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Some Considerations for the Applicability of Seawater as Mixing Water in Concrete

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ABSTRACT

According to the report of the WMO, more than half of world population would not have enough drinking water by 2025. In order to save drinking water, the usage of seawater in concrete industry seems imperative. In the present study, the possibilities of seawater as a material of concrete were discussed based on the literature-based and experimental investigations. As the results of literature-based study, more than half of papers collected in this study had positive opinion about concrete mixed with seawater by adding the mineral admixture such as blast furnace slag (BFS). Also some results of long term exposure tests indicated the high possibility of utilization of seawater as a material of concrete. Moreover the experimental data obtained in this study indicated that the addition of BFS might contribute significantly to the corrosion resistance of steel bar due to low oxygen environment around steel bar as well as chloride immobilization.

Keywords. Reinforced Concrete, Mixed with Seawater, Corrosion, BFS, Water Shortage

INTRODUCTIONS

The rapid growth of world population, in addition to the climate change may have serious impacts on resources around the world. Fresh water for example will be a scarcity and it might be very difficult to obtain it at some regions in the world. According to the report of World Meteorological Organization (WMO), more than half of the world population would not be able to get enough drinking water by 2025.

Here, in concrete industry, several billion tons of fresh water is annually used, as mixing, curing and cleaning water, around the world. From the view point of saving fresh water, the authors believe that the possibilities of using seawater as mixing water in concrete should be investigated seriously. Additionally, if the use of seawater as a concrete material is permitted, it will be very convenient and economical in the construction, especially in the coastal works. However, in most of the reinforced concrete standards, the use of seawater is not permitted due to the risk of early corrosion of reinforcement, induced by Cl in seawater compounds.

The authors would like to show various possibilities of concrete mixed with seawater on the literature-based and experimental investigations.

LITERATURE-BASED INVESTIGATIONS

Outline of literature survey. First of all, the published papers related to concrete mixed with seawater were analysed. These papers were collected by the data base of Japan Science and Technology Agency (JST), and published from 1974 to 2011. During this literature survey, a total of 68 papers (English: 32 papers, Japanese: 36papers) have been analysed. The distribution of annual publication on this topic is shown in Figure 1. Throughout this figure, it can be understood that the investigation of concrete mixed with seawater has been conducted so far, more than 40 years, with almost constant number of publications per year.

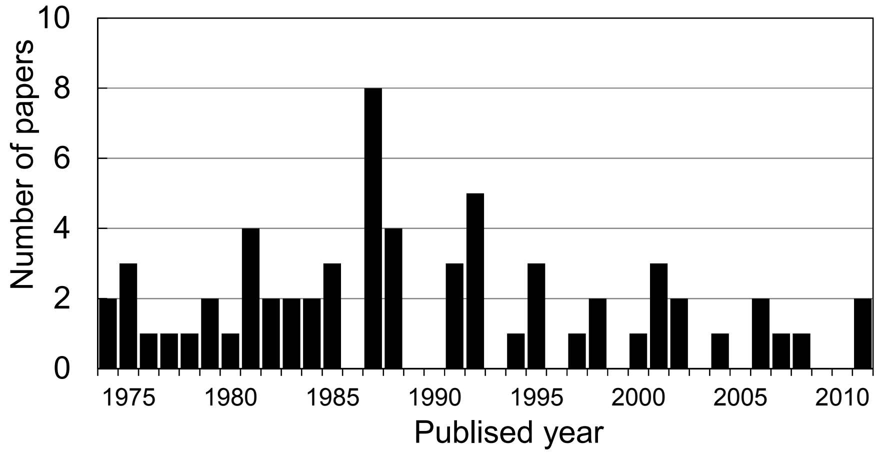
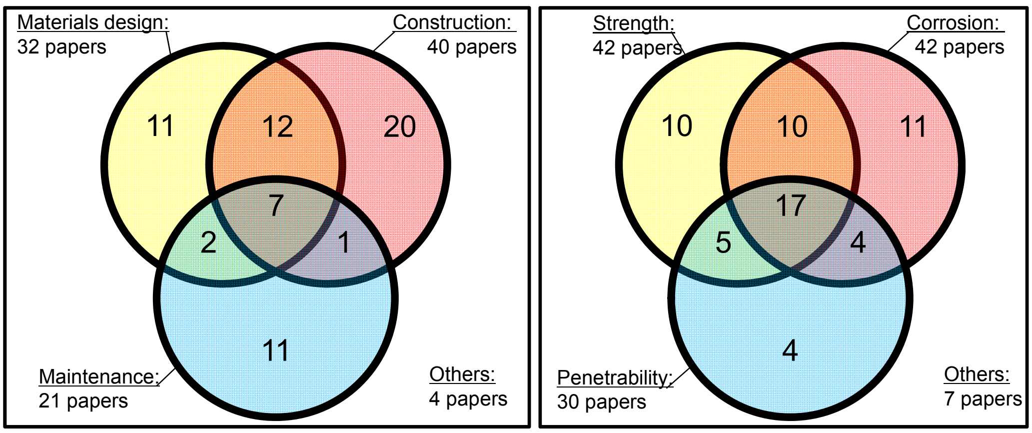


