

**AN EXPERIMENTAL STUDY ON PENETRATION OF CHLORIDE IONS INTO CONCRETE
AND CORROSION OF REINFORCING BARS IN VARIOUS MARINE ENVIRONMENTS**

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Nobufumi TAKEDA



Shigeyuki SOGO



Shigemi SAKODA



Takashi IDEMITSU

Exposure tests on concrete in marine environments were conducted over a period of 10 years to establish a rational design method for concrete structures that takes account of the durability. In these tests, the penetration of chloride ions, the corrosion of reinforcing bars, and changes in concrete quality were investigated. The following findings were obtained: (1) Chloride ion distribution can be predicted using the chloride ion diffusion coefficient (D_c) and the surface chloride ion concentration (C_o) obtained from exposure tests; (2) The rate of chloride ion penetration in marine environments is fastest in the splash zone, followed by the underwater and atmospheric zones; (3) In marine environments, properly treated construction joints and cracks under 0.1mm in width do not significantly advance reinforcement corrosion for an exposure period of up to 10 years.

Key words: diffusion coefficient, exposure test, marine environment, penetration of chloride ions, reinforcing bar corrosion

Nobufumi Takeda is a deputy chief research engineer at the Technical Research Institute of Obayashi Corporation, Tokyo, JAPAN. He obtained his D.Eng. from Kyushu Institute of Technology in 1999. His research interests include the durability design and durability improvements of concrete structures. He is a member of the JSCE and JCI.

Shigeyuki Sogo is a General manager at the Technical Research Institute of Obayashi Corporation, Tokyo, JAPAN. He obtained his D.Eng. from Kyushu Institute of Technology in 1991. His research activities relate to the development of special concreting methods such as underwater concrete, mass concrete, and self-compacting concrete, and the durability design of concrete structures. He is a member of the JSCE and JCI.

Shigemi Sakoda is a professor in the School of Marine Science and Technology of Tokai University, Tokyo, JAPAN. He obtained his D.Eng. from Tokai University in 1992. He has been involved in research on the properties of concrete with inferior quality aggregates and the durability of concrete in marine environments. He is a member of the ACI, JSCE, and JCI.

Takashi Idemitsu is a professor at Kyushu Institute of Technology, Fukuoka, JAPAN. He obtained his D.Eng. from Kyushu Institute of Technology in 1992. His research interests include prestressed concrete using reinforcing bars, self-compacting concrete, and the quality assurance of concrete structures. He is a member of the JSCE and JCI.

1. INTRODUCTION

In order to design concrete structures for a marine environment with a proper consideration of durability, it is vital to clarify the rate of chloride penetration into concrete and the rate of reinforcement corrosion. There have been numerous reports on both these topics, mainly based on investigations of structures constructed in marine environments and exposure tests in such environments [1]. According to these reports, chloride ion concentration, moisture content, and oxygen supply in the concrete all affect the corrosion of reinforcing steel, and the splash zone is generally considered to be the severest environments with regard to concrete structure durability, followed by the underwater and atmospheric zones. It has also been reported that the chloride ion limit, at which reinforcement corrosion begins to occur, lies between 1.2 and 2.5 kg/m³[2],[3]. Further, estimation of long-term chloride ion penetration has been attempted by measuring chloride ion concentrations near surfaces and using the diffusion coefficient of chloride ions in Fick's diffusion equation [4],[5],[6].

However, in a report in which a number of investigations of chloride penetration into concrete in various marine environments were analyzed, it is pointed out that chloride ion concentrations in marine structures vary widely even in environments that may be classified into the same category [7],[8]. In addition to these wide variations, the marine environment varies according to geographical location, position of the structure, and the arrangement of structure members, making it difficult to correlate their influence on the rate of chloride penetration and progress of reinforcement corrosion. This has hampered the elucidation of the effects of different marine environments and construction parameters, such as cracks and construction joints, on chloride ion penetration in concrete and reinforcement corrosion.

In this study, exposure tests on concrete specimens in different marine environments, i.e., the splash zone, underwater, and the atmospheric zone, were conducted over a period of 10 years with the aim of establishing a rational design method for concrete structures in marine environments taking into account durability. This paper reports on the estimation of chloride penetration and rate of reinforcement corrosion based on the results of these exposure tests, and the following issues are discussed:

- (1) Influence of different environmental conditions on the quality of concrete, chloride ion penetration, and reinforcement corrosion
- (2) Influence of types of cement on concrete quality, chloride ion penetration, and reinforcement corrosion
- (3) Influence of cracks and construction joints on the rate of reinforcement corrosion

2. METHODS OF EXPERIMENT AND ANALYSIS

2.1 Outline of experiment

Three experiments were implemented with the following aims:

- Experiment I: Experiment to elucidate the effects of different environmental conditions
- Experiment II: Experiment to elucidate the effects of cement types
- Experiment III: Experiment to elucidate the effects of cracks and construction joints

For each experiment, concrete specimens encasing reinforcing steel were exposed to different marine environments for 10 years. Changes in the quality of concrete, chloride ion penetration, and reinforcement corrosion over time were investigated periodically. **Table 1** gives the combinations of experimental conditions, such as exposure, type of cement, and presence of cracks and construction joints. Four exposure conditions were selected: splash zone, atmospheric zone, underwater, and inland. Three cements were used: ordinary portland cement, Type B blast-furnace slag cement, and sulfate-resistant portland cement. Specimens with cracks or construction joints were also prepared using ordinary portland cement and were exposed to the same four environmental conditions.

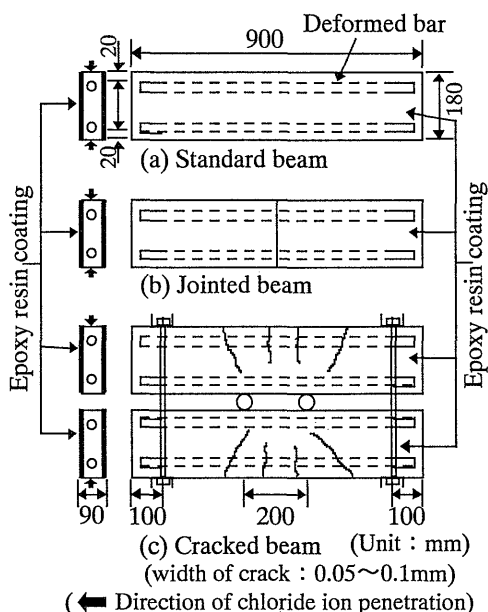


Fig.1 Type, Shape and Size of Beam Specimens

Table 1 Combinations of Experimental Conditions

Types of specimen	Types of cements	Exposure environments			
		Splash zone	Atmospheric zone	Underwater	Inland
Standard beam	Ordinary portland cement (OP)	○	○	○	○
	Type B blast-furnace slag cement (BB)	—	○	○	—
	Sulfate-resistant portland cement (SR)	—	○	○	—
Cracked beam	Ordinary portland cement (OP)	○	○	○	○
Jointed beam	Ordinary portland cement (OP)	○	○	○	○

Table 2 Physical Properties and Chemical Composition of Cements

Properties Types of cements	Specific gravity	Blaine fineness (cm ² /g)	Chemical compositions (%)							
			Ig.loss	Insol.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃
Ordinary portland cement	3.15	3,300	0.5	0.3	21.7	5.3	3.0	64.7	1.3	2.2
Type B blast-furnace slag cement	3.04	3,440	0.9	0.5	25.2	7.3	2.2	57.5	2.8	1.7
Sulfate-resistant portland cement	3.18	3,370	0.8	0.1	22.1	4.1	4.5	64.3	1.0	1.9

Table 3 Properties of Aggregates

Materials	Properties
Fine aggregate	Land sand , Specific gravity : 2.58 Absorption : 1.64% , Fineness modulus : 2.67
Coarse aggregate	Crushed stone , G _{max} : 15mm Specific gravity : 2.66 , Absorption : 1.09%

2.2 Specimens

a) Composition, shape, and size

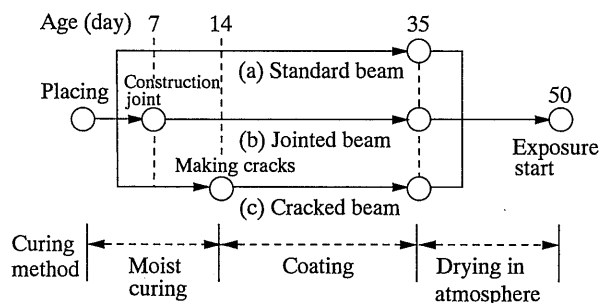
Three types of specimen were prepared for exposure: reinforced concrete beams for investigation of reinforcement corrosion (RC specimen), plain concrete cylinders for compression tests, and plain concrete cylinders for chloride penetration analysis. The reinforced concrete beams were 9 by 18 cm in cross-sectional size and 90 cm in length, as shown in **Fig. 1**. These beams had deformed reinforcing bars embedded with a cover depth of 2 cm. These were SD 295/D19 bars with transverse ribs conforming to JIS G 3112. Both sides and ends of the beams were coated with a thick-film epoxy resin to allow chloride ion penetration only from both edges. Whereas cylinders for the compression tests were 10 cm in diameter and 20 cm in height, those for chloride penetration analysis were 15 cm in diameter and 15 cm in height. The curved surface and one end of each cylinder for chloride penetration were coated with a thick-film epoxy resin to allow chloride ion penetration only from one end.

