Pergamon

Cement and Concrete Research, Vol. 26, No. 5, pp. 781-790, 1996

0008-8846/96 $15.00 + .00

PII S0008-8846(96)00039-7

DETERMINATION OF CHLORIDE DIFFUSION COEFFICIENT AND GAS PERMEABILITY OF CONCRETE AND THEIR RELATIONSHIP

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(Refereed)
(Received June 9, 1995; in final form February 21, 1996)

ABSTRACT

Chloride diffusion coefficient and gas permeability of concrete were experimentally determined. The relationship between them is discussed. Chloride diffusion coefficient was determined using saturated concrete by an accelerated electrical testing method. The chloride diffusion coefficient was found to be controlled by the water-to-cement ratio with about 2.2 times higher chloride diffusion coefficient for concrete with the water-to-cement ratio of 0.6 as compared with that of 0.4 water-to-cement ratio. Gas permeability was greatly influenced by the degree of saturation of the concrete. A correlation was found between chloride diffusion coefficient and gas permeability. Lightweight aggregate concrete was tested and compared with normal weight concrete with respect to chloride diffusion and gas permeability.

Introduction

Transport properties of concrete are important and deserve thorough investigation as they significantly influence the durability of concrete. Water, carbon dioxide gas, and chloride ions are considered to be primal substances degrading the integrity of concrete structures as a result of their transport through and subsequent interaction with cement hydrates and embedded steel reinforcement. Water permeability is of importance for concrete for water retaining or submerged structures. Concrete above ground and exposed to the atmosphere should have a low gas permeability so as to prevent carbonation that results from the penetration of carbon dioxide gas into the concrete. In addition, lower gas permeability can be desirable for concrete structures confining radioactive waste material so as to reduce the risk of emission of radiation. For the case of concrete structures in marine and other salt-laden environments, chloride permeability can be used to predict service performance of the concrete under corrosive conditions. Mobility of free chloride ions via water saturated pores in concrete needs to be understood in relation to the corrosion of steel reinforcement embedded in the concrete cover.

The permeability of concrete is determined experimentally using various flowing media according to the anticipated design requirements. Recently, attempts have been made to study the relationship between different concrete permeabilities with such flowing substances as gas, water, and chloride ions (1,2,3,4). The outcome of these studies will help to estimate the per meability of one particular substance from the other permeabilities. The transport property of concrete is influenced by the internal framework of capillary pores in the concrete, which is primarily controlled by the water-to-cement ratio and the degree of hydration. It is generally accepted that a higher porosity and better continuity of pores result in a higher permeability. In addition to geometric features of the pore structure in concrete, the moisture condition within the pores will have a pronounced effect on concrete permeability. Water molecules present in pores prevent the flow of gas through the concrete while chloride ions can easily pass through water-filled pores. Furthermore, interaction involving an electrochemical phenomenon will occur between the surface of a cement paste solid and a flowing medium.

In this study the gas permeability was determined for concrete subjected to various drying procedures and hence having different degrees of saturation at time of test. The gas permeabilities of these concretes were compared with the chloride diffusion coefficient which was determined on saturated concrete by an accelerated electrical testing method. In addition, in order to simulate field conditions all concrete specimens were tested under an axial compressive loading condition. Furthermore, lightweight aggregate concrete was tested and compared with normal weight concrete.

Experimental Methods

Specimen Preparation. Mix proportions and the properties of fresh and hardened concrete are shown in **TABLE 1**. Normal weight and lightweight concretes with water-to-cement ratios of 0.4 and 0.6 were tested (hereinafter normal weight concrete and lightweight concrete with water-to-cement ratios of 0.4 and 0.6 are abbreviated as NW04, NW06, LW04 and LW06, respectively). Ordinary portland cement was used (CSA A-5 Type10). Natural gravel (maximum size : 12.5 mm, specific gravity : 2.68 and absorption : 1.02 %) and sand (specific gravity : 2.68, absorption : 1.14 % and fineness modulus : 2.71) were used as the coarse and fine aggregate respectively for normal weight concrete. For lightweight concrete expanded shale aggregate (specific gravity : 1.58 and absorption : 12.0 %) was used as the coarse aggregate and the same sand as mentioned above was used as fine aggregate. The lightweight coarse aggregate was presoaked for 24 hours prior to mixing. All aggre-