Figure 1. Number of papers related to concrete mixed with seawater. (published from 1974 to 2011)

These papers were classified into different topics as defined in Figure 2. Figure 2.(a) shows the results related to the objective fields of the paper such as materials design, construction or maintenance. Also the results of investigated items such as strength, corrosion or penetrability of concrete is shown in Figure 2.(b). From these figures, it can be seen that the properties of concrete mixed with seawater have been widely investigated from several aspects up to now.



(a) Objective fields **(b) Investigated items**

Figure 2. Objective fields and investigated items (Total number: 68 papers)

Results obtained in literature surveys. The noteworthy results of the surveys are summarized in Table 1. In the case of fresh concrete properties, seawater may affect some properties such as setting time. Thus some studies suggested the use of appropriate chemical admixtures in order to obtain the proper workability of concrete mixed with seawater (Kaushik, 1995).

Also, it can be summarised that the strength of the concrete mixed with seawater is initially higher than that with fresh water. Then, the difference of strength after the long term exposure due to the type of mixing water becomes small. For example Mori et al. (1981) reported that the difference of strength between concrete mixed with seawater and fresh water is relatively small after 10 years of exposure test. Additionally, according to Yamamoto (1980), the concrete mixed with seawater may show higher strength compared with fresh water mixing under the environment below 15 ºC.

On the other hand, the use of seawater is considered as risky because the large amount of Cl in concrete easily generates steel corrosion. For example, Neville (2001) recommend that the seawater should not be used as mixing water for concrete reinforced by steel bars because of the high risk of corrosion. However the results of the long term exposure tests conducted by Port and Airport Research Institute in Japan indicated that the amount of Cl measured in concrete after 20 years of exposure is not affected by the mixing water (Fukute, 1990) and the negative influence of seawater used as mixing water is relatively decreasing with age (Otsuki, 1985).

Figure 3 shows the time dependent changes of corroded areas (Otsuki, 2011). 5 different kinds of cement were considered in the experiment. Also, the amounts of SO_3 were changed. As mixing water, fresh water and seawater were used. The size of the specimen was 150mm diameter and 300mm height. 3 round steel bars of 9mm diameter were used for reinforcement, with a concrete cover depth of 30, 50 and 70mm. After the curing, these specimens were exposed to tidal zone. The corroded area of steel bars were measured using a planimeter and percentages against steel bars' surfaces were calculated. For each condition 3 to 5 steel bars were tested and the values were averaged.

From this figure, we can see that the influence of cement type is much larger than that of mixing water. Also, it is clearly recognized that the influence of mixing water is negligible especially after 20 years exposure. The corrosion resistant of BFS and alumina cement can be recognized far better than those of OPC, HSC and MHC even mixed with seawater.

From this 20 years' exposure test, the kind of mixing water has little influence on the corrosion and the specimens with BFS are far better than those with OPC, HSC and moderate cement notwithstanding the kind of mixing water.