The reinforced specimens included some with a construction joint (jointed beams) and some with bending cracks (cracked beams) prepared for exposure in experiment III. Jointed beams had a construction joint at mid-length. At 7 days after placement of the first half, the joint surface was wirebrushed to a depth of 0.5 mm or deeper to remove the laitance layer, and the second half with identical mixture proportions was placed. Cracked beams, with four to five pre-formed cracks per beam, were fastened into jigs to maintain the crack width at 0.05 to 0.1 mm at the surface.

Table 4 Mix Proportions and Properties of Fresh Concrete

Symbol	Types of cement	Gmax (mm)	W/C (%)	s/a (%)	Unit weight (kg/m ³)					Fresh concrete	
					W	C	S	G	Ad*	Slump (cm)	Air content (%)
OP	Ordinary portland cement	15	50.0	48.0	166	332	847	935	1.04	12.0	5.0
BB	Type B blast-furnace slag cement				162	324	851	935	1.01	10.5	4.4
SR	Sulfate-resistant portland cement				166	332	849	937	1.04	13.0	4.1

* Ad : air-entraining and water-reducing agent

**Fig.2** Flow of Specimen Preparation

b) Materials and mixture proportions

The following three types of cements were used: ordinary portland cement, Type B blast-furnace slag cement, and sulfate-resistant portland cement. **Table 2** gives the physical properties and chemical compositions of these cements. Land sand and crushed stone were used as the fine and coarse aggregates, respectively, in every experiment. **Table 3** gives the properties of the aggregates. An air-entraining and water-reducing agent containing modified lignosulfonate as the main component was used as a chemical admixture.

Table 4 gives the concrete mixture proportions and the properties of the fresh concrete. Concretes made using ordinary portland cement, Type B blast-furnace slag cement, and sulfate-resistant portland cement are hereafter referred to as “OP,” “BB,” and “SR,” respectively.

Whereas OP, BB, and SR were used in experiments I and II, only OP was used in experiment III. All concretes were proportioned to have a water cement ratio of 50%, a cement content of around 332 kg/m³, a slump of 12.0 ± 1.5 cm, and an air content of 4.5 ± 1.5% in consideration of the maritime conditions.

c) Preparation of specimens

Figure 2 shows the flow of specimen preparation from concrete placing to the beginning of exposure, as well as the curing methods. The specimens were wet-cloth-cured up to an age of 14 days. They were then dried in preparation for epoxy coating on the specified surfaces, air-dried, and exposed to the marine environment at an age of 50 days. Beams to be precracked were loaded at an age of 14 days such that one of the permeable edges formed the tension edge, thus inducing bending cracks. After unloading, pairs of cracked beams were fastened together with jigs as shown in **Fig.1** before being coated on both sides.

2.3 Exposure conditions

The exposure site was a breakwater in Shimizu Harbor, Shizuoka Prefecture. **Figure 3** shows the location of the exposure site. **Figure 4** and **Table 5** indicate the exposure positions of the specimens on

the breakwater and the conditions to which each position was exposed, respectively. The marine environments were three: the splash zone between high and low tide (splash), in the atmosphere and subjected to salt spray only during the strong winds (atmospheric), and in the sea at a depth of 11 m (underwater). An inland site was also selected at a point 30 km from the coastline with little influence from air-borne chloride ions (inland). Whereas specimens were exposed to all four environments (splash-zone, atmospheric, underwater, and inland) in experiments I and III, the environments for experiment II were only atmospheric and underwater.

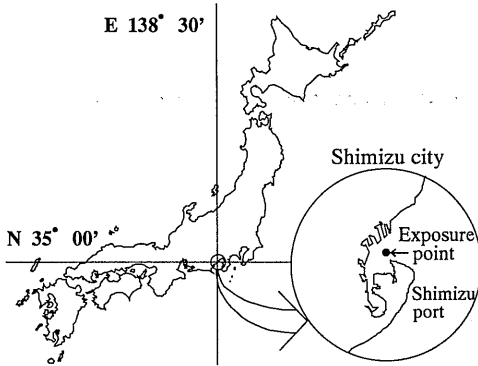


Fig.3 Location of Exposure Site

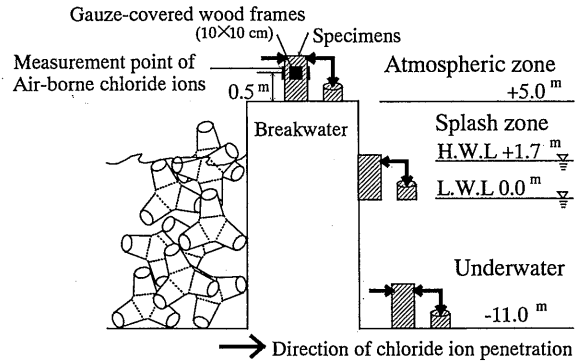


Fig.4 Exposure Positions of Specimens on Breakwater

Table 5 Environmental Conditions of Exposure Positions

Environment	Environmental conditions		
A Splash zone	Between H.W.L (+1.7m) and L.W.L (0.0m)	Level 500m off Shimizu port	
B Atmospheric zone	Zone 5m higher than L.W.L Affected by spindrift and sea breeze		
C Underwater	Depth of seawater	: 11m	Average temperature : 16.0°C Precipitation : 2360mm/year
	Seawater properties :		
	Average temperature	: 18.4°C	
	pH	: 8.29	
	Chloride ion concentration	: 18.4‰	
D Inland	30km from coastline (Kiyose, Tokyo)		
	Average temperature	: 15.3°C	
	Precipitation	: 1460mm/year	

Also set up on the breakwater were a capture vessel for air-borne chloride ions as proposed by the Public Works Research Institute of the Ministry of Construction [9], and four gauze-covered wooden frames. These were positioned 0.5 m above the top of the breakwater, so were in the atmospheric zone. The amounts of air-borne chlorides (NaCl equivalent) from four directions were measured using these devices every month from July through December 1995. The measurements are shown in Fig.5. The values varied widely depending on direction, with the maximum and minimum of the averaged catch over the period in one direction being 1.5 and 0.32 mg/dm²/day, respectively. The average of air-borne chloride ions from all directions over the period was 0.77 mg/dm²/day. The average of air-

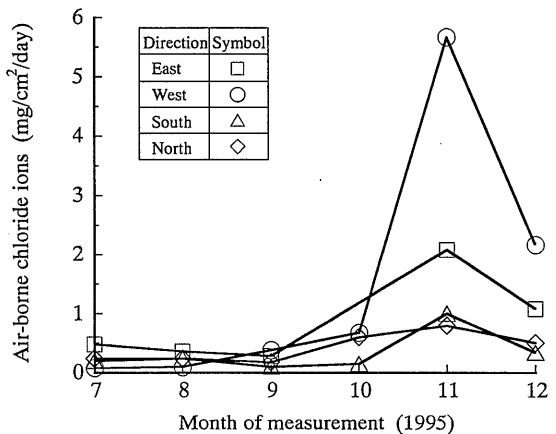


Fig.5 Result of Measurements of Amount of Air-borne Chloride Ions

borne chloride ions from all directions measured using the capture vessel was 0.22 mg/dm²/day.

2.4 Measurements and methods

The measurements made and methods used are given in **Table 6**, and the times of each measurement are given in **Table 7**. Compressive strength and progress of reinforcement corrosion were measured by recovering specimens from the sites at 1, 3, 6, and 10 years of exposure. The chloride ion concentration was quantitatively analyzed in terms of total salts by potentiometric titration with chloride ion-selective electrodes, using concrete drill dust samples from each 2 cm in depth at 1 and 6 months and 1, 2, 3, 4, 6, and 10 years of exposure. The chloride ion concentration was expressed as a percentage by weight of concrete. Corrosion of reinforcing steel was evaluated by cleaving the beams and measuring the ratio of corroded area to total reinforcement surface area.

