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9. A Study on the Durability of Concrete Exposed in Marine Environment for 20 Years

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Synopsis

In this study, long term durability of marine concrete is investigated. This study was started in 1970 at Port and Harbour Research Institute, Ministry of Transport, Japan. Many specimens with several different factors, such as type of cement, mixing water and cover thickness of reinforcing steel in concrete, were fabricated and exposed under marine environment. During 20 years' exposure, several properties of concrete and reinforcing steel have been tested both chemically and physically. From the test results, several important conclusions were derived. In this paper, some findings from a series of tests are presented.

Key Words: Concrete, durability, marine environment, corrosion of reinforcing steel, mixing water

9. 海洋環境に20年間暴露されたコンクリート耐久性に関する研究

福 手 　 勤・濱 田 秀 則

要　旨

　　海水の作用を長時間受けるコンクリートにおいて，セメントや練りまぜ水の種類の違いがコンクリートの強度特性，化学組成，鉄筋の腐食特性などに及ぼす影響について調べることを目的として，各種コンクリート供試体を製作し，わが国の一般的な海洋環境と考えられる久里浜湾において20年間の暴露試験を実施した。本研究は，暴露試験の結果に，物理的，化学的，電気化学的な考察を加えてとりまとめたものである。

キーワード：コンクリート，耐久性，海洋環境，鉄筋の腐食，練りまぜ水

Contents

1. Introduction

Unexpectedly early deterioration of concrete structures which have been believed to have semi-permanent durability has often been reported; it is becoming a serious social problem. As the main reasons of the early deterioration of concrete structures, the following reasons are pointed out: the use of insufficiently clean sea sand, the use of an admixture containing high content of salt, alkali aggregate reactions, insufficient construction control, etc.

Therefore, materials for concrete are severely regulated by Japan Society of Civil Engineers (JSCE), Architectural Institute of Japan, Japanese Industrial Standard (JIS) and so on.

Against the corrosion of the reinforcement in concrete structures, such as harbour structures and marine structures which are influenced significantly by salt, more care is necessary than in general land structures [1], [2]. For the deterioration of concrete caused by sulfate contained in seawater, care is also necessary. In order to make clear the phenomenon and to confirm the validity of the countermeasures, long-term continuous survey is required, since the corrosion and the deterioration phenomenon progress gradually with time.

As examples of long-term systematic tests on the durability of concrete exposed to marine environments, experiments performed by the Norway Institute of Technology in Trondheim Bay, Norway, since 1936 [3] and by the Corps of Engineers in Treat Island, Maine, U.S.A. [4] are well-known In Japan, when the breakwater in the Port of Otaru, Hokkaido, was constructed in 1896, Dr. Isamu Hiroi made many mortar test specimens; they have been kept in seawater, tap water and air, and the changes in their strength have been surveyed for nearly 100 years [5], [6]. Since all of them have been maintained and controlled steadily for a ling time, they have contributed valuable information to the researchers of concrete durability.

As for existing long-term exposure tests, since the techniques of investigating the effects of internal and external chloride on the durability of concrete and of the electrochemical characteristics of reinforcement have only recently been established, these subjects have been little discussed.

In 1970, the Port and Harbour Research Institute (PHRI), Ministry of Transport, Japan, started exposure tests of various concrete test specimens in Kurihama Bay, which can be considered to exhibit a typical environmental condition in Japan. During these twenty years, the effects of type of cement as well as mixing water on the long-term strength characteristics of concrete, chemical composition of concrete and corrosion characteristics of reinforcement have been surveyed. This research entails physical, chemical and electrochemical consideration of the test results up to 20 years. Some parts of the test results up to 5 and 10 years were reported in the reference [7] and [8].

2. Environmental Condition of Exposure Site for Specimens

As for the exposure environment, a tidal zone, which has more serious impication than a submerged zone with respect to concrete deterioration, was selected. For the actual exposure, a tidal pool in PHRI which can simulate tidal movement was used. The tidal pool is supplied with seawater and drained by a pump twice a day, and the tide movement is simulated based on a 1.5 m tidal range. The seawater in the tidal

pool is pumped up from Kurihama Bay contiguous to Tokyo Bay; the average temperature of the seawater is about 24°C in the summer and about 8°C in the winter. The test specimens were set up within the scope of L.W.L. ± 0~1.3 m. The test specimens are not splashed in the pool.

3. Preparation of Test Specimens

(1) Materials Used

Seven types of cement, namely, ordinary portland cement (symbol: N0, N2), high early strength portland cement (H0), moderate heat portland cement (M0), blast furnace slag cement B-class in JIS R 5211 (B0, B2) and aluminous cement (AL), were used. As for the N0, H0, M0 and B0, the three brand cements on the market are mixed in equal quantities respectively. In the N2 and B2, the quantity of gypsum phosphate of 2% by weight of sulfur trioxide (SO_3) was added to the N0 and B0 respectively [9]. The AL was on the market. **Tables 1~3** show the chemical composition and physical test results of the cement. The SO_3 quantities of the N2 and B2 exceed the quality standard of JIS R 5210 and 5211.

