Numerical modeling of concrete carbonation under wide range of environmental conditions

Sabet Divsholi Bahador

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CARBONATION UNDER WIDE RANGE OF
ENVIRONMENTAL CONDITIONS**

Sabet Divsholi Bahador

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SCHOOL OF CIVIL AND ENVIRONMENTAL ENGINEERING
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A thesis submitted to the Nanyang Technological University
in fulfilment of the requirement for the degree of
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2008

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SUMMARY

Carbonation and chloride penetration in concrete has been a subject of research interest for many years. Carbonation and chloride penetration can make severe damage in reinforced concrete. The problem with corrosion in reinforced concrete is a very real one. It can affect service life of concrete structures significantly. In urban area and industrial area with the high concentration of CO_2 the problem of carbonation is the main deterioration mechanism. Several parameters and variables can affect the rate of carbonation in concrete structures. For purpose of modeling, understanding all the variables and process before the start of corrosion is important.

A new mathematical model for carbonation of concrete is proposed in this study. This model can cover many parameters affecting the carbonation rate of concrete. The input data for this model include chemical composition, physical properties and mineral characteristics of Portland cement and mineral admixtures, water/cement ratio, aggregate/cement ratio, maximum aggregate size, curing condition (period, temperature, relative humidity), preconditioning (period, temperature), CO_2 concentration, exposure time and the ambient conditions. The output of this model is depth of carbonation after defined period of time. A new model for the prediction of degree of pozzolanic activity of mineral admixtures has been proposed and studied in this work. Also the effect of crack on increasing the rate of carbonation of concrete has been considered. To verify the effect of preconditioning and mineral admixtures on saturation degree and drying rate, an experimental work was done and by monitoring the total weight loss during drying-wetting process, the drying rate and final saturation degree of concrete with various mix proportions were studied. The pore structure of concrete with various mix proportions and in various conditions was also studied by using mercury intrusion porosimeter (MIP).

The prediction ability of the proposed model is much better compared to the existing models and this model can predict the carbonation depth of concrete under the wide range of the environmental conditions.

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LIST OF SYMBOLS

pH	=	The acidity or alkalinity of a solution, numerically equal by 7 for neutral condition
ρ_c	=	Specific density of cement
ρ_a	=	Specific density of aggregate
ρ_w	=	Specific density of water
MW	=	Molar weight
FA, LFA	=	Low calcium fly ash
FH	=	High calcium fly ash
SF	=	Silica fume
CSF	=	Condensed silica fume
$GBFS$	=	Granulated blast-furnace slag
$BFSC$	=	Blast-furnace slag cement
$EPMA$		Electron probe x-ray microanalysis
NIR	=	Near-infrared ray
w/c	=	Water cement ratio
a/c	=	Aggregate cement ratio
x	=	Depth from exposed surface
t	=	Time
D_{e,CO_2}, D_{CO_2}	=	(Effective) CO_2 gas diffusivity
T	=	Temperature
R_0C	=	Rate of carbonation
RH	=	Relative humidity
RH_{10}	=	The internal relative humidity at 10 mm depth from surface
IRH	=	Internal relative humidity
RHa	=	Ambient relative humidity
$D(w)$	=	water diffusivity

H_{en}, H', H_c	=	Environment relative humidity, equivalent relative humidity and absolute relative humidity.
e	=	Pozzolanic ratio
f	=	Saturation degree of the pores
d_K	=	Kelvin diameter
w	=	Thickness of water film inside of pores
f_d	=	The fraction of pore size distribution
f_K	=	The volume of completely filled pores, i.e., $d < d_K$
f_w	=	The volume of aqueous film of the pores with diameter $d > d_k$
a_s	=	The specific surface area of pores
LOI	=	Loss on ignition
ε_{air}	=	The volume of entrapped air
d	=	Equivalent diameter of the intruded pores
γ	=	Surface tension of mercury
θ	=	Angle of contact between the mercury and the pore walls
p	=	Pressure at which a given increment of mercury intrudes into the pore system
σ_c	=	The compressive strength
A	=	Area of loaded surface
F_i	=	Hydration degree of PC compounds
α_{bf}, α_f	=	Maximum activity, hydration degree of mineral admixtures
n, n_i, n_j	=	Constant
$K_{H,i}, K_{H,j}$	=	Constant
α_{RH}	=	Air curing coefficient
R	=	Universal gas constant
α_T	=	Curing temperature coefficient
E_a	=	The activation energy (minimum energy required for product formation)

m_i	=	Weight fraction of component i
m_{cl}	=	Weight fraction of clinker
$f_{c,p}$	=	Fraction of CaO in pozzolanic material
$f_{s,p}$	=	Fraction of gypsum in pozzolanic material
α_j	=	Degree of pozzolanic activity
a, b	=	Constant
ε_0	=	Initial porosity
$\varepsilon(t)$	=	Porosity at time t
$\Delta\varepsilon_H(t)$	=	Reduction in porosity due to hydration
$\Delta\varepsilon_C$	=	Reduction in porosity due to carbonation
W	=	Total amount of water in mix design
a_T	=	Exposure temperature coefficient
$\Delta\bar{V}_{C_3S}$	=	Difference in molar volume between solid reaction product and solid reactants for C_3S
$\Delta\bar{V}_{C_2S}$	=	Difference in molar volume between solid reaction product and solid reactants for C_2S
$\Delta\bar{V}_{C_3A,s}$	=	Difference in molar volume between solid reaction product and solid reactants for C_3A
$\Delta\bar{V}_{C_4AF}$	=	Difference in molar volume between solid reaction product and solid reactants for C_4AF
$\Delta\bar{V}_{CH}$	=	Difference in molar volume between solid reaction product and solid reactants for $Ca(OH)_2$
$\Delta\bar{V}_{CSH}$	=	Difference in molar volume between solid reaction product and solid reactants for CSH
ε_p	=	Porosity of cement paste
A	=	Al_2O_3
S	=	SiO_2

$\bar{S}$	=	Gypsum
C	=	CaO
r_D	=	Dissolution rate of $Ca(OH)_2(s)$
r_{CH}	=	Carbonation rate of $Ca(OH)_2$
H	=	Henry's constant
K_{sp}	=	Solubility of ion
K_T	=	Arrhenius law for exposure temperature
r_{CSH}	=	Carbonation rate of CSH
$r_{H,CSH}$	=	Hydration rate of CSH
x_C	=	Carbonation depth
S_f	=	Final saturation degree
$S(x)$	=	Saturation degree in depth x from drying surface

CHAPTER

1

INTRODUCTION

1.1 Background

Concrete is the most widely used construction material. Its success can be attributed to its low cost and satisfactory performance in service. Durability of concrete is much superior to its main competitors, steel and timber. In the last decades, however, the instance of unsatisfactory durability of concrete structures has increased at an alarming rate, especially in the most developed parts of the world.

The most common durability problem is corrosion of the reinforcing steel in reinforced concrete. Corrosion reduces the available cross sectional area of a reinforcing bar and its strength. Since the volume of the corrosion products exceeds by far that of the corroding metal, this causes spalling of the concrete covering the reinforcement bars (Papadakis, 1989).

In concrete, reinforcing bars are protected from corrosion by a thin oxide layer which is formed and maintained on their surface due to highly alkaline environment of the surrounding concrete i.e. pH value around 13. The alkalinity of the concrete is due to the $Ca(OH)_2$, one of the important hydration products which is produced during hydration of cementitious material (Papadakis, 1989).

In maritime or coastal environments, and when deicing salts come in contact with concrete at the surface, chloride penetration is the main mechanism that induces corrosion of concrete. In all other cases, and especially in CO₂ rich urban environment, carbonation of the concrete is the main mechanism leading to steel corrosion (Papadakis, 1991, 1).

Carbonation of concrete has been the interested topic of research for many years. There are many invaluable experimental data on carbonation depth of concrete in natural and accelerated test. Also various mathematical models have been proposed to predict the depth of carbonation.

1.2 Objective

The objective of this study is to predict the carbonation depth of concrete based on accelerated and natural carbonation test results. The important parameters on carbonation test results will be used to develop a general carbonation model. The proposed model will have the ability to predict most of accelerated and natural carbonation test results regardless of their preconditioning and exposure condition. The parameters include the chemical and physical properties of cementitious materials such as oxide composition and particle size distribution, the mix proportion, the curing condition like type of curing, curing temperature and curing period, and environmental condition such as CO₂ concentration, temperature, relative humidity and the moisture content of concrete (as presented in Figure 1-1).

Figure 1-1 Schematic presentation of this research

1.3 Scopes

The scope of this study is to propose a general mathematical model for carbonation of concrete. This model will have the ability to predict most of carbonation test result regardless of their conditions. And it also can define a service life design based on Singapore exposure condition.

1.4 Organisation

This report is set up as follows: Chapter 2 reviews the carbonation process and drying process in concrete. The effective parameters on concrete carbonation will be studied in chapter 3. In chapter 4 study of drying process of concrete will be presented. Carbonation of concrete includes the finite difference method (FDM) software to predict the carbonation depth is offered in chapter 5. And the final chapter contains the conclusion and the recommendations for future studies.

CHAPTER

2

LITERATURE REVIEW

2.1 Chemical composition of cement

2.1.1 PC composition

The properties of concrete depend on the quantities and qualities of its components especially cementitious materials. ASTM C 150 defines Portland cement as "hydraulic cement" produced by pulverizing clinkers consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an inter ground addition." The manufacture and composition of Portland cements, hydration processes, and chemical and physical properties have been repeatedly studied and researched, with innumerable reports and papers written on all aspects of these properties.

ASTM C 150 and AASHTO M 85 present the standard chemical requirements for each type of cement. The compounds in Portland cement are denoted by ASTM as tricalcium silicate (C_3S), dicalcium silicate (C_2S), tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). However, it should be noted that with effects of burn temperatures, quenching, oxygen availability, and other real-world kiln conditions, the actual components are often complex chemical crystalline and amorphous structures. The behavior of each type of cement depends on the content of these compounds.

Characterization of these compounds, their hydration, and their influences on the behavior of cements are presented in full detail in many books. Some of the most complete references dealing with the chemistry of cement include those written by Bogue (1955) and Taylor (1964). Different analytical techniques such as X-ray diffraction and analytical electron microscopy are used by researchers in order to understand the hydration of cement and to improve the properties of cementitious material.

The Bogue equations for estimating the theoretical or potential compounds of Portland cement are as follows.

$$C_3S = 4.07 (CaO) - 7.60 (SiO_2) - 6.72 (Al_2O_3) - 1.43 (Fe_2O_3) - 2.85 (SO_3) \quad (2.1)$$

$$C_2S = 2.87(SiO_2) - 0.75(C_3S) \quad (2.2)$$

$$C_3A = 2.65(Al_2O_3) - 1.69(Fe_2O_3) \quad (2.3)$$

$$C_4AF = 3.04(Fe_2O_3) \quad (2.4)$$

$$C\bar{S}H_2 = 2.15(SO_3) \quad (2.5)$$

ASTM C 150 and AASHTO M 85 have specified certain physical requirements for each type of cement. These properties include 1) fineness, 2) soundness, 3) consistency, 4) setting time, 5) compressive strength, 6) heat of hydration, 7) specific gravity, and 8) loss of ignition. Each one of these properties has an influence on the performance of cement in concrete. The fineness of the cement, for example, affects the rate of hydration. Greater fineness increases the surface available for hydration, causing higher early strength and more rapid generation of heat (the fineness of Type III is higher than that of Type I cement) (U.S. Dept. Trans. 1990).

The initial concentration of compound i ($i = C_3S, C_2S, C_4AF, C_3A$) in PC can be calculated from the weight fraction of compound i in the clinker (m_i/m_{cl}) and mix proportions, i.e. cement content (c) or w/c ratio, a/c ratio, and the volume fraction of entrapped or entrained air ε_{air} in concrete (Papadakis, 1991, 2).

$$[i]_0 = \frac{m_i/m_{cl}^{C(1-\varepsilon_{air})}}{MW_i} = \frac{m_i/m_{cl}\rho_c(1-\varepsilon_{air})}{MW_i(1+\frac{w\rho_c}{c\rho_w}+\frac{a\rho_c}{c\rho_a}+\frac{p\rho_c}{c\rho_p})} \quad (2.6)$$

In which ρ_c, ρ_w, ρ_a and ρ_p (kg/m^3) are the densities of cement, water, aggregate and pozzolanic materials respectively, and MW_i is the molar weights of compound i given in Table 2-1.

Table 2-1 Molar weights of cement compounds

Compound	C_3S	C_2S	C_4AF	C_3A
Molar weight $MW_i \times 10^3$ (kg/m^3)	228.30	172.22	485.96	270.18

2.1.2 Mineral admixtures

In this work the following three groups will be studied.

1-Fly ash

Fly ash is the combustion residue in coal-burning electric power plants, which flies out with the flue gas stream and is removed by mechanical separators, electrostatic precipitators, or bag filters. It has been used as a pozzolanic addition in concrete or as a Portland cement additive, due to economical and technological benefits.

Low-calcium fly ash (LFA) is produced by burning anthracite or bituminous coal. LFA is categorized as a normal pozzolanic, a material consisting of silicate glass, modified with aluminum and iron (Papadakis, 1999, 1).

High-calcium fly ash (HFA) is the combustion residue in electric power plants burning lignite or sub-bituminous coal. It essentially consists of alumina silicate glass modified by the presence of large amounts of calcium and magnesium. It can be categorized as cementitious material when CaO is higher than 20% (Papadakis, 2000).

2-Silica fume

Silica fume (SF) or microsilica is industrial by-product, from electric arc furnace producing silicon and ferrosilicon alloys. SF belongs to the category of high pozzolanic material because it consists essentially of silica in noncrystalline form with a high specific surface, and thus exhibits excellent pozzolanic activity (reaction with calcium hydroxide). It is mainly used to improve the mechanical properties and the durability of concrete (Papadakis, 1999, 2).

3-Granulated blast furnace slag (GBFS)

The use of granulated blast-furnace slag (GBFS) as supplementary cementitious material for production of cement is economical and ecological. According to European standard for cement, a blast-furnace slag cement (BFSC) may contain 95 wt% GBFS. Therefore the characteristic of the cement is strongly affected by GBFS. The chemical composition, structure and crystallinity, the fineness, and particle size distribution of the GBFS are the main important factors affecting the pozzolanic activity of these materials. It is well known that blast furnace slag cement (BFSC) has been manufactured by intergrinding of GBFS with cement clinker or by separate grinding (Wang, 2005).

2.2 Carbonation of concrete

2.2.1 Methods to measure carbonation depth

-pH indicator

One of the most common methods for measuring the carbonation depth of concrete is by spraying a sample cross section, i.e., a section parallel to the direction of carbonation, with a pH indicator. In this method, a 1–2% water–alcohol solution of phenolphthalein will be used, which produces a pink stain (typical of phenolphthalein

in an alkaline medium) in areas with a pH higher than 9, while the areas with a pH < 9 (where carbonation has occurred) remain colorless (Seatta, 2005).

Figure 2-1 Carbonation depth by phenolphthalein (Geraldine, 2006)

-EPMA analysis (electron probe X-ray microanalysis)

This method is based on image processing and it can identify the carbonated area with different color, as the image shown in Figure 2-2.

Carbonation depth

Figure 2-2 Carbonation depth by EPMA (Hisashi, 2005)

-Near infrared spectral imaging system

It is one of the new methods introduced by Hisashi Kanada and Taketo Uomoto to predict depth of different deterioration of concrete (Hisashi, 2005).

The benefits of this method are as follow:

- No pretreatment, direct measurement.
- Applicability for field inspection
- Reduction of componential analysis
- Operator's skill is not required
- Large area measuring
- Remote and non-destructive inspection
- Nonuse of chemical agent
- Low-cost componential analysis

The basic idea of this method is the specific wave length will be absorbed in different condition as follow.

Carbonation, neutralization

The $Ca(OH)_2$ in cement paste absorbs near infrared ray at 1410 nm wave length.

Chloride content

Absorbance of near infrared ray at 2266 nm wave length increases by increasing the chloride content.

Deterioration due to sulfuric acid attack

The $CaSO_4(H_2O)_2$ absorbs near infrared ray at 1750 nm wave length.

This model is still under further investigations.

-Gammadensimetry

Gammadensimetry is an accurate and nondestructive measurement; the idea is based on absorption of the gamma rays emitted by a radioactive source of cesium (Geraldine, 2006).

Some other methods are **neutron radiography** and **radioactive carbon dioxide** more information about these methods is available in some references (Richardson, 1988).

2.2.2 Factors affecting carbonation rate of concrete

Factors affecting carbonation rate of concrete reported by researchers as follow:

1. Exposure time

Almost all of the theoretical models claim that a square root relationship exists between time and depth of carbonation.

2. Mix proportion

- w/c ratio

w/c ratio has significant effect on carbonation rate by changing porosity and pore connection; lower w/c ratio leads to lower porosity and lower pore connection and finally lower depth of carbonation.

- a/c ratio

Most of the works on the effect of a/c ratio shows that higher a/c ratio in constant w/c ratio leads to a higher depth of carbonation (Papadakis, 1991, 1).

- Chemical composition of cement (PC, BFSC, SFC, FAC)

The total carbonatable materials depend on chemical composition of the cement. Generally replacement of the PC by mineral admixtures is known to increase the rate of carbonation by consuming the calcium hydroxide. But large variation of carbonation depth of concrete depends on the chemical compositions and physical properties of mineral admixtures as expected.

3. Curing condition

- Curing period

Longer period of curing leads to higher amount of carbonatable material and also lower porosity and pore connection and

therefore lower depth of carbonation is expected.

- Curing temperature

The curing temperature affects the pore structure of cement paste. In higher curing temperature, the volume of hydration products will decrease. In result, it causes higher porosity. Meanwhile higher rate of hydration in higher temperature is expected and in short curing period, it can be an advantage.

- Air curing

Curing in air will decrease the hydration degree. It causes higher porosity, higher pore connection and decrease in amount of carbonatable material. Therefore it can increase the depth of carbonation significantly.

4. Concrete characteristic

- Porosity and pore size distribution

Higher porosity leads to higher air permeability, lower saturation degree and in result higher depth of carbonation is expected.

- Saturation degree

Saturation degree has direct effect on carbonation of concrete, higher saturation degree will increase the rate of reaction of compounds with CO_2 but also will decrease the diffusivity of gaseous CO_2 , then only in the critical level of saturation degree the carbonation depth will be maximum.

- Preconditioning

Preconditioning has significant effect on result of accelerated carbonation test. Based on type of preconditioning the measured depth of carbonation will be varied significantly. Knowing the details of preconditioning in accelerated test will help to predict the carbonation depth in natural condition from accelerated test results more accurately.

- Crack

Crack can increase the available area for penetration of harmful

chemical agent into concrete. Higher carbonation depth is expected in higher cracked sections.

5. Exposure condition

- Relative Humidity

Ambient relative humidity has direct effect on saturation degree and water movement rate in concrete. the rate of diffusivity of chemical agents and reaction rate is controlled by this parameter.

- CO₂ concentration

Square root relationship between CO₂ concentration and carbonation depth has been proposed by most of the researchers.

- Exposure Temperature

Higher ambient temperature can increase the rate of reaction of CO₂ with hydration products. Therefore in the same degree of saturation and relative humidity, it can increase the depth of carbonation.