Table 6 Measurement Items and Methods

Items	Methods
Compressive strength	- Compressive strength test (JIS A 1108) - Specimens : diameter 10cm , length 20cm
Neutralization	Measure the depth of zones uncolored by phenolphthalein solution spray
Chloride ion content	- Quantitative determination of total salts by potentiometric titration with chloride ion-selective electrodes - Sampling of concrete drill dust from each 2cm in depth
Reinforcing bar corrosion	Sketch corroded parts and evaluate percentage corroded area to total reinforcement surface area
Chemical composition	Powder X-ray diffraction analysis
Porosity (pore size distribution)	- Mercury intrusion method by porosimeter - Measurement range of pore diameter : $3.0 \times 10^{-9} \sim 3.0 \times 10^{-5} \text{ m}$

Table 7 Measurement Period

Measurement item	Exposure term							
	1M	6M	1Y	2Y	3Y	4Y	6Y	10Y
Compressive strength			○		○		○	○
Neutralization			○		○		○	○
Chloride ion content	○	○	○	○	○	○	○	○
Reinforcing bar corrosion			○		○		○	○
Chemical composition								○
Porosity								○

2.5 Method of estimating chloride ion penetration

Movement of chloride ions into concrete dose not simply depend on diffusion of chloride ions, but is known to be macroscopically describable as diffusion. Many models have been proposed for chloride ion movement into concrete [5],[10],[11],[12],[13]. When the boundary condition is the chloride ion concentration at the surface (C_0) and is constant, the solution of Fick's diffusion equation can be expressed as Eq. (1). When expressing the movement of chloride ions into concrete in a marine environment using this equation, the diffusion coefficient (D_c) in Eq. (1) takes account of such phenomena as concentration and fixation of chloride ions and suction of water, as these are included in the diffusion phenomenon and are dealt with as macroscopic diffusion. For this reason, this diffusion coefficient is referred to here as the "apparent diffusion coefficient."

In this paper, the movement of chloride ions by means other than diffusion is included in the diffusion phenomenon to simplify the movement of chloride ions as much as possible, thereby grasping the trend in long-term indices of chloride ion movement. The changes in the chloride ion concentration at the surface (C_0) and apparent diffusion coefficient (D_c) in Eq. (1) were investigated for up to 10 years of exposure under these assumptions. C_0 and D_c in Eq. (1) were calculated by the least squares method from the chloride content distribution measured for each exposure period. However, if the penetrability of chloride ions is assumed to change over time, then D_c changes accordingly, and the value of D_c determined in this manner will indicate an average of changing diffusion coefficients over the period from the beginning of exposure to the time of measurement. In other words, the value may reflect the influence of penetrability of chloride ions prior to the time of measurement.

$$C = C_o \left\{ 1 - \operatorname{erf} \left(\frac{x}{2\sqrt{D_c \cdot t}} \right) \right\} \quad (1)$$

where x = depth from the surface (cm)
 t = elapsed time (s)
 C = chloride ion concentration at depth x from the surface (%)
 C_o = chloride ion concentration at the surface ($x = 0$) (%)
 D_c = apparent diffusion coefficient of chloride ions (cm^2/s)
 erf : error function, $\operatorname{erf}(Z) = \frac{2}{\sqrt{\pi}} \cdot \int_0^Z e^{-t^2} \cdot dt$

3. INFLUENCE OF ENVIRONMENTAL CONDITIONS AND CEMENT TYPE ON PROPERTIES OF CONCRETE IN MARINE ENVIRONMENTS

3.1 Influence of exposure conditions

a) Appearance of specimens

Photograph 1 shows the appearance of cylinder specimens exposed to the splash-zone environment for 10 years. Organisms such as shellfish became attached to the splash and submerged specimens, and particularly on splash specimens. Cracks and rust exudations due to reinforcement corrosion were observed on the splash and submerged reinforced specimens, both those with precracks and joints and others. No cracks or rust exudations were observed on atmospheric and inland reinforced specimens. No sign of deterioration was observed in the appearance of any plain concrete specimen in any of the environments.



Photo. 1 Appearance of Cylinder Specimens at 10 Years of Exposure (Splash Zone)

b) Changes in compressive strength

The changes in compressive strength of concrete made using ordinary portland cement (OP) are shown in **Fig. 6**. The compressive strength before exposure (at 50 days) was approximately 45 N/mm^2 . The compressive strength of atmospheric cylinders took nearly the same course over time as standard-cured cylinders, increasing by about 10% after 10 years of exposure. The compressive strength of splash cylinders increased in the first year by about 20% compared with the pre-exposure strength and leveled off thereafter up to 10 years. The compressive strength of submerged cylinders was 10% higher at 3 years of exposure, but was 4% lower at 6 years, and eventually 8% lower at the end of the 10-year test period. Inland cylinders showed few changes in their compressive strength over 10 years.

The compressive strengths of the cylinders in all marine environments except the inland environment were higher than those of standard-cured specimens for up to 3 years. At 10 years of exposure, however, the ratio of compressive strength to that of standard-cured specimens was 1.12, 1.02, 0.83, and 0.89 in the splash, atmospheric, underwater, and inland zones, respectively. This suggests wide-ranging compressive strength changes over time depending on the environment. In addition to the wetness of the site, various other factors are thought to synergistically influence the compressive strength of concrete exposed to a marine environment, including the amount of ettringite formed through reaction with sulfates in the seawater and the amount of calcium leaching into the seawater.

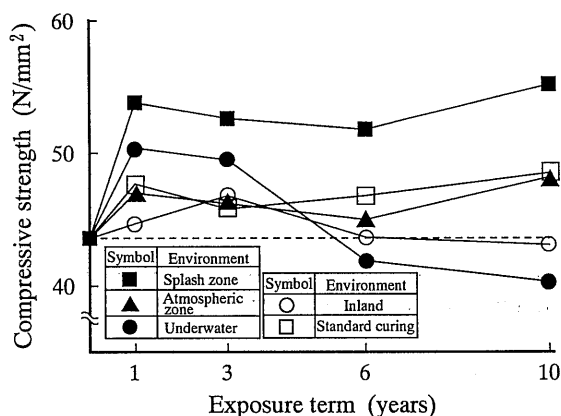


Fig.6 Changes in Compressive Strength over Time

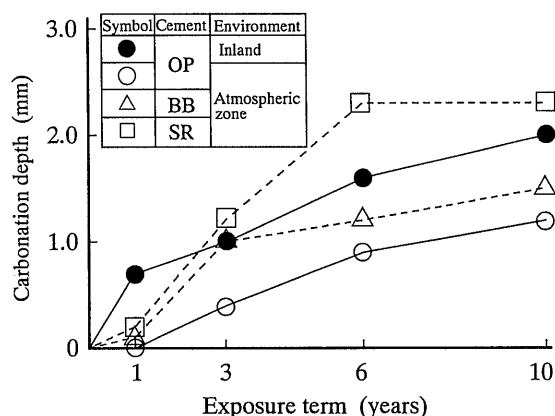


Fig.7 Changes in Carbonation Depth over Time

c) Progress of carbonation

Figure 7 gives the measurements of carbonation depth. At 10 years of exposure, no carbonation was observed in splash and submerged beams, while the carbonation depths of atmospheric beams and inland beams were 1.2 mm and 2.0 mm, respectively. Progress of carbonation may therefore be affected by its wetness. In all environments, alkalinity was maintained at the reinforcement depth (2 to 4 cm in depth).

d) Powder X-ray diffraction analysis

Figure 8 shows the results of powder X-ray diffraction analysis of OP specimens after 10 years of exposure in the four environments. A comparison of the X-ray diffraction intensities of calcium hydroxide (Ca(OH)_2) in the surface range (0 to 2 cm in depth) shows that intensities for splash and underwater specimens are lower than those for atmospheric and inland specimens. This suggests leaching of Ca(OH)_2 from near the surface of splash and underwater specimens into the sea. When exposed to the underwater environment, leaching of Ca(OH)_2 can be expected to cause losses in compressive strength. The tendencies exhibited by underwater specimens were also observed in splash specimens, but Friedel's salt was detected near the surface (within 2 cm of the exposed surface). Ettringite was not clearly detected in any of the environments.

