

CORROSION EVALUATION OF REINFORCING BAR IN SEA WATER MIXED MORTAR BY ELECTROCHEMICAL METHOD

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ABSTRACT

Sea water has a potential to be used as mixing water. However, sea water contains high chloride ion concentration which can lead to accelerate corrosion of reinforcement. In order to investigate the effect of sea water as mixing water and partial replacement of cement by Blast Furnace Slag (BFS) on corrosion rate of reinforcement, electrochemical testing such as half-cell potential and polarization curve were conducted. The results show that sea water mixing reduced the passivity of reinforcing bar. However, partial replacement of cement by BFS can reduce the risk of corrosion.

Keywords: electrochemical method, sea water, corrosion

1. INTRODUCTION

Reinforced concrete structures in generally should be avoided from usage of sea water. The high chloride ion concentration, along with the presence of oxygen and water, leads to the acceleration of the corrosion process. Furthermore, the use of sea water as mixing water for reinforced concrete proposed more corrosion compared to the tap water as mixing water [1]. On the other hand, sea water has potential to be used as mixing water. However, in the case sea water used as mixing water, it is not recommended for reinforced concrete [2]. N. Otsuki reported, partial replacement of cement by BFS showed good performance when sea water is used as mixing water in view point of durability[3]. In order to investigate the effect of sea water used as mixing water and partial replacement of cement by BFS on corrosion rate of reinforcement, the experimental laboratory study was carried out. Corrosion activity of reinforcing bar can be evaluated by the electrochemical methods such as half-cell potential and polarization curve.

content of mortar mixed with natural sea water is 3.35 kg/m³ where according to the JSCE standard that the chloride corrosion threshold for corrosion initiation is 1.2 kg/m³ [4].

Table 1 Physical Properties

Material	Density, g/cm ³	F.M.
OPC	3.16	-
BFS 4000	2.91	-
Sand	2.58	2.77
Sea Water	1.03	-

Table 2 Physical Characteristics and
Chemical Component

Items	OPC	BFS
Density, g/cm ³	3.16	2.91
Blaine fineness, cm ² /g	3390	4000
MgO, %	1.2	5.32
SO ₃ , %	2.23	-
LOI, %	2.15	0.33
Total alkali, %	0.51	-
Chloride, %	0.019	0.006

2. EXPERIMENTAL DETAILS

2.1 Materials

The specimens were made with Ordinary Portland Cement (OPC) and Blast Furnace Slag (BFS). The physical properties are shown in Table 1. Further, the physical characteristics and chemical component are presented in Table 2.

2.2 Mixture Proportions

The mix proportions of mortar are summarized in Table 3. The water to binder ratio (W/B) of mortar was 50%. There is three type mix, consisted OPC with tap water mixing for control, OPC with sea water mixing and BFS with sea water mixing. The chloride

Table 3 Mix Proportions

Material	Mix-1	Mix-2	Mix-3
W/B, %	50	50	50
s/a, %	45	45	45
Tap water, kg/m ³	255	-	-
Sea water, kg/m ³	-	255	255
Cement, kg/m ³	510	510	255
BFS, kg/m ³	-	-	255
Sand, kg/m ³	1508	1525	1515

2.3 Specimen Design

The dimension of the specimen is 150mm x 100mm x 150mm. Deformed bar with diameter D-13 mm and plain bar φ13 mm with cover thickness 50 mm were casted. The summary of reinforcing bar type is

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described in Table 4. Two reinforcing bars were embedded in each specimen. There are three types of reinforcing bar; plain steel, epoxy-coated and stainless steel as shown in Photo 1. In the middle part of epoxy-coated reinforcing bar was damaged artificially. Moreover, variation of specimen were presented in Table 5. The specimen demolded after one day placing, then immediately cured in the water until 28 days. After that, five side surfaces of specimen were coated by epoxy resin before subjected to the dry-wet cycle. Furthermore, specimens were set into the dry-wet cycle condition after 28 days. One cycle was 7 days, consisted of 2 days drying (air dry) and 5 days wetting (immersed in tap/sea water). The summary of various curing types it's shown in Table 6.

