

Chapter 2

Literature Reviews

2.1 General

This chapter presents literature reviews relevant to carbonation of concrete with fly ash. The rate of carbonation depends on properties of binders, mix proportion, curing period of concrete, ambient relative humidity and carbon dioxide concentration and moisture concentration in concrete. The size of the specimen is also a factor since the moisture released by the reaction of carbon dioxide with calcium hydroxide must diffuse out in order to preserve hygral equilibrium between inside of the specimen and the atmosphere. If the diffusion is too slow, the vapor pressure within the concrete rises to saturation and the diffusion of carbon dioxide into the paste is practically stop (Mays 1992). In deed, carbonation is affected by moisture condition in concrete in two ways. Dry calcium hydroxide reacts very slowly with carbon dioxide. The reaction is much faster and more complete when a surface film of water, saturated with the solid, is present on the grains of hydroxide. Very dry concrete therefore carbonates at a slower rate than semi-dry concrete does. On the other hand, if the pores of the paste are completely filled with water, the carbon dioxide gas must diffuse by dissolving in water, in which the diffusion rate is considerably much less than that through air (Neville 1995).

2.2 Parameters Influencing Carbonation of Concrete

2.2.1 Water to binder ratio

It is obvious that one of the most significant parameters influencing carbonation of concrete is water to binder ratio. This is because the higher water to binder ratio induces the higher porosity in pore system of paste matrix and thus the higher diffusivity of carbon dioxide. Uomoto and Takada (1993) and Sulapha et al. (2003) concluded that water to cement ratio of concrete affected degree of carbonation in concrete. Carbonation rate increased with an increase in water to cement ratio. Roy et al. (1999) found that the lower grade of concrete (higher water to cement ratio and lower cube strength) showed larger carbonation depths than the higher grade concrete.

2.2.2 Use of pozzolanic materials

Ho and Lewis (1987), Uomoto and Takada (1993), and Sulapha et al. (2002) found that the influence of using fly ash as a replacement material in concrete increased the rate of carbonation due to increasing of porosity in concrete. Hobbs (1988) investigated the influence of 35% replacement of two fly ashes on carbonation rate, depth of carbonation, and strength development of concrete. He concluded that the depth of carbonation in concrete at similar water to binder ratio or similar binder content was higher in fly ash concretes than in normal cement concretes. Papadakis et al. (1992) proposed that carbonation depth at a given time and ambient relative humidity is approximately proportional to the paste porosity and inversely proportional to the square root of the total concentration of CaO in concrete. Both of these effects contributed to the increased

carbonation depth in pozzolanic cement concrete, in comparison to that in Portland cement concrete with the same water to binder ratio.

In contrast to the adverse effect that pozzolan replacement has on carbonation depth and porosity, Papadakis (2000) reported that the partial replacement by the pozzolan of aggregate rather than of cement had a favorable effect. In addition, when compared to the low-CaO fly ash at the same replacement level, specimens incorporating high-CaO fly ash showed better carbonation resistance. Atis (2002) reported that fly ash concrete made with 50% replacement, which had a much lower water to binder ratio than the cement-only concrete, could show a lower or comparable carbonation depth when compared with the cement-only concrete. Malholtra et al. (2000) reported that after 10 years of exposure, the depth of carbonation in concrete with low water to binder ratio (0.27-0.29) and replaced by 57% of fly ash in total binder, was negligible.

2.2.3 Type of cement

Meyer (1968) found that concrete made from sulphate-resisting cement or Portland blast furnace cement had higher depth of carbonation than those made from ordinary Portland cement type I. Horiguchi et al. (1993) conducted tests on concrete made with binary and ternary blended cement consisted of three types of Portland cement (normal Portland cement, moderate heat Portland cement, belite-type low heat Portland cement) with blast-furnace slag and fly ash. It was found that the change in rate of carbonation depended on the blending ratio of Portland cement or cement content. The rate of carbonation decreased when the blending ratio of Portland cement decreased. Kobayashi and Uno (1989) conducted accelerated carbonation tests on mortar specimens made using a range of cement types. It was found that the rate of carbonation increased with greater alkali contents in the cement. This trend was also confirmed through the accelerated carbonation tests and exposure tests in the atmosphere using concrete specimens conducted also by Kobayashi and Uno (1990).

