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The Effect of Calcium Nitrite Coating as Corrosion Inhibitor in Seawater-Mixed Mortar

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ABSTRACT

Utilization of seawater as mixing and curing water is normally prohibited in reinforced concrete structures because seawater contains high chloride ion concentration which can accelerate corrosion of steel bars in concrete. Seawater, however, has a possibility for mixing water by adding supplementary substance to prevent corrosion, e.g. calcium nitrite. The aims of this study is to evaluate the effectiveness of calcium nitrite-based inhibitor (CNI) as coating for inhibiting corrosion in seawater-mixed concrete with several parameters such as type of coated steel bar and supplementary cementitious material (SCMs). Various CNI coating concentration were applied to mortar paste as coating of steel bar. Moreover, Ground Granulated Blast Furnace Slag (GGBFS) was used as SCMs. As the comparison, OPC seawater-mixed mortar specimens from previous research were also prepared. Specimens were exposed to dry and wet cycles: drying in natural laboratory temperature for 5 days and immersion in seawater for 2 days. Corrosion risk was investigated by electrochemical measurement such as half-cell potential, polarization resistance and anodic-cathodic polarization. These data demonstrate a steady-state corrosion rate and the efficiency of corrosion inhibitors. As a result, overall, CNI-coated specimens show a well performance to prevent the corrosion behavior.

Keywords: calcium nitrite, corrosion inhibitor, seawater, steel reinforcing.

1. INTRODUCTION

The United Nations [1] estimate that in 2050 the world will get an additional about 3.5 billion population, with the largest growth in developing countries which have experienced the crisis of pure water. Hence, the use of fresh water is only for primary needs. In the field of concrete, billions tons of fresh water consumed annually for mixing, curing and washing purposes. Although seawater, covering around 96.5% of the total water on earth, is really abundant, it is proper to be considered. The main problem of seawater utilization as mixing water is steel corrosion. In recent decades, corrosion of reinforcement bar has well known as the most harmful damage in reinforced concrete structure. The corrosion of reinforcing bar is ascribed as the main cause of deterioration in reinforced concrete performance. Reinforced concrete structures undergo deterioration due to chloride attack which causes corrosion of reinforcement bar. Although all standards in the world inhibit using seawater as mixing water for reinforced concrete, some researchers reported not so bad to use of seawater with mineral admixtures. One of the practiced methods popularly used for controlling steel corrosion in concrete is the corrosion inhibitors.

The most widely used corrosion inhibiting admixture is calcium nitrite-based inhibitor

(CNI) [2]. CNI can be applied either as coating of concrete [3] or as coating of steel bar. This study was carried out to evaluate the effectiveness of CNI as coating for inhibiting corrosion in concrete. The electrochemical measurement was used to investigate the corrosion risk such as half-cell potential polarization resistance, and anodic-cathodic polarization curve.

2. EXPERIMENTAL PROGRAM

2.1 Specimen Design

The mortar specimens were made with Ordinary Portland Cement (OPC) and supplementary cementitious materials, Ground Granulated Blast Furnace Slag (GGBFS) with surface area of 4000 cm^2/g. Seawater was used as mixing water and sea sand that taken from natural sea environment directly. The dimension of specimens was 150mm × 100mm × 100mm with 50mm cover depth.

This research consists of CNI specimen series and non-CNI specimen series. For Series 1, CNI was applied into entire seawater-mixed mortar (w/b 50%). And for Series 2, CNI was applied as coating of steel bar only. The steel bars were coated by tap water and CNI-mixed mortar (w/b 40%) and then embedded into the seawater-mixed mortar (w/b 50%). 1.5 liter and 3 liter of CNI solution, containing 20%-30% of CN, were mixed into 1 m^3 of fresh mortar.

Table 1 CNI specimen series

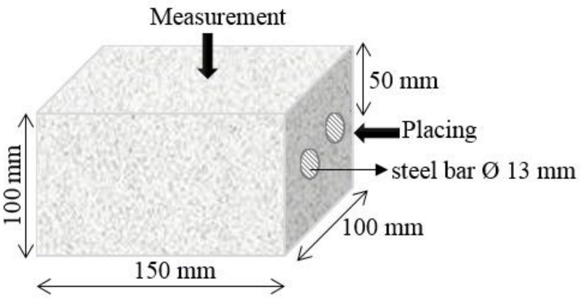
Type	Name	Coating (w/b 40%)			Mortar (w/b 50%)		
		Binder		CNI (L/m³)	Binder		CNI (L/m³)
		OPC	BFS		OPC	BFS	
Series 1	0-N	-	-	-	o	-	0
	0-B	-	-		-	o	
	1.5-N	-	-	-	o	-	1.5
	1.5-B	-	-			o	
	3-N	-	-	-	o	-	3
	3-B	-	-		-	o	
Series 2	0-NN	o	-	0	o	-	-
	0-BB	-	o		-	o	
	1.5-NN	o	-	1.5	o	-	-
	1.5-BB	-	o		-	o	
	3-NN	o	-	3	o	-	-
	3-BB	-	o		-	o	