Table 4 Reinforcing Bar Type

Reinforcing	Size
Epoxy-coated Damage (D)	D13
Epoxy-coated No Damage (ND)	D13
Stainless steel	D13
Plain steel	φ13

Table 5 Variation of Specimen

Type	Specimen Name	Curing Type			
		I	II	III	IV
N	N-EC-D	○		○	
	N-EC-ND			○	
	N-SS			○	
	N-PS	○		○	
N	N-EC-D		○		○
	N-EC-ND		○		○
	N-SS		○		○
	N-PS		○		○
B	B-EC-D		○		○
	B-EC-ND		○		○
	B-SS		○		○
	B-PS		○		○

Notation: N = Ordinary Portland Cement
 EC = Epoxy-coated steel bar
 SS = Stainless steel bar
 PS = Plain steel bar, B = Blast Furnace Slag
 ND = No Damage, D = Damage

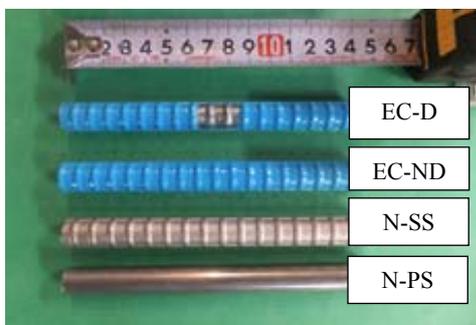


Photo 1 Reinforcing bar

2.4 Experimental Methods

An electrochemical technique by half-cell potential measurement to determine corrosion risk of

reinforcing bar in concrete. The corrosion potential, E_{corr} (half-cell rebar/concrete) is measured as potential difference (in voltage) against a reference electrode (half-cell) [5]. A more negative voltage reading is interpreted to mean that the embedded bar has more excess electrons, and there is, therefore, a higher potential that the bar is corroding [6]. Assessment on Grades of corrosion risk for reinforcing bar based on half-cell potential is given in Table 7 according to ASTM C876-09 [7].

Table 6 Type of Curing

Type	Mix	Curing	Dry-wet Cycle (2/5)
I	T	T	T
II	S	T	T
III	T	S	S
IV	S	S	S

Notation: T = tap water; S = sea water

Table 7 Corrosion probability (ASTM C876-09)

Half-cell Potential (V, CSE)	Corrosion Activity
$-200 < E$	90% no corrosion probability
$-350 < E < -200$	uncertainty
$E < -350$	90% corrosion probability

Polarization curve measurement was conducted to obtain condition of passivity film and oxygen supplies in the concrete. At present, measurement of the polarization curve takes about 40 minutes and the specimen should be immersed in a solution [8]. Judgment standard of passivity Grade is proposed for the polarization curve obtained by the immersion method based on the findings of Otsuki [9] as presented in Table 8.

Table 8 Grade of passivity film associated anodic polarization curve [9]

Grade	OPC	BFS
Grade 0	potential 0.2-0.6V, current density is over 100 $\mu\text{A}/\text{cm}^2$ at least one time	no passivity exist
	potential 0.2-0.6V, current density is 10-100 $\mu\text{A}/\text{cm}^2$	
Grade 2	potential 0.2-0.6V, current density is over 10 $\mu\text{A}/\text{cm}^2$ at least once but not to qualified to Grade 1 and 3	certain degree of passivity exist
	potential 0.2-0.6V, current density is 1-10 $\mu\text{A}/\text{cm}^2$	
Grade 4	potential 0.2-0.6V, current density is over 1 $\mu\text{A}/\text{cm}^2$ at least once but not qualified to Grade 1, 2 and 3.	excellent passivity exist
	potential 0.2-0.6V, current density is less than 1 $\mu\text{A}/\text{cm}^2$	

In addition, chloride ion concentration was measured at certain depths of specimens. The

specimen were cut in three layers from the surface of concrete, with 10 mm thick for each layer and crushed into powder. The amount of chloride ion concentration in concrete was determined based on JSCE-G573-2003.