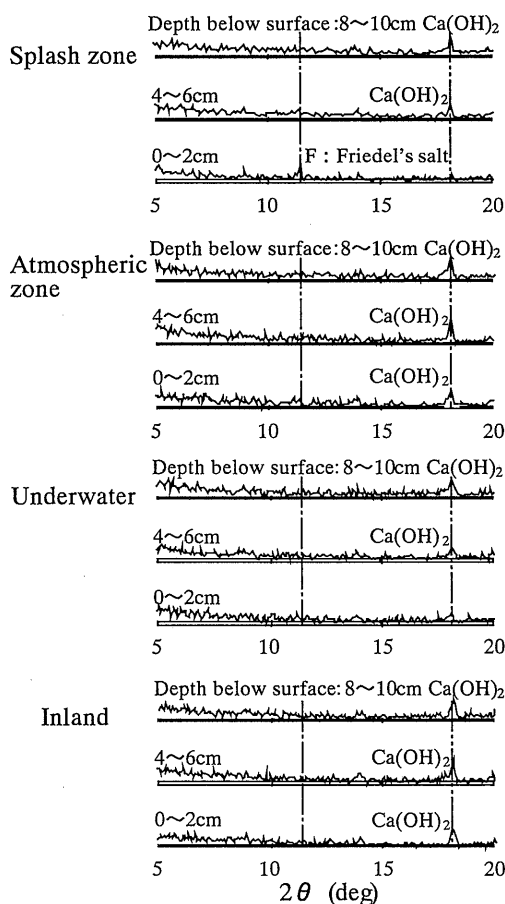


Fig.8 Result of Powder X-ray Diffraction Analysis (OP, after 10 Years of Exposure)

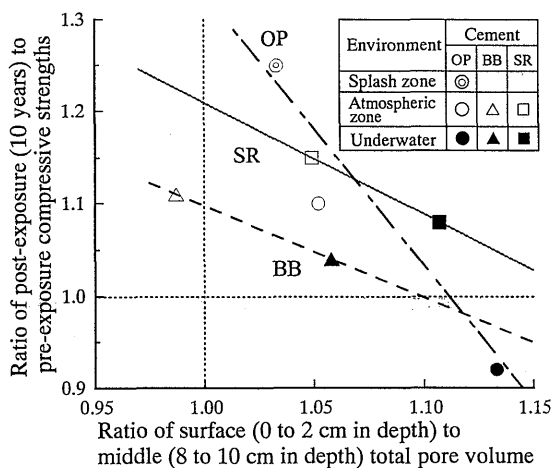


Fig.9. Relationship between Ratio of Surface to Middle Total Pore Volume and Ratio of Post-exposure to Pre-exposure Compressive Strength

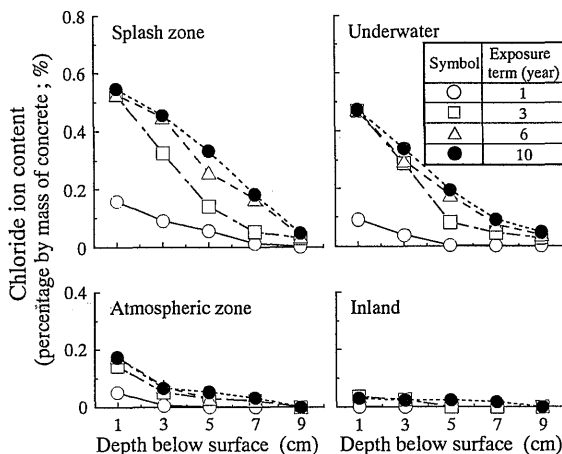


Fig.10 Changes in Chloride Ion Content Distribution Over 10 Years (OP)

e) Pore volume

Figure 9 shows the relationship between surface (0 to 2 cm in depth) to middle (8 to 10 cm in depth) total pore volume and the ratio of post-exposure (10 years) to pre-exposure compressive strength. The total pore volume refers to the total volume of pores $30\text{ \AA}$ to $30\text{ }\mu\text{m}$ in equivalent diameter. The total pore volume near the surface tended to be larger than that in the middle for all cement types. This tendency was more evident in underwater specimens than in atmospheric specimens. Submerged OP specimens exhibited a total pore volume 13% larger near the surface than in the middle. In the case of OP specimens in the splash and atmospheric zones, the differences were 3% and 5%, respectively. This may be because $\text{Ca}(\text{OH})_2$ in the concrete exposed to seawater leached into the seawater, increasing the total pore volume near the surface. According to this X-ray diffraction analysis, leaching of $\text{Ca}(\text{OH})_2$ from concrete also takes place in specimens in the splash zone, but the difference between the total pore volume near the surface and that at 8-10 cm in depth is inappreciable. This may be affected by the fact that shellfish and other organisms cling to concrete surfaces in the splash zone, filling relatively large pores of specimens.

The compressive strength ratio after 10 years of exposure decreased more significantly as the surface-to-middle total pore volume ratio increased. The pore volume measurements also suggest that $\text{Ca}(\text{OH})_2$ loss has an effect on the compressive strength loss of submerged specimens.

f) Changes in chloride ion content over time

The changes in the distribution of chloride ion content (as a percentage of mass of concrete) over 10 years are compared among the four environments in **Fig. 10**. At any time during the period, the chloride ion content was the highest in the splash zone, followed by the underwater and atmospheric environments. **Figure 11** shows the distribution of increments in chloride ion content with depth from the exposed surface during four time spans: from the beginning to 1 year, from 1 to 3 years, from 3 to 6 years and from 6 to 10 years. Up to 3 year, the increments near the surface (0-3cm) are relatively high, but the increments in the deeper range became relatively large there after.

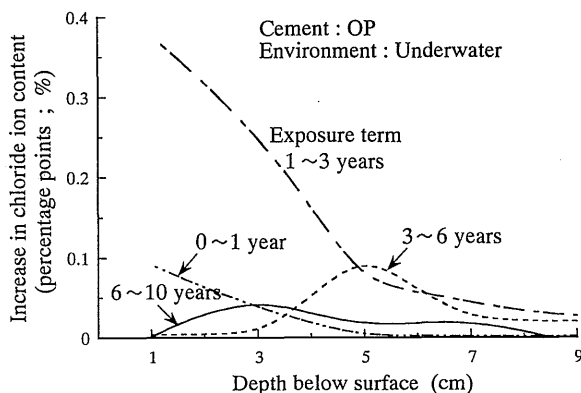


Fig.11 Distribution of Increase in Chloride Ion Content (OP)

Figure 12 shows the surface chloride ion concentration (Co) calculated from the measurements using Eq. (1) as well as approximation curves. In all environments, the surface chloride ion concentration increases with time up to an exposure period of 3 years and levels off thereafter. When exposed to the splash zone, the surface chloride ion concentration at 10 years was 0.70% by mass of concrete (around 16 kg/m^3), whereas for underwater and atmospheric specimens the figures were 0.57% (around 14 kg/m^3) and 0.22% (around 5 kg/m^3), respectively.

The time-related changes in surface chloride ion concentration were approximated using Eq. (2). In this approximation equation, the ultimate surface chloride ion concentration (Co^*) and coefficient α for each environment are the values indicated in **Fig. 12**. The ultimate surface chloride ion concentration (Co^*) was highest in the splash zone, followed by the underwater and atmospheric zones. These results are similar to those reported by Sugiyama et al [14]. The differences in coefficient α with environment were relatively small. As in past reports [8],[15],[16], these experiments also confirmed the strong correlation between environment and surface chloride ion concentration.

$$Co(t) = Co^* (1 - \exp^{-\alpha \cdot t}) \quad (2)$$

where $Co(t)$ = surface chloride ion concentration after an exposure period of t years (%)
 Co^* = ultimate surface chloride ion concentration (%)
 α = coefficient
 t = exposure period (years)

Figure 13 shows the changes in apparent diffusion coefficient (Dc) over time, as determined similarly to the case of Co and the approximation curves. The apparent diffusion coefficient of chloride ions diminishes with time in all environments. The fall in the first 3 years tends to be large, but becomes more moderate thereafter. The apparent diffusion coefficients after a 10-year exposure period were $7 \times 10^{-8} \text{ cm}^2/\text{s}$, $4.3 \times 10^{-8} \text{ cm}^2/\text{s}$, and $2.4 \times 10^{-8} \text{ cm}^2/\text{s}$ in the splash, underwater, and atmospheric zones, respectively, so the fastest rate of penetration of chloride ions is in the splash zone, followed by the underwater and atmospheric zones.

X-ray diffraction analysis and pore volume measurements revealed the leaching of Ca(OH)_2 and a large increase in total pore volume near the surface of underwater specimens, suggesting that the concrete surface has a porous microstructure. However, the chloride ion penetration was found to be lower than in the splash zone. This may be because more chloride ions penetrate into concrete in the splash zone than in the seawater under the influence of effects other than diffusion, such as cyclic drying and wetting due to tidal wetting and the impact of chloride ions against the concrete surface caused by waves. This leads to a higher apparent diffusion coefficient in the splash zone.