Since one of the subjects of the research is the evaluation of the durability of

Table 1 Chemical component of cement

cement	igloss (%)	insol. (%)	Al_2O_3 (%)	Fe_2O_3 (%)	S_iO_2 (%)	CaO (%)	MgO (%)	SO_3 (%)	Na_2O (%)	K_2O (%)	S (%)	fcao (%)
N0	0.8	0.3	5.5	3.1	21.7	64.7	1.3	2.0	0.30	0.57	—	0.9
N2	1.7	0.3	5.2	2.9	20.7	63.3	1.2	3.9	0.27	0.56	—	0.9
H0	1.1	0.5	5.2	2.7	20.6	65.3	1.2	2.5	0.37	0.54	—	0.9
M0	0.8	0.2	4.5	3.8	23.5	63.4	1.2	1.7	0.28	0.48	—	0.5
B0	0.4	0.7	9.7	2.1	25.7	54.1	3.2	2.4	0.46	0.51	0.4	0.3
B2	1.3	0.6	9.3	2.0	24.4	53.2	3.0	4.3	0.44	0.48	0.4	0.4

Table 2 Physical properties of cement (N0, N2, H0, M0, B0, B2)

Type of Cement	Specific gravity	Specific surface area (cm²/g)	Setting time			Flow (mm)	Compressive strength (kgf/cm²)		
			W/C (%)	Initial (h-m)	Final (h-m)		3d.	7d.	28d.
N0	3.14	3180	27.5	2-28	3-28	250	131	226	422
N2	3.12	3570	27.8	2-50	3-50	249	159	231	380
H0	3.13	4290	29.0	2-23	3-26	259	226	338	447
M0	3.19	3260	25.5	3-02	4-27	255	90	146	317
B0	3.04	3850	28.8	3-34	5-10	255	97	152	346
B2	3.00	4100	29.0	3-54	5-52	253	95	152	325

Table 3 Physical properties of cement(AL)

Chemical component (%)			Specific gravity	Specific surface area (cm²/g)	Flexural strength (1 day) (kgf/cm²)	Compressive strength (3 days) (kgf/cm²)
Al_2O_3	Fe_2O_3	CaO				
60.6	2.5	32.5	2.98	4230	67.2	468

seawater mixed concrete, tap water (symbol: W) and seawater (symbol: S) were used as mixing water of concrete. The chemical composition of the seawater is shown in **Table 4**. In this paper, the kind of concrete is hereinafter abbreviated by pairing cement with mixing water, for example (AL, W).

Table 4 Chemical component of sew water used for concrete mixing

Specific gravity (20°C)	pH (20°C)	Chemical component (mg/1)						
		Na	K	Ca	Mg	Cl	SO₄	CO₃
1.024	8.03	10125	387	376	1180	17136	2412	65

As for coarse aggregate and fine aggregate, river gravel (maximum size: 25 mm) and river sand produced at the Sagami River, Kanagawa Prefecture were used.

All the concrete was mixed with water reducing agent as admixture; for (AL, W), air entraining agents were also used. As for the reinforcement, ⌀9 mm round bars specified in JIS G 3112 were used in a brilliant condition; the black layer was removed.

(2) Fabrication of Test Specimens

For the test of compressive strength, corrosion of reinforcement and mix potential, cylindrical test specimens (⌀15 × 30 cm) were fabricated using the concrete presented in **Table 5**.

As for the test specimens used for the measurement of the corrosion of reinforcement and mix potential, the three reinforcements were embedded with a cover thickness of 2 cm, 4 cm and 7 cm as shown in **Fig. 1**. Lead wires were soldered to the reinforcements of the test specimens for mix potential measurement.

The concrete was mixed by 200 liter forced mixing type mixers; the mixing and placing were done in a 20°C constant temperature room. The concrete was cast in two layers; each layer was compacted with vibrators.

(3) Curing of Test Specimens

The casted concrete test specimens were kept in the constant temperature room. At the age of one day, the molds were removed, and moved into a standard curing water tank (water temperature: 21°C) where they were cured for six days (In the case of H0, they are cured for three days). Then, they were moved into the tidal pool mentioned in 2. and a series of exposure tests was started. However, in the case of (AL, S), the molds were removed at age of 4 days, and they were moved into the tidal pool. In the case of (AL, W), the molds were removed at the age of one day, and moved into the tidal pool.

Table 5 Specified mix proportion of concrete

Cement	Water	G_{max} (cm)	Slump (cm)	Air (%)	W/C (%)	S/a (%)	Unit quantity (kg/m3)					
							W	C	S	G	WE (1)	AE (cc)
N0	W	25	66	34	52.7	37.0	153	290	740	1261	2.9	—
	S	25	56	32	53.4	36.0	155	290	718	1277	2.9	—
N2	W	25	64	40	54.5	37.0	158	290	734	1251	2.9	—
	S	25	51	34	55.2	36.0	160	290	713	1270	2.9	—
H0	W	25	37	39	53.1	37.0	154	290	738	1258	2.9	—
	S	25	57	31	55.2	36.0	160	290	711	1263	2.9	—
M0	W	25	65	48	52.4	37.0	152	290	742	1264	2.9	—
	S	25	46	40	53.1	36.0	154	290	720	1280	2.9	—
B0	W	25	35	30	52.4	37.0	152	290	738	1258	2.9	—
	S	25	40	38	53.1	36.0	154	290	716	1274	2.9	—
B2	W	25	42	38	54.8	37.0	159	290	729	1242	2.9	—
	S	25	47	41	55.5	36.0	161	290	708	1258	2.9	—
AL	W	25	63	31	52.1	37.0	151	290	737	1256	2.9	20
	S	25	51	35	52.8	36.0	153	290	716	1272	2.9	—

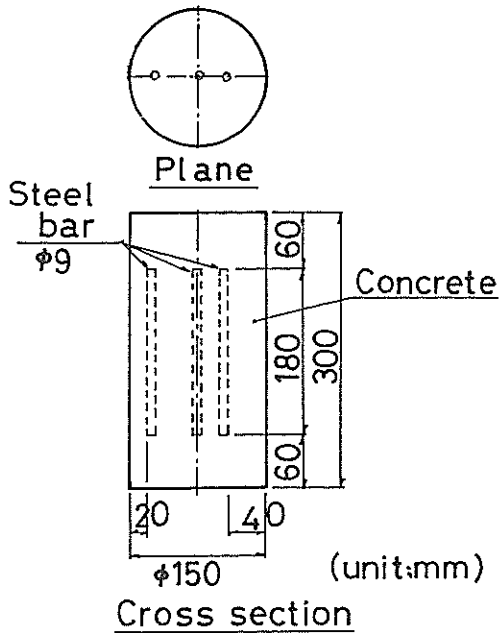* Slump and Air content are measured values.