2.2.4 Paste content

Loo et al. (1994) and Russell et al. (2001) reported that by comparing mixtures with the same water to binder ratio, the effect of paste content on carbonation depth was insignificant. The content of paste or the aggregate slightly affected the carbonation depth of concrete, although CO₂ must diffuse through the interconnected pores within the paste matrix. Carbonation resistance of mixtures was more significantly affected by the quality of paste than by the amount of paste.

2.2.5 Type and content of aggregates

Papadakis (1991) stated that carbonation depth slightly increased with increasing aggregate to cement ratio because the larger ratio led to the lower CH in the concrete mix. He also found that for the same aggregate to cement ratio, the different in sand to aggregate ratio had no effect on carbonation. In addition, Richardson (1988) reported that the lightweight coarse aggregate could provide a short circuit through which the carbonation front advanced rapidly. However, the problem did not arise if the cement paste was dense.

2.2.6 Curing period

Fattuni (1988) and Parrott (1996) found that rate of concrete carbonation depended on water-curing period. Carbonation decreased when the water-curing period was increased. Ho and Lewis (1987) and Wee et al. (1999) added that this tendency was significant for concrete cured within seven days. They found that concrete remained practically unaffected upon curing period when the period was extended beyond seven days. Balayssac et al. (1992) also added that increasing of curing period to three days was sufficient for concretes with cement content higher than 380 kg/m^3 . Concrete with low cement content (or high water to cement ratio) had to be cured longer than those having higher cement content. The choice of curing time depended on cement content and must be adjusted to concrete design.

2.2.7 Pore structure

Horiguchi et al. (1993), Malami et al. (1994), and Sulapha et al. (2002) demonstrated a significant relation between carbonation depth and porosity of concrete, in which carbonation rate increased when the total pore volume increased. Roy et al. (1999) also added that concrete that had larger pores had higher carbonation rate than concrete that had smaller pores.

2.2.8 Compressive strength

Loo et al. (1994), Chi et al. (2002), and Atis (2003) found that there was a strong relationship between carbonation depth and compressive strength of concrete, in which the depth of carbonation decreased with an increase in compressive strength. This finding appears to be logical since both carbonation and compressive strength are significantly controlled by the pore structure of concrete. However, there is controversy over the effect of compressive strength on fly ash concrete, i.e. Wesche (1991) concluded that concretes of equal strength with and without fly ash had similar carbonation resistance levels, but Ho and Lewis (1987) stated that if the comparison of mixes was based equal 28-day compressive strength and common binder content or water to binder ratio, then fly ash concrete was found to have lower resistance to carbonation.

2.2.9 Ambient temperature

In general, it is found in a normal chemical reaction that elevated temperature can accelerate the reaction. Papadakis (1991) reported that for a constant relative humidity, the increase in carbonation due to increasing environmental temperature (from 22 to 42 °C) was small because the rate of the carbonation process was mainly governed by diffusion of carbon dioxide, which was very weakly sensitive to temperature. This report is also in agreement with the observation of Loo et al. (1994).

2.2.10 Relative Humidity

Higgins (2000) found that carbonation and corrosion rates were affected in many different ways by humidity. The rate of carbonation was fastest in dry environment and was negligible under wet condition. Cahyadi and Uomoto (1993) showed that from 50 to 100% RH, the increase of environmental relative humidity decreased carbonation of concrete. However, it had to be noticed that from 50 to 30% RH, the decrease of

environmental relative humidity might not decrease carbonation of concrete especially in normal concentration of carbon dioxide. Roy et al. (1999) indicated that the effects of relative humidity on carbonation were complex with maxima in carbonation depths being measured at both 75 and 92% RH. This was possibly due to difference in mechanisms of carbonation in the accelerated tests. Russell et al. (2001) reported that maximum carbonation occurred at 55% RH and when RH increased from 55 to 75%, a decrease in carbonation depth was observed.

2.2.11 Carbon Dioxide Concentration

It is obvious that increasing of carbon dioxide concentration causes the increasing of carbonation rate penetrating into concrete because carbon dioxide diffuses from surrounding environment that has higher concentration into concrete that has lower concentration. However, this would appear to apply up to a certain critical carbon dioxide level. Richardson (1988) stated that accelerated curing through high level of carbon dioxide produced different effects than normal curing. This would be due to the formation of calcium bicarbonate as opposed to calcium carbonate. The implication of this is that accelerated test using very high carbon dioxide concentrations may not be a valid method of modeling long term environment behavior. Loo et al. (1994) found that the effect of concentration of carbon dioxide was greater on specimens with lower 28-day compressive strength. The carbon dioxide ranging from 7 to 18% did not affect the rate of carbonation of concrete specimens significantly when the compressive strength is greater than 40 MPa.