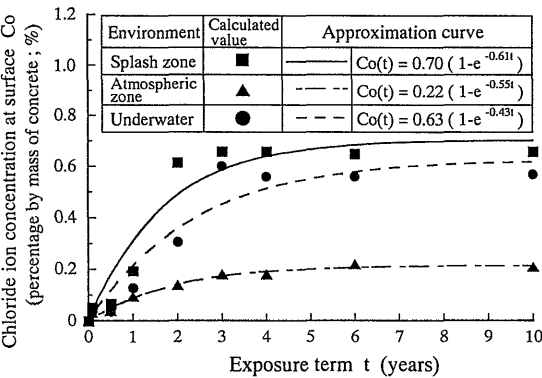


Fig.12 Changes in Surface Chloride Ion Concentration over Time and Approximation Curves (OP)

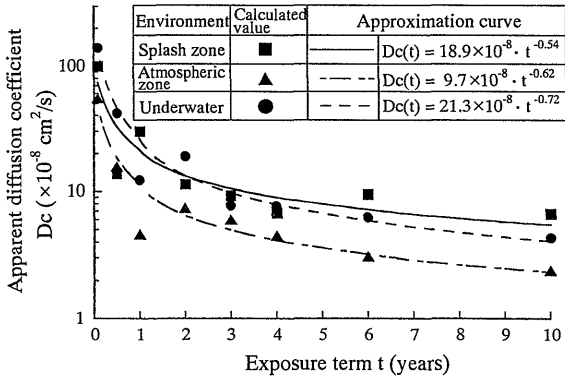


Fig.13 Changes in Apparent Diffusion Coefficient over Time and the Approximation Curves (OP)

The changes in apparent diffusion coefficient over time were approximated using Eq. (3). In this approximation expressing time-related changes in apparent diffusion coefficient, coefficients D_c^* and β for each environment are the values shown in Fig. 13. Over a long period, the apparent diffusion coefficient approaches a limit value, and this is highest in the splash zone, followed by the underwater and atmospheric zones. This suggests that the environment also affects apparent diffusion in concrete. The tendency of the apparent diffusion coefficient to fall over time has been reported in past studies [8],[14],[17],[18]. This may be attributed to the high penetration of chloride ions at an early stage in marine environments and the increase in the denseness of the concrete microstructure over time.

$$D_c(t) = D_c^* \cdot t^{-\beta} \quad (3)$$

where $D_c(t)$ = apparent diffusion coefficient after an exposure period of t years (cm^2/s)
 D_c^* = coefficient
 β = coefficient
 t = exposure period (years)

Accordingly, the surface chloride ion concentration and apparent diffusion coefficient are strongly affected by environmental conditions. Also, these values can be approximated by Equations (2) and (3), and can be estimated to a certain extent if the exposure periods and environmental conditions are known. For a more accurate estimation, the water-cement ratio and curing temperature should also be taken into account.

g) Progress of reinforcement corrosion

Figure 14 shows the state of corrosion of the reinforcing steel in RC specimens without precracks or construction joints after an exposure period of 10 years. The ratio of corroded area at 10 years was highest in splash zone specimens, followed by underwater and atmospheric specimens. Corrosion was limited to the surface of the reinforcement in all environments, and no pitting corrosion was observed. The changes in reinforcement corrosion ratio over an exposure period of 10 years are shown in Fig. 15. In the splash zone, corrosion was first observed after an exposure period of 1 year and it increased over time until the corrosion ratio reached more than 25% after 10 years. In submerged specimens, corrosion first appeared at 3 years but scarcely increased up to 10 years. In the atmospheric specimens, corrosion was observed for the first time after a period of 10 years.

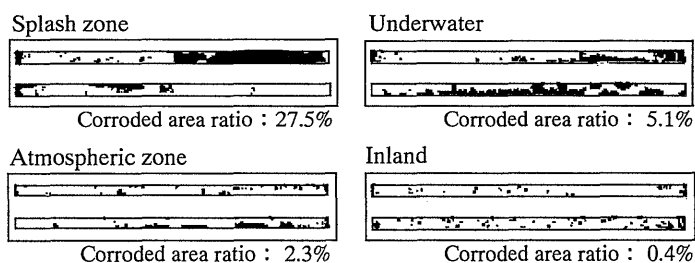


Fig.14 State of Corrosion of Reinforcing Steel after 10 Years of Exposure

Figure 16 shows changes in the chloride ion content at the depth of the reinforcement (2 to 4 cm below the surface). In all environments, the chloride ion content at this depth scarcely increased after the first 3 years of exposure. Chloride contents at the reinforcement after 10 years were 0.06% (around 1 kg/m^3), 0.34% (around 8 kg/m^3), and 0.46% (around 10 kg/m^3) by mass of concrete in the atmospheric, underwater, and splash zones, respectively.

The chloride ion penetration rate and oxygen supply are said to affect the onset and progress of corrosion. As shown in Fig.15, it was confirmed in this experiment that corrosion progresses more rapidly in the splash zone, where both are high, than in the air and underwater. The corrosion ratio in

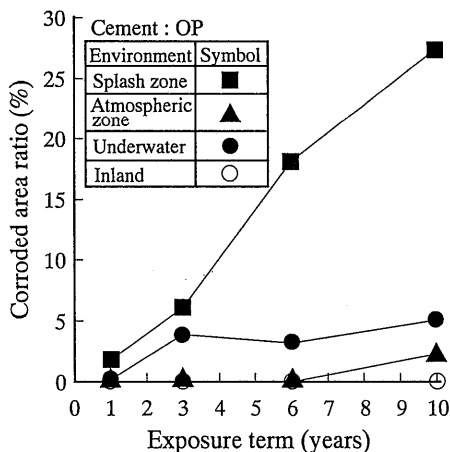


Fig.15 Changes in Corroded Area Ratio of Reinforcement over Time

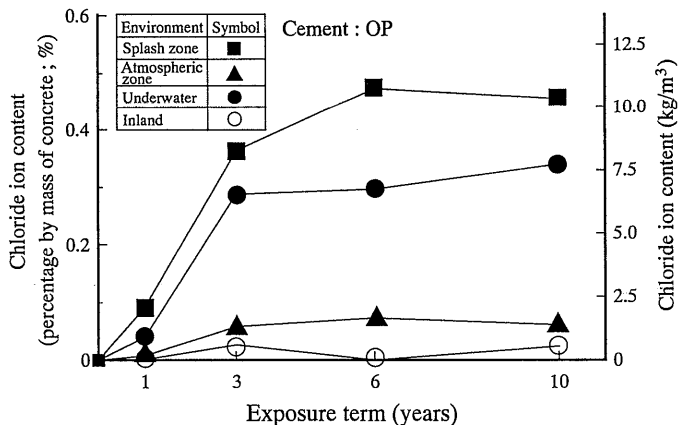


Fig.16 Changes in Chloride Ion Content at Reinforcement Depth over Time

atmospheric specimens was as low as 2% after an exposure period of 10 years, though more than 1.2 kg/m³ of chloride ions had been present near the reinforcement after the first 3 years.

In the marine environments studied in these experiments, reinforcement corrosion was most intense in the splash-zone specimens up to an exposure period of 10 years, followed by underwater and atmospheric specimens. Reinforcement corrosion in submerged specimens started early due to the high chloride ion content, but the low oxygen supply inhibited its propagation. The time to onset of reinforcement corrosion in atmospheric specimens was long, but the high oxygen supply may lead to a higher rate of corrosion than in submerged specimens for exposure periods over 10 years.

3.2 Effects of cement type

a) Compressive strength

Figure 17 shows the time-related changes in compressive strength of concretes made using OP, SR, and BB cements. When submerged, SR and BB specimens began to lose compressive strength after the first 3 years as in the case of OP specimens, but at 10 years, they were both 5% higher than the values before exposure. The loss in compressive strength of submerged SR and BB specimens was less than that of OP specimens.

