ACCELERATED CARBONATION TEST OF CONCRETE

by

Halit YAZICI

July, 1998

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ACCELERATED CARBONATION TEST OF CONCRETE

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by

Halit YAZICI

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M. Sc. THESIS EXAMINATION RESULT FORM

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

Embedded steel in reinforced concrete members is protected from corrosion by alkaline composition of the concrete which is provided mainly by the dissolution in the pore water of the $Ca(OH)_2$. However, this positive property of the concrete may be lost in time due to carbonation of hydrated components of cement especially, $Ca(OH)_2$ which is converted to $CaCO_3$ with diffusion of CO_2 from the environment into the concrete pore system during carbonation process. This phenomenon is accepted one of the main factors determining the service life of the reinforced concrete members.

This study includes comprehensive research on carbonation process, factors affecting carbonation rate, its modifications on micro-structure and behaviour of the cement paste and concrete. Furthermore, an elementary Accelerated Carbonation Test Apparatus (ACTA) was developed and some preliminary tests were conducted on various types of cement mortar or concrete specimens.

ÖZET

Betonarme elemanlarda, beton içine gömülü olan çelik, betonun alkali ortamı sayesinde korozyondan korunur. Betonun alkalinitesi büyük ölçüde çimentonun hidratasyonundan kaynaklanan ve gözenek suyu içinde çözünmüş $Ca(OH)_2$ tarafından sağlanır. Fakat, betonun bu olumlu özelliği zaman içinde karbonatlaşma adı verilen bir kimyasal reaksiyon sonucu ortadan kaybolabilir. Özellikle, $Ca(OH)_2$ ortamda bulunan CO_2'in betonun gözenek sistemine işlemesiyle $CaCO_3$'a dönüşür. Ortamın pH derecesini düşüren ve donatının paslanmasına yol açan bu olgu betonarme elemanların servis ömürlerini belirleyen önemli faktörlerden biri olarak kabul edilir.

Bu çalışmada karbonatlaşma olayı; olayın gelişimini etkileyen faktörler, karbonatlaşmanın çimento hamuru ve betonun iç yapısında meydana getirdiği değişiklikleri içerecek şekilde, kapsamlı biçimde incelenmiştir. Ayrıca, laboratuvar ortamında olayı hızlandırarak gerçekleştirmek amacı ile basit bir deney düzeneği oluşturulmuş ve bazı ön deneyler gerçekleştirilmiştir.

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CHAPTER ONE
INTRODUCTION

As the corrosion of embedded steel which can cause breaking of the steel, cracking or spalling off the concrete cover, is one of the major causes of the deterioration of reinforced or prestressed concrete structures, carbonation is accepted one of the main durability problems. It is well known that corrosion risk of embedded steel in carbonated concrete is higher than those of uncarbonated.

In a simplified term, the process of conversion of calcium hydroxide to calcium carbonate due to reaction with the atmospheric carbon dioxide that diffuses from the environment into the concrete pore system and combines with water, forming carbonic acid which then reacts with the alkali hydroxides (sodium, potassium), forming carbonates is called *carbonation*. In other words, carbonation is a chemical reaction that can occur in the concrete, mortar, or hardened cement paste if sufficient moisture and CO_2 are exist. But as a result of past experimental researches show that not only $Ca(OH)_2$, but also all of the hydrated components of cement, except gypsum, can be carbonated and different products from $CaCO_3$ and water are produced such as silica gel, gypsum and aluminium hydroxide.

There are different factors that affect progress of carbonation. Some of them are concerning with composition of concrete such as, chemical and mineralogical composition of cement, water/cement ratio, amount of cement and curing conditions, etc. Some of them are environmental factors such as, ambient CO_2 concentration, ambient relative humidity for outdoors, unsheltered concrete, the cycles of rain, snow and ambient temperature, etc. Therefore, the degree of pore saturation is a controlling factor for carbonation. In completely saturated concrete diffusion of gas is negligible. On the other hand, in dry concrete CO_2 cannot be converted to carbonic acid so in both cases reaction of carbonation

is impeded practically. Furthermore, experimental results show that carbonation is maximum at relative humidities around 50%.

It is increasingly realised that more money and resources are being allocated to repair and to rehabilitate concrete structures as a result of inadequate durability rather than inadequate strength. Corrosion of steel reinforcement is the most serious durability problem for reinforced concrete structures. Normally, reinforcement is protected from corrosion by a thin oxide layer that forms on its surface. However, the stability of this passive oxide layer is depended on the alkalinity corresponds to a pH value. The pH value of the concrete is greater than 12.5 and it is provided by the dissolution in the pore water of even a very small amount of the solid $Ca(OH)_2$ in the hardened cement gel. Sodium and potassium oxides also contribute a little to the alkalinity. A reduction in the pH value of the pore water below 9.5 causes depassivation of the steel bars, due to the dissolution of their protective surface oxide layer. The pH of the pore water drops at a certain point in the concrete to an equilibrium value about 8.3 which is below depassivation threshold, when all the quantity of dissolved $Ca(OH)_2$ in the cement gel is converted to $CaCO_3$. After that the corrosion processes can develop if sufficient moisture and O_2 are exist in the media. Due to this process, carbonation is accepted one of the main factors that affect the service life of reinforcement concrete structures.

Carbonation creates considerable modifications in the microstructure of the mortar, cement paste and concrete. The radii of some pores and specific surface values decrease, mechanical strengths increase. Also, the gas diffusion coefficients decrease and due to the result of these positive changes in the pore structures the durability of plain concrete can be improved by carbonation. However, all of these changes depend on various factors such as, water/cement ratio, amount of cement, mineralogical composition of cement, cure, etc. Furthermore, experimental results show that the paste in mortar and concrete more porous than the corresponding plain paste so, decreasing porosity, one of the positive changes of carbonation is more pronounced in plain paste than those of mortar and concrete.

Carbonates which form as a result of chemical reactions, have three different forms that are vaterit, calsite and aragonit. Increase in volume, due to carbonates, are in order 19%, 12% and 3% consecutively. Although, increase in volume, carbonation also cause shrinkage

which has not been explained yet sufficiently. However, there are different theories. One of the approach states that carbonation shrinkage occurs due to the evaporation of water which is produced by chemical reactions. Another theory claims that the dissolving of crystals of $Ca(OH)_2$ under compressive stress, deposit in pores free from stress and consequently, the compressibility of the cement paste increases. Carbonation increases the shrinkage at intermediate humidities, but not 100 per cent or 25 per cent. Therefore, the sequence of drying and carbonation greatly affects the total magnitude of shrinkage. Simultaneous drying and carbonation produces lower total shrinkage than when drying is followed by carbonation. As the carbonation process occurs very slowly, cracks due to carbonation shrinkage apply to the surface layer of the concrete and are not structurally significant. Furthermore, creep strains increase during carbonation possibly because the Calcium Silicate Hydrate (CSH), the main load-bearing skeleton of hardened cement paste, is converted to new compounds during carbonation so, extra creep occurs. Whereas, carbonation before loading reduces the amount of creep in concrete. This is probably due to the reduction in porosity resulting from deposition of the carbonation reaction products in the pores.

Various formulas have been developed by different investigators about the penetration rate of carbonation. Moreover, the depth of the carbonation front in concrete can be measured in a variety of ways; by X-ray diffraction, infrared spectroscopy, electron microscopy, thermogravimetry, differential thermal analysis or using indicators (phenolphthalein, thymolphthalein). The phenolphthalein test is the simplest and most popular and is carried out by spraying a freshly split surface of the concrete with a mixture of phenolphthalein (0.1% alcohol solution). The essence of this procedure is that such colour indicators show different colours in different pH regions. Such as, phenolphthalein appears colourless on the carbonated layer while appears an intensive red on the uncarbonated layer of the concrete. Thymolphthalein which is a more dependable indicator, can also be used as an alternative of phenolphthalein.

As the corrosion of the reinforcement is one of the most important factor that influence the service life of reinforced or prestressed concrete structures, some passive and active realkalization methods are developed to reinstate alkalinity of the carbonated concrete. Passive method consist of application lime-cement mortar coating. Experimental research

shows a high alkalinity may be restored in a carbonated zone if sufficient moisture is available in the pore system. Furthermore, it postpones the carbonation rate required for fully penetrate the concrete coating and diffusion of CO_2 is more difficult. Active realkalization method is similar with the cathodic corrosion protection method by direct current. But this method have some negative effects such as alkali-aggregate reaction if concrete aggregate has active silica or reinforcement steel may become brittle due to hydrogen reaction. Furthermore, the bond between concrete-reinforcement may weaken.

Besides its negative effects for reinforced or presstressed concrete members, carbonation can cause some positive modifications for concrete members without reinforcement. First of all, easy soluble $Ca(OH)_2$ is converted to hard soluble $CaCO_3$ and due to its products, pore volume of the OPC concrete may be decreased by carbonation. Although, fixing $Ca(OH)_2$ with puzzolonic reaction is more preferable, in some cases, to improve durability of concrete members which will be immersed or contact with water during their service life, are exposed to the atmosphere to being carbonated before using at their own places.

CHAPTER TWO
IMPORTANCE OF CARBONATION

Carbonation of concrete is known to be one of the most threating event when it causes corrosion of the rebars. Steel corrosion is one of the main causes of concrete damage, and hence carbonation in reinforced concrete is a phenomenon that has to be feared. However, carbonation is a very slow process to observe, and some characteristics of carbonated concrete still hidden (De Ceukelaire & Van Nieuwenburg, 1993).

2.1. What's Durability

Besides its ability to sustain loads, concrete is also required to be durable. The durability of concrete can be defined as its resistance to deterioration resulting from external and internal causes. The external causes include the effects of environmental and service conditions which concrete is subjected, such as weathering, chemical actions. The internal causes are the effects of salts, particularly chlorides and sulphates, in the constituent materials, interaction between the constituent materials, such as alkali-aggregate reaction, volume changes, absorption and permeability.

Figure 2.1 which shows the interrelations between the main factors influencing durability. It can be seen from Figure 2.1 that the combined transportation of heat, moisture and chemicals, both within the concrete mass and in exchange with the surroundings (the microclimate), and the parameters controlling these transport mechanisms, constitute the principal elements of durability (Jackson, 1988; CEB, 1992).

The presence of water or moisture is the single most important factor controlling the various deterioration processes, apart from mechanical deterioration. The transport of water within the concrete is determined by the pore type, size and distribution and by cracks (microcracks and macrocracks). Thus, controlling the nature and distribution of pores and

cracks is essential. In turn, the type and rate of degradation processes for concrete (physical, chemical and biological) and reinforcing or prestressing reinforcement (corrosion) determine the resistance and rigidity of the materials, the sections and the elements making up a structure. The surface conditions of the structure are also determined in this way, and this is reflected in the safety, the serviceability and the appearance of a structure; i.e. these processes determine the performance of the structure.

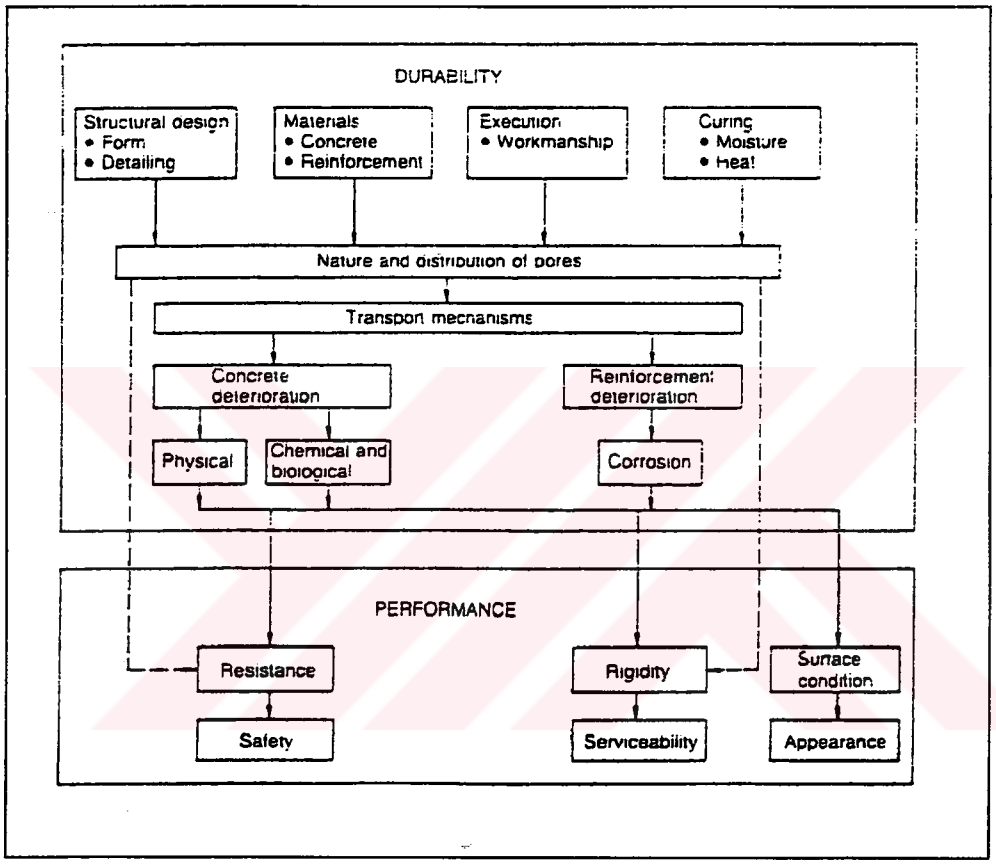

Figure 2.1 Relationship between the concepts of concrete durability and performance

In order to produce durable concrete care should be taken to select suitable constituent materials. It is also important that the mix contains adequate quantities of materials in proportions suitable for producing a homogeneous and fully compacted concrete mass (Jackson, 1988; CEB, 1992).

2.2 Transport Mechanisms in Concrete

2.2.1 Transport Mechanisms

In nearly all chemical and physical processes influencing the durability of concrete structures, two dominant factors are involved: transport within the pores and cracks, and water. The transport of gases, the transport of water, dissolved agents and the binding mechanisms are important. The rate extent and effect of the transport are largely dependent on the pore structure and on the microclimate at the concrete surface. In this context, pore structure signifies the amount of pores and the pore size distribution.

The pore structure and crack configuration, the filling of pores and cracks with water, are determining factors in respect of the transport of water, gases and dissolved substances. In addition, the rate of transport depends considerably on the transport mechanisms. In the event of chemical binding mechanisms being involved, the chemical composition of the cement and the properties of the aggregates are also of importance.

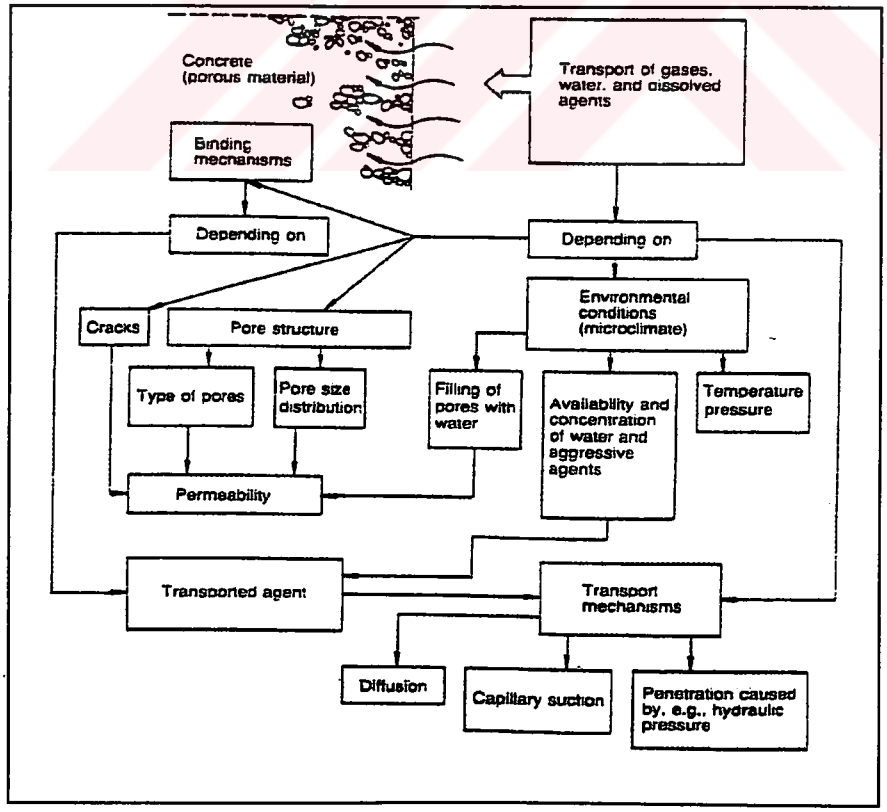

Figure 2.2 Transport phenomena in concrete

All transport mechanisms are mainly a function of the pore structure and crack configuration, and are determined by the same processes The transport phenomena in concrete is briefly presented in Figure 2.2 (CEB, 1992).

2.2.2 Pore Structure of Concrete

In addition to the microclimate, permeation is influenced by the pore structure of cement paste. For a characterization of open pore structure with regard to the substance into and within porous building materials, two parameters will be of importance: open porosity and pore size distribution. Open porosity means pores which are interconnected so that transport of liquids or gases and/or the exchange of dissolved substances is possible. It corresponds to the maximum reversible water content, and in the case of cement paste, lies in the region of 20-30 %.

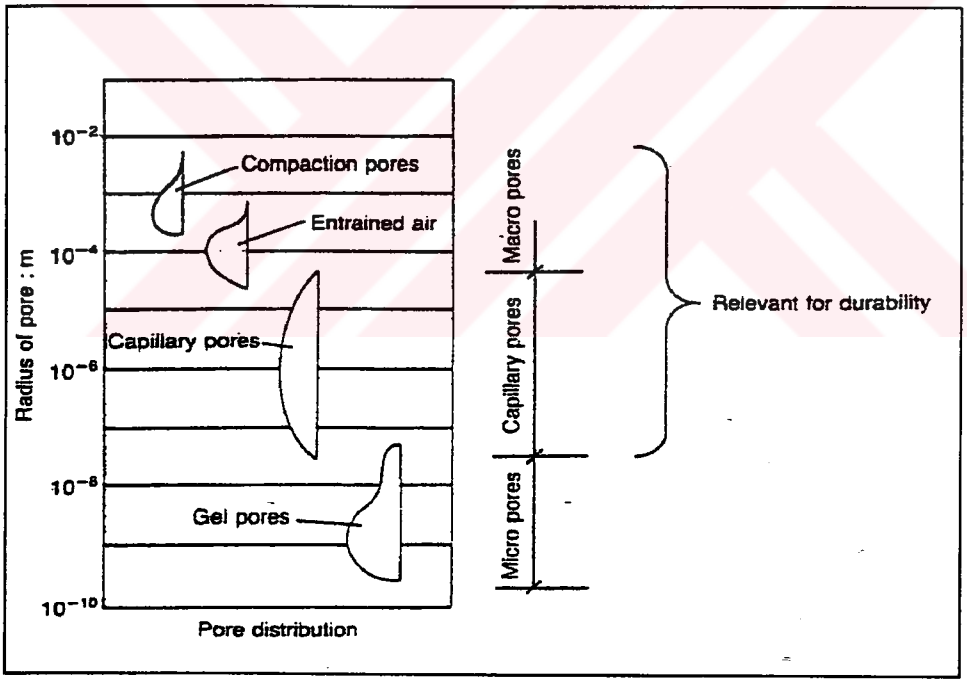

Figure 2.3 Pore size distribution

The pore size distribution particularly influences the rate of the transport. The size of pores in the cement paste range over several orders of magnitude. According to origin and characteristics, the pores are described as compaction pores, air pores, capillary pores or gel pores. Expressed more general terms, it appears to be convenient to classify them as macropores, capillary pores and micropores. The capillary pores and macropores are

particularly relevant with regard to durability. In general, the resistance of concrete to chemical and physical influence is considerably reduced with increasing quantity of capillary pores. Figure 2.3 shows pore size distribution of the concrete (CEB&RILEM, 1983; CEB, 1992)

2.2.3 Interaction Between Pores and Water

Free surfaces of solids (e.g. pore surfaces) exhibit a surplus of energy (the surface energy) due to a lack of binding components to the adjacent molecules. In cement paste pores, this surface energy causes the water vapor molecules within the pores to adsorb onto the pore surface, the thickness of the water film depending on the degree of humidity within the pores.

Due to the fact that the ratio between surface area and volume of the pores increases with decreasing pore radius, the quantity of water adsorbed relative to the pore volume will also increase, until at a certain limit value of the pore radius, the pores with smaller radii are completely filled water. This process is called *capillary condensation*. The limit value of the pore radius, depends primarily on the water content of the air in the pore which, all else being constant, is proportional to the humidity of the air surrounding the concrete.

As a result of the high proportion and small radii of the gel pores concrete exhibits comparatively high water content even when the humidity of the surrounding air is relatively low. Increasing the humidity of the air will cause the larger pores to be filled with water, thus reducing the pore space available for diffusion of gases. Consequently, the permeability of the concrete with regard to gases will decrease considerably with growing water content and, in the case of almost water-saturated concrete, the diffusion of gases (e.g. carbon dioxide and oxygen) becomes practically negligible (CEB, 1992).

2.2.4 Transport Mechanisms in Humid Air

The larger pores in concrete surrounded by air are filled with air, depending on the humidity of ambient air. The surface of these pores is coated with a water film bound by adsorption. Any transport processes of gases, water or substances dissolved in water are

diffusion processes under these ambient conditions. Diffusion processes are induced by tendency for differences in concentrations to equilibrate.

Carbon dioxide diffuses into the concrete due to a chemical reaction between the carbon dioxide and the concrete developing at the pore walls, which causes the concentration within the pores to be reduced. A similar process applies with oxygen when it is consumed during corrosion.

Diffusion of water or water vapour will always take place when the ambient humidity changes or when the concrete is drying out.

The diffusion of substances dissolved in water (e.g. chloride ions) will develop in the water film at the pore surface or in the water-filled pores. Due to the decreasing film thickness and the decreasing proportion of water-filled pores, respectively, the diffusion rate of substances dissolved in water will be substantially reduced with decreasing moisture content of the concrete.

2.2.5 Transport Mechanisms: Rain and Splash Water

In the case of wetting of concrete surfaces (e.g. rain and splash water), water transport is of major importance because of capillary suction, saturation will quickly be achieved. Solutes are transported by the water; the diffusion of gases is practically impeded.

The effect of capillary suction depends on the surface energy of the pore surface. The tendency to adsorb water onto the surface will, in the case of a surplus of water, result in suction being initiated. The height of capillary rise in vertical capillaries is determined by an equilibrium between the binding forces of the surface and the weight of the water column in the capillary. As far as suction in horizontal direction is concerned, the depth of penetration will primarily depend on there being an excess of water at the concrete surface and on the duration of this situation.

Water is adsorbed by concrete through capillary suction at a considerably higher rate than it is disposed of by evaporation (CEB&RILEM, 1983; CEB, 1992).

2.3 Protection Effect of Concrete

2.3.1 The pH Value

Pure water contains a little amount hydrogen (H^+) and hydroxide (OH^-) ions. Ion concentration reaches 10^{-14} Mol in one litre water which has the same amount of these ions. In other words, there is a 10^{-7} Mol H^+ and 10^{-7} Mol OH^- in it which is neutral. Negative logarithm that base on ten, is 7 called *The pH value*. The pH value which shows the amount of H^+ ions in the solution, changes from 0 to 14. If concentration of H^+ ions is higher than 10^{-7} in the solution that called *acidity* (pH < 7). In this case, of course concentration of OH^- ions is lower. On the contrary, if concentration of H^+ ions is lower than 10^{-7} in the solution that called *alkaline* (pH > 7). In other words, concentration of OH^- ions is higher. Figure 2.4 gives a brief summary about the formation of pH value (Kavalalı, 1994).

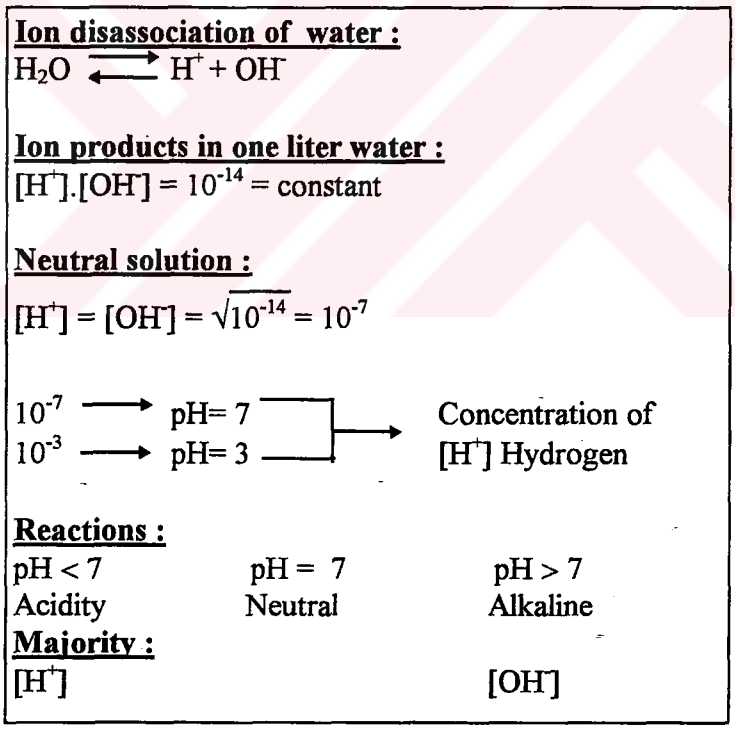

Figure 2.4 Ion disassociation of water

2.3.2 Alkaline Protection Media

Some metals, like aluminium and copper are corroded in normal atmospheric conditions until the oxide film develops. Corrosion is prevented by the oxide film that protects underlying metal surface. This protective passive oxide film also forms on the surface of iron but it is unstable in normal atmospheric conditions unless there is an alkaline media. Corrosion which destroys the surfaces of iron, do not start in the alkaline environment. This passive layer impedes the dissolution of iron, Thus corrosion of reinforcement is impossible, even if all other preconditions for corrosion are fulfilled (mainly moisture and oxygen). Figure 2.5 shows schematically protection of reinforcement by alkalinity of concrete (CEB&RILEM , 1983; Kavalalı, 1994).