Also there are some reports describing the actual application of concrete mixed with seawater around the world. For example, Novokshchenov (1995) reported the deterioration of reinforced concrete structure in marine environment constructed in the Arabian Gulf in 1977. This structure was seriously deteriorated due to steel corrosion. However, according to the authors, this deterioration may not be due to Cl derived from mixing water only, but also to the sever environment, especially sulphate attack. Besides, the water-cement ratio of concrete was relatively high (0.52-0.74) and ordinary Portland cement was used as cement. In the case of the low water-cement ratio such as 0.27 (Gayner, 1979) or the use of proper mineral admixture such as BFS (Ozaki, 1984), the steel corrosion in concrete mixed with seawater can be avoided even in the existing reinforced concrete structures.

Table 1 Noteworthy results in literature reviews

Items	Noteworthy results
Mix proportion	When fresh pastes are exposed to seawater their surfaces rapidly become coated with an almost impenetrable layer of brucite. The protective layers allow the hydration and pozolanic reactions to proceed without being disrupted significantly by seawater attack. (Jensen, 1988) No significant transformation of hydration phases from CAH_{10} to C_3AH_6 is found for alumina cement concrete mixed with seawater. It shows a dense (almost nonporous) microstructure at the inner and outer regions of the specimens, and also a dens (almost nonporous) steel-concrete interface compared with the same mixed with fresh water. (Tarek, 2004)
Fresh property	Seawater decreases the setting time of cement by 30-75% as the concentration of the mixing seawater increases from 1N to 10N therefore the use of suitable retarding admixtures is recommended in such cases. (Kaushik, 1995)
Strength	The difference of the strengths of concrete mixed with seawater and fresh water is small after 10 years exposure test. (Mori, 1981) Seawater affects the gain in strength of cement when used for mixing. It increases the early strength up to 7 days but ultimately the strength decreases by about 13% at 28 days. (Kaushik, 1995) There was no significant difference of the strength in seawater between cement and fly ash cement until 28 days' duration. (Noma, 1994) The strength of concrete with BFS cement is higher than that with OPC after immersing natural seawater. The density of concrete specimen becomes lowest in the case of BB cement. (Yoda, 1981) The strength of concrete mixed with NaCl under low temperature (under 15ºC) become higher than that without NaCl.(Yamamoto, 1980)
Penetrability	50 % of the Cl in concrete mixed with seawater is fixed in cement hydrates. (Kobayashi, 1984) It was found that the concrete, which was made from BFS and volcanic ash and appeared to contain sea sand, had scarcely deteriorated at all, even though it had been exposed to seawater environment for 60 years. The volcanic ash used during the mixed improved the water tightness of the concrete by pozolanic reaction, and seems to be useful in controlling the deterioration of concrete. Although sea sand was used in the mixing of concrete, there was no evidence of severe corrosion of the reinforcing bars. (Ozaki, 1984) The amount of Cl measured in concrete after 20 years' exposure is not affected by the mixing water. (Fukute, 1990)
Corrosion	Although sea sand was used in the mixing of concrete, there was no evidence of severe corrosion of the reinforcing bars. (Ozaki, 1984) The influence of initial content of Cl in concrete is not largely influenced on the corrosion of steel bar in concrete. Also concrete with alumina cement or BFS cement have high resistance against Cl penetration or steel corrosion in concrete. (Fukute, 1990) The corrosion of steel bar in concrete with seawater tends to be higher than that with fresh water and it is depends on the cover depth. No distinct corrosion was observed at uncracked section, providing concrete mixed with the service water and concrete cover of 40 cm. Reinforcing bars at cracked section corroded by 35 percent among whole crack width of less than 0.1mm and half of them showed distinct observed corrosion. (Seki, 1976) The negative influence of the Cl in the mixing water (in the materials used) is relatively decreasing with age. The influence of curing condition, crack and kind of cement is larger than the usage of seawater.(Otsuki, 1985)
Anti-corrosive materials	The addition of 2% $NaNO_2$ to the mortar effectively counters the risk of corrosion in reinforcements embedded on concrete mixed with seawater. The addition of nitrite, whether during the making of mortar specimens or by subsequent immersion in solutions containing the inhibitor, provide ineffective for passivating strongly rusted surfaces. (González, 1998) The use of calcium nitrite-based corrosion inhibitor was an effective and relative low-cost method to protect the reinforcing steel from corrosion under an aggressive seawater exposure. The addition of a calcium nitrite-based corrosion inhibitor in concrete accelerated cement hydration, increased the erly age strength, reduced the late age strength, and resulted in slightly higher expansion.(Lee, 1997) Bamboo reinforcement has high strength and durability but the low bonding strength between concrete and bamboo and generation of fungus should be solved. (Horii, 2007)
Carbonation	The rate of carbonation of concrete mixed with seawater is lower than that with fresh water.(Nakajima, 1981)
Freezing and thawing	The resistance against freezing and thawing decrease when the Cl content becomes over 0.5 % of cement. (Yamato, 1987)