2.2.12 Cracks

Richardson (1988) discussed that the behavior of carbon dioxide in a crack was different to the behavior of carbon dioxide in contact with a concrete surface exposed to the atmosphere. Both situations involved interfacial contact of carbon dioxide and concrete, in which reaction was sustained by a constant source of carbon dioxide under certain conditions. However, the effective diffusion coefficient of carbon dioxide in the crack differed from that in air and this coefficient might not be constant. Whereas the supply of carbon dioxide to the surface concrete in contact with the atmosphere was effectively limitless, the volume of carbon dioxide in a crack was constrained by the crack width and the rate at which carbon dioxide penetrated the crack from atmosphere. Also the carbon dioxide in the crack must attack two concrete surfaces and so the intensity of the attack was further reduced.

2.3 Moisture Distribution in Concrete

Carbonation is largely affected by moisture distribution in concrete. If the pores of the paste are completely filled with water, the carbon dioxide gas must diffuse through water, in which the diffusion rate is considerably much less than that through air. The diffusion of carbon dioxide is practically stopped and the carbonation rate is considerably low. During drying, water migrates from concrete by the diffusion of the water vapor through the interconnected capillary concrete pores. However, for a very dry concrete, dry calcium hydroxide reacts very slowly with carbon dioxide. Thus the carbonation rate is also low. Some of the literatures involving moisture movement in concrete are presented as follows.

Powers, T.C. (1958) stated that permeability of concrete depended on the size, distribution, and continuity of the pores. In addition, water flowed more easily through the capillary pores than through the much smaller gel pores. Therefore, the permeability of cement paste was controlled by its capillary porosity.

Tangtermsirikul et al. (1992) proposed a model for water movement due to drying with considering effect of structural change due to carbonation. The model was based on Fick's law of diffusion by the assumption that when concrete subjected to drying, water in the concrete was considered to move through the pore structure according to the gradient of vapor pressure regarded to vary with relative humidity in pore of concrete. It was concluded that for saturated concrete, amount of evaporable water was smaller in the carbonation portion than in noncarbonated portion due to the reduction of pore volume in the carbonated area.

Kim and Lee (1999) measured the internal relative humidity in drying concrete specimens at early ages. The variation of relative humidity due to self-desiccation in sealed specimens was also measured. It was found that moisture distribution in low-strength concrete with high water to cement ratio was mostly influenced by moisture diffusion due to drying rather than self-desiccation. In contrast, for high-strength concrete with low water to cement ratio, self-desiccation had a considerable influence on moisture distribution.

Rico (2000) proposed the study of moisture transport properties. Due to the difficulties in measuring the relative humidity within concrete, global measurements of weight loss were made. A three-dimensional finite element formulation in terms of the relative humidity in the pores was employed in order to solve the governing nonlinear diffusion equation, which was described along with the physical mechanisms involving the moisture diffusion. The weight losses of the specimens were calculated using the desorption isotherm that related the humidity in the pores to the water content. The evolution of the weight loss of the mortar specimens was compared to test data and the parameters that led to an acceptable global fit were determined in his study.

Ayano et al. (2000) developed a new method to determine hygral diffusion and film coefficient. The distribution of relative humidity in pore system of concrete at any arbitrary time during drying was determined by experimental approach. The hygral diffusion coefficient could be expressed both as a function of moisture content and as a function of relative humidity.

Wong et al. (2001) investigated water movement in cement-only concrete. The water diffusion and sorptivity tests, together with the accelerated water permeability test were performed. The effects of pore humidity, ambient temperature, environmental relative humidity, applied hydrostatic pressure gradient, and water to cement ratio were also explored. The study of water movement had practical implications on the prediction of transport and distribution of aggressive chemical agents in concrete, as well as on the development of rational and quantitatively assessment for concrete structures exposed to different climatic and environmental conditions.