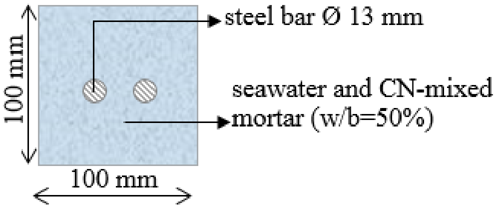
*CNI contains main component 20-30% of calcium nitrite

As the comparison, non-CNI specimens from previous research were also prepared [3]. The mortar specimens were made with Ordinary Portland Cement (N) with three kinds of water to binder ratio, 40%, 50% and 60%. The specimens N40-T, N50-T, and N60-T were using tap water as mixing water while the specimens N40-S, N50-S, and N60-S were using seawater as mixing water. All specimens were treated by dry-wet cycle which consists of 5-days dry and 2-days wet in seawater. The lists of specimens are shown in Table 1 and Table 2.

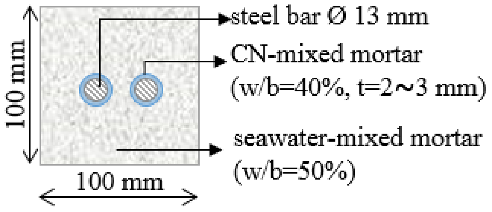
Table 2 Non-CNI specimen series

Name of Specimens	Mixing Water		Water to Cement Ratio (%)
	Tap water	Seawater	
N40-T	o		40
N40-S		o	40
N50-T	o		50
N50-S		o	50
N60-T	o		60
N60-S		o	60





(a) Series 1



(b) Series 2

Fig. 1. Specimen size

2.2 Experimental Program

Half-cell potential test was conducted to investigate corrosion risk. According to ASTM C 876[4], the limitations suggested are (1) higher than -200 mV represents 90% probability no corrosion, (2) from -350 mV to -200 mV represents uncertain of corrosion, and (3) less than -350 mV represents 90% probability of corrosion. The half-cell potential test was conducted around one hour after the wet cycle.

Polarization curve measurement was conducted to obtain condition of passivity film. 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. In the measurement of anodic-cathodic polarization curve, the potential of the steel bar (E_{corr}) was shifted to ±700 mV from the natural potential. Judgments standard of passivity grade is proposed for the anodic polarization curve obtained by the immersion method based on the finding of N. Otsuki [5] as shown in Fig. 2 and Table 3. In addition, polarization resistance was conducted to estimate the current density of specimens where the judgement based on CEB [6] that shown in Table 4.

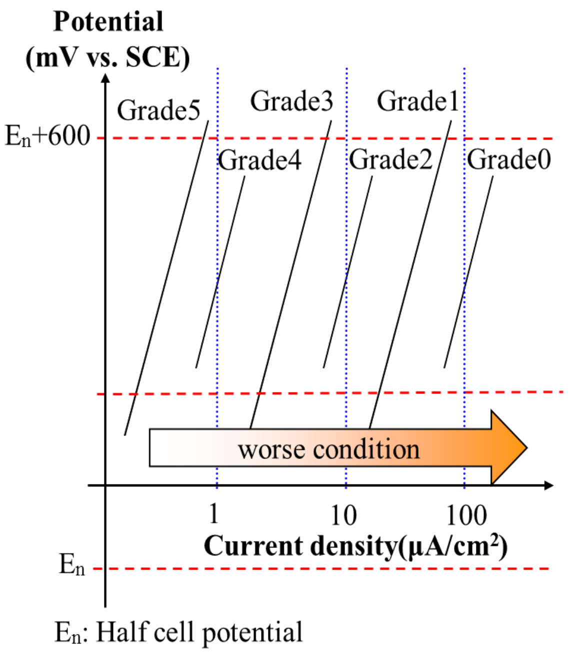


Fig. 2. Grade of passivity film associated anodic polarization curve

Table 3. Grade of passivity

Grade	Condition	Passivity
Grade 0	potential 0.2-0.6V, current density is over 100 μA/cm² at least one time	no passivity exist
Grade 1	potential 0.2-0.6V, current density is 10-100 μA/cm²	certain degree of passivity exist
Grade 2	potential 0.2-0.6V, current density is over 10 μA/cm² at least once but not to qualified to Grade 1 and 3	
Grade 3	potential 0.2-0.6V, current density is 1-10 μA/cm²	
Grade 4	potential 0.2-0.6V, current density is over 1 μA/cm² at least once but not qualified to Grade 1, 2 and 3.	
Grade 5	potential 0.2-0.6V, current density is less than 1 μA/cm²	excellent passivity exist