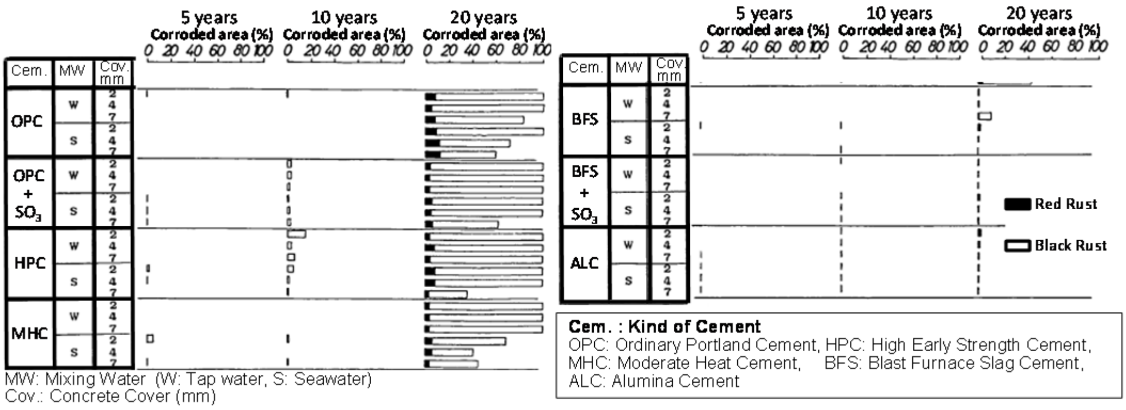


Figure 3. Time dependent changes of corroded areas (%). (Otsuki, 2011)

Positive and negative opinions against seawater used in reinforced concrete. From the above discussions, it can be seen that there have already been wide information about the properties of concrete mixed with seawater, and that the negative influence of seawater used as mixing water is relatively low in long term exposure to marine environment, compared to fresh water mix by using proper materials. However the use of seawater in reinforced concrete is still prohibited around the world.

In this chapter, the positive and negative opinions against concrete mixed with seawater obtained in literature-based study were discussed. Figure 4 shows positive and negative opinions against concrete mixed with seawater analyzed taking in account different cement types. From this figure, in the case of OPC, the percentage of negative opinion was larger than that of positive opinion although the percentage of positive and negative opinion in the total was almost same. In the case of BFS or FA, it seemed like the use of mineral admixture in concrete mixed with seawater shifted the opinions from negative to positive. So it was important to clarify the effect of mineral admixtures against the steel corrosion embedded in concrete and quantitatively evaluate the durability of reinforced concrete mixed with seawater. In the next chapter, the fundamental experiments were conducted in the laboratory and the effect of BFS on the resistance to chloride attack in reinforced concrete mixed with seawater was clarified.