3. RESULT AND DISCUSSION

3.1 Control Conditions

Fig.1 shows half-cell potential value of specimen with curing Type I (tap water mixing; tap water curing) as control. Two types of reinforcing bar was embedded, plain steel (PS) and epoxy-coated with damage (EC-D). Properties of fresh mortar with slump flow 135.5 mm and air content 5.2%. Measurement time 0 weeks mean just after placing and 1/7 weeks means one day after placing. In the initial age just after placing, the half-cell potential value was less than -350 mV, and then increased after one day. This indicates, the half-cell potential value becomes more positive after hydration of cement. The reinforcing steel epoxy-coated with small damage and plain steel show no corrosion, based on half-cell potential test value higher than -200 mV.

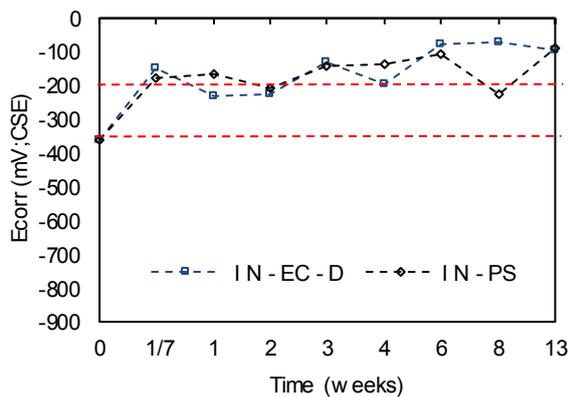


Fig.1 Half-cell potential (Type I)

Anodic polarization curve is related to quality of passivity film. When the current density becomes larger, the Grade of passivation film becomes worse. On the other hand, cathodic polarization is related to diffusion of oxygen. When the current density becomes larger, it is indicating that the level of oxygen supply becomes larger.

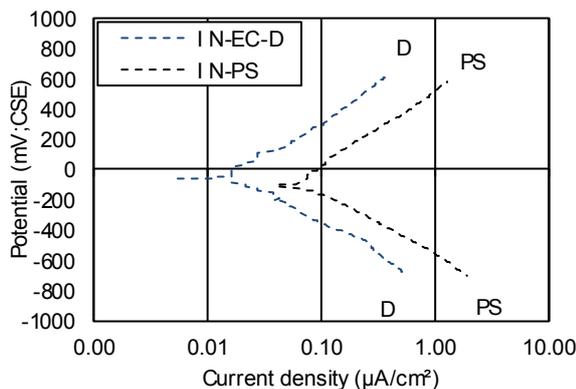


Fig. 2 Polarization curve (Type I – 13 weeks)

The result of polarization curve for Type I (tap water mixing; tap water curing) is shown in Fig.2. The epoxy-coated reinforcing bar (D) shows good performances than reinforced plain steel (PS). The anodic polarization curve for reinforced epoxy-coated showed lesser current density than $1 \mu\text{A}/\text{cm}^2$ categorized Grade 5 (excellent passivity exists). Furthermore, reinforced plain steel showed current density is over $1 \mu\text{A}/\text{cm}^2$ categorizes as Grade 4 (certain degree of passivity exist). Both reinforcing bar showed good passivity, due to the usage of tap water.