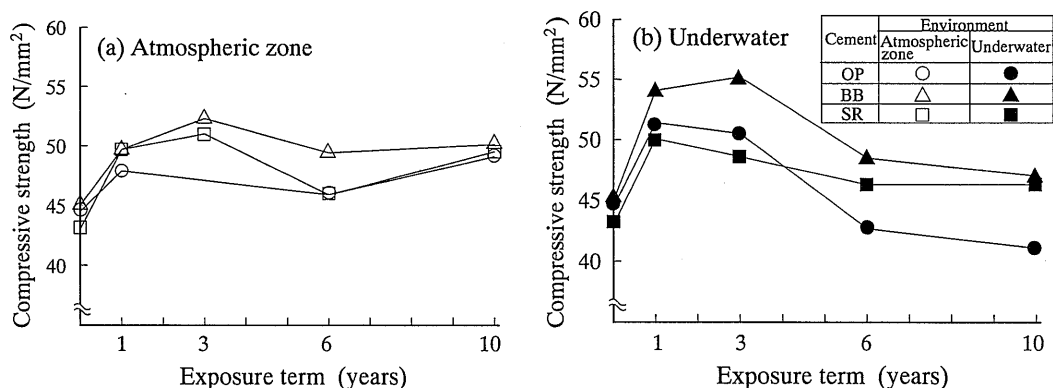


Fig.17 Time-related Changes in Compressive Strength of Concrete Made with Different Cements

b) Pore volume measurement and powder X-ray diffraction

As shown in **Fig. 9**, the total pore volume of SR and BB specimens submerged for 10 years was higher near the surface (2 cm from the surface) than in the middle (8 to 10 cm below the surface) by approximately 10% and 5% in SR and BB specimens, respectively. Whereas the total pore volume of SR specimens showed a similar tendency to that of OP specimens, BB specimens exhibited small losses in total pore volume, as their low initial $\text{Ca}(\text{OH})_2$ content limits the leaching of $\text{Ca}(\text{OH})_2$. This presumably explains the smaller fall in compressive strength than with OP and SR specimens.

Powder X-diffraction revealed that the diffraction intensities of $\text{Ca}(\text{OH})_2$ near the surface (0 to 2 cm in depth) of SR and BB specimens submerged for 10 years were low, as with OP specimens, suggesting that it leached into the sea.

c) Chloride ion penetration

Figure 18 shows the state of chloride ion penetration in specimens made with different cements and exposed to the marine atmosphere or seawater. Similarly to OP specimens, the chloride ion contents in SR and BB specimens were higher in submerged specimens than in specimens exposed to marine air. In the sea, the chloride ion content in BB specimens was higher than that in OP specimens near the surface, but lower beyond 3 cm below the surface. The chloride ion distribution in SR specimens was similar to that in OP specimens in all environments.

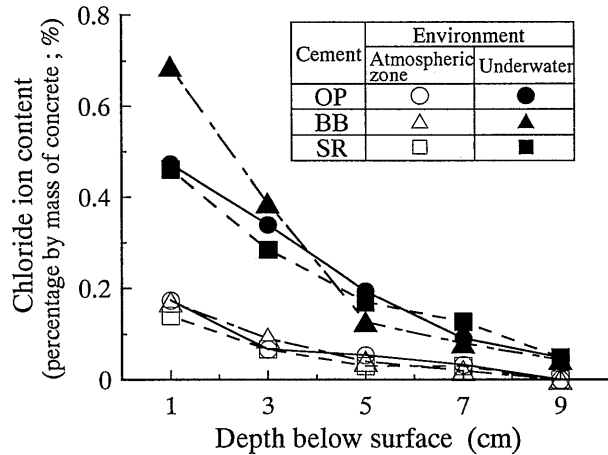


Fig.18 Chloride Ion Penetration of Concretes Made with Different Cements

Figures 19 and 20 show the time-related surface chloride ion concentration and apparent diffusion coefficient with approximation curves, respectively, determined from the distribution of chloride ion content using Eq. (1). All cements exhibited small changes in surface chloride ion concentration after the first 3 years of exposure. When exposed to marine air, no marked differences were observed between cement types with regard to surface chloride ion concentration at 10 years. When submerged, however, the surface chloride ion concentration in BB specimens was 0.95% (around 21 kg/m^3), whereas that of OP and SR was 0.60% (around 14 kg/m^3). The apparent diffusion coefficient of all cement types diminished over time. SR specimens exhibited apparent diffusion coefficients similar to OP specimens up to 10 years both in marine air and underwater. The apparent diffusion coefficients of BB specimens were similar to OP specimens in the air, but these were lower when submerged, illustrating BB's effect of inhibiting chloride ion penetration throughout the exposure period.

d) Reinforcement corrosion

Figure 21 shows the time-related changes in chloride ion content at the reinforcement depth in specimens containing different cements. The cement type had no appreciable effect on chloride ion content in atmospheric specimens. In the sea, the chloride ion concentration near the reinforcement in OP and SR specimens leveled off after the first 3 years, but that of BB specimens continued to gradually increase thereafter.

Figure 22 shows the changes in ratio of corroded area over time in concretes made of different cements. Corrosion in submerged BB specimens commenced later than in OP specimens, and its area was found to be smaller than in OP specimens after 10 years. The corrosion ratio of submerged SR specimens was smaller than that of OP specimens up to 6 years, but converged at 10 years. In the atmospheric environment, no appreciable differences in corrosion ratios by cement type were observed after

exposure for 10 years. In other words, within the range of experimental exposure, BB had a certain inhibiting effect on reinforcement corrosion in submerged specimens when compared with OP, whereas SR was similar to OP in terms of corrosion-inhibiting effect.

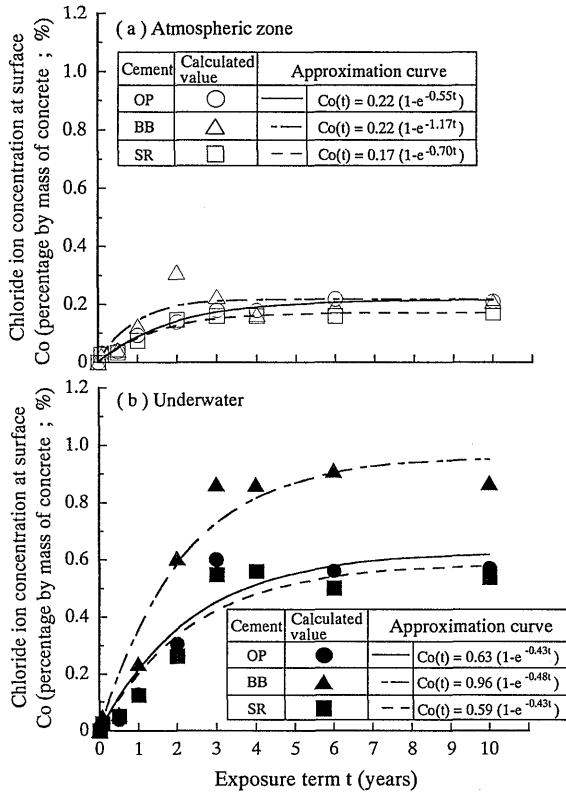


Fig.19 Time-related Surface Chloride Ion Concentration with Approximation Curves for Concretes Made with Different Cements

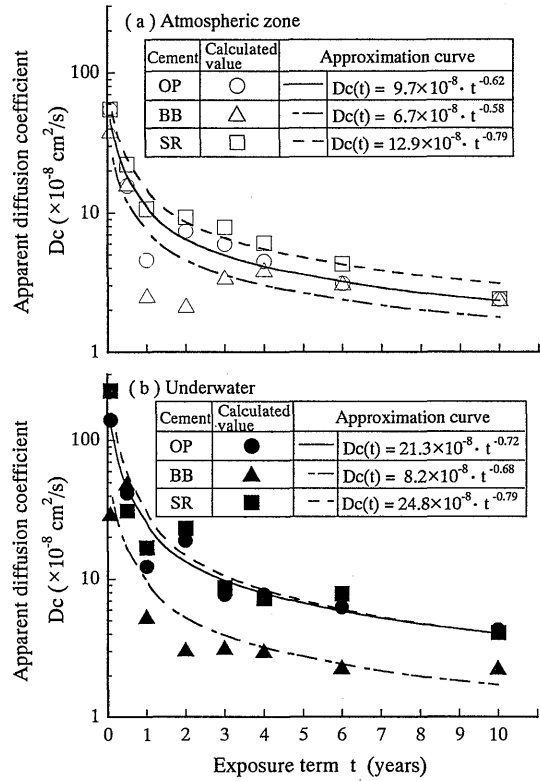


Fig.20 Time-related Apparent Diffusion Coefficient with Approximation Curves for Concretes Made with Different Cements

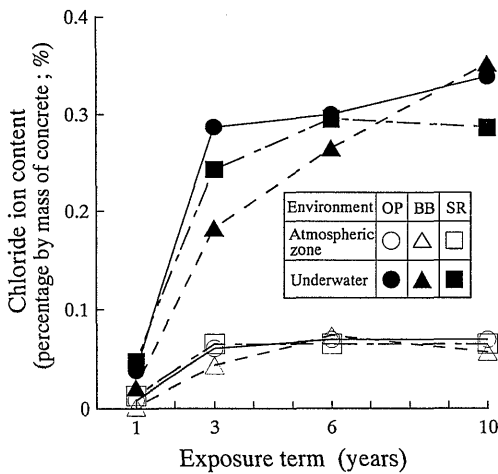


Fig.21 Time-related Changes in Chloride Ion Content at Reinforcement Depth in Specimens Containing Different Cements