TABLE 1

Mix Proportion and Properties of Fresh and Hardened Concrete

	Mix proportions[#1]								Fresh concrete			Strength
Mix	W/C	C	W	F.A.	C.A.	S	AE	WR	Slump	Air	Unit wt.	28-day[#2]
No.		(kg/m³)				(%)	(mL/m³)		(mm)	(%)	(kg/m³)	(MPa)
NW04	0.4	460	184	745	888	46	234	534	65	7.0	2298	42.4(0.40)
LW04	0.4	460	184	745	504	46	237	855	115	6.5	1837	35.7(1.37)
NW06	0.6	305	184	876	888	50	50	0	75	7.0	2314	27.0(0.23)
LW06	0.6	305	184	876	504	50	50	0	75	6.0	1934	24.7(0.60)

#1: F.A. – fine aggregate, C.A. – coarse aggregate, S – fine and coarse aggregate ratio by volume, AE – air entrained agent, WR – superplastisizer.

#2: The entry is an average of three core cylinders (standard deviation).

gates were mixed at a saturated surface dry condition based on 24 hours submersion in water and each of the water-to-cement ratios was calculated on the basis of aggregates being saturated surface dry. The volume of coarse aggregate per cubic meter was maintained constant in all mix designs, thereby the volume ratio of mortar matrix to coarse aggregate was constant. In order to achieve adequate workability of the fresh concrete a high range water-reducer (Superplastisizer) was used for NW04 and LW04. Also, an air entraining agent was used to obtain the air content of 5 to 7%.

A cylindrical hollow concrete specimen with outside and inside diameters of 150 mm and 75 mm, respectively, was used for permeability testing. The wall thickness was then 37.5 mm. In addition, the height of the hollow cylinder was 230 mm after cutting with a diamond saw to remove approximately 20 mm from the top and bottom.

Gas permeability was measured using concrete specimens with various degrees of saturation, in which seven different drying procedures were employed after being cured for three to four months in the curing room (temperature: about 24 °C, humidity: > 95%). The applied drying conditions were : Series A - 45 days in a laboratory air, Series B - 90 days in a laboratory air, Series C - 180 days in a laboratory air, Series D - one month in a laboratory air followed by 1 day in an oven at 60 °C, Series E - one month in a laboratory air followed by 5 days in an oven, Series F - one month in a laboratory air followed by 7 days in an oven, and Series G - one month in a laboratory air followed by the oven dry to constant weight. For each specimen subjected to the respective drying method the porosity is defined in this study as follow:

$$p = \frac{loss\ of\ weight}{total\ volume\ of\ concrete} \times 100 \tag{1}$$

where p is the porosity of concrete after a specific drying procedure (%). The total volume of concrete was 3050 cm^3 and the loss of weight was the amount of water lost (cc) by the drying in each method. Therefore the porosity is a single function of the loss of weight of concrete by each drying method. An epoxy adhesive was used for capping the top and bottom of gas permeability specimens. The top surface was sealed including the hole by the epoxy while there was a small hole left on the bottom for inlet of the gas.

The accelerated electrical chloride permeability test was conducted on concrete under a moist condition after being cured in the curing room for three to four months. The entire bottom surface was coated and capped with an epoxy adhesive, thereby sealing the center hole for testing of chloride permeability. Also capping with sulphur was done for the top surface as well.

