- Technical Paper -

EFFECTIVENESS OF CALCIUM NITRITE AS CORROSION INHIBITOR FOR STEEL BAR COATING IN SEAWATER-MIXED MORTAR

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ABSTRACT

The attack of aggressive agents, such as chloride, is known to jeopardize the durability of concrete structures as it triggers corrosion in steel bars. Thus, the use of seawater in concrete-mixing has remained prohibited despite its high accessibility. In this study, Calcium Nitrite solution is initially added to the seawater-mixed concrete. Using non-destructive methods, its effectiveness as a coating for steel bar in seawater-mixed mortar is investigated. The results showed a pronounced effect of the different concentrations of Calcium Nitrite on the potential, besides, a better effect was found in the steel bar coated specimen.

Keywords: seawater-mixed mortar, corrosion, Calcium Nitrite, electrochemical measurement

1. INTRODUCTION

Because of its high impact on the durability of concrete structures, the corrosion of steel bars is a critical problem in need of solutions in engineering fields. When corrosion initiates in the reinforcing steel, the formation of cracks occurs after the expansion of the steel from its original diameters. However, the presence of cracks in concrete promotes the ingress of aggressive agents in vicinity of the reinforcing steel; therefore, it accelerates corrosion. Especially in marine environments, this issue is not foreign as it causes great damage.

However, the use of concrete consumes a huge amount of water across the world despite its scarcity, which is also a further issue in the field. Statistics suggest that some 2.1 billion m^3 of fresh water are comprised into the ten million of concrete worldwide every year [1]. The use of seawater as mixing water has been considered due to the great potential in its accessibility and quantity. Still, problems were raised as its use adds to the total volume of chloride in the original mix proportion of concrete, which is limited to 0.30kg/m^3 or less than 0.60kg/m^3 according to the JIS A 5308 for civil engineering concrete structures. In addition, chloride contamination into the original mix is also proven to be even more aggressive than the same quantity of chloride ingress during the service life [2]. As a result, the use of seawater as a mixing water in concrete is still forbidden in most existing standards.

The use of seawater-mixed concrete with the use of some cementitious materials such as Ground Granulated Blast Furnace Slag (GGBFS) and Fly Ash (FA) admixtures have also been explored in the past few years and showed some successful use in attempt to improve the quality of concrete [3]. Nevertheless, even concrete of good quality is reported to not withstand the attack of chloride when it is exposed to marine environments. Several types of corrosion prevention methods were then developed to tackle this issue, namely, the use of anodic protection such as corrosion inhibitors, stainless steel, epoxy coating or the use of cathodic protection, such us sacrificial anode cathodic protection. Over the last few years, the use of Calcium Nitrite Inhibitor has been of interest for its simplicity in usage, its cost effectiveness and its appreciated effect [4].

This study is a continuation of the effect of Calcium Nitrite for steel bar coating as corrosion inhibitor in seawater-mixed concrete [5]. In this paper, its effectiveness is investigated after 3 years of exposure. Investigations were undertaken using non-destructive electrochemical measurement.

2. TEST PROGRAMS

2.1 Specimen Materials

The experimental works incorporate two series of 12 specimens with a dimension of 120 mm x 135 mm x 135 mm. Ordinary Portland cement (OPC) and Ground Granulated Blast Furnace Slag (GGBFS) were used as a binder and sea sand was used as fine aggregates in the mortar mix. A reinforcing bar of 13mm was used for all specimens, with a concrete cover of 50mm.

All surfaces of each specimen except one surface for the measurement were coated with epoxy resins. The casting was done in the direction parallel to the rebar (Fig. 1).

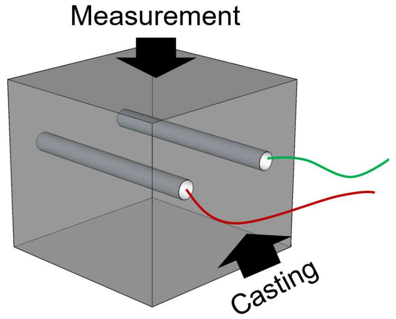

Fig. 1 Specimen outline
(120 mm x 135 mm x 135 mm)

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The characteristics of the materials used in this study are summarized in Table 1.