Fig. 1 Dimension of specimen

4. Test Methods

Main test items and methods are as follows

(a) Compressive Strength of Concrete

The test was carried out according to JIS A 1108 at initial stage and at the age of one, 5, 10 and 20 years. The above initial stage means the age of 28 days, as a rule, however the exception is as follows; in the case of (AL, W), it means one day, in the case of (AL, S), it means 4 days, and in the case of H0, it means 7 days.

(b) X-ray Diffraction Analysis

At the age of 20 years, to confirm the crystal minerals in concrete, X-ray diffraction was performed. The samples tested were taken at two places of 1 cm and 7.5 cm inside from the surface at the center in the height-direction of the concrete test specimens. They were crushed into powder.

(c) Carbonation Depth of Concrete

Carbonation depth of concrete was measured in accordance with the phenolphthalein method at 1, 5, 10 and 20 years.

(d) Corroded Area of Reinforcement in Concrete

Measurements of the corroded area of reinforcement were performed on the three to five specimens of reinforcement at each cover thickness, at 5, 10 and 20 years.

As for the reinforcement taken out from the concrete test specimens, visible rust was traced and the corroded area was measured with planimeters. From the results, the rate of corroded area for the surface area of reinforcement was calculated.

(e) Mix Potential of the Reinforcement in Concrete

The mix potential of reinforcement was measured on the same test specimens in January, April, July and October annually, up to 20 years of aging from the start of exposure test. The measurements were performed by immersing the test specimens in the seawater completely. Seawater silver chloride electrodes were used as reference electrodes.

(f) Anodic Polarization of Reinforcement in Concrete

The anodic polarization of reinforcement was performed for each mix and each cover, at 10, 15 and 20 years. The concrete at the top of the test specimens were removed by chipping, and lead wires were connected to the exposed reinforcement and covered with epoxy resin. The measurements were performed by immersing the test specimens in the sea water. As for a reference and a counter electrode, a saturated calomel electrode and a stainless steel plate were used respectively.

From the shape of anodic polarization curve, the conditions of the passivity of the reinforcement were classified from grade-0 (poor passivity) to grade-5 (good passivity), which can be a useful indicator to evaluate the state of passive film of the reinforcement [10].

(g) Salt Content in Concrete

Salt content in concrete was tested at 10, 15 and 20 years. Five to ten grams of concrete near each reinforcement (depth: 2 cm, 4 cm, 7 cm) of the test specimens was sampled; the coarse aggregate was removed; the rest was pulverized under 105μm. Water soluble chloride ion from these samples were extracted using the 24-hour extraction method in 20°C distilled water [10], and quantitative analysis was performed according to the silver chromate-absorptiometric method [11].

(h) Diffusion Coefficient of Oxygen in Concrete

The diffusion coefficient of oxygen in concrete was surveyed in accordance with

the Japan Concrete Institute method [12] for each mixture at 20 years of aging. As for the test specimens, 2 cm in thickness between 3 and 5 cm from the the top and bottom of concrete test specimens were used as test specimens. The diffusion coefficient was measured when the ratio of water saturation was 0, 60 and 80%.

5. Test Results and Discussion

(1) Strength Characteristics of Concrete
(a) Surface properties of concrete
The surface properties of concrete were observed at 5, 10 and 20 years; at 5 and 10 years, only stains and rough surfaces were recognized; while, at 20 years cracks and spalling were recognized in some test specimens. Many fine cracks and spalling were recognized on the surface of most test specimens by portland cement, while they were not recognized on the surface of the test specimens by blast furnace slag cement and aluminous cement.

The main causes for the cracks and spalling development are considered to be caused by ettringite having expansibility. The details are described in c) with respect to the reason for decrease in strength.

No difference in cracks and spalling was recognized between test specimens that were immersed in tap water and those that were immersed in seawater.

(b) Compressive strength of concrete
Figure 2 shows the time-dependent change of the compressive strength f'_c of seawater mixed concrete. **Figure 3** shows the time-dependent change in the strength ratio (hereinafter, called initial strength ratio), which divides the strength at each stage by the initial strength f'_{c0} of each mixture. **Figure 4** shows the change of the initial strength ratio of tap water mixed concrete. As for the relation between the aging and strength, it increases up to 5 years in most test specimens; however, after 5-years of aging the strength has a tendency to fall gradually; at the age of 20 years the strength is less than the initial strength. The tendency of concrete to lose strength
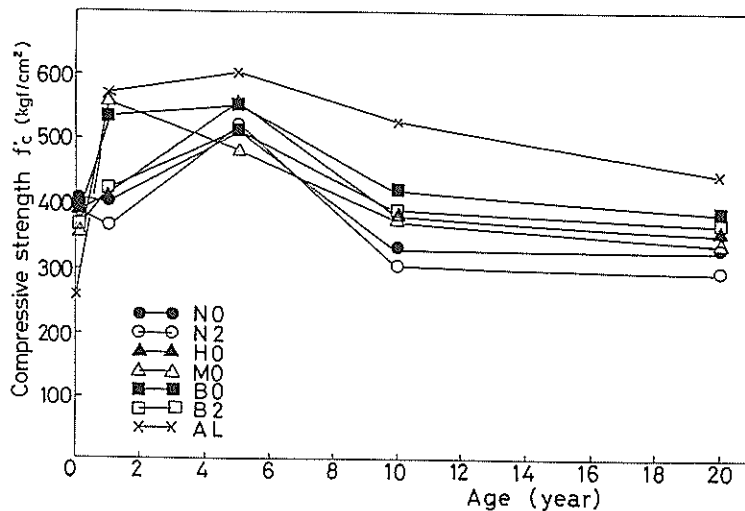

