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Effect of calcium nitrite-based corrosion inhibitor in preventing corrosion of embedded steel in concrete

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Abstract

Due to the corrosion inhibition effect and compatibility with concrete properties, calcium nitrite solution has been widely used, in North America and Asia,. However, investigation has often been restricted to tests using a macrocell corrosion monitoring or measuring corrosion rate in an aqueous condition. This study concerns the assessment of the inhibition effect of calcium nitrite-based corrosion inhibitor using a polarisation method and its influence on the chloride transport, compressive strength and setting time of concrete.

The calcium nitrite-based corrosion inhibitor significantly reduced the corrosion rate of steel in chloride contaminated mortar and raised the chloride threshold level, ranging from 0.22% to 1.95% by weight of cement, while nitrite-free specimen produced the threshold level ranging from 0.18% to 0.33%. It was observed that concrete specimens containing the corrosion inhibitor produced the higher total charge passed in a rapid test for chloride ion permeability. An increase in the dosage of corrosion inhibitor resulted in a decrease in the concrete setting time. In addition, the compressive strength at early ages was increased by corrosion inhibitor, but in a long term (900 days), decreased to the level for 28 days.

Keywords: Chloride; Corrosion; Inhibitor; Permeability; Compressive strength

1. Introduction

It is well known that steel in concrete is protected from corrosion by a microscopically thin oxide layer (passive film: γ-$Fe_2O_3 \cdot H_2O$) that is formed in the highly alkaline condition of concrete pore solution [1,2]. This protective film suppresses the iron dissolution to negligibly low values, and furthermore this oxide is insoluble and highly stable. However, steel corrosion, even in well-constructed concrete, can be active when chlorides continuously accumulate at the depth of the steel. Once corrosion initiates, the corrosion propagates rapidly. Subsequent corrosion of steel produces rust products, which have the volume of 3–8 times greater than an original metal [3]. This generates the stress causing cracking and spalling of the concrete cover, which further accelerates corrosion.

To prevent or at least mitigate the corrosion of embedded steel in concrete exposed to a chloride environment, calcium nitrite-based corrosion inhibitors have been widely used since the middle of 1970s. Its prominent inhibiting effect has been reported in the majority of previous studies [4–8], showing an increase in the chloride threshold level and in the corrosion-free life of concrete structure. Moreover, calcium nitrite has been preferred over other corrosion inhibitors (sodium nitrite, sodium benzoate), because of its compatibility with concrete properties. When added to concrete, sodium nitrite and sodium benzoate lower concrete strength [9], and the inhibition effect of stannous chloride was marginal [10]. In determining the minimal dosage of calcium nitrite to prevent corrosion, the concentration ratio of nitrite to chloride ions has been generally preferred, which is often regarded as being 0.5–1.0 [11–13]. However, the influence of calcium nitrite on the concrete properties concerning durability, for example the long term development of strength or chloride penetration has been rarely reported so far, while investigation on inhibition effect has been extensively performed using a galvanic cell or monitoring the corrosion rate in an aqueous environment (i.e., beaker tests).

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The present study concerns the inhibition effect of commercially available calcium nitrite-based corrosion inhibitors, by measuring the corrosion rate of the embedded steel rebar in mortar. To assess the influence of corrosion inhibitors on concrete quality, the development of compressive strengths at 7, 28, 60 and 900 days, setting time and ion permeability were measured. Also, based on the calculated chloride threshold level for corrosion inhibitor, the corrosion-free service life was evaluated.

2. Experimental works

The present study has employed three commercial corrosion inhibitors (i.e., ACI, DCI and NR 1200), which consist of 30% of calcium nitrite and about 2% of calcium nitrate. The pH of corrosion inhibitors ranges from 11.2 to 