- Exposure type (indoor, sheltered from rain, expose to rain, cyclic condition)

The various empirical equations and coefficients were offered by various researchers. In general agreement regardless of relative humidity, the depth of carbonation for these conditions can be compared as follow:

$$x_{Indoor} > x_{sheltered} > x_{expose\ to\ rain}, x_{cyclic\ condition}$$

In which x is the carbonation depth.

All the coefficients and empirical equations proposed by various researchers can be valid only for their environmental conditions. However there is no general coefficient or equation to predict the depth of carbonation in general conditions.

Some other factors like aggregate characteristic, construction quality, roughness of concrete surface highlighted by various researchers. The effects of these parameters in normal concretes are negligible (Richardson, 1984).

2.2.3 Summary of carbonation models

The various researches have been done on carbonation of concrete in experimental works or mathematical models and various carbonation models have been proposed by the researchers. In most of these models a few factors considered. Therefore they can not predict the depth of carbonation in general condition properly.

Generally the models can be divided into two main groups, simple and complex models.

-Simple models (explicit models)

Usually these models contain of one explicit formula predicting the carbonation depth at given time t . A common feature of all these theoretical models is the square root relationship which is presented as follow

$$x = k\sqrt{t} \quad (2.7)$$

Which x =depth of carbonation, t =exposure time and k =coefficient which depends on various factors.

By considering the carbonation of $Ca(OH)_2$ and based on Fick's first law for diffusion of aggressive agent, the simple equation to predict the depth of carbonation proposed as follow

$$x = \sqrt{\frac{2D_{CO_2}[CO_2]t}{[Ca(OH)_2]}} \quad (2.8)$$

In this equation, D_{CO_2} is effective diffusivity of CO_2 . And $[CO_2]$, $[Ca(OH)_2]$ show the molar content of CO_2 and $Ca(OH)_2$ respectively.

Some other researchers believe on carbonation of other compounds in concrete and based on this idea the following equations has been presented by Papadakis

(Papadakis, 1989).

$$x = \sqrt{\frac{2[CO_2]_0 D_{e,CO_2} t}{[Ca(OH)_2]_0 + 3[CSH]_0 + 3[C_3S]_0 + 2[C_2S]_0}} \quad (2.9)$$

The main problem with equation (2.9) is that the total carbonatable material decreases by increasing the curing time. Due to this problem it can not simulate the effect of curing properly. Also some other researchers did not record the carbonation of all compounds in cement paste. Grove showed that in the PC concrete, only $Ca(OH)_2$ and CSH will participate in carbonation reaction (Groves, 1990). Then the equation (2.9) will be as follow

$$x = \sqrt{\frac{2[CO_2]_0 D_{e,CO_2} t}{[Ca(OH)_2]_0 + 3[CSH]_0}} \quad (2.10)$$

The main issue in Papadakis work is the type of preconditioning he used before start of carbonation test, this problem will be discussed later on this thesis.

Another explicit equation offered by Uomoto as follow (Uomoto, 1993)

$$x = (2.084 - 0.8471 \log C) \times e^{(8.748 - \frac{2563}{T})} \times (2.39 \left(\frac{w}{c}\right)^2 + 0.446 \frac{w}{c} - 0.398) \times \sqrt{Ct} \quad (2.11)$$

In which C is the CO_2 concentration (%). In this simple equation the effect of ambient temperature is considered. According to experimental works on carbonation of concrete in natural and accelerated test this equation can predict a bigger range of carbonation data. But due to high saturation degree before start of this work, the proposed equation by Uomoto cannot simulate the effect of CO_2 concentration properly.

One of the good experimental studies has been done by Russell and Basheer (Russell, 2001). They kept their samples in oven at $40^\circ C$ for 1, 2 and 4 weeks as preconditioning to reach the desired saturation degree of 75%, 65% and 55% respectively. Then they sealed all the faces of the samples and kept them 6 more weeks in oven to achieve a uniform saturation degree in concrete. And finally they

proposed the following equation for the rate of concrete carbonation.

$$R_0C = \beta_0 + \beta_1[\log(APl_i)] + \beta_2(f_{cu}) + \beta_3(RH_{10}) + \varepsilon_1 \quad (2.12)$$

In which R_0C shows the rate of carbonation, APl_i shows the initial measurement of the air permeability, RH_{10} the relative humidity at 10 mm from expose surface, f_{cu} compressive strength of concrete, and finally $\beta_0, \beta_1, \beta_2, \beta_3, \varepsilon_1$ are constant.

The correlation coefficient for this equation is 0.781. It shows that this equation can not simulate their experimental study properly. For higher w/c ratio, higher rate of drying is expected. Using the same length of drying as preconditioning for different w/c ratio was one of the weak points of this study. Also 1, 2 and 4 weeks drying in oven by 40°C was not enough to bring the moisture content as low as desire levels for 75%, 65% and 55%.

- Complex Models

In the last decades, many complex models have been developed in order to simulate the carbonation process numerically. The general approach is to collect mass balances. Most of this models used finite elements method and moving boundary to predict the depth of carbonation (Muntean, 2005).

Burkan Igor offered a model involves the effect of heat transfer and moisture transport to measure the depth of carbonation of concrete. The basic idea of this model is based on start from $t=0$ condition and increase the time by Δt . The boundary conditions will be checked each time (Burkan, 2004). One of the strong points of his work is working on effect of crack on carbonation of concrete. But the weaknesses of his work are that he considered $Ca(OH)_2$ as only carbonatable material. And instead of theoretical and defined procedure, most of relations were based on numerical methods. Also insufficient number of parameters is the main problem of this work.

One of the other complex models offered by Sietta, the finite element method applied both in time and two dimensional spaces with considering the effect of

moisture and heat flow. This model is developed very well. But the basic theories he used in his work was not strong. Some other complex models offered by Ishada (2004) and Bary (2004).

Many experimental works have been done in this topic. Although the authors did not offer any simulation models for concrete carbonation, their experimental data are valuable.

2.3 Drying process of concrete

2.3.1 Effect of moisture movement on concrete deterioration

The modeling of complex fluid movements within unsaturated concrete samples is always topical because many points remain unclear due to the complexity of the pore structure and all the physicochemical interaction between different phases (Monlouis, 2004). There is increasing concern that moisture movement contribute to most of the deterioration process in the concrete such as chloride and carbonation induced corrosion, leaching, acid and sulphate attacks, alkali silica reaction and freeze-thaw attacks. Therefore it has decisive effect on the performance of concrete (Wong, 2001).

The moisture reduction of concrete structures in dry service environment will increase the risk of shrinkage and cracking. So, it is very important to predict the distribution and moisture change in concrete structures for durability problems (Zhengwu, 2006).

Due to important of this issue, several models have been proposed to predict the moisture movement and moisture distribution in concrete. In most of the works, the internal relative humidity distribution is the main interested parameter. But the saturation degree of concrete is the more important parameter. It's due to the pore blockage caused by condensed water which can affect the rate of deterioration mechanisms.

Lots of parameters are effective on drying rate of concrete and the final saturation degree. Due to complexity of the effect of different parameters on rate of drying, proposing a general model is difficult. Investigation of different parameters separately will help to identify how each of these parameters can affect the overall process. It will help to decide which one is more effective and can be used to improve the behavior of concrete.

The drying rate and the saturation degree depend on pore structure and environment relative humidity. And the pore structure of the concrete depends on w/c ratio, a/c ratio, curing period, type and percentage of mineral admixtures.

There are few works on the effect of mineral admixtures on drying rate and the saturation degree of concrete. The effectiveness of mineral admixtures depends on the particle size, chemical composition and the mineral characteristics.

One of the main concerns of this work is the effect of saturation degree of concrete on accelerated carbonation test. To predict the carbonation depth in natural condition based on accelerated data, Papadakis offered the following relation (Papadakis, 1989).

$$\frac{\text{Depth of carbonation (accelerated test)}}{\text{Depth of carbonation (natural condition)}} = \sqrt{\frac{[CO_2]_{ac.}}{[CO_2]_{na.}}} \quad (2.13)$$

Ceukelaire (1992) did the test in both natural and accelerated condition by 10% and 0.03% CO₂ concentration. According to Papadakis equation (2.13) the relation coefficient should be $\sqrt{\frac{10}{0.03}} = 18.25$. But the relation coefficient for his work was between 6 and 13.

Also Uomoto (1993) did the test in both conditions with 0.07%, 1%, 10% CO₂ concentration and based on Papadakis relation the coefficient should be $\sqrt{\frac{1}{0.07}} = 3.78$, $\sqrt{\frac{10}{0.07}} = 11.95$ respectively. But based on his experimental work the relation coefficients are much smaller.

Table 2-2 Different relation coefficients in Ceukelaire work

RH%	Carbonation depth(mm) after exposure in 10% CO ₂	Carbonation depth(mm) after exposure in 0.03% CO ₂	Relation coefficient
90	4.9	0.5	9.8
80	5.6	0.5	11.2
70	7.5	0.8	9.375
60	8.0	0.6	13.33
50	8.5	1.4	6.07
40	6.8	0.9	7.55

Table 2-3 Different relation coefficients in Uomoto work

Initial curing (days)	w/c	x_c (mm) 0.07% CO ₂	x_c (mm) 1% CO ₂	x_c (mm) 10% CO ₂	$\frac{x_c(1\%)}{x_c(0.07\%)}$	$\frac{x_c(10\%)}{x_c(0.07\%)}$
0	0.7	1.78	4.63	11	2.6	6.18
0	0.6	1.23	3.29	7.05	2.675	5.73
0	0.5	0.67	1.87	4.14	2.791	6.18
5	0.7	0.79	2.62	5.51	3.316	6.97
5	0.6	0.62	1.6	3.61	2.58	5.82
5	0.5	0.27	0.82	1.72	3.03	6.37

In his work, Roy (1999) measured the carbonation depth for accelerated carbonation test by 6% CO₂ is 2 to 6 times more than natural condition. It is much lower than the Papadakis prediction which is equal to 14 times.

This apparently big and unpredictable error in these predictions is due to different saturation degree at the start of accelerated carbonation test. Before starting the mathematical modeling, having a good observation of saturation degree is necessary.

2.3.2 Saturation degree of concrete

The saturation degree of concrete f is the fraction of the pore volume filled with water. The fraction of the pore volume available for diffusion of gases is equal to $(1 - f)$. All pores with diameter less than Kelvin Diameter d_k (μm) are completely filled with water, while the walls of all pores with diameter d exceeding d_k will be covered by a continuous film of water, of thickness w .

$$w = \frac{cx d_w}{[1+(c-1)x](1-x)} (1 - x^{d/2d_w}) \quad (2.14)$$

$$d_k = 2w + \frac{A}{T \ln(\frac{1}{x})} \quad (2.15)$$

In which $x = RH/100$, the constant A is equal to 0.6323 for noncarbonated material and 0.2968 for carbonated, C is the BET-constant for the particular temperature and water vapor-solid surface system (assume $C=100$ for non-carbonated concrete and $C=1$ for carbonated concrete), $d_w = 3 \times 10^{-4} \mu m$ is the molecular diameter of water (Papadakis, 1991, 2). The equations (2.14) and (2.15) are depending on each other. For solving them the approximate equation proposed by Hagymassy can be useful (Hagymassy, 1969).

$$w = 0.000425 [-\log(\frac{RH}{100})]^{-0.31} \quad (2.16)$$

The completely filled pores, i.e., $d < d_k$ take up the following fraction of the total pore volume.

$$f_k = \int_{-\infty}^{\log d_k} f_d d (\log d) \quad (2.17)$$

The aqueous film of the pores with diameter, $d > d_k$ occupied the following fraction of the total volume of the pores (f_d is the function of pore size distribution)

$$f_w = \frac{2cx d_w}{[1+(c-1)x](1-x)} \int_{\log d_k}^{\infty} \frac{1}{d} (1 - x^{d/2d_w}) f_d d (\log d) \quad (2.18)$$

The saturation degree will be equal to $f = f_k + f_w$.

Effect of ambient relative humidity on saturation degree

The relation between saturation degree and external (ambient) relative humidity for w/c ratio of 0.25 and 0.5 has been presented in Figure 2-3 (Maekawa, 1999, p 79). This data shows different level of saturation degree for different w/c and in the same relative humidity for lower w/c ratio, the saturation degree is higher. But because the 105°C was used to achieve these saturation degrees, these values are much lower than the natural absorption-desorption curves. This issue will be further discussed later on this thesis.

Figure 2-3 Saturation degree for different relative humidity and w/c ratio

Relation between saturation degree and relative humidity for cement paste and mortar was investigated by Papadakis. Figure 2-4 shows the experimental data by Papadakis for the saturation degree and relative humidity.

Figure 2-4 Saturation degree of mortar and cement paste in different relative humidity

Papadakis also showed that the saturation degree in the same level of relative humidity is lower for higher w/c ratio (Papadakis, 1991, 2).

2.3.3 Methods to study the moisture movement in concrete

There are many methods to study the moisture movement in concrete. These methods can be broadly classified into three groups (Parrott, 1988).

1. Overall weight change measured on test specimens
2. Weight change corresponding to selected depths from the exposed surface
3. Measuring the internal relative humidity at selected depths

The overall weight change is one of the methods used by various researchers. It can be useful in the case of natural surrounding environment. The internal relative humidity can be measured in different depth by different type of probe. The basic idea of this method is to make a hole at specific depth of sample and the probe will be inserted to measure the internal relative humidity in that particular depth. The main

problem with measuring the internal relative humidity is the higher recorded value of internal relative humidity for higher w/c ratio. In higher w/c ratio, the rate of drying is faster and lower saturation degree is expected. Gravimetric methods can also be used to determine moisture content profiles after splitting the specimens at selected sections.

2.3.4 Summary of previous models

As the moisture distribution in concrete is one of the important parameter to control the penetration rate of aggressive agent in concrete, different models have been proposed to predict the saturation degree and moisture distribution in concrete.

One of the first models for moisture diffusivity and saturation degree was proposed by Kasperkiewicz (1972). He proposed the following equation to calculate the rate of diffusion of moisture from concrete surface.

$$D(w) = aw^2 + bw + c \quad (2.19)$$

Where a, b and c are the experimental coefficients. With this equation, he calculated the distribution of saturation degree in concrete.

Another work was done by Bazant and Najjar (Bazant, 1972) and they proposed the following equation to obtain the diffusion of the moisture from concrete.

$$C = C_1 \left(\alpha_0 + \frac{1-\alpha_0}{1+\alpha_1^n(1-H')^n} \right) \text{ where } \alpha_1 = \frac{1-H_{en}}{1-H_c} \quad (2.20)$$

In this equation C_1, α_0, n are the empirical coefficients and H_{en}, H', H_c are environment relative humidity, equivalent relative humidity and absolute relative humidity. And then they used moving boundary idea to measure internal relative humidity distribution. Later Wong (2001) and West (2005) worked on this equation to improve coefficients and boundary conditions.

Ayano used exponential behavior for moisture diffusion from concrete as follow (Ayano, 2000).

$$D(w) = a \times e^{b(1-w)} \quad (2.21)$$

Verdier used different exponential behavior for moisture diffusion from concrete as follow (Verdier, 2004).

$$D(w) = A \times e^{bw} \quad (2.22)$$

Parrott has worked on this subject for a long time and three different equations have been proposed by him. His focus was to predict the internal relative humidity instead of the saturation degree of concrete. The first equation he proposed was as follow (Parrott, 1988)

$$RH = 100 - \left(1 - e^{-\frac{1.42}{(d+0.01)^2}}\right)(100 - RHA) \quad (2.23)$$

Where RHA is the ambient relative humidity, t (days) is the drying time and d (mm) is the depth from drying surface. Then he offered his second equation as follow

$$RH = RHA + \frac{(100-RHA)}{(1+\frac{t}{b})} \quad (2.24)$$

Where the parameter $b = d^{1.35}(70 - e)(\frac{w}{c} - 0.19)/8$, d is the depth from drying surface (mm), and e is percentage of PC replaced by fly ash or slag. McDonald and Roper run experimental work and they proposed new coefficient for parameter b in this equation as follow (McDonald, 1991).

$$b = d^{0.85}(128 - e)(\frac{w}{c} - 0.03)/11.4 \quad (2.25)$$

But Parrott in his next paper and also in answer of McDonald wrote that this equation is not working well and he proposed the new equation as follow (Parrott, 1991).

$$f(r) = e^{-kT} = (r - r_a)(100 - r_a) \quad (2.26)$$

Where $k = 0.8 - 0.14T + 0.01T^2$, $T = \frac{t}{t_{1/2}}$, k diminishes from 0.8 to 0.4 as T change from 0 to 4. $t_{1/2} = 10jd$ for $t_{1/2} < 414$ days, and $t_{1/2} = 3jd + 290$ for $t_{1/2} \geq 414$ days. $j = 1, 0.56$, and 0.53 for PC, fly ash and GBFS respectively.

But as it has been mentioned before, measuring the internal relative humidity leads to record the higher value of internal relative humidity in higher w/c ratio. But the drying rate is faster for higher w/c ratio and lower saturation degree is expected.

Due to importance of this issue, the drying process in concrete considering the preconditioning will be studied in chapter 4. In chapter 3 the effective parameters on the carbonation of concrete will be studied. Some of these parameters will be used to simulate the drying of concrete later on chapter 4.

CHAPTER

3

CARBONATION OF CONCRETE

3.1 Carbonatable materials

Total carbonatable materials can play a significant role on carbonation rate of concrete. Higher amount of carbonatable materials result in lower rate of carbonation. The total carbonatable materials depend on total cementitious materials and the hydration degree of these materials. The hydration of PC and pozzolanic reactions of mineral admixtures has been presented in the following.

Hydration of PC

All major compounds of Portland cement can react with water to produce different type of hydration products. The hydration reactions of Portland cement in the presence of gypsum are proposed as follow (Papadakis, 1991, 2).

Hydration degree of compounds

Hydration degree of four major compounds of cement can be calculated by following equation (Papadakis, 1991, 2).

$$F_i = 1 - (1 - K_{H,i}t(1 - n_i))^{1/(1-n_i)} \quad (3.5)$$

Where t is time after mixing and the coefficients are described in Table 3-1.

Table 3-1 Coefficient for hydration degree of PC in equation (3.5)

Compound	C_3S	C_2S	C_4AF	C_3A
n_i	2.65	3.1	3.81	2.41
$K_{H,i}(day^{-1})$	1.17	0.16	1	2.46

Equation (3.5) has been verified by using experimental data obtained by Brunauer (1964) as shown in Figure 3-1.

Figure 3-1 Hydration degree of cement major component

Air curing

In related experiment for air curing, Parrott et al reported that hydration continued for $\frac{w}{c} = 0.59$ pastes at relative humidity as low as 55%. The hydration degree was

measured after 14 and 90 days of exposure to various relative humidity, and the values were compared with the saturation degree of continuously saturated specimens. The ratio α_{RH} , the saturation degree for a sample hydrated at a defined relative humidity to the saturation degree of a sample hydrated under saturated conditions was approximated by a power law relationship (Parrott, 1986).

$$\alpha_{RH} = \left[\frac{RH - 0.55}{0.45} \right]^4 \text{ for } RH > 0.55 \text{ and for } RH \leq 0.55 \text{ then } \alpha_{RH} = 0 \quad (3.6)$$

Figure 3-2 Air curing coefficient

Effect of temperature on hydration rate

Various works have been done by researchers to simulate the effect of temperature on hydration rate. Based on their experimental data, the following equation is adopted by authors.

$$\alpha_T = e^{\frac{E_a}{R} \left(\frac{1}{293} - \frac{1}{T} \right)} \quad (3.7)$$

Where R is the universal gas constant ($R = 8.314 \frac{J}{mol.k}$) the average of activation energy according to experimental data is equal to $E_a = 38.2 \frac{kJ}{mol}$ (Bentz, 1997), (Kada-Benameur, 2000), (Ma, 1994), and T is the absolute temperature.