Table 4. The criteria of the polarization resistance

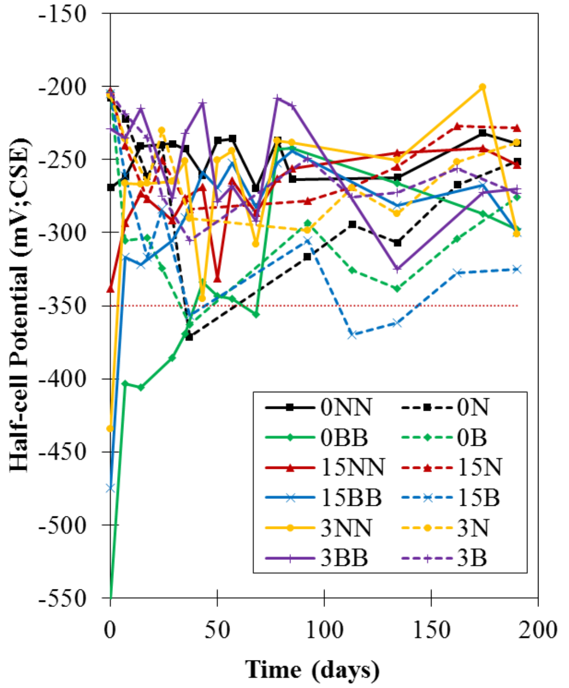
Corrosion current density I_{corr} (μA/cm^2)	Corrosive estimation
$I_{corr} < 0.2$	Low corrosion rate
$0.2 \leqq I_{corr} < 0.5$	Low to medium corrosion rate
$0.5 \leqq I_{corr} < 1$	Medium to high corrosion rate
$1 < I_{corr}$	High corrosion rate

3. RESULT AND DISCUSSION

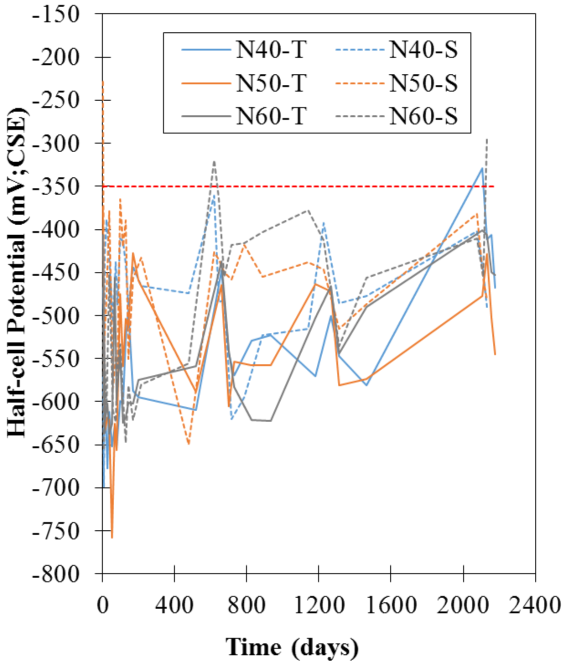
3.1 Half-cell potential

Just after demold, Series 1 more positive half-cell potential value. However the values were decreased gradually during hydration phase and recovery after 28 days, the same tendency with the finding of Omar [7]. Meanwhile, Series 2 has more negative half-cell potential value, similar to the normal trend. The value recovery gradually during hydration process, 28 days.

From Fig. 3(a), the potential of Series 1 are around -320 mV to -220 mV. Generally, the potential of Series 2 have more positive value. This may be a sign that CN-coated is worth to prevent the corrosion. The potential of Series 2 specimens are range between -300 mV to -200 mV after 120 days. Even the potential deviation between these two types of specimens are quite small, the better performance of Series 2 can be seen clearly.



