CORROSION SCIENCE AND TECHNOLOGY, Vol.4, No.2(2005), pp.69~74

Experimental Study on CO_2 Diffusivity in Cementitious Materials

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The carbonation of concrete is one of the major factors that cause durability problems in concrete structures. The rate of carbonation depends largely upon the diffusivity of carbon dioxide in concrete. The purpose of this study is to identify the diffusion coefficients of carbon dioxide for various concrete mixtures. To this end, several series of tests have been planned and conducted. The test results indicate that the diffusion coefficient increases with the increase of water-cement ratio. The diffusion coefficient decreases with the increase of relative humidity at the same water-cement ratio. The diffusion of carbon dioxide reached the steady state within about five hours after exposure. The content of aggregates also influences the diffusivity of carbon dioxide in concrete. It was found that the diffusion coefficient of cement paste is larger then that of concrete or mortar. The quantitative values of diffusivity of carbon dioxide in this study will allow more realistic assessment of carbonation depth in concrete structures.

***Keywords** : carbonation, gas diffusivity measurement system, diffusion coefficient, relative humidity*

1. Introduction

During the service life the deterioration of concrete structures occurs with various physical and chemical factors including acid or salt attack, alkali-aggregate reaction and freezing-thawing reaction. Especially, steel corrosion is the most important degradation process in reinforced concrete structures.

When corrosion occurs in reinforced concrete, the strength of concrete structure falls due to reducing the effective cross sectional area of reinforced steel. And for the severe case the concrete cover spalls by expansion of steel. From the viewpoint of corrosion, chloride penetration is the main mechanism of corrosion in marine environment or when deicing salts contact with the concrete surface. In other cases, carbonation of concrete is the main mechanism leading to reinforced steel corrosion. From the corrosion model of Tuutti, steel corrosion occurs during propagation period after the initiation period in concrete.[1] Here, the initiation period means that the chloride ions diffuse to the steel in concrete or the carbonation process reaches to it.

Generally the concrete carbonation is known that the reaction of between environmental carbon dioxide and carbonatable constituents of hardened cement paste forces the low pH in concrete.[2),3)] On the other hand, the shrinking core model has been used in the chemical engineering when the rate of movement of boundary is slow relative to transport rates of the material.[4)] Since the carbonation process of concrete is also that the change rate of carbonation front is slower than the diffusion rate of CO_2, this model is effective to explain the carbonation process. In this case, because the boundary moves slowly, the process of mass transport is always considered as steady state, this assumption is often known as continuing of standstill.

From the shrinking core model it is known that the carbonation depth with time is affected by CO_2 diffusivity, CO_2 concentration and amounts of carbonatable materials besides time. Especially, because the amounts of carbonatable materials can be predicted from mix design and the CO_2 concentration is usually constant, it is clear that the reasonable consideration of CO_2 diffusivity is one of the most important factors to predict the carbonation depth of concrete structure. Therefore, Papadakis et al. have attempt to predict the CO_2 diffusivity from the measure of N_2 diffusivity and Houst et al.[5)] develop the measuring system of gas diffusivity under unsteady state conditions.[6)] But, since the test results of CO_2 diffusivity through concrete is insufficient yet, in this study the test method is proposed to measure the CO_2 diffusivity through concrete under steady state and through the CO_2 diffusivity tests the factors affecting the diffusion are discussed.

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2. Experimental

2.1 Measurement scheme for CO_2 diffusion coefficient

The testing method of Schwiete and Ludwig using the test gases oxygen and nitrogen is well suited to obtaining the diffusion coefficient of oxygen for concrete specimens of cylindrical shape.[7] In this study the measurement system is designed for measuring gas diffusion coefficient when the gas diffusion through concrete specimen reaches the steady state, and the measurement can be estimated according as carbon dioxide concentration in the nitrogen is measured with time by the analyzer based on principle of light-absorption. Also since the carbon dioxide diffusion rate affecting carbonation process depends on relative humidity, the measuring equipment is designed to measure gaseous diffusion coefficient by controlling relative humidity of inflow gas, and it can control the size of specimens from 5 mm to 5 cm. Fig. 1 and Fig. 2 presents the gas diffusivity measurement system and the diffusion cell, respectively.

