

Possibility of Sea Water as Mixing Water in Concrete

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Abstract: In the near future, fresh water will be very difficult to get and scarce. It is said that in 2025 half of the mankind will live in the areas where fresh water is not enough. Also, UN and WMO (World Meteorological Organization) are predicting five billion people will be in short of even drinking water. Also, in the present, there are some areas where sea water or chloride contained sand are used as mixing water with or without intension. The authors believe that the possibilities of using sea water as mixing water in concrete should be investigated seriously. In this paper, the authors would like to show various possibilities of using sea water as mixing water as mixing water in RC (reinforced concrete) members. The possibilities are shown as follows: (1) mixed with pozzolanic materials (Blast furnace slag powder, etc.) expecting to fix the free chloride ion; (2) Mixed with corrosion inhibitor; (3) reinforced with stainless steel or corrosion resistant reinforcement; and (4) used in very dry or submerged conditions.

Key words: Sea water, blast furnace slag, corrosion behavior, stainless steel, hydration products.

1. Introduction

Besides shown in the introduction, the authors have investigated chloride attack in marine environment. In these investigations, the authors compared durability of concrete with OPC (ordinary Portland cement) and BFS (blast furnace slag) cement and mixed with fresh water and sea water. The results (the authors will show the research in the later chapter) showed "there is not so much difference with the concrete mixed with fresh water, even though mixed with sea water [1], but the difference between the concrete with OPC and BFS cement is very large. Also, the BFS cement concrete mixed with sea water showed better durability than the OPC concrete mixed with fresh water."

Inspired by the fact, the authors believe there are various possibilities of using sea water as mixing water from the point of concrete technology.

In this paper, the following possibilities are introduced:

(1) Mixed with pozzolanic materials (Blast furnace slag powder, etc.) expecting to fix the free chlorideion;

(2) Mixed with corrosion inhibitor;

(3) Reinforced with stainless steel or corrosion resistant reinforcement;

(4) Used in very dry or submerged conditions.

2. Mixed with Various Kind of Cement

In 1969, around 200 specimens were manufactured to examine the effect of sea water as mixing water and exposed in tidal zone. The followings show the specimens, materials, test results and considerations [2].

2.1 Materials and Manufacturing Specimens

(1) Materials

As cements, Ordinary Portland cement, High Early Strength cement, Moderate cement, Blast Furnace Slag cement and Aluminate cement were used. Also, the amounts of SO_3 were changed. Some cements contained 2% more SO_3 than the others.

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As mixing water, tap water and sea water were used. The chemical components of sea water are shown in Table 1.

River gravel was used for coarse aggregates, and the maximum size was 25 mm. Also, river sand was used as fine aggregate.

The used steel bars were 9 mm diameter round bars which were conformed to the Japan Industrial Standard. The steel bars were treated by 2% ammonium citrate to be no rust and shiny surface;

(2) Manufacturing specimens

The mix proportions of concrete are shown in Table 2.

The size of the specimen was 15 cm diameter and 30 cm height. There were specimens for strength, potential measurement and steel corrosion. Also three steel bars were embedded in the specimens for potential and corrosion, whose covers were 2, 4 and 7 cm as shown in Fig. 1;

(3) Curing

The specimens were de-molded one day after

 Table 1
 Chemical compositions of sea water as mixing water.

casting, except specimens with aluminate cement in that case they were de-molded four days after casting. After de-molding, the specimens were cured in under water (21 degree) until seven days old after casting. Then the specimens were exposed in tidal condition.

2.2 Test Items

(1) Compressive strength

Compressive strengths were measured at the ages of seven days (only for high early strength cement concrete), 28 days, one year, five years, 10 years and 20 years. The tests were performed according to Japan Industrial standards. In a same condition, three specimens were tested and the test data were averaged;

(2) Corroded areas of steel bars

Corroded areas of steel bars were measured using a planimeter and percentages against steel bars' surfaces were calculated. For each conditions three to five steel bars were tested and the values were averaged;