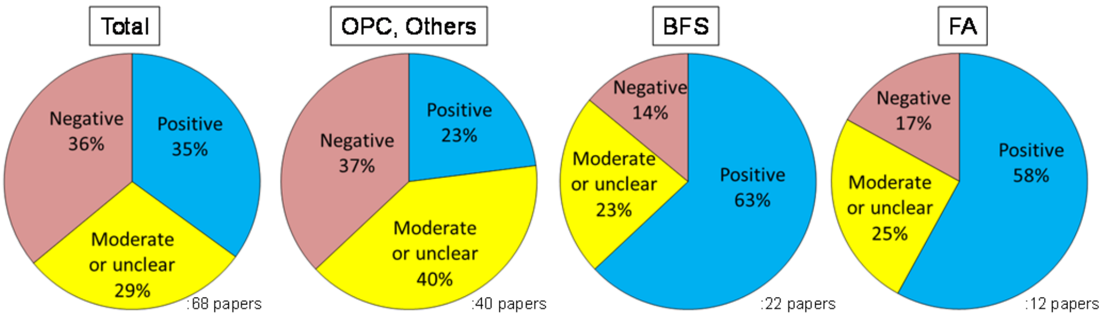


Figure 4. Positive and negative opinions against concrete mixed with seawater using total and each cement.

STEEL CORROSION IN CONCRETE MIXED WITH BFS AND SEAWATER

Experimental procedures. In this section, the resistance of steel corrosion in concrete mixed with seawater due to chloride attack was evaluated using the experimental data obtained by authors. The Cl content, the cathodic/anodic polarization behaviour and the time dependent change of corrosion current density of steel bars in concrete were investigated in order to understand the resistivity to corrosion of steel bars in concrete mixed with seawater.

The specimen used in this investigation was mortar and concrete. The both of water cement ratio of specimen were 0.5. The mix proportions of mortar and concrete specimens are shown in Table 2(a) and (b). In order to evaluate the effect of BFS on the corrosion of steel bars in concrete, a part of the ordinary Portland cement was replaced by BFS, at 0, 40 and 55 % ratio.

The specimens were mixed with fresh water or artificial seawater. The chemical composition of artificial seawater is given in Table 3.

Table 2 Mix proportion of concrete and mortar specimen. (W/C=0.5)

(a) concrete specimen for the evaluation of Cl^- contents

No.	BFS Ratio (%)	Mixing water	s/a (%)	Unit of weight (kg/m³)					C x (%)		Slump (cm)	Air (%)
				W	C	BFS	S	G	AW	AE		
OPC- F	0	Fresh	42	171	342	0	764	1052	1.4	0.017	7.0	3.0
B40- F	40			171	205	137	748	1047	1.4	0.021	10.5	3.0
B55- F	50			171	154	188	748	1044	1.2	0.021	7.5	2.9
OPC-S	0	Sea		171	342	0	764	1052	1.4	0.017	7.0	3.0
B40-S	40			171	205	137	748	1047	1.4	0.021	13.0	3.1
B55-S	50			171	154	188	748	1044	1.2	0.021	10.5	3.1

(b) mortar specimen for the evaluation of corrosion situation

No.	BFS Ratio (%)	Mixing water	S/C (%)	Unit of weight (kg/m³)			
				W	C	BFS	S
OPC- F	0	Fresh	2.0	311	622	0	1245
B40- F	40			305	366	244	1220
B55- F	50			303	272	333	1210
OPC-S	0	Sea		311	622	0	1245
B40-S	40			305	366	244	1220
B55-S	50			303	272	333	1210

W: water (fresh water or seawater), C: ordinary Portland cement (density: 3.14g/cm³, surface area: 4660cm²/cm³), BFS: blast furnace slag (density: 2.89g/cm³, surface area: 4200cm²/cm³, activity index (28days): 94%), S: natural river sand (density (SSD): 2.60g/cm³, water adsorption ratio: 2.20%, F.M. 2.59), G: crushed stone (density (SSD): 2.65g/cm³, water adsorption ratio: 1.09%, F.M. 6.71), AW: Air entraining water reducing agent, AE: Air entraining agent, Seawater: artificial seawater mixed with chemicals shown in Table 3.

Table 3 Chemical composition of artificial seawater.