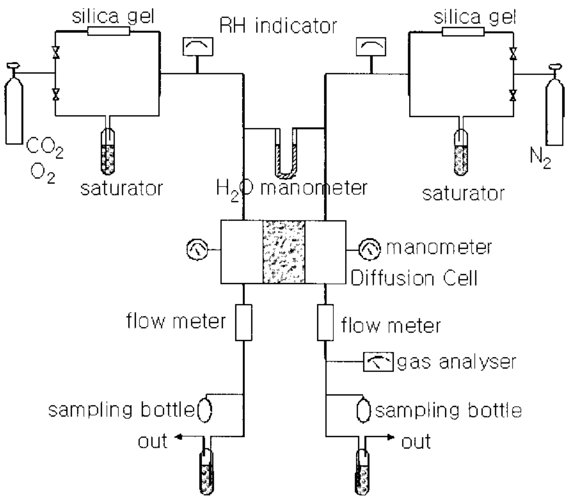


Fig. 1. Gas diffusion measurement system

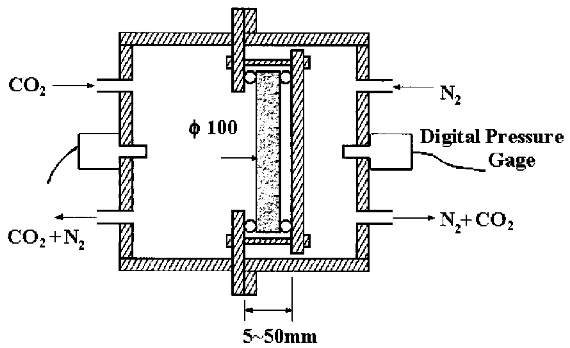


Fig. 2. Gas diffusion cell

On the other hand, it is important to maintain the equivalent pressure and flow rate both sides in Fig. 1 for assurance of mass transport caused by partial pressure. So the pressure and the flow rate of both sides maintain 0.2 kgf/cm^2 and 200 cc/min, respectively.

The test procedures are as follows.

a. The equipment should be equipped in the indoors preserving temperature constant.
b. The thickness and measurement area (or the diameter of measurement) is measured by calipers and so on.
c. It is inputted the nitrogen gas into the one side of the specimen and the CO_2 gas in the same pressure into the other side of specimen constantly.
d. When the concentration of CO_2 in the nitrogen gas is going to be constant according to time, it can be judged the steady state reaches, and measure the concentration of CO_2 in the nitrogen gas.
e. Calculate the diffusion coefficient by following equation.[5]

$$D_A = \frac{Q f_A L}{(1-f_A)A} \qquad (1)$$

Where, D_A = diffusion coefficient of gas A (m^2/s)
Q = flow rate of gas B (m^3/s)
fA = molar ratio of gas A in gas B
L = thickness of specimen (m)
A = cross sectional area (m^3)

f. From the each result in same condition, calculate the average value of the carbon dioxide diffusivity.

2.2 Test materials and mix design

Table shows the physical properties of aggregates used in this study. Generally, the specific gravity of fine aggregates and of coarse aggregates is 2.50~2.65 and 2.55~2.70, respectively. The fineness modulus of aggregates is good when the fine modulus of fine aggregate is 2.3~3.1 and that of coarse aggregates is 6~8. Therefore it is supposed that used aggregates in this study have the good quality.

Table 2 shows the used mix design in this study. On the other hand, tests perform with the mortars that water to cement ratio and aggregate to cement ratio is 0.5 and 2, respectively and the hydrated cement pastes that water to cement ratio is 0.5.

Table 1. Physical characteristics of used aggregate

Kinds of aggregate	Specific gravity	Absorption	Fineness modulus
Fine	2.56	2.18	2.85
Coarse	2.60	0.94	6.51

Table 2. Detailed mix design

W/C	Cement (kg/m^3)	Water (kg/m^3)	Fine aggregate (kg/m^3)	Coarse aggregate (kg/m^3)
0.42	425	179	714	895
0.50	315	158	748	1076
0.58	277	161	726	1117

2.3 Test variables and standard specimens

Tests perform with ordinary Portland cements and major variables are water to cement ratio (0.42, 0.50, 0.58) and relative humidity (10%, 45%, 75%, 90%). Also, knowing the influences of aggregate size tests are performed with the mortar and the hydrated cement paste that water to cement ratio is 0.50. In case of concrete, the tests of diffusion coefficient of carbon dioxide are also performed with completely carbonated specimens because the carbonation of concrete has been processed with the carbonation front between carbonation area and non-carbonation area.

