[2111] 超高耐久性コンクリートの開発

DEVELOPMENT OF HIGHLY DURABLE CONCRETE

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1. INTRODUCTION

In an ordinary atmospheric environment, corrosion of reinforcing steel in a concrete structure can occur when carbon dioxide permeates the concrete and the protective film of the steel is destroyed. Thus the rate of carbonation in concrete can be a significant factor in influencing the durability of the concrete structure. In urban areas, such as Tokyo or Osaka, sulfurous acid gas from the exhaust of automobiles is diffused in the atmosphere which greatly lowers the pH of rainwater falling in these areas. The penetration of this rainwater into concrete surfaces hastens the carbonation of the concrete and creates a problem. According to the results of recent measurements, the pH of rainwater in the Tokyo district is about 3.0. There have been many examples of exposed concrete surfaces being attacked by the strong acidity (1).

Since carbonation of concrete results from the reaction between carbon dioxide and sulfurous acid in the atmosphere and calcium hydroxide in cement hydration products, the predominant concept in the past had been that this reaction was unavoidable. In view of this situation, the authors conducted studies principally on the use of chemical actions with the objective of providing a means of prolonging the lives of concrete structures by reducing the rate of carbonation.

2. EFFECTS OF A WATER-INSOLUBLE GLYCOL ETHER DERIVATIVE ON CONCRETE DURABILITY

As reported in a previous paper (2), the authors found that addition of a water-insoluble glycol ether derivative reduced drying shrinkage of concrete to approximately half of conventional air-entrained concrete. Even only this effect seems to be favorable to durability of concrete structures, since shrinkage cracks sometimes can be a major cause of corrosion of reinforcing steel in concrete. In addition, it was also found that this glycol ether derivative worked as an antifoaming agent in a fresh concrete system, and a result, expelled entrapped air in concrete, making concrete dense. In general, the fundamental measures for improving the durability of concrete are to make the concrete as dense as possible

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and to minimize contact with external environmental conditions. Consequently, the water-insoluble glycol ether derivative having the effect of reducing the total volume of air in concrete, and moreover, reducing the volumes of individual air bubbles was considered effective for improving the durability of concrete.

A change in the constitution of concrete will first of all alter the permeability of concrete. Therefore, it was decided to make comparison studies of the permeabilities of concrete containing a glycol ether derivative and air-entrained and plain concrete of identical strength levels.

Permeability Test

The permeability test was performed determining the depth of permeation of water when a constant water pressure of 0.98 MPa was applied for 48 hours to a cylindrical specimen 150 mm in diameter and 150 mm in height. The calculation of the coefficient of permeability was by the following equation based on the diffusion equation.

$$\beta_i^2 = \alpha \times \frac{D_m^2}{4 \times t \times \xi^2} \quad (\alpha = 175.7,\ \xi = 1.163) \qquad (1)$$

where, β_i^2 : coefficient of diffusion ($10^{-2} \times mm^2/sec$)
D_m : average permeation depth (x 10 mm)
t : pressurized time (sec)

The test results are given in Table 1. As is clear from Table 1, the permeability of concrete containing a glycol ether derivative is extremely small compared with that of air-entrained concrete. Because of this, it may be expected that concrete containing this compound is durable against penetration by various corrosive substances.

From such a point of view, accelerated carbonation tests and chloride ion penetration tests were carried out regarding concrete containing this water-insoluble glycol ether derivative.

Accelerated Carbonation Test

Mortar specimens (40 x 40 x 160 mm) were made under the conditions of water-cement ratio 0.50 and cement-sand ratio 1:2. Ordinary portland cement (specific gravity 3.16) was used. The glycol ether derivative were added to the mortar in amount of 2% and 4% by weight of cement.