Chemicals	NaCl	$MgCl_2$-$6H_2O$	Na_2SO_4	$CaCl_2$	KCl	$NaHCO_3$
Weight (g/L)	24.54	11.10	4.09	1.16	0.69	0.20

The quantity of water soluble Cl in concrete was measured using JCI method (SC-4). The test samples were taken from the middle of cylindrical concrete specimens (diameter: 100mm, height: 200mm) after submerged to seawater for 7days. In the meantime, electrochemical measurements for evaluating the corrosion phenomena of steel bars in mortar mixed with seawater were also conducted. The mortar specimens, with 3 round steel bars (Φ13mm, cover depth: 10mm) embedded, were exposed to sprayed environment of 3.0% NaCl solution at 50°C. Here the cathodic/anodic polarization curve and polarization resistance were electrically measured as shown in Figure 5. Electric current was applied between steel bar (WE: working electrode) and stainless plate (CE: counter electrode) in the measurement of the cathodic and anodic polarization curve with 1.0mV/sec of the sweep speed. On the other hand, the polarization resistance was measured by AC impedance method using high frequency (10kHz) and low frequency (10mHz) alternative current and corrosion current density was calculated with 0.0209V of Stern-Geary constant (Stern, 1957).

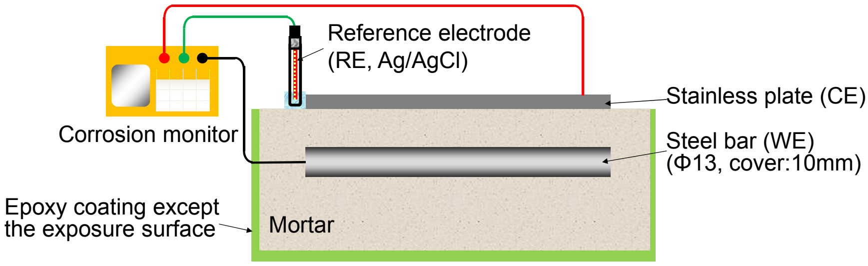
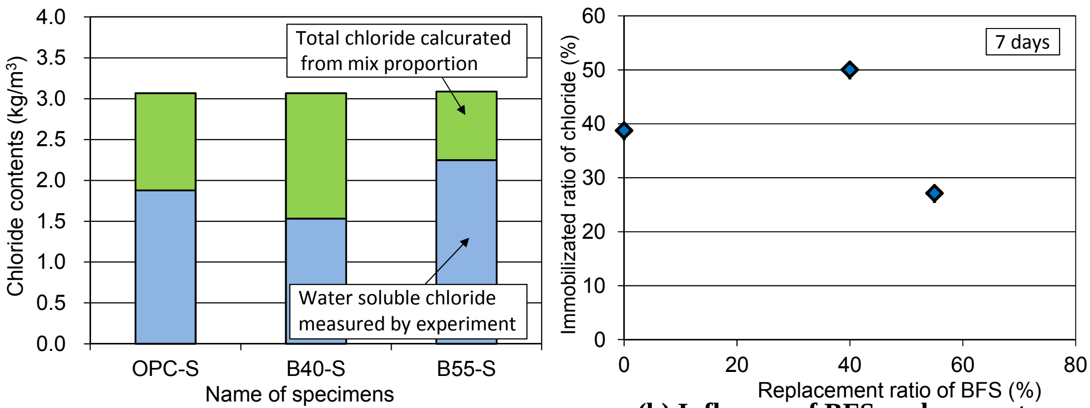


Figure 5. Measurement of polarization curves and polarization resistance.

Cl in concrete mixed with seawater. The large amount of Cl may cause the corrosion of steel bars in concrete. Especially the quantity of water soluble Cl is the most important factor in the corrosion of steel bars in concrete, because it destroys directly the passivation film around steel bars. Therefore it is necessary to clarify the water soluble Cl content in concrete in order to understand the corrosion phenomena. Since BFS cement is considered to have a high ability of Cl immobilization, the authors can assume that the usage of BFS may be effective to concrete mixed with seawater. Therefore the influence of BFS replacement on the ability of immobilization was investigated here.