2.2 Specimen Outline

In Series 1 (CNI-Mortar specimens), Calcium Nitrite was added to the entire mortar mix with a water to cement ratio of 50%, and seawater (with 4.7736 kg/m3 of Chloride concentration vs. mortar) was used as mixing water as presented in Fig. 2. In Series 2, Calcium Nitrite was applied to the mortar for coating using tap water as mixing water, with a water to binder ratio of 40% as seen in Fig. 3. The thickness of the coating is about 3 mm. For the specimen, seawater was used as mixing water with a water to binder ratio of 50%.

For both series of specimens, respectively 1.5 liters/m^3 and 3 liters/m^3 of Calcium Nitrite solution was used containing 20% to 30% of Calcium Nitrite, as represented in Table 2 and Table 3. Series 1 and Series 2 were prepared in 2019 (Series 1= 31 months; Series 2= 30months).

2.3 Specimen Condition

The curing process of both Series were done by wrapping with wet towels, then they were stored in a controlled room maintained at 20º C for 28 days.

For Series 2, before the actual casting, the reinforcing bars were first coated with CNI-mortar, wrapped with wet towels, as presented in Fig. 4, and cured for 28 days.

After curing, the specimens were put under a dry-wet cycle for the first 7 months for series 1 and eight months for series 2 and the progress of corrosion was monitored at the laboratory room conditions. Dry-wet cycle, performed by immersing the specimens in a seawater, was used to simulate aggressive marine environments and to accelerate the initiation and progression of corrosion of steel bars. Then, both series specimens were stored in the laboratory at room conditions for 17 months and the actual conditions of the specimen were measured for 2 months under room conditions at a constant temperature of 20ºC. The

Table 1 Properties of materials

Material	Physical properties	
Ordinary Portland Cement	Density, [g/cm^3]	3.16
Ground Granulated Blast Furnace Slag	Surface area, [cm^2/g]	4000
Fine Aggregate (Sea sand)	Density, [g/cm^3] (SSD condition)	2.54
	Water Absorption, [%]	1.09
Round steel Bar	SS400 (Ø 13 mm)	
AE Water Reducer	Polycarboxylate ether-based	
AE Agent	Alkylcarboxylic type	

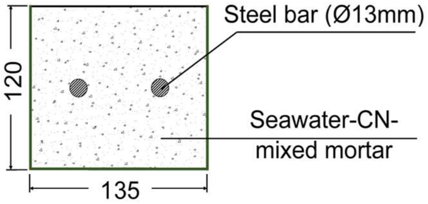

Fig.2 Series 1 – CNI-mortar specimen

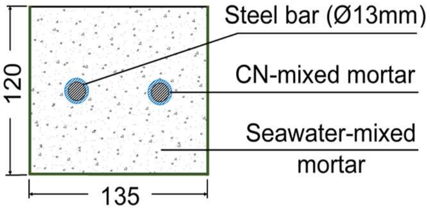

Fig.3 Series 2 – CNI-coating specimen

Fig.4 Steel coating and curing - Series 2

Table 2 Mix proportion of the mortar - Series 1 and Series 2

Specimen Name		CNI (l/m³)	W/C (%)	Unit Weight (kg/m³)			
				Seawater	OPC	GGBFS	Sand
Series 1	0N	0	50	255	510	-	1525
	1.5N	1.5					
	3N	3					
	0B	0	50	255	255	255	1515
	1.5B	1.5					
	3B	3					

Table 3 Mix proportion of the coating mortar - Series 2

Specimen Name		CNI (l/m³)	W/C (%)	Unit Weight (kg/m³)			
				Tap Water	OPC	GGBFS	Sand
Series 2	0NN	0	40	232	581	-	1508
	1.5NN	1.5					
	3NN	3					
	0BB	0	40	232	291	291	1514
	1.5BB	1.5					
	3BB	3					

specimens were subjected again to 5 days of dry and 2 days wet cycle under atmospheric conditions.