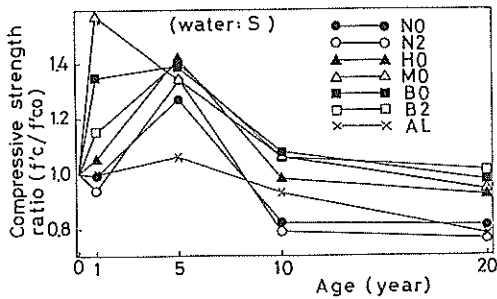**Fig. 2** Strength of concrete mixed with sea water

Fig. 3 Compressive strength ratio
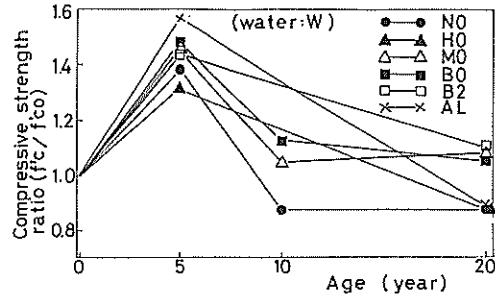f'c/f'co (mixed with sea water)

Fig. 3 Compressive strength ratio
f'c/f'co (mixed with sea water)

when exposed to seawater has been reported often [3], [13], [14].

The initial strength ratio at the age of 20 years was 0.76 to 0.94 in the portland cement group, 0.98 to 1.01 in the blast furnace slag cement group, and 0.79 in aluminous cement. The initial strength ratio of the blast furnace slag cement was relatively high; this means that the strength loss is less than other cements. **Figure 5** shows the time-dependent change of the compressive strength ratio (hereinafter, called the seawater/tap-water strength ratio) using seawater and tap water as mixing water. Since concrete mixed with seawater at slightly stronger than the mix puma strength ratio of most test specimens at 28-days aging was more than 1.0. However, later, the compressive strength ratio declined toward 1.0, and at 20 years of aging it ranged from 0.92 to 1.03. Thus, since the seawater/tap-water strength ratio of portland cement and blast furnace slag cement group became about 1.0 at long-term aging, it is considered that the use of seawater for mixing is independent of the compressive strength of the long-term aging of concrete. This was also reported by Gjorv [3].
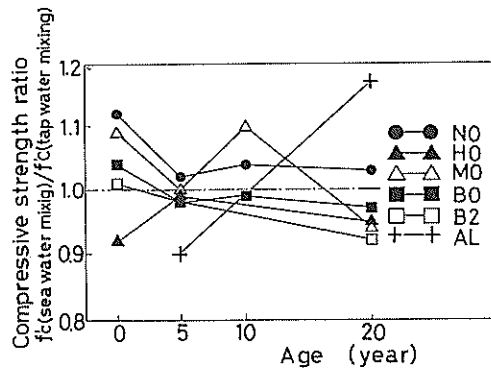
Fig. 5 Compressive strength ratio (mixed with sea water v.s. tap water)

Aluminous cement shows a very unique tendency compared to the portland cement and blast furnace slag cement group. The delay of the development of strength of (AL, S) is supposed to be caused by the formation of aluminate chloride; this phenomena has already been documented [15], [16]. And it will be discussed in d) that seawater/tap-water strength ratio of alminous cement at 20 years exceeds 1.0 remarkably. It is supposed that gypsum in cement does not affect the strength of concrete.

(c) Cause of the decrease in strength of the concrete with portland cement and blast furnace slag cement group

It is said that in the portland cement and blast furnace slag cement group, at a relatively early aging in seawater, chloride ions which penetrate into concrete react with calcium hydroxide, and then the concrete is made porous causing decrease in strength. While, at an advanced aging, C_3A in concrete reacts with sulphuric acid ion in seawater and ettringite is generated, it is said that the expansion-failure of the surface of the concrete causes decrease in strength.

Figure 6 shows the results of the X-ray diffraction analysis of the concrete at 20 years of aging. From **Fig. 6**, the following may be said.

① The ettringite was recognized in all samples; there is hardly a difference among the generated quantity by the types of cement and mixing water.

② The Friedel's salt was recognized in all samples. However, it was not detected in the center of the specimens mixed with blast furnace slag cement and tap water. It may be suggested that the rate of penetration of a chloride ion in this mixture is slow.

③ Calcium hydroxide was not detected on the surface of all the test specimens; particularly concrete mixed with portland cement and tap water calcium hydroxide was not detected even in the center of the test specimens. It was found that calcium hydroxide remains near the center of the specimens of the the concrete with blast furnace slag cement group and the concrete mixed with

Cement	Water	(cm)	Ettringite	Friedel's salt	CaCO$_3$	Ca(OH)$_2$
NO	W	1	+	++	+	
		3	+	++	+	
		5	+	++	+	
		7.5	+	++	+	
	S	1	+	++	+	
		7.5	+	++	+	+
N2	W	1	+	++	+	
		7.5	+	++	+	
	S	1	+	++	+	
		7.5	+	+	+	+
HO	W	1	+	++	+	
		7.5	+	++	++	
	S	1	+	++	+	
		7.5	+	++	+	+
MO	W	1	+	++	+	
		7.5	+	+	+	
	S	1	+	++	+	
		7.5	+	++	+	+
BO	W	1	+	++	+	
		3	+	+	++	
		5	+	+	+	+
		7.5	+		+	+
	S	1	+	++	+	
		7.5	+	+	+	+
B2	W	1	+	++	+	
		7.5	+		+	+
	S	1	+	+	+	
		7.5	+	+	+	+

+ : CPS (Counts per Second) is less than 500
++ : CPS (Counts per Second) is ranged
     from 500 to 2000

Fig. 6 X-ray analysis (N0,N2,H0,M0,B0,B2)

seawater. These results suggest the following; the elusion of calcium hydroxide from the concrete surface can be reduced by using the blast furnace slag cement or seawater as mixing water, but it can not be avoided under a marine environment over 20 years.