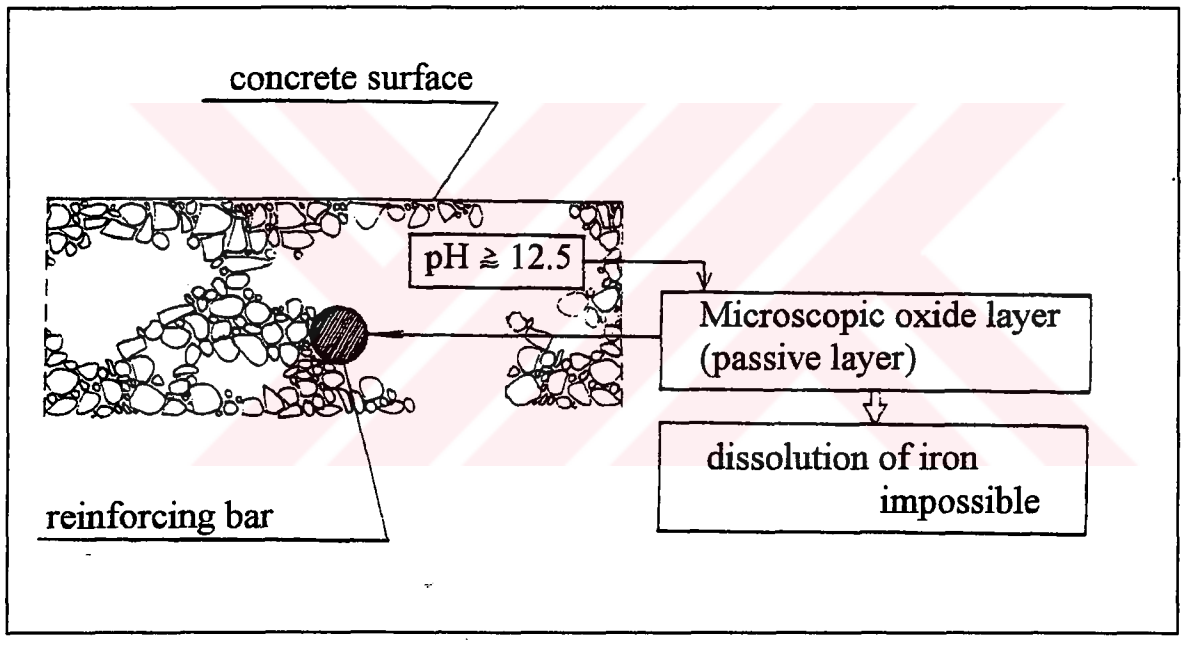

Figure 2.5 Protection of reinforcement by alkalinity of concrete

The passive oxide film has an approximately 50 μm thickness and it contains iron ions (Fe^{2+}, Fe^{3+}), oxide and hydroxide ions. Solution that contains ions called *electrolyt*. Figure 2.6 shows that if the pH value of the electrolyt above 9.5, passive layer has a protection effect even a great deal of oxygen exists in the surrounding environment (Kavalalı, 1994; Baradan, 1996).

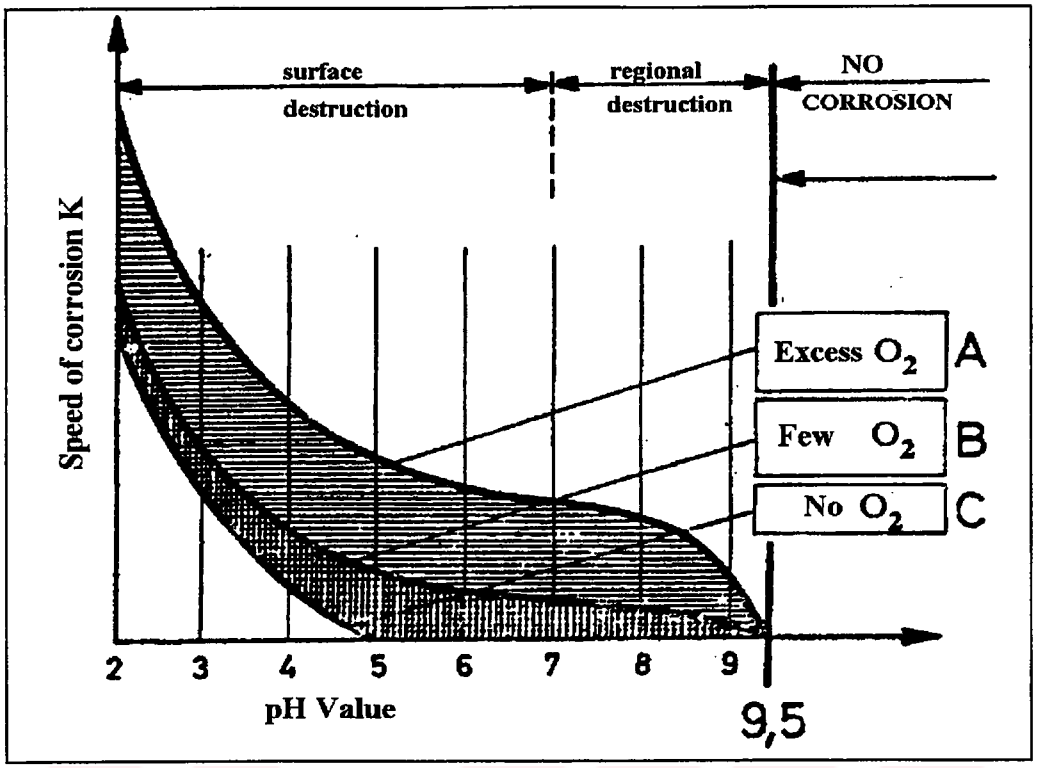

Figure 2.6 Relation between electrolytical corrosion and the pH value of the electrolyt

2.3.3 Friedel's Salt and Binding Capacity of Concrete for Chloride Ions

The concrete has a certain chemical binding capacity for chloride ions, depending on the chloride concentration in the pore water. However, not all the chlorides can be bound. Part of the chloride can be chemically bound by the cement to form the *Friedel's salt.* Considerable evidence from laboratory investigations and field structures, however, suggest that, the C_3A and tetra-calcium aluminoferrite (C_4AF) phases of the cement are responsible for the binding of chloride ions to form *Friedel's salt*, $3CaO.Al_2O_3.CaCl_2.10H_2O$, and its ferrite analogue, $3CaO.Fe_2O_3.CaCl_2.10H_2O$ (Suryavanshi&Swamy, 1996).

The disassociation of the bound chlorides in the form of Friedel's salt, during the service life of concrete structure, subjects the steel to a greater corrosion risk. This is because, out of the total chlorides (free chlorides + bound chlorides) only free-chlorides are responsible for the depassivation of the reinforcement steel. This emphasizes the need for Friedel's salt to remain stable during the service life of a concrete structure. Therefore it is of importance that after carbonation bound chlorides are released again so that the chloride content in the

pore water and, consequently, the corrosion risk caused by chlorides will increase considerably.

The critical chloride content indicating incipient danger of corrosion depends on various parameters. Therefore, there is no single generally valid value of critical chloride content existing.

If concrete is not carbonated, 0.4% Cl^- related to cement weight is a good criterion for incipient danger of corrosion. But, as illustrated on the opposite in Figure 2.7 , the critical value can be much higher, as well as lower, depending on the indicated influences. As prestressing steels are more sensitive to corrosion, a lower limit of about 0.2% Cl^- related to the cement weight is recommended for prestressed structures. Therefore, the danger of corrosion will increase after carbonation of concrete, even with chloride contents ranging below 0.4%.

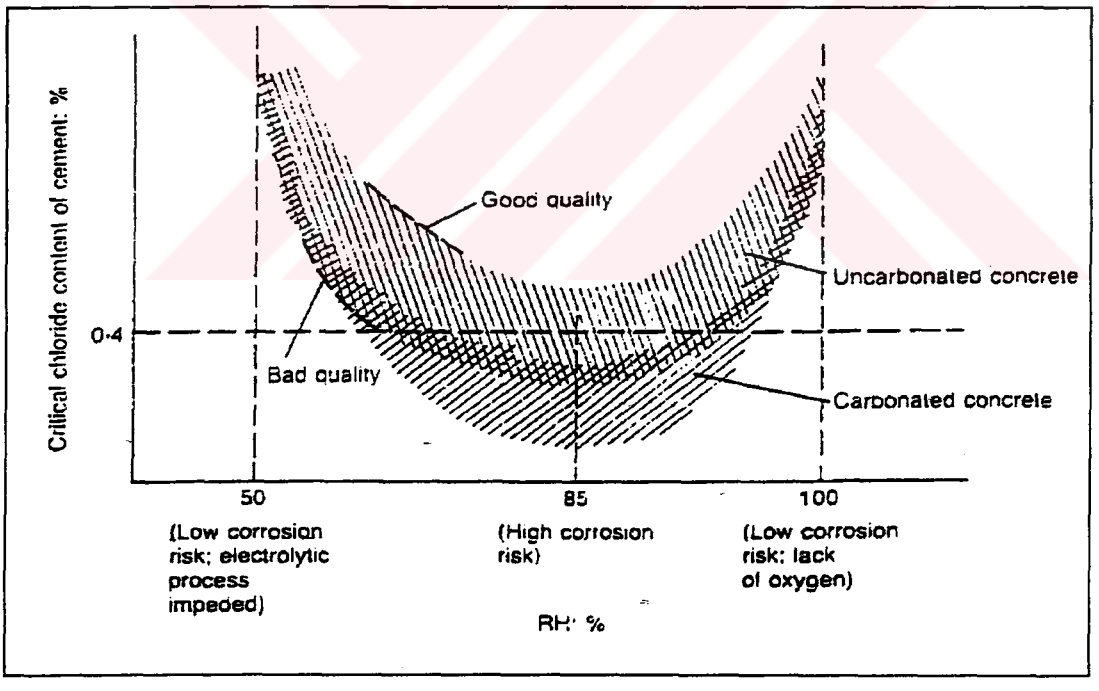

Figure 2.7 Variation of critical chloride content with environment

With increasing cement content the binding capacity of concrete both for CO_2 and chlorides will be increased. However, within the normal range of cement content the

penetration rates of carbonation and chlorides are influenced to a considerably lower extent by the cement content than by the W/C ratio, the quality of compaction and curing.

Mainly, the most usual blending agents; natural pozzolans, blast furnace slags, fly ashes, silica fumes, have the common properties that are slow hardening at early age and distinct hardening later on (post-hardening). That means blended cements are more curing-sensitive than Portland cements.

If the post-hardening is guaranteed by adequate curing, a lower permeability of concrete can be achieved by using blended cements compared with portland cements. In this way especially the resistance against chloride penetration can be improved.

But, inadequate curing may lead to a poor quality of the concrete cover (permeability, binding capacity), especially if cements with high percentages of blending agents (e.g. 80% slag, 50% fly ash, 30% silica fume) are used (CEB&RILEM, 1983; CEB, 1992; Suryavanshi&Swamy, 1996).

2.4 Hydration of Cement and Sources of Alkaline Media

Concrete is a highly alkaline material. This is largely due to the presence of soluble $Ca(OH)_2$, although sodium and potassium oxides also contribute a little. As a result of the chemical changes which take place in the kiln, several compounds are formed in the cement. Although only four of them are generally considered to be important. The two calcium silicates, C_3S and C_2S, which are contribute most to the physical properties of concrete, form similar products that are Calcium Silicate Hydrates (CSH) and $Ca(OH)_2$ during hydration. Amount of $Ca(OH)_2$ that is formed by C_3S, is 3 times higher than it is formed by C_2S. Table 2.1 shows the main chemical compounds of cements and their reactions of hydration. (Jackson, 1988; Baradan, 1996)

Table 2.1 Main chemical compounds of Portland cements and their reactions of hydration

Name of Compounds	Chemical Composition	Usual abbre-viation	Reaction of hydration
Tricalcium silicate	$3CaO.SiO_2$	C_3S	$2(3Cao.SiO_2) + nH_2O \longrightarrow 3CaO.2SiO_2.(n-3)H_2O + 3Ca(OH)_2$
Dicalcium silicate	$2CaO.SiO_2$	C_2S	$2(2Cao.SiO_2) + nH_2O \longrightarrow 3CaO.2SiO_2.(n-1)H_2O + Ca(OH)_2$
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A	$3CaO.Al_2O_3 + 6H_2O \longrightarrow 3CaO.Al_2O_3.6\ H_2O$ + heat $3CaO.Al_2O_3.6\ H_2O + Ca(OH)_2 + 6H_2O \longrightarrow 4CaO.Al_2O_3.13\ H_2O$
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	$4CaO.Al_2O_3.Fe_2O_3 + (n+6)H_2O \longrightarrow 3CaO.Al_2O_3.6\ H_2O + CaO.Fe_2O_3.nH_2O$

Free-lime which is exist in the cement reacts with water so, alkaline media of cement paste is enriched.

$$CaO + H_2O \longrightarrow Ca(OH)_2 \qquad (2.1)$$

Except $Ca(OH)_2$, alkaline oxides that are KOH, NaOH also increase the pH value of the concrete (Kavalalı, 1994).

$$\text{Alkaline phases of clinker} + H_2O \longrightarrow KOH,\ NaOH \text{ and others} \qquad (2.2)$$

From Figure 2.8 to 2.12 show some products of hydration of cement according to the electron microscopy (Houst,1993).

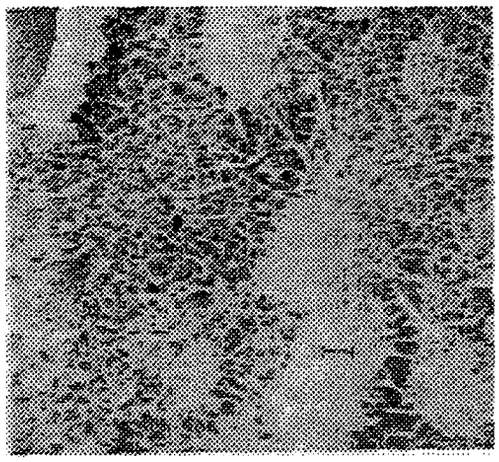

Figure 2.8 CSH components of Portland cement mortar (W/C= 0.6, hydrated for 14 days at 24°C).

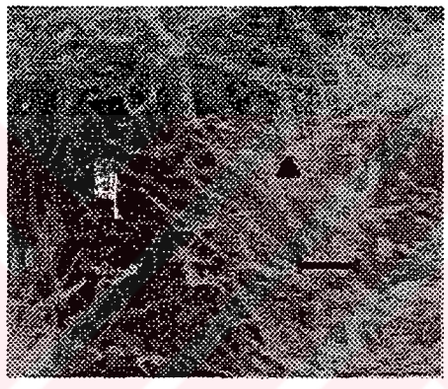

Figure 2.9 Pores and CSH gel of Portland cement paste (W/C= 0.6, hydrated 185 days at 40°C)

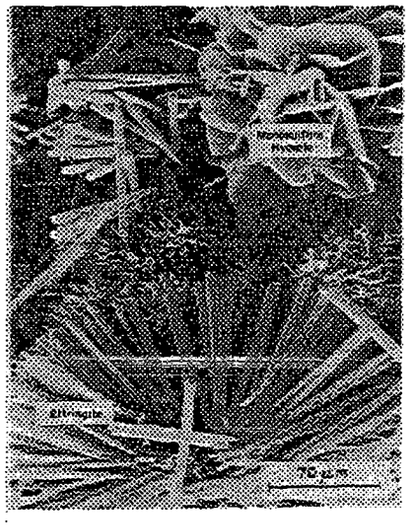

Figure 2.10 Hexogonal crystals of monosulfate aluminate and crystals of ettringite

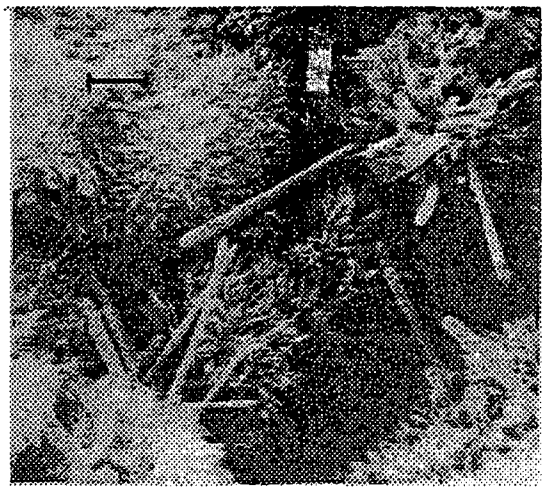

Figure 2.11 CSH gel and ettringite of Portland cement paste (W/C= 0.6, hydrated 2 days at 24°C)

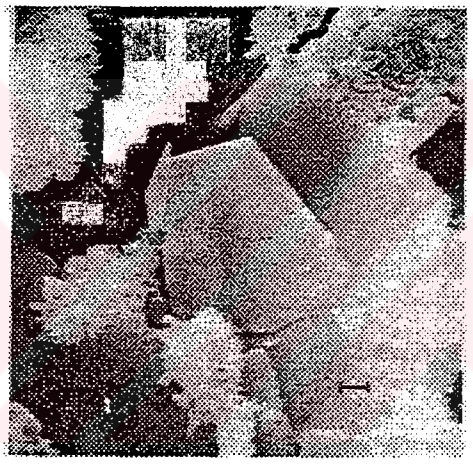

Figure 2.12 Crystals of $Ca(OH)_2$ and CSH of Portland cement paste (W/C= 0.6, hydrated 5 days at 24°C)

Due to carbonation or by the action of chloride ions the pH-value may be reduced locally or over greater surface areas. If the pH-value of concrete drops to 9.5 in the regions close to the reinforcements, or if the chloride content exceeds a critical value, the passive layer will get lost. Consequently, corrosion of reinforcement is possible, if sufficient moisture and oxygen are available as shown Figure 2.13 schematically (CEB&RILEM, 1983).

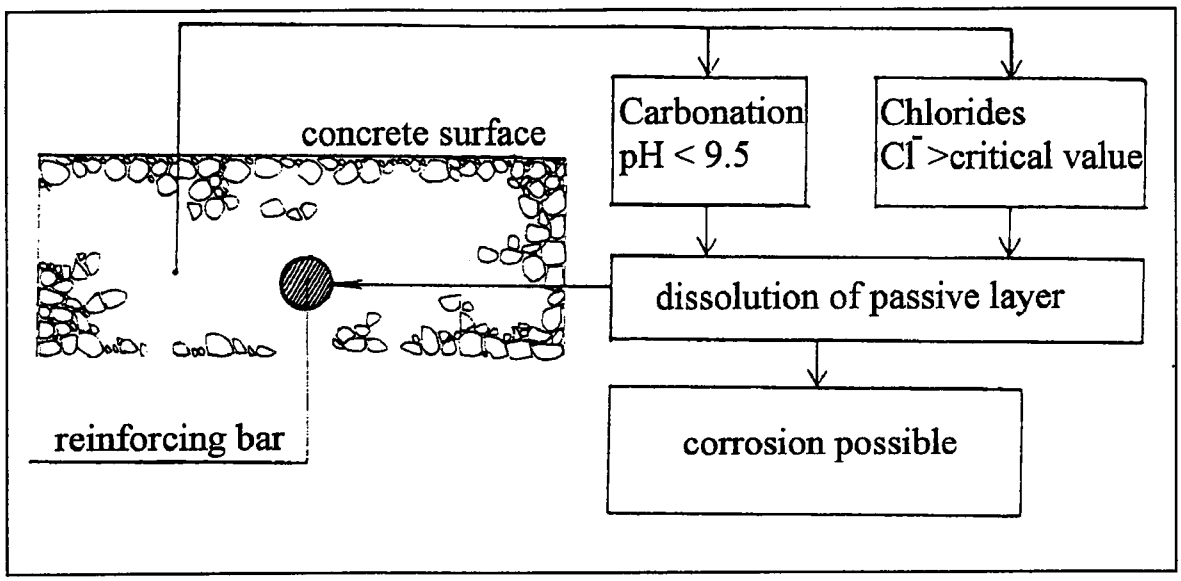

Figure 2.13 Corrosion of reinforcement after dissolution of passive layer

2.5 Carbonation of Concrete

Some gases in the atmosphere may turn to acid form. Especially CO_2 and SO_2 have tendency to develop into strong acids in three step reactions.

1. Step : Penetration to the pore system of cement paste

2. Step: Reactions with pore water

$CO_2 + H_2O \longrightarrow H_2CO_3$ (Carbonic acid) (2.2)

$SO_2 + H_2O \longrightarrow H_2SO_3$ (Sulfuric acid) (2.3)

3. Step: Acids react with the alkaline components of cement paste.These components exists in the pore water in dissolved form.

Acid + Alkaline $\longrightarrow$ Salt + Water

Atmosphere in industrial areas usually, contains 1000-2000 mg/m^3 CO_2 and 0.1-0.2 mg/m^3 SO_2. These are the major sources of carbonation effect. The most important formula of reactions can be simplified, as below;

$$Ca(OH)_2 + CO_2 \xrightarrow{H_2O} CaCO_3 + H_2O \quad (2.4)$$

$pH \approx 12.6$ $\qquad$ $pH \approx 8.3$

CO_2 must penetrate deeper into the concrete layer in order to repeat this reaction. The building up of $CaCO_3$ layer in outer surfaces, some what slows the process.

The pH value of calciumcarbonate is about 8.3. In this case, the corrosion protection effect of cement paste is loosen since $8.3 < 9.5$. The passive layer becomes unstable. This reaction is called *carbonation* because of the last product, that is calciumcarbonate.

General opinion that carbonation only is based on lime is not correct since, except gypsum, all of the hydrated components of cement can be carbonated.

Cement phase is rich in terms of $(OH)^-$. It is interesting that, if concentration of $(OH)^-$ ions are high, the solubility of $Ca(OH)_2$ decreases and crystallation forms. This solid formation of $Ca(OH)_2$ cannot react with carbonic acid unless there is other alkaline elements present in the media that are NaOH or KOH.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O \quad (2.5)$$

and Na_2CO_3 reacts with $Ca(OH)_2$ as a second stage

$$Na_2CO_3 + Ca(OH)_2 \longrightarrow CaCO_3 + 2NaOH \quad (2.6)$$

Due to Reaction 2.5, concentration of $(OH)^-$ decreases so, solubility of $Ca(OH)_2$ increases and Reaction 2.6 grows easily. Hard soluble $CaCO_3$ precipitates. During the Reaction 2.6, NaOH arises again so, Reaction 2.5 repeats.

Hydrated components of cement that are calcium silicate hydrate, mono calcium alumino sulfate and tricalcium alumino sulfate (ettringite) are also carbonated while acting sodium carbonate (Na_2CO_3) and carbonation of these components produce calcium carbonate

($CaCO_3$), sodium hydroxide (NaOH) and water (H_2O). Therefore, silica gel and gypsum ($CaSO_4.2H_2O$) also are produced by reaction of CSH with Na_2CO_3, aluminium hydroxide ($Al(OH)_3$) are also produced by reaction of alumino sulfates.

It can easily be understood from the above equations that, carbonation starts with the production of Na_2CO_3. In other words, alkali content of cement (NaOH, KOH) is very important. As a matter of fact, Kobayashi and Uno stated that carbonation of structures has been progressing with increasing rates when the method of manufacturing cement in Japan was converted to dry system. Authours explain this situation with higher alkali content of cement (Kobayashi&Uno, 1989; Kobayashi&Uno, 1990; Houst, 1993).

Calciumcarbonate is stable and dissolves hardly in water. Volumes of $CaCO_3$ are larger than replaced components (20%) so that they fill the pore structure of the concrete. If $Ca(OH)_2$, which must exist to protect the alkaline media in the pores, is present for a long time, carbonation progress slowly within the concrete mass. A little amount of $Ca(OH)_2$ is enough to saturate the pore water. Due to this fact, the pH value of the concrete drops quickly when $Ca(OH)_2$ is used up. Figure 2.14 shows the correlation between pH value and time (Kavalalı, 1994).

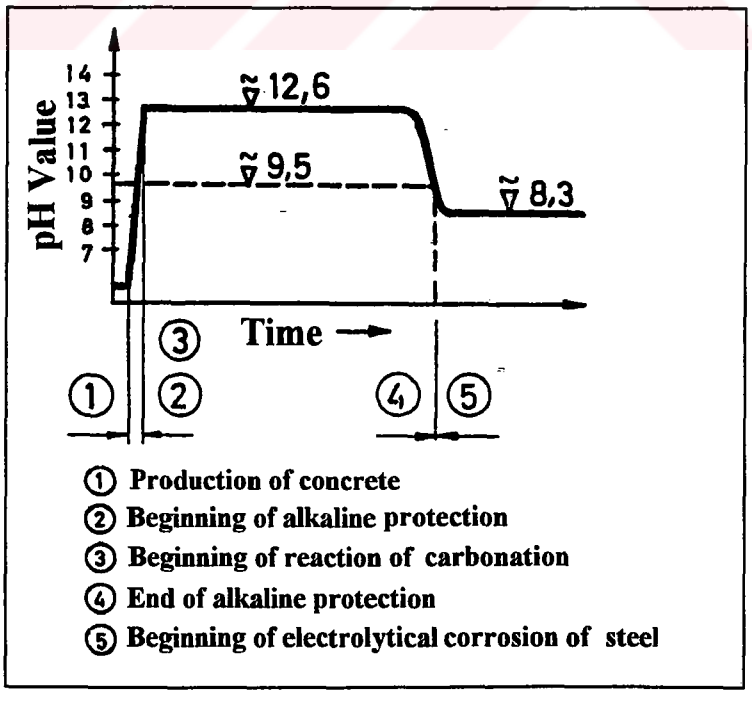

Figure 2.14 Schematic correlation between pH value and time in the concrete cover

For the diffusion of CO_2 into the concrete mass the equilibrium pressure of reactions must be lower than CO_2. In fact, partial pressure of CO_2 in the atmosphere is always higher than equilibrium pressure of hydrated components. In other words, all of the hydrated components may be carbonated. Since, among hydrated components, $Ca(OH)_2$ has the lowest equilibrium pressure Reactions 2.5 and 2.6 have a priority.

If CO_2 acts for a long time, hard-soluble calciumcarbonate turns to easy-soluble calciumhydrocarbonate which can be removed by washing. Thus with the incorporation of new CO_2 more $Ca(OH)_2$ is used up in two stages as shown below;

$$CaCO_3 + CO_2 + H_2O \longrightarrow Ca(HCO_3)_2 \qquad (2.7)$$

$$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3 + 2\,H_2O \qquad (2.8)$$

Finally, carbonation causes dissolving of Friedel's salt and unification property of cement paste with Cl^- ions is loosen.

The elements of the reaction are; a water film and continual diffusion of CO_2. Therefore carbonation do not occur under water (CO_2 does not exist) and relative humidities below 30% (Although, at the high level of pollution, vapour condensation is not sufficient). Carbonation reaches to a maximum speed at the relative humidity of 50%.

The most important corrosion risk of embedded reinforcement steel occurs at the relative humidity of 50-85 %. Rains and capillary vapour condensation fills up pores with water so, the diffusion of CO_2 into the paste becomes slower. Therefore, concrete structures which are exposed to the atmosphere but protected from rain, carbonate 2~3 times faster than those are not protected. It has been reported that covered sides of sloped concrete slabs of 60 cm thickness carbonated 10 times faster than their exposed sides during early ages (Kavalalı, 1994; Akman, 1997).

2.5.1 The Rate of Carbonation

The CO_2, penetrates from the surface to the interior parts of the concrete. Consequently, carbonation starts from the concrete surface and penetrates slowly towards the depths of

the concrete. The speed-determining process is the diffusion of CO_2 into concrete. (CEB&RILEM, 1983).

Various formulas have been developed by different investigators about penetration rate of carbonation. General structure of various formulas may be stated as below.

$$x_k = c\sqrt{t}$$

X_k= Carbonation depth from the surface, (mm)

t = Time, (year)

c = Coefficient, depending on material and atmospheric condition

These formulas can be use to estimate the rest of service life of structure or affects of surface treatment of the concrete on the service life of the structure (Papadakis&Fardis&Vayenas, 1992; Kavalalı, 1994; Baradan, 1996).

2.6 Factors Affecting Carbonation

There are various factors that affect the rate of carbonation. They may be summerized as below.

2.6.1 Water/Cement Ratio

Factors affecting the pore structure of concrete and mortar, are also important for the diffusion of CO_2. Among these factors water/cement ratio is the first order. High W/C ratio causes increased voids, easier diffusion of gas and higher hydration of cement at the hardened concrete. So carbonation rate increases with greater W/C ratios. On the other hand, the voids also increase at the very low W/C ratio due to the difficulty of obtaining well placed and compacted concrete (Akman, 1997).

2.6.2 Curing Conditions

The other factor affecting the void structure of concrete is curing conditions. Hydration products that are cured in moist conditions reduce the voids of concrete. Due to this fact,

carbonation rate is related with the conditions of curing. If there is a lack of moist curing, an increase with the carbonation rate will be expected.