2.4 METHODS

Electrochemical measurement is popular as it gives an appropriate state of corrosion of reinforcing steel without requiring the concrete to be destroyed. Besides, most of the reaction happening inside of concrete as it corrodes is mainly electrochemical [2]. The use of the combination of the three methods: half-cell potential, current density, and polarization curve, is common as it provides different aspects of the corrosion of steel.

Series of testing were performed at the end of a wetting cycle. More specifically, at the end of one cycle for half-cell potential (every 7 days) and after 4 cycles of dry-wet for polarization curve and current density measurements (every month). The specimens were covered with a wet towel to ensure their moisture at least 30min before and during each testing.

(1) Half-cell Potential E_{corr}

Half-cell potential is a practical and sufficiently rapid electrochemical method used to assess or monitor the probability and progress of corrosion in reinforced concrete. The measurement was proceeded using an impedance multimeter and a reference electrode based on the ASTM C876-15 [6]. The reference electrode adopted was a Saturated Calomel Electrode (SCE) and the measurements were performed at room temperature. Afterward, the results from the measurements were converted to Copper Sulfate Electrode (CSE) value at 25ºC using the following equation:

$$E_{CSE} = E_{SCE} - 74 - 0.66 \times (t-25) \qquad (1)$$

Where,

E_{CSE} : Potential value in CSE (mV)
E_{SCE} : Potential value in SCE (mV)
t : Temperature (ºC)

(2) Current Density, I_{corr}

Current density measurement was done to investigate the corrosion rate in the steel bar. A portable rebar corrosion meter (SRI-CM-III) Shikoku Institute with Ag/AgCl for reference electrode was used for the measurements. The data were obtained straightforwardly by reading from the apparatus. The corrosion rate related to the current density in the steel is summarized according to the CEB standard [7]. The measurement were performed every month, however, the results shown is this paper are at 31 months and 30 months, respectively for Series 1 and Series 2.

(3) Polarization Curve

In this study, to determine the passivity state of the steel in the concrete, polarization curve measurement was performed. The grade of passivity is determined as a function of the current density; the larger the current density, the worse the grade of passivity (Fig. 5). Polarization curve by immersion in water, a method introduced by Otsuki [8], was employed for the tests. A potentiostat, a function generator and a data logger were employed in the measurement and a Saturated Calomel Electrode was used as a reference electrode. The passivity grade of the steel was afterward judged following the method proposed in Table 6. This paper records the data of the measurement done at the 31 months for Series 1 and 30 months for Series2.

Table 4 Half-cell potential range related to corrosion probability (ASTM C876)

Half-Cell Potential (E_{corr}) (mV; CSE)	**Probability of Corrosion**
$E_{corr} > -200$ mV	10%
$-350 < E_{corr} < -200$	Uncertain
$E_{corr} < -350$	90%

Table 5 Corrosion current density I_{corr} Criteria (CEB Standard)

Polarization Resistance (kΩ.cm²)	**Current Density (μA/cm²)**	**Corrosion Penetration (mm/year)**	**Corrosion Rate**
>130	<0.2	<0.0023	Very Low
52 - 130	0.2 - 0.5	0.0023 - 0.0058	Low to Medium
16 - 52	0.5 - 1	0.0058 - 0.0116	Medium to High
26	>1	>0.0116	Very High