Accelerated Chloride Permeability Test with an Electrical Potential Difference. For the purpose of accelerating chloride permeability tests, an electrical potential of 15 volts was applied to the inner and outer surfaces of a thick-walled cylindrical hollow concrete specimen. During the chloride permeability testing concrete specimen was subjected to a sustained axial load of about 20 percent of the maximum strength to simulate field conditions. The electrical chloride permeability test arrangement is depicted in **FIG. 1**.

Under the given electrical field, chloride ions having a negative charge migrate into the wall of the concrete approaching the positive pole placed inside the well of the hollow specimen. Thus, the speed of chloride ions passing through the full thickness of concrete was increased. The inside solution was a 0.3 N sodium hydroxide solution and its alkalinity was maintained above 11 pH in the course of chloride permeability testing. This alkali solution was used as a

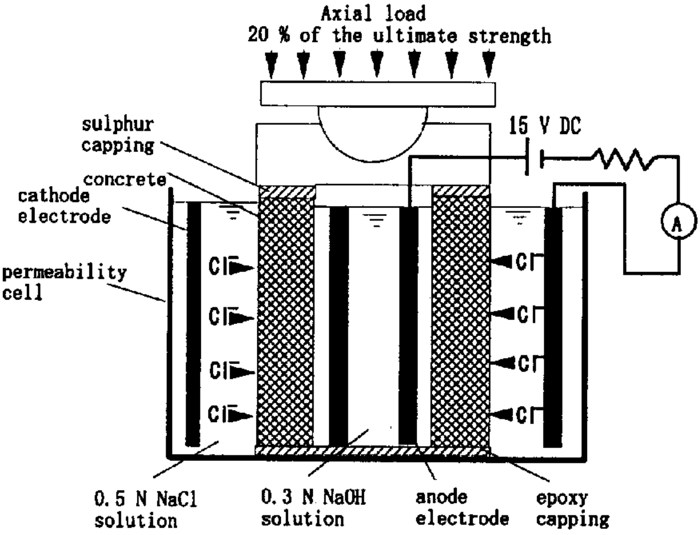

FIG. 1.
Accelerated chloride permeability test.

neutral solution in the inside well of specimen in order to prevent the evolution of chlorine gas and the dissolution of the anode electrode (5). The concentration of chloride ions in the inside neutral solution was measured at an interval of 12 or 24 hours. It was expected that the amount of chloride ions accumulating in the NaOH solution would increase consistent with an increase in time elapsed after a certain transition period (steady state). The linear relationship with respect to the increase of chloride ions and elapsed time in a steady state permitted calculation of the diffusion coefficient of chloride ions for concrete tested. For calculating the chloride diffusion coefficient in an accelerated chloride permeability test, with an electrical potential, the Nernst-Planck equation may be used (6,7,8,9). In this study the equation was modified to account for a radial flow in a cylindrical tube as shown in Eq. **(2)**

$$D = V_2 \frac{dC_2}{dt} \frac{\ln(r_1/r_2)}{2\pi h \frac{zFV}{RT} C_1} \tag{2}$$

where D is the diffusion coefficient of chloride ions (cm^2/s), $V_2(dC_2/dt)$ is the rate of the increasing amount of chloride ions in the inside solution in a steady state and obtained from the test (mol/s), z is the valency of chloride ions (-1), F is the Faraday constant (9.65×10^4 Coulomb/mol), R is the gas constant (8.314 J/(K mol)), T is the absolute temperature (293 K), V is the applied voltage (15 V), C_1 is the concentration of chloride ions in the NaCl solution (maintained constant at 0.5 N through test), r_1 and r_2 are the outside and inside radii respectively, (75 mm and 37.5 mm), and h is the effective height of specimen.