3.2 Effect of Sea Water Mixing

Fig.3 shows half-cell potential value of specimen with curing Type II (sea water mixing; tap water curing). There are four type reinforced steel embedded in this condition, epoxy-coated with small damage (EC-D) and no damage (EC-ND), stainless steel (SS) and plain steel (PS). Properties of fresh mortar sea water mixing with slump flow 133.5 mm and air content 5.4%. In addition, properties of fresh mortar sea water mixing with partial replacement of cement by BFS with slump flow 158 mm and air content 5.5%. The same pattern is obtained as shown in Fig.1. In the early age after placing, the half-cell potential value was less than -350 mV and increased after one day. All measurement data can be categorized an increasing probability of corrosion. This is due to the chloride ion existing in mortar from mixing water. Moreover, the trend value of half-cell potential along with increasing age of specimen shows more positive than -200 mV. This is considered that tap water as curing water could increase the resistance of concrete against. In this group, reinforced steel epoxy-coated showed the best performance in the corrosion resistance.

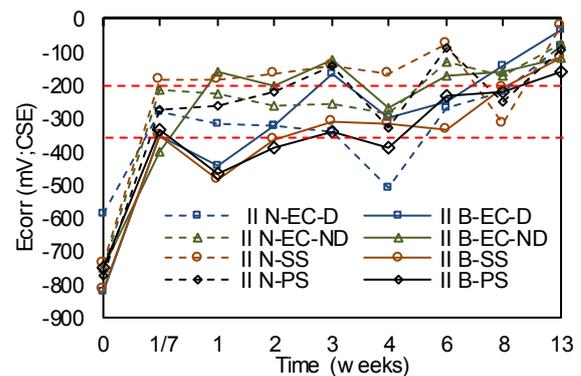


Fig.3 Half-cell potential (Type II)

For specimens using sea water as mixing water, anodic and cathodic polarization curve is shown in Fig.4. The best performance is exhibited by reinforced steel epoxy-coated, for anodic polarization curve whose current density shows value less than $1 \mu\text{A}/\text{cm}^2$ categorized as Grade 5 (excellent passivity exists). It is indicates that sea water mixing increase the current density than tap water as mixing water. The increasing of current density is about 9.2%, as obtained that is $1.31 \mu\text{A}/\text{cm}^2$ with tap water mixing and $1.43 \mu\text{A}/\text{cm}^2$

with sea water mixing. On the other hand, partial replacement of cement by Blast Furnace Slag provided passivity film better than Ordinary Portland Cement. All specimens with BFS have smaller current density than OPC. Obtained current density is $1.18 \mu\text{A}/\text{cm}^2$ with BFS. Similar trend is also shown in cathodic polarization curve, in which BFS exhibited smaller current density than OPC. This indicates that partial replacement of cement with BFS show smaller oxygen supply.

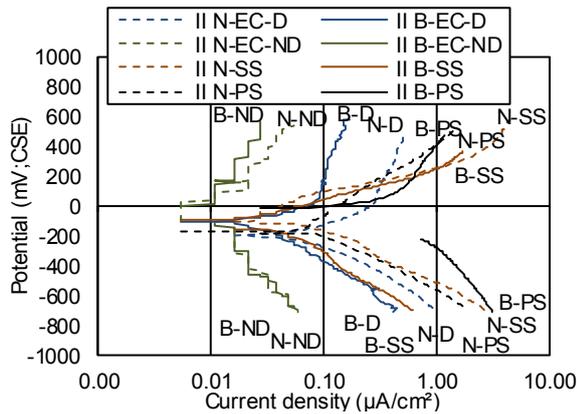


Fig. 4 Polarization curve (Type II – 13 weeks)

3.3 Effect of Sea Water Curing

Fig.5 shows half-cell potential value of specimen with curing Type III (tap water mixing; sea water curing). Variation of reinforced steel is same with curing Type II. The phenomenon in the initial age also continued where potential value was less than -350 mV just after placing and increased after one day. The half-cell potential value showed constant at range between -200 mV and -350 mV. These series is likelihood to the real condition, where concrete are directly exposed by sea water. The effect of sea water as curing water generates uncertainty or increasing probability of corrosion with potential value between -350 mv and -200 mV. The best performance in corrosion resistance is shown by stainless steel (SS), where potential value became more positive than -200 mV and indicated low potential corrosion.