The results of experiments which have been reported by Ballim, demonstrate the negative effects of inadequate early-age curing of concrete in Figure 2.15. The sensitivity of concrete containing ground granulated blast furnace slag (GGBS) to the duration of curing is also clearly shown.

Figure 2.15 also shows the standard 28-day compressive strengths obtained for the concrete tested. It can clearly be observed that the rate of deterioration of a particular concrete cannot be determined from its compressive strength alone. This fact proves the error in specifications for durability that are based on compressive strength only (Ballim, 1996; Akman, 1997).

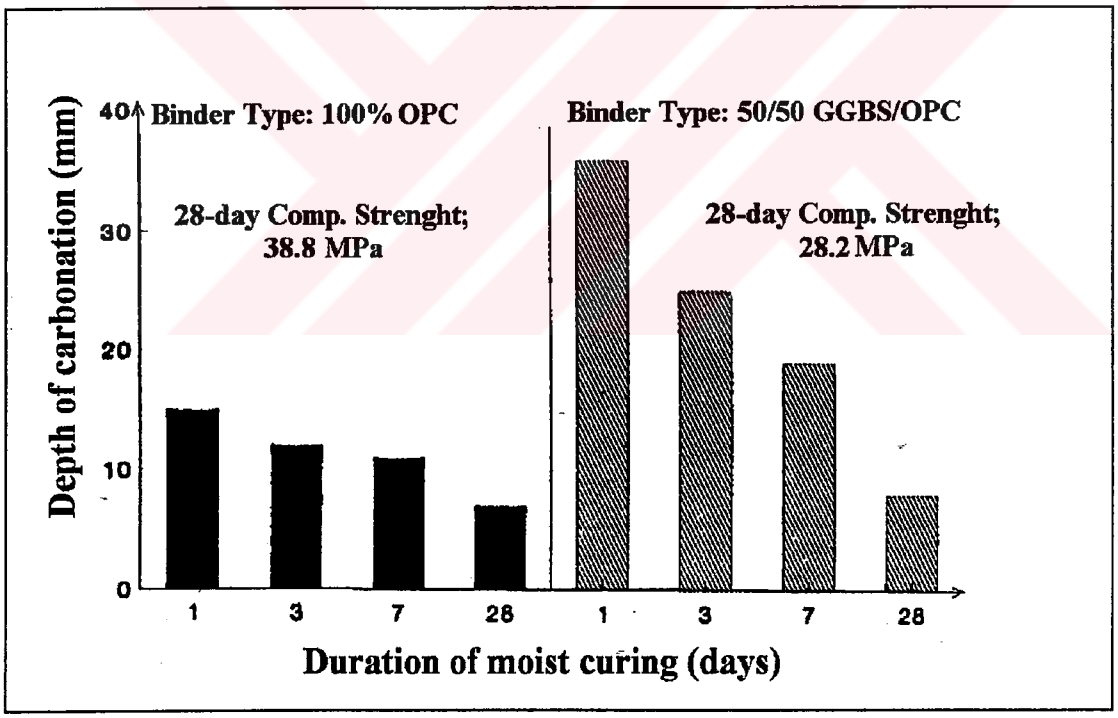

Figure 2.15 Effect of early-age curing on the depth of accelerated carbonation

2.6.3 The Amount of Cement

In concretes with high cement content, the amount of hydration products increases and the diffusion of carbonic gas becomes difficult. Therefore, the speed of carbonation decreases. On the contrary, in low dosage concrete, grains of aggregate approach at each

other, diffusion coefficients of gas drop sharply and become discontinuous. And the diffusion of gas is easier because of insufficient amount of grains of cement to fill the voids between the grains of gravel and voids between cement and aggregate (Akman, 1997).

2.6.4 The Moisture Content of The Concrete and The Relative Humidity

The rate of carbonation depends also on the moisture content of the concrete and the relative humidity of the ambient media. The moisture released by the reaction of CO_2 with $Ca(OH)_2$ must diffuse out in order to preserve hygral equilibrium between the inside of specimen and the atmosphere. If diffusion is too slow the vapour pressure within the concrete rises to saturation and the diffusion of CO_2 into the paste is practically stopped (Neville, 1975).

When pores are saturated, the diffusion of CO_2 into the paste becomes harder. On the other hand, the carbonation process can not develop in the dried concrete because there is insufficient water in the pores within the cement paste for CO_2 to form carbonic acid (Neville, 1975; Akman, 1997).

The results of the measurements of the carbonation depth that are reported by De Ceukelaire and Van Nieuwenburg, are presented in Table 2.2. These values are used to sketch the diagram in Figure 2.16. Two curves are drawn; one for the exposure to the CO_2-enriched atmosphere, and the other for the exposure to the normal atmosphere. The carbonation depth reaches a maximum value at the relative humidity of 50% as can be observed from Table 2.2. This is the case, for the 10 % CO_2 atmosphere as well as in the 0.03 % CO_2 environment. This is a confirmation of the findings of other authors situating the maximum carbonation velocity at relative humidity levels between 50 and 70 % (De Ceukelaire & Van Nieumenburg, 1993).

Table 2.2 Carbonation depths of at different R.H. levels after 21 days

Relative Humidity	Carbonation depth (mm) after exposure in 10 % CO_2	Carbonation depth (mm) after exposure in 0.03 % CO_2
90 %	4.9	0.5
80 %	5.6	0.5
70 %	7.5	0.8
60 %	8.0	0.6
50 %	8.5	1.4
40 %	6.8	0.9

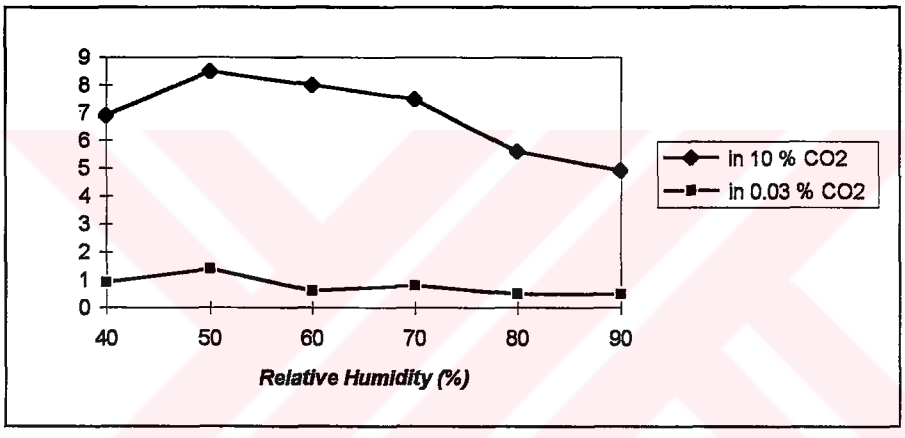

Figure 2.16 The depth of carbonation in relation to the relative humidity in the climate box

2.6.5 Concentration of CO_2

The carbonation process is accelerated by the concentration of CO_2. The rate of carbonation increases within the places like, garages, tunnels, cinemas, etc. Figure 2.16 also shows that the difference between the carbonation depths of CO_2 in an enriched atmosphere and in the normal atmosphere.

High concentration of CO_2 can cause some confusion concerning the comparability of the normal carbonation process and the accelerated carbonation process. Possibly, there is a substantial difference of the microstructural consequences. Moreover, excessive concentration of CO_2 can cause slower carbonation (De Ceukelaire&Van Nieumenburg, 1993; Akman, 1997).

2.6.6 The Temperature of Ambient Media

The speed of carbonation increases with the elevated temperatures at normal temperatures levels. However, excessive temperatures have reverse effects due to drying and due to the decreases of solubility of the gas (Akman, 1997).

2.6.7 The Alkali Content of Cement

It is confirmed through accelerated carbonation tests and exposure tests that were made by Kobayashi and Uno; that the rate of carbonation of concrete is higher with the higher the alkali content of cement, and it is pointed out that alkali in cement, is a factor newly found to have an influence on carbonation of concrete.

Figure 2.17 shows the influences of alkali content in cement on the depth of carbonation of concrete and the results of 16 weeks of accelerated carbonation. It may be comprehended from this Figure that the depth of carbonation increases more or less linearly as the alkali content of cement, that is the value R_2O, becomes higher.

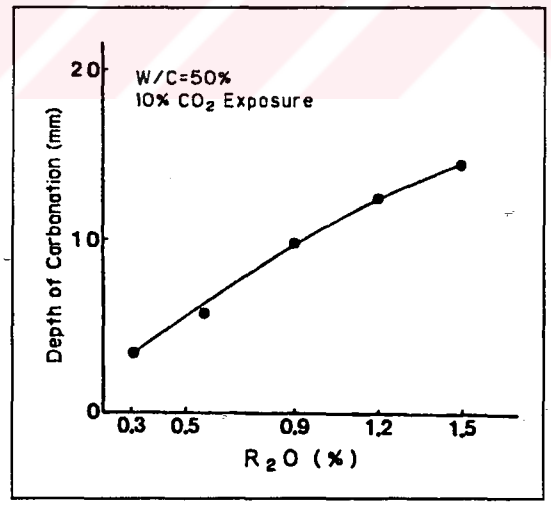

Figure 2.17 Depth of carbonation R_2O relationship (16 weeks accelerated carbonation)

Figure 2.18 shows the effects of water / cement ratio and alkali content of cement on the rate of carbonation. It is clear from this figure that; the rate of carbonation of concrete with water/cement ratio of 0.5 and R_2O of 1.2 %, is approximately equal to the

rate of carbonation of concrete with water/cement ratio of 0.6 and R_2O of 0.57 %. The rate of carbonation of concrete with water cement ratio of 0.4 and R_2O of 1.2 % is approximately equal to the rate of carbonation of concrete of water/cement ratio 0.5 and R_2O of 0.57 %. In other words, with regard to the carbonation of concrete, the influence of an 0.6 percentage point increases in alkali content of cement in terms of R_2O is equivalent to increase in water/cement ratio of 0.1 (Kobayashi & Uno, 1990).

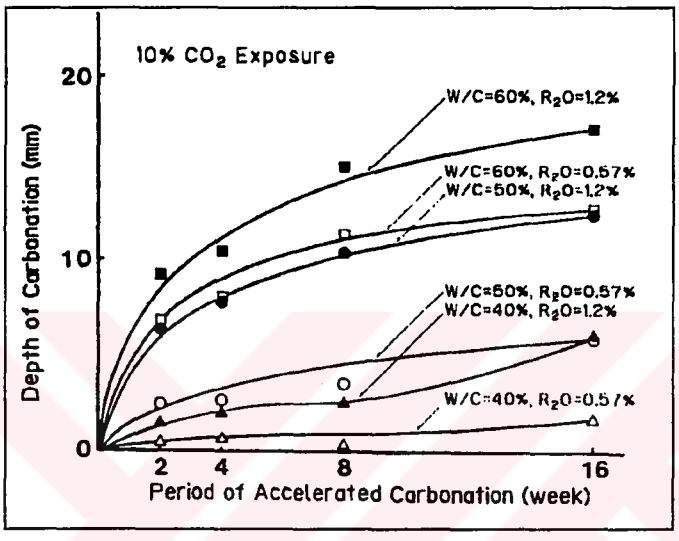

Figure 2.18 Effect of R_2O and water/cement ratio on progress of carbonation

The above mentioned factors that influence the carbonation of concrete, mortar or cement paste are presented in Table 2.3 briefly.

Table 2.3 Factors affecting carbonation and their influence.

FACTOR	INFLUENCE
Water/Cement ratio	The higher the W/C ratio, the higher the carbonation rate
Cure	Inadequate earl-age curing causes an increase in carbonation rate, especially, if blended cements or blended agents are used
The amount of cement	The higher the cement content, the lower the carbonation rate
Relative humidity	Carbonation reaches its maximum value at 50 % relative humidity. No carbonation at dry or saturated conditions.
Concentration of CO_2	The speed of carbonation increases with the higher concentration of CO_2
Temperature	The speed of carbonation increases with the elevated temperatures at normal temperatures levels
The alkali content of cement	The higher the alkali content of cement, the higher the carbonation rate

2.7 Effect of Carbonation on Micro-Structure

The pore structure of Portland cement paste, mortar and concrete was studied by Winslow and Liu. The results show that at similar degrees of hydration, the paste in concrete is more porous than similar paste hydrating in the absence of aggregate. The difference is more pronounced as the hydration increases. This difference would be even greater if the pastes were compared at equal ages since the paste in the concrete hydrated more rapidly than the plain paste. Moreover, within a sample type, accelerating or retarding the hydration by changing the temperature did not significantly changing the intruded pore volume of the paste when all pastes were allowed to hydrate equally. Not only are the total intruded pore volume the same for different hydration situations, but distributions of the pore volumes are also similar. The only variable that altered the pore volume, within a type of sample, was the water/cement ratio.

In this research, all samples were tested at two different degrees of hydration : approximately 9.5% and 14.5% non-evaporable water content. Summary of average data for samples shown in Table 2.4. All samples were hydrated at 20 °C (Winslow&Liu, 1990).

Table 2.4 Summary of average data for samples

Sample type	W/C	Age at test (days)	Non-evaporable Water Content	Total Intruded Pore Volume (cm^3/g)
Less Hydrated Saples				
Paste	0.45	1.5	0.099	0.277
Mortar	0.45	0.9	0.091	0.285
Concrete	0.45	0.9	0.098	0.307
Paste	0.55	1.1	0.093	0.352
Mortar	0.55	1.1	0.093	0.348
Concrete	0.55	1.1	0.090	0.339
More Hydrated Samples				
Paste	0.45	21.0	0.148	0.191
Mortar	0.45	20.0	0.148	0.229
Concrete	0.45	20.0	0.148	0.242
Paste	0.55	21.0	0.148	0.241
Mortar	0.55	11.0	0.145	0.294
Concrete	0.55	14.0	0.141	0.287

it can be observed that the pore size distributions of the paste in mortar and concrete have similar characteristics as those of plain pastes from Figures 2.19 to 2.22. However, the paste in mortar and concrete is more porous than the corresponding plain paste. This difference is much more pronounced in the case of the more hydrated samples. Much of the additional pore volume occurs in pores with diameters greater than the threshold diameter of the plain paste. This result indicates that the presence of the aggregate does influence the micro-structure of the paste that forms around it.

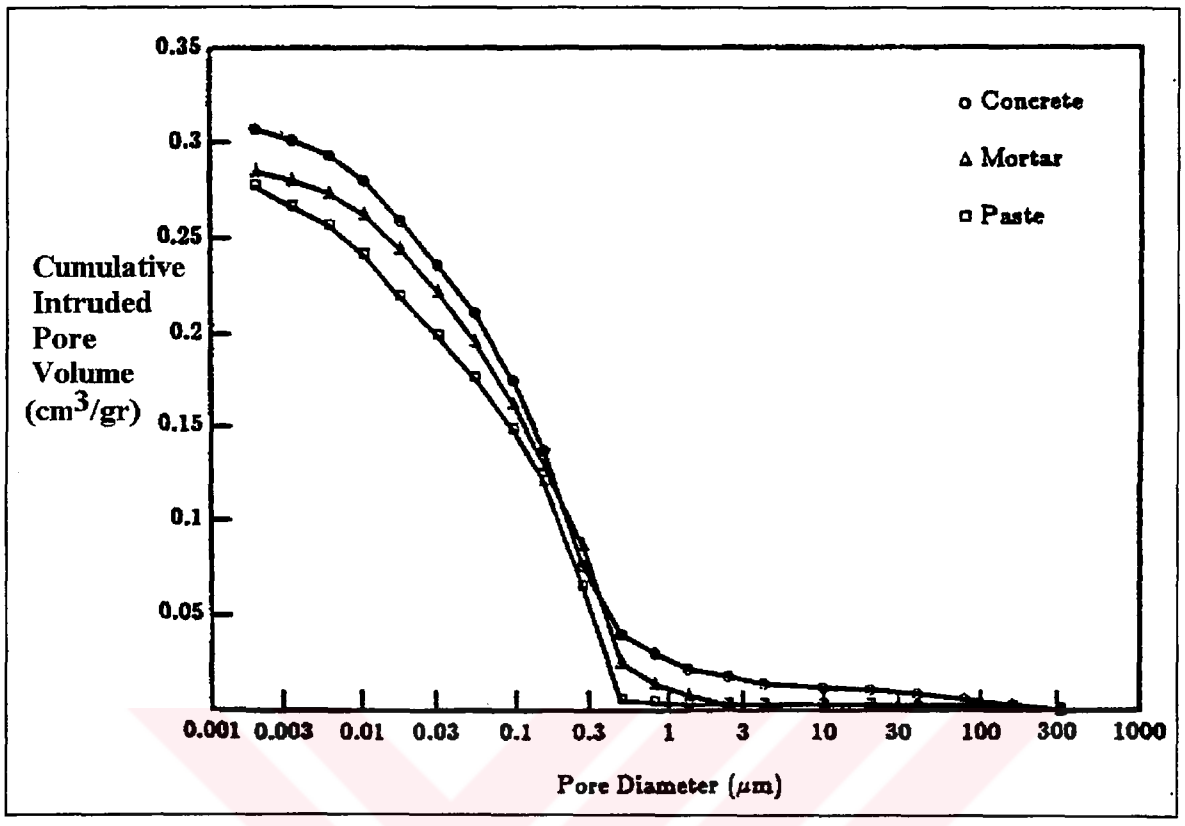

Figure 2.19 Pore structure of less hydrated samples, W/C= 0.45

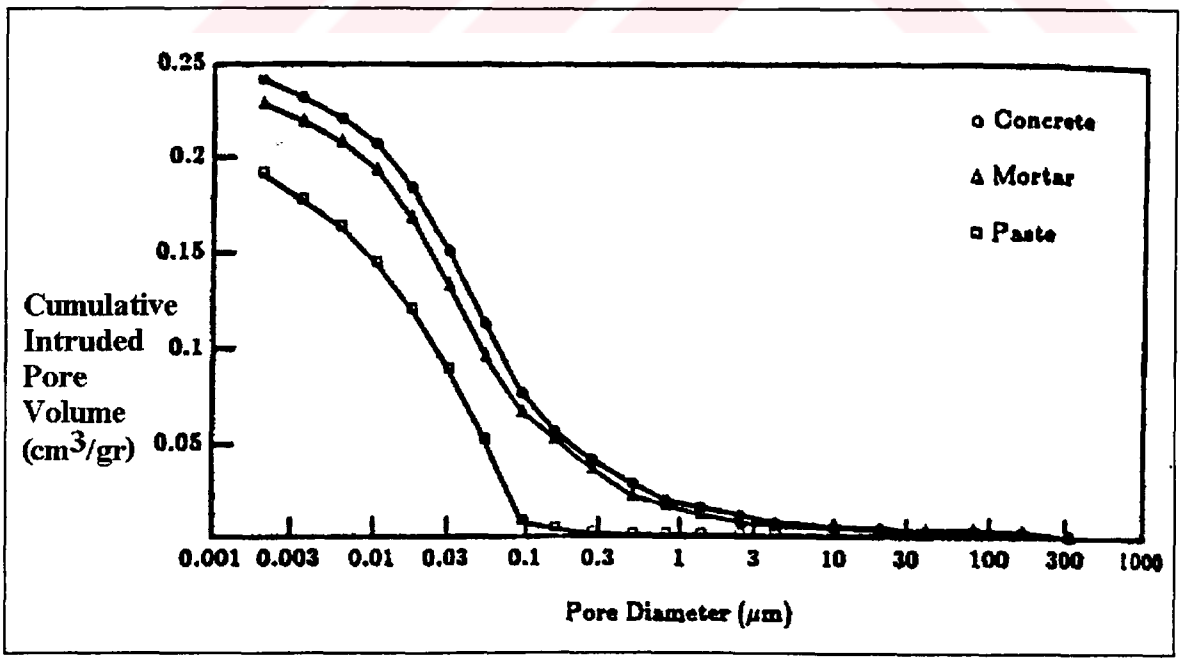

Figure 2.20 Pore structure of more hydrated samples, W/C= 0.45

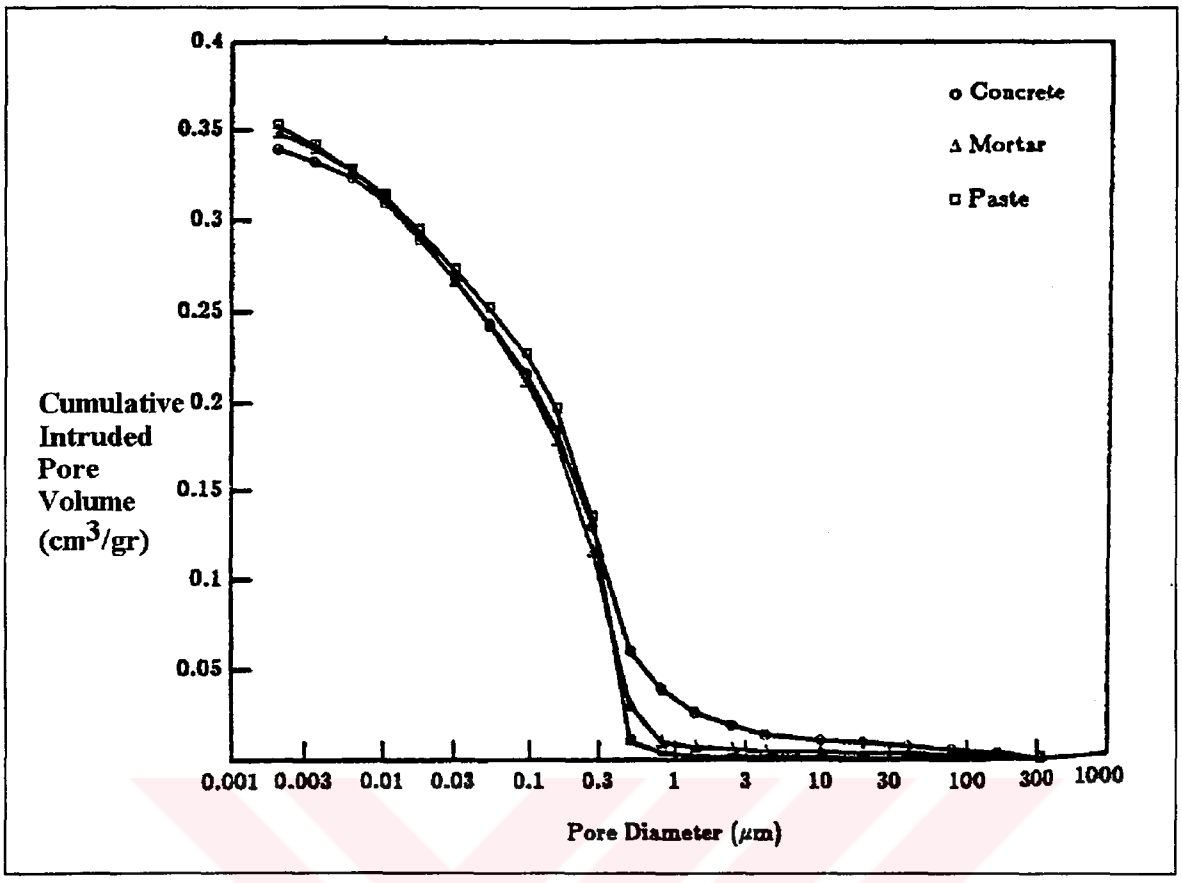

Figure 2.21 Pore structure of less hydrated samples, W/C= 0.55

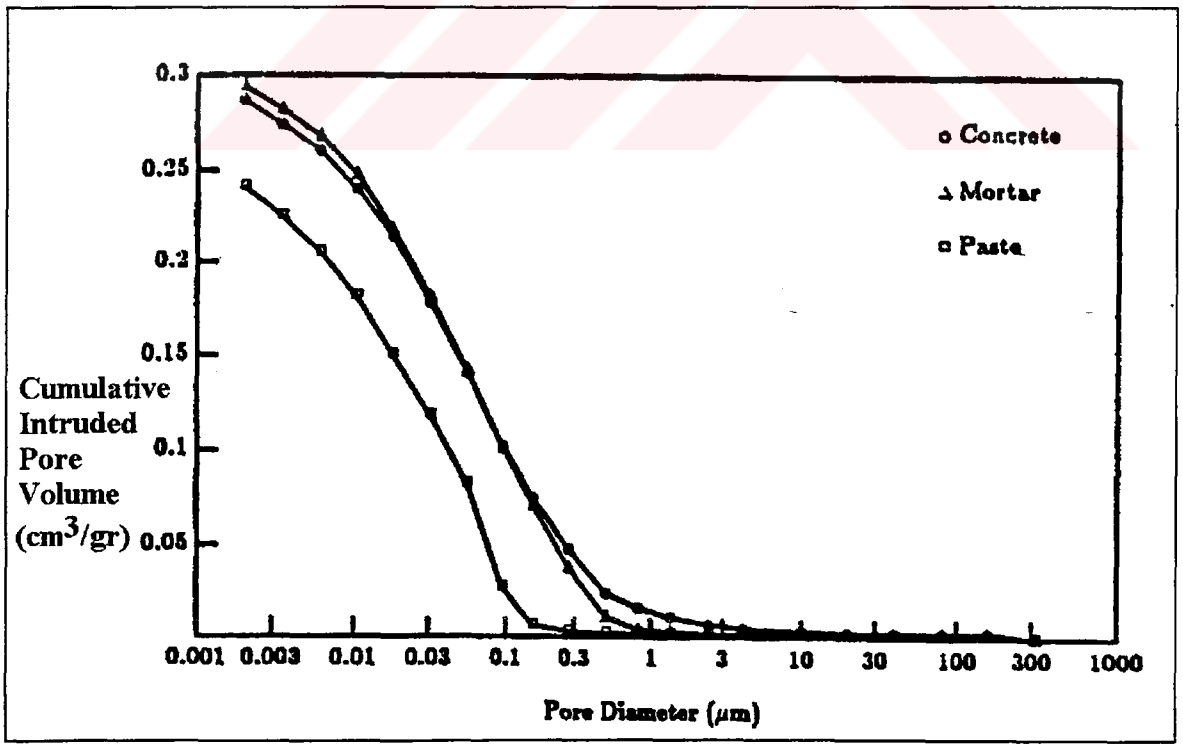

Figure 2.22 Pore structure of more hydrated samples, W/C= 0.55

There are two aspects to this result. One is that the additional pore volume in concrete paste lies in the largest pore size range. These are the pores that are most likely to affect properties such as permeability and durability in an adverse way.

The other important aspect is that the pore structure of plain paste is not a good model for the porosity of the paste as it exists in concrete.

The results of this study show that the paste that develops in a mortar has pore structure that is much closer to that which develops in concrete than that of plain paste. The similarity is more pronounced in the more mature samples. This finding is not unexpected, because the fine aggregate, possessing the majority of the surface area of the total aggregate, would be expected to be the major factor in any alteration of the paste. A practical consequence of this is that the pore structure of the paste in mortar may be an adequate model for that in concrete, and is much easier to study (Winslow&Liu, 1990).

Carbonation creates considerable modifications in the micro-structure of the cement paste and concrete. The radii of some pores and specific surface values decreases significantly after carbonation.

Carbonation results in the formation of new solid compounds which are deposited in the pores of the matrix, while the original phases of the hydrated cement paste are decomposed. These changes in the mineralogical composition are accompanied by changes in the pore structure.

Carbonates which become as a result of chemical reactions, have three forms that are vaterit, calsite and aragonit. Increase in volume, due to carbonates, are in order 19 %, 12 % and 3%. Calsite has a thermodynamic stability at normal temperature levels but others are stable over 30 °C. These volume changes cause significantly reduction of pore volume and specific surface (Akman, 1997).