After mixing, the mortar was left in molds for a period of 24 hours. The specimens were then stripped and cured for 14 days at 20°C, 100% R.H. The specimens were then placed in an atmosphere of 30°C, 60% R.H. with a carbon dioxide concentration of 5%, in order to evaluate the degree of carbonation at various ages. The evaluation of the degree of carbonation was done by spraying a mixture of 1% phenolphthalein and 99% ethyl alcohol on fractured surfaces of mortar specimens which were broken in flexure. Those portions of the specimens which experienced a color change to red

Table 1 PERMEABILITY TEST RESULTS OF CONCRETE
WATER PRESSURE: 0.98MPa
PRESURIZED TIME: 48hr

ADMIX. (dosage)	AV. PENETRATION DEPTH (mm)	DIFFUSION COEFFICIENT ($\times 10^{-2} mm^2/sec$)
PLAIN	37.2	26.0
AE	30.0	16.9
GLYCOL ETHER (2%)	19.4	7.1
GLYCOL ETHER (4%)	19.6	7.2

TABLE 2 DEPTH (mm) OF CARBONATION OF MORTAR CONTAINING GLYCOL ETHER DERIVATIVE

ADMIX. AGE	2 WEEKS	4 WEEKS	8 WEEKS
PLAIN	5.5 (1.00)	8.0 (1.00)	9.5 (1.00)
GLYCOL ETHER (2%)	3.7 (0.67)	6.2 (0.78)	6.8 (0.72)
GLYCOL ETHER (4%)	3.1 (0.56)	5.0 (0.63)	5.4 (0.57)

FIGURES IN ( ) RATIOS TO PLAIN CONCRETES were judged as not being carbonated.

Table 2 gives the results of accelerated carbonation tests. As these test results clearly show, the progress being approximately 60% of plain mortar. This is roughly equal to the ratio of average permeation depth (D_m) obtained from permeability tests.

Accordingly, it is thought the effect of inhibiting carbonation of mortar with this glycol ether derivative is due to the lowering of the permeability of the mortar.

<u>Chloride Ion Penetration Test</u>

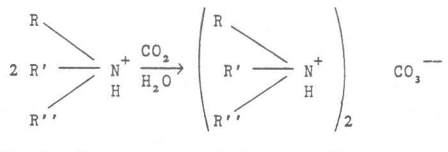
The glycol ether derivative was added at rates of 2% and 4% by weight of cement to mortar of the same mix conditions as in the accelerated carbonation test and the degree of penetration of chloride ions was examined. The specimen dimensions were 40 x 40 x 160 mm.

After mixing the mortar it was held in molds for 24 hours. Following this, curing was performed for 14 days in air of 20°C and 100% R.H.. Next, drying was done for 7 days at 20°C and 60% R.H., and then the specimens were immersed in saturated NaCl solution for 14 days. After this procedure, the specimens were broken, and 0.1% fluorescein-sodium aqueous solution and 0.1N silver nitrate aqueous solution were sprayed on, and those areas which changed color to white were measured.

The results of chloride ion penetration tests are given in Table 3. It can be seen from these results that the degree of chloride ion penetration in concrete containing the glycol ether derivative is extremely slow compared with ordinary concrete. The ratio of chloride ion penetration depth is close to the ratio of D_m in permeability tests, and it is thought that an action similar to inhibition of carbonation worked against penetration of chloride ions.

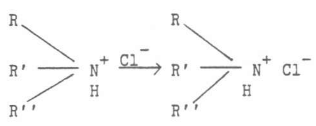
3. PRINCIPLES OF CONCRETE CARBONATION INHIBITION AND CHLORIDE ION ABSORPTION BY AN AMINO ALCOHOL DERIVATIVE

Generally speaking, there are many chemical compounds which possess the capacity to absorb carbon dioxide. In the chemical industry field, such compounds are utilized for desulfurization and deoxidization in petroleum refining. An amino alcohol derivative is typical of such compounds, and the process of carbon dioxide absorption is indicated by the following reaction formula.


(2)

(R indicates hydrogen or alkyl radical)

These amino alcohol derivatives are also effective in absorbing chloride ions, as shown by the following reaction formula:


(3)

As is shown by the reaction formula above, an amino alcohol derivative possesses the extremely favorable property of absorbing both carbon dioxide (and other acidic gases) and chloride ions which adversely affect the durability of concrete structures. Accordingly, it was thought that the durability of concrete structures might be improved by adding these compounds to concrete.

From such a point of view, accelerated carbonation tests and chloride ion penetration tests were carried out by the same methods as described in the preceding chapter regarding concrete containing an amino alcohol derivative. The amino alcohol derivative used in this test was polyhydroxyalkylated alkylenepolyamine compound.