Determination of Gas Permeability of Concrete Subjected to Different Drying Conditions. The flowchart of the gas permeability test is illustrated in **FIG. 2**. Nitrogen gas pressure

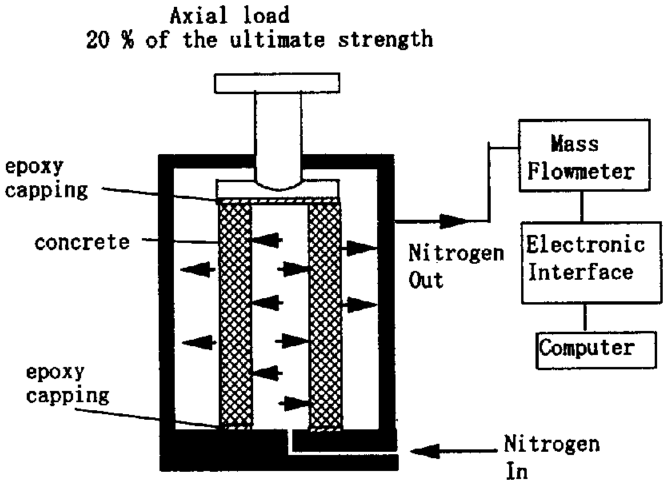

FIG. 2.
Gas permeability test.

of 0.63 MPa was applied to the inner circumferencial surface of the cylindrical hollow concrete specimen and the pressure differential was maintained between the outer and inner surfaces of the specimen. This high applied gas pressure level was selected to avoid the effect of gas slippage which would otherwise occur at lower pressure levels within the concrete (1).

Volumetric gas flow rate was determined at atmospheric pressure and at the room temperature (about 20 °C) after the flow of gas became steady state. An axial static load of about 20 percent of the maximum strength was applied to the specimen during testing. This was done to simulate field conditions. Using the volumetric gas flow rate the gas permeability was calculated as follows (8,11).

$$k = -\frac{\mu Q p_1 \ln(r_1/r_2)}{\pi h(p_1^2 - p_2^2)} \tag{3}$$

where k is the intrinsic permeability and defined as the gas permeability (m^2) in this study, Q is the volumetric gas flow rate (cm^3/s) obtained by the test, p_1 is the atmospheric pressure (0.1 MPa), p_2 is the applied nitrogen gas pressure (0.63 MPa), and μ is the viscosity of the nitrogen gas (1.74×10^{-5} Pa s at 20 °C).

Results and Discussion

Chloride Diffusion Coefficient of Concrete Determined by Electrical Method. **FIG. 3** shows the results of the accelerated chloride permeability test with an electrical potential of 15 volts. The increase in chloride ions in the inside neutral solution with time is shown. The rate of the increasing amount of chloride ions in the inside solution became constant with time after about 7 days had elapsed for NW04 and LW04. A steady state condition

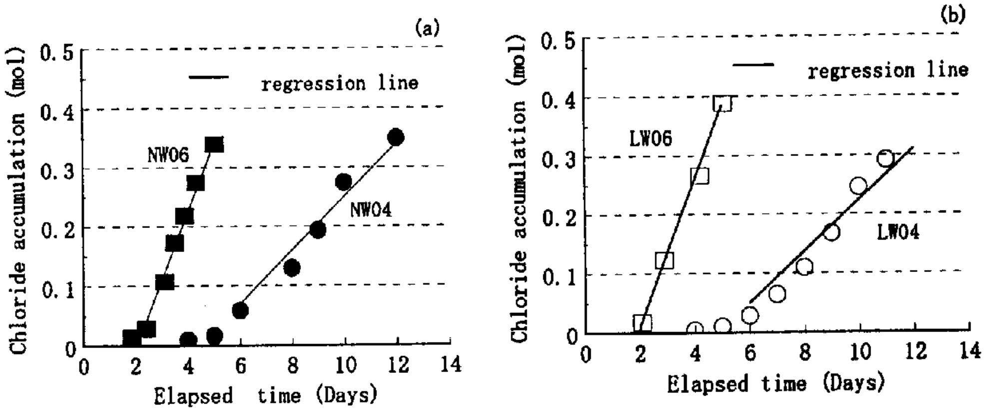

FIG. 3.
Accelerated chloride permeability test results: (a) normal weight concrete, (b) lightweight concrete.