Figure 6(a) shows the Cl content in concrete mixed with seawater after 7 days. Here total chloride content of Cl is calculated from mix proportion of concrete. From this, the water soluble Cl content varied according to the replacement ratios of BFS. The influence of BFS replacement ratio on immobilization of Cl in concrete calculated from Cl content is shown in Figure 6(b). The highest rate of immobilized Cl was obtained with 40 % replacement of BFS and almost half of Cl was immobilized in the cement hydrates. From the viewpoint of the initial situation of Cl, it was estimated that the 40 % replacement of BFS was the most efficient against steel corrosion in concrete mixed with seawater.



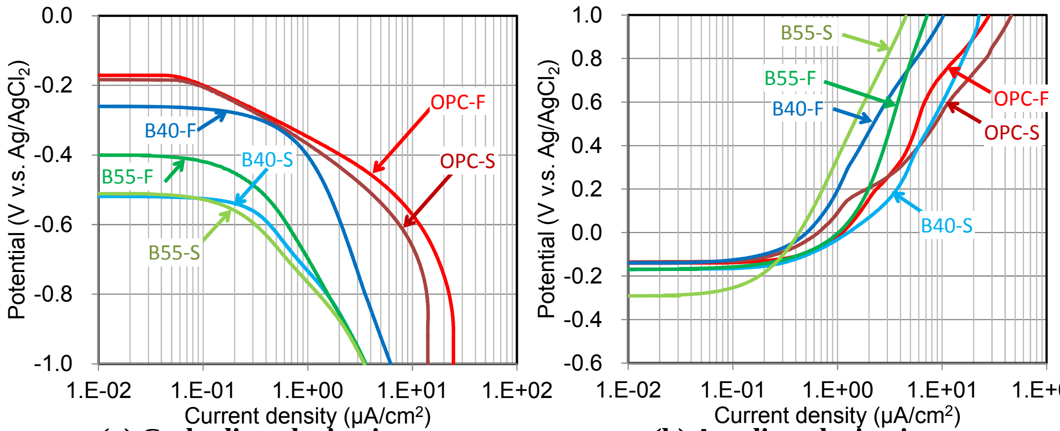
(a) Cl content

(b) Influence of BFS replacement on immobilization of Cl

Figure 6. Initial content and immobilization ratio of Cl in concrete mixed with seawater (after 7days).

Cathodic and anodic polarization phenomena. The corrosion progresses based on the anodic and cathodic reactions and the rate of corrosion is decided by the balance of these reactions. Therefore cathodic and anodic polarization phenomena are also important to evaluate the corrosion of steel bars in concrete mixed with seawater. The cathodic and anodic polarization curves about 140 days of exposure to acceleration environment, when the steel corrosion had already started due to external Cl penetration in OPC concrete mixed with fresh water, were measured as shown below.

Figure 7 (a) shows the cathodic polarization curves of steel bars in mortar with different replacement ratio of BFS. From this, it was confirmed that the cathodic polarization curve went to left-down side of the graph with the increase of the replacement ratio, which indicated that the oxygen content around steel bar decreased when the higher replacement of BFS got higher. It was considered that this phenomenon was derived from the low pore volume of cement matrix in BFS mortar and the reduction action of BFS powder in concrete. Especially BFS power was produced under reductive atmosphere and oxidation number of Fe or Mn in BFS tended to low (Nippon Slag Association, 2012). Then, it was considered that the amount of oxygen around the steel bar in BFS decreased. Thus, from the viewpoint of cathodic polarization phenomena, it was estimated that the higher replacement of BFS was effective against steel corrosion in concrete mixed with seawater. On the other hand, Figure 7 (b) shows the anodic polarization curves of steel bars in mortar. From this, the current density of steel bar with OPC in anodic polarization tended to be larger than that with BFS. Especially the steel bars in concrete with more than 55 % replacement ratio of BFS seemed to have better passive film even if concrete was mixed with sea water. Considering the basic cathodic and anodic polarization phenomena, it seems that the higher replacement ratio of BFS has better corrosion resistance against chloride attack.