The results of measurements on accelerated carbonation at various ages are given in Table 4, and the results on chloride ion penetration in Table 5. As these results show, the carbonation reaction progresses very slowly and the chloride ion penetration is very small in mortar containing the amino alcohol derivative. Since this amino alcohol derivative does not seem to affect the strength of mortar and hence to change the fundamental property of the mortar matrix, it may be concluded that the effects seen in the above tests attributes to the carbon dioxide and chloride ion absorption property of the amino alcohol derivative.

TABLE 3 DEPTH OF CHLORIDE ION PENETRATION IN CONCRERE CONTAINING GLYCOL ETHER DERIVATIVE

ADMIX. AGE	PENETRATION DEPTH (mm)	RATIO TO AE
PLAIN	28.4	0.83
AE	34.3	1.00
GLYCOL ETHER (2%)	23.2	0.68
GLYCOL ETHER (4%)	19.7	0.57

TABLE 4 DEPTH (mm) OF CARBONATION OF MORTAR CONTAINING AMINO ALCOHOL DERIVATIVE

ADMIX. AGE	2 WEEKS	4 WEEKS	8 WEEKS
PLAIN	6.0 (1.00)	8.6 (1.00)	10.7 (1.00)
AMINO ALCOHOL (4%)	2.4 (0.40)	3.8 (0.44)	5.4 (0.50)

TABLE 5 DEPTH OF CHLORIDE ION PENETRATION IN MORTAR CONTAINING AMINO ALCOHOL DRIVATIVE

ADMIX.	PENETRATION DEPTH (mm)	RATIO TO PLAIN CONCRETE
PLAIN	11.3	1.00
AMINO ALCOHOL (4%)	6.9	0.61

4. LIFE EXPECTANCY OF STRUCTURES COMPOSED OF HIGHLY DURABLE CONCRETE

As described above, concrete containing these two derivatives shows highly durable properties compared with ordinary concrete. Thus the extent of prolongation of life span at actual structures should be known. For this purpose the life expectancy system for reinforced concrete structure seems to be useful. Outline and fundamental concept of the system are described in References 4 and 5. Although only structures situated under ordinary environmental conditions are the objective in this system and the system has been used mainly for design of cover thickness for reinforcement, we can calculate the life span of structures composed of concrete containing these two admixtures.

The relationship of progress of carbonation of concrete and cover thickness for reinforcing steel with scattering is conceptually shown in Fig. 1. The items below are the given conditions in Fig. 1.

1) The average value Ct of depth of carbonation is expressed as

$$Ct = \alpha \cdot \beta \cdot \gamma \cdot \sqrt{t} \qquad (4)$$

where, Ct: depth of carbonation
α : coefficient dependent on environmental condition
β : coefficient dependent on finishing materials

γ : coefficient dependent on internal factors of concrete, determined by Kishitani's equation as shown below,

$$\text{when} \quad x \geqq 0.60 \qquad \gamma = \frac{R\ (x - 0.25)}{\sqrt{0.3\ (1.15 + 3x)}} \qquad (5)$$

$$\text{when} \quad x < 0.60 \qquad \gamma = 0.37R\ (4.6x - 1.70) \qquad (6)$$

R : coefficient determined by variety of aggregate and cement
x : water cement ratio of concrete

2) The scatter in depth of carbonation is a normal distribution, and in terms of variation V, is constant without regard to age.
3) The scatter in thickness of cover is a normal distribution.
4) Reinforcing steel embedded in outdoor surface of concrete would be corroded when carbonated zone reaches the surface of the steel. The reinforcing steel in indoor surface of concrete would be corroded when carbonated zone reaches 20 mm beyond the surface of the steel.

Regarding the distribution of depth of carbonation, the average value and standard deviation are increased with age to become overlapped with the distribution of cover thickness for reinforcement, and corrosion of reinforcing steel begins at the overlapped area (Fig. 2). On the basis of these concepts the probability of steel corrosion can be obtained as a function of cover thickness, carbonation depth and age.

In this system the effect of glycol ether and amino alcohol derivatives may attribute to the reduction of R in equations (5) and (6). Coefficient R represents the ratio of carbonation depth in highly durable concrete to that in ordinary concrete having the same water cement ratio as highly durable concrete.