④ Calcium carbonate generated by the reaction of calcium hydroxide on carbon dioxide was recognized in all samples.

From the above results, the decrease in strength of the portland cement and blast furnace slag cement group under marine environment, particularly the portland cement group, are supposed to be caused by the expansion due to generated ettringite formation. From the results of the X-ray diffraction test, there is no sign that seawater mixed concrete is less durable than tap water mixed concrete.

(d) Strength of concrete with aluminous cement

As for aluminous cement, CA, which is the main chemical component, reacts with water, and converts into stable C_3AH_6 and $2AH_3$ through a semi-stable compound such as CAH_{10}. It is said that the conversion makes porous the organization of hydration hardening body and increases in void causes the release of the crystallization water resulting in decrease in strength.

Figure 7 shows the generative minerals confirmed by X-ray diffraction in the samples using aluminous cement in the same way as c); in the concrete C_3AH_6 and $2AH_3$ was recognized. From this, it was confirmed that the conversion from CAH_{10} into C_3AH_6 and $2AH_3$ caused the decrease in strength of concrete.

Mixing Water	Sampling depth (cm)	CAH_{10}	C_3AH_6	$2AH_3$
W	1.0	++		+
	7.5	+	++	++
S	1.0	++		+
	7.5	++	+	++

+ : CPS (Counts per Second) is less than 500

++ : CPS (Counts per Second) is ranged from 500 to 2000

Fig. 7 X-ray analysis (AL)

Meanwhile, when comparing the outer layer of test specimens with the center, CAH_{10} remains to a smaller degree in the center of the tap water mixed concrete. While there is no sign of C_3AH_6 in the outer layer, and much was recognized in the center of the tap water mixed concrete. Similarly there is also no sign of $2AH_3$ in the outer layer, while much was recognized in the center. Eventually, much CAH_{10} remains in the outer layer having much effects from seawater and in the seawater mixed concrete; this indicates that there is a small quantity of conversion to C_3AH_6 and $2AH_3$.

Based on these results, seawater as mixing water contributes to reduce the conversion and to inhibit the decrease of long-term strength though seawater causes retardation of hardening and setting of aluminous cement at the initial stage of aging. The results indicate the tendency as shown in **Fig. 5**.

(2) Carbonation Rate of Concrete

Figure 8 shows the relation between the average value x of the maximum carbonation depth at the cross section of the concrete test specimens and age t, and a-value of the approximate expression of $x = a \sqrt{1} \ t$. Though a little difference in the carbonation depth caused by the difference of the types of cement was recognized, there was almost no effect as a result of mixing water. It is said that the carbonation rate of concrete in the air is 0.79 of high-early strength portland cement and 1.41 of blast furnace slag cement B-class when ordinary portland cement is 1.0 [19]. In this research, the same tendency was recognized. In **Fig. 8**, the calculation curve for concrete in the air by Kishitani's formula [20] is shown, in which the carbonation ratio R is 1.0 and the water cement ratio is 52.7%. The carbonation rate at the tidal zone obtained in these tests is much smaller than that in the air; according to the approximate expression, its value is equivalent to about 40% of that in the air. By the approximate expression, the maximum carbonation depth at 50-years of aging is about 0.7 cm.
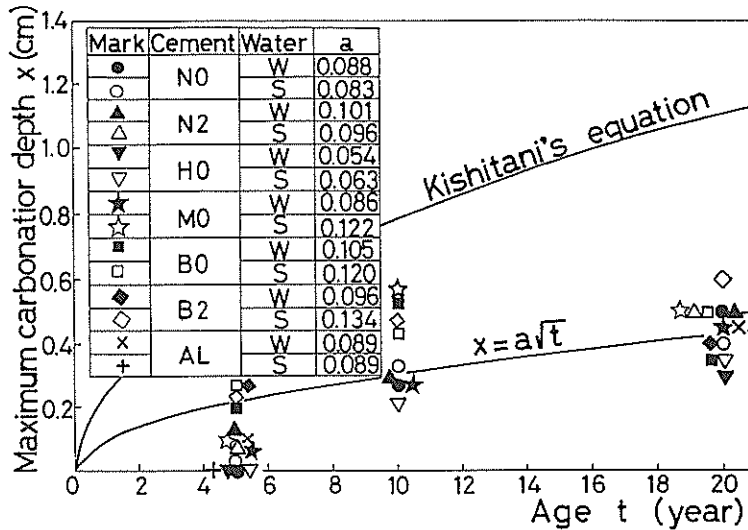

Mark	Cement	Water	a
◉	NO	W	0.088
○		S	0.083
▲	N2	W	0.101
△		S	0.096
▼	HO	W	0.054
▽		S	0.063
★	MO	W	0.086
☆		S	0.122
■	BO	W	0.105
□		S	0.120
◆	B2	W	0.096
◇		S	0.134
×	AL	W	0.089
+		S	0.089

Fig. 8 Depth of carbonation

(3) Corrosion Condition of Reinforcements in Concrete
(a) Corroded area

Figure 9 shows the ratio of corroded area of reinforcements. Each value is the mean value of the measured values of three to five specimens of reinforcement under the same conditions. When measuring the corroded area, rust was classified into black rust and red rust. Black rust is considered to contain a great deal of Fe_3O_4, while red rust is considered to contain a great deal of $FeOOH$. However, no correlation between differences in rust-color and depth of corrosion was found. And at 20 years of aging a black thin layer in which there was no sectional defects was found. Its area was included in the black coloured rust area at 20 years of aging in the figure.