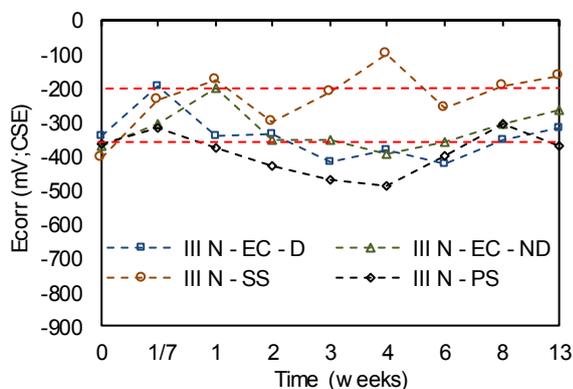


Fig.5 Half-cell potential (Type III)

The effect of sea water as water curing on polarization curve for Type III (tap water mix; sea

water curing) is described in Fig.6. Reinforced plain steel bar in Fig. 4 showed that current density is over $1 \mu\text{A}/\text{cm}^2$ with certain degree of passivity exist as Grade 4. On the other hand, reinforced plain steel bar in Fig. 6 showed current density almost over $10 \mu\text{A}/\text{cm}^2$ a categorized as Grade 3. It is considered that sea water curing increase the amount of chloride ion ingress into mortar and increase current density. The others reinforcing bar showed same pattern with type III. The best performance in passivity is shown by reinforced epoxy-coated steel bar.

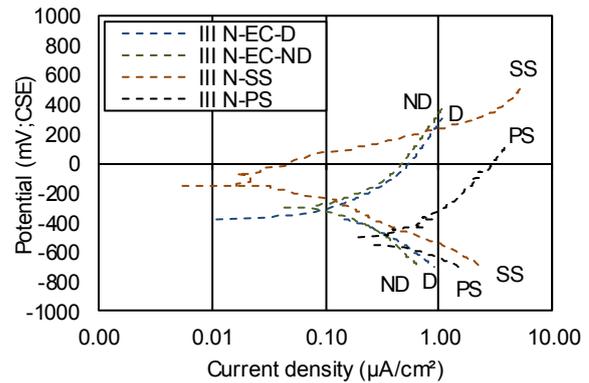


Fig. 6 Polarization curve (Type III – 13 weeks)

3.4 Effect of Sea Water Mixing and Curing

Fig.7 shows half-cell potential value of specimen of Type IV (sea water mixing; sea water curing). From this figure, it can be understood that sea water mixing and sea water curing increase probability of corrosion. It was observed that all data showed more negative than -200 mV, it indicates a high potential corrosion indicating 90% probability of corrosion. It seems that the high amount of chloride ions in mortar was caused by the use of sea water as water mixing and curing. When the chloride level reached the threshold and oxygen is supplied into mortar, corrosion initiated earlier than another series. Overall, stainless steel embedded in mortar showed the best performance in corrosion resistance. It can be seen from the potential value upper -350 mv.

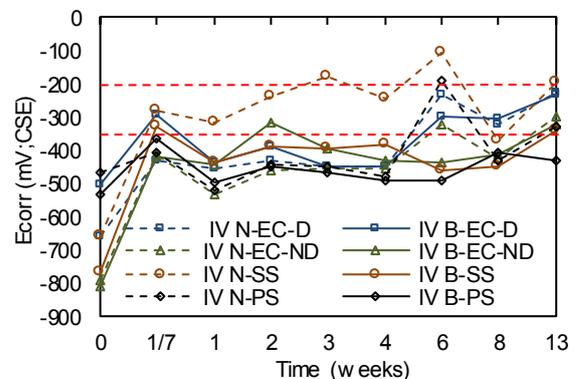


Fig.7 Half-cell potential (Type IV)