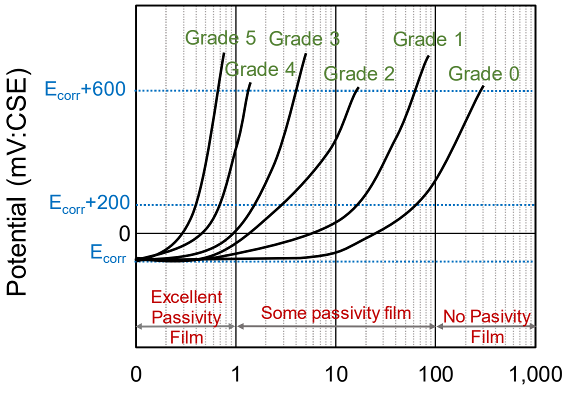

Fig.5 Grade of passivity

Table 6 Grade of passivity related to current density

Grade	**Potential**	**Current density**	**Passivity state**
0		$I_{corr} > 100\mu A/cm^2$ at least one time	No Passivity film
1	E_{corr}+200mV to E_{corr}+600mV	$10 < I_{corr} < 100\mu A/cm^2$	some passivity film
2		The anodic curve cut the 10 μA/cm²	
3		$1 < I_{corr} < 10$ μA/cm²	
4		The anodic curve cut the 1μA/cm²	
5		$I_{corr} < 1\mu A/cm^2$	Excellent Passivity film state