(a) CNI specimens



(b) Non-CNI specimens

Fig. 3. Half-cell potential value

From Fig. 3(b) the non-CNI specimens, it is clear that seawater curing induced the negative potential values even using tap water as mixing water. The potential values of all specimens are below than -350mV which is the sign of 90% corrosion probability even in the early age. After 6 years measurement, the trend is still under -350mV in all cases. The trend is contrary with calcium nitrite specimens. The usage of BFS and calcium nitrite can increase the potential value into more positive value. Meanwhile, in this case, the high water to binder ratio did not give significant effect on potential.

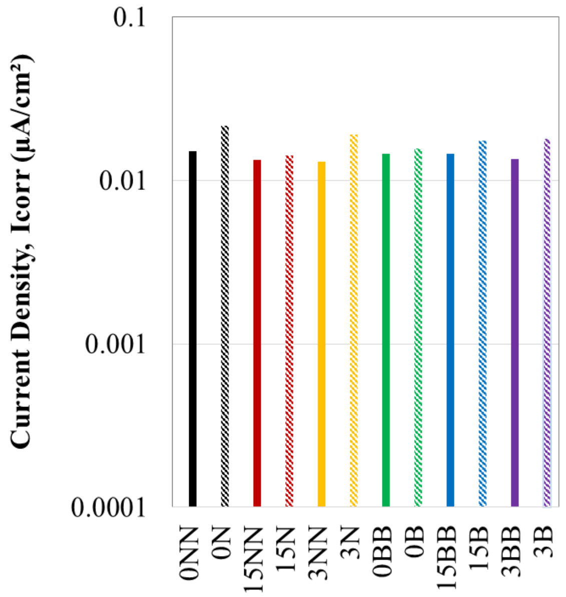
3.2 Current Density

Fig. 4(a) shows the current density value. The current density of all cases after 200 days is below than 0.2μA/cm^2 which is estimated the low corrosion rate based on CEB reference. Series 1 did not show a clear tendency of calcium nitrite content. Thus, blast furnace slag as supplementary cementitious materials did not give significant effect to current density value. The current density (I_{corr}) values of the Series 2 are lower than those of Series 1. In Series 2, the trend is clear, that is, the higher calcium nitrites content the lower current density. The steel bar was coated by mortar paste with low water to binder ratio, 40%, and used tap water as mixing water too. These condition might be the reason Series 2 have lower current density compared the others.

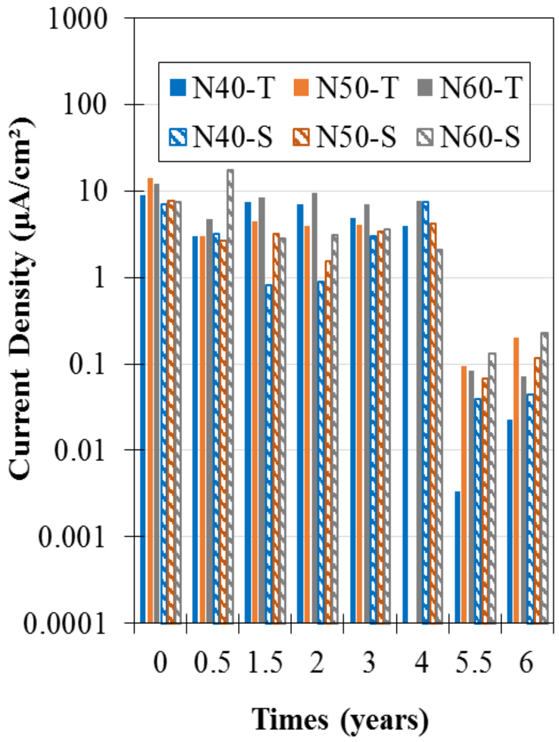
Fig. 4(b) shows the maximum current density of non-CNI specimens. In the early age, the maximum current densities are quite high range from 5μA/cm^2 to 10μA/cm^2 which is estimated the high corrosion rate. Around 5 and half years, the current density reduced significantly. After long term evaluation, the specimens that were mixed with seawater showed a clear trend, that is, the higher water to binder ratio, the higher current density values.

3.3 Polarization Curve

As known, the higher current density, the lower passivity grade is. Based on Fig. 5 and Fig. 6, generally, the current density of Series 1 is higher than those of Series 2. As the result, passivity grade of Series 1 are lower than Series 2. However, from the Series 1, samples with BFS show better trend compared to samples with OPC. On the other hand, Table 5 shows the grade passivity of non-CNI specimens. At the early age, the grade passivity of specimens is quite low, even for tap-water mixing specimens. N50-T and N60-T are using tap-water as mixing water but the passivity grade of those specimens is Grade 2 at the early age.