Fig. 8 shows polarization curve of type IV (sea water mixing; sea water curing). Reinforced epoxy-

coated steel shows good performance whose current density less than $1 \mu\text{A}/\text{cm}^2$ and it is categorized as Grade 5 (excellent passivity exist). Meanwhile reinforced plain steel shows the worst passivity film. Reinforced plain steel gave current density $4.0 \mu\text{A}/\text{cm}^2$, which is categorized as Grade 3 (certain degree of passivity exist), 200% larger than control specimen with $1.31 \mu\text{A}/\text{cm}^2$. This means that plain steel is prone to corrosion by use of sea water as mixing water and curing water. In addition, partial replacement of cement by Blast Furnace Slag shows better performance to reduce risk of corrosion and restrict the oxygen supplies than Ordinary Portland Cement. In specimen with reinforcing plain steel (PS) by BFS, with current density is $2.21 \mu\text{A}/\text{cm}^2$ and in specimen by OPC current density is $4.0 \mu\text{A}/\text{cm}^2$.

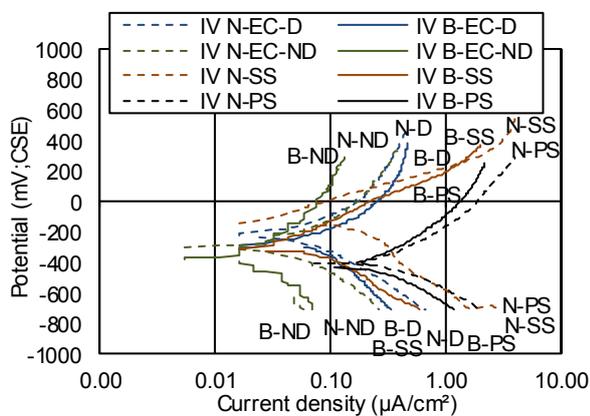


Fig. 8 Polarization curve (Type IV)

3.5 Chloride Ion Profile

Chloride ion concentrations at various depths from the surface of specimen are shown in Fig. 9, Fig. 10 and Fig. 11. The chloride ion profile for type I was not measured. The chloride ion distribution for type II (sea water mixing; tap water curing) is presented in Fig. 9. At the surface, chloride ion content is lower than certain depth of the mortar. It indicates that chloride contained in sea water as mixing water has undergone washing process as a result of the use of tap water as curing water. In contrast, on the type III and IV higher chloride content at the surface than certain depth of the mortar is found as shown in Fig. 10 and Fig. 11.

Fig. 10 shows the result of chloride ion distribution for type III (tap water mixing; sea water curing). The chloride ion distribution for type IV (sea water mixing; sea water curing) is presented in Fig. 11. Partial replacement of cement with Blast Furnace Slag shows positive effect of chloride ion ingress. The specimen with BFS gave lower chloride content than OPC. In the specimens with BFS, the chloride content in the surface were 10.80 kg.m^3 (IV B-EC-D), 11.17 kg.m^3 (IV B-EC-ND), 11.33 kg.m^3 (IV B-SS) and 12.77 kg.m^3 (IV B-PS) smaller than with OPC, 11.86 kg.m^3 (IV N-EC-D), 13.27 kg.m^3 (IV N-EC-ND), 12.90 kg.m^3 (IV N-SS) and 13.47 kg.m^3 (IV N-PS). This trend also continues at 3 cm of depth. If 1.2 to 3.0

kg/m^3 of chloride content is a threshold value for corrosion initiation, from Fig. 11, it can be seen that reinforcement without protection such as plain steel has started to corrode if cover concrete is smaller than 30 mm. Partial replacement of cement with BFS showed good performance to prevent the chloride ingress into mortar.