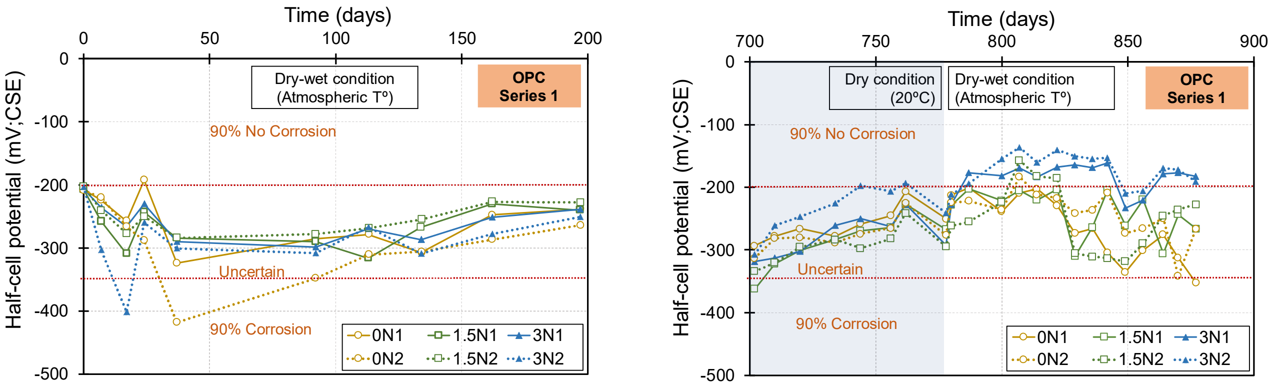

Fig.6 Half-cell Potential-Series 1- OPC specimen

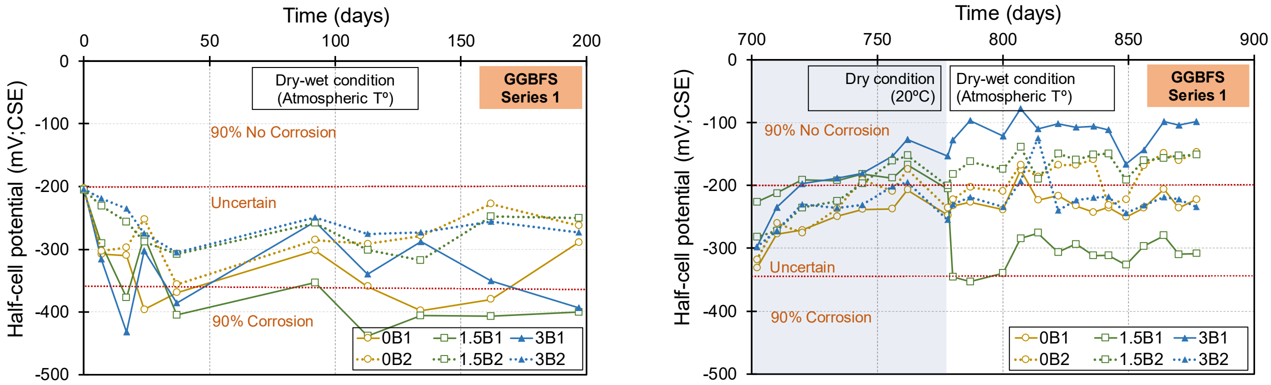

Fig.7 Half-cell Potential-Series 1 - GGBFS specimen

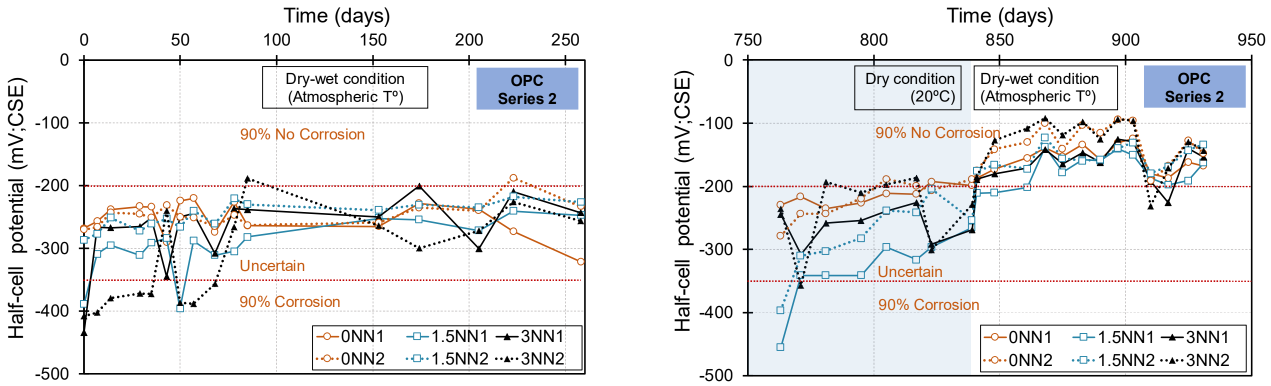

Fig.8 Half-cell Potential-Series 2 - OPC specimen

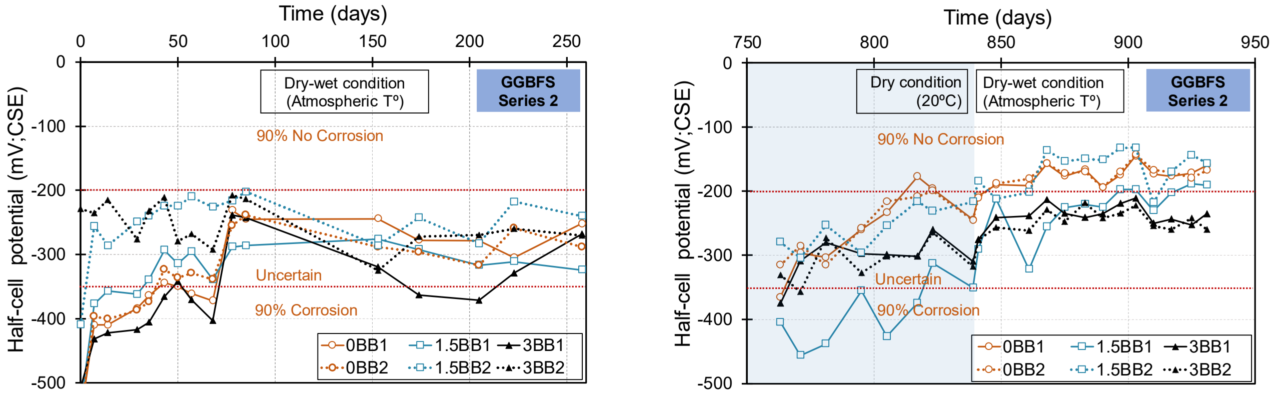

Fig.9 Half-cell Potential-Series 2 - GGBFS specimen

3. RESULTS AND DISCUSSION

3.1 Half-cell Potential

From Fig. 6, the potential of Series 1 shows a higher value after demolding (0 month of age). However, a slight decrease was observed during the hydration phase, which is consistent with previous research [9]. The potential gradually recovers, nevertheless, the average trend did not exceed the threshold value of the uncertain zone of corrosion (<200mV). In Series 2, however, the opposite trend is observed (Fig 7). The potential value decreased from its initial value after demolding during the hydration period, before it slightly recovers again. After being stored under laboratory conditions for several months, the specimens were monitored again. The specimens were first put under 20 ºC room under dry conditions to assess their actual conditions and measurement were done once a week. After 2months, it was put under wet and dry cycle again.