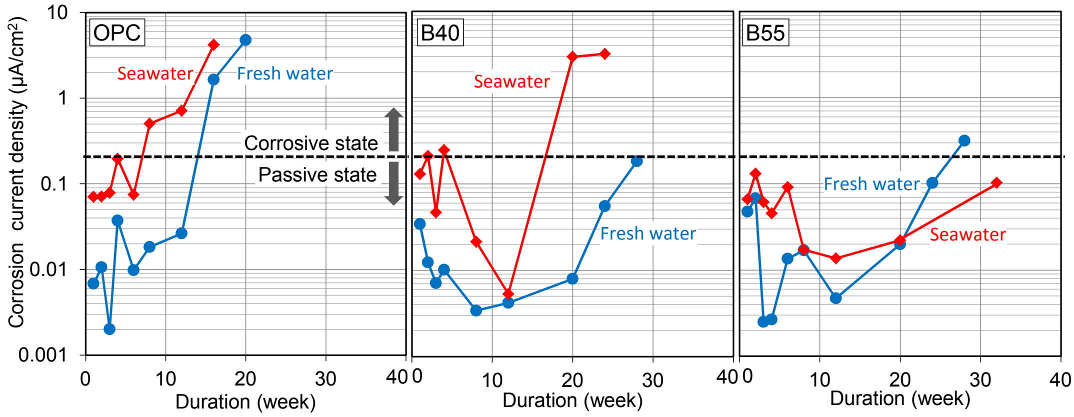


(a) Cathodic polarization curve **(b) Anodic polarization curve**

Figure 7. Cathodic polarization and oxygen diffusivity of concrete mixed with/without seawater.

Steel corrosion in concrete mixed with seawater. As the result of the literature study shown in Figure 3, BFS concrete mixed with seawater has high resistivity against chloride attack even after 20 years exposure to marine environment. In this section, the effect of BFS on the corrosion behaviour of steel bars in concrete was discussed using the data obtained in this study. The time dependent changes of steel bars in concrete under accelerated condition of chloride attack (50°C, spray of 3.0 % NaCl solution) is shown in Figure 8. In this graphs, 0.2 $\mu A/cm^2$ of the corrosion current density (dashed line) indicates the judgment criteria of corrosion proposed by CEB. In the case of OPC, the corrosion current density increased with the time and this tendency of seawater mixing was much faster than that of fresh water mixing. However, the periods over the criteria of CEB became longer as the BFS replacement ratio got higher. Also the difference between seawater and fresh water became smaller with the increase of replacement ratio especially at longer duration.

It was considered that the higher resistivity to corrosion of steel bars in mortar was due to the properties of BFS concrete, such as the Cl immobilization, low porosity and the low oxygen effect. Especially the tendency of corrosion resistivity of steel bar corresponded with the result of cathodic polarization phenomenon. Therefore it can be assumed that BFS was one of the effective additives for concrete mixed with seawater from the viewpoint of corrosion protection, and this effect derives from the low oxygen effect in the cement matrix as well as Cl immobilization.



dashed line : Judgment criteria of corrosion proposed by CEB,

larger than 0.2μA/cm^2 : Corrosive state, lower than 0.2μA/cm^2 : Passive state

Figure 8 Time dependent change of corrosion current density of steel bar under 3 % NaCl sol. sprayed condition at 50 °C

CONCLUSIONS

In the present study, the possibilities of using seawater mixed concrete were discussed based on the literature-based study and experimental investigations. As the results of literature-based study, more than half of papers collected in this study had a positive opinion toward concrete mixed with seawater by adding the mineral admixture such as BFS. Also the results of long term exposure test indicated the high possibility of utilization of seawater as a material of reinforced concrete. Moreover the experimental data indicated that the introduction of BFS might contribute significantly to the corrosion resistance of steel bar due to low oxygen environment around steel bar as well as Cl immobilization phenomena. Thus, it could be concluded that the steel corrosion in concrete mixed with seawater and BFS was not remarkably different from normal concrete.

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