Figure 3-3 shows the behavior of the equation (3.7) for different temperature

Figure 3-3 Behavior of the equation (3.7) for different temperature

The simulation of hydration degree can be improved by including the effect of air curing and hydration temperature as follow.

$$F_i = \alpha_{RH} (1 - (1 - K_{H,i} \alpha_T t (1 - n_i))^{1/(1-n_i)}) \quad (3.8)$$

Effect of air curing and curing temperature on hydration degree of C_3S is presented in Figure 3-4 and 3-5 respectively.

The behaviors are match with the expectation and experimental data's. Considering these effects strongly improve the prediction ability of the simulation model of carbonation as these parameters are affecting the total carbonatable materials and the porosity of the concrete samples.

Figure 3-4 Effect of air curing on hydration degree

Figure 3-5 Effect of curing temperature on hydration degree

3.1.2 Pozzolanic activity of mineral admixtures

Generally the pozzolanic reactions of mineral admixtures are as follow

Some notes and assumptions for using the above equations have been proposed by various researchers as follow.

1- In equation (3.9), the main issue is how many percent of CaO will participate in this reaction. The following theories proposed by various researchers.

- All CaO, it means $\alpha_C=1$ proposed by Mehta (Mehta, 1983)
- Equal to $(\frac{f_{c,p}-f_{s,p}}{f_{c,p}})$ (CaO content of pozzolanic material minus gypsum content of pozzolanic material divided by CaO content of pozzolanic material) proposed by Papadakis in his different paper (Papadakis, 2000).
- Equal to pozzolanic activity proposed by author

Assuming the CaO activity equal to pozzolanic activity shows better prediction of the reactions for various types of mineral admixtures. Therefore the activity of CaO in equation (3.9) is adopted equal to pozzolanic activity.

2- Due to low CaO content in silica fume and also low-calcium fly ash, equation (3.9) can be neglected for these two cases.

3- In equations (3.11) and (3.12), A is related to Al_2O_3 content. Due to low Al_2O_3 content of silica fume, both equations can be ignored for case of silica fume.

4- For fly ash, it depends on $C\bar{S}H$ content and each or both equations (3.11) and (3.12) can be used as follow.

- If $C\bar{S}H$ content is less or equal to the amount needed for reaction of C_3A in

cement paste, the equation (3.12) will be used.

- If the $C\bar{S}H$ is higher than the amount needed for cement reaction but lower than needed for completion of the Al_2O_3 , reaction (3.12) will be process partially
- If $C\bar{S}H$ content is higher than the amount needed for cement paste and Al_2O_3 content, the reaction (3.12) will not process.

But generally most of the gypsum in Portland cement is consumed during the hydration of C_3A and there is no more gypsum to react with Al_2O_3 . The pozzolanic reactions will not start in initial hours when most of gypsum is consumed. Due to these facts and for the simplification, the equation (3.11) can be neglected for the entire mineral admixture. This assumption will not affect the accuracy of simulation.

5- The most iron in pozzolanic material is crystalline phase hematite and/or magnetite, and does not participate in the reactions. Therefore equation (3.13) can be ignored for mineral admixtures (Papadakis, 2000).

Based on above considerations, the above equations can be reduced to three equations of (3.9), (3.10) and (3.12).

Degree of pozzolanic activity of mineral admixtures

For calculation of pozzolanic activity of mineral admixtures, it is necessary to have good understanding on this process. Papadakis (Papadakis, 2000) used the constant rate model for pozzolanic activity of mineral admixtures and his model was based on glass content of pozzolanic materials.

In his work, the degree of pozzolanic activity of mineral admixtures after one year curing was assumed to be equal to glass phase content. This equation only shows trend line and it is not fit on an experimental data. In reality the curing period is limited to a few days and this equation cannot predict the degree of pozzolanic activity of mineral admixtures for short curing period.

If the glass phase content is measured by using the direct methods, the maximum pozzolanic activity of mineral admixtures can be equal to glass phase content. However, the X-ray diffraction method is used by most of the researchers to measure mineral characteristic of mineral admixtures. The result of the X-ray diffraction method can shows the percentage of crystalline phase. Then the mineral admixtures will have the maximum pozzolanic activity as follow:

$$\alpha_b = (1 - \text{crystalline phase content}) \quad (3.14)$$

In which α_b is the maximum pozzolanic activity of mineral admixture in the presence of enough calcium hydroxide after long curing period.

The degree of pozzolanic activity of mineral admixtures up to one year of curing can be calculated by using the same equation as equation (3.8) and with including the maximum pozzolanic activity of mineral admixtures.

$$\alpha_j = \alpha_b \times \alpha_{RH} (1 - (1 - K_{H,j} \alpha_T t (1 - n_j))^{1/(1-n_j)}) \quad (3.15)$$

The coefficients (K_H and n) for each mineral admixture are presented in Table 3-2.

Table 3-2: Coefficient for calculating degree of pozzolanic activity of mineral admixtures

Mineral admixture j	Silica Fume	Slag	High Calcium Fly Ash	Low Calcium Fly Ash
n_j	2.9	6	2.8	6
$K_{H,j}(\text{day}^{-1})$	$\frac{1}{\sqrt{250d_n}}$	$\frac{1}{\sqrt{50d_n}}$	$\frac{1}{\sqrt{100d_n}}$	$\frac{1}{\sqrt{100d_n}}$

In which d_n (μm) is the average particle size of mineral admixture. Achieving this activity depends on the availability of calcium hydroxide. The equations (3.10) and (3.12) cannot proceed without calcium hydroxide. It means that the degree of pozzolanic activity of mineral admixtures is affected by the production rate of calcium hydroxide.

In some of the experimental works only the specific surface area has been reported and the average particle size did not measured or reported. To study these data, it is important to obtain the average particle size from the specific surface area. Ji (Ji, 2003), described the relation between the specific surface area and the average particle size as follow:

$$d_n = \frac{88287}{A} - 3.5737 \quad (3.16)$$

In which d_n is the average particle size in μm and A is the specific surface area in cm^2/g .

If the chemical composition of mineral admixture is known, by using these equations for given curing period, the optimum amount of mineral admixture can be calculated. It means that the extra amount beyond the optimum value will not participate in pozzolanic reactions. It just plays the role of filler material in concrete.

Figure 3-6 shows the degree of pozzolanic activity of silica fume with various average particle sizes. As it is shown, condensed silica fume (larger particle size) has much lower degree of pozzolanic activity compared to as produced silica fume (smaller particle size).

Figure 3-6 The degree of pozzolanic activity of silica fume in the presence of enough $\text{Ca}(\text{OH})_2$ and $\alpha_b=0.95$

3.1.3 Molar concentration of carbonatable materials

The molar concentration of the carbonatable materials for PC at time t after mixing has been proposed as follow (Papadakis, 1999, 1).

$$[\text{Ca}(\text{OH})_2] = \frac{3}{2} [C_3S]_0 F_{C_3S} + \frac{1}{2} [C_2S]_0 F_{C_2S} - 2[C_4AF]_0 F_{C_4AF} \quad (3.17)$$

$$[\text{CSH}] = \frac{3}{2} [C_3S]_0 F_{C_3S} + \frac{1}{2} [C_2S]_0 F_{C_2S} \quad (3.18)$$

$$[C_3S] = [C_3S]_0 (1 - F_{C_3S}) \quad (3.19)$$

$$[C_2S] = [C_2S]_0 (1 - F_{C_2S}) \quad (3.20)$$

Figure 3-7 shows the typical concentration of these materials in different curing period.

Figure 3-7 Concentration of carbonatable material

In his experimental work, Groves (Grove, 1990) showed that Ca(OH)_2 and CSH are carbonated simultaneously and the carbonation of unhydrated C_3S , C_2S does not occur. This assumption coincides with most of the experimental results on carbonation of concrete.

Based on above sentences and the equations (3.9), (3.10) and (3.12) for pozzolanic reactions and equation (3.15) for the degree of pozzolanic activity of mineral admixtures, the carbonatable materials in blended cement concrete can be calculated as follow:

$$[\text{Ca(OH)}_2] = \frac{3}{2} [\text{C}_3\text{S}]_0 F_{\text{C}_3\text{S}} + \frac{1}{2} [\text{C}_2\text{S}]_0 F_{\text{C}_2\text{S}} - 2[\text{C}_4\text{AF}]_0 F_{\text{C}_4\text{AF}} - \frac{3}{2} \alpha_j [\text{SiO}_2]_0 - 4\alpha_j [\text{Al}_2\text{O}_3]_0 + \alpha_j [\text{CaO}]_0 \quad (3.21)$$

$$[\text{CSH}] = \frac{3}{2} [\text{C}_3\text{S}]_0 F_{\text{C}_3\text{S}} + \frac{1}{2} [\text{C}_2\text{S}]_0 F_{\text{C}_2\text{S}} + \frac{1}{2} \alpha_j [\text{SiO}_2]_0 \quad (3.22)$$

In which F_i is the hydration degree of compound i calculated by using equation (3.8) and α_j is the degree of pozzolanic activity of mineral admixtures calculated by equation (3.15).

Chapter 3 Carbonation of concrete

The physical and chemical composition of the mineral admixtures and the mix proportions in Papadakis works has been presented in Table 3-3 and Table 3-4 respectively (Papadakis, 1992).

Table 3-3 Physical and chemical properties of materials in Papadakis work

	Cement	SF	FL	FH
Mean Diameter μm	14.0	0.36	13.9	12.6
BET (m ² /kg)	1300	18000	1200	6200
Density(kg/m ³)	3130	2260	2250	2660
Chemical Analysis (%)				
SiO_2	20.10	90.90	53.50	39.21
Al_2O_3	4.25	1.12	20.40	16.22
Fe_2O_3	3.49	1.46	8.66	6.58
CaO	63.20	0.69	3.38	22.78
Free CaO	1.48	0.024	0.36	5.18
Other characteristics (%)				
Insoluble residue (%)	0.11	62.85	78.4	30.88
Glass phase (%)	-	96	75	50

Table 3-4 Mix proportions of concrete in Papadakis works

	PC	FL1	FL2	FL3	FH1	FH2	FH3	SF1	SF2	SF3
C (kg/m ³)	514.6	514.6	514.6	514.6	514.6	514.6	514.6	514.6	514.6	514.6
W (kg/m ³)	257	257.	257.4	257.4	257.4	257.4	257.4	257.4	257.4	257.
P (kg/m ³)	0	51.5	102.9	154.4	51.5	102.9	154.4	25.7	51.5	77.2
Agg. (kg/m ³)	1543	1482	1421	1360.6	1492.1	1440.5	1388.8	1513	1483	1452
w/c	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50	0.50
p/c	0	0.1	0.2	0.3	0.1	0.2	0.3	0.05	0.1	0.15
a/c	3	2.88	2.76	2.64	2.90	2.80	2.70	2.94	2.88	2.82

The Figures 3-8, 3-9 and 3-10 show the prediction results and experimental results of the amount of calcium hydroxide in concrete made of silica fume, low calcium fly ash and high calcium fly ash in Papadakis works (Papadakis, 1999, 1), (Papadakis, 1999, 2), (Papadakis, 2000) respectively.

The prediction results are in good agreement with experimental results and the correlation coefficient is 0.90.

Figure 3-8 Prediction of the calcium hydroxide content for silica fume replacement in Papadakis work

Figure 3-9 Prediction of the calcium hydroxide content for low calcium fly ash replacement in Papadakis work

Figure 3-10 Prediction of the calcium hydroxide content for high calcium fly ash replacement in Papadakis work

The physical and chemical composition of the mineral admixtures and the mix proportions in Saeki works has been presented in Tables 3-5 and 3-6 respectively (Saeki, 2005).

Table 3-5 Chemical and physical properties of materials in Saeki work

	Density $\frac{kg}{m^3}$	surface area Blaine $\frac{m^2}{kg}$	Chemical composition (%)					
			SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
Cement	3150	326	22.2	4.9	3	64	1.3	2.1
FA a	2260	290	49.6	25.9	5.7	11.6	2.3	0.4
FA b	2340	313	66.2	27.2	2.5	1.1	0.5	0
FA c	2160	284	51.2	25.5	5.3	10.6	2.2	0.5
Slag a	2880	436	31.8	13	0.2	43.2	6	2.1
	2880	603	31.8	13	0.2	43.2	6	2.1
Slag b	2890	427	32.8	12.5	0.4	41.9	7	2
	2890	596	32.5	12.6	0.4	41.9	7	2.2
Slag c	2890	406	32.6	15.5	0.3	42.3	5.7	2
	2890	610	32.4	15.7	0.2	42.8	6.3	2

Table 3-6 The mix proportions of mortar in Saeki work

Pozzolan	$w/(c + p)$	$a/(c + p)$	C (kg/m ³)	P (kg/m ³)	W (kg/m ³)	Agg. (kg/m ³)
Fly ash	0.55	0.3	401.5	172.1	315.5	1262.5
Fly ash	0.55	0.5	286.8	286.8	315.5	1226.7
Slag	0.55	0.5	286.8	286.8	315.5	1294.8
Slag	0.55	0.7	172.1	401.5	315.5	1286.2

Figure 3-11 Prediction of the calcium hydroxide content for different slag replacement in Saeki work

Figure 3-12 Prediction of the calcium hydroxide content for different fly ashes in Saeki work

Figure 3-11 and 3-12 show that the prediction results are in good agreement with experimental results for three types of fly ash by 30% replacement and two types of slag with 50% replacement and the correlation coefficient is 0.88.

3.2 Diffusivity of CO₂ in concrete

Carbon dioxide can penetrate into concrete in gas phase or liquid phase. The diffusion of oxygen and carbon dioxide is 10^4 to 10^5 times faster in the gas phase as in solution (Lawrence, 1981). Therefore it can be concluded that diffusion in gas phase is more important in process of carbonation. As it was proposed by different researchers, the gas diffusivity of concrete depends on the porosity and the moisture content.

3.2.1 Porosity of concrete

The porosity of concrete is defined as the ratio of pore volume to the total volume of concrete. It will decrease with time due to the processes of cement hydration, pozzolanic reactions and carbonation (Papadakis, 1991, 2).

$$\varepsilon(t) = \varepsilon_0 - \Delta\varepsilon_H(t) - \Delta\varepsilon_P - \Delta\varepsilon_C \quad (3.23)$$

In which ε_0 is initial porosity and $\Delta\varepsilon_H(t)$ is the reduction of porosity due to hydration and $\Delta\varepsilon_C(t)$ is the reduction of porosity due to carbonation.

Initial porosity ε_0 of concrete can be calculated as follow

$$\varepsilon_0 = W/\rho_w + \varepsilon_{air} = \frac{\frac{w\rho_c}{c\rho_w}(1-\varepsilon_{air})}{(1+\frac{w\rho_c}{c\rho_w}+\frac{a\rho_c}{c\rho_a}+\frac{p\rho_c}{c\rho_p})} + \varepsilon_{air} \quad (3.24)$$

In which $\rho_c, \rho_w, \rho_a, \rho_p, c, w, a, p$ are densities of cement, water, aggregate, pozzolan and cement, water, aggregate and pozzolanic content of concrete, respectively. The volume fraction of entrapped air, denoted by ε_{air} , can be estimated as function of maximum aggregate size (ACI, 211.1-91).

Table 3-7 Percentage of entrapped air for different aggregate size

MSA(mm)	9.5	12.5	19	25	37.5	50	75	150
Entrapped air (%)	3	2.5	2	1.5	1	0.5	0.3	0.2

3.2.1.1 Effect of curing temperature on morphology of hydration products

Porosity measurement on the C_3S – *paste* was carried out by Bentur et al. They have revealed from the volume balance concept that the capillary porosity will increase at higher curing temperature for the same hydration degree. It is due to decreases the volume of hydration products (Bentur, 1979). The following coefficient is proposed to simulate the effect of curing temperature on porosity of concrete.

$$a_T = e^{-28 \times 10^{-6} T^2} \quad (3.25)$$

In which T is curing temperature in centigrade. Figure 3-13 shows the reduction in volume of hydration product in higher temperature.

Figure 3-13 Effect of curing temperature on porosity of concrete

Considering this effect, the equation for porosity of concrete can be improved to following format.

$$\varepsilon(t) = \varepsilon_0 - a_T(\Delta\varepsilon_H(t) - \Delta\varepsilon_P(t)) - \Delta\varepsilon_C \quad (3.26)$$

3.2.1.2 Reduction in porosity due to hydration, pozzolanic reactions and carbonation

The molar volume of the solid hydration products in equations (3.1) to (3.4) exceeds that of the solid reactants. The $\Delta\bar{V}_{C_3S}$, $\Delta\bar{V}_{C_2S}$, $\Delta\bar{V}_{C_3A}$, $\Delta\bar{V}_{C_4AF}$ are the difference in molar volume between solid product and solid reactants in the hydration reaction (Papadakis, 1991, 2). Table 3-8 shows the molar difference of solid reaction and solid reactants for equation (3.1) to (3.4) respectively.

Table 3-8 Molar difference of solid products and solid reactants in PC reactions

	$\Delta\bar{V}_{C_3S}$	$\Delta\bar{V}_{C_2S}$	$\Delta\bar{V}_{C_3A}$	$\Delta\bar{V}_{C_4AF}$
$\Delta\bar{V} \times 10^6 (m^3/mol)$	53.28	39.35	112.79	155.86

Then $\Delta\varepsilon_H(t)$ can be calculated by following equation.

$$\Delta\varepsilon_H(t) = [C_3S]_0 F_{C_3S} \Delta\bar{V}_{C_3S} + [C_2S]_0 F_{C_2S} \Delta\bar{V}_{C_2S} + [C_3A]_0 F_{C_3A} \Delta\bar{V}_{C_3A} + [C_4AF]_0 F_{C_4AF} \Delta\bar{V}_{C_4AF} \quad (3.27)$$

The $\Delta\varepsilon_P$ is reduction in porosity due to pozzolanic reactions and it can be calculated as follow:

$$\Delta\varepsilon_P = \alpha_j [SiO_2] \Delta\bar{V}_{SiO_2} + \alpha_j [CaO] \Delta\bar{V}_{CaO} + \alpha_j [Al_2O_3] \Delta\bar{V}_{Al_2O_3} \quad (3.28)$$

The molar difference between the solid reactant and solid products of pozzolanic reaction for equations (3.9), (3.10) and (3.12) has been presented in Table 3-9 respectively.

Table 3-9 Molar difference of solid reactant and solid products in pozzolanic reactions

	$\Delta \bar{V}_{CaO}$	$\Delta \bar{V}_{SiO_2}$	$\Delta \bar{V}_{Al_2O_3}$
$\Delta \bar{V} \times 10^6 (m^3/mol)$	16.19	≈ 0	114.26

As it has been shown in Table 3-6 and Papadakis experimental work (Papadakis, 1999, 2), the reduction in porosity due to equation (3.10) is assumed to be zero.