Effect of carbonation and rate of hydration on micro-structure of cement paste can be seen Figure 2.23 that was reported by Gunter, Bier and Hilsdorf. In diagram the cumulative pore volume of carbonated and non-carbonated zones in hydrated paste samples was plotted

as a function of the pore radius. The samples have been cured in water up to an age of 7 days. Subsequently they were stored in air at 20 °C, 65 % r.h., CO_2 content 0.03% and 2.0 %, respectively. Figure 2.23 shows the cumulative pore volume of the pastes immediately at the end of the 7 day curing period and after approximately half a year of drying. For Portland cement paste samples taken from the interior parts of the specimens continued hydration without carbonation caused a reduction in total pore volume and a shift to smaller pore sizes (curve 1 and 2). For the samples taken from the carbonated surface regions total pore volume and pore size are substantially reduced even more (curves 3 and 4) (Gunter& Bier&Hilsdorf, 1987).

Figure 2.23 also shows the effect of CO_2 concentration on the pore size distribution for pastes made of Portland cement. Carbonation causes a pronounced reduction in total pore volume which is slightly larger for the higher CO_2 concentration.

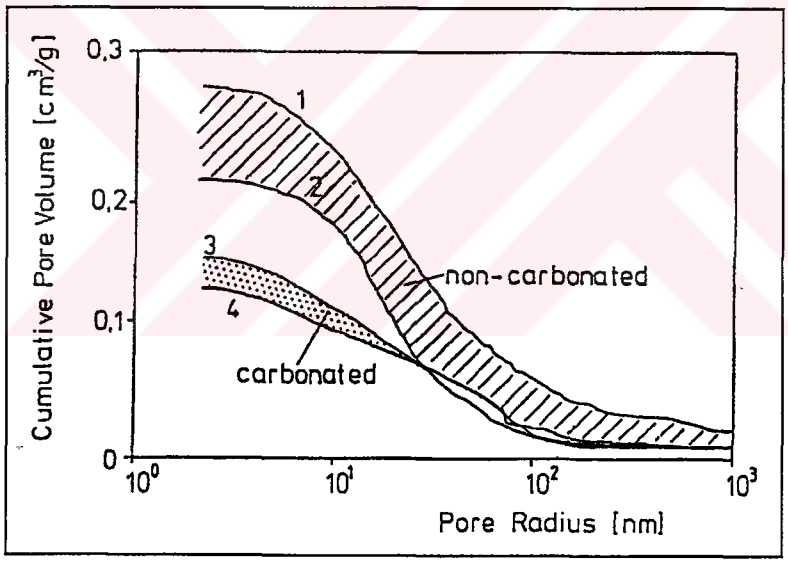

Figure 2.23 Effect of carbonation on cumulative pore volume of cement paste made of PC

In Figure 2.23, W/C ratio of specimens is 0.50. Curve 1 shows 7 days old non-carbonated specimen. Curve 2 shows 6 months old non-carbonated specimens. Curve 3 shows 6 months old specimen carbonated at 0.03 percent CO_2. Curve 4 shows 1 month old specimen carbonated at 2 percent CO_2 (Gunter et.al., 1987).

It was reported by Houst as a result of experimental research that the accelerated carbonation of hardened cement paste and mortars leads to large modification of the porous system. The lower the water/cement ratio or, in other words, the porosity, the higher the reduction of porosity. The pore-size distributions, measured by mercury intrusion porosimetry, show that the pores of all sizes are affected. Therefore in hardened cement paste (hcp) of W/C ≤ 0.5, the volume of the pores with a radius < 0.1 μm especially decreases. The BET (Brunauer-Emmett-Teller) specific surface area was also reduced of 50 % by carbonation (Houst, 1993).

Figure 2.24; Figure 2.25 and Figure 2.26 show pore size distribution of carbonated and non-carbonated hcp at different W/C ratios.

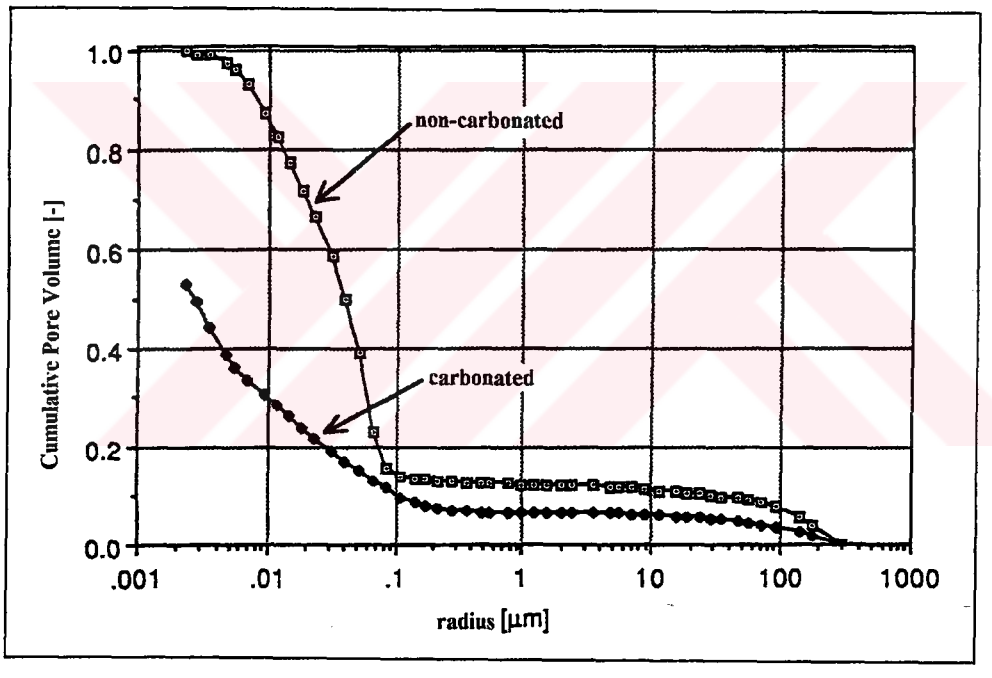

Figure 2.24 Pore size distribution of carbonated and non-carbonated hcp at W/C=0.4

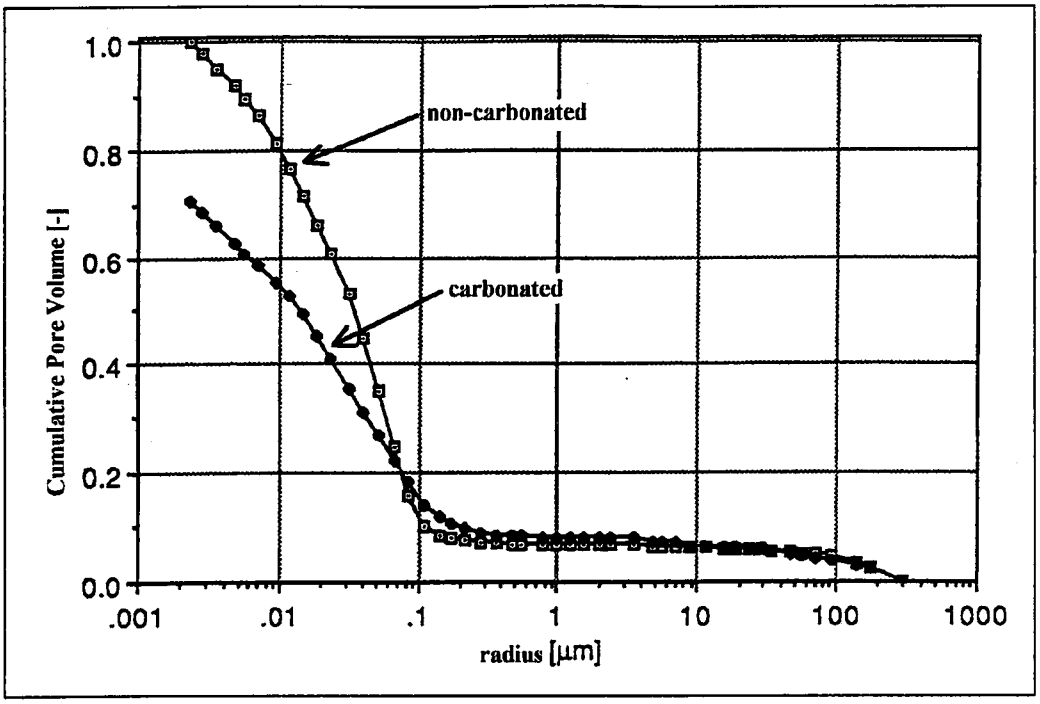

Figure 2.25 Pore size distribution of carbonated and non-carbonated hcp at W/C=0.5

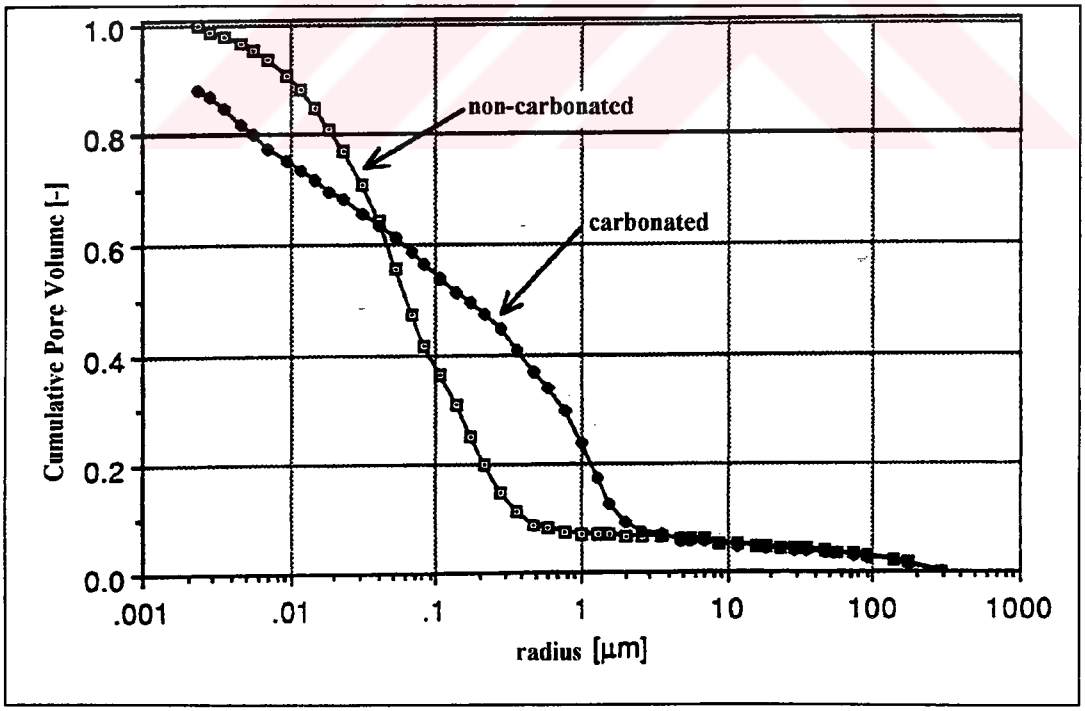

Figure 2.26 Pore size distribution of carbonated and non-carbonated hcp at W/C=0.8

The porosity of the studied mortars by Houst was little modified by carbonation. This is due to the high level of large pores in these mortars, which is much higher than that of hcp.

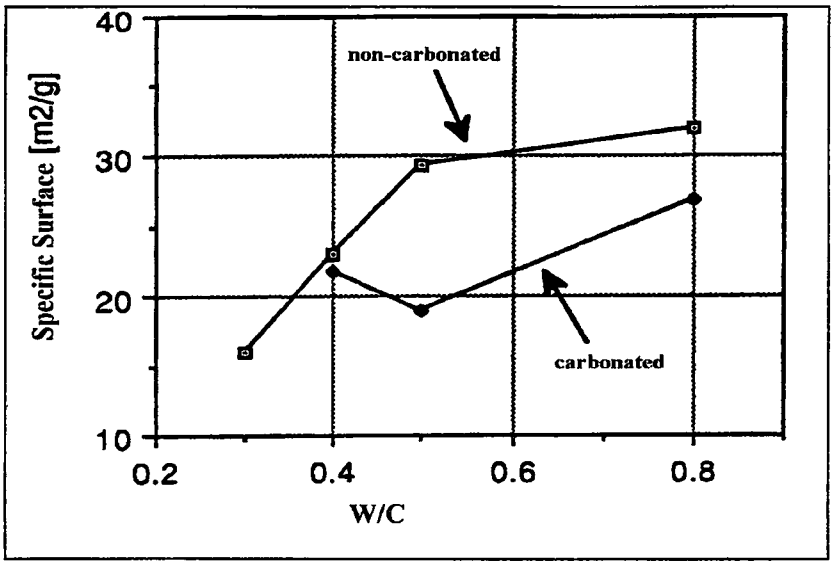

Figure 2.27 Influence of carbonation on specific surface with regard to pores

Figure 2.27 shows specific surface values carbonated and non-carbonated samples that have different W/C ratios. It is clear from Figure 2.27 that specific surface values of samples decreases with progress of carbonation.

2.8 Carbonation Shrinkage

An adequate explanation has not been done yet about carbonation shrinkage. However, there are different theories. One of the approach states that carbonation shrinkage occurs due to evaporation of water which is produced by chemical reactions. Another theory claims that the dissolving of crystals of $Ca(OH)_2$ under compressive stress and deposit in pores free from stress, and consequently, the compressibility of the cement paste is increases. In this theory it is accepted that carbonation of the hydrates present in the gel does not contribute to shrinkage. Hovewer, carbonation of the hydrates can be cause shrinkage. So, both approaches can be accepted as valid theories (Akman, 1997; Neville, 1981).

Carbonation is accompanied by an increase in the weight of the concrete and by shrinkage. When concrete dries and carbonates simultaneously, the increase in weight on

carbonation may at some stage give the misleading impression that the drying process has reached the stage of constant weight, i.e. equilibrium. Figure 2.28 shows loss-of weight of concrete due to drying and carbonation graphically.

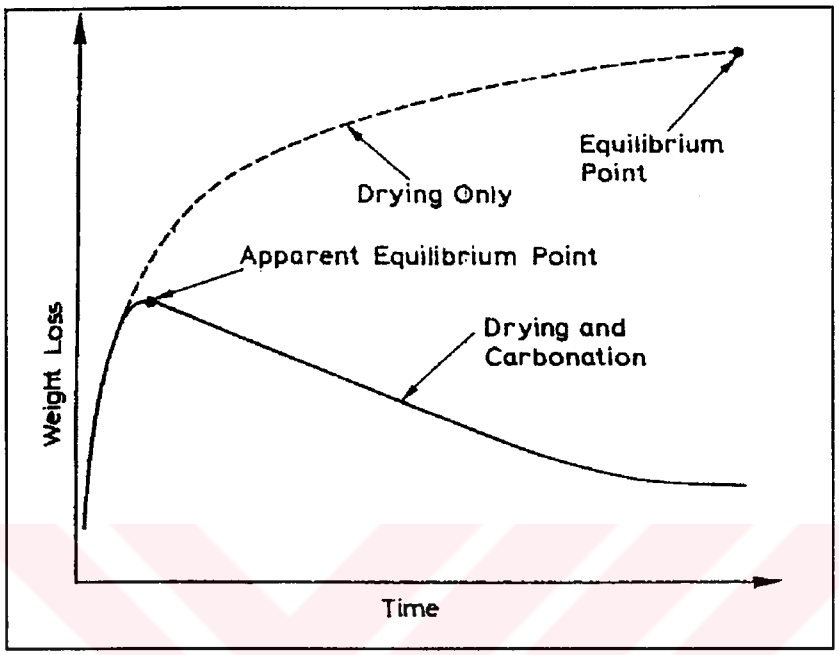

Figure 2.28 Loss of weight of concrete due to drying and carbonation

Figure 2.29 shows the drying shrinkage of mortar specimens dried in CO_2-free air at different relative humidities, and also the shrinkage after subsequent carbonation. Carbonation increases the shrinkage at intermediate humidities, but not at 100 per cent or 25 per cent. In the latter case, there is insufficient water in the pores within the cement paste for CO_2 to form carbonic acid. On the other hand, when the pores full of water the diffusion of CO_2 into the paste is very slow; it is also possible that the diffusion of calcium ions from the paste leads to precipitation of $CaCO_3$ with a consequent clogging of surface pores.

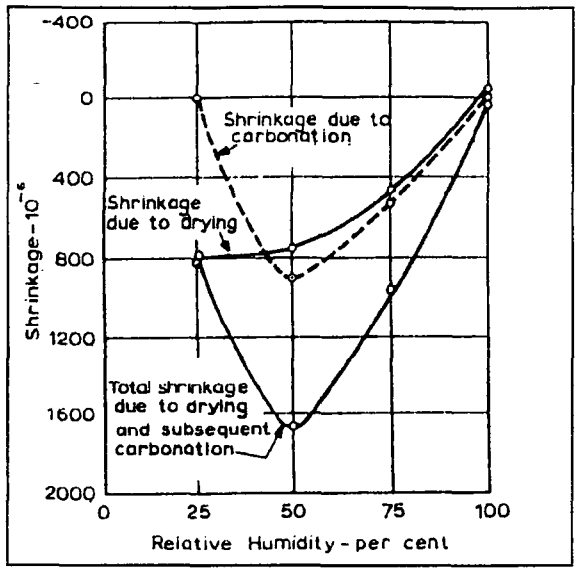

Figure 2.29 Drying shrinkage and carbonation shrinkage of mortar at different relative humidities.

The sequence of drying and carbonation greatly affects the total magnitude of shrinkage. Simultaneous drying and carbonation produces lower total shrinkage than when drying is followed by carbonation. Figure 2.30 shows influence of the sequence of drying and carbonation of mortar on shrinkage.

Carbonation shrinkage of high-pressure steam cured concrete is very small.

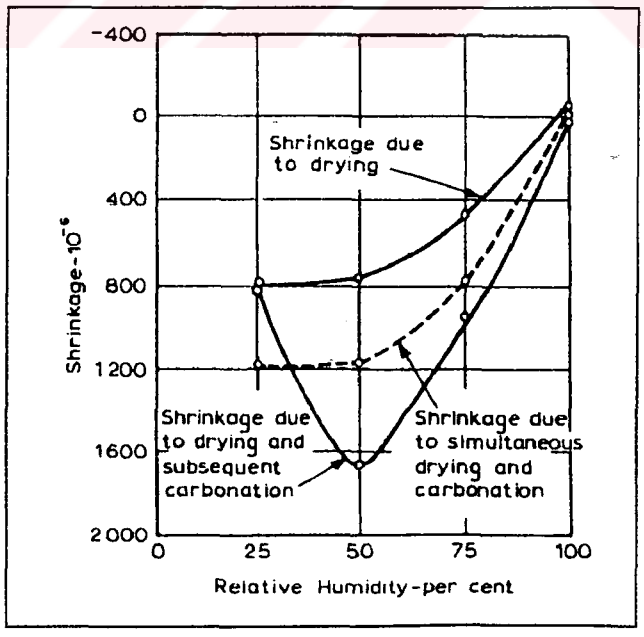

Figure 2.30 Influence of the sequence of drying and carbonation of mortar on shrinkage.

When concrete is subjected to alternating wetting and drying in air containing CO_2, shrinkage due to carbonation (during the drying cycle) becomes progressively more apparent. The total shrinkage at any stage is greater than if drying took place in CO_2 -free air, so that carbonation increases the magnitude of shrinkage and may contribute to crazing of exposed concrete.

However, carbonation of concrete prior to exposure to alternating wetting and drying reduces the moisture movement, sometimes by nearly a half. A practical application of this is pre-carbonate precast products immediately after demoulding by exposing them to flue gases. Concrete with a small moisture movement is then obtained (Neville, 1981).

2.9 Creep Due to Carbonation

Carbonation, the formation of carbonates due to the presence of carbon dioxide in the atmosphere, changes the structure of hardened cement paste, causing a gain in weight and shrinkage. In the case of structural concrete, only the surface layer becomes carbonated and, although this is important with respect to corrosion of reinforcement steel, the volume carbonated is a small proportion of the total volume of the concrete. In the laboratory, however, the carbonated volume can become a substantial proportion of the volume of the specimen. It seemed possible that carbonation might affect the creep of laboratory specimens. The possible effects of carbonation upon the creep of small laboratory specimens was studied by Parrott, using prisms of hardened cement paste with a water/cement ratio of 0.47.

The test results clearly indicate that carbonation during a creep test on hardened cement paste substantially increase creep strains. Similar behavior is to be expected for concrete, although the magnitude of any increase in creep will depend upon time and upon size of specimen (Parrott, 1975).

Creep strains (i.e.total time-dependent strains minus control specimen strains) of loaded specimens strains and changes in weight of both loaded and control specimens are shown from Figure 2.31 to Figure 2.33.The carbonating control specimens exhibited a considerable shrinkage accompanied by a gain in weight. The weight changes of loaded and

corresponding control specimens were virtually the same for both carbonating and non-carbonating groups. The creep strain of the carbonating specimens was 70% greater than that of the non-carbonating specimens after seven weeks under load. In another experiment using the same apparatus and method, but with specimens having a higher drying surface to volume ratio, virtually identical results were obtained by Parrott. Furthermore, a similar increase in creep was also measured in tests where carbonation began 29 days after loading. Thus, for example, the increase in creep after three weeks of carbonation were 50 %, 45 % and 50 % for the three experiments (Parrott, 1975).

Thermal analysis and carbon dioxide measurements indicated that the calcium hydroxide was converted to calcium carbonate and this seemed, from measurements of pore structure, to be deposited in the spaces left by calcium hydroxide and in the fine pores; there was no indication of carbonates being deposited in the largest pores.

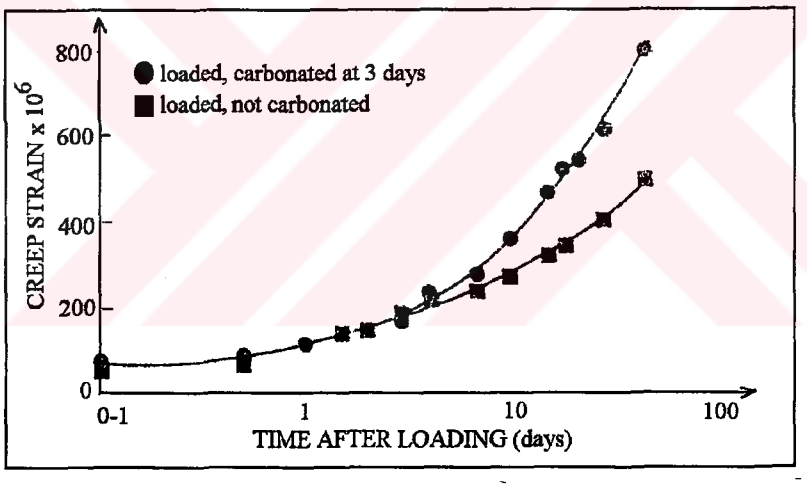

Figure 2.31 Creep strain of the specimens

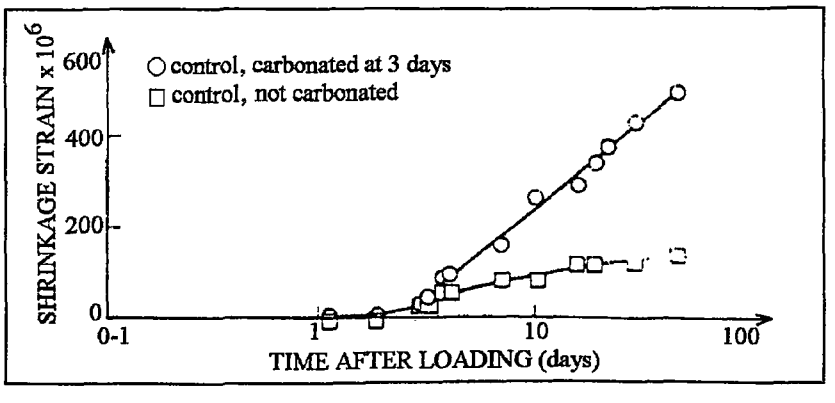

Figure 2.32 Shrinkage strain of the specimens

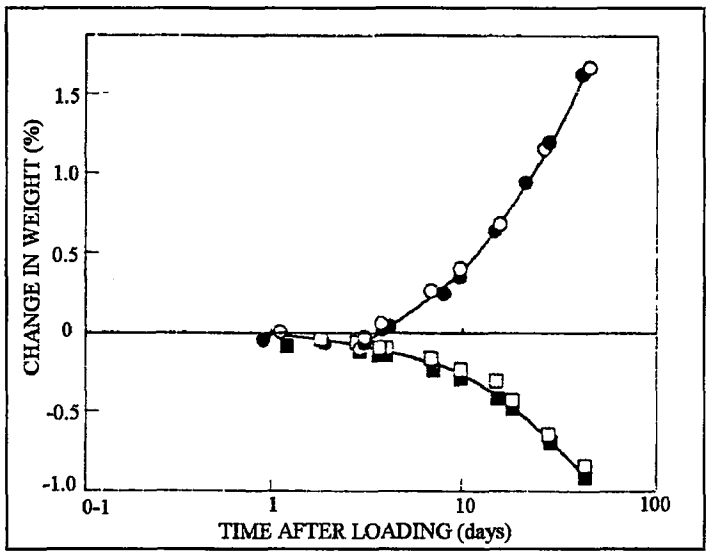

Figure 2.33 Weight changes of the specimens

The CSH and calcium hydroxide, which constitutes a proportion of the hydrated cement, forms part of the load-bearing skeleton of hardened cement paste and the extra creep during carbonation results from its loss of load-bearing ability during chemical conversion. This is similar to the explanation of carbonation shrinkage. Increase in creep of a loaded material have been previously observed by Greenwood and Johnson in a range of metals with different crystal structures (Parrott,1975).

It should be noted that, carbonation before loading reduces the amount in creep of concrete. This is probably due to the reduction in porosity resulting from deposition of the carbonation reaction products in the pores of hardened cement paste. Such an explanation is consistent with the measured increases in strength that resulted from carbonation (Parrott, 1975; Akman, 1997).

2.10 Corrosion of Reinforcement

As is known, steel in concrete is protected against corrosion by the fact that, owing to the alkalinity of the pore water (pH= 12.5 - 13.5) a microscopic oxide layer is formed on the steel surface preventing the anodic dissolution of iron.

If this pH-value drops below pH= 9 due to carbonation or the chloride content exceeds a certain critical value, the passivated coating and, consequently, the corrosion protection will be lost locally or over greater surface areas.

Excluding the case of chlorides being added to the concrete mix, corrosion of reinforcement will only be possible after carbonation or a harmful amount of chlorides has reached the surface of the reinforcement.

The initiating processes (carbonation, chloride penetration) and the deterioration process (corrosion of reinforcement) are influenced by different parameters. Therefore, if one is looking for answer of questions of service life, the initiation period and the propagation period must be treated separately. The situation is presented schematically in the Figure 2.34.