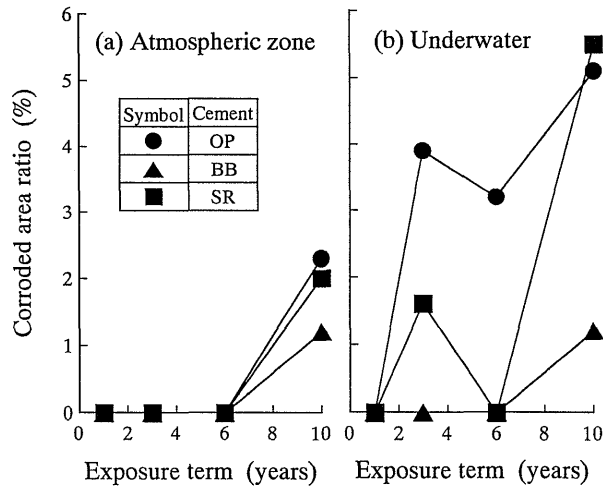


Fig.22 Changes in Corroded Area Ratio Over Time in Concretes Made with Different Cements

4. INVESTIGATION INTO METHODS OF ESTIMATING CHLORIDE ION CONTENT AND REINFORCEMENT CORROSION

4.1 Estimation of chloride ion content

If the apparent diffusion coefficient in Fick's diffusion equation were constant and independent of time, then concrete's resistance to chloride penetration would not change over time. However, the apparent diffusion coefficient evidently changes with time, as described in the previous chapter. Concrete's chloride penetration properties are therefore variable with time. The apparent diffusion coefficient calculated from the accumulation amount of chloride ions in the concrete after, say, exposure for 10 years does not represent a property of the concrete at the 10 year point, but is rather an averaged property for the period. As noted in Chapter 2, the apparent diffusion coefficient thus determined will include the effect of chloride ion penetrability prior to measuring the chloride ion content, including the early stage during which chloride ions penetrate rapidly into the concrete.

Figure 23 shows the chloride ion content distribution in OP specimens exposed to the underwater environment for 10 years as estimated from the surface chloride ion concentration (C_o) and the apparent diffusion coefficient (D_c) obtained at 1, 3, 6, and 10 years using Eq. (2) and (3), respectively. Whereas the estimated chloride ion distribution differs widely from the measured values when using C_o and D_c data obtained at 1 or 3 years, it agrees better with the measured values when using the data obtained at 6 years. This is because, when calculated using Eq. (2) and (3), C_o is lower and D_c is higher before 6 years than the values at 10 years, as shown in **Figs. 12 and 13**, but these values converge at around 6 years and thereafter.

Figure 24 shows the chloride ion distribution at 1, 3, 6, and 10 years as estimated from C_o and D_c data obtained at 10 years. The small C_o value at 1 year led to a large error between the estimated and measured values. At 3 to 6 years, the estimated chloride ion content was lower than the measured values, due to the D_c values being smaller than the actual values.

These results indicate that the accuracy of estimation can be improved by using C_o and D_c values obtained after exposure for the longest possible time span. Conversely, D_c obtained from a long-term experiment may lead to underestimation of the earlier chloride penetration.

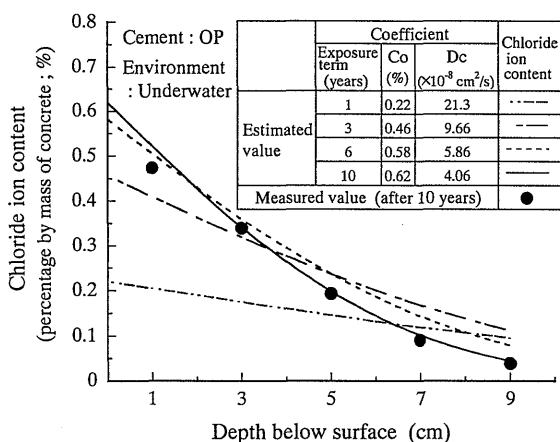


Fig.23 Chloride Ion Distribution at 10 Years Estimated from the C_o and D_c Data Obtained at 1,2,3,6, and 10 Years

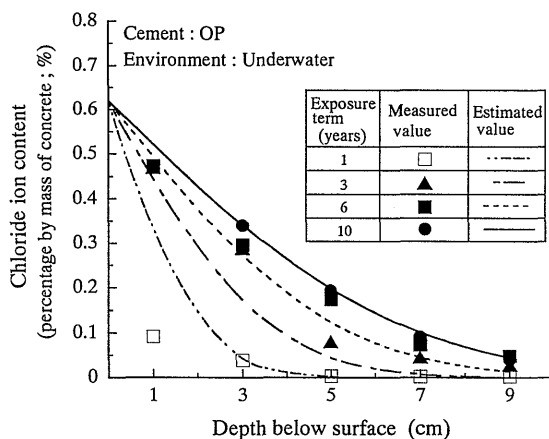


Fig.24 Chloride Ion Distribution at 1,3,6, and 10 Years Estimated from C_o and D_c Data Obtained at 10 Years

In actual practice, a surface chloride ion concentration and apparent diffusion coefficient obtained from an experiment over 5 to 6 years appears to be adequate for estimating chloride ion penetration after a relatively long exposure period of more than 10 years, as the values have nearly converged by this time and the resulting estimate falls on the safe side.

Figure 25 shows the chloride ion distribution in concrete made using OP and BB after exposure periods of 50 and 100 years as estimated using the above-mentioned equations for estimating C_o and D_c . When BB is used for a typical underwater marine structure in which the reinforcement cover is 75 to 100 mm, it is estimated that the chloride ion content is held to a low level at near the reinforcement even after 100 years, and that the chloride content is lower than with OP.

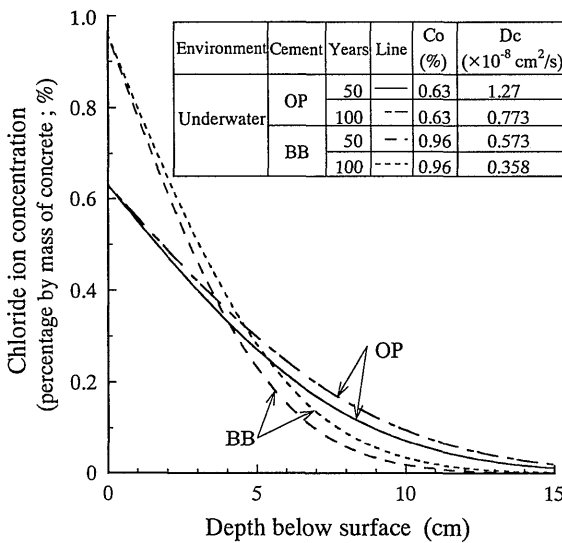


Fig.25 Estimated Chloride Ion Distribution after Exposure for 50 and 100 Years

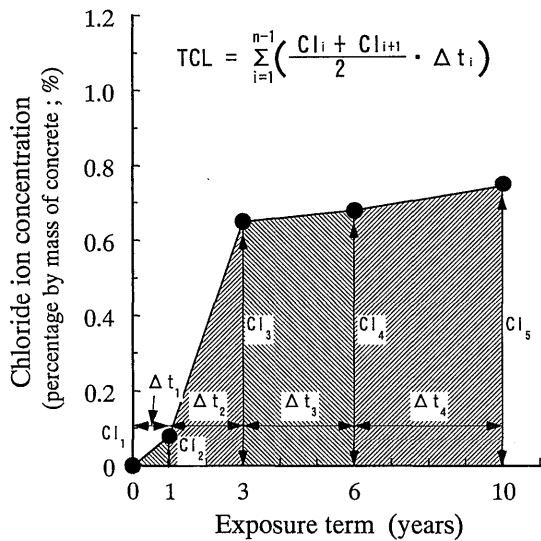


Fig.26 Calculation Method for Total Chloride Ion Factor (TCL)

4.2 Estimation of corroded area of reinforcement

The ratio of reinforcement corroded area in concrete exposed to the splash-zone environment for 10 years was around 25%, and there was no marked profile loss. Nevertheless, corrosion-induced cracks were observed. It follows that even a relatively small corroded area ratio can threaten the durability of reinforced concrete. The authors therefore attempted to estimate the reinforcement corrosion ratio as an index of the durability of reinforced concrete.