As shown in the Figure, regardless of the type of cement, the corroded area at the age of 5 and 10 years was very low. The corroded area of blast furnace slag cement and aluminous cement at 20 years of aging was low, while that of portland cement was high.
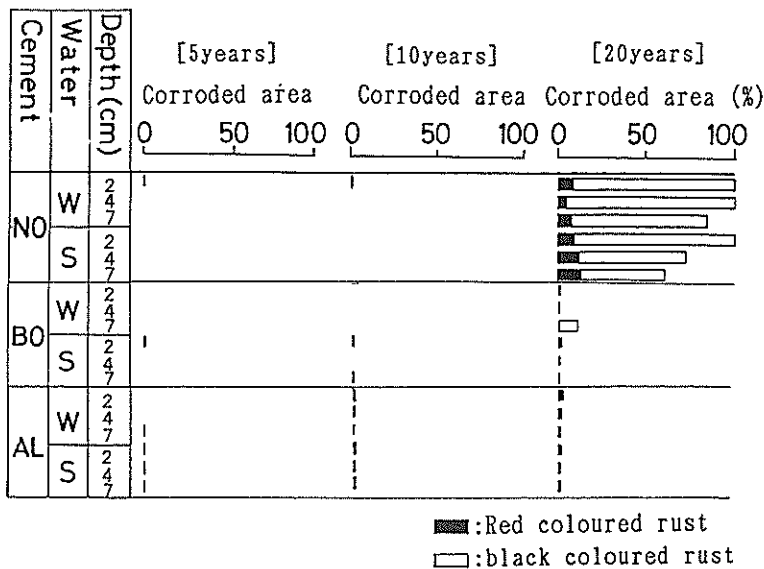
Fig. 9 Corroded area of steel bars

The reason is that the black layer mentioned above was included.

Though the amount of red rust on the reinforcements in the concrete mixed with seawater and portland cement at 20 years was a little greater than that of tap water mixed concrete, it can be considered that the type of mixing water had no effect on the amount of corrosion of reinforcement. Based on this, there seems to be little difference between the seawater mixed concrete and tap water mixed concrete in their effect on corrosion of reinforcement, at least in tidal zone.

On the other hand, the effect of the type of cement was significant; this effect was particularly obvious at 20 years of aging. As for the corroded area ratio of the reinforcements for the concrete with portland cement group, large amounts of red and black rust were recognized. Meanwhile, blast furnace slag cement was confirmed to be excellent in corrosion prevention. In aluminous cement which is weak in alkalinity and has fear of corrosion of reinforcement, there was almost no recognizable rust [21]. Also, the corrosion of reinforcement seems to be affected very little by an increase in quantity of gypsum in the cement.

As for the effect of cover thickness, the reinforcement using portland cement was affected a little at 20 years of aging; however, this effect was much smaller than that due to the type of cement.

From the the ratio of corroded area of the reinforcements in the concrete, the following results were obtained.
- Rust generation was observed in the reinforcements in the concrete with portland cement at about 20 years of aging even with a covering of 7 cm.
- Blast furnace slag cement and aluminous cement were more resistant to the corrosion of reinforcement than portland cement.
- Differences in the type of cement had a large effect on the corroded area.
- The use of seawater as the mixing water did not affect the corroded area very much.
- The effect of differences in covering thickness less than 7 cm on the corroded area was smaller than that of the differences in the type of cement.

(b) Judgment of the grade of passivity

The results of the grade of passivity of the reinforcements, as judged from the anodic polarization curve, are presented in **Table 6**. From the table, it can be seen that as in the tendencies of the corroded area, the effect of the type of cement was more significant than that of the mixing water or covering depth. That is, the grade of passivity of the rein-forcements in the concrete which used the blast furnace slag cement or aluminous cement had better values than portland cement. Clearly, this corresponds to the small value of corroded area in the concrete with blast furnace slag group cement or aluminous cement.

Table 6 Grade of passivity

Cement	Water	Depth (cm)	Grade of Passivity	
			15 years	20 years
N0	W	2	2	2
		4	2	2
		7	2	2
	S	2	1	2
		4	2	2
		7	2	2
M0	W	2	2	2
		4	2	2
		7	2	2
	S	2	2	2
		4	2	2
		7	2	2
B0	W	2	4	4
		4	4	5
		7	4	5
	S	2	4	4
		4	4	5
		7	4	5
AL	W	2	—	5
		4	—	5
		7	—	5
	S	2	—	5
		4	—	5
		7	—	5

(c) Time-dependent change in mix potential with time

A typical change in mix potential with time is shown in **Fig. 10**. The value for each year is an average of the measured values for the three test specimens in January, April, July and October of the measuring period.

In short-term aging, there was a small difference between the values for seawater mixed and those for tap water mixed, but in long-term aging the values for seawater
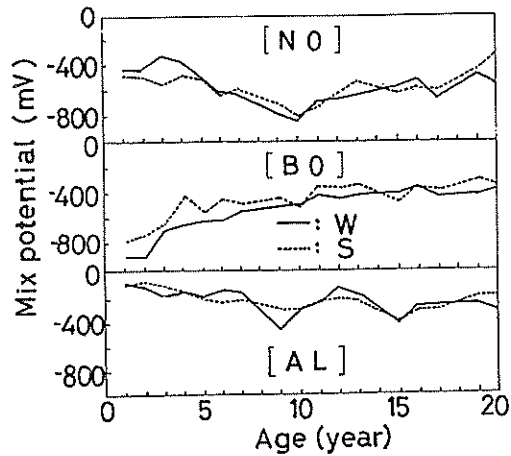
Fig. 10 Change of mix potential

mixed were the same as those for tap water mixed.