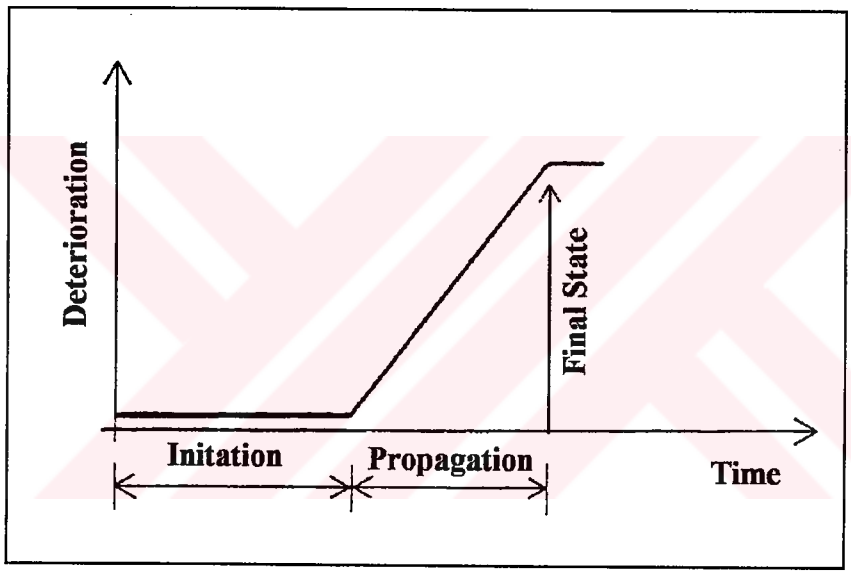

Figure 2.34 General deterioration scheme

During the initiation period carbonation, chlorides or other harmful agents will penetrate towards the reinforcement. During the propagation period the reinforcement will corrode, the final state being reached, if a certain limit of deterioration is exceeded. The final state means, that the end of the life time has been reached or repair measures are necessary.

An electro-chemical corrosion element consists of cathode and anode that must be connected together both electrically and electrolytically. As regard reinforcement embedded in concrete, the reinforcing bar will act as an electrical conductor and the pore water of the concrete as electrolyte.

Anode and cathode may be found on the steel surface either close together (micro element) or at locally separated places (macro element), a fact that requires the conductivity of the electrolyte (pore water) to be given special consideration.

Simplified, the corrosion process can be separated into two single processes, the cathodic and anodic process.

The anodic process is the real dissolution of iron. Positively charged iron ions pass into solution:

Anodic process: $Fe \longrightarrow Fe^{++} + 2e^{-}$ (2.9)

The surplus electrons in the steel will combine at the cathode with water and oxygen to form hydroxide ions.

Cathodic process : $2e^{-} + 1/2\ O_2 + H_2O \longrightarrow 2(OH)^{-}$ (2.10)

After some intermediate stages the iron and hydroxide ions will be combine to form rust which can be written theoretically as Fe_2O_3.

$4Fe + 3O_2 \longrightarrow 2Fe_2O_3$ (2.11)

During the corrosion process only oxygen is consumed to produce the corrosion products. Water is necessary only to enable the electrolytic process to take place.

Depending on the environmental conditions, the following parameters may be controlling factors in the determination of the corrosion rate:

- supply of oxygen at the cathode (diffusion from the surface)
- electrolytical conductivity of concrete (water content, concrete mix)
- cathodic polarization resistance
- relation between anodically and cathodically acting surface areas (in connection with electrolytical conductivity)

Figure 2.35 shows electro-chemical corrosion of reinforcement in a concrete schematically.

As a consequence of the interrelations corrosion will not occur, neither in dry concrete (electrolytical process impeded) nor in water-saturated concrete (loss of oxygen), even passive layer at the surface of the reinforcement has been destroyed.

Within the anodically acting areas, the passive layer must be destroyed, the cathodic process however can take place, even if the passive layer is intact.

In the case of chloride-corrosion, this effect causes the called pitting corrosion, because the passive layer will be dissolved only over small surface areas, so that small anodic areas and huge cathodic areas will exist on the surface, a fact that causes substantial reductions in section of the reinforcement. In addition, the chloride ions will act as a catalyst in the pit and accelerate the dissolution of iron in the anodically acting pit.

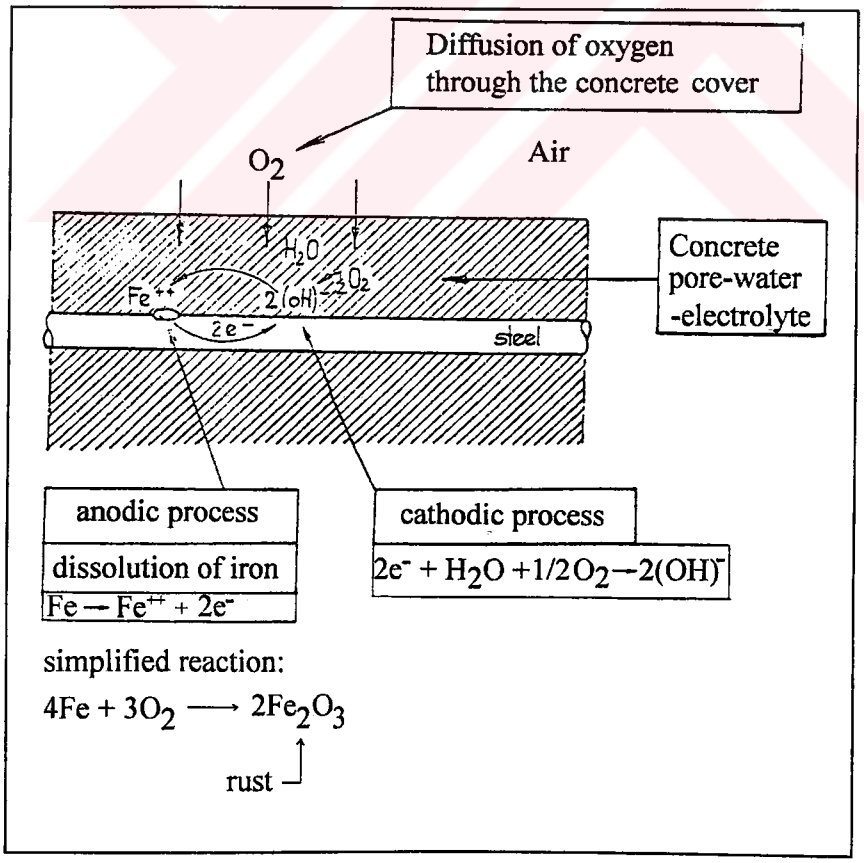

Figure 2.35 Electro-chemical corrosion of reinforcement

The conditions leading to corrosion and the interrelations influencing the corrosion rate are shown in Table 2.4

If the passivation on the steel surface is destroyed within a strictly confined area, e.g. within the region of cracks in concrete or peaks of carbonation that reach to the surface of the reinforcement, then the situation and distribution of anodically and cathodically acting bar regions will become an important factor with regard to the rate of corrosion. The theoretical possibilities are explained in Figure 2.36 with 3 models.

Table 2.5 Electro-chemical corrosion of steel in concrete pre-conditions and interrelations

Pre-conditions	Depending on	Influenced by	Possibilities to prevent corrosion or to decrease corrosion rate
electrical conductivity of steel to convey electrons	exist in all cases	-	-
potential differences on the steel surface to start the electrochemical process	exist in all cases	-	-
electrolytical conductivity of concrete to convey hydroxide ions	amount of H_2O in concrete	environmental conditions, permeability of concrete	increase of concrete cover
anodic dissolution of iron to induce electro-chemical process	PH<9 caused by carbonation or aggressive anions (Cl^-)	concrete cover, permeability of concrete, concrete mix, cracks, crack-widths	decrease in permeability of concrete
oxygen in the electrolyte to form rust products	diffusion of oxygen from the surface of concrete to the surface of steel	concrete cover, permeability of concrete, amount of H_2O in concrete, cracks	(to a certain extent limitation of crack widhts)

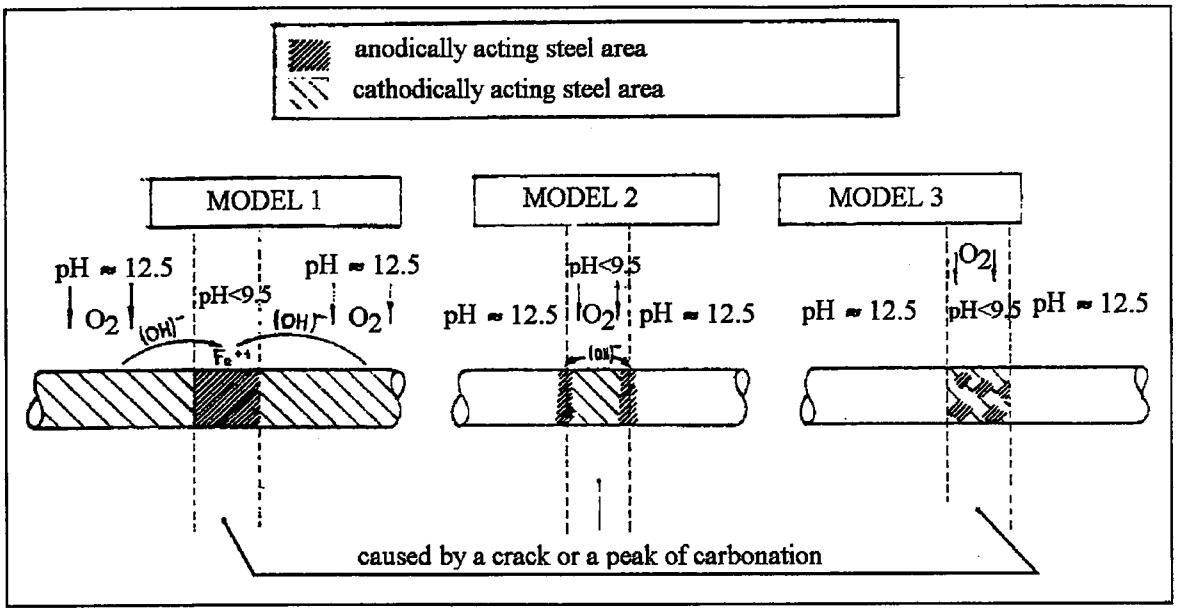

Figure 2.36 Models of the corrosion process in the region of locally reduced alkanity of concrete

A combination of the three models can be observed in practice.

In the region of concrete cracks it should further be considered that owing to the slip existing between steel and concrete, the active steel surface will not be confined to the actual cross-section of the crack.

Depending on the specific environmental and concrete conditions, the maximum corrosion rate can be assumed in the range between 60 and 200 μ/year (CEB&RILEM, 1983).

2.10.1 Influence of Cracks

Within the region of cracks carbonation can penetrate to the reinforcement at a higher rate than in uncracked concrete. In reinforcement concrete construction the width of cracks cannot be limited to such an extent that corrosion during the whole service life of the structure could be completely ruled out. Yet, the width of cracks is no longer to be regarded as a major factor in corrosion protection of the reinforcement. Carbonation in the region of smaller cracks, will reach the reinforcement only at a later time than in that of wider cracks. From this point, however, the rate corrosion is almost independent of the crack width, as the diffusion of oxygen is in general not influenced by the width of cracks.

Corrosion normally tends to cause only a small reduction of the bar diameter so that a sufficiently long service life is to be expected, provided that the bars applied are not too thin.

The thickness of concrete cover is of major importance due to the fact that with increasing thickness of cover the risk of concrete being spalled off by corrosion products will be reduced.

Cracks proceeding transverse to the reinforcement are less harmful than longitudinal cracks (related to the direction of the reinforcement). This is due to fact that in the case of transverse cracks corrosion is confined to a small surface area, so that the risk of spalling off of the concrete cover will not exist.

No reliable findings are reported on the danger of corrosion of reinforcement of structural elements in soil or immersed in water (not sea water). It can, however, be assumed that the reinforcement of structural elements permanently surrounded by wet soil (without aggressive substances) or submerged is not likely to corrode, as the concrete will not or hardly not carbonate. Yet, the danger of corrosion appears to be existent at the soil/air or water/air interface respectively, and here particularly in those regions where dry conditions change into wet ones, involving carbonation of concrete on one hand and on the other hand accelerated corrosion to take place at the reinforcement.

All the processes influencing corrosion of reinforcement are more or less controlled by diffusion processes:

Carbonation: diffusion of CO_2

Penetration of chlorides: diffusion of chlorides

Corrosion of reinforcement: diffusion of O_2

Therefore, the major parameter in connection with corrosion and protection of the reinforcement is the quality of the concrete cover. This quality can be defined as thickness of concrete cover and permeability of concrete cover (CEB&RILEM, 1983).

2.11 Realkalization

As the corrosion of the reinforcement is important for service life of structure, some passive and active realkalization methods are developed to reinstate alkalinity of the carbonated concrete.

Passive method consist of application of lime-cement mortar coating. Provided that its water/cement ratio is relatively low and its lime content high, a lime-cement mortar coating of the usual thickness around 20 mm is found to be an extremely effective means of postponing or even preventing carbonation-induced corrosion initiation. It postpones the onset of concrete carbonation by the time required for carbonation to fully penetrate the coating, and it retards its further penetration into the concrete because atmospheric CO_2 has to travel further to reach the carbonation front. Its effectiveness is not reduced very much even if it is applied to the concrete surface several months or even a few years after the end of the concrete curing period. Application of such surface coating to carbonated concrete several years old arrests advancement of the carbonation front and reinstates alkalinity of the carbonated concrete region to its high value above the threshold of steel depassivation. In fact, such an application of a mortar coating may appreciably prolong the service-life of already carbonated concrete, hence may be considered as an effective, easy and inexpensive repair method for carbonation-afflicted concrete. In this method, lime-cement mortar coating must be kept wet for a long time to penetrate Ca^{++} and OH^- ions to deeper layer of concrete. Only pore water reinstates alkalinity of the carbonated concrete so; effective contribution of coating may be lost with drying (Papadakis et al, 1992; Akman, 1997).

Experimental research that is made by Bier, Kropp and Hilsdorf, shows a high alkalinity may be restored in a carbonated concrete zone by application of a cement mortar overlay. If sufficient moisture is available in the pore system the diffusion of alkaline substances from the overlay into the carbonated zone will raise the pH of the pore solution to a high alkaline level. However realkalizition is not limited to restoring a high alkalinity but involves also phase transformations in the carbonated matrix. In Figure 2.37 results from infrared spectroscopy (IRS) shows that CSH prevailing in the original, not carbonated matrix was decomposed by carbonation to form calcium carbonate (CC) and silica gel (SH). In a

realkalized matrix, silica gel disappears and those of CSH are reestablished in the presence of calcium carbonate. These results show that the amorphous and finely distributed silica gel is highly reactive and forms new CSH-like phases with penetrating alkalies. The existing calcium carbonate remains unaffected.

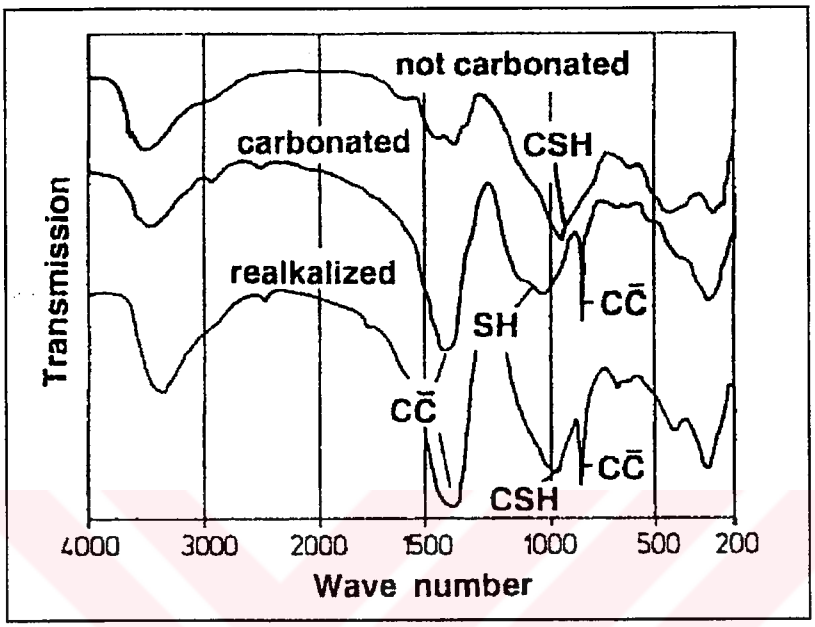

Figure 2.37 IRS-transmission of non-carbonated, carbonated and realkalized cement paste matrix

The reformation of CSH phases in the realkalized zone also changes the pore structure as shown in Figure 2.38. with increasing duration of realkalization a reduction of the coarse pores with $10<r<100$ nm occurs, and new very fine pore spaces are created with $r<10$ nm. This observation may be explained by the growth of CSH-like phases in the pores of reactive silica gel. Due to these modifications the realkalized zone becomes much denser than the original or carbonated matrix (Bier et.al., 1989).

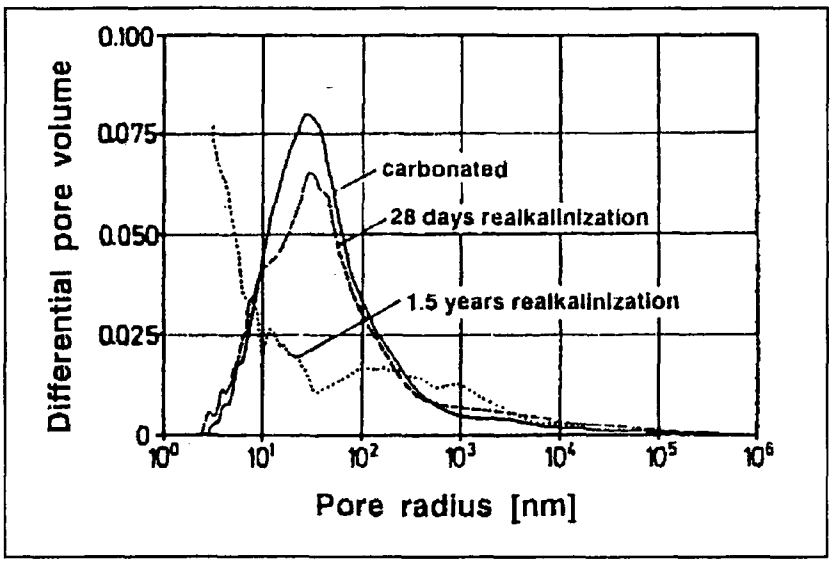

Figure 2.38 Differential pore size distribution in carbonated and realkalized cement paste matrix of Portland Blast Furnace Slag Cement (PBFSC) concrete

Active realkalization method is like cathodic corrosion protection method with direct current. A current conducting mesh as the anode (e.g. made out of copper wires, which are coated with a conducting polymer.) which is plastered close to the surface, is saturated with electrolyte which consist of sodium carbonate. Direct current with 1 A/m^2 is applied for 3-7days so, Na^+ and OH^- ions penetrate to the concrete and raise the pH value of the concrete to 11. But this method have some negative effects such as alkali-aggregate reaction if concrete aggregate has an active silica or reinforcement steel may become brittle due to hydrogen. Furthermore, the bond between concrete-reinforcement may weaken (Kavalalı, 1994; Akman,1997).

2.12 Research Techniques

There are various research techniques for determining the rate of carbonation. As the carbonated and uncarbonated portions of the concrete have different pH values, the most popular and easy method is using indicators that show different colours in different pH regions.

Carbonation results in the formation of new solid compounds while the original phases of the hydrated cement paste are decomposed. As, the structure of carbonated cement paste, mortar or concrete is different from those of uncarbonated, some techniques which have

been used in a material science, can be used to determine, identify or estimate the structure of components of carbonated or uncarbonated cement paste, mortar or concrete and carbonation rate. These techniques are mentioned below briefly.

2.12.1 Using Indicators

Carbonation of the concrete may, besides other methods, be rendered visible by simply spraying colour indicators onto the fresh concrete surfaces. The essence of this procedure is that such colour indicators show different colours in different pH regions. For investigations on the carbonation of concrete phenolphthalein ($C_{20}H_{14}O_4$), among others, proved useful as it appears colourless with a pH value below 8.3, but shows an intensive red color pH values over 8.3. With the progress of carbonation the pink colouring gradually disappears over the newly exposed surface. Thymolphthalein ($C_{28}H_{30}O_4$) which is a more dependable indicator, can also be used as an alternative of phenolphthalein. In such situation, uncarbonated layer of the concrete (pH >9.3) presents dark blue color while carbonated layer (pH < 9.3) shows no color at all (Baradan, 1996).

The alkalinity interface does not run exactly parallel to the concrete surface but will vary more or less in relation to the inhomogeneities of the concrete.

Figure 2.39 shows a drilling core sample sprayed with phenolphtalein. The parts that are dark grey color indicates the high alkaline area that are not affected by carbonation (Kavalalı, 1994).

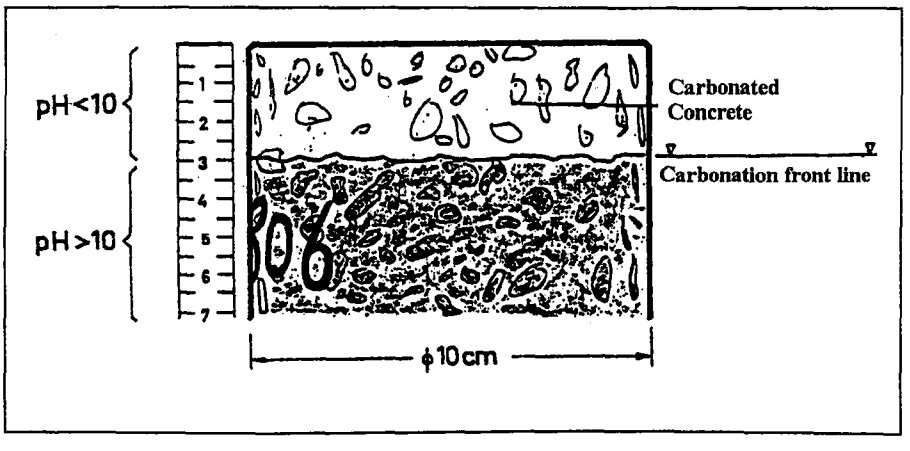

Figure 2.39 Drilling core sprayed with phenolphtalein

2.12.2 X-ray Diffraction

X-ray diffraction is one of the established techniques used in cement science. It is capable of identifying, estimating and elucidating the structure of many unhydrated and hydrated phases of cement. It cannot, however, be efficiently used for CSH and other phases which are extremely fine grained and nearly amorphous. In such investigations other techniques may be usefully employed. X-ray diffraction is applied to follow the kinetics of hydration of cement both in the presence and absence of admixtures. Various hydration products that are formed at higher temperatures may be identified by X-rays. Another possible application of X-rays is for the determination of the specific surface area of hydrated portland cement by low angle X-ray scattering (Ramachandran, 1976).

2.12.3 Differential Thermal Analysis

This technique (DTA) was originally conceived by Le Chatelier in 1887 and was modified by Roberts-Austen. In DTA the heat effects associated with physical or chemical changes are recorded as a function of temperature or time, as the substance is heated at a uniform rate. Exothermic or endothermic reactions caused by reactions such as crystal inversion, dehydration, decomposition and chemical reactions are detected by DTA. The method has been used for both qualitative and quantitative work in cement chemistry. Identification, kinetics and study of the mechanism of reactions are some of the applications of this technique. In many instances this technique detects a substance that may not be observed X-ray diffraction.

2.12.4 Thermogravimetry

Thermogravimetry analysis (TGA) permits determination of weight changes that occur when a sample is continuously heated at a uniform rate. It differs from the static or semi-static method in which the sample is held at a constant temperature for a desired length of time. In cement chemistry it has been applied in conjunction with differential thermal analysis to follow hydration reactions. The TG method may be used to estimate free lime in hydrated Portland cement and it generally yields a lower value that obtained by chemical methods. The TG method cannot be applied to detect phase transformations in which no loss in weight occurs (Ramachandran, 1976).

2.12.5 Electron Microscopy

Optical microscopy has been used extensively in cement chemistry for the examination of cement clinkers and aggregates used in concrete. However, many materials of interest in cement chemistry are too small for resolution in the optical microscope and in such cases the electron microscope is very useful. The resolution of this microscope may be in the order 8-25 Å. Electron diffraction of the sample may also be obtained with this instrument.

The scanning electron microscope (SEM) has played a significant role in the understanding of the microstructure of hydrated cementitious systems. The technique consist of narrow electron beam scanning the surface of specimen. The scattered electrons are collected by a detector and the amplified signal controls the brightness of a spot on the cathode ray tube. The SEM has a large depth of focus but its resolution is only about 200 Å. The depth of focus enables examination of a sample in a three-dimensional arrangement. Clear indications have been obtained of the presence of hexagonal crystals of $Ca(OH)_2$ and calcium monosulphate aluminate hydrate in the hydrated cement systems. Needles of ettringite and calcium silicate hydrate have also been reported, the former being larger than the latter. The general morphology of CSH is dependent on various factors such as the hydration period, water/solid ratio, temperature, presence of admixture, etc. It may be a mass of irregular small plates.

In addition to study of the morphology of the material, some elements such as Ca, Si and Al present in the hydrated cement may be estimated using some attachments to the SEM (Ramachandran, 1976).

2.12.6 Surface Area Determination

The specific surface area of unhydrated portland cement is usually determined by Blaine air permeability method. Portland cement has to conform to certain minimum finess requirements and a cement with a higher specific surface area will promote high early strengths. The values obtained by using the air permeability method are different from those derived from Wanger, Andreasen and nitrogen adsorption methods.

The determination of specific surface area of hydrated portland cement is much more involved. One of the methods suggested is based on the adsorption of H_2O adsorbed vapour. The method uses the well-known BET (Brunauer-Emmett-Teller) equation for the determination of the amount of adsorbed water required to form a monomolecular layer over the solid.

The validty of this method has been questioned because the adsorption-desorption isotherms for water vapour are not identical at low relative pressures. Part of the water is taken up by the interlayer spaces in hydrated cement. It appears that this limitation does not apply if N_2 is used as the adsorbate.

2.12.7 Mercury Porosimetry

The properties of cement and concrete not only depend on the solid phase but also on the nature of the void or pore space.

Porosity and pore-size distribution of materials may be determined by adsorption techniques. A mercury porosimeter is used to determine pore size in the range 25 Å-1000 μm. The principle of the mercury porosimeter consists of determining the quantity of mercury depends on the applied pressures. The minimum pore diameter penetrated by the mercury depends on the applied pressure. For example, at 5 psi pores of 35 μm diameter are penetrated whereas at 60,000 psi pores down to 30 Å diameter intruded.

2.12.8 Infrared Absorption Spectroscopy

Infrared spectroscopy has been extensively used for organic compounds. The technique has been used with some success in the detection of organic admixtures present in cement. It can also be used for differentiating the principal components of portland cement and for investigating the structural changes occurring during hydration (Ramachandran, 1976).

CHAPTER THREE
SPECIAL TOPICS ON CARBONATION

3.1 The Effect of Pozzolans and Admixtures on Carbonation

In the past, many experimental researches have been done by different investigators to observe effect of different pozzolans and admixtures on carbonation rate. Some of them are mentioned below briefly.

3.1.1 Blast Furnace Slag

Some investigations have been carried out into the effects of cement replacement by ground granulated blast furnace slag or Portland blast furnace slag cement on the carbonation rate of concrete and their effects on micro-structure in the past. Because, this type of cement has a major market share in some countries such as Netherlands.

The quality and performance of site-stored concrete blocks was investigated by Osborne where the concretes incorporates different levels of ground granulated blast furnace slag as cement replacement. The data showed that the plain OPC concretes had carbonated less than the slag cement concretes, there being little or no carbonation for OPC concretes with cement contents of 350 or 450 kg/m^3 and only 3-4 mm after 3 years of exposure for the 250 kg/m^3 concretes. There was a slight increase in the levels of carbonation for the block A series of concretes compared to the block B concretes, due to the more complete protection afforded by the polystrene insulation on the B series of concrete blocks during the first 7 days of hydration prior to exposure which restricted both water vapour losses and carbonation (Osborne, 1989).