On the other hand, the test specimens, which are made from sawing the standard specimens with a 100 mm in diameter and a 200 mm in diameter, are a cylindrical shape with a 100 mm in diameter and a 10 mm in thickness. The 10 mm in thickness is adopted to guarantee the completely carbonation of specimen in a short term.

All specimens is mixed by mechanical mixer. The mold is removed after 24 hours from mixing time and during 28 days they are cured in a water tank maintained 20±2 ℃ temperature.

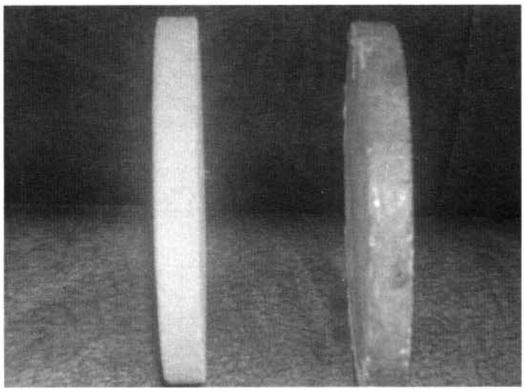


Fig. 3. Standard specimen

Table 3. Salts for maintaining constant relative humidity

Kinds of salts	Silica gel	Potassium carbonate K_2CO_3	Sodium chloride NaCl	Potassium sulfate K_2CO_3
RH	10±0.5%	43.2±0.4%	75.3±0.1%	97.3±0.5%

For the purpose of measuring the diffusion coefficient according to relative humidity, specimens place in vacuum desiccators, which remains in constant relative humidity, until they are constant weight.[8)] And the sides of specimens are coated with epoxy for the one dimensional flow. Fig. 3 shows the standard specimen in this study and Table 3 presents the salts for maintaining constant relative humidity from the ASTM standard. In Table 3, the result of silica gel has been gained from test results.

3. Results and discussion

3.1 Time to steady state condition

Fig. 4 shows that the diffusion of carbon dioxide reaches steady state condition with the various kinds of specimens. From these results, the diffusion of carbon dioxide reaches the steady state within about five hours in all concrete specimens after exposure. Also, in case of mortars and cement pastes, the time to steady state condition is 3~5 hours and these results are in accordance with concrete specimens.

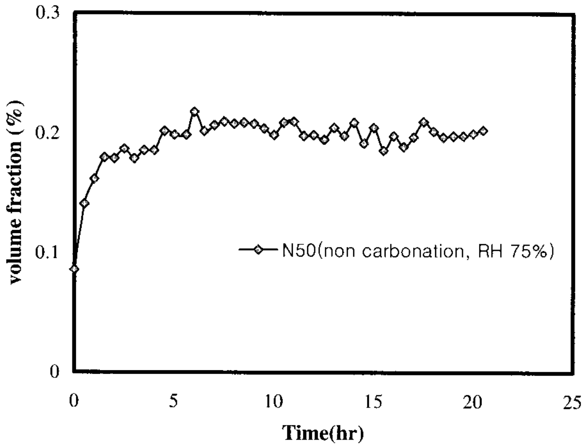
3.2 Influence of water to cement ratio

Fig. 5. shows the influence of water to cement ratio to the diffusion coefficient of carbon dioxide in concrete. The test results indicate that the diffusion coefficient increases with the increase of water to cement ratio, but the increasing ratio according to water to cement ratio is small when the relative humidity is high. It is supposed that the variation of pore structures caused by the change of water to cement ratio has little affected diffusion of carbon dioxide in concrete because the most of pores are filled with water when the relative humidity is high.