was attained after about 2 days for NW06 and LW06. A linear regression line was determined after the transition period. The slope is the flow rate of chloride ions for each concrete mix. The chloride flow rate so obtained was 6.54 × 10^{-7} mol/s and 14.2 × 10^{-7} mol/s for NW04 and NW06, respectively, and 7.27 × 10^{-7} mol/s and 15.6 × 10^{-7} mol/s for LW04 and LW06, respectively. These flow rates were then used to calculate the diffusion coefficient of chloride ions using **Eq. (2)**. The diffusion coefficients were 10.6 × 10^{-9} cm^2/s and 23.1 × 10^{-9} cm^2/s for NW04 and NW06, respectively, and 11.8 × 10^{-9} cm^2/s and 25.3 × 10^{-9} cm^2/s for LW04 and LW06, respectively. These values of chloride diffusion coefficients appeared to agree with others (9). It was found that the effect of the water-to-cement ratio on chloride diffusion coefficient was significant in this study. The chloride diffusion coefficients of normal weight and lightweight concrete were increased by a factor of about 2.2

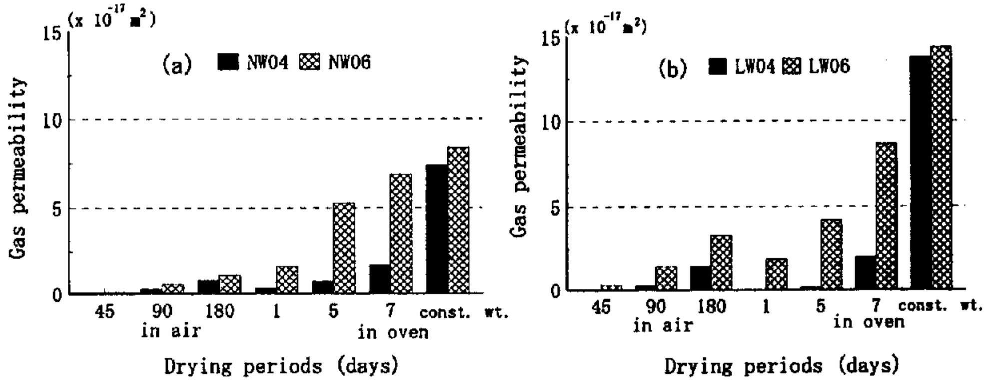

FIG. 4.
Effect of air dry and oven dry on gas permeability (a) normal weight concrete, (b) lightweight concrete.

when the water-to-cement ratio increased from 0.4 to 0.6 for each type of concrete. Thus, as generally recognized, this accelerated chloride permeability test with an electrical potential of 15 V shows that a higher water-to-cement ratio results in a higher chloride diffusion coefficient. In addition, lightweight concrete had a similar chloride diffusion coefficient to normal weight concrete with equal water-to-cement ratios. This indicates a negligible effect of the porous aggregate on the transport of chloride ions through lightweight concrete.

Gas Permeability of Concrete Subjected to Different Drying Procedures. The result of gas permeability testing is shown in **FIG. 4** and **FIG. 5**. **FIG. 4** shows an increase in gas permeability of concrete with an increase in the drying period in the air and the oven, respectively. For NW04 and LW04 subjected to drying in air alone, the gas permeability was increased by a factor of 16.0 and 48.3, respectively, as the drying period was extended from 45 days (Series A) to 180 days (Series C). Similarly for NW06 and LW06 the increment factor is 8.6 and 10.7, respectively, when Series A is compared with Series C. Also concrete subjected to drying in an oven at 60 °C after one month's air dry shows 4.8, 4.2 and 4.6 times higher gas permeability for NW04, NW06 and LW06, respectively, as the oven-drying period was increased from 1 day (Series D) to 7 days (Series F). For LW04 the gas permeability rapidly increased by a factor of 13.5 with an increase in the period of oven drying from 5 days (Series E) to 7 days (Series F). This study, therefore, shows a significant effect of drying on gas permeability.