The carbonation depth for both series of concretes (A and B) increased as the level of slag replacement for OPC increased from 40 to 70 %. However samples with the lowest

cement content of 250 kg/m^3 had carbonated with a 12 mm depth for the 70 % slag blend, compared with 6.5 mm (350 kg/m^3) and 3.5 mm (450 kg/m^3) for these higher cement content concretes at the same level of slag after 2,5 years. Figure 3.1 shows the effect of cement content and level of slag replacement on depth of carbonation for blast furnace slag cement concretes, used 300 mm blocks A and B series.

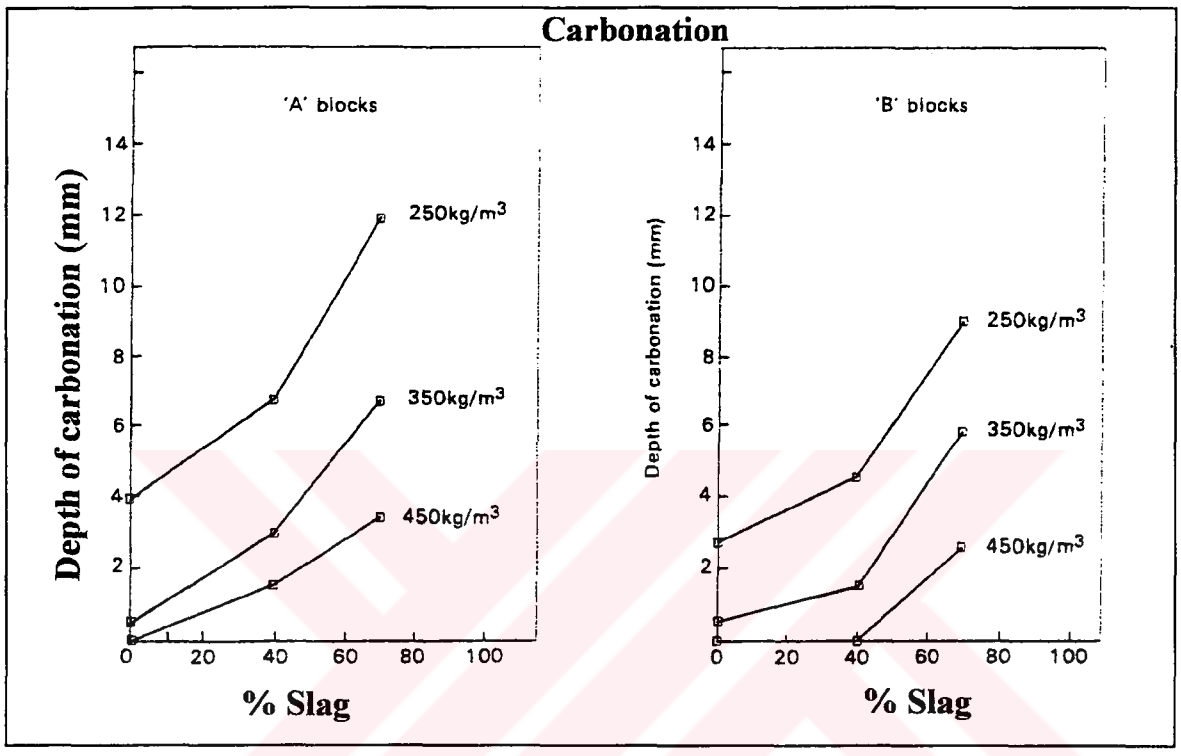

Figure 3.1 The effect of cement content and level of slag replacement on depth of carbonation of concretes

According to Osborne's research, the two main factors influencing the depth of carbonation were the level of slag replacement for Portland cement and the environmental conditions in which the concretes were situated. Carbonation was greater in the higher slag content cements especially if associated with a sheltered or drying micro-climate, However, in general, gas and water permeability decreased with increased Portland cement content and replacement levels were reduced from 70 to 50 % (Osborne, 1989).

During the hydration of Portland cement and granulated slag in Portland blast furnace slag cement finely dispersed calcium silicate hydrates are formed as the major constituent of

hydrated cement paste. With increasing slag content of the cement, more CSH phases are formed, contributing to the well known dense pore structure of pastes made of PBFS cements (Bier & Kropp & Hilsdorf, 1989).

Upon carbonation of the hydrated cement paste, all alkaline compounds are decomposed to form carbonates. Furthermore, the decomposition of CSH results in the formation of a porous silica gel.

Experimental research was made by Bier, Kropp and Hilsdorf about the effect of slag cement on micro-structure of carbonated and non-carbonated concrete.

In an experimental investigation, different types of hydrated cement paste, mortars and concretes manufactured with Portland cement and Portland blast furnace slag cements with different slag contents subjected to carbonation and resulting changes in the pore structure monitored. These tests demonstrated that the silica gel formed during carbonation shows pores in the range of approximately 300 nm pore radius. Where large quantities of silica gel are formed carbonation leads to a coarser pore structures compared to the original structure. Permeability of these systems then increases significantly. the porous silica gel, however, proved to be reactive. Upon access of alkalies, new CSH phases may be rebuilt with a very fine pore size distribution with pore radii $r<10$ nm.

Carbonation of the alkaline compounds in hardened cement paste (hcp) is a diffusion controlled process depending on the penetration of CO_2 into the pore system of the matrix. Especially large capillary pores enable an easy access of CO_2 to the matrix. Also the chemical composition of the cement must be regarded. The major compound is given by the CaO content of the cement. Therefore, with decreasing CaO content of the cement a higher depth of carbonation is observed.

Carbonation results in the formation of new solid compounds which are deposited in the pores of the matrix, while the original phases of the hydrated cement paste are decomposed these changes in the mineralogical composition are accompanied by changes in the pore structure. For Portland cement pastes Figure 3.2 shows that the distinct peak in the differential pore size distribution is reduced, and the pore volume intruded by mercury

decreases significantly. Therefore, carbonation led to a denser pore structure. This effect was even slightly increased by accelerated carbonation (2 percent CO_2). For pastes made of PBFSC with high slag content, a different behavior was observed by Bier et al. Figure 3.3 shows that the peak of the pore size distribution is shifted after carbonation towards coarser pores and no reduction in the pore volume occurred. Similar to the PC pastes accelerated carbonation increases the changes in the pore structure.

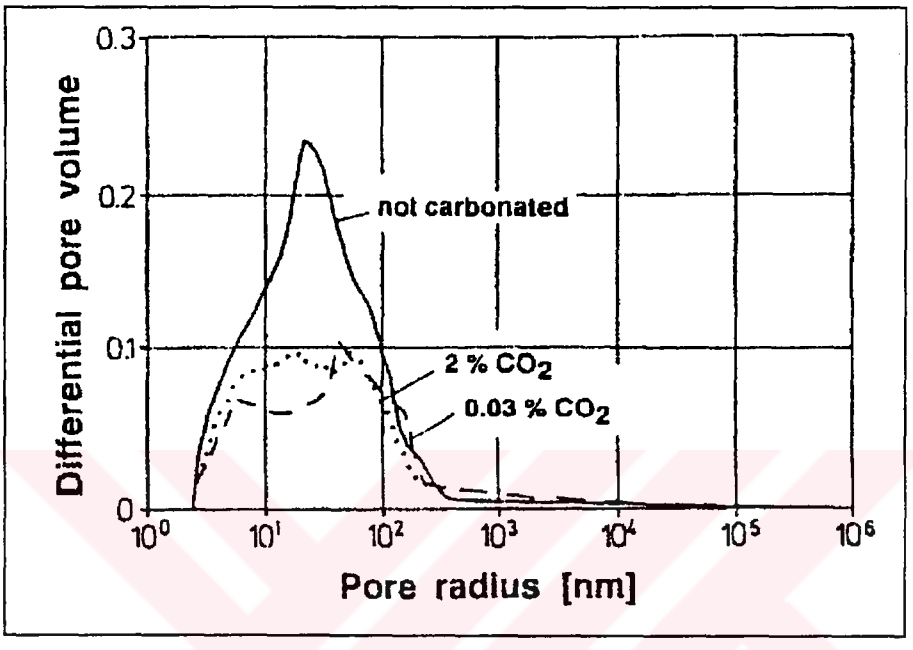

Figure 3.2 Differential pore size distribution in carbonated hcp made of OPC

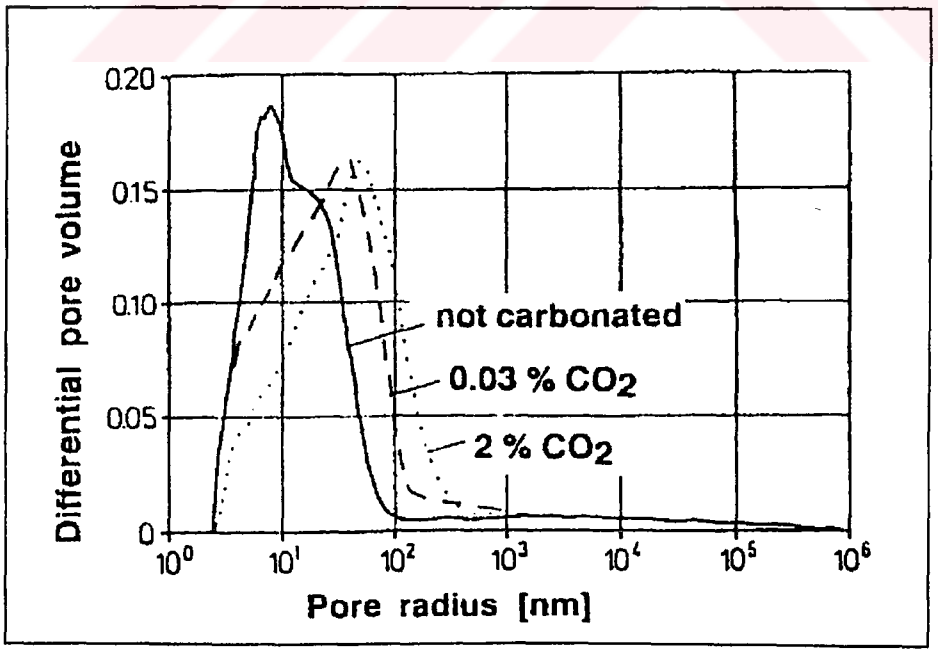

Figure 3.3 Differential pore size distribution in carbonated hcp made of PBFSC with a slag content of 50 percent by mass

The decomposition of the CSH results in the formation of a hydrous silica gel. In hydrated cement paste systems where much silica gel was formed upon carbonation the coarse pores of the silica gel cause the shift of the pore size distribution towards coarser pores whereas the very fine pores of the silica gel were not detected by Mercury intrusion porosimetry (MIP). In pastes no coarsening of the pore structure was observed because the amount of silica gel formed is too small. Aside from these pores detectable by MIP also finer pores must exist because of the large specific surface area given by nitrogen adsorption.

Comparing the permeability of the different cement mortars before carbonation took place Figure 3.4 shows that the denser pore structure of cements containing granulated slag exhibits a lower permeability than Portland cement mortars. However, the changes in the pore structures due to carbonation are reflected in the permeability. Whereas the denser pore structure of a carbonated Portland cement paste matrix reduces the permeability, for PBFSC an increase of the permeability by two orders of magnitude was observed. These results indicate a continuous pore system in the silica gel formed during carbonation (Bier et.al., 1989).

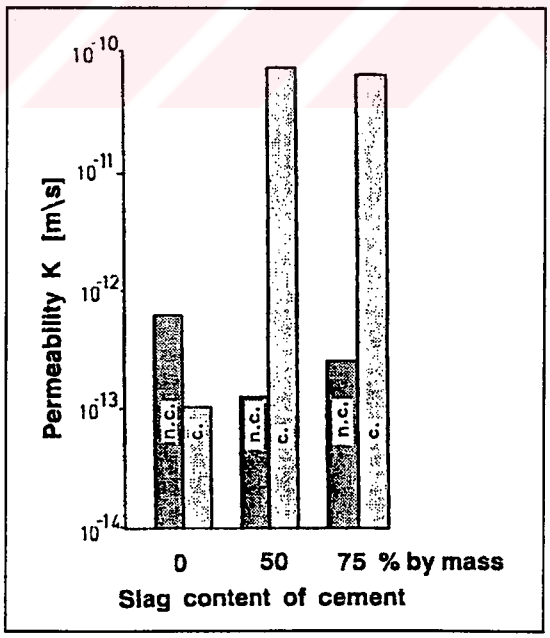

Figure 3.4 Permeability of non-carbonated and carbonated mortars manufactured with different cements

3.1.2 Fly Ash

It was shown that even relatively high strength concrete (C45) made with ordinary Portland cement (OPC) of typical C_3A content may not provide adequate protection to steel reinforcement in an aggressive marine environment. Fly ash concretes of similar strength were considerably more resistant to penetration of chloride ions. The improvement was related to the increasing contents of fly ash. Consequently, fly ash concrete was found to have substantially improved durability compared with OPC concrete in this environment (Thomas&Matthews, 1992).

It was suggested that the mechanisms for chloride penetration was initially sorption into the dry concrete, followed by ionic diffusion with chemical interaction (binding of chlorides by hydrates) in the saturated concrete at later ages. The increased resistance of fly ash concrete to chloride ion penetration results from decreased diffusivity and increased capacity to bind chloride ions.

The mechanisms of carbonation is likely to consist mainly of gaseous diffusion combined with chemical interaction. The chief chemical interaction is the reaction of CO_2 with $Ca(OH)_2$ liberated during cement hydration. In fly ash concrete the quantity of $Ca(OH)_2$ will be significantly reduced by the lower quantities of OPC and consumption by the pozzolanic reaction. Hence, the extent of chemical interaction (and binding of CO_2) will be reduced compared with OPC concrete.

According to Thomas and Matthews's research, concretes with a range of fly ash levels (0-50%) were exposed to various treatments during the first 28 days. After that the concretes were stored either internally or externally (sheltered) and the rate of carbonation was monitored. The results emphasize the importance of adequate curing for concrete durability, especially in the presence of fly ash. In some cases increasing the initial curing period from 1 to 7 days had the effect of reducing carbonation by 50 %. Concretes with up to 30 % fly ash carbonated to a similar or slightly greater degree compared with OPC concretes of the same strength grade.

The progress of carbonation with time for concrete samples is shown in Figure 3.5 for internal and Figure 3.6 for external storage.

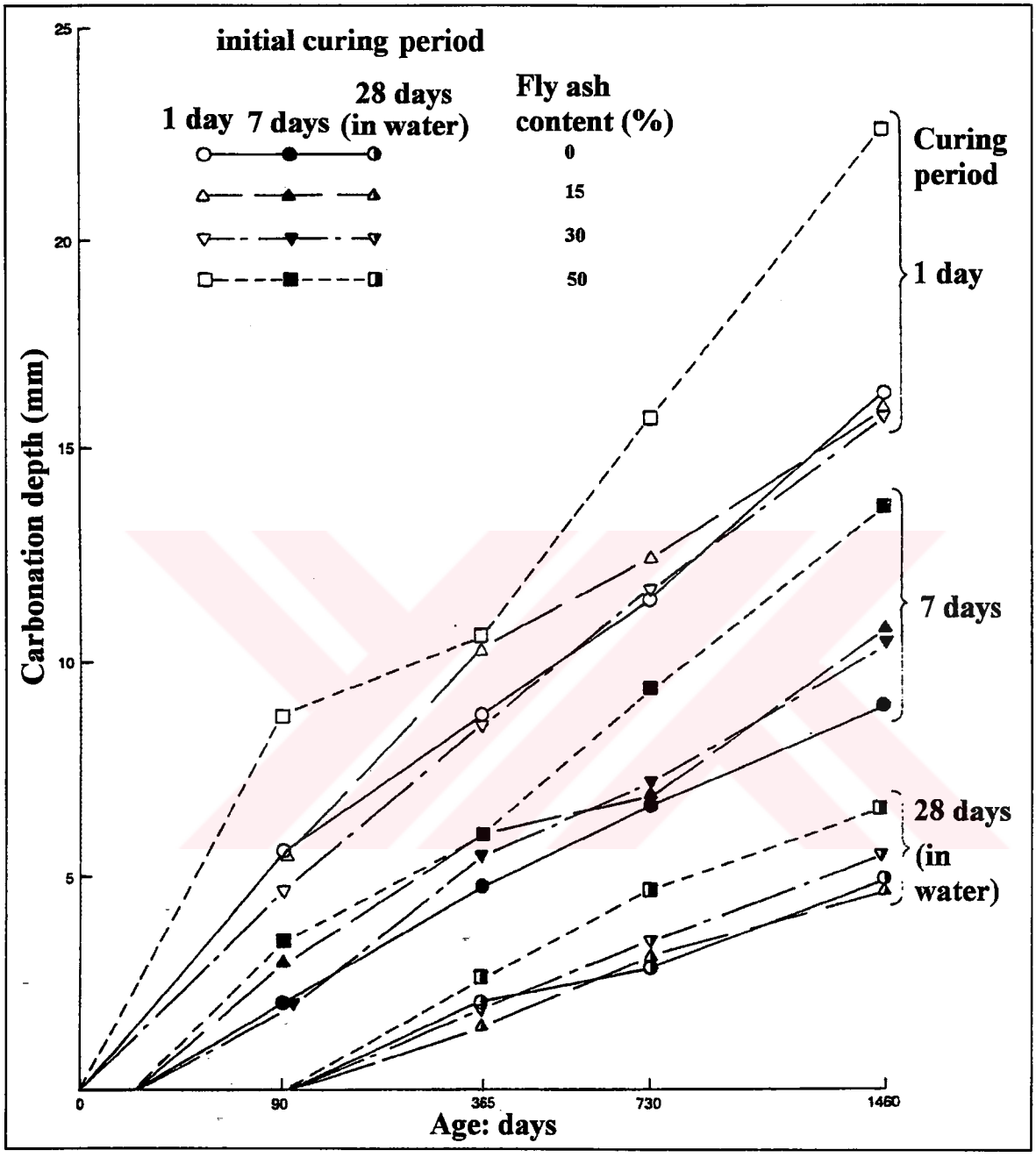

Figure 3.5 Carbonation of internally stored concretes (20 °C and 65% RH)

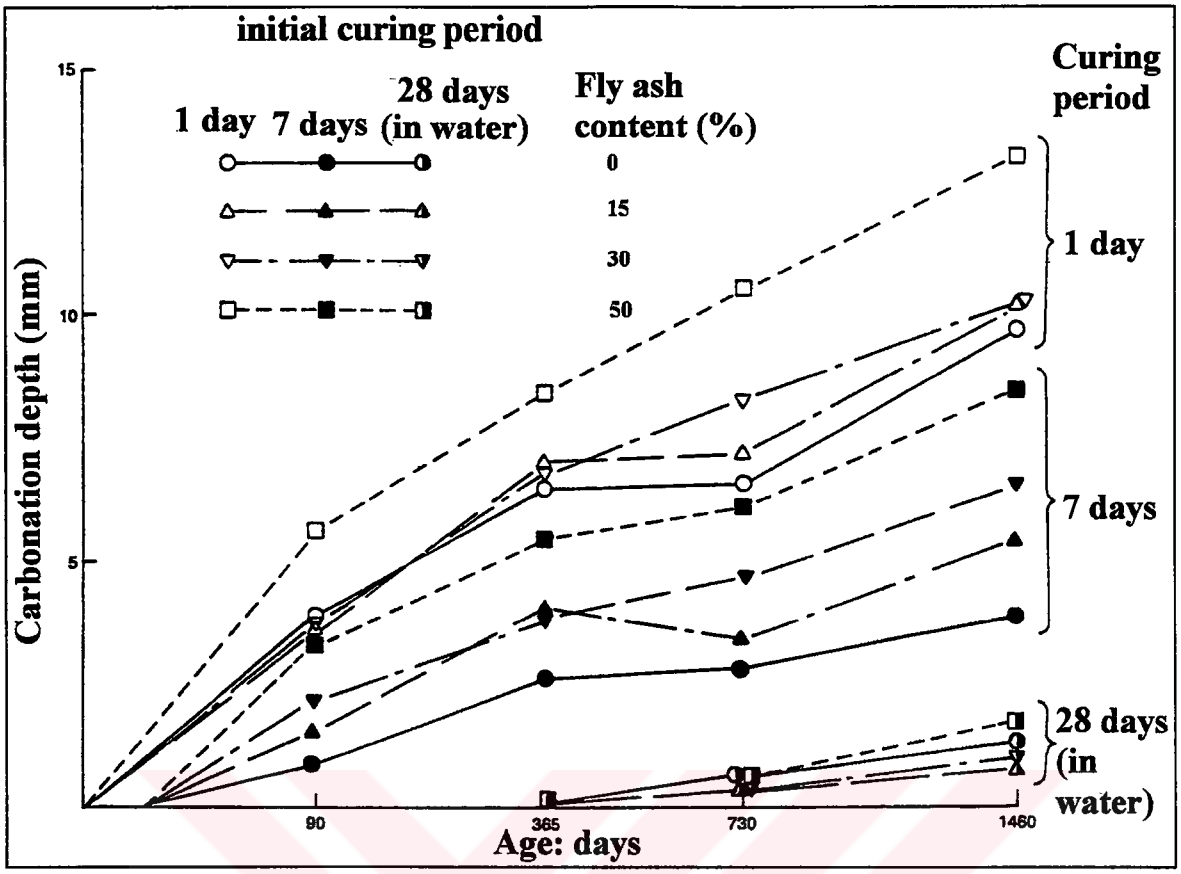

Figure 3.6 Carbonation of externally stored concretes (sheltered from rain)

The depth of carbonation increases proportionally with the square root of time for internally stored concretes, and a similar, but less marked, trend may be discerned for the concretes stored outside. Concretes stored in water for 28 days do not carbonate immediately on exposure, and little significant carbonation was observed for these concretes after 90 days of internal exposure or 365 days of external exposure. These delays obviously reflect the time taken for the concretes to dry out sufficiently to permit the ingress of carbon dioxide (Thomas&Matthews, 1992).

Specimens stored externally but sheltered from rain, carbonate on average 40% less than specimens of the same concrete stored internally (at 20 °C and 65% RH). However, the initial curing period has a pronounced effect on carbonation in both storage environments. For concretes cured for just 1 day, the depth of carbonation after 2 years is nearly twice that of concretes moist-cured for 7 days and 3 times that of rate of concretes cured for 28 days in water.

The results in Figure 3.5 and Figure 3.6 indicate that carbonation is increased considerably for concretes with the higher levels of fly ash (50%), especially when poorly cured. The carbonation of concretes containing lower levels of fly ash (15-30%) is generally similar to or slightly higher than that of the no fly ash concretes.

In this research, specimens were cured for 24 hours in their molds under damp sacking and polythene, in the laboratory at 20 °C. After 24 hours all the specimens were demolded and subjected to one of the following treatments up to age of 28 days.1 day cure; air-stored immediately after demoulding, 7 day cure; moist-cured under damp sacking and polythene for a further 6 days before air storage, water cured; immersed in water until test.

Another experimental research was made by Ying-yu and Qui-dong to observe effects of carbonation on micro-structure.

Figure 3.7 and 3.8 show pore size distribution of mortar specimens which was taken from this investigation. It can be seen from Figure 3.7 that for the blended cement mortars contaning 40% of fly ash, the decrease of porosity mainly happens in the region where porosity of the pores whose radii are below 320 Å, but the porosity of those pores with radii between 320-4000 Å increases slightly and this observation was explained by authors with contraction cracks caused by carbonation (Ying-yu &.Qui-dong, 1987)

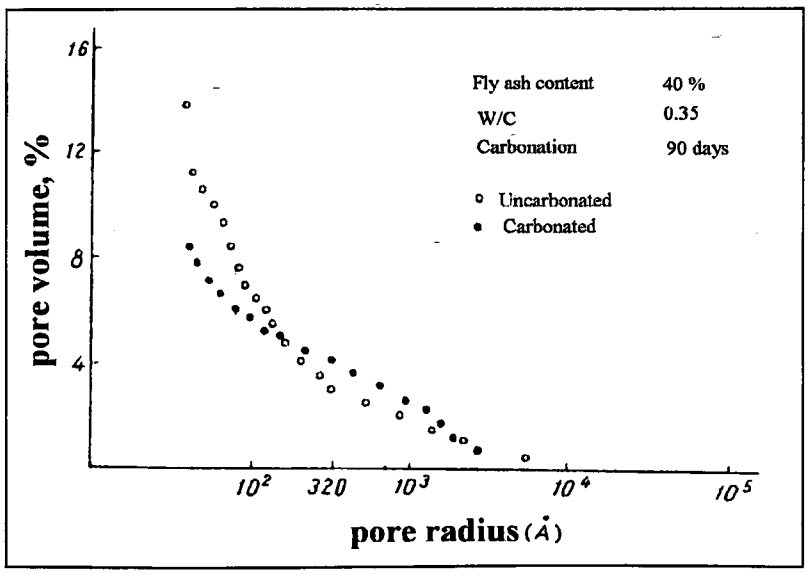

Figure 3.7 Integral curves of pore size distribution

From Figure 3.8, carbonation mainly decreases the porosities of those pores with radii below 630 Å but for those with radii over 1000 Å, the porosities before and after carbonation are almost the same. According to above analyses, it is believed that the active pores are mainly those whose radii are smaller than 630 Å. However, the pores with radii over 1000 Å which are inactive pores with the increases of these pores, the diffusion rate of CO_2 increases greatly. However, the capacity of the mortar to adsorb CO_2 increases a lesser degree, as a result, these pores reduce the carbonation resistance of mortar. Decreasing these pores would increase the carbonation resistance of mortar.

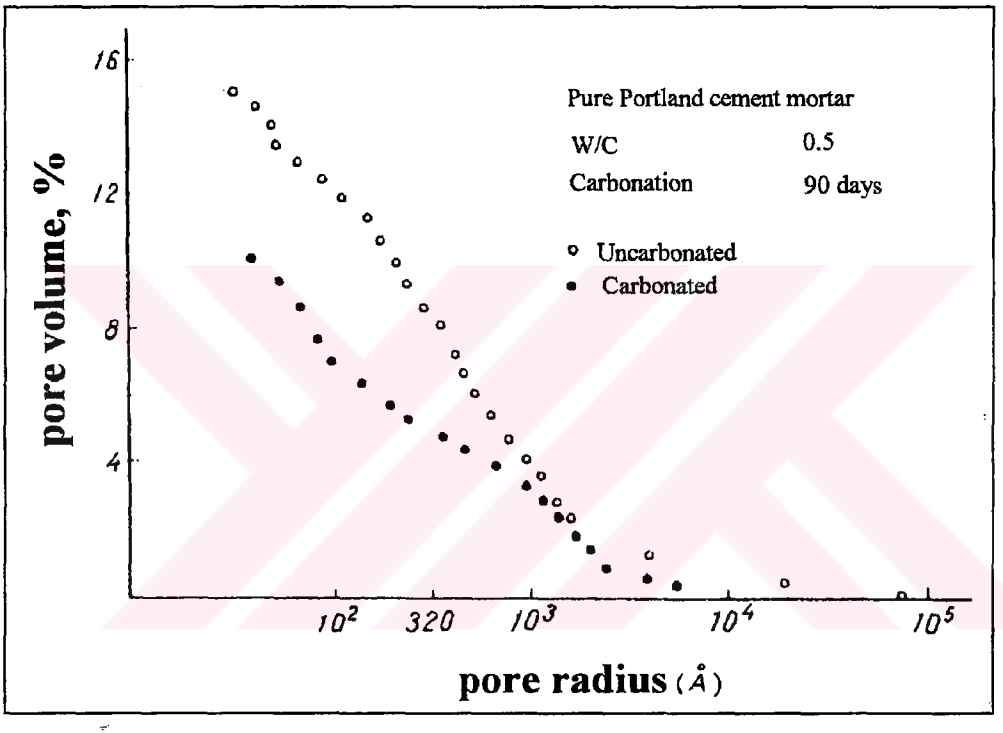

Figure 3.8 Integral curves of pore size distribution

3.1.3 Combination of Blast Furnace Slag and Fly Ash

The effects on carbonation of replacement by fly ash of Portland cement in concrete are well established. The increase in the carbonation rate when Portland cement is replaced by fly ash. The effects on carbonation of combination Portland blast furnace slag cement and fly ash were investigated by Bijen and Selst.