The term $\Delta \varepsilon_c$ is due to the fact that the molar volume of the solid product of the carbonation of $Ca(OH)_2$ and CSH is increased by $\Delta \bar{V}_{CH} = 3.85 \times 10^{-6} m^3/mol$ and

$\Delta \bar{V}_{CSH} = 15.39 \times 10^{-6} \frac{m^3}{mol}$ respectively. Therefore $\Delta \varepsilon_c$ can be calculated as follow (Papadakis, 1991, 2).

$$\Delta \varepsilon_c = [Ca(OH)_2] \Delta \bar{V}_{CH} + [CSH] \Delta \bar{V}_{CSH} \quad (3.29)$$

3.2.1.3 Porosity of cement paste

The porosity of cement paste $\varepsilon_p(t)$ will be calculated by assuming all the porosity of concrete concentrate in cement paste (Papadakis, 1991, 2). The porosity of cement paste of PC and blended cement concrete can be calculated by equations (3.30) and (3.31) respectively.

$$\varepsilon_p(t) = \frac{w/\rho_w + \varepsilon_{air} - \Delta \varepsilon_H - \Delta \varepsilon_c}{\frac{c}{\rho_c} + \frac{w}{\rho_w}} \quad (3.30)$$

$$\varepsilon_p(t) = \frac{w/\rho_w + \varepsilon_{air} - \Delta \varepsilon_H - \Delta \varepsilon_p - \Delta \varepsilon_c}{\frac{c}{\rho_c} + \frac{w}{\rho_w} + \frac{p}{\rho_p}} \quad (3.31)$$

3.2.2 Moisture content of concrete

As reported by different researchers, effective gas diffusivity depends on moisture

content and w/c ratio. The significant effect of relative humidity can be taken into account by considering the diffusivity as function of the saturation degree of pores, which also include the effect of pore size distribution. Alternatively, the effective diffusivity for uniform saturation degree is proposed as a function of $(1 - \frac{RH}{100})^2$ (Papadakis, 1991, 1).

3.2.3 Effective gas diffusivity of concrete

Various attempts have been done to measure and simulate the diffusivity of gas in concrete. In Papadakis work, regression analysis of the experimental data for PC yielded to the following expression for the effective diffusivity of CO_2 and O_2 ($\frac{m^2}{s}$).

$$D_{e,CO_2} = 1.64 \times 10^{-6} \varepsilon_p^{1.8} (1 - RH)^{2.2} \quad (3.32)$$

$$D_{e,O_2} = 1.92 \times 10^{-6} \varepsilon_p^{1.8} (1 - RH)^{2.2} \quad (3.33)$$

Where ε_p is the porosity of cement paste, and D_{e,CO_2} and D_{e,O_2} are the effective diffusivity of CO_2 and O_2 respectively.

This model is fit to Papadakis experimental data for relative humidity values (RH) above 50%. For lower RH values significant deviations were observed (Papadakis, 1991, 2).

In Papadakis work, the moisture content was assumed to be equal to desired level and uniform. But in reality and in most of the cases the distribution of moisture content plays a significant role in diffusivity of concrete. Based on the trend lines and also by reviewing the experimental results, the values recorded by Papadakis are higher due to damage in pore structure caused by 105°C oven drying. Then lower diffusivity for undamaged pore structure is expected.

The new equation based on Papadakis equation is proposed by author. In this equation, effect of moisture content prior to test and the effect of damage caused by oven drying have been considered. This equation can give better prediction for natural carbonation test and the accelerated tests.

$$D_{e,CO_2} = 3.3 \times 10^{-6} f(pre) \varepsilon_p^{2.75} (1 - RH)^{2.2} \quad (3.34)$$

$f(pre)$ in equation (3.34) is the function of damage caused by preconditioning and the function of saturation degree before the start of carbonation test. It can be described as follow:

$$f(pre) = (S_f/S)^4 \times f(d) \quad (3.35)$$

In which $f(d)$ is the function of damage and $(S_f/S)^4$ is related to saturation degree.

In the case of high temperature oven drying, by assuming that the sample was dried up to required level, the function of saturation degree is equal to one and the function of preconditioning will be equal to the function of damage. The function of damage can be calculated as follows:

$$f(d) = 1 + 0.005(T - 293)(1 - (t + 1)^{-1.5}) \quad (3.36)$$

$f(d) \geq 1$, T is the absolute environment temperature ($^{\circ}K$) and t is the drying period (days).

S_f is the final saturation degree in specific relative humidity. It is obvious that if the carbonation start right after curing when the sample is fully saturated or long time after curing period when the saturation degree is equal to S_f , are two different conditions and the $(1 - RH)^2$ can not simulate the effect of moisture content on diffusivity of concrete for these cases properly. By considering the function of saturation degree this problem will be solved. The saturation degree depends on pore structure of concrete and environmental relative humidity. This parameter will be studied in next chapter.

The behavior of the function of damage for different temperature has been presented in figure 3-14.

Figure 3-14 Function of damage in different temperature

Effect of mineral admixtures on diffusivity of concrete

The intrinsic diffusion rate at which ions or molecules are transported in concrete depends on the size and connectivity of the pore system. The pozzolanic addition may further promote the pore disconnection.

The micro pores content (pores with diameter less than 20 nm) of replacing 10% of aggregate by silica fume has been measured much higher than PC concrete with the same total porosity (Papadakis, 1999, 2). Same result for the case of replacing 10% of aggregate by low-calcium fly ash reported by Papadakis (Papadakis, 1999, 1). For the case of replacing 10% of aggregate by high-calcium fly ash the micro pores content measured much higher than PC concrete. Taking into account its lower total porosity, it is established as a denser and finer pore structure (Papadakis, 2000).

It can be concluded that the main effect of pozzolanic material on pore structure of concrete is related to finer pore size distribution and also lower pore connection. As

result, the lower diffusivity and water movement in blended cement is expected.

For blended cement with $0.38 < w/(c + p) < 0.58$, Papadakis offered the following equation (Papadakis, 2000).

$$D_{e,CO_2} = 6.1 \times 10^{-6} \varepsilon_p^3 (1 - RH)^{2.2} \quad (3.37)$$

Where ε_p is the porosity of blended cement. Equation (3.37) is fitted on Papadakis experimental data and also shows the trend line for blended cements. However, the effectiveness of replacing PC with mineral admixture depends on the chemical composition, glass phase content, percentage of replacement and the curing period. The pore structure can be finer or coarser compared to PC concrete with the same w/c and a/c ratios.

By neglecting the effects of the types, the percentages, the quality of mineral admixtures, and curing period on the diffusivity of CO₂ in concrete, the error of prediction increases significantly.

Figure 3-15 shows the experimental data of the average pore diameter of concrete with the various mineral admixtures, the percentage of replacement, and the curing period obtained by using Mercury Intrusion Porosimeter. The total porosity is similar for these cases.

As it has been shown, the pore structure of blended cement concrete depends on the activity of mineral admixture, the percentage of replacement, and the curing period. The average pore diameter in blended cement concrete can be higher or lower than PC concrete. For instance, using the low quality low-calcium fly ash in this experimental work resulted in higher average pore diameter compared to PC concrete.

Figure 3-15 The effect of curing period, percentage and type of cementitious materials on average pore diameter of concrete

The following equation is proposed for calculating the CO₂ diffusivity in blended cement concrete.

$$D_{e,CO_2} = 3.3 \times 10^{-6} f(pre) \varepsilon_p^{2.75} (1 - \alpha_j \sqrt{e})^{(2.3 - 2\alpha_j e)} (1 - RH)^{2.2} \quad (3.38)$$

Where D_{e,CO_2} is the CO₂ diffusivity of concrete ($\frac{m^2}{s}$), RH is the exposure relative humidity, α_j is the degree of pozzolanic activity of mineral admixtures, $e = \frac{P}{(P + C)}$ is the percentage of pozzolanic content to total cementitious materials.

For instance for the effect of GBFS ($d_n=9 \mu m$, glass content=100%) with 10%, 30% and 50% replacement on CO₂ diffusivity in comparison to PC concrete with different curing period has been presented in Figure 3-16. Here for simplification, it is assumed that $f(pre) = 1$ and the relative humidity is equal by 60%.

Figure 3-16 The effect of GBFS replacement on CO₂ diffusivity in concrete

As it has been shown in Figure 3-16, the percentage of replacement and the curing period is very important parameter in CO₂ gas diffusivity. Figure 3-17 and 3-18 show the effect of up to 15% normal silica fume and condensed silica fume replacement on CO₂ diffusivity of concrete.

Figure 3-17 The effect of SF replacement on CO₂ diffusivity in concrete

Figure 3-18 The effect of CSF replacement on CO_2 diffusivity in concrete

Figure 3-19 and 3-20 show the effect of up to 30% replacement of high and low quality fly ash on CO_2 diffusivity in concrete.

Figure 3-19 The effect of high quality fly ash replacement on CO_2 diffusivity in concrete

Figure 3-20 The effect of low quality fly ash replacement on CO₂ diffusivity in concrete

As it has been shown in figure 3-18, the condensed silica fume can only improve the pore structure of concrete in long curing period and the particle size can play a significant role in diffusivity of CO₂ in concrete. As shown in Figures 3-19 and 3-20, the quality of mineral admixtures is a very important parameter which affects their pozzolanic activity.

This new equation for diffusivity of CO₂ in concrete can simulate the effect of various parameters more clearly and also the final model for carbonation of concrete has better prediction ability by using this new equation. The effect of type, percentage of replacement and the quality of the mineral admixture on pore structure of concrete will be studied in next chapter.

3.2.4 Effect of crack on diffusivity of CO₂ in concrete

Crack will occur whenever the tensile strain exceeds the tensile strain capacity. The cracks in concrete generally can be divided into two main groups, the cracks before

hardening and the cracks after hardening. The cracks before hardening are generally due to plastic shrinkage or plastic settlement or the constructional movement. The cracks after hardening are due to drying shrinkage, crazing, structural design, physical impact, or corrosion.

These cracks have different width, depth and concentrations. For instance the crazing cracks are normally the high concentration surface cracks and normally do not have any significant effect on durability of concrete. The plastic shrinkage cracks are normally between 0.1 to 3 mm wide and 10 to 50 mm deep. These cracks may be significantly harmful for increasing the rate of carbonation and chemical ingress. The structural cracks are mostly the result of the flexure. These cracks normally have big crack width. These cracks are normally deep and continue beyond the steel bars. The details of calculating the crack spacing and crack width for various affecting parameters have been presented in BS 8007:1987.

The cracks in common projects are normally the combination of flexure cracks, accidental overloading cracks, crazing cracks, alkali silica reaction and chloride ingress cracks. Also the quality of the construction may play a significant role in crack depth and width. Regardless of the reason that the crack happen, the crack width can play significant role on durability of concrete. If the crack width is smaller than critical level around 0.3 mm, it can be healed in process of hydration or carbonation, or the concrete expansion. It also can be useful to prevent the further cracks due to expansion of concrete.

As mentioned above, different type of cracks have different width and depth. The effect of crack can be simulated by increasing the available area for penetration of CO_2 up to crack depth. In the theoretical approach if the length, width and depth of all cracks are available, the available penetration area can be calculated. The cracks can be described by the width of w , length of l and the height of h .

The schematic of crack is presented in Figure 3-21.

Figure 3-21 Schematic of crack in concrete structures

Figure 3-22 shows the simulation of crack by using the average values for width, depth and height.

Figure 3-22 Simulation of crack in concrete structures

As shown in Figure 3-22 the width of crack can be assumed to decrease linearly from w in surface to zero in depth h . The total porosity in the cracked area for this single crack can be calculated as follow:

$$A_{Cracked\ Concrete} = A_P + A_{Crack} \quad (3.39)$$

In which, A_P and A_{Crack} are the area of the pores and the area of the cracks respectively.

For the element with height of d_z in Figure 3-18 and with using the boundary conditions, the width of element can be calculated as follow:

$$w_z = w\left(\frac{h-z}{h}\right) \quad (3.40)$$

The porosity of cement paste in cracked section can be calculated as follow:

$$\varepsilon_{Crack} = \int_0^h A_P d_z + \int_0^h w_z L d_z \quad (3.41)$$

In the equation for CO₂ diffusivity in concrete, it is assumed that porosity is homogeneous. But it is clear that the porosity in near surface especially for reinforced section is higher compared to average value for porosity of the concrete. But this issue will remain same for cracked and uncracked sections. Then the increase in total porosity can be shown as follow:

$$\Delta\varepsilon_p = \int_0^h w_z L d_z \quad (3.42)$$

By using the equation (3.40) the increase in total porosity can be calculated as follow

$$\Delta\varepsilon_p = \int_0^h w_z L d_z = \int_0^h w\left(\frac{h-z}{h}\right) L d_z = \int_0^h w L d_z - \int_0^h \frac{wz}{h} L d_z = wLz \Big|_0^h - \frac{wz^2}{2h} \Big|_0^h$$

Then

$$\Delta\varepsilon_p = whL - \frac{whL}{2} = \frac{whL}{2} \quad (3.43)$$

Equation (3.43) represents the effect of one specific crack on total porosity of concrete. In actual cases all the cracks do not have the same width or even same height and length. If the total number of the cracks is equal by i , the total increase in the porosity of concrete can be calculated as follow:

$$\Delta\varepsilon_p = \sum_1^i \frac{w_i h_i L_i}{2} \quad (3.44)$$

The diffusivity of CO₂ in concrete is controlled by saturation degree of the pores but it is not the case in the cracks. Then the diffusivity of CO₂ in cracked concrete for PC and blended cements can be calculated as follow:

$$D_{e,CO_2} = 3.3 \times 10^{-6} \times [f(pre)(1 - \alpha_j \sqrt{e})^{(2.3-2\alpha_{je})} \times \varepsilon_p^{2.75}(1 - RH)^{2.2} + (\varepsilon_{Crack}^{2.75} - \varepsilon_p^{2.75})] \quad (3.45)$$

To illustrate the effect of crack on CO₂ diffusivity in concrete, three simplified cases of crack with assumption of all cracks has the same length, width and depth, in comparison with uncracked section is simulated. The details of this cracked sections for the sample with area of 1 m×1 m and with w/c=0.5& a/c=3 (W=252 kg/m³, C=504 kg/m³, Agg. = 1512 kg/m³ and ε_{air} = 1%) and the curing period equal by 3 days has been presented in Table 3-10.

Table 3-10 The details of the cracked sections

Condition	Case number	Crack width (mm)	Crack depth (mm)	Crack length (mm)	Crack spacing (mm)
Without crack	1	0	0	0	0
Low cracking	2	0.5	10	400	60
Medium cracking	3	1.5	20	600	50
Severe cracking	4	3	30	800	40

By using the finite difference method the diffusivity of CO₂ in concrete in different depth from surface by assuming the homogeneous distribution of concrete porosity can be calculated. Figure 3-23 shows the diffusivity of the CO₂ in concrete in different depth from surface for these four cases.

Figure 3-23 The effect of different cracking on diffusivity of CO₂ in concrete

The increase in carbonation depth of concrete for these cases will be studied in chapter five.

3.3 Carbonation reactions

3.3.1 Carbonation of Ca(OH)₂

The carbonation of concrete has several steps from penetration of CO₂ in concrete, dissolution of CO₂ in pores water and formation of acid, dissolution of Ca(OH)₂ in pores water and finally the carbonation reaction.

The first step is dissolution of Ca(OH)₂ inside of pores water, this reaction will start from initiation of hydration and it is a two way reaction.

Rate of $\text{Ca}(\text{OH})_{2(s)}$ dissolution

The rate of $\text{Ca}(\text{OH})_{2(s)}$ dissolution can be calculated approximately by the following equation.

$$r_D = \left(\frac{1}{2}\right) \varepsilon f_w k_s a_{s,CH} ([OH^-]_{eq} - [OH^-]) \quad (3.47)$$

In the above expression, ε is concrete porosity, f_w is volume fraction of pores occupied by aqueous film, the k_s is the mass transfer coefficient for the dissolution of $\text{Ca}(\text{OH})_2$, $a_{s,CH}$ represents the exposed surface area of $\text{Ca}(\text{OH})_2$ per unit volume of concrete, and $[OH^-]$ is the local concentration of OH^- in the liquid phase of pores.

The rate of dissolution of $\text{Ca}(\text{OH})_{2(s)}$ is not important for the simulation of carbonation because as it will shown later on in chapter five, in mass balance of $\text{Ca}(\text{OH})_2$ this parameter will be eliminated from both side of mass balance equation.

The other equations for the process of carbonation are presented as follow.

Rate of carbonation of $\text{Ca}(\text{OH})_2$, r_{CH} is determined in the volume of liquid phase in pores (Papadakis, 1989). From following equation the rate of carbonation of $\text{Ca}(\text{OH})_2$ can be calculated.

$$r_{CH} = 10^{-5} HRT k_2 [OH^-]_{eq} [CO_2] \quad (3.52)$$

For calculation of this rate per unit volume of concrete, it should be multiplied by

ε_w . The f_w is the volume fraction of pores occupied by water film.

In this equation, H is Henry's constant for CO_2 and equal to $33 \frac{mol}{m^3 \cdot bar}$ (at $T=25^\circ C$), R is universal gas constant and equal to $8.314 \frac{L \cdot kpa}{K \cdot mol}$, T is temperature in Kelvin, k_2 is rate constant between CO_2 and OH^- equal to $8.3 \frac{m^3}{mol \cdot s}$ (at $T=25^\circ C$).

The $[OH^-]_\infty$ is the OH^- concentration in a saturated $Ca(OH)_2$ solution equal to $56 \frac{mol}{m^3}$ (obtained from solubility constant, $k_{SP, Ca(OH)_2} = 8.8 \times 10^{-5} \text{ molar}$)
 $[CO_2]$ is the molar concentration in gas phase in $\frac{mol}{m_{gas}^3}$.

Rate of $Ca(OH)_2$ diffusion

In aqueous solution, the $Ca(OH)_2(aq)$ diffuses from region with higher concentration of OH^- to those with lower, with a diffusivity $D_{e, Ca(OH)_2(aq)}$, of the order of $10^{-13} \frac{m^2}{s}$. This diffusion takes place in the aqueous phase of the pores. This value is much smaller than the diffusion rate of aggressive agent and also carbonation rate. Therefore this rate can be neglected from the process.

3.3.2 Carbonation of CSH and unhydrated components

The carbonation of CSH and unhydrated C_3S, C_2S of hardened cement paste may take place according to the following equations.

These reactions may be processed by the rates equal to r_j , $j = CSH, C_3S$, and C_2S (in moles of constituent j per unit volume of concrete, per second) as follows.

$$r_j = K_j a_s [j] \bar{V}_j [CO_2] \quad (3.56)$$

In which $[j]$ is the molar concentration of constituent j (in moles per unit volume of concrete), $\bar{V}_j$ is molar volume ($\bar{V}_{CSH} = 150 \cdot 10^{-6} \text{ m}^3/\text{mol}$, $\bar{V}_{C_3S} = 71.3 \cdot 10^{-6} \text{ m}^3/\text{mol}$, $\bar{V}_{C_2S} = 52.2 \cdot 10^{-6} \text{ m}^3/\text{mol}$), and K_j is the rate constant for reaction of constituent j with CO_2 (m/s). By using the result of accelerated exposure condition with 100 percent of CO_2 , this value was recorded and K_j is equal to 10^{-9} m/s (Papadakis, 1991, 1).