As shown in the previous chapter, reinforcement corrosion can propagate even while the chloride ion content at reinforcement depth scarcely increases. This suggests that the degree of corrosion cannot simply be estimated from the chloride ion content at a certain time. Though oxygen supply should be taken into consideration, the environmental conditions selected for this study were limited, and the water-cement ratio was equalized to estimate the corroded area. As shown in **Fig. 26**, the sum of the products of the mean chloride ion content near the reinforcement multiplied by the exposure period calculated at yearly measurements is defined as the total chloride ion factor (TCL), and is calculated using Eq. (4).

$$TCL = \sum_{i=1}^{n-1} \left(\frac{Cl_i + Cl_{i+1}}{2} \cdot \Delta t_i \right) \quad (4)$$

where TCL = total chloride ion factor (%·year)
 Cl_i = measured chloride ion content at i -th time increment (%)
 Δt_i = time interval between measurements at i -th and $(i+1)$ th time increment (years)
 n = number of measurements of chloride ion content

Figure 27 shows the relationship between total chloride ion factor and corroded area ratio for concretes made with different cements. In the case of OP, the total chloride ion factor at the reinforcement depth in the splash and underwater zones is 7 times and 5 times that in the atmospheric zone, respectively, after an exposure period of 10 years. A linear relationship is observed between total chloride ion factor and corroded area ratio for each environment. As the total chloride ion factor increases, the corroded area ratio exhibits an increasing tendency. Corroded area ratios of up to 30% can be estimated to a degree from the total chloride ion factor, if the environmental conditions are known.

In the splash zone, the same total chloride ion factor leads to a higher corroded area ratio than underwater. This suggests a strong effect of oxygen supply on corrosion propagation. Despite the high oxygen supply, corrosion is retarded in the marine atmosphere due to the low total chloride ion factor.

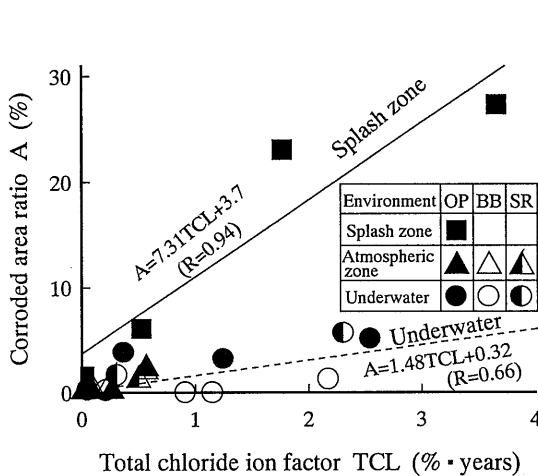


Fig.27 Relationship between Total Chloride Ion Factor and Corroded Area Ratio

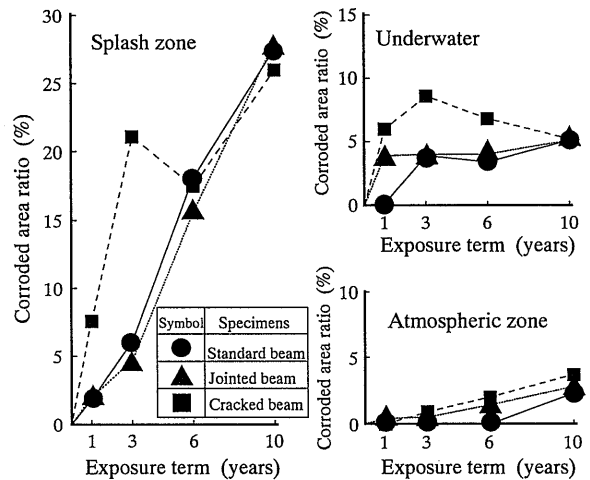


Fig.28 Time-related Changes in Corroded Area Ratio in Specimens with Cracks or Construction Joints

5. EFFECTS OF CRACKS AND CONSTRUCTION JOINTS ON REINFORCEMENT CORROSION

Figure 28 shows the time-related changes in corroded area ratio for specimens with induced cracks and construction joints. The state of reinforcement corrosion in cracked specimens after exposure for 10 years is shown in **Fig. 29**. Corrosion in cracked beams in the splash and underwater zones began earlier than in uncracked beams, but eventually led to corrosion ratios similar to those of cracked beams at 10

years. When the initial crack width was 0.05 to 0.1 mm, the cracks did not significantly accelerate corrosion up to 10 years in any of the environments in this experiment.

Figure 30 shows the state of reinforcement corrosion at 10 years in beams having a construction joint. Corrosion tended to start at the joint in all environments and was concentrated near the joint up to 6 years. By 10 years, however, corrosion had propagated to other parts of the reinforcement. Nevertheless, the corroded area ratio of beams with a construction joint was similar to that of monolithic beams at 10 years in all environments. Accordingly, properly treated construction joints may not significantly accelerate corrosion in marine environments.

Over a 10-year exposure period, the splash zone is the harshest environment for concrete with minute cracks 0.05 to 0.1 mm in width or properly treated construction joints, followed by the underwater and atmospheric environments. In this respect, cracked and jointed concrete is similar to plain reinforced concrete.

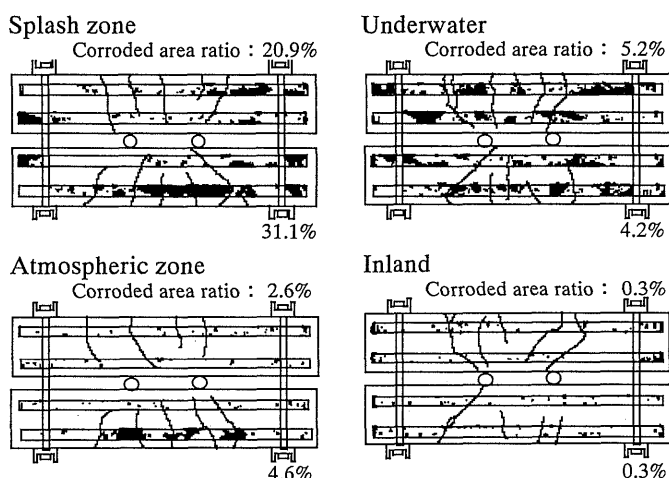


Fig.29 State of Reinforcement Corrosion in Cracked Beams at 10 Years

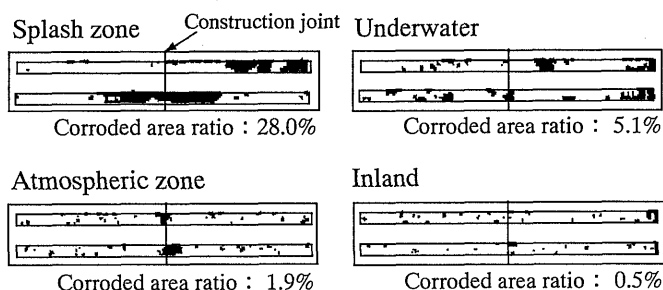


Fig.30 State of Reinforcement Corrosion in Beams with Construction Joint at 10 Years

6. CONCLUSION

Concretes made using different types of cement and also concrete samples with induced cracks and construction joints, were exposed to various marine environments for 10 years. An investigation of

these concrete revealed the following:

- (1) Whereas the compressive strength of concrete scarcely changed in the marine atmosphere over an exposure period of 10 years, that of submerged concretes tended to decrease after the first 3 years.
- (2) In the marine environments selected for these experiments, the rate of chloride ion penetration was highest in the splash zone, followed by the underwater and atmospheric zones.
- (3) In the marine environments selected for these experiments, the rate of reinforcement corrosion propagation was highest in the splash zone, followed by the underwater and atmospheric zones.
- (4) Type B blast-furnace slag cement was found to inhibit chloride ion penetration when compared with ordinary portland cement. When the same concentration of chloride ions was present in submerged specimens, the propagation of reinforcement corrosion was slower in specimens made with Type B blast-furnace slag cement than in specimens made with ordinary portland cement.
- (5) The surface chloride ion concentration in the diffusion equation tends to increase over time, while the apparent diffusion coefficient of chloride ions tends to decrease. However, these changes become less significant after the first 3 years. Both surface chloride ion concentration and apparent diffusion coefficient are strongly affected by environmental conditions.
- (6) Changes in the surface chloride ion concentration and apparent diffusion coefficient of chloride ions can be predicted using approximation equations. Long-term chloride ion content is roughly predictable from the surface chloride ion concentration and the apparent diffusion coefficient if the type of marine environment and cement type are taken into account.
- (7) The ratio of reinforcement corrosion was found to correlate with the product of chloride ion content and time in each environment. Corroded area ratios of up to 30% may be estimated to a certain degree using this index.
- (8) It is considered that properly treated construction joints and cracks of up to 0.1 mm in width do not significantly accelerate corrosion of reinforcement in any marine environment.

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