2.4 Modeling and Prediction of Carbonation in Concrete

Carbonation is one of several ageing phenomena which affect the properties of concrete. Several theories exist, attempting to describe the relationship between carbonation depth and concrete age. Many field and laboratory observations have also been recorded. It is clear that the relationship is non-linear. A frequently used relationship is that the ingress of carbonated layer proceeds proportionally with the square root of time (Richardson 1988). This relationship facilitates the prediction of carbonation of concrete under a particular set of conditions and can be applied for both outdoor and controlled accelerated conditions. This relationship has been widely used by numerous researchers (Wee et al. 1999, Castrol et al. 2000, Russell et al. 2001). The equation that relates the depth of carbonation front (D) with time (t) is given as follow.

$$D = A \cdot \sqrt{t} \quad (2.1)$$

where A is a measure of concrete quality and is greater for poor concrete. Under a specific condition, A is usually formulated to have relationship with the compressive strength of concrete. The effect of different curing regimes can be accounted for by the use of compressive strength at the beginning of the carbonation test instead of the standard 28-day compressive strength of concrete (Loo et al 1994, Sulapha et al. 2002, Atis 2003).

Furthermore, many attempts have tried to formulate semi-microscopic models for simulating the carbonation in concrete. The mechanisms and processes of carbonation were discussed in those models. Those models can be applied for various cases of environments and mix proportions of concrete. Some of those literatures are presented as follows.

Papadakis et al. (1991a, 1991b) presented a mathematical model based on the physicochemical processes in concrete carbonation. These processes included the diffusion of carbon dioxide in the gas phase of concrete pores, its dissolution in the aqueous film of these pores, the diffusion of dissolved $\text{Ca}(\text{OH})_2$ in pore water, its ultimate reaction with the dissolved carbon dioxide, and the reaction of carbon dioxide with C-S-H and with the yet unhydrated C_3S and C_2S . In addition, the parallel processes of production of materials susceptible to carbonation during the hydration of cement and of reduction of concrete porosity during hydration and carbonation were included in the model.

Seiki et al. (1991) performed an accelerated carbonation test to explain mechanisms of carbonation in concrete. The depth of carbonation correlated to the amount of evaporated water. The amount of calcium hydroxide and calcium carbonate, pore volume, and pore size distribution depended on exposure duration in the accelerated chamber. The depth of carbonation decreased due to the diffusion of calcium hydroxide from non-carbonated portion to carbonated portion under wetting condition. Based on these test results, the diffusion equations for water, carbon dioxide, calcium hydroxide were proposed and finite difference method was used for numerical analysis. The depth of carbonation of concrete could be predicted by analyzing those diffusion equations.

Saetta et al. (1993) described the governing equations of moisture, heat, and carbon dioxide flows through concrete within the framework of a distributed parameter model. The coupling terms and the non-linearity of the problem were taken into account and a numerical procedure based on the finite element method was developed to solve the set of equations.

Sarja and Vesikari (1996) introduced a stochastic equation for determining depth of carbonation by relating carbonation to square root of time, in which the slope or carbonation rate factor depended on the compressive strength, binder agents, cement content, and environmental conditions (humidity and temperature). Loo et al (1994) proposed a similar model. However, the rate of carbonation was formulated to have relationship with the standard compressive strength, carbon dioxide concentration, environmental temperature, and curing period.

Jiang et al. (2000) investigated the carbonation process and the factors affecting concrete carbonation. A mathematical model based on carbonation process for predicting the carbonation depth of high-volume fly ash (HVFA) concrete was developed. An accelerated carbonation test was conducted on ordinary Portland cement concrete and HVFA concrete. The depths of carbonation predicted from the model were compared with the test results. It was shown that the effective water to binder ratio and the cement content were the key factors affecting HVFA concrete carbonation. The increase of curing period could improve the carbonation behavior of HVFA concrete. The carbonation behavior of HVFA concrete with appropriate mix proportion could meet the requirements of structural concrete. The agreement between test results and the prediction from the model was proved to be satisfactory for predicting the evolution of carbonation depth with time.

Steffens et al (2002) developed a theoretical model to predict carbonation of concrete structures. The model described movement and retention of heat, moisture, and carbon dioxide by means of balance equations and diffusion law. The balance equations were coupled and took into account the interaction between different transport and storing processes. A new mathematical formulation of the function of moisture in balance faithfully represented the moisture-storing properties of porous media. The evolutionary equation of the reaction of carbon dioxide was derived from reaction kinetics that were described by Arrhenius's function. The model was solved by means of a numerical method using a finite element concept and numerical time integration technique.