Density (20°C)	рН (20°С)	Chemical compositions (mg/l)										
		Na	K	Ca	ı	Μ	[g	Cl		SO_4	CO	3
1.024	8.03	10,125	387	37	76 1,180		180	17,136		2,412	65	
Table 2	Mix proporti	ons of concre	te.									
Cement	Mixing water	G.max (mm)) Slump (cm)	Air (%)	W/C	S/a	Unit amount					
type							W	С	S	G	Ad(l)	AE(c.c.)
OPC	Freshwater	25	6.6	3.4	52.7	37.0	153	290	740	1,261	2.9	
	Seawater	25	5.6	3.2	53.4	36.0	155	290	718	1,277	2.9	-
OPC+SO ₃	Freshwater	25	6.4	4.0	54.5	37.0	158	290	734	1,251	2.9	-
	Seawater	25	5.1	3.4	55.2	36.0	160	290	713	1,270	2.9	-
НРС	Freshwater	25	3.7	3.9	53.1	37.0	154	290	738	1,258	2.9	-
	Seawater	25	5.7	3.1	55.2	36.0	160	290	711	1,263	2.9	-
Moderate	Freshwater	25	6.5	4.8	52.4	37.0	152	290	7742	1,264	2.9	-
	Seawater	25	4.6	4.0	53.1	36.0	154	290	720	1,280	2.9	-
BFS	Freshwater	25	3.5	3.0	52.4	37.0	152	290	738	1,258	2.9	-
	Seawater	25	4.0	3.8	53.1	36.0	154	290	716	1,274	2.9	-
BFS+SO ₃	Freshwater	25	4.2	3.8	54.8	37.0	159	290	729	1,242	2.9	-
	Seawater	25	4.7	4.1	55.5	36.0	161	290	708	1,258	2.9	-
Aluminate	Freshwater	25	6.3	3.1	52.1	37.0	151	290	737	1,256	2.9	20
	Seawater	25	5.1	3.5	52.8	36.0	153	290	716	1,272	2.9	-

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<u>Cross-section</u> Unit ; m m Fig. 1 Outline of the specimen for corrosion test.

(3) Corrosion depths of steel bars

Corrosion depths of steel bars were measured at the ages of 20 years using a thickness gauge.

2.3 Test Results and Considerations

(1) Compressive strengths

The compressive ratio was defined as the ratio between the compressive strength of concrete mixed with sea water and that mixed with tap water. The time dependent changes of the compressive strength ratios were shown in Fig. 2. From this figure, the ratios were somewhere between 0.9 to 1.1, and the influence of mixing water was not so much.

(2) Corroded areas of steel bars

The time dependent changes of corroded areas were shown in Fig. 3. As shown from this figure, the influence of the kind of cement is much larger than those of mixing water. Also, it is clearly recognized that the influence of mixing water is negligible.

The corrosion resistant ability of BFS cement can be recognized far better than those of OPC, HSC and moderate cement even mixed with sea water.

(3) Corrosion depths

The corrosion depths after 20 years' exposure are shown in Fig. 4. As shown from this figure, the influence of the kind of cement is larger than that of mixing water. The corrosion depth with BFS is less than the others' no matter the kind of mixing water.

2.4 Summary

From this 20 years' exposure test, the kind of mixing water has little influence on the strength and corrosion. Especially about corrosion, the specimens with BFS is far better than with OPC, HSC and moderate cement notwithstanding the kind of mixing water. So, in tidal zone, there is a possibility using sea water as mixing water, considering the kind of cement.



Fig. 2 Time dependent changes of compressive strength ratios (mixed with sea water/mixed with tap water).

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Fig. 3 Time dependent changes of corroded areas (%).

Cement	M.W	Cover 2cm	Cover 4cm	Cover 7cm					
Maximum corrosion depth (mm) 0 0.2 0.4 0.6 0 0.2 0.4 0.6 0 0.2 0.4 0.6									
OPC	W	• •		• ••					
	S	**		*					
OPC + SO3	W	• • •	***						
	S	•• •	***	••					
нрс	W		• •	• •					
	S	•• •	••	•• •					
Moder ate	W	•••	• •	•• •					
	S			••••					
	W		• ••	• • •					
BFS	S	-		٤					
BFS + SO3	W								
	S			7					
Alum inate	W	-	·· ·						
	S	•••	••	••					

W: Tap water as mixing water

S: Sea water as mixing water **Fig. 4 Corrosion depths of steel bars after 20 years' exposure.**

3. Mixed with Corrosion Inhibitor

It is reported that the NO2-/Cl- ratio is around 1.0, the steel bars can be protected from corrosion, and the surface of the steel bars are passivated [3]. In the case

of the mix proportions shown in Fig. 2, the chloride contents are around 2.74 kg/m³ and 77.2 mol/m³. This is calculated by the water content (160 kg/m³) and chloride concentration of the used sea water (17,100 ppm).