In his experimental work Grove (Grove, 1990) showed that $Ca(OH)_2$ and CSH are carbonated simultaneously and the carbonation of unhydrated C_3S, C_2S does not occur. This assumption agrees with most of the experimental results on carbonation of concrete.

3.3.3 Partially carbonated portion of concrete

In low relative humidity, reaction rate is relatively slow and penetration of CO_2 is relatively fast. Therefore CO_2 can penetrate to the deeper parts and reacts with $Ca(OH)_2$ of deeper parts, although the outer part has not yet been fully carbonated. It will reduce the depth of fully carbonated where the pH is lower than critical value for corrosion of steel bars. The coefficient will be presented later on this thesis to solve the issue of low relative humidity with decreasing the predicted depth of carbonation.

3.3.4 The pH calculation

The value of $Ca(OH)_2(aq)$ is always lower than its saturated condition and it can be calculated from solubility constant, $K_{sp} = [Ca^+][OH^-]^2 = 8.8 \times 10^{-5} \text{ molar}$. Then it

is equal to $Ca(OH)_2(sat.) = 0.028 \text{ molar}$.

The other alkalis in concrete like Na_2O, K_2O can increase the pH value. But the amount of this alkali content commonly is less than 1% of cementitious material. Therefore they can be ignored in pH calculation. In process of carbonation and in monitoring mass balance the value of pH can be calculated from following equation.

$$pH = 14 + \text{Log}(2 \times Ca(OH)_2(aq)) \quad (3.57)$$

Then pH of concrete in saturated condition of $Ca(OH)_2$ can be calculated as follow:

$$pH = 14 + \log(2 \times 0.028) = 12.71.$$

3.4 Effect of ambient exposure condition on carbonation

Effect of ambient condition can be simply divided into

- 1 Type of exposure
- 2 Condition of exposure

Type of exposure can be indoor condition, outdoor and sheltered from rain, and outdoor and exposed to rain.

Generally, highest depth of carbonation recorded in indoor condition due to higher CO_2 concentration. The lowest value of carbonation depth recorded in exposed to rain condition because of the high level of moisture content. The value of carbonation depth for sheltered condition is higher than exposed to rain (Thomas, 1992).

Some researchers approximately compared the carbonation depth of these different conditions together. For instance 50% and 25% of indoor condition carbonation depth is reported for outdoor sheltered from rain and outdoor exposed to rain respectively. It is clear that the outdoor condition depends on local climate, number of rainy days and some other parameters. This comparison is not meaningful for various conditions. However it is clear that the depth of carbonation in indoor condition is higher than two other cases. It is the critical condition which can be used for design purposes.

Condition of exposure is related to relative humidity, temperature, and CO₂ concentration of condition. As it is reported by Richardson (1988), most of researchers believe that the most favoring relative humidity for carbonation is around 50%, and the value between of 50% to 65% reported by some other researchers.

The CO₂ concentration for normal atmospheric is around 0.03% to 0.035%, and for indoor condition the value between of 0.03% to 0.1% reported by different researchers (Loo, 1994), (Houst, 2002). For urban and suburban area the value between 0.07% and 1% is reported by some of the researchers. And it can be shown that in heart of big cities the problem of carbonation is one of the most severe one (Nischer, 1984), (Tuuti, 1982).

In higher temperature higher rate of reaction and higher depth of carbonation is expected. Some researchers claim that effect of temperature on rate of carbonation can be described by Arrhenius law as follow.

$$K_T = A \exp (-B/T) \quad (3.58)$$

Where T=absolute temperature (°K) and the amount of this relation for specific temperature will be equal by one.

In his experimental work, Uomoto (1993) used this equation for simulation of the effect of environment temperature. In this work, different coefficient has been calculated for the temperature T=25°C, then this equation set to be one on this temperature. Considering the effect of environment temperature on rate of reaction can improve the prediction ability of the model. Further verification by experimental work will be presented later on this thesis.

$$K_T = \exp (8.6-2563/T) \quad (3.59)$$

Effect of low relative humidity on carbonation rate

As mentioned above, in lower relative humidity the rate of reaction is lower. But according to CO_2 diffusivity equation, highest CO_2 diffusivity in lowest relative humidity is expected.

Figure 3-24 shows the weakness of the Papadakis model (Papadakis, 1991,2) in prediction of the carbonation depth for low relative humidity.

Figure 3-24 Problem of Papadakis model for low relative humidity

In prediction results, with reduction in relative humidity, the carbonation depth will increase. But as the experimental data shows, the maximum depth of carbonation will occur in relative humidity around 50%.

As it claimed by Papadakis, Danckwerts measured the rate of reaction in equation (3.52), in bulk aqueous solution with dimensions orders of magnitude larger than molecular dimensions. This is not the case in concrete pores. Where the dimensions of micro pores are the order of angstrom, and the aqueous film thickness on the walls of larger pores is typically 1 to 3 molecular dimensions. The coefficient proposed for reduction of rate of reaction in low relative humidity can effectively increase the

accuracy of predictions. This coefficient is proposed as follow:

$$k = \sqrt{\frac{1}{S^{\ln(S)}}} \quad (3.61)$$

In which S is the saturation degree of concrete. This coefficient and its effectiveness on prediction ability of the carbonation model will be presented in chapter five.

CHAPTER

4

STUDY ON DRYING PROCESS OF CONCRETE

4.1 Experimental study

4.1.1 Materials and mix proportions

The cement used in the experiments was the type II Portland cement manufactured in China. The oxide and compound composition are listed in Table 4-1 and Table 4-2 respectively. The specific surface area was $1.8 \text{ m}^2/\text{g}$.

Table 4-1 Oxide composition of cement

Oxide	Content (%)
<i>CaO</i>	63.0
<i>SiO₂</i>	21.5
<i>Al₂O₃</i>	5.5
<i>Fe₂O₃</i>	4.5
<i>SO₃</i>	1
<i>MgO</i>	2
Other Oxides	1.5
<i>Loss on ignition</i>	1.00

Table 4-2 Compound composition of cement

Compound composition	Content (%)
C_3S	46.75
C_2S	26.6
C_3A	6.9
C_4AF	13.7

Three types of mineral admixtures have been used in this experimental study. The low calcium fly ash (LFA) imported from Malaysia, the condensed silica fume (CSF) provided by Grace Construction and the granulated blast furnace slag (GBFS) imported by Engro Company from China were the mineral admixtures in this work. The physical and chemical properties of these mineral admixtures presented in Table 4-3.

Table 4-3 Physical and chemical characteristics of mineral admixtures

Mineral admixtures	CSF	LFA	GBFS
<i>Physical properties</i>			
Specific Surface Area (m^2/g)	0.71	1.35	2.1
Particle Mean Diameter (μm)	28.5	19.5	9.2
Density (kg/m^3)	2200	1950	2720
<i>Chemical analysis (%)</i>			
SiO_2	92	50	36
Al_2O_3	2	23	9
Fe_2O_3	2	9	1
CaO	1	3	44
SO_3	0.3	1	1
MgO	1	2	8

The characteristic of these materials were examined by particle size analyzer and the X-ray diffraction test. Figure 4-1 shows the particle size distribution and the average particle size of the mineral admixtures in comparison to Portland cement. As shown the GBFS has finer particle size distribution compare to PC but the particle size distribution of LFA and CSF is coarser.

Figure 4-1 Particle size distribution and average particle size of mineral admixtures in comparison to cement type II

Figure 4-2, 4-3 and 4-4 show the XRD results for GBFS, CSF and LFA respectively.

Figure 4-2 The XRD results for GBFS

Figure 4-3 The XRD results for CSF

Figure 4-4 The XRD results for LFA

The number of the counts in GBFS and CSF is very low and it means no crystalline phase in these two materials is detectable but the number of the counts in LFA is considerably high and the crystalline phases are the Quartz and Mullite. Due to this reason the glass phase content and the quality of this LFA is lower compared to two other mineral admixtures.

The water reducer Cormix® P4 provided by Grace Construction has been used for some of the mix proportions in this experimental work. Cormix® P4 is an aqueous solution of modified lignosulfonates which promotes more complete hydration of Portland cement.

The natural sand and coarse aggregate were used in this experiment and the aggregate size namely was 0-5 mm for sand and 5-20 mm for coarse aggregate.

The water used in the experiments was Singapore tap water.

4.1.2 Specimen preparation

To achieve the scope of this experimental study on drying rate in concrete with

Chapter 4 Study on drying process of concrete

considering the preconditioning effect for PC and blended cements more than 300 samples with 21 different mix proportions have been cast. Table 4-4 shows the mix proportions in ratios and quantities.

Table 4-4 The details of mix proportions

Mix name	W/(C+P)	a/c	P Type	p/(c+p)	W (kg/m ³)	C (kg/m ³)	P (kg/m ³)	Sand (kg/m ³)	Agg. kg/m ³	SP %
C0	0.5	3	-	0	254	514	0	741	762	0
C1,C4	0.5	3	-	0	251.5	503	0	830	679	0
C6	0.5	4	-	0	212	424	0	848.5	848.5	
C3	0.5	5	-	0	182.2	365	0	820	1002	0
C2	0.4	3	-	0	210.5	526	0	710	869	0.25
C5	0.6	4	-	0	244.2	407	0	976.8	651.2	0
SI-1	0.5	3	GGBG	0.1	250.5	451	50	751.5	751.5	0
SI-2	0.5	3	GGBS	0.3	249	348	150	747	747	0
SI-6	0.5	3	GGBS	0.5	248.5	248.5	248.5	894.6	596.4	0
SI-3	0.5	4	GGBS	0.5	209	209	209	836	836	0
SI-4	0.6	4	GGBS	0.5	241	201	201	804	804	0
SI-5	0.4	4	GGBS	0.5	174.5	218	218	872.5	872.5	0.50
Sf-1	0.5	3	CSF	0.05	250.5	476	25	751.5	751.5	0
Sf-2	0.5	3	CSF	0.1	249.5	449	50	748.5	748.5	0
Sf-3	0.5	3	CSF	0.15	248.5	422	75	745.5	745.5	0
Sf-4	0.4	3	CSF	0.15	209.2	445	78	798	798	0.50
Sf-5	0.6	4	CSF	0.15	241.2	341.7	60.3	804	804	0
FI-1	0.5	3	LFA	0.1	249	448	50	747	747	0
FI-2	0.5	3	LFA	0.2	246.5	394.4	98.6	739.5	739.5	0
FI-3	0.5	3	LFA	0.3	244.2	341.9	146.5	732.6	732.6	0
FI-4	0.4	3	LFA	0.3	205.5	359.5	154	770.2	770.25	0.50
FI-5	0.6	4	LFA	0.3	237.6	277.25	118.8	792	792	0

The samples were prepared by mixing in a mixer for 3 minutes by one-third of water and then continue mixing for 4 more minutes by rest of water. The fresh concrete was poured into steel cube moulds of 100×100×100 mm and 150×150×150 mm in three layer and each layer compacted by tamping rod on vibrating table. The sample were sealed by plastic sheet to prevent the water evaporation and removed from the molds after 24 hours. Some of the samples were then submerged in water at ambient temperature (25°C-30°C) until the related curing ages were achieved. The curing ages for different specimens varied from 0 day water curing (1 day in mold) to 89 days water curing (90 days curing).

Sample preparation of MIP test

The pore structures of samples were measured by mercury intrusion porosimeter (MIP). After reaching to specific condition which has been planned, the samples from different mix proportion with various curing periods from near surface and from center of the samples has been taken. The sample has been broken to small particle with dimension of about 4-6 mm. Then the samples were immersed in acetone in order to extract the free water and further were dried in vacuum desiccator.

4.1.3 Equipments and procedures

Relative humidity monitoring

For monitoring the effect of temperature on drying process and also monitoring of exposure condition in outdoor, indoor without air-conditioning and indoor with air-condition the thermometer and hygrometer were used. This device can measure maximum and minimum humidity and temperature in one day. Two devices were used to monitor different exposure condition.

MIP test

Mercury intrusion porosimeter 9400 Series was used for this experiment. The MIP test consists of two steps of analysis. One is low pressure analysis. The other is high pressure analysis. For case of low pressure the sample was evacuated to 50 μmHg and the pressure was generated up to 30 Psia by nitrogen gas gradually to force the mercury into the pores on the surface of the sample. Then the weight of penetrometer was measured to calculate assembly weight and installed in high pressure port to perform high pressure analysis, the maximum pressure in high pressure is about 60,000 Psia.

The MIP measures the volume distribution of pores materials by mercury intrusion. Mercury porosimetry is based on capillary law governing liquid penetration

into small pores. This law, in the case of non-wetting liquid like mercury and cylindrical pores is expressed by the Washburn equation (Washburn, 1921) as follow.

$$d = \frac{4\gamma \cos \theta}{p} \quad (4.1)$$

Where

d = Equivalent diameter of the intruded pores

γ = Surface tension of mercury

θ = Angle of contact between the mercury and the pore walls

p = Pressure at which a given increment of mercury intrudes into the pore system

The volume of mercury penetrating pores is measured as a function of applied pressure and this serve as a unique characterization of the pore structure. Pores are rarely cylindrical; hence the above equation constitutes a special model which may not best represent pores in actual materials. However its use is generally accepted as the best practical means, otherwise it would be most complex problem.

The surface tension of the mercury was taken as 0.485 N/m and the advancing contact angle is assumed to be 130.0° (Cook, 1993). In this process, the following parameters were determined: (Roy, 1999)

- 1- Total intrusion volume
- 2- Total pore area
- 3- Median pore diameter
- 4- Average pore diameter
- 5- Apparent and bulk density

Compressive strength test

To investigate the effect of the mineral admixtures and the quality of concrete samples, compressive strength test was performed on the samples. For the 100 mm cube samples the load were applied with a rate of 150 kN/min to the samples. The compressive strength was calculated by equation (4-2).

$$\sigma_c = \frac{F}{A} \quad (4.2)$$

4.1.4 Various exposure conditions

The exposure temperature and relative humidity and variance of these data's can affect the drying rate of concrete.

Most of the experimental works done on drying rate of concrete operate under well laboratory conditions and with present of nitrogen gas to prevent carbonation of concrete and investigation of the level of moisture condition in real local climate was the concern of this part of experiment.

The environment monitoring for indoor condition with and without air-conditioning and outdoor and sheltered from rain were operated for more than one year and average values of temperature and relative humidity are shown in Table 4-5. The profile of variances of data is shown in Figure 4-5 and 4-6.

The variation of relative humidity and temperature is assumed to be linear in duration of days. The average values in Table 4-5 has been calculated based on this assumption. This assumption is pretty acceptable for Singapore with very low variation of relative humidity.

Figure 4-5 Average temperature variances in duration of monitoring

Figure 4-6 Average relative humidity variances in duration of monitoring

Table 4-5 The average temperature and relative humidity for different exposure

Condition	Average Temperature	Average RH
Indoor	27.5°C	73%
Outdoor without air-condition	26.5°C	75%
Indoor with air-condition	19.5°C	75%

To understand how these three different exposure condition can affect the drying rate of concrete, Figure 4-7 shows the drying rate of concrete with $w/c=0.5$, $a/c=3$ and 14 days of curing in these three different conditions.

Figure 4-7 Sample weights loss in indoor and outdoor and air-con condition and the expected level

Based on Figure 2-3 for w/c ratio equal to 0.5 and in drying process, the desired saturation degree will be around 50% for relative humidity equal to 74%. This desired level has been shown in comparison with different drying conditions in Figure 4-7.

As shown in Figure 4-7, the higher daily variation of relative humidity in outdoor condition compared to indoor without air-condition did not make any difference as

long as the average values of relative humidity remain similar for two conditions. It can be concluded that the average value of relative humidity can play main role and daily variation of relative humidity does not have a significant effect of moisture condition.

Loo (1994) did accelerated carbonation test and he used 13 days to 71 days local Singapore climate condition as preconditioning before start of accelerated test for RH equal to 65%. As presented in Figure 4-7, the drying ages of around 7 or 8 month is enough for the 100 mm cube sample with 3 dimensional drying in relative humidity around 73% to reach to its uniform saturation degree.

Figure 4-7 shows the expected level of saturation degree proposed by Figure 2-3 is much lower than the measured value in this experiment. It can be due to the possible damage caused by preconditioning on pore structure of concrete.

4.2 Results and discussions

In the next four sections the main scopes of this experiment and the results of the experiment for effective parameters on drying rate of concrete will be reviewed

4.2.1 The effect of preconditioning on concrete pore structure

Monitoring the 105°C oven drying

As some of the researchers used the 105°C oven drying as preconditioning before carbonation test or gas permeability test, knowing the level of moisture content in 105°C oven drying is important. Figure 4-8 shows the moisture content in 105°C oven drying.

One day oven drying offered as preconditioning for relative humidity equal to 65%. Figure 4-8 shows that it is acceptable to assume that the saturation degree after one day oven drying in 105°C is equal to desired level for 65% relative humidity.

After around 7 days of drying the sample will be totally dry. But two issues here are the non uniform moisture distribution in concrete and the possible damage of concrete pore structure and micro cracks in concrete. The fast drying by 105°C will defiantly results the non uniform moisture distribution in concrete. The second issue will be investigated by MIP test and monitoring the rate of weight loss during the drying after rewetting.

Figure 4-8 The rate of moisture loss in 105°C oven drying

Study on effect of 105°C oven drying on pore structure by drying after rewetting

The drying after rewetting is a very good method proposed by author to measure the degree of damage caused by oven drying on pore connection of concrete. the general idea of this method is to monitor the drying rate of concrete in special preconditioning. Then rewet the sample to initial state and finally monitor its second drying in comparison to the samples without any preconditioning. Figure 4-9 shows the case that the preconditioning was to keep the sample in indoor condition.

Figure 4-9 Drying after rewetting for indoor condition

After 50 days of drying in indoor condition sample submerge in water for 10 days and then return to normal condition for second round of drying. The sample did not reach to its previous weight even after 10 days submerged in water but it was enough to assume that the sample is totally wet. As shown in Figure 4-9, the rate of drying after rewetting is slower than the sample dried in indoor condition. It is due to older age of sample and continuing hydration due to high relative humidity of ambient and also ten more days submerging in water.

Figure 4-10 shows the sample oven dried in 105°C for seven days and then rewetting for 13 days compared to sample dried in indoor condition. It was found that the 105°C oven drying can increase pore connection of concrete. In order to control the relative humidity and temperature, after rewetting, 3 of the samples dried in 105°C kept in oven at 40°C and RH=50% in same time with the sample without any preconditioning. Figure 4-11 shows this second case. It is clear that the same results can be obtained from Figure 4-11.

Figure 4-10 Effect of 105°C on rate of drying after rewetting compare to indoor condition

Figure 4-11 Effect of 105°C on rate of drying after rewetting compare to 40°C oven drying condition

Study on effect of 105°C oven drying on pore structure by MIP test

For these conditions three or more sample taken from near surface and from center of samples. The carbonation process will start from surface and aggressive agent will penetrate from surface. Then having the porosity near surface is important on carbonation rate especially in accelerated test.