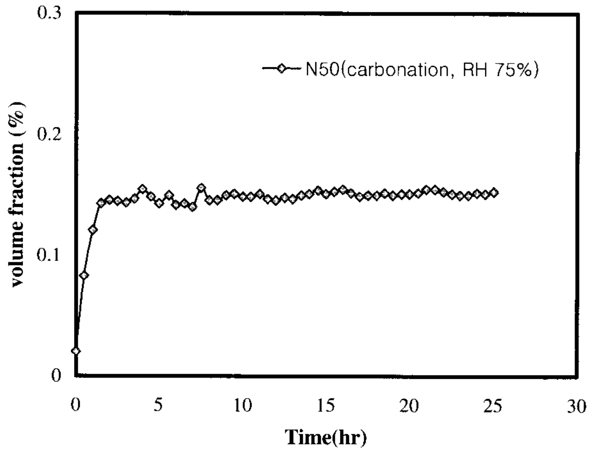
3.3 Influence of relative humidity

From the Fig. 6. it is known that the influence of relative humidity to the diffusion coefficient of carbon dioxide in concrete. The diffusion coefficient decreases with the increase of relative humidity at the same water to cement ratio, but the change of diffusion coefficient of carbon dioxide with the relative humidity is small when the water to cement ratio is lower. It is supposed that the open pore, which is possible to diffuse gas, is little because concrete matrix is dense when the water to cement ratio is lower and therefore the influence of relative humidity to diffusion coefficient decreases when the water to cement ratio is lower.

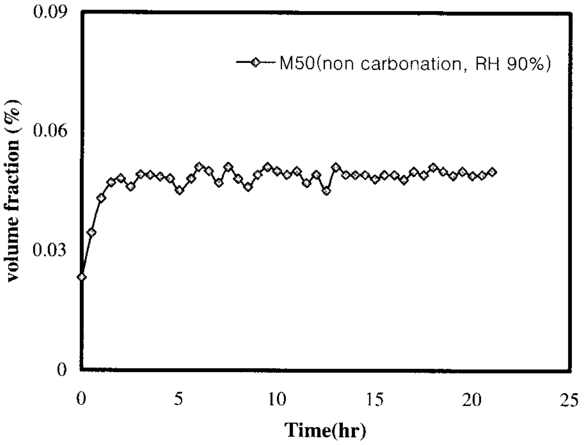
Fig. 7. shows that the diffusion coefficient of carbon dioxide in carbonated concrete is lower more or less than that in non-carbonated concrete but the influence of relative humidity to diffusion coefficient of carbon dioxide



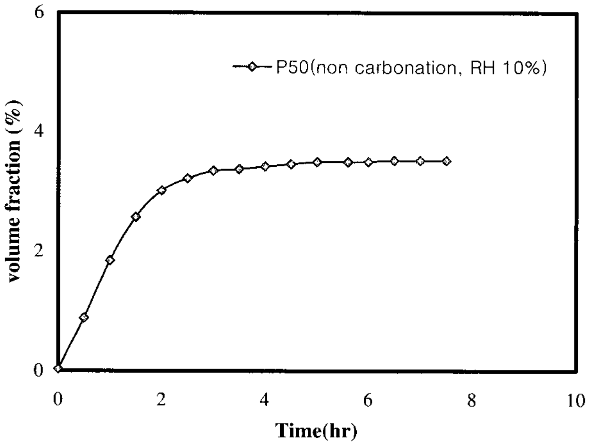
(a) Concrete (NC, w/c 0.5, RH 75%)



(b) Concrete (C, w/c 0.5, RH 75%)

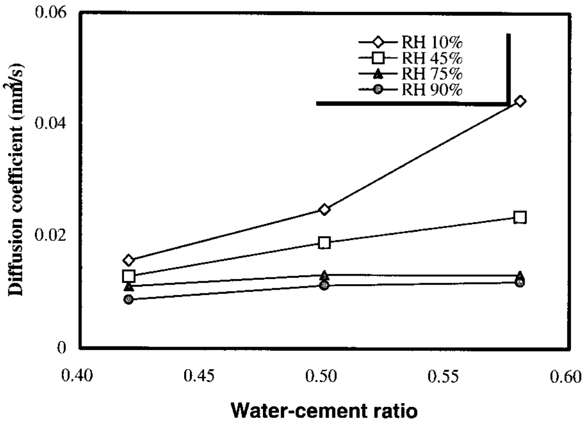


(a) Mortar (NC, RH 90%)

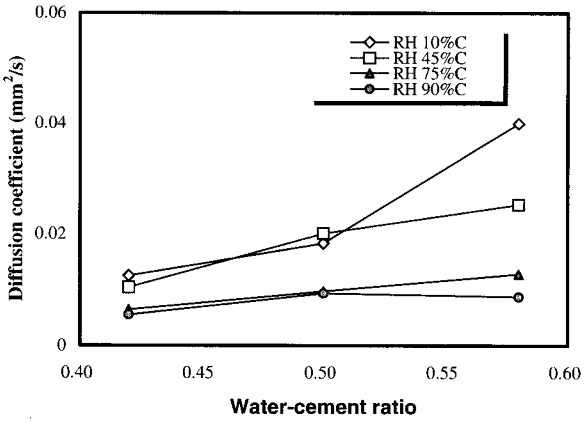


(b) Hydrated cement paste(NC, RH 10%)