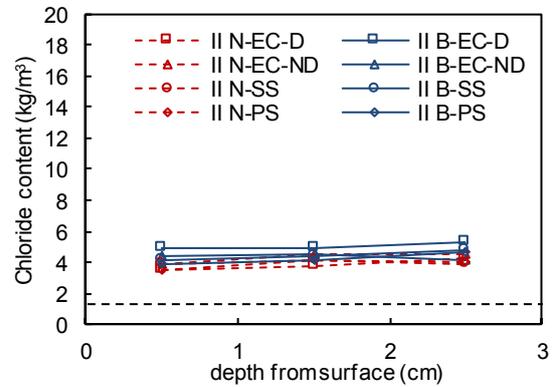


Fig.9 Chloride ion profile for Type II

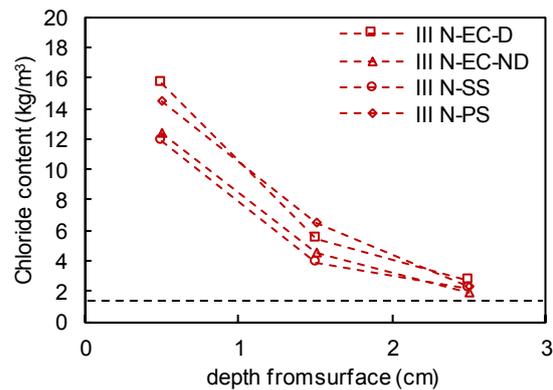


Fig.10 Chloride ion profile for Type III

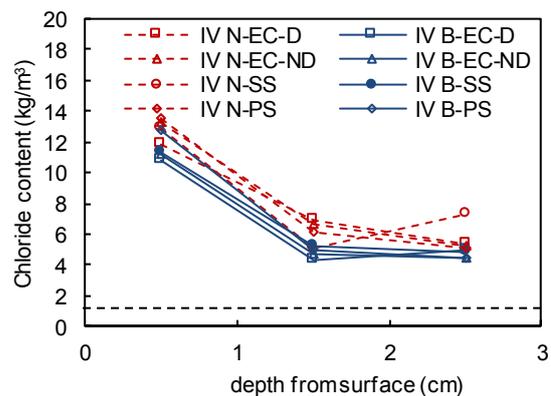


Fig.11 Chloride ion profile for Type IV

3.6 Corrosion Condition

After 13 weeks, specimens were crushed to observe corrosion condition. In the specimen II N-PS (sea water mixing; tap water curing) and IV N-PS (sea water mixing; sea water curing), corrosion initiated, even only as dots corrosion. This results indicate that

mortar with OPC have high corrosion risk when use sea water as mixing water. Specimen used partial replacement of cement by BFS also contain high of chloride content. However corrosion not occurred. It seems that BFS prevented diffusion of oxygen. The results show that sea water mixing reduced corrosion resistance of reinforcement. However, partial replacement of cement by BFS can reduce the risk of corrosion.

4. CONCLUSIONS

Both chloride diffusion and corrosion of reinforced concrete is particularly important in view point of durability of marine concrete. Sea water used as mixing water and also partial replacement of cement by BFS showed different result on corrosion activity. Based on the investigation, the following conclusions are drawn:

1. Both sea water as mixing and curing water give significant effect on corrosion activity. It could change transition form of steel from passive to active corrosion due to existing chloride ion. Corrosion can start as far as enough oxygen and water are supplied.
2. Partial replacement of cement by Blast Furnace Slag can reduce the risk of corrosion by reducing diffusion of oxygen. Partial replacement of cement by BFS could also decrease the permeability and ingress of chloride ion.
3. It is really recommended to use corrosion inhibitor of reinforced steel such as epoxy-coated to protect reinforcing steel from corrosion when sea water is used as mixing or curing water. Furthermore, reinforcing stainless steel bar as reinforcement also recommended because the critical chloride ion concentration of stainless steel (SUS304-SD) is 15 kg /m³.
4. Long term observation is required to check the trend of potential more negative with corrosion current density increment versus time. In addition, to understand the trend of corrosion due to use of sea water as mixing water.

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