When drying in indoor condition, the average pore size at near surface is slightly bigger than at the center of the samples. The indoor condition can be used as reference for oven drying conditions. Figure 4-12 represents the pore size distribution of center and near surface of concrete samples kept in indoor condition

Figure 4-12 Pore size distribution in near surface and center of samples dried in indoor condition

Figure 4-13 shows the cumulative intruded pore volume of samples kept in normal condition for near surface and center of specimens. Figure 4-13 shows that the center and near surface have similar total porosity.

Figure 4-13 Cumulative intruded pore volume for samples dried in indoor condition

The MIP result for samples taken from near surface and center of samples kept in 105°C for 5 days presented in Figures 4-14 and 4-15.

Figure 4-14 Pore size distribution of samples oven dried in 105°C for 5 days

Figure 4-15 Cumulative intruded pore volume in 5 days 105°C oven drying

Figures 4-14 and 4-15 show that long oven drying in 105°C can severely damage the pore structure of concrete especially in center, because the sample forced to lose all the water. It damages the internal pore structure more severely. As it mentioned before, one day 105°C oven drying used by most of researcher as preconditioning before accelerated tests. Figures 4-16 and 4-17 show the effect of one day 105°C oven drying on pore structure of concrete in center and near surface of samples.

Figure 4-16 Pore size distribution for one day 105°C oven drying

Figure 4-17 Cumulative intruded pore volume in one day 105°C oven drying

Figures 4-16 and 4-17 show the effect of one day 105°C oven drying on pore structure of concrete in near surface and center of the samples. This oven drying can damage the near surface pore structure severely but it is not long enough to damage the pore structure of concrete at the center of samples significantly. Due to this reason, the air permeability of samples oven dried for 1 day in 105°C is lower than the samples dried in oven with 105°C for 5 days. But the carbonation process will start from surface of samples. Because of this, both one day and 5 days oven drying can cause a big error in measuring depth of carbonation in accelerated test.

The effect of these two oven drying condition on the average pore diameter of concrete is presented in Figure 4-18. As mentioned above, the pore structure in near surface for both these cases damage severely and it can affect on rate of deterioration mechanisms in concrete.

The saturation degree of concrete is affected by pore structure of concrete and the ambient relative humidity. Damage in pore structure caused by preconditioning will decrease saturation degree of concrete.

Figure 4-18 The effect of 105°C oven drying on the average pore diameter of PC

As it has been shown in Figures 2-3 and 2-4, for a long time, researchers believe that the absorption and desorption follow two different curves. But these curves are the result of the different degree of damage caused by different period of oven drying. Figure 4-19 shows the instant absorption and desorption curve as a result of oven drying in comparison with natural drying and wetting process.

Figure 4-19 The instant absorption and desorption curves produced by oven drying compared to natural drying-wetting process

During desorption process, the sample is exposed to 105°C oven drying for limited period and before starting of absorption, the sample is totally dried. This later long drying causes the higher damage in pore structure of the concrete.

Figure 4-20 shows the total weight loss of the sample dried in natural condition compared to absorption and desorption rate for the sample with 5 days and 1 day oven drying preconditioning.

Figure 4-20 Comparison of the sample weight loss in indoor condition for various preconditioning

In Figure 4-20, comparing sample 1 and 2, it shows that sample 2, which is suffering from long 105°C oven drying, has much faster drying rate in indoor condition (after rewetting) compared to sample 1 which is dried directly in indoor

condition. Comparing sample 2 and sample 3, it shows that the final saturation degree in absorption and desorption is quite similar since the samples have similar pore structure. Comparing sample 4 with samples 2 and 3, it shows that a shorter oven drying period leads to less damage and higher final saturation degree but the value is still significantly lower than sample 1. Case 6 shows the expected saturation degree for indoor condition in this experiment. It is higher than the value reported by Figure 2-3. The saturation degree for the sample with $w/c=0.5$ and $a/c=3$ dried in indoor condition with $RH=73\%$ was around 0.63 (sample 1), for the sample with 5 days of 105°C oven drying the saturation degree was around 0.32 (samples 2&3). For the sample with 1 day of 105°C oven drying the saturation degree is around 0.42 (sample 4). In some experimental results the values 0.42 and 0.32 is mistakenly reported as saturation degree in desorption and sorption of concrete in this RH. As mentioned these lower values are the result of damage caused by oven drying. Some of the researchers like Neithalath (Neithalath, 2006) used a sorption equation to simulate drying of concrete. Some of researchers like Gopalan (Gopalan, 1996) and Khatib (Khatib, 2004) used oven drying as preconditioning before sorption test. Comparing the sample 4 and sample 6 show that the rate of sorption is highly depends on moisture content of the sample prior to sorption test. Even using the same period of drying will not lead to same moisture content as the drying rate is affected by pore structure of concrete. Sorption results can be used to compare various pore structures and simulate the drying rate if the moisture content is similar.

Monitoring the 40°C oven drying

Monitoring of 40°C oven drying condition can be very important because most of researchers believe that drying in 40°C does not damage pore structure of concrete. Some of the researchers like Russell (Russell, 2001) used this condition as preconditioning of accelerated carbonation test.

Study on effect of 40°C oven drying on pore structure by drying after rewetting

Figure 4-21 shows the rate of drying in 40°C after rewetting compared to sample

without any preconditioning. Only slightly increase in rate of drying is observed in this case. But generally it can be assumed that there is no significant increase in rate of drying after oven drying in 40°C.

Figure 4-21 Drying after rewetting for 40°C

It cannot show that the oven drying in 40°C does not damage the pore structure. As presented in equation (3.36), the damage caused by oven drying does not only depend on temperature but also on the period of drying.

Study on effect of 40°C oven drying on pore structure by MIP test

As mentioned above, since the increase in rate of drying is not significant, it is necessary to identify any possible damage by doing MIP test.

Figures 4-22, 4-23 and 4-24 show the porosity of samples oven dried in 40°C for near surface and center of specimen.

Figure 4-22 Pore size distribution in long period 40°C oven drying

Figure 4-23 Cumulative intruded pore volume in long 40°C oven drying

Figure 4-24 The effect of 40°C oven drying on the average pore diameter of PC

It is clear in Figures 4-22, 4-23 and 4-24, even oven drying in 40°C can damage the pore structure of concrete but the damage is not severe. Moreover the rate of drying after rewetting does not increase significantly. It can be concluded that oven drying in 40°C can be used much safer than oven drying in 105°C. But the period of drying to achieve the desired level of saturation degree must be considered.

Galle (2001) in similar work done for center of specimen reports that freeze drying will not damage the pore structure of samples taken from center of specimen. The freeze drying technique is commonly used in many industrial areas like soil engineering, food industry, and biology. In the experimental procedure sample were first frozen (-195°C) by immersion in liquid nitrogen for 5 minutes. This quick quenching process at very low temperature allows generating ice microcrystals. After freeze drying, sample were introduce in an Alpa I/5 Martin Christ type freeze dryer in which temperature and vacuum pressure will kept at -40°C and to 10^{-1} Pa, respectively. But there is no data about the effect of freeze drying on microstructure of near surface of specimen and also whether this method will increase the pore connection and rate of drying after rewetting.

As mentioned above, the temperature higher than 40°C can damage the pore structure of concrete.

4.2.2 The effective parameters on drying rate of concrete

The drying rate and the saturation degree of concrete mainly depend on the pore structure of concrete and the environment conditions. The pore structure of concrete is affected by w/c ratio, a/c ratio, curing period, mineral admixture characteristic, percentage of mineral admixture replacement and preconditioning. Different sets of experiment have been done to indentify the effect of these parameters on drying rate of concrete.

To check the repeatability and the accuracy of the monitoring of the weight loss, the same mix proportion (C0, C1, and C4) have been cast for three times. The comparison of the result for different curing period and environment condition shows that the

process of weight loss of concrete is very good repeatable and predictable. Figure 4-25 shows the comparison of these three mix proportions with 14 days of curing. Data presented is based on Indoor (RH=73% & T=27°C) condition and 100 mm cube.

Figure 4-25 Repeatability of the process of the weight loss

The w/c ratio has clear effect on pore structure of concrete. Lower w/c ratio leads to denser pore structure, lower total porosity and smaller pore size and slower rate of drying is expected.

Figure 4-26 shows the effect of different w/c ratio on the sample weight of the concrete samples.

Figure 4-26 Sample weight for various w/c ratios and drying periods

The faster rate of weight loss for higher w/c may be the result of higher water content. Due to this reason the ratio of water loss to possible water loss (saturation degree) for different w/c ratio has been reviewed in Figure 4-27.

Figure 4-27 Total water loss to possible water loss for various w/c ratios

As shown in Figures 4-26 and 4-27 higher w/c ratio leads to faster rate of drying. The w/c ratio has significant effect on saturation degree of concrete. The cumulative intrusion of mercury in concrete samples for these three cases has been shown in Figure 4-28.

Figure 4-28 Cumulative intruded pore volume with different w/c ratio

In longer curing period the denser pore structure is expected. Figure 4-29 shows the sample weight for PC concrete samples with different curing periods.

Figure 4-29 Sample weight for various curing and drying periods

As shown in Figure 4-29, in longer curing period, due to higher hydration degree of cementitious materials, lower total porosity and lower rate of drying are expected.

The sample weight curves for different w/c ratios and curing periods are totally distinguished, repeatable and predictable. The lower w/c ratio and longer curing period leads to denser pore structure and lower rate of drying of concrete.

Figure 4-30 shows the effect of various w/c ratios and different curing periods on the sample weight loss.

Figure 4-30 Effect of w/c ratio and curing period on the weight loss

Figure 4-31 shows the same data for $w/c=0.5$ and $a/c=3$ with comparing the total water loss to possible water loss (saturation degree). The effect of curing period on final saturation degree is negligible, but it has considerable effect on rate of drying. The possible water loss is calculated by using the hydration degree equation (3.8) and by assuming the non-evaporable water for fully hydrated cement equal by 0.23 (Neville, 2005, p 26).

The effect of a/c ratio is the most complex behaviour to describe. For the same w/c ratio, higher a/c ratio leads to lower water content and lower initial total porosity. But in longer curing period due to lower cementitious material, the reduction in porosity is lower and the total porosity can be even higher compared to the concrete with lower a/c ratio. Due to the effect of interfacial transition zone (ITZ) near aggregates surface,

the average pore size is higher for higher a/c ratio. Figure 4-32 shows average pore size for various a/c ratios by MIP test.

Figure 4-31 Effect of curing period on final saturation degree and drying rate

Figure 4-32 The effect of a/c ratio on average pore diameter

The higher a/c ratio will lead to faster drying rate. Figure 4-33 shows the effect of a/c ratio on drying rate of concrete samples.

Figure 4-33 The effect of a/c ratio on drying rate of concrete

As shown in Figure 4-33, for longer period of curing the effect of aggregate content is less significant.

In blended cement concrete the pore structure is highly affected by the activity of mineral admixtures and the curing period. The general perception that the blended cement concrete has lower pore connection and finer pore size distribution can be completely wrong if the quality of blended cement is low and the curing period is insufficient. Due to this reasons, knowing all the characteristics of mineral admixtures before concluding any results is very important. In blended cement concrete, similar to PC concrete, the effect of curing period on the final saturation degree is negligible but the replacement percentage and the activity of mineral admixtures can significantly affect the saturation degree and drying rate of concrete. For instance, the low calcium fly ash used in this experiment has low glass content and big particles which lead to a

low activity in reacting with cementing component. The low quality of this fly ash leads to lower compressive strength up to 28 days of curing. Figure 4-34 shows the compressive strength results for different percentage of this fly ash replacement.

Figure 4-34 The effect of LFA replacement on compressive strength of concrete

Figure 4-35 shows the effect of this fly ash replacement on drying rate of concrete.

Figure 4-35 Effect of fly ash replacement on drying rate of concrete

The MIP test for 28 days curing shows the higher total porosity and bigger pore size distribution for higher percentage of this fly ash replacement. Figures 4-36 and 4-37 show the pore size distribution and the total porosity respectively.

Figure 4-36 Pore size distribution with different percentage of fly ash replacement

Figure 4-37 Cumulative intruded pore volume with different fly ash replacement

The condensed silica fume with mean particle diameter of 28.5 μm has been used in this experiment. This silica fume showed to be effective on pore structure of concrete only after longer period of curing. Figure 4-38 shows the effect of 15% condensed silica fume replacement after 1 day and 14 days of curing on total weight loss of concrete.

Figure 4-38 Effect of condensed silica fume replacement and curing period on sample weight of concrete

Big particle size of this condensed silica fume results in not significant increase in compressive strength in comparison to PC. Figure 4-39 shows the compressive strength of concrete made by different percentage of this condensed silica fume.

Figure 4-39 The effect of CSF replacement on compressive strength of concrete

The MIP test results do not show any effect on average pore size of concrete by replacing this condensed silica fume. The volume increase in reaction of SiO_2 by PC compounds is equal by zero. Then higher total porosity for higher percentage of replacement of condensed silica fume is expected and recorded. But as shown in Figure 4-38, although the total porosity is higher but the pore connection is lower and lower drying rate is recorded. Figure 4-40 shows the increase in total porosity as results of different parentage of condensed silica fume replacement with 28 days curing.

Figure 4-40 Cumulative intruded pore volume with different CSF replacement

High quality GBFS with mean particle size of $9.2 \mu\text{m}$ has been used in this experiment. This GBFS is shown to be very effective on reducing the pore connection and average pore size of concrete. Higher percentage of replacement of this GGBS results in better pore structure of concrete. The total porosity remained almost same but the average pore size was much smaller and the pore connection also was much lower. The good quality of this GBFS resulted in higher compressive strength even by replacing 50% of PC by GBFS. Figure 4-41 shows the compressive strength of concrete by replacing various percentages of GBFS.

Figure 4-41 The effect of GBFS replacement on compressive strength of concrete

Figure 4-42 shows the cumulative intrusion for various percentage of GBFS replacement after 28 days curing. As shown, the total porosity remains similar for these cases.

Figure 4-42 Effect of GBFS replacement on cumulative intrusion by MIP test

The GBFS replacement effectively decreases the average pore diameter. Figure 4-43 shows the effect of different percentage of GBFS replacement on average pore diameter of the samples.

Figure 4-43 Effect of GBFS replacement on average pore diameter by MIP

The total weight loss has been dropped in result of replacing PC with the various percentages of GBFS. Higher percentage of GBFS results in lower weight loss and slower rate of drying as shown in Figure 4-44.

Figure 4-44 Effect of percentage of GBFS replacement on sample weight

Beside the effect of w/c ratio, the mineral quality and the percentage of replacement are the main parameters affecting the saturation degree of concrete. The effect of w/c ratio on saturation degree of concrete with the normal slump range is pretty predictable and the experiment shows the repeatability of the results as well. As mentioned above, the effect of mineral admixtures on saturation degree is related to quality of mineral admixtures and the percentage of replacement. The Figure 4-45 shows the variation of the final saturation degree in indoor condition for the blended cement concrete in this experiment.

Figure 4-45 Variation of saturation degree for different mineral admixtures and different percentages of replacement

As shown the effect of mineral admixtures on saturation degree is highly affected by its quality and the percentage of replacement and generating a general conclusion needs more experimental works.

4.3 Simulation of drying rate of concrete

For the normal slump PC concrete without any preconditioning, the final saturation degree is predictable.

$$S_f = 1 - e^{\frac{\frac{w}{c}-1}{1.4 \ln(\frac{1}{RH})}} \quad (4.1)$$

Equation (4.1) has good prediction ability on author's experimental data. The behavior of this model for different w/c ratio and RH has been presented in Figure 4-46.

Figure 4-46 Saturation degree of concrete in different w/c ratio and relative humidity

The same trend for the effect of w/c ratio on saturation degree of concrete for different relative humidity has been reported by Papadakis. The only difference is that the reported saturation degree for different w/c ratio and relative humidity is lower in Papadakis works and it is due to the 105°C oven drying that he used as preconditioning for his samples which result to severe damage in pore structure of concrete.

The higher a/c ratio results in lower saturation degree but to quantify the effect is complicated. The following equation can show the trend line of the effect of a/c ratio on final saturation degree of concrete.

$$S_f = 1 - e^{\frac{\frac{w}{c}-1}{1.27 \times (\frac{a}{c})^{0.1} \ln(\frac{1}{RH})}} \quad (4.2)$$

The final saturation degree of blended cement concrete has been calculated by using Figure 4-45. For other works, it can be obtained by comparing the weight loss of blended cement by control PC and from extrapolation of weight loss curves. This value can be roughly calculated as follow

$$S_f = (Gp^{0.3}(1 + K_H))^{10e} \times (1 - e^{\frac{\frac{w}{c}-1}{1.27 \times (\frac{a}{c})^{0.1} \ln(\frac{1}{RH})}}) \quad (4.3)$$

In which Gp is the glass phase content, K_H is coefficient depends on type of mineral admixture as presented in Table 3-2 and e is the pozzolanic ratio. The saturation degree of concrete in the depth x from drying surface can be calculated as follow:

$$S_{(x)} = S_f + \frac{(1 - S_f)}{(1 + \frac{t}{0.7x^{1.8} \times b \times F \times (1 - 1.3 \frac{w}{c})})} \quad (4.4)$$

The S_f is the final saturation degree which described above. x is the depth from drying surface (mm), t is the drying time (days), F is the average hydration degree calculated by equations (3.8) and (3.15), b is equal to 3 and 1 for 1-dimensional and 3-dimensional drying respectively.

By using the equation (4.4) the total weight loss of concrete for one and three dimensional drying can be calculated as follow:

$$W_t = 4 \int_0^D \int_0^D S(x) dy dx \quad (4.5a)$$

$$W_t = 4 \int_0^D \int_{S(x_1)}^{S(x_2)} f(x, y) dy dx \quad (4.5b)$$

In which W_t is the total weight loss and D is the maximum distance from the drying surface.

Reduction in saturation degree by time for different w/c ratio and curing period in comparison to simulation result by using the equations (4.1) to (4.5) has been presented in Figure 4-47. The reduction in the saturation degree of concrete for various w/c ratios and curing periods is pretty distinguished and predictable.

Figure 4-47 Saturation degree of concrete for various w/c ratios and curing periods

Figures 4-48 and 4-49 show the the reduction in saturation degree of concrete in 1-dimensional and 3-dimensional drying. Figure 4-48 shows the PC concrete with w/c=0.6, a/c=4 and 4 days of curing and Figure 4-49 shows the blended cement concrete with 50% GBFS replacement, w/c=0.6, a/c=4 and 4 days of curing. To study the 1-dimensional drying a thick layer of bitumen were used to cover four surface of specimenes.

Figure 4-48 Saturation degree of PC concrete in 1-D and 3-D

Figure 4-49 Saturation degree of GBFS concrete in 1-D and 3-D

Equation (4.4) can predict the drying rate of concrete with good accuracy. The behaviors presented by this model fulfill the expected trend lines in experimental works.

Figure 4-50 shows the distribution of saturation degree in PC concrete with $w/c=0.5$ and $a/c=3$ with 28 days curing in the indoor condition with $RH=73\%$ for different drying period and distance from drying surface up to 100 mm.

Figure 4-50 Distribution of saturation degree of PC in different drying ages

The effect of curing period on internal saturation degree distribution has been presented in Figure 4-51. The higher curing period results in denser pore structure, higher saturation degree and slower drying rate.