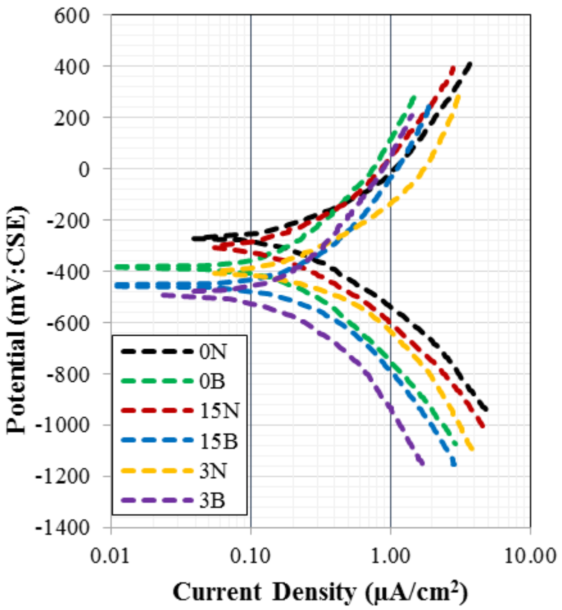


(a) CNI specimens

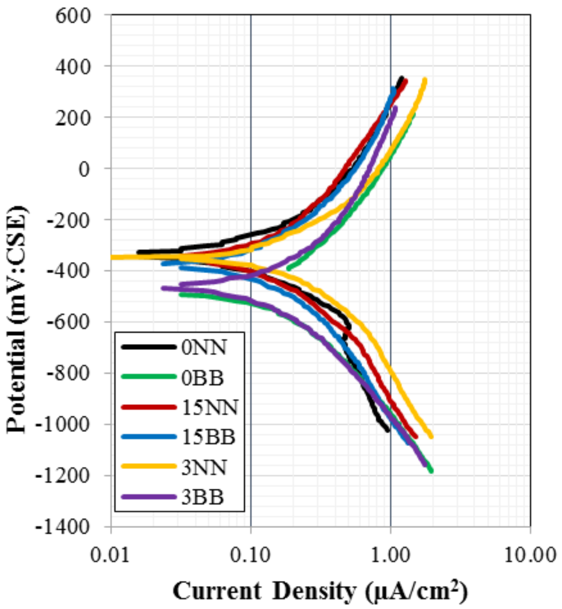


(b) Non-CNI specimens

Fig. 4. Current density value



(a) Series 1



(b) Series 2

Fig. 5 Polarization curve of CNI specimens

Table 5. Summary of "Grade of passivity"

	Exposure (years)							
	0	0.5	1.5	2	3	4	5.5	6
	Passivity Grade							
N40-T	3	4	3	3	4	4	-	3
N40-S	3	4	5	5	4	3	4	3
N50-T	2	4	4	4	4	-	2	2
N50-S	3	4	4	4	4	4	2	2
N60-T	2	4	3	3	3	3	3	3
N60-S	3	2	4	4	4	4	3	3

4. CONCLUCION

This study was carried out to evaluate the effectiveness of CNI as coating for inhibiting corrosion in seawater mixed-concrete with several parameters such as type of coated steel bar and supplementary cementitious material (SCMs). Various CNI coating concentration were applied to mortar paste as coating of steel bar. Moreover, Ground Granulated Blast Furnace Slag (GGBFS) with surface area of 4000 cm^2/g was also used as SCMs. As comparison, previous specimens were also prepared. Finally, following conclusion could be derived:

1. Overall, Series 2 show the better performance based on half-cell potential and this result is coincided with the relatively low current density value.
2. The usage of calcium nitrite as additional substance for coating can reduce corrosion rate.
3. The utilization of calcium nitrite into entire specimens gives positive affect to passivity grade. The passivity grades of Series 1are lower than Series 2.
4. The usage of Blast Furnace Slag (BFS_{4000}) as supplementary cementitious material (SCMs) does not give effect on corrosion rate. However, it gives significant effect on grade of passivity. Specimens with BFS show better condition of passivity grade than specimens with OPC.
5. Seawater curing induced the negative potential values even using tap water as mixing water.
6. Water to binder ratio did not give significant effect on potential value.

Overall, the usage of calcium nitrite into coating component only is enough to avoid corrosion in seawater-mixed concrete. In the other words, seawater-mixed concrete is possible to produce by proper handling such as the addition of calcium nitrite as corrosion inhibitor and the usage blast furnace slag as supplementary cementitious material. However, this result is focus on early age only, the long term investigation is necessary to carry out in the further research.

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