Also, same kind of corrosion inhibitor contains 35% Ca(NO₂)₂ in the solution. The manufacturer showed the properties of concrete (strength, setting time, etc.) have no problem adding the inhibitor up to 20 liter/m3, and it means 4.9 kg/m³ and 106.5 mol/m³. Then the NO₂⁻/Cl⁻ ratios can be up to 1.38.

It means there is a good possibility using sea water as mixing water with corrosion inhibitor.

4. Reinforced with Stainless Steel or Corrosion Resistant Steel Bars

According to the Standard Specification for Concrete Structures (JSCE — Japan Society of Civil Engineers), critical chloride ion concentration of carbon steel bars is 1.2 kg/m³ [3]. Chloride ion content in sea water mixing concrete is calculated to be 2.74 kg/m³. Therefore, carbon steel bars cannot be used. Corrosion-resistant steel bars will be used there. There are epoxy-coated bar and stainless steel bar in corrosion-resistant steel bars. For epoxy-coated reinforcing bar, corrosion occurs when chloride ion concentration on the steel bar under the epoxy-coating film exceeds 1.2 kg/m³ [4]. If there are scratches on the coating, corrosion occurs from the area. Critical chloride ion concentration for stainless steel bars (Clim) are different depending on the grade of stainless steel's corrosion resistance [5].Critical chloride ion concentrations of stainless steel bars provided in JIS G 4322, as shown in Fig. 5, are much higher than 2.74

kg/m³. If appropriate structure design (cover, W/C, etc.) is performed, the sea water mixing concrete is considered to be available. In addition in carbonated concrete, critical chloride ion concentration of SUS410-SD, most cost-effective stainless steel bar, is 3 kg/m³, which can be used in environments with chloride ion concentration does not increase due to salinity ingress [6]. As mentioned above, for reinforcement corrosion, sea water mixing concrete can be used by using stainless steel reinforcing bars.

5. Hydration Properties of Cement Using Sea Water as Mixing Water

As shown in Chapter 2, BFS has an advantage in using sea water as mixing water. So in this chapter, the reaction ratios, pore volumes and compressive strength of early ages are shown in the case of BFS with sea water and fresh water.

The results of slag reaction ratio tests of BFS cement (Type C) mixing with sea water and freshwater are shown in Fig. 6. Specimens were prepared with BFS cement paste whose replacement ratio of BFS to OPC was 70% and water cement ratio was 0.5. Size of the specimens was $10 \times 10 \times 40$ mm and pre-curing was carried out for 24 hours. At a set time, the specimens were crushed to prepare the powder specimens passing through the 150 µm sieve for the each chemical analysis.



Fig. 5 Recommended value of JSCE and experimental result value of critical chloride ion concentration of stainless steel bars, C_{lim} : threshold chloride ion concentration of stainless steel bars.



Age[log_days]

Fig. 6 Influence of mixing with sea water on slag reaction ratio on BFS cement.



Fig. 7 Influence of mixing with sea water on pore volume on BFS cement.



Fig. 8 Influence of mixing with sea water on compressive strength on BFS cement.

Mixing with sea water raises the BFS reaction ratio compared to mixing with fresh water for the entire period. The increasing has the largest value at 1st day, since then, reduced and remained.

The results of mercury intrusion porosimetry (pore volume measurement) of BFS cement mixing with sea

water and fresh water are shown in Fig. 7. Total pore volume was decreased by mixing with sea water compared to data of 1st day. BFS reaction ratio with sea water was larger than that of fresh water. Therefore, total pore volume with sea water decreased compared to fresh water.

The results of compressive strength tests of BFS cement mixing with sea water and fresh water are shown in Fig. 8. BFS cement was strengthened in entire period by mixing with sea water. Strength depends on the micropore structure, accordingly, the representative index is the total pore volume and the pore diameter. It is concluded that mixing with sea water decreases the amount of pores, and then strength of BFS cement with sea water was increased.

6. Conclusions

From the test results and discussions shown above. The authors are confident to safely use sea water as mixing water. The countermeasures of using sea water as mixing water are as follows:

(1) Use BFS cement or other blended cement instead of OPC;

(2) Use corrosion inhibitor;

(3) Reinforced with stainless steel or corrosion resistant reinforcement.

Nowadays, the design method is changing to "Performance based design", so if the performance in the expected life can be proved over the required level, the concrete mixed with sea water can be used.

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