The effect of w/c on distribution of saturation degree is shown in Figure 4-52. As described above and as presented in Figure 2-3, the lower w/c ratio results in slower rate of drying. And due to the denser pore structure, the higher saturation degree for lower w/c ratio is expected.

Figure 4-51 Distribution of saturation degree for various curing periods in indoor condition

Figure 4-52 Distribution of saturation degree of PC concrete for various w/c ratios

As mentioned in previous section, the effect of blended cement concrete on pore structure and saturation degree of concrete depends on its quality and the percentage of replacement. Figure 4-53 shows the distribution of saturation degree for the blended cements of this experimental work in comparison with PC concrete.

Figure 4-53 Distribution of saturation degree for different blended cements

In next chapter by using the effective parameters on carbonation of concrete and the drying and saturation degree model, the carbonation depth of concrete under various conditions will be calculated.

CHAPTER

5

SIMULATION OF CONCRETE CARBONATION

5.1 Mathematical model

The mathematical model developed herein applies to one-dimensional geometry, i.e., to an infinite slab or wall of thickness $2L$, include the cracked sections, with both surfaces exposed to an external atmosphere with concentration of $CO_2 = [CO_2]_0$.

Nevertheless, the model can be applied to beam or columns with planar external surface, with the exception of the corner regions. For extension to two-or-three-dimensional geometry, only the diffusion terms, and the boundary conditions, have to be generalized.

5.1.1 Mass balance and boundary conditions

The mathematical model can be based on the following differential mass-balance of the gaseous CO_2 , solid and dissolved $Ca(OH)_2$, CSH, an unhydrate silicates which account for the production, diffusion, and consumption of these substances.

- **First Simplification**, unhydrate silicate will not participate in carbonation reactions. Then these terms can be neglected from mass balances.

Mass balance of CO_2 is as follow.

$$\frac{\partial}{\partial t} [\varepsilon(1-f)CO_2] = \frac{\partial}{\partial x} \left(D_{e,CO_2} \frac{\partial [CO_2]}{\partial x} \right) - \varepsilon f_w r_{CH} - 3r_{CSH} \quad (5.1)$$

Mass balance of solid $Ca(OH)_2$ is as follow.

$$\frac{\partial}{\partial t} [Ca(OH)_2(s)] = r_{H,CH} - r_D \quad (5.2)$$

Mass balance of dissolved $Ca(OH)_2$ is as follow.

$$\frac{\partial}{\partial t} \{ \varepsilon f [Ca(OH)_2(aq)] \} = \frac{\partial}{\partial x} (D_{e,Ca(OH)_2(aq)} \frac{\partial [Ca(OH)_2(aq)]}{\partial x}) - \varepsilon f_w r_{CH} + r_D \quad (5.3)$$

- **Second Simplification** the $Ca(OH)_2(aq)$ diffusion terms at the right-hands-side of equation (5.3) is negligibly small for relative humidity less than about 90 percent, so the equations (5.2) and (5.3) can be added, yielding to the following equation.

$$\frac{\partial}{\partial t} [Ca(OH)_2] = r_{H,CH} - \varepsilon f_w r_{CH} \quad (5.4)$$

In which the concentration $[Ca(OH)_2]$ is that of the entire $Ca(OH)_2$, solid or dissolved.

Mass balance of CSH is as follow.

$$\frac{\partial}{\partial t} [CSH] = -r_{CSH} + r_{H,CSH} \quad (5.5)$$

In which x is the distance from the exposed surface of the concrete and t denotes time.

As mentioned before the term r_{CH} is referring to unit volume of the liquid phase of those pores which are partially filled with water and partially filled with air. So, it must be multiplied by the volume εf_w to be converted to rate per unit volume of concrete. The other terms, $\varepsilon(1-f)$, εf in above equations, have similar justification.

Boundary condition

All these equations are from a system of partial differential equations in space and

time. This system is considered to hold from the point in time at which hydrothermal equilibrium is established between the external environment and the concrete pores, which is considered to coincide with the end of the period of moist curing. That particular point in time is taken as $t=0$. Prior to it, and for time period equal to the duration of moist curing t_{cu} , only the hydration reactions are considered to take place.

Then at $t=0$ the “initial” concentration of $Ca(OH)_2(aq)$, $Ca(OH)_2(s)$, CSH , denoted by $[Ca(OH)_2(aq)]_0$, $[Ca(OH)_2(s)]_0$, and $[CSH]_0$, have been established through the mass of concrete. The initial concentration of $Ca(OH)_2(aq)$ is equal to one-half the concentration of OH^- at saturation, $[OH^-]_{eq}$ while that of $Ca(OH)_2(s)$ is equal to the total initial concentration of $Ca(OH)_2$ minus $[Ca(OH)_2(aq)]_0$. The initial value of porosity is equal to $\varepsilon = \varepsilon_0 = \varepsilon_{(t=0)}$. The initial conditions of the problem are as follow.

$$\text{At } t = 0 : \{ [CO_2] = 0, [Ca(OH)_2(s)] = [Ca(OH)_2(s)]_0, [Ca(OH)_2(aq)] = [Ca(OH)_2(aq)]_0, [CSH] = [CSH]_0, \varepsilon = \varepsilon_0 \} \quad (5.6)$$

And the boundary equations will be as follow.

$$\text{At the surface } x = 0: [CO_2] = [CO_2]_0, \frac{\partial [Ca(OH)_2(aq)]}{\partial x} = 0 \quad (5.7)$$

$$\text{At the symmetry axis } x = L: \frac{\partial [CO_2]}{\partial x} = 0, \frac{\partial [Ca(OH)_2(aq)]}{\partial x} = 0 \quad (5.8)$$

By mass balance equations and each time, equations (5.7) and (5.8) for boundary conditions, and equation (3.57) for pH calculation the depth of carbonation can be calculated. Generally these equations can be solved numerically, as instance Runge-Kutta scheme. By discrimination in space and time, replacement of the derivatives t and x by the corresponding finite differences and using step by step integration. The integration time step must be very small, the order of 30 sec. Most of the rates in equations are very large, which means that the corresponding processes occur very fast.

-**The third simplification** derivation of term $\varepsilon(1-f)[CO_2]$ in concrete pores is always small. The gaseous phase of pores is in connection with environment and always the amount of not reacted CO_2 in gaseous phase can be assumed to be equal to environment concentration. Then the left side of equation (5.1) can be assumed equal to zero.

In this equation, except within a very small part ∂x (partially carbonated part) of the interval from 0 to L, either $[CO_2] = 0$ or $[Ca(OH)_2(aq)] = [Ca(OH)_2(s)] = [CSH] = 0$ should exist. The implication is that a carbonation front separating the region over which $[CO_2] \neq 0$.

The concentration of $Ca(OH)_2$ solid and dissolved, and CSH are zero due to their complete carbonation, from the region over $[CO_2] = 0$ and the concentration of the other substances are equal to their initial value.

5.1.2 Depth of carbonation

The above mass balance and boundary conditions are based on uniform moisture content. Based on this assumption if the carbonation front is at the distance x_c from the concrete surface then for noncarbonated region:

$$[CO_2] = 0, [Ca(OH)_2] = [Ca(OH)_2]_0, [CSH] = [CSH]_0, x > x_c$$

And in the completely carbonated region

$$[Ca(OH)_2] = [CSH] = 0, 0 \leq x \leq x_c$$

In this latter region, the effective diffusivity of CO_2 is constant and equal to D_{e,CO_2}^C , which corresponds to fully carbonated concrete, so there also exists

$$\frac{d^2[CO_2]}{dx^2} = 0, i. e., [CO_2] = [CO_2]_0(1 - x/x_c), 0 \leq x \leq x_c$$

Now all the above equations and boundary conditions can be cast in neighborhood of the carbonation front into the following format:

$$\frac{d}{dx} \left(D_{e,CO_2} \frac{d[CO_2]}{dx} \right) + \frac{d}{dt} ([Ca(OH)_2 + 3[CSH]]) + (2r_{H,C_4AF} + 4r_{H,C_3A}) = 0$$

All terms in above equation will be multiplied by dx_C as follow.

The first: $(D_{e,CO_2} d[CO_2]/dx)_{x_C^+} = +D_{e,CO_2}^C [CO_2]_0/x_C$

The second: $(\frac{dx_C}{dt})\{[Ca(OH)_2] + 3[CSH]\}_{r(x_C^+)} = (\frac{dx_C}{dt})([Ca(OH)_2]_0 + 3[CSH]_0)$

-Fourth simplification the third part will be zero as it is infinitesimally small. Therefore, there finally exists.

$$x_C \frac{dx_C}{dt} = \frac{D_{e,CO_2}^C [CO_2]_0}{[Ca(OH)_2]_0 + 3[CSH]_0} \quad (5.9)$$

Equation (5.9) can be integrated, under the initial condition $x_C = 0$ at $t = 0$, yielding to the following equation.

$$x_C = \sqrt{\frac{2D_{e,CO_2}^C [CO_2]_0}{[Ca(OH)_2]_0 + 3[CSH]_0} t} \quad (5.10)$$

By using equations (3.59) and (3.60) for environment temperature and the low relative humidity condition, the following explicit equation for calculation of carbonation depth of concrete is proposed as follow:

$$x_C = e^{(8.6 - \frac{2563}{T})} \sqrt{\frac{2D_{e,CO_2}^C [CO_2]_0}{S^{\ln(S)} [Ca(OH)_2]_0 + 3[CSH]_0} t} \quad (5.11)$$

These additional terms can decrease the error of prediction on all experimental data significantly. The involve parameters in this equation are as follow:

1- Material

- Oxide composition of PC
- Mineral admixtures (Chemical composition, fineness, glass content)

2- Mix design

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- w/c ratio
- a/c ratio
- p/c ratio
- Maximum aggregate size to calculate ε_{air} entrapped air.

3- Curing

- Curing condition (air curing or water curing)
- Curing period
- Curing temperature

4- Prior drying conditioning

- Drying period
- Drying temperature (to estimate the damage of pore structure)

5-Crack condition

- Crack depth
- Crack width
- Crack spacing

6- Environment condition

- CO₂ concentration
- Relative humidity
- Temperature

7- Exposure time

For using this equation, the oxide composition of cement, mix proportion of concrete, curing condition, drying condition and environment conditions are needed.

The calculation procedure will be as follow

- 1 Calculation of cement compounds from Bogue equations (2.1) to (2.5).
- 2 Calculation of initial molar concentration of compound from equations (2.6).
- 3 Calculation of the hydration degree by equation (3.8) for PC and using equation (3.15) for mineral admixtures.
- 4 Using equations (3.21) and (3.22) for calculation of initial molar concentration of carbonatable material.
- 5 Calculation of initial porosity from equation (3.24).
- 6 Calculation of reduction in porosity due to hydration and carbonation from

equations (3.27) to (3.29).

- 7 Porosity of cement paste ε_p from equations (3.30) or (3.31).
- 8 Diffusivity of CO_2 from equation (3.38) for uncracked concrete and equation (3.45) for cracked concrete.
- 9 If the moisture content is uniform and equal to desired saturation degree, the carbonation depth can be calculated by using equation (5.11). If the moisture content is not uniform the carbonation depth cannot be calculated by explicit equation. By using the finite difference method and calculating the saturation degree in different depth from surface by using equation (4.4), the carbonation depth will be calculated. Also for cracked section the carbonation depth cannot be calculated by explicit equation and by using finite difference method and using the equation (3.45) for diffusivity of cracked section, the carbonation depth can be calculated. The schematic of finite difference method presented as follow:

For simplification the carbonation depth generally can be shown as follow

$$x_{C(t)} = e^{(8.6 - \frac{2563}{T})} \sqrt{\frac{2D_{e,CO_2}[CO_2]_0}{S^{\ln(S)}[Ca(OH)_2]_0 + 3[CSH]_0}} t = \sqrt{abD_e t} \quad (5.12)$$

D_e is the diffusivity of cracked or uncracked concrete which can be calculated by equations (3.45) or (3.38) respectively. b represents the coefficients related to moisture content of concrete. It can be calculated by equations (3.60) and (4.4).

$a = e^{(8.6 - \frac{2563}{T})} \sqrt{\frac{2[CO_2]_0}{[Ca(OH)_2]_0 + 3[CSH]_0}}$ represents the constant parameters in equation (5.11).

Then by using the time step equal by Δt , $t_1 = 0$, $x_c = x_1 = 0$ and t_d initial drying time, the carbonation depth can be calculated as follow:

$$t_1 = 0 \rightarrow b_{(x=0, t=t_d+t_1)}, D_{e(0)} \rightarrow x_1 = \sqrt{abD_e t_1} = 0$$

$$t_2 = t_1 + \Delta t \rightarrow b_{(x=x_1, t=t_d+t_2)}, D_{e(x_1)} \rightarrow x_2 = x_1 + \sqrt{abD_e t_2} - \sqrt{abD_e t_1}$$

$$\begin{aligned}
t_3 &= t_2 + \Delta t \rightarrow b_{(x=x_2, t=t_d+t_3)}, D_{e(x_2)} \rightarrow x_3 = x_2 + \sqrt{abD_e t_3} - \sqrt{abD_e t_2} \\
&\cdot \\
&\cdot \\
&\cdot \\
t_n &= t_{n-1} + \Delta t \rightarrow b_{(x=x_{n-1}, t=t_d+t_n)}, D_{e(x_{n-1})} \rightarrow x_n = x_{n-1} + \sqrt{abD_e t_n} - \\
&\sqrt{abD_e t_{n-1}}
\end{aligned}$$

To illustrate these calculations the simple case with assumption of uniform saturation degree and uncracked section for Papadakis experimental work will be reviewed. Table 5-1 shows the composition of the cement compounds in Papadakis work.

Table 5-1 Compounds of Portland cement in Papadakis work

Compound	C_3S	C_2S	C_4AF	C_3A	Gypsum
Percent	38.58	35.2	7.24	11.36	5.1

- Mix proportion of concrete as follow, w/c=0.65, a/c=3, $\varepsilon_{air} = 1\%$.
- Environmental conditions as follow, RH=65%, T=25°C, CO₂=50%.
- Curing period is equal to 90 days and by equation (3.8) the hydration degree can be calculated. The hydration degrees are as follow

Curing time	F_{C_3S}	F_{C_2S}	F_{C_3A}	F_{C_4AF}
90 days	0.96	0.81	0.97	0.86

- By using equation (2.6) initial molar concentration of cement compound can be calculated as follow:

$$[C_3S]_0 = \frac{0.3858 \times 3160(1-0.01)}{228.3 \times 10^{-3}(1+0.65 \times 3.16+3 \times 3.16/2.6)} = 0.789 \times 10^3 \text{ mol/m}^3$$

$$[C_2S]_0 = \frac{0.352 \times 3160(1-0.01)}{172.22 \times 10^{-3}(1+0.65 \times 3.16+3 \times 3.16/2.6)} = 0.954 \times 10^3 \text{ mol/m}^3$$

$$[C_4AF]_0 = \frac{0.0724 \times 3160(1-0.01)}{485.96 \times 10^{-3}(1+0.65 \times 3.16 + 3 \times 3.16/2.6)} = 0.0695 \times 10^3 \text{ mol}/m^3$$

- By using equation (3.24) the initial porosity can be calculated as follow.

$$\varepsilon_0 = \frac{\frac{w\rho_c}{c\rho_w}(1-\varepsilon_{air})}{(1+\frac{w\rho_c}{c\rho_w}+\frac{a\rho_c}{c\rho_a}+\frac{p\rho_c}{c\rho_p})} + \varepsilon_{air} = \frac{0.65 \times 3.16/1(1-0.01)}{(1+0.65 \times 3.16 + 3 \times 3.16/2.6)} + 0.01 = 0.313$$

- By using equation (3.17) and (3.18) initial molar concentration of carbonatable materials can be calculated as follow

$$[Ca(OH)_2] = \frac{3}{2} \times 789 \times 0.96 + \frac{1}{2} \times 954 \times 0.81 - 2 \times 69.5 \times 0.86 = 1403 \text{ mol}/m^3$$

$$[CSH] = \frac{1}{2} \times 789 \times 0.96 + \frac{1}{2} \times 954 \times 0.81 = 765 \text{ mol}/m^3$$

- By using equations (3.27) and (3.29) reduction in porosity due to hydration and carbonation can be calculated as follow

$$\Delta\varepsilon_H(90) = 789 \times 0.96 \times 53.28 \cdot 10^{-6} + 954 \times 0.81 \times 39.35 \cdot 10^{-6} + 196 \times 0.97 \times 112.79 \cdot 10^{-6} + 69.5 \times 0.86 \times 155.86 \cdot 10^{-6} = 0.101$$

$$\Delta\varepsilon_C = [Ca(OH)_2]\Delta\bar{V}_{CH} + [CSH]\Delta\bar{V}_{CSH} = 1403 \times 3.85 \cdot 10^{-6} + 765 \times 15.39 \cdot 10^{-6} = 0.0171$$

- By using equations (3.30) and (3.31) the porosity of concrete and cement paste can be calculated as follow

$$\varepsilon_c(t=90) = \varepsilon_0 - \Delta\varepsilon_H(t) - \Delta\varepsilon_C = 0.313 - 0.101 - 0.0171 = 0.192$$

$$\varepsilon_p(t=90) = \frac{w/\rho_w + \varepsilon_{air} - \Delta\varepsilon_H - \Delta\varepsilon_C}{\frac{c}{\rho_c} + \frac{w}{\rho_w}} = \frac{0.192}{(\frac{467}{3160} + \frac{303.5}{1000})} = 0.425$$

- By using equation (3.35), function of damage as results of overnight 105°C oven drying is equal by $f(d) = 1.18$.
- From equation (3.38) the effective gas diffusivity of CO₂ can be calculated
- Molar concentration of CO₂ is equal to $[CO_2]_0 = \frac{\frac{50}{100}}{0.0224} = 22.32 \frac{\text{mol}}{m^3}$ (the

volume of ideal gas is equal by $22.4 \frac{\text{lit}}{\text{mol}}$)

The calculated depth of carbonation by equation (5.11) in comparison by Papadakis experimental data presented in Figure 5-1.

Figure 5-1 Carbonation depth of concrete

For higher aggregate content higher carbonation depth is expected, Figure 5-2 shows the simulation results by equation (5.11) and experimental data by Papadakis for different aggregate content.

Figure 5-2 Effect of aggregate content on carbonation rate of concrete

For longer curing period, higher carbonatable material content and lower porosity is expected. Therefore lower carbonation depth is expected. Figure 5-3 shows the simulation results for different curing periods.

Figure 5-3 Effect of curing period on carbonation depth

As mentioned before the main problem with Papadakis model is the weakness of this model to predict the carbonation depth for ambient relative humidity lower than 50%.

Figure 5-4 shows the behavior of equations (5.11) and Papadakis model for his experimental data.

Figure 5-4 The comparison of equations (5.11) and Papadakis model on his experimental data

Figure 5-4 shows that the new model can predict the depth of carbonation for low relative humidity with good accuracy.

The crack will increase the available area for penetration of CO_2 in concrete. as it mentioned before, the cracks are usually complicated. For simplified cases of crack which is presented in Table 3-10, the carbonation depth at different time can be calculated.

Figure 5-5 shows the carbonation rate of concrete in the different cracked sections.