Fig. 4. Time to steady state condition



(a) In case of non-carbonated concrete



(b) In case of carbonated concrete

Fig. 5. Variation of diffusion coefficient according to water to cement ratio

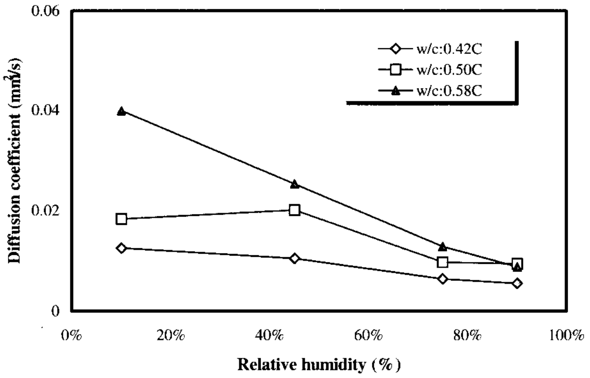
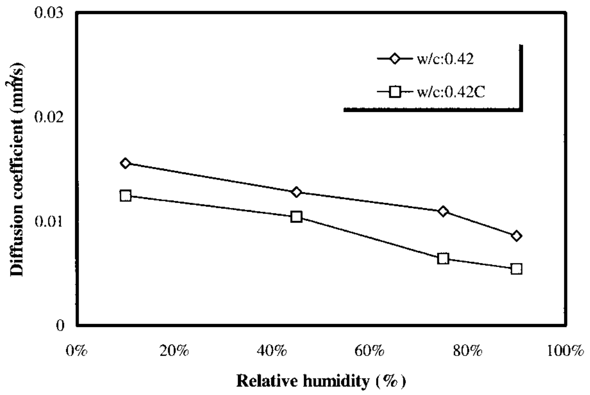
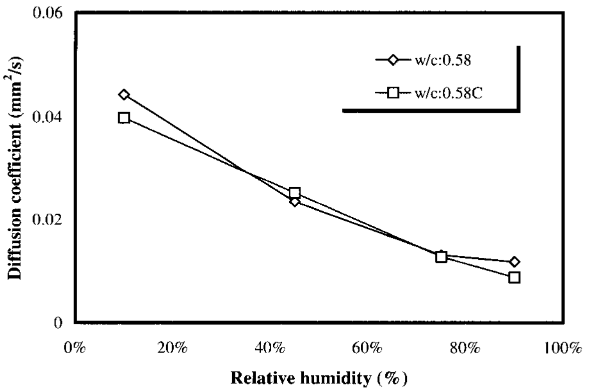


Fig. 6. Variation of diffusion coefficient according to relative humidity



(a) Water to cement ratio 0.42



(b) Water to cement ratio 0.58

Fig. 7. Influence of carbonation conditions to diffusion coefficient

has the same tendency with both carbonated and non-carbonated specimen. On the other hand, from the Fig. 7(b), when the water to cement ratio is 0.58 the diffusion coefficient of carbon dioxide almost coincides with two cases and it is supposed that the change of pore structure caused by carbonation has little affected diffusion of carbon dioxide in concrete because the concrete with high water to cement ratio is not dense.

3.4 Diffusion coefficient of mortar and hydrated cement paste

Fig. 8 and fig. 9 show that the diffusion coefficient in hydrated cement paste is larger than that in concrete and mortar. Because porosity per unit volume of hydrated cement paste is much more than that of concrete or mortar and therefore absolute amounts of pore in hydrated cement paste is large, these results are supposed rational.

From Fig. 8, the diffusion coefficient of carbon dioxide in mortar is smaller than that in concrete except that relative humidity is 10 %. These coincide the diffusion coefficient test of oxygen under relative humidity 60 % performed by Kobayashi.9 But, from the viewpoint of porosity, these results are a contrast to the case of hydrated cement paste.