As seen in Fig. 6, for Series 1, the potentials are on average between -200 mv and -350 mV (zone of uncertain corrosion). The effectiveness of Calcium Nitrite in Series 1 OPC specimens is more pronounced and the higher the quantity of CNI, the better the potential of the rebar, which agrees with the results in previous research [10]. For the GGBFS specimens of Series 1(Fig. 7), the trend of the potential varies from the zone of 90% no corrosion to the zone of uncertain corrosion (-200 mV to -350 mV), which is more performant compared to the result of the OPC specimens. Though some of the rebar shows less performance compared to other rebars, the effect of the CNI is also observed but is not as straightforward as the results seen in Series 1 OPC specimens.

In Series 2, the potential of the OPC specimen has significantly shifted to a more positive value from the zone of uncertain corrosion to the zone of 90% no corrosion probability after it had been set under dry-wet cycle (Fig. 8). Nonetheless, the effect of the difference in concentration of CNI could not be distinguished due to the similar values shown but all specimens. For the GGBFS specimens, the potential shows a more positive value from -300 mV to -100 mV, as illustrated in Fig. 9. The effect of the CNI, however, shows the opposite trend to the specimen Series 1, as the specimens with a higher concentration of CNI shows a lower value of potential.

Moreover, from both Series, the trend of the effect of temperature is also observed. The half-cell potential decreases with increasing temperature and increases as the temperature drops. A similar result was reached in previous research. These results show that the CNI-coating specimens are more effective compared to CNI-mortar specimen. [11] It can be assumed that the use of lower water to binder ration and taper water has a role to play in this result along with the use of CNI.

3.2 Current Density

Fig. 10 and Fig. 11 illustrate the results from polarization resistance measurements at the 31 months for Series 1 and 30 months for Series 2. The chart shows that the current density of both Series 1 and Series 2 is under 0.2 μA/cm^2, which indicates a low corrosion rate after referring to Table 5. These results are probably due to the young age of the specimen.

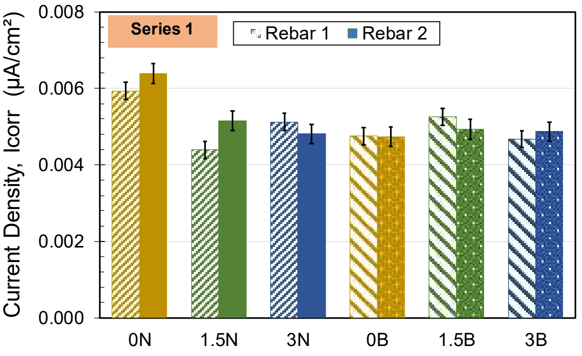

Fig.10 Current Density at 31 months - Series 1

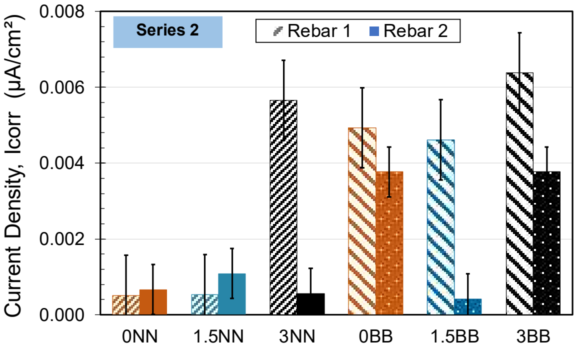

Fig.11 Current Density at 30 months- Series 2

Moreover, comparing Series 1 and Series 2, it can be clearly seen that the specimen with coating has significantly lower current density, which implies a lower corrosion rate; especially for the specimen 0NN and 15 NN. Therefore, it could be assumed that the use of coating in this study is still effective even without the use of CNI. These current density results are consistent with the Half-cell potential results. Besides, similar to the results in the half-cell potential, the effect of the CNI could not be understood perfectly from the current density results.