FIG. 5 shows an exponential increase in the gas permeability of concrete with an increase in porosity. Thus, it was found that the gas permeability of concrete is, to a great extent, influenced by the porosity which is a single function of the amount of water evaporated and lightweight aggregate internal structure in this study. In general, water in pores of larger size can be removed faster as a result of an ordinary drying method. Thus, the flow of gas would occur predominantly through the larger pores filled partially or completely by air. The gas permeability then increased exponentially with progressive drying in air or in the oven.

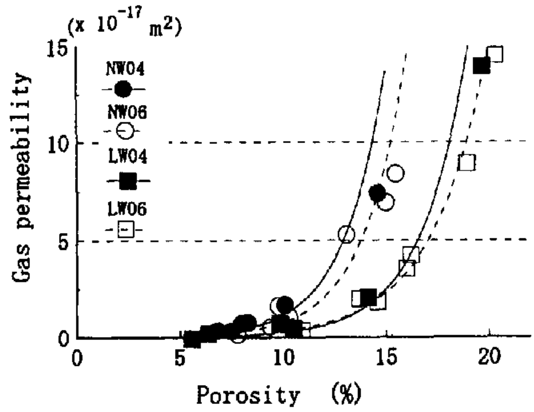

FIG. 5.
Effect of porosity on gas permeability.

The water-to-cement ratio also had a marked effect on gas permeability. Gas permeability of concrete with the water-to-cement ratio of 0.6 was higher than that of concrete with the water-to-cement ratio of 0.4. This was especially observed for cases of shorter drying periods in air and oven. The effect of the water-to-cement ratio on gas permeability is attributed to the fact that the amount of water evaporated due to drying was much larger for NW06 and LW06 than that of NW04 and LW04 even though the same drying method was used. Therefore, a larger loss of water for concrete with a higher water-to-cement ratio resulted in a higher gas permeability. However, the difference in gas permeabilities of concretes with water-to-cement ratios of 0.4 and 0.6 became small in case with Series G, in which drying of the concrete continued in an oven to constant weight: the ratio of gas permeability of NW06 to that of NW04 is about 1.2 and likewise the ratio of gas permeability between LW06 and LW04 is about 1.1. In addition, the gas permeability of lightweight concrete was higher than that of normal weightconcrete although such severe drying condition may not be encountered by concrete in service. This indicates the presence of pores and microcracks sufficient in size and continuity for the flow of gas to occur easily even in concrete with a low water-to-cement ratio of 0.4 if the concrete was dried in an oven to constant weight. It is reported that a rapid increase in gas permeability is more evident for a low water-to-cement concrete due to the development of microcracks when the concrete is subjected to continuous drying in an oven to constant weight (2).

Relationship between Chloride Diffusion Coefficient and Gas Permeability. The relationship between chloride diffusion coefficient and gas permeability was investigated, in which saturated concrete specimens were used for measuring the chloride diffusion coefficient while the gas permeability was determined on concrete specimens subjected to various drying methods (Series A to G). **FIG. 6 (a)** and **(b)** show the result of this study. The gas permeability shown in **FIG. 6 (a)** was on concrete specimens subjected to air drying alone for 45 to 180 days : Series A, B and C, while **FIG. 6 (b)** shows the gas permeability of concrete subjected to oven drying following air drying : Series D, E, F and G. Each Series has four plots representative of normal weight and lightweight concrete with