It is generally accepted that fly ash from bituminous coal meeting the requirements at ASTM C 618 (Class F fly ash) is a pozzolanic material. This means that the fly ash particles react in Portland cement concrete with lime and water. Cementitious products are formed.

For ordinary Portland cement this reaction only occurs after one or more weeks. It has been shown that this period is due to the fact that the pH of the pore water is initially too low to initiate fly ash reaction. In general at 20 °C it appears the fly ash dissolves significantly only when the pH is reaching a level of 13.2 or a hydroxyl ion concentration of 3000 mg/l (Bijen&Selst, 1991).

Figure 3.9 shows that for an ordinary Portland cement (OPC) and water/cement ratio of 0.45 at 20 °C this level is reached in about 100 hours. The Figure 3.9 shows that the ordinary Portland blast furnace slag cement (OPBFSC) investigated shows a pH development hardly reaching the level of 13.2. Taking into account that replacement of cement by fly ash decreases the pH somewhat. It is clear that fly ash reactivity in Portland blast furnace slag cement is to be low. Furthermore, between cements differences in pH developments can be observed.

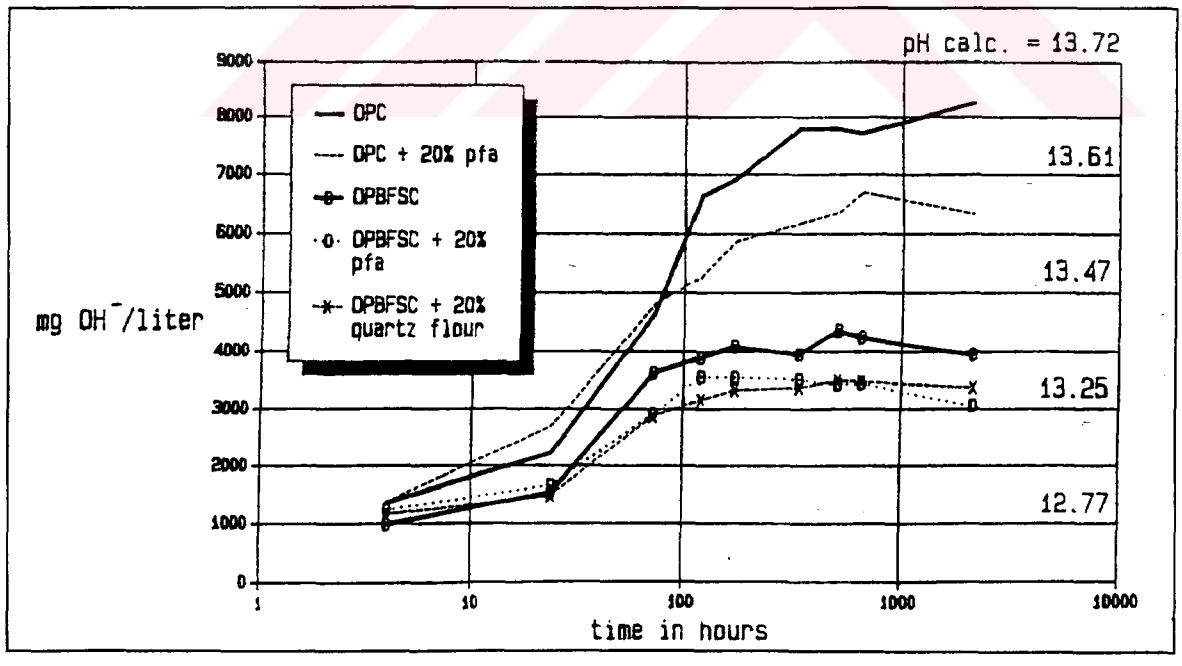

Figure 3.9 Development of the OH^- concentration and pH in time for ordinary Portland cement (OPC) and ordinary Portland blast furnace slag cement (OPBFSC) and without cement replacement at 20 °C

Figure 3.10 shows results of the laboratory program for OPBFSC with various replacement percentage cured for 7 days under water and subsequently exposed outdoors for two years. It can be seen Figure 3.10 replacement increases carbonation.

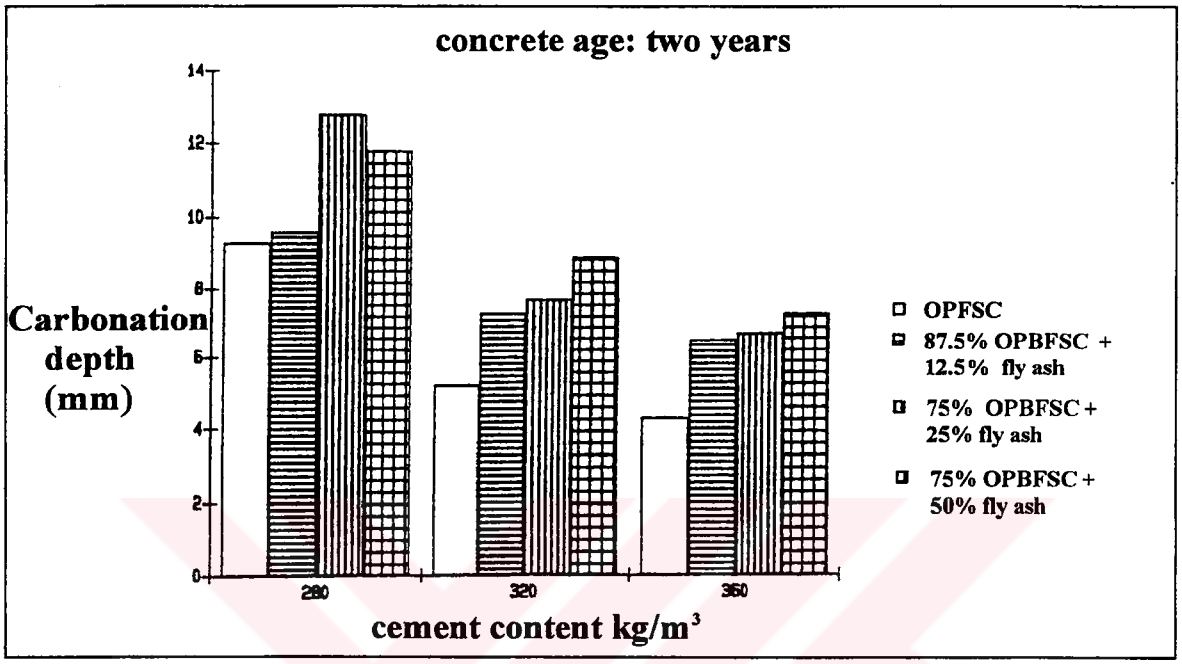

Figure 3.10 Carbonation depth after two years for concretes with OPBFSC with and without fly ash cured for seven days under water of 20 °C and subsequently exposed outdoors

Figure 3.11 shows carbonation depths after two years of outdoor exposure of laboratory program specimens with 320 kg/m^3 OPBFSC and 240 OPBFSC + 80 kg/m^3 fly ash and 1, 7, 28 or 90 days of wet curing. Prolonged wet curing more than 7 days has hardly any effect on carbonation depth. The first 7 days are dominant.

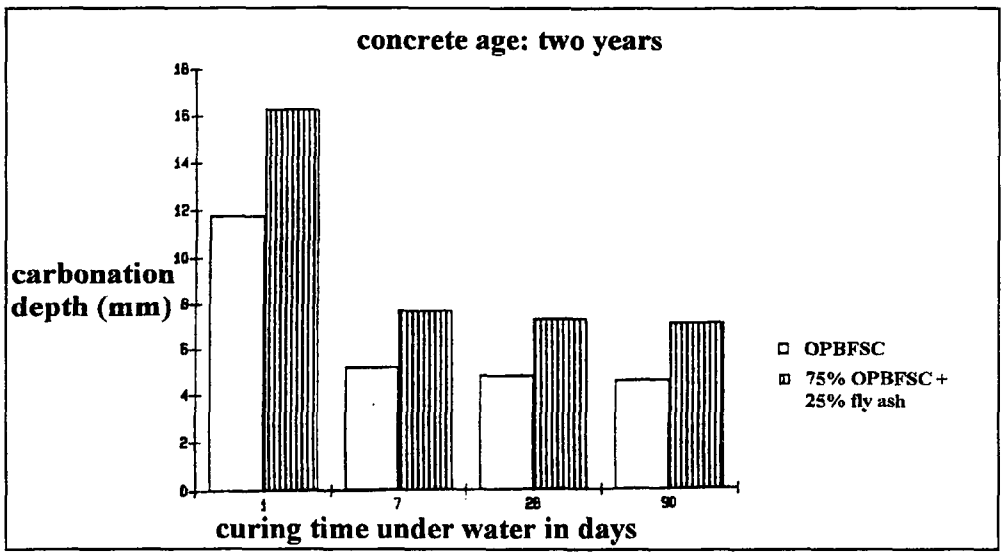

Figure 3.11 Carbonation depth after two years of exposure outdoors for specimens of 320 kg/m^3 OPBFSC with and without fly ash cured 1, 7, 28 of 90 days under water of 20 °C

Carbonation depth as a function of time for concrete with 320 kg/m^3 cement + fly ash for various cement types at 0 and 25% cement replacement are shown in Figure 3.12. Cement replacement for ordinary Portland cement concrete has only a minor effect on carbonation rate but is relatively large for the OPBFSC (Bijen&Selst, 1991).

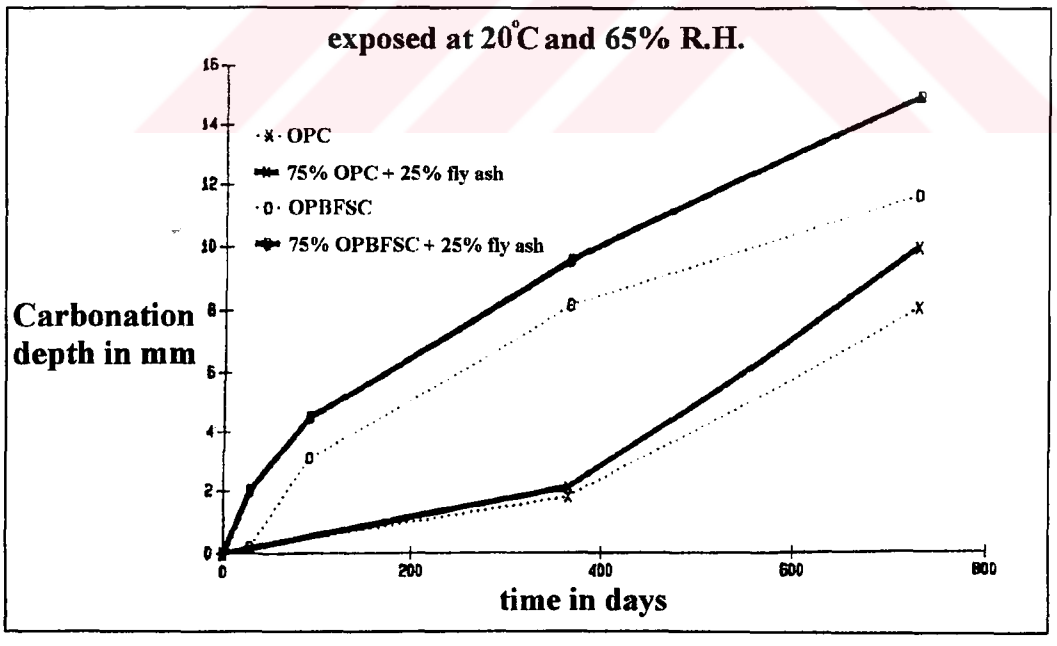

Figure 3.12 Carbonation depth development as a function of time for concrete with 320 kg/m^3 (cement plus fly ash) for OPC and OPBFSC and 0 or 25 percent cement replacement cured for seven days in water of 20 °C and subsequently exposed to 20 °C and 65 percent R.H.

3.1.4 Superplasticizing Admixture

Effect of Superplasticizing admixture on carbonation rate was reported by Dhir, Tham and Dransfield. In this research, the 100 mm cube specimens were subjected to an accelerated carbonation at 4% concentration of CO_2 with 20 °C temperature and 55% relative humidity.

After a period of 20 weeks, specimens were removed and split open to test phenolphthalein spray. The result obtained with this system, when compared with those obtained with the specimens exposed the normal United Kingdom outdoor exposure, in general tended to suggest an equivalence of 1 week accelerated test to 1 year outdoor exposure effect. The depths of carbonation recorded at the conclusion of the tests were shown plotted against the 28-day strength of concrete in Figure 3.13. Both normal and superplasticised concretes exhibit a similar trend with regard to effect of strength in reducing the depth of carbonation. However, superplasticised concrete mixes have less depth of carbonation for given design strength than the corresponding concrete mixes, with percentage difference increasing as the design strength of the two concretes is increased. This probably reflects of reduced air permeability of superplasticised concrete mixes arising from their lower mix water contents compared to the normal mixes having similar strengths and water/cement ratios (Dhir&Tham&Dransfield, 1987).

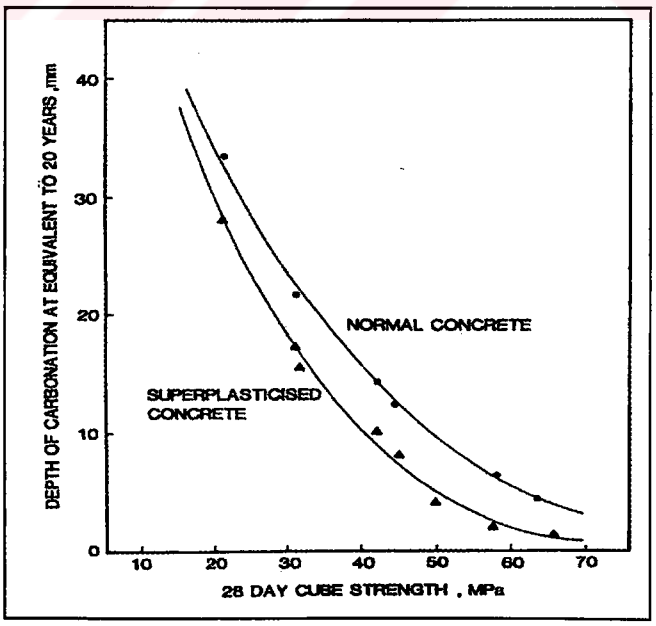

Figure 3.13 Relationship between the depth of carbonation and strength of concrete

3.2 Decomposition of Hydrated Cement Components During Carbonation

In the literature there are different researches about decomposition of hydrated cement components during carbonation. Some of them are mentioned below briefly.

3.2.1 Ettringite

It is well known that ettringite is found in the hydration products of ordinary Portland cement, especially, in the cases of a special rapid-hardening Portland cement and the blast furnace slag cement mixed with an amount of gypsum, ettringite is one of the main product which acts a binder.

The stability of ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) in contact with CO_2 gas has been studied using synthesized ettringite by Nishikawa, et al. It was reported that by the carbonation with excess water, ettringite clearly decomposed to gypsum, calcium carbonate, and alumina gel. The apparent carbonation rates were calculated from the amount of calcium carbonate (Nishikawa&Suzuki&Ito&Sato&Takebe, 1992).

It has been suggested that ettrigite decomposed to calcite, gypsum and alumina gel by carbonation as follows:

$$3CaO.Al_2O_3.3CaSO_4.32H_2O + 3CO_2 \longrightarrow 3CaCO_3 + 3(CaSO_4.H_2O) + Al_2O_3.xH_2O + (26\text{-}x)H_2O \quad (3.1)$$

(ettringite) (gypsum) (alumina gel)

The stability of ettringite and monosulphate in water solution with various values of pH was studied by Gabrisova et al. Measurements showed that the boundary for the disappearance of ettringite is pH= 10.7 and for monosulphate pH= 11.6. At lower values of pH, only gypsum and aluminum sulphate were present in the system (Gabrisova & Havlica & Sahu, 1991).

3.2.2 CSH

The phenomenon of CSH in hardened cement paste being decomposed through carbonation was investigated by Kobayashi, Suziki and Uno. It was reported that CSH is decomposed to $CaCO_3$, SiO_2 and H_2O by the carbonation.

In 1984, one of the authors took core specimens to investigate the strength of concrete from the reinforced concrete foundation of 5-storey housing apartment 10 years after completion. X-ray diffraction and the thermal analysis were conducted on samples taken out of the discolored and non-discolored portions of the cores. Figure 3.14 shows the results of the X-ray diffraction tests. It is clearly seen in these diagrams in that sharp peaks was observed in the non-discolored portion which indicate existence of $Ca(OH)_2$ as well as $CaCO_3$, but in the discolored portion, no diffraction peak for $Ca(OH)_2$ is observed at all. On the other hand, Table 3.1 shows the results of the thermal analysis and measurement of the quantity of $Ca(OH)_2$ and $CaCO_3$. The weight of $CaCO_3$ in the discolored portion was accounted for 34-37% of the total weight of the sample. If the whole amount of $Ca(OH)_2$ in the non-discolored portion is assumed to have turned to $CaCO_3$, the weight percentage of $CaCO_3$ should be around 20% anyway, therefore, $CaCO_3$ equivalent to 14-17% of the total weight of the sample should have been supplied from somewhere other than $Ca(OH)_2$. If it is taken into consideration that the sample on which the thermal analysis was conducted was not purely hydrated cement but includes a certain amount of sand particles, the value of 14-17% of the total weight of the specimen was supposed to be too large. In this case the authors had an idea that this might be derived from $CaCO_3$ that had been formed by carbonation of CSH and verified it (Kobayashi, Suziki and Uno, 1994).

Table 3.1 Results of Thermal Analysis

Kind of sample	$Ca(OH)_2$ (wt%)	$CaCO_3$ (wt%)
A- Non-discolored	7.0	10.4
A- Discolored	0	37.3
B- Non-discolored	5.3	13.5
B—discolored	0	34.4

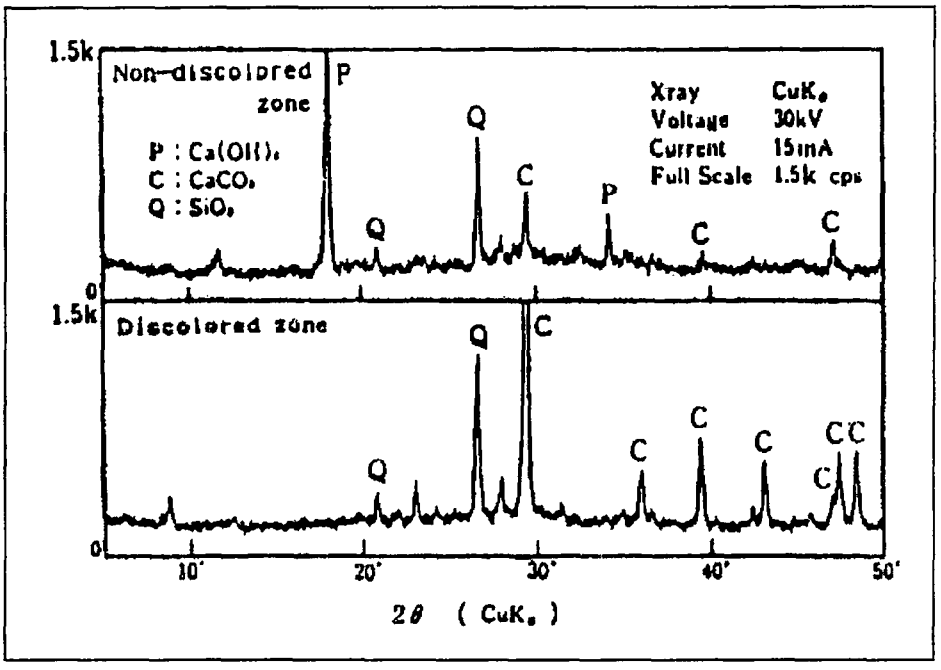

Figure 3.14 X-ray diffraction patterns of samples taken from non-discolored and discolored zone

3.2.3 Friedel's Salt

The experimental investigation was made by Suryavashi and Swamy to explain the role of atmospheric carbonation on the stability of the Friedel's salt in chloride contaminated structures. For this purpose, four different types of concrete slabs with thickness of 150 mm, were subjected to chloride penetration over a total period of about three years and then exposed to atmospheric carbonation for almost same period.

Figure 3.15 shows X-ray diffractograms for 0-5 mm and 45-65 mm depth intervals. The diffractogram for the 0-5 mm depth interval shows the absence of potlandite ($Ca(OH)_2$), ettringite ($3CaO.Al_2O_3.3CaSO_4.32H_2O$) and Friedel's salt, although it is natural to expect Friedel's salt at this depth interval due to presence of large quantities of acid soluble chlorides. The absence of potlandite is explained by its chemical reaction with the atmospheric CO_2 in the presence of moisture to form calcium carbonate (calcite, aragonite and vaterit). The ∝-quartz was believied to be formed by the sand used in producing of concrete.

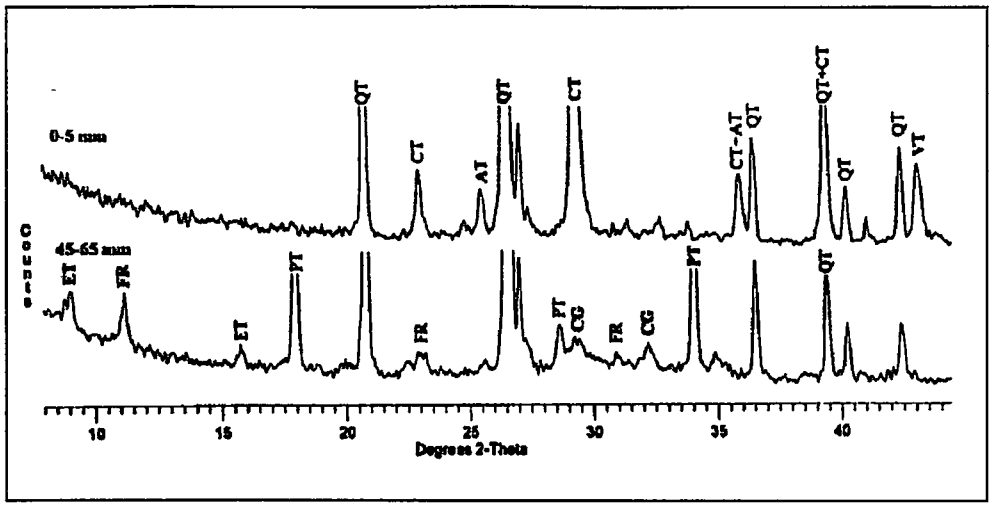

Figure 3.15 XRD diffractogram for slab

Key words in Figure 3.15 are ET:Ettringite, FR: Friedel's salt, PT: Portlandite, QT: ∝-Quartz, AT: Aragonite, CT: Calcite, CG: CSH gel and VT: Vaterite.

In this research, according to XRD and DTA results suggest that the stability of Friedel's salt to be pH dependent on the alkalinity of the concrete surrounding it. The solubility of Friedel's salt increases with the degree of carbonation of the concrete. The solubility of the Friedel's salt is in accordance with the equilibrium given below. Note that, $Al(OH)^-_4$ is an aluminium containing ion known to exist in concrete.

$$3CaO.Al_2O_3.3CaCl_2.10H_2O \leftrightarrow 4Ca^{2+} + 2Cl^- + 4OH^- + 2Al(OH)_3 \quad (3.2)$$

$$Al(OH)_3 + OH^- \leftrightarrow Al(OH)^-_4 \quad (3.3)$$

From the above solubility equilibrium for the Friedel's salt it is clear that, in the event of a drop in alkalinity due to carbonation, the chlorides from Friedel's are released into the pore solution. Thus, in the presence of carbonation attack the steel reinforcement in chloride contaminated concrete structure is at a higher corrosion risk. This may also explain the corrosion risk presented by the presence of chlorides at low concentrations, which is generally negligible in uncarbonated concrete, but became increasingly significant on carbonation (Suryavanshi&Swamy, 1996).

CHAPTER FOUR
EXPERIMENTAL PROGRAM

The Second stage of this research was to test the effects of cement type, curing conditions and maturity of concrete on carbonation rate by accelerated test methods. A rather simple accelerated test apparatus proposed by Ballim (1996) has been developed for this purpose. The Properties of the materials, concrete mix designs, information about the accelerated carbonation test apparatus and other related details are given in this Chapter.

4.1 Aggregate

Crushed stone of maximum size 31.5 mm was used as coarse aggregate, and sand as fine aggregate in all concrete mixtures. Sieve analyses were carried out for two grades crushed stones and sand. Test results are given Table 4.1 and Table 4.2. Furthermore, the other physical properties of the fine and coarse aggregates are given in Table 4.3. The sieve analyses tests were performed according to TS 707.

Table 4.1 Results of sieve analyses of coarse and fine crushed stone

Sieve size	Grams retained		Cumulative grams retained		Cumulative per cent retained		Cumulative per cent passed	
(mm)	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine
31.5	-	-	-	-	0	0	100	100
16	5138	50	5138	50	98	3	2	97
8	124	658	5262	708	100	41	0	59
4	-	958	-	1666	100	97	0	3
2	-	59	-	1725	100	100	0	0
1	-	-	-	-	100	100	0	0
0.5	-	-	-	-	100	100	0	0
0.25	-	-	-	-	100	100	0	0

Table 4.2 Results of sieve analysis of sand

Sieve size (mm)	Grams retained	Cumulative grams retained	Cumulative per cent retained	Cumulative per cent passed
8	30	30	3	97
4	133	163	14	86
2	216	379	32	68
1	291	670	57	43
0.5	321	991	85	15
0.25	137	1128	96	4
Pan	42	1170	100	0

Table 4.3 Physical Properties of aggregates

	Fine crushed stone	Coarse crushed stone	Sand
Bulk specific gravity (dry)	2.694	2.694	2.633
Bulk specific gravity (saturated surface-dry)	2.705	2.705	2.660
Water absorption (%)	0.439	0.439	1.0
Unit weight, loose (kg/m^3)	1390	1422	1478
Unit weight, compacted (kg/m^3)	1581	1585	1615
Materials finer than (No. 200 - 74 μm)	-	-	3.6
Organic impurities (NaOH)	-	-	Clean

Both coarse and fine aggregates were combined to a specific grading to keep a uniform grading for each mixture. The blend consist of 25 % coarse crushed stone, 25 % fine

crushed stone and 50 % sand. The grading and composition of the aggregates blend are given in Table 4.4. Moreover, the gradation curves of the aggregates blend and the standard limits are presented graphically in Figure 4.1.