Figure 5-5 The effect of crack on carbonation rate of concrete

Figures 5-6 and 5-7 show the experimental results obtained by Papadakis (Papadakis, 1989), (Papadakis, 2000), Masuda (Masuda, 1993), Parrott (Parrott, 1988), Loo (Loo, 1994), Thomas (Thomas, 1992), and others in comparison with the simulation results for PC and blended cement concrete. The range of the various parameters is shown in Table 5-2.

Table 5-2 The range of various parameters used in experimental works.

Parameter	Minimum	Maximum
w/c	0.35	0.7
a/c	3	8.4
Curing period (days)	1	365
Curing temperature (°C)	5	30
Curing relative humidity	65%	95%
CO ₂ concentration	0.03%	50%
Environment temperature (°C)	20	40
Environment RH	35%	80%
Silica fume replacement	0	15%
Fly ash replacement	0	50%
Slag replacement	0	50%
Preconditioning	Various type of preconditioning from drying in natural condition to 105°C and etc.

Figure 5-6 The experimental data versus the simulation results for PC concrete

Figure 5-7 The experimental data versus the simulation results for blended cement concrete

For some samples, the detailed information of the preconditioning process is not reported. In these cases, the average values for function of damage and function of saturation degree are assumed.

Figures 5-6 and 5-7 show that the prediction results are in good agreement with the experimental results for wide range of environmental conditions obtained by many researchers.

The explicit equation for measuring the depth of carbonation in uniform relative humidity was presented above. By considering the variation of moisture content by depth from drying surface and non uniform distribution of moisture at the start of carbonation test, the calculation will be more complicated. Due to this reason, the software has been developed to calculate the carbonation depth of concrete in general condition.

5.2 Software developing

As mentioned above, the calculation of carbonation depth for general condition with finite difference method and small increment of time is very time consuming. Due to this reason the software has been developed to calculate the carbonation depth of concrete in general condition. Different project can be defined and for each project, up to four different conditions can be compared together. Figure 5-8 shows the page to define new project in this software.

The parameters involved, the inputs and the results will be reviewed.

5.2.1 Parameters, input data and results

Chemical composition

As shown in Figure 5-9, various type of PC can be defined and later can be used in the simulation. The chemical composition, mean particle size and density are the input parameters in this page. Later by Bogue equations the cement compounds will be calculated.

Carbonation Software Version 1.2

Project Materials Condition Analysis Results Print Help

Save Ctrl+S
Project Ctrl+N
Close Ctrl+C

Define project

Project No	Project Name
101	Study on effect of curing PC
102	Study on effect of slag type
103	study on effect of saturation
104	Study on aggregate content
105	Study on SF replacement
106	Study on quality of FL
107	Study on slag(low Curing)
108	Study on slag different curing
109	Study on Singapore con
110	Study on software

Number 101

Name of Project Study on effect of curing PC

Created by

Creation date

Close Delete Edit Save New

Nanyang Technological University

Exit

Figure 5-8 Defining a new project

Carbonation Software Version 1.2

Project Materials Condition Analysis Results Print Help

Cement
mineral admixture

Cement Composition

No	Name cement	CaO	SiO2	Al2O3
101	China	65	21	5
102	Singapore cement	63	21	6

Number 101

Name of Cement China

CaO 65 %

SiO2 21 %

Al2O3 5 %

Fe2O3 4.5 %

MgO 1 %

SO3 2 %

Residue 0.5 %

Mean particle size 14.7 um

density 3150 kg/m3

Close Delete Edit Save New

Nanyang Technological University

Exit

Figure 5-9 Input data for chemical composition of cement

Figure 5-10 shows the page for input data of mineral admixtures. The input data are the chemical composition, physical properties and mineral characteristic.

One of the four types of silica fume, slag, high calcium fly ash or low calcium fly ash must be chosen for any of the mineral admixtures. Different type of mineral admixture can be defined and effect of all affecting parameters can be investigated later by this software.

Carbonation Software Version 1.2

Project Materials Condition Analysis Results Print Help

Mineral Admixtures

No	Mineral admixtures	Type	TypeC	CaC
101	low quality HFA	High Calcium Fly Ash	01	
102	w Grase condensed SF	Silica Fume	04	
103	SlagEngro	Slag	03	
104	SF	Silica Fume	04	
105	high quality LFA	Low Calcium Fly Ash	02	
106	low quality LFA	Low Calcium Fly Ash	02	

Number: 101

Mineral Admixtures: low quality HFA

Type: High Calcium 1

CaO: 11 %

SiO₂: 44 %

Al₂O₃: 7 %

Fe₂O₃: 5 %

MgO: 6 %

Glass phase: 0.75 (0-1)

Mean particle size: 12 um

density: 2200 kg/m³

Buttons: Close, Delete, Edit, Save, New

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Exit

Figure 5-10 Input data for mineral admixtures characteristic

The next step is to identify the mix proportions. Figure 5-11 shows the related page for input data of mix proportions. The mix proportions can be entered as percentage or the exact quantities.

The Figure 5-12 shows the page related to input data of conditions. The curing condition (RH, temperature and curing period), oven drying condition, natural drying condition and simple types of cracks are also defined.

Carbonation Software Version 1.2

Project Materials Condition Analysis Results Print Help

Mix proportion
Define condition

Mix proportion

No	Name	Max agg	W/(c+p)	P/(c+p)
101	PC	20	0.5	0
102	C2	12	0.4	0
103	50% mineral	20	0.5	0.5
104	10% mineral	20	0.5	0.1
105	w/c=0.65,a/c=3	20	0.65	0
106	w/c=0.65,a/c=5	20	0.65	0
107	w/c=0.65,a/c=8	20	0.65	0
108	w/c=0.65,a/c=4	20	0.65	0
109	30% mineral	20	0.5	0.3
110	5% mineral	20	0.5	0.05

Number

Name of mix pro.

Max. aggregate size mm

by percentage

w/(c+p)

e=p/(c+p)

a/(c+p)

by weight

Cement kg/m3

pozzolanic kg/m3

water kg/m3

Aggregate kg/m3

Aggregate density kg/m3

Close Delete Edit Save New

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Exit

Figure 5-11 Input data for mix proportions

Carbonation Software Version 1.2

Project Materials Condition Analysis Results Print Help

Mix proportion
Define condition

Define Condition

No	Name of condition	ing
101	papadakis	
102	ac-short drying	
103	1 curing	
104	90 curing	
105	uniform-with drying	
106	uniform-without dryi	
107	not uni-co2=0	
108	n uni-co2=300	
109	1 day	
110	10 days	

Number

Name of condition

Curing Details

Curing RH %

Curing Temperature

Curing period

☐ Oven Drying

Temperature

Period

natural expouser condition

Drying period days

Drying condition

RH %

CO2 Con. in drying period %

Crack details (1m-1m section)

width

hieght

crack spacing

crack length

☐ Assume the uniform Saturation degree and equal to Sf

Close Delete Edit Save New

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Exit

Figure 5-12 Input data for curing, drying and cracking conditions

In each time of analysis up to four different cases can be analysis and compared together. Then the next step is to choose different cases under different project. Figure 5-13 shows the page related to defining different cases.

Finally as shown in Figure 5-14 in the analysis page, the CO₂ concentration, carbonation period and the time step will be chosen. This can be accelerated or natural carbonation, with or without preconditioning. Smaller time step results in higher accuracy but longer calculation time.

Carbonation Software Version 1.2

Project Materials Condition **Analysis** Results Print Help

Define Case Analysis

Define Case

Project No	Project Name
102	Study on effect of slag type
103	study on effect of saturation
104	Study on aggregate content

Case No	Case name	Cement name
113	a/3=3	China
114	a/c=5	China
115	a/c=8	China
116	a/c=4	China

Number: 113

Case Name: a/3=3

Cement: China

Mineral admixture:

Mix proportion: w/c=0.65, a/c=3

condition: 1 year

Close Delete Save New

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Exit

Figure 5-13 Input data for defining the different cases

Carbonation Software Version 1.2

Project Materials Condition Analysis Results Print Help

Analysis condition

Case No	Case name	Cement name	anic
113	a/3=3	China	
114	a/c=4	China	
115	a/c=5	China	
116	a/c=8	China	

Project: Study on aggregate cc

CO₂ Concentration: 50 %

Carbonation Period: 20 days

Time step: 300 second

Run Analysis

Carbonation...

Analysis is complete

OK

Close

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Exit

Figure 5-14 Input data carbonation condition and analysis time step

The results are divided in five different pages. The summary of calculations and final carbonation depth is presented in Figure 5-15. The Ca(OH)_2 , CSH and total carbonatable materials are obtained for different cases. Figure 5-16 shows the Ca(OH)_2 content for different cases as example of these pages. Figure 5-17 shows the carbonation depth of concrete for the different cases.

These following figures show the effect of aggregate content on the carbonation depth of Portland cement concrete. For these cases the curing period is 90 days and the w/c ratio is equal by 0.5. All the samples are assumed to have one year of natural drying with CO₂ concentration of 0.03% and then 20 days of accelerated carbonation with 50% CO₂. The time step is assumed to be equal to 300 seconds. It is less than 0.0002 times of carbonation period.

Figure 5-15 The summary of calculation results

Figure 5-16 The Ca(OH)₂ content in different aggregate content

Figure 5-17 The carbonation depth of concrete with different a/c ratio

5.2.2 Example of using the software

Now by having this software, the carbonation depth for natural condition can be calculated. Some of the complicated conditions like the effect of mineral admixtures on carbonation depth of concrete and the effect of moisture content on carbonation depth of concrete also can be investigated.

As mentioned before there is big difference between the accelerated carbonation results of Roy (1999), Uomoto (1993), Loo (1994) and Papadakis (1989) has been recorded. The main reason for this difference is the different moisture content of concrete before starting the carbonation test.

Four different cases will be defined as follow. In the first case the carbonation starts after curing immediately like the case of Roy's experimental work. The second case is defined as 50 days natural drying with 0.03 % CO₂ concentration like the case of Loo. Loo kept his sample in indoor condition between 13 to 71 days prior to accelerated carbonation test. For the third case, sample was kept in indoor condition

with 0.03 percent CO_2 concentration for one year before starting the carbonation test. Papadakis oven dried his samples in 105°C over night and after that he kept them for few days to reach the uniform saturation degree. Case four is defined as case with 12 hours 105°C and uniform saturation degree. Figure 5-18 shows the carbonation depth for these cases. Case three has higher initial carbonation depth because of one year natural carbonation before starting the accelerated test.

Figure 5-18 The carbonation depth of concrete with different preconditioning

Figure 5-18 shows why different carbonation depth in different accelerated carbonation test is recorded. For these cases the relative humidity is 65%, which is the favorable condition for all above researchers. In this relative humidity, the preconditioning used by Papadakis shows to have nearest prediction compared to sample with one year of natural drying.

By replacing the mineral admixtures, the total carbonatable materials will decrease. The main benefit of mineral admixtures is to reduce the pore size and pore

connection of concrete. With the damage caused by oven drying this only benefit will be ignored and higher carbonation depth will be recorded. But based on quality of mineral admixture, the percentage of replacement and the curing period, carbonation depth can be same or even lower than the carbonation depth of Portland cement concrete.

Figure 5-19 shows the reduction in total carbonatable materials by replacing the 10%, 30% and 50% of PC with high quality GBFS (glass phase content=100% and $d_n=9\text{ }\mu\text{m}$).

Figure 5-19 The total carbonatable materials with different percentage of GBFS replacement

The Figure 5-20 shows the carbonation depth for the above cases. All the cases have one year of natural drying with 0.03 percent CO_2 and 20 days of accelerated carbonation depth with 50% CO_2 concentration.

Figure 5-20 The carbonation depth of concrete by different percentage of GBFS replacement with 90 days curing

Figure 5-20 shows replacing 10% and 30% of PC with this GBFS results in lower carbonation depth if the samples dried in natural condition. But for the sample with 50% GBFS replacement the carbonation depth was higher. By considering the improvement in quality of concrete against alkali silica reaction, chloride penetration and other durability issues, using the optimum percentage of mineral admixtures can be very economical, ecological and important. The quality of mineral admixture and the curing period is also very important parameter on carbonation rate of concrete.

Replacing 15% of PC with normal silica fume after 14 days curing resulted in lower carbonation depth in natural condition. But replacing of the same amount of condensed silica fume results in higher carbonation depth. Figure 5-21 represent this case.

In the above case for GBFS the samples had 90 days of curing. In reality the curing period is limited to a few days. Figure 5-21 shows the carbonation depth for the same cases but with three days of curing.

Figure 5-21 The carbonation depth of concrete by 15% normal and condensed silica fume replacement with 14 days curing

Figure 5-22 The carbonation depth of concrete by different percentage of GBFS replacement with 3 days curing

Chapter 5 Simulation of concrete carbonation

As shown in Figure 5-22, the curing period can also plays very significant role on the carbonation rate of blended cement concrete. In this particular case for 10% GBFS, 8 days and for 30% GBFS 14 days curing can result in same carbonation depth in comparison to PC with same curing ages.

As mentioned in chapter four, in Singapore indoor condition the average relative humidity is around 73% and the temperature is around 27°C. By increasing the level of CO₂ gases in the last 15 years, the average value of 0.05% CO₂ for outdoor condition and 0.07% for public indoor condition over the next 100 years is expected. The minimum cover of the uncracked concrete with various w/c and a/c ratios for the indoor condition as described above will be calculated. The calculation results for three different curing periods with CO₂=0.07% are shown in Table 5-3. The natural sand and the coarse aggregate with maximum size of 20 mm are used in the calculations.

Table 5-3 Minimum concrete cover for different mix proportions in Singapore condition for 100 year life span

Case No:	Mix Proportion			Estimated Slump (mm)	1 day curing	3 day curing	7 day curing
	w/c	a/c	Cement (kg/m^3)		Minimum concrete cover (mm) for 100 years life span		
1	0.4	3	530	30-40	49	35	29
2	0.5	3	500	90-110	54	40	33
3	0.5	4	420	60-70	59	44	37
4	0.5	5	360	30-40	64	48	41
5	0.6	3	475	140	57	43	37
6	0.6	4	400	90-110	62	47	41
7	0.6	5	350	60-70	67	51	44

In the above cases the concrete assumed to be uncracked but for the short curing period and the thick concrete cover, the crack is unavoidable and the carbonation depth can increase 10-15 % due to the non structural cracks.

Chapter 5 Simulation of concrete carbonation

In underpasses and building parking lots the condition is more critical. Table 5-4 shows the comparison of the carbonation rate in indoor condition and parking lots.

Table 5-4 comparison of the carbonation rate in public indoor and parking lots and underpasses

	Public indoor	Parking lots and underpasses
CO ₂ concentration	0.035-0.1%	0.07 to 1 %
Average T (in Singapore)	27°C	28.5°C
Average RH (in Singapore)	73%	69%
CO ₂ concentration in cal.	0.07%	0.2%
Carbonation depth for w/c=0.5, a/c=3, 3 days curing and after 10 years of natural carbonation	12.7 mm	22.4 mm

In underpasses and parking lots the CO₂ concentration is higher and normally the temperature is higher and the relative humidity is lower (in Singapore condition it is nearer to critical value of RH). Then based on these three parameters faster rate of carbonation in parking lots and underpasses compare to indoor areas are expected.

The above calculation shows that the concrete carbonation can be very important problem in the long term exposure in Singapore condition. Carbonation can affect the durability of concrete significantly.

In short curing condition, replacing the mineral admixtures will increase the carbonation depth of concrete. Then using this material should be done with accurate calculations to result in better quality in the long period of exposure.

CHAPTER

6

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORKS

6.1 Conclusions

In this study a new numerical model and software for carbonation of concrete made of Portland cement or blended cement is proposed. The carbonation mechanism is very complex and many parameters are involved. The parameters considered in this model are the chemical, physical and mineral characteristic of PC and mineral admixtures, mix proportion (w/c, a/c, maximum aggregate size), curing condition (curing period, relative humidity and temperature), the exposure conditions (temperature, relative humidity and CO₂ concentration), the preconditioning (pore structure damage, saturation degree), the reduction of reaction rate due to lack of moisture in low relative humidity and the presence of crack in concrete.

In this study it was found that the main reason for variation of results of accelerated carbonation test is mainly because of saturation degree and damage caused by preconditioning. In this work a simulation model to measure the saturation degree of concrete in different time and depth has been proposed. By using this simulation, the carbonation model is able to predict the depth of carbonation in accelerated and natural condition more accurately.

In relative humidity less than 50%, the carbonation depth is lower. It was found that by considering the effect of low rate of reaction in low relative humidity this issue will be solved.

Chapter 6 Conclusions and recommendations for future works

It also was found that the effect of mineral admixtures on pore structure of concrete and carbonation depth is affected by quality of mineral admixture, particle size distribution and glass phase content and the curing period of concrete. New equation for degree of pozzolanic activity was proposed and used in this model to improve the ability of the model to predict the effect of mineral admixture on carbonation of concrete. New equation for diffusivity of CO_2 in blended cement concrete was proposed. This equation will help to predict the carbonation depth of blended cement concrete with various characteristic in wide range of environmental conditions.

The prediction ability of this proposed model is much better compared to the existing models and this model can predict the carbonation of concrete under the wide range of the conditions.

6.2 Recommendations for future works

The equation related to effective gas diffusivity of concrete is based on equation proposed by Papadakis. In his experimental work, Papadakis used the 105°C oven drying as precondition which can damage the pore structure and decrease the saturation degree of concrete. However the effect of saturation degree and the damage due to preconditioning are considered in new equation, but it still needs to be verified by experimental results.

The effect of percentage and quality of mineral admixture on carbonation depth of concrete by considering the saturation degree of concrete is needed to be verified by experimental works. It will help to check the accuracy of the carbonation model for blended cement concrete.

This existing model can predict the effect of crack on carbonation rate of concrete by assuming all the cracks has the same length, width and depth. This model needs to be improved for more complex situation where the crack depth and length is varied among the concrete section. Finally the numerical model needs to be verified by experimental data.

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APPENDIX: AUTHOR'S LIST OF PUBLICATIONS AND AWARDS

Sabet Bahador, H. C. Jong, "Effect of preconditioning of concrete under accelerated test", proceeding of 31st Our World in Concrete and Structures, August 2006, Singapore, pp 127-134.

Sabet Bahador, H. C. Jong, "The effect of environment conditions on concrete carbonation (numerical model)", The proceeding of the 5th conference on New Technologies for Urban Safety of Mega Cities in Asia, 16-17 November 2006, Phuket, Thailand, pp 405-414.

Sabet Bahador, H. C. Jong, "Study on moisture transport and pore structure of PC and blended cement concrete by monitoring the weight loss during the drying process", accepted, 32st Our World in Concrete and Structures.

Sabet Bahador, H. C. Jong, "Study on properties of the concrete contained Ground Granulated Blast furnace Slag", accepted, The First International Conference on Recent Advances in Concrete Technology, Washington D.C., USA.

Sabet Bahador, H. C. Jong, "The numerical model for hydration and carbonation of PC and blended cement concrete under the wide range of environmental conditions", to be submitted.

Sabet Bahador, H. C. Jong, "Study on the saturation degree and pore structure of PC and blended cement concrete in different environmental conditions", to be submitted.

M.C BAUCHEMIE Award 2006, 31st conference on Our World in Concrete and Structures 16-17 August, 2006 for the paper "Effect of preconditioning of concrete under accelerated test".