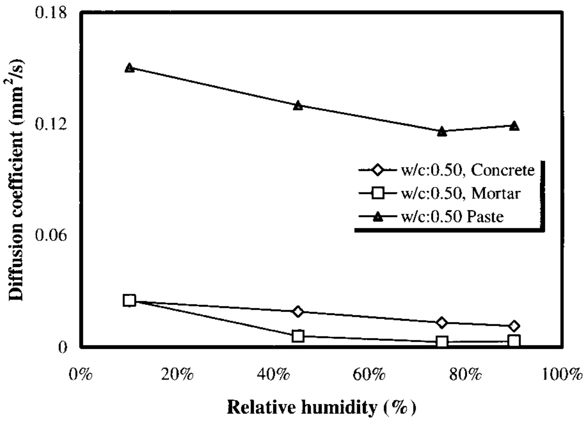


Fig. 8. Variation of diffusion coefficient according to RH with various materials

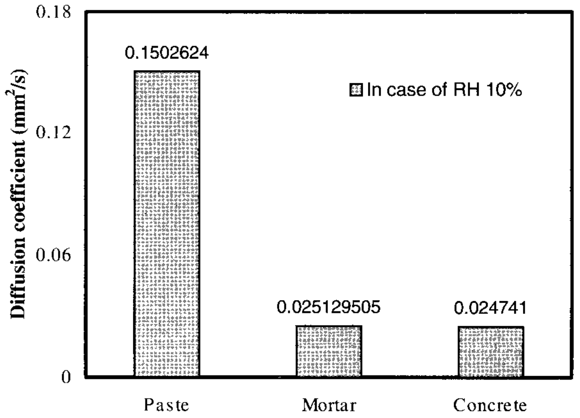


Fig. 9. Diffusion coefficient of carbon dioxide in case of 10% relative humidity

Fig. 9 compares the diffusion coefficient of carbon dioxide in concrete, mortar and hydrated cement paste when relative humidity is 10 % and from this it is known that the diffusion coefficient of carbon dioxide in mortar is a little larger than that in concrete. Because the influence of microstructure including porosity affects the gas diffusion absolutely when relative humidity is 0 %, the result of Fig. 11 may have been affected the difference of porosity per unit volume. But, in case of Fig. 10, when relative humidity is over 45 % the diffusion coefficient of carbon dioxide in mortar is smaller than that in concrete and this implies that relative humidity has largely influence on diffusion coefficient of mortar than concrete. That is to say, the diffusion coefficient of carbon dioxide has been largely affected by the difference of porosity due to composition of materials when relative humidity is very low, but the influence of other factors on it becomes larger in proportion to the degree of relative humidity. Theory of ITZ (interfacial transition zone) is one of the possibilities. In case of concrete, it is supposed that the microstructures are different from mortar or hydrated cement paste because of coarse aggregate. Consequently, since the adsorption isotherms of concrete are different from mortar or hydrated cement paste, it is resulted that the change of diffusion coefficient of carbon dioxide due to increasing of relative humidity in concrete is smaller than in mortar.

4. Conclusions

The carbonation is one of the most important degradation processes in concrete structures and it is affected by many parameters including time, gas diffusion rate, ambient CO_2 concentration and amounts of carbonatable materials in concrete. But the study of CO_2 diffusivity is insufficient yet. Therefore the purpose of this paper is to study diffusion coefficient of carbon dioxide in various cementitious materials by developing the measurement system of gas diffusion coefficient and especially to analyze the influence of relative humidity on it.

The following conclusion can be drawn from this study.

(1) In case of high relative humidity, the variation of pore structures caused by the change of water to cement ratio has little affected diffusion of carbon dioxide in concrete because the most of pores are filled with water.

(2) The diffusion coefficient decreases with the increase of relative humidity at the same water to cement ratio, but the change of diffusion coefficient of carbon dioxide with the relative humidity is small when the water to cement ratio is lower. It is supposed that the open pore is little when the water to cement ratio is lower.

(3) The diffusion coefficient in hydrated cement paste is larger than that in concrete and mortar. It is supposed that the porosity per unit volume of hydrated cement paste is much more than that of concrete or mortar.

(4) The diffusion coefficient of carbon dioxide in mortar is smaller than that in concrete except that relative humidity is 10%. It is supposed from that the adsorption isotherms of concrete are different from mortar or hydrated cement paste because of the influence of ITZ.

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