3.3 Polarization Curve

In Series 1, the difference between the anodic polarization curve is not significant (Fig. 12). Nevertheless, the specimens with GGBFS show better passivity grade compared to the OPC Specimen. The effect of the CNI is also not straightforward. The cathodic polarization curve shows that oxygen diffusion is much higher in the OPC specimens than those of the GGBFS. From series 02, the effect of the concentration of CNI solution could not be differentiated as the specimen shows the same value, as shown in Fig. 13.

In addition, the effect of the use of GGBFS could not be depicted. An interesting trend in these results is the low current density shown by the OPC specimen without CNI solution (0NN). For the oxygen permeability, similar to the results in series 1, the diffusion of oxygen is more limited in the GGBFS specimen, except for the 0NN specimen. Table 7 summarizes the grade of passivity of each specimen. It shows the presence of excellent passivity film in each steel bar of Series 1 and Series 2, noted as grade 5.

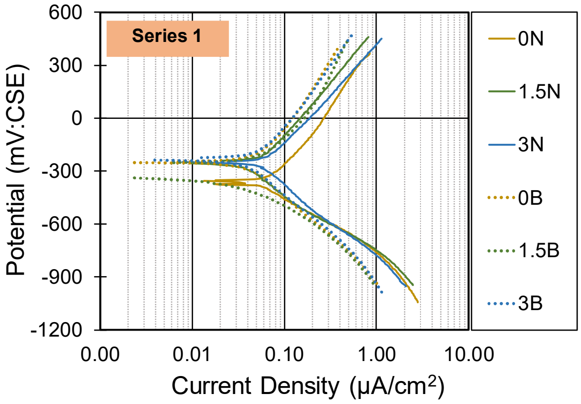

Fig.12 Polarization curve at 31 months – Series 1

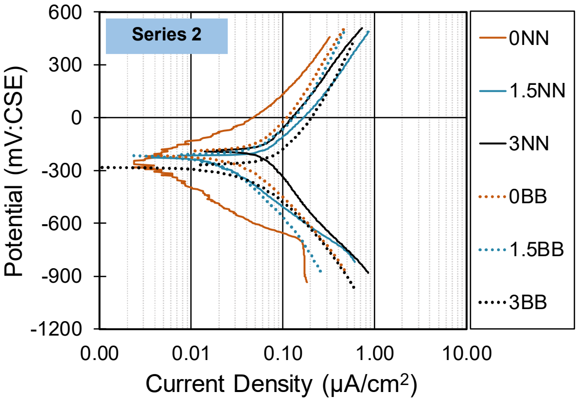

Fig.13 Polarization curve at 30 months – Series 2

Table 7 Passivity grade Series 1 and Series 2

Grade of Passivity Series 1 :					
0N	1.5N	3N	0B	1.5B	3B
5	5	5	5	5	5
Grade of Passivity Series 2					
0NN	1.5NN	3NN	0BB	15BB	3BB
5	5	5	5	5	5

On average, from the cathodic polarization curve, the CNI-coating (Series 2) shows better performance in terms of limitation in the oxygen permeability.

4. CONCLUSIONS

In this study, the effect of different concentration of CNI-coating on seawater-mixed mortar was evaluated, electrochemical measurement. The results showed:

(1) A prominent effect of the difference in concentration of CNI on the potential of the reinforcing bar in Series 1 Fig. 6, though it is not clear based on the polarization curve and the current density results.

(2) A substantially higher potential in Series 2 compared to Series 1 proving the effectiveness of coating in seawater-mixed mortar and the difference in water to cement ratio on the mortar for coating and the mortar for specimen. (Fig. 7)

(3) Based on the results from the half-cell potential and current density, it could be suggested that the combination of the use of OPC with CNI as a coating mortar and GGBFS as casting mortar with 1.5 liters/m^3 of CNI could be a good method to improve the corrosion resistance for seawater mixed mortar.

For a better understanding of the research, the long-term effectiveness of the CNI-coating on seawater-mixed concrete is still required.

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