Table 4.4 Grading and composition of aggregates blend

	Blend	Standard limits (TS 1277)		
Sieve size (mm)	Cumulative per cent passed	Cumulative per cent passed (upper)	Cumulative per cent passed (ideal)	Cumulative per cent passed (lower)
31.5	100	100	100	100
16	75	89	80	62
8	63	77	62	38
4	44	65	47	23
2	34	53	37	14
1	22	42	28	8
0.5	8	28	18	4
0.25	2	15	8	2
Pan	0	0	0	0

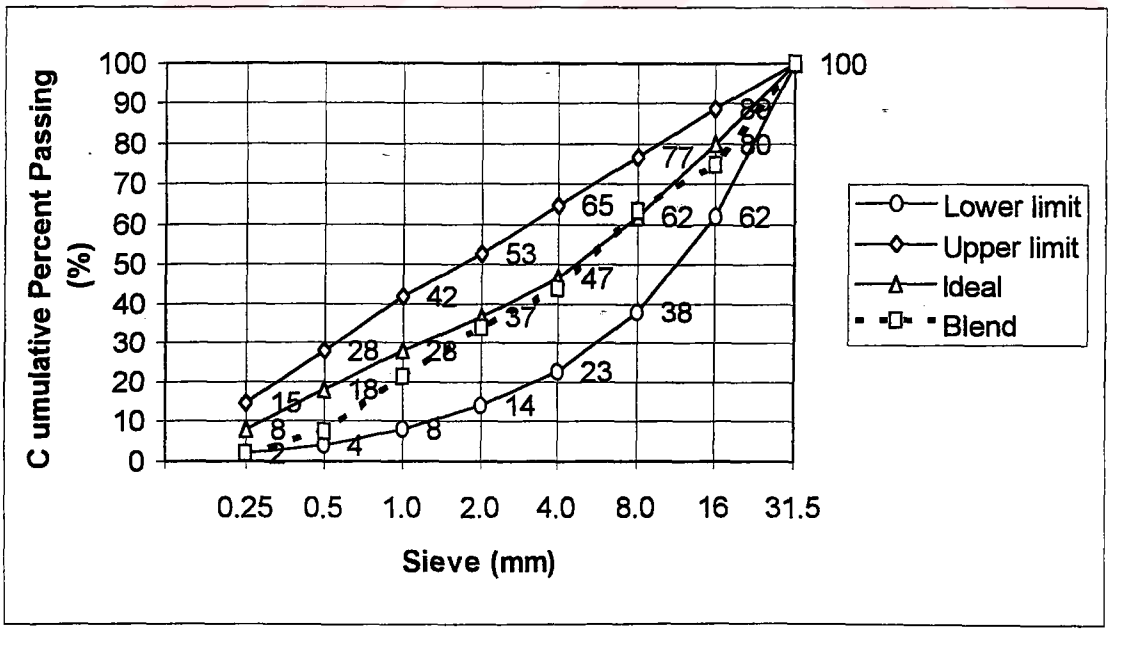

Figure 4.1 The grading curve of the aggregates blend and standard limits

4.2 Cement

Four different types of cement were used in concrete designs in same quantities to observe their effects on carbonation rate. The cements that are used in concrete mixtures are Portland Cement 32.5 (PC32.5), Portland Cement 42.5 (PC42.5), Portland Puzzolona Cement 32.5 (TC32.5) and Portland Fly Ash Cement 32.5 (UKC32.5). All of them were procured from Batıçim Cement Plant in İzmir. The chemical composition and physical properties of these cements are presented in Table 4.5. The test data was provided by Batıçim.

Table 4.5 Physical properties and chemical analysis of cement

Physical Analysis				
	PC32.5	**PC42.5**	**TC32.5**	**UKC32.5**
Specific gravity	3.09	3.10	2.86	2.87
Surface area, Blaine, cm/g^2	3411	3480	5043	3719
Initial setting time (hr-min)	1.55	1.50	2.20	3.20
Final setting time (hr-min)	3.05	2.50	3.25	5.45
2-days compressive strength, (Mpa)	20.2	21.0	16.0	17.5
7-days compressive strength, (Mpa)	35.9	38.7	25.8	32.4
28-days compressive strength, (Mpa)	44.5	47.3	34.6	46.1
Chemical Analysis, (%)				
Al_2O_3	5.20	5.57	8.08	10.57
Fe_2O_3	3.00	3.04	3.44	3.53
CaO	63.31	63.57	43.98	50.95
MgO	1.30	1.21	0.92	1.11
SO_3	2.34	2.25	2.29	1.78
K_2O	0.91	0.88	1.55	0.97
Na_2O	0.11	0.09	0.10	0.08
Cl^-	0.0177	0.0177	0.0443	0.0243
Insoluble residue	0.34	0.66	31.72	15.57
Loss on ignition	1.37	2.13	3.64	2.18

4.3 Concrete Mixtures

Four series of concrete mixtures were designed to have a slump of 80 ± 15 mm and an air content of 1%. The proportioning of the concrete mixtures were made according to TS 802 (Design of Concrete Mixes). The quantities of the concrete ingredients were measured with sufficient accuracy. The moisture contents of fine and coarse aggregates were measured before preparing concrete mixtures to make adjustment in water contents if necessary to maintain the desired saturated-surface dry conditions for the aggregates. The mixing procedure of fresh concrete was accomplished in 40 lt vertical axis type of drum mixer. The descriptions and compositions of four different concrete types studied in this research are presented in Table 4.6.

Table 4.6 Mix proportions of concretes

	A series	B Series	C series	D Series
Concrete type	BS18(B225)	BS18(B225)	BS18(B225)	BS18(B225)
Cement type	PC32.5	PC42.5	TC32.5	UCK32.5
Water/Cement ratio	0.5	0.5	0.5	0.5
Cement (kg)	350	350	350	350
Water (lt)	162	162	162	162
Coarse crushed stone (kg)	475	475	468	469
Fine crushed stone (kg)	475	475	468	469
Sand (kg)	933	933	921	921
TOTAL (kg/m^3)	2395	2395	2369	2371

4.4 Specimens Preparation, Curing and Test Procedure

Experiments were conducted by using two types of specimens. One type consisted of cylinder specimens of 150 mm diameters and 300 mm heights which were used to determine the compressive strength of each series. The other consisted of cube specimens of 150 mm which were used to take core specimens of 50 mm diameters. Two core specimens were taken from each cube to use in accelerated carbonation test. Core specimens were placed in

accelerated carbonation apparatus at the age of 7 and kept for 21 days. This procedure was repeated at the age of 28 days.

The molds were oiled prior to placing concrete. Cylinder specimens were cast in three layers whereas cube specimens were cast in two layers. Each layer being compacted with 25 stokes using 16 mm diameter rodding bar. After demolding, each series of specimens were divided into two groups before the curing period. Half of them were kept in water while rest of them were exposed to the laboratory atmosphere until the test days. Experiments were conducted with limited number of specimens since, the accelerated carbonation test apparatus has not enough space to take a large number of core specimens at the same time. Table 4.7 gives the information about the number, size, curing condition and other details of specimens according to test type for each series.

Table 4.7 Details of specimens according to test type for each concrete mix

Test	Compressive strength			
Specimens size and type	150/300 mm Cylinder			
Age of test	7 days		28 days	
Cure type	in water	no-cure	in water	no-cure
Number of specimens	1	1	1	1
Total	4			
Test	Accelerated carbonation test			
Specimens size and type	150 mm cube			
Cure type	in water		no-cure	
Number of specimens	1		1	
Total	2			
Core specimens size and type	50/150 mm cylinder		50/150 mm cylinder	
Age of test	7	28	7	28
Number of specimens	1	1	1	1
Total	4			

4.5 The Accelerated Carbonation Test Apparatus and Other Devices

Figure 4.2 shows accelerated carbonation test apparatus (ACT) which consists mainly of an accelerated carbonation chamber and a compressed air cylinder. The carbonation chamber has a inlet and outlet valve in order to fill or empty the chamber and pressure gauge to measure the pressure in the chamber. The compressed air cylender has two outlet valve in order to control the flowing gas mixture (10% CO_2 and normal air) and two pressure gauges to measure the pressures in the cylinder and outlet tube.

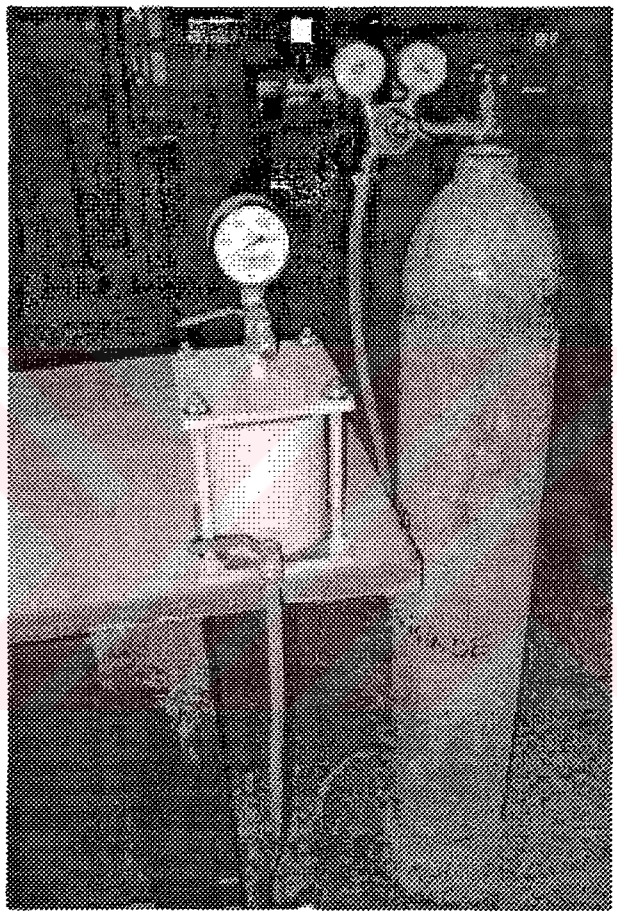

Figure 4.2 The Accelerated Carbonation Test Apparatus (ACT)

Figure 4.3 shows the core machine that was used to take 50 mm diameter core specimens from 150 mm concrete cubes. The core specimens were then cut down 10 cm height in order to obtain h/d ratio of 2 by a sawing machine that is shown in Figure 4.4.

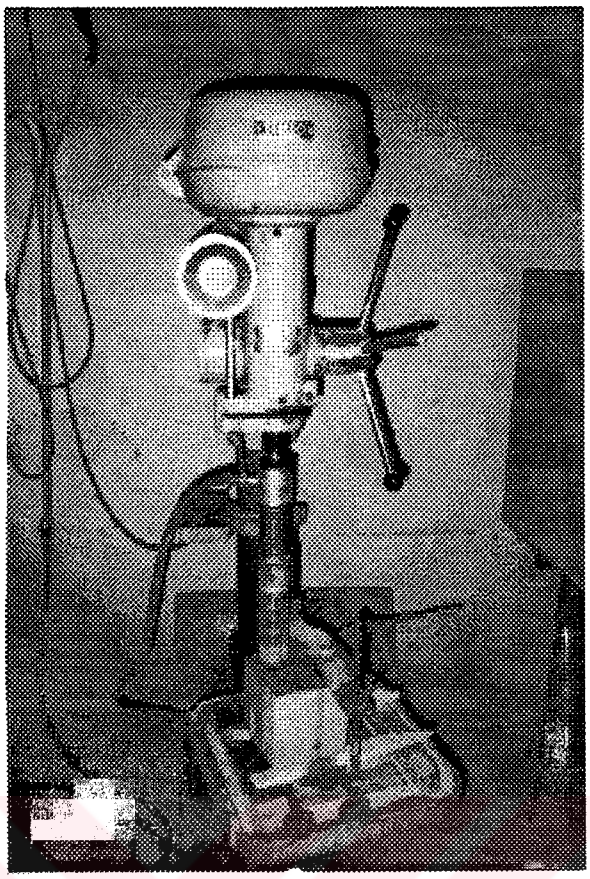

Figure 4.3 The Core Machine

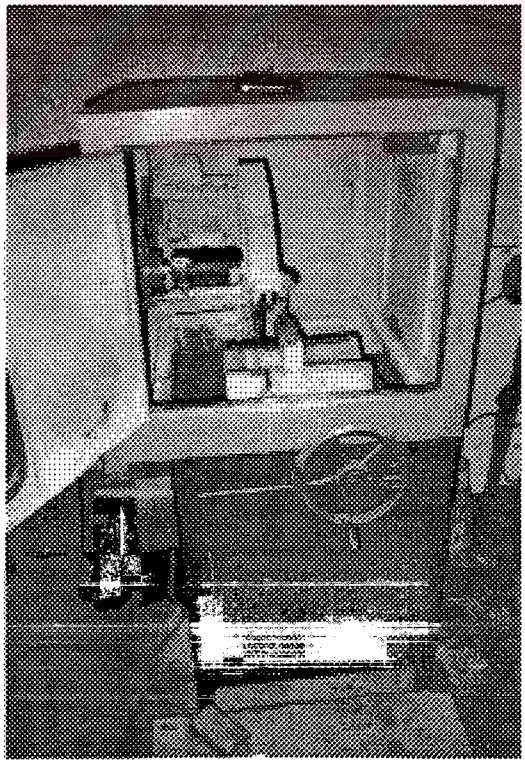

Figure 4.4 The Sawing Machine

Figure 4.5 shows the curing cabinet which was used to maintain constant temperatures and relative humidities with using different saturated salt solutions. In the second stage of experimental studies the carbonation chamber was attached to the curing cabinet in order to control the temperature and humidity conditions.

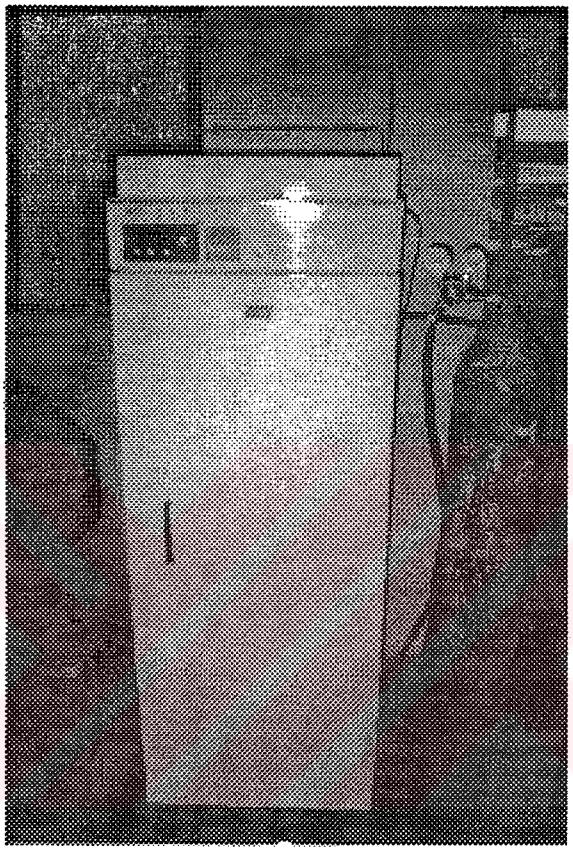

Figure 4.5 The Curing Cabinet with ACT Apparatus

Figure 4.6 shows the curing cabinet with air compressor. Figure 4.7 shows the Accelerated Carbonation Chamber in the curing cabinet and fan adapter.

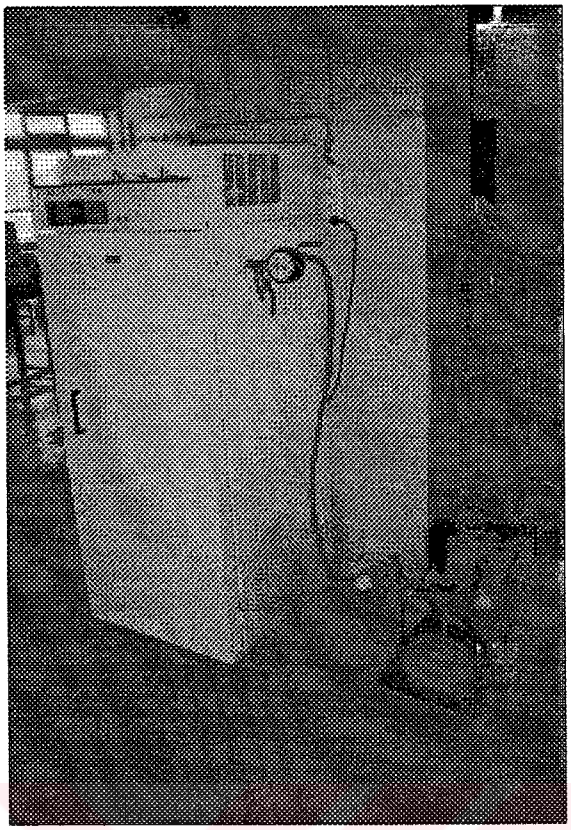

Figure 4.6 The Curing Cabinet with Air Compressor

Figure 4.7 The Accelerated Carbonation Test Apparatus and Fan Adapter

Accelerated Carbonation Test Procedure

Concrete mixes of B and C series were prepared at the same dates in order to test the core specimens simultaneously. Two core specimens were drilled from B series concrete cubes of two different curing conditions for a seven days period. One group of the cube specimens were kept in standard curing conditions while the others had been exposed to laboratory's atmosphere conditions. The same process had been repeated for the C series of concrete mixes. The cylinder core specimens of 150 mm height and 50 mm radius were sawed to 100 mm of height. The core specimens were placed in the ACT apparatus's chamber after drying to constant weight at 105 °C. In order to clean the air in the chamber the outlet valve of the CO_2 cylinder and inlet and outlet valves of the chamber were kept open. After maintaining the steady flow of the gas the outlet valve closed. The inlet valve was also closed as soon as the pressure in chamber reaches to 2 kPa. The specimens were kept in the chamber for 21 days. During this period the pressure level was increased to the desired level whenever it was necessary. After the testing period, core specimens were taken out of the chamber and split perpendicular to their heights. Thymolphthalein ($C_{28}H_{30}O_4$) has been sprayed on the freshly cut and dried surfaces. The penetration depth of colorless region has been measured in order to determine the rate of carbonation. However, some of the specimens showed traces of carbonation, while a large number of others do not. Due to these inconsistent test results, some modifications has been designed on Ballim's simple ACT apparatus. Most of the modifications were based on controlling the ambient relative humidity in the chamber.

First of all, the relative humidity of the gas mix was found extremely dry in the CO_2 cylinder measured at the outlet valve. In order to raise the level of ambient humidity, a cup full of water was placed in the bottom of the chamber. The relative humidity of the chamber has been measured by means of a probe of an electronic relative humidity gauge. In this case, the level of r.h. has been recorded about 90% in the outlet region. This value probably reaches to values up to 100% in the closed chamber which is not a suitable range for the progress of carbonation. As the carbonation reaches its maximum speed at 50% r.h. and it is impeded practically at dry or saturated conditions, a saturated sponge placed in the bottom of the chamber in order to obtain this media. However, this modification did not bring totally successful results.

A container filled with saturated sodium dichromate ($Na_2Cr2O_72H_2O$) which provides 50 % r.h. at 37 °C was placed in the ACT chamber. The chamber was also kept in a curing cabinet to maintain a constant temperature. However, this modification also did not bring totally successful results.

Excessive temperatures which have reverse effects due to drying and decreasing of solubility of the gas, may have been one of the reason for unsuccessful test results. So, ambient temperature was decreased from 37 °C to 20 °C at which saturated sodium dichromate provides 55 % relative humidity. Moreover, considering Accelerated Carbonation Chamber was small closed media and it did not have circulation system to circulate gas mix, it was decided that the curing cabinet may be used as the accelerated carbonation chamber so that the specimens could be kept in it during carbonation test. without chamber. To realize this modification, the inlet valve, the outlet valve and presure gauge were put on the curing cabinet . In order to test, whether the CO_2 gas mix leaked from the curing cabinet, the air compressor was attached to the inlet valve and it was filled with air. During this period pressure in the curing cabinet did not increase, in other words, according to the results of this trial, it was determined that the curing cabinet was not impermeable enough for the gas. So, this modification was also cancelled.

Finally to provide circulation of the CO_2 in the Accelerated Carbonation Chamber, a small fan with 12 volt adapter was placed in the chamber. And the modified system was put in the curing cabinet similar to the previous trials with saturated sodium dichromate at 20°C and 55 % relative humidity. This modification, among others, bring some successful test results.

After all these trials, various modifications did not help to provide meaningful test results. Due to the lack of time, the initial test program has been canceled. Nevertheless, the test trials has proved that a simple ACT apparatus proposed by Ballim does not reveal consistent test results. These results indicate that the accelerated carbonation tests of concrete should be executed by means of a more sophisticated apparatus that controls the ambient humidity and temperature conditions.

CHAPTER FIVE
CONCLUSION

Besides its ability to sustain loads, concrete is also required to be durable. Carbonation is known to be one of the most important durability problem for reinforced or prestressed concrete structures. There are different factors that affect carbonation process and some important positive characteristics of concrete are modified by carbonation which were explained in the Thesis. To improve carbonation resistance of concrete, in other words, to slow down the speed of carbonation reaction, some measures which may be taken into account at the design level or at the application level are mentioned below briefly.

It is very vital that sufficient concrete cover has to be chosen so that the carbonation front does not reach the reinforcement in the uncracked area during the predicted service life. The minimum values of concrete covers given in the codes should be increased by a tolerance value which depends on the quality control during execution and the curing measures. Recommended tolerance value changes from 5 mm to 10 mm according to environmental conditions.

Quality of concrete and thickness of concrete cover which depend mainly on W/C ratio, compaction and curing, has a major importance. If the surface layer of concrete has a high value of permeability, caused by inadequate design and application with locally reduced concrete cover may cut down the durability. One of the main factors that influences the permeability of concrete is the water/cement ratio. In the case of the W/C exceeds 0.6, the permeability will increase considerably due to the increase in capillary pores. All of past experimental data show clearly that increase in W/C causes an in increase carbonation rate. To improve the carbonation resistance of concrete, working with the lower W/C ratio which causes denser concrete mass, is necessary. The application of water-reducing admixtures may help to decrease the water amount. As the poor compaction or rock pockets may also

cause increase in the permeability to such an extent that any protection for the reinforcement will be lost, fresh concrete must be compacted using exterior or internal vibrators. Gaps for inserting of vibrator and sufficient bar spacing should be provided for appropriate concreting and compaction. Dimensions of cross sections should be enlarged if necessary.

According to recent experimental researches, curing measures are one of the main factors that can determine the carbonation resistance of concrete. Insufficient early age curing, especially in the first seven days, causes increase in carbonation considerably. Due to insufficient curing which can cause early drying of the concrete surface, the permeability of the surface layer of concrete may be increased. The depth of the influenced layer depends on the degree of drying, however, it is often deeper than the concrete cover. As the wind and high temperatures are very dangerous for early drying, curing measures must begin after concreting and are not permitted to be interrupted. Moreover, the curing sensitivity of the concrete increases with the increasing W/C ratio and decreasing cement content. The most usual blending agents; natural pozzolans, blast furnace slags, fly ashes, silica fumes, have the common properties that are slow hardening at early age and distinct hardening later on. That means concretes with blended agents or blended cements are more curing sensitive than plain concrete. In other words, increased carbonation rate is expected for concrete with blended agents than plain concrete due to lack of curing.

With increasing cement content, the binding capacity of concrete for CO_2 and the amount of hydration products increases, denser concrete mass is obtained therefore, the penetration speed of the carbonation reaction decreases significantly. In fact, codes generally insist on a minimum cement content of 300 kg/m^3, independent from the cement type. To obtain more durable concrete against carbonation penetration, one of the easiest and effective method is increasing cement content. However, it should not be forgotten that within the normal range of cement content the penetration rates of carbonation are influenced by the cement content than by the W/C ratio, the quality of compaction and curing.

Carbonation of the alkaline compounds in hardened cement paste is a diffusion controlled process depending on the penetration of CO_2 into the pore system of the matrix. Especially

large capillary pores enable an easy access of CO_2 into the matrix. Also, the chemical composition of the cement must be regarded. With decreasing CaO and increasing alkali oxides content of the cement a higher depth of carbonation is observed. Moreover, according to the past experiments, the increase in carbonation rate is observed when Portland cement is replaced by puzzolonic materials or blended cements is used and this is more pronounced with increasing replacement level possibly because, the quantity of $Ca(OH)_2$ will be significantly reduced by the lower quantities of OPC and consumption by the pozzolanic reaction in concretes with puzzolonic materials. Furthermore, carbonation results in the formation of new solid compounds which are deposited in the pores of the matrix, while the original phases of the hydrated cement paste are decomposed. Therefore, the pore structure of concrete can be changed by carbonation. Generally, carbonation led to a denser pore structure in OPC concretes whereas a different behavior can be observed when blended agents are used such as, with high slag content carbonation led to coarser pore structure. As a result of this knowledge, to increase the carbonation resistance of concrete, it can be recommended that replacement level of blending agents must be limited. Furthermore, before using new materials (cements, blending agents, additives, admixtures, aggregates) or new technologies, not only mechanical strengths alone, but also the results with respect to durability must be checked.

Superplasticised concrete mixes have less depth of carbonation than plain concrete mixes at the similar strength grade. This probably reflects of reduced air permeability of superplasticised concrete mixes due to their lower mix water contents compared to the normal mixes having similar strengths and W/C ratios. However, there are different admixtures in the marketing to improve some characteristics of concrete against different attacks which depend on environmental conditions in which concrete is subjected. It has not been encountered enough experimental researches about effects of these admixtures on carbonation rate in the literature. However, it can be expected that using water-reducing admixtures or surface treatment of the concrete with chemical materials or paintings to close capillary pores so that penetration of CO_2, O_2 or Cl^- are broken down, can cause decreasing carbonation rate and increasing carbonation resistance. Furthermore, experimental researches show that application lime-cement mortar coating to the surface layer of the concrete is easy and inexpensive method to increase carbonation resistance. Because, it postpones and slows down the reaction due to diffusion of CO_2 so that

corrosion initiation period is postponed or even prevented. The other positive effect of this coating is that it can be reinstate alkalinity of carbonated concrete region even application of a few years after the end of concrete curing period if sufficient moisture being kept for a long time.

Within the region of cracks carbonation can penetrate to the reinforcement at a higher rate than in uncracked concrete. In reinforcement concrete construction the width of cracks cannot be limited to such an extent that corrosion during the whole service life of the structure could be completely avoided. However, it is recommended that the single crack width at exterior concrete members should not exceed 0.5 mm. Furthermore, a minimum amount of reinforcement must be used to avoid extremely wide cracks. However, using reinforcement for crack control is not enough and recommendable. For corrosion and carbonation protection, an increase in the critical widths by increasing the concrete covers preferable.

If above mentioned measures are not sufficient to improve durability with respect to carbonation, it may be necessary directly protection the reinforcement. The most effective methods are epoxy-coatings and cathodic protections.

Apart from explaining controlling factors of carbonation rate and effects of carbonation on hardened cement paste, mortar or concrete in detail, testing a rather simple accelerated carbonation apparatus was also one of the major objectives of this thesis. The experimental phase of this research was consisted of two stages. First, a simple accelerated carbonation test apparatus was developed according to Ballim's research and then some preliminary tests were conducted using different types of cements at different ages and curing conditions to check the working of the apparatus. The second stage experimental program was conducted to observe the effects of cement type, curing conditions and age of concrete on carbonation rate. It was clear from all of these test results that this elementary ACTA do not work properly. Since, indications of carbonation was observed from some of these samples whereas a large number of others did not show any evidence of carbonation. Although, some modifications were made on the ACTA especially to keep the relative humidity around 50%, continuously successful test results from this simple ACTA were not provided. In spite of the fact that, carbonation is a complex chemical reaction depending on

a lot of factors all of which must be regarded and this simple ACTA has not got relative humidity and temperature controlling systems to keep the r.h. and temperature constant, using this ACTA for further researches appears to be difficult unless some modifications being made on it especially to control the r.h. and temperature while considering the other environmental factors such as concentration and pressure of CO_2, etc.

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