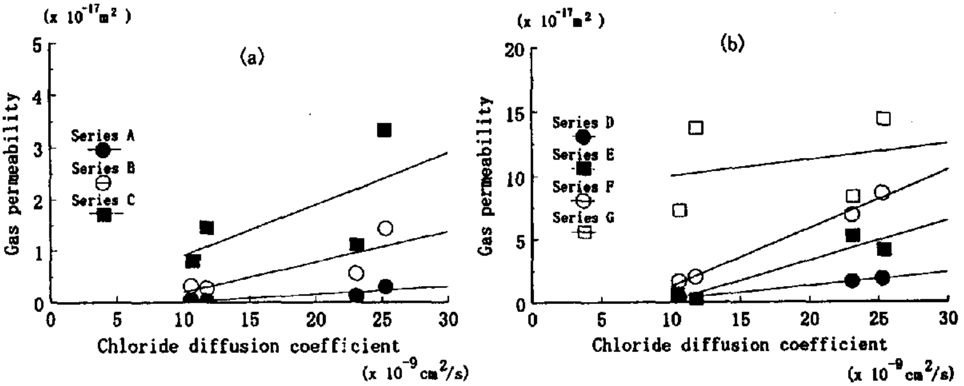

FIG. 6.

Relationship between chloride diffusion coefficient and gas permeability: (a) air dry for gas permeability concrete, (b) oven dry for gas permeability.

water-to-cement ratios of 0.4 and 0.6. It was found that the correlation between chloride diffusion coefficient and gas permeability depends significantly upon the drying methods for gas permeability. A better correlation was found when the chloride diffusion coefficient was compared with the gas permeability of concrete that was dried in air alone or in the oven for relatively short periods of time. As for the correlation of the chloride diffusion coefficient and the gas permeability for concrete dried in air alone (see **FIG. 6 (a)**), the coefficients of determination (R square) were 0.76, 0.68 and 0.44 for Series A, B and C, respectively. When the chloride diffusion coefficient was compared with the gas permeability of concrete that was subjected to the oven drying for 1, 5 and 7 days after one month in air drying (see **FIG. 6 (b)**), the coefficients of determination were 0.99, 0.89 and 0.99 for Series D, E and F, respectively. However, the R square was significantly lower, i.e., 0.06 for Series G in the gas permeability test where the concrete was dried in an oven to constant weight.

It seems that a correlation between chloride diffusion coefficient and gas permeability may exist in the case where the water-to-cement ratio has a significant effect on the gas permeability. In particular, the water-to-cement ratio of concrete significantly influenced the gas permeability of concrete specimens subjected to relatively shorter drying periods in the air and in the oven. The correlation was due to the fact that the chloride diffusion coefficient was also influenced significantly by the water-to-cement ratio. On the other hand, the correlation became poor with a longer period of drying for gas permeability specimens. This could have resulted from microcracks in concrete induced by drying when measuring gas permeability. Longer drying periods allowed more microcracks to occur in concrete resulting in higher gas permeability that led to a poorly correlated gas permeability with chloride diffusion coefficient. Thus, when investigating the relationship between chloride diffusion coefficient and gas permeability, consideration should be given to the effect of drying method and hence the effect of microcracks on gas permeability. Therefore, within the range of this study, the gas permeability correlated better with the chloride diffusion coefficient of saturated concrete (on the basis of the R-square larger than 0.68), when the gas permeability of concrete dried in laboratory air for up to 90 days or dried in an oven at 60 °C for up to 7 days after air drying for one month, was used for this correlation.

Conclusions

1) Chloride diffusion coefficient of saturated concrete, which was measured by an accelerated electrical method with the electrical potential of 15 volts, increased by a factor about 2.2 times as the water-to-cement ratio increased from 0.4 to 0.6. Lightweight concrete showed a comparable chloride diffusion coefficient to that of normal weight concrete with equal water-to-cement ratio. Chloride diffusion coefficients of concrete determined in this electrical method were within 10 to 25 × 10^{-9} cm^2/s.
2) Gas permeability was greatly influenced by the procedures used to dry the concrete and it increased exponentially with open porosity. The effect of increased water-to-cement ratio on gas permeability was more pronounced in the case of shorter drying periods than longer drying periods in the air and in the oven.
3) Within the range of this study, a correlation may exist between chloride diffusion coefficient of saturated concrete and gas permeability of concrete subjected to air drying for less than 90 days or for oven drying for less than 7 days.

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