The tendencies of the change in mix potential depended on the type of cement used. As for the mix potential of the reinforcements in the test specimens which used N0, the potential had a tendency to move to the base side up to 10 years of aging and to move to the noble side after that. As for those which used B0, the potential had a tendency to gradually move to the noble side up to 20 years of aging. And, as for those which used AL, the potential had a tendency to move to the base side up to 20 years of aging.

The tendencies of the changes in the potential differ depending on the type of cement used is considered to be mainly caused by differences in the oxygen amount around the reinforcement. The corrosion reaction is expressed by the following formulas (1) and (2); the anode reaction (1) and cathode reaction (2) progress equivalently.

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{1}$$

$$1/2O_2 + H_2O + 2e^- \rightarrow 2OH^- \tag{2}$$

The mix potential is interpreted to be the potential at the intersection of the anodic and cathodic polarization curves. Since the cathodic reaction is controlled by oxygen, as shown in formula (2), the cathodic polarization curve is changed by the quantity of oxygen around the reinforcement; even in the case where the anodic polarization curve is constant, the mix potential is changed.

Figure 11 shows imaginary anodic and cathodic polarization curves for objects using N0, B0 and AL. In the anodic polarization curve, since the reinforcements have a good passivity at the initial aging, this is expressed as Ao in the Figure. However, this is thought to change to A1 and A2 due to the effect of salt, after the passage of 10 years to 20 years of aging. And, as was shown in b), where the grade of passivity of the reinforcements depended on the type of cement, the anodic polarization curve also depends on the type of cement. On the other hand, though the cathodic polarization curve is Co at the initial aging, the oxygen density rises with the progress of aging, and it is thought to change to C1 and C2. Also, the quantity of oxygen around the reinforcement
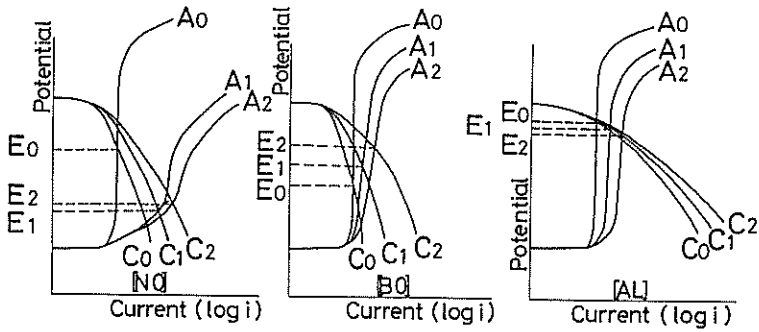
Fig. 11 Assumed polarization curves of steel bars

depends on the type of cement. If the magnitude of the oxygen diffusion is largest for AL followed by N0 and B0 in that order, the cathodic polarization also depends on the type of cement, as shown in the Figure. Therefore, it can be considered that the mix potential Eo, E1 and E2, which changes with the passage of time, also depends on the type of cement. The experimental results of diffusion of oxygen are to be shown in (4) c).

(4) Chloride Ions and Oxygen in the Concrete

(a) Chloride ion content in the concrete

Figure 12 shows the water soluble chloride ion as a weight percentage for mortar. In the mix conditions used here, concrete mixed with seawater contained chloride ions of 0.22 to 0.24% (2.59 to 2.76 kg per $1m^3$ concrete) of the mortar weight in the fresh concrete state. This value is more than four times the 0.6 kg/m^3 which is considered as allowable chloride content in fresh concrete. As shown in Fig. 12, in the concrete which used ordinary portland cement, the chloride content averaged 1.4% at 10 years of aging, 1.75% at 15 years of aging and 2.0% at 20 years of aging. When comparing these values with that of the fresh concrete, these values are 6.1, 7.6 and 8.7 times greater, respectively. And, in N0, since there is little increase in the chloride content between 10 years and 20 years of aging, the chloride ions in the concrete are thought to nearly reach a condition of saturation at around 10 years of aging.
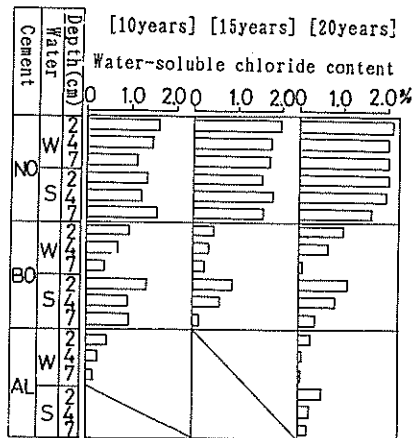

Fig. 12 Water soluble content in concrete

On the other hand, the chloride content in B0 and AL was much lower than that in N0; the chloride ion content at the age of 20 years was only 30% of that of N0 on the average. It is said that B0 is strongly resistant to the penetration of chloride ions due to their minute composition [18]; this was confirmed by our research.

As for the effect of the use of seawater as the mixing water on the chloride ion content in the concrete, no effect was recognized on N0; however, B0 and AL were affected a little because the amount of chloride penetration from the seawater is small. However, this effect was much smaller than that of cement type.

As for the effect of cover thickness on chloride ion quantity, there was no effect with N0, the same as with the case of mixing water. In contrast with B0 and AL, the effect of the cover thickness was remarkable; if a sufficient cover thickness is used a cover can prevent the penetration of salt.