According to various experimental data, the average value of R was determined at about 0.4 when the glycol ether derivative and the amino alcohol derivative were added to concrete in amounts of 3% and 1%, respectively. On this basis several examples were obtained as Fig. 3 and 4 showing the aimed cover thickness and life span of structure under the condition that no finishing materials are put on the surface of concrete, and P = 10%. As is clearly seen in these Figs., the life span of structure

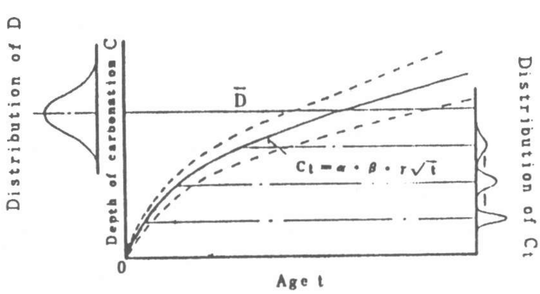


Fig.1 Relations Between Carbonation Depth With Age and Cover Depth

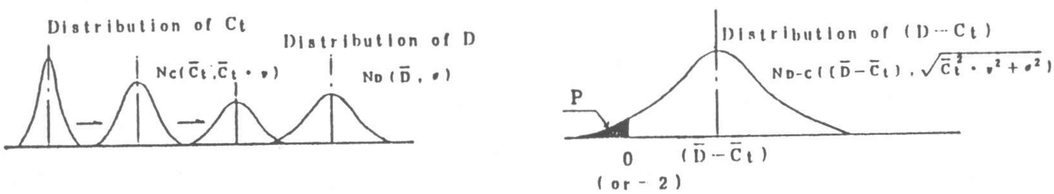


Fig.2 Concept of Progress of Carbonation and Corrosion of Reinforcement

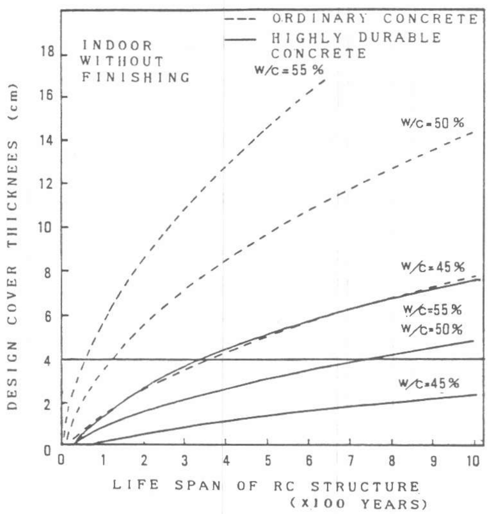


Fig.3 Life Expectancy of Reinforced Concrete Structure (Indoor)

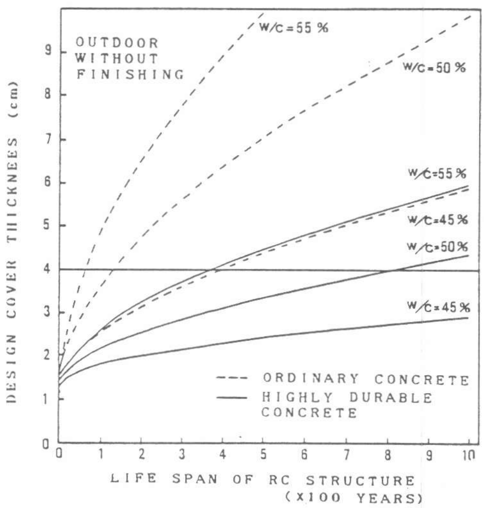


Fig.4 Life Expectancy of Reinforced Concrete Structure (Outdoor)

composed of highly durable concrete can be estimated at several hundred years if the aimed cover thickness is greater than 4 cm, and water cement ratio is smaller than 50%.

5. CONCLUSIONS

1) The progress of carbonation and penetration of chloride ions are extremely slow in concrete containing the glycol ether derivative.

2) An amino alcohol derivative used for desulfurization and deoxidization during petroleum refining demonstrates an ability to absorb carbon dioxide and chloride ions even when added to mortar or concrete.

3) Carbonation and penetration of chloride ions in mortars containing these amino alcohol derivatives proceed at an extremely slow rate.

4) Through the life expectancy system for reinforced concrete structure it was estimated that the life of the structure could be prolonged to several hundred years by utilization of these two derivatives.

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