From these results, the following points became clear:

In the case where seawater acts on concrete for a long time, the salt penetration resistance of portland cement is lower than that of blast furnace slag cement and aluminous cement. It was also found that the use of seawater as mixing water had little effect on the chloride ion content in the mortar.

(b) Relationship between chloride content and the corroded area of reinforcement

Figure 13 shows the relationship between the water soluble chloride content around the reinforcements and the corroded area. Since the corrosion reaction progresses in a complicated relationship with factors such as oxygen supply and moisture in addition to chloride content, the relationship between chloride content and corroded area is not determined unconditionally. However, as shown in **Fig. 13**, when the water soluble chloride content exceeds 1.5% in mortar weight, there was a clear tendency towards an increase in the corroded area.
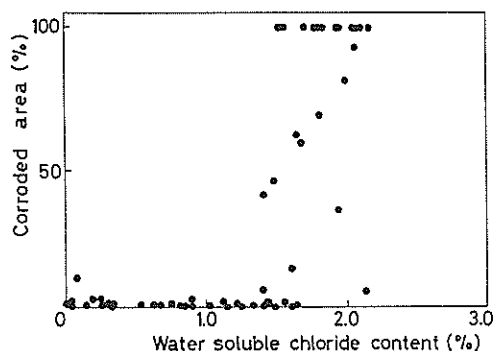

Fig. 13 Relationship between chloride content in concrete and corroded area of steel bars

(c) Diffusion coefficient of oxygen

Measured results of the diffusion coefficient of oxygen, which controls the cathodic reaction, are shown in **Fig.14**. Each value is an average value of samples taken from the top and the bottom of the test specimens.

As shown in the figure, mixing water had no recognizable effect on the diffusion coefficient of oxygen, but there were recognizable effects based on the type of cement. The average diffusion coefficients for each type of cement in the case saturation of 0% were as follows:
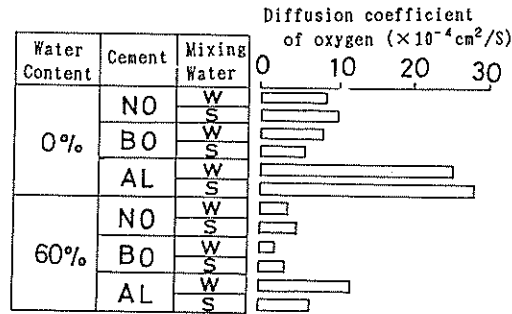
Fig. 14 Diffusion coefficient of oxygen of concrete

portland cement   : 9.35×10^{-4} to 10.57×10^{-4} cm²/s
blast furnace slag cement   : 6.99×10^{-4} to 9.06×10^{-4} cm²/s
aluminous cement   : 26.80×10^{-4} cm²/s

The average diffusion coefficient for blast furnace slag cement was a little lower than that for portland cement. In contrast, that for aluminous cement was remarkably higher. This can be explained by high porosity due to the conversion of mortal of aluminus cement. Also, in the case of water saturation of 60%, the diffusion coefficient becomes smaller than that of saturation of 0%, but the effects of the type of cement showed the same tendencies. This supports the ideas relating to the cathodic polarization curve mentioned in (3) c).

In the case of aluminous cement, despite that the amount of penetrated chloride ions was small, the diffusion coefficient of oxygen was large. The following reason for this can be considered. This might be due to the difference in pore size distribution of each mix; the apparent coefficient of diffusion of chloride ion has a strong relation with the pore size less than 20 A in radius [22], on the other hand the coefficient of diffusion of oxygen has a relation with the pore size larger than 1 μ m in radius [22].

6. Conclusion

The results of the exposure test for a 20 year period under a marine environment (tidal zone) can be summarized as follows:

(1) In the concretes using portland cement, such as ordinary, high-early-strength and moderate heat types, there were many recognizable fine cracks and fine spalling on the surface at the age of 20 years. On the other hand, cracks and spalling found on the surface of the concretes using blast furnace slag cement B-class and aluminous cement were few in number.

(2) The compressive strength of concrete increases up to about 5-years of aging, and after this gradually decreases. At 20 years of aging most specimens had a tendency to be below their initial strength. There were no differences in compressive strength due to differences in mixing water with long-term aging.

(3) Based on the corroded area and the the grade of passivity, it was clear that the corrosion of the reinforcements in the concrete using portland cement progresses up to 20 years of aging. Corrosion is significantly affected by the type of cement used; it was seen that the corrosion in concretes with blast furnace slag cement and aluminous cement was less than that in concrete with portland cement. It

was clear that there was almost no recognizable effect on the corrosion of reinforcements due to differences in mixing water.

(4) As for preventing the penetration of salt, the concretes using blast furnace slag cement and aluminous cement were much better than these using portland cement. There was a small recognizable effect of the mixing water on the chloride ions content in the concretes using blast furnace slag cement B-class and aluminous cement at 20 years of aging, but there was no effect on the concrete using portland cement.

(5) There was no effect of mixing water on the diffusion coefficient of oxygen in the concrete. On the other hand, there was a recognizable effect of the type of cement used on the diffusion coefficient; the concrete with the lowest diffusion coefficient was blast furnace slag cement, while the one with the highest cofficient was aluminous cement.

(6) Within the scope of this test, even when gypsum phosphate with 2% in SO3 weight was added to ordinary portland cement and blast furnace slag cement B-class, there was no recognizable effect on the durability of the concrete.

(7) In this series of experiments for 20 years, concrete using blast furnace slag cement and aluminus cement show very excellent performance against sea-water attack and corrosion of reinforcement. Furthermore, it was found that sea water as mixing water of concrete has little effect on the durability of concrete and corrosion of reinforcement, when concrete has been exposed in tidal zone for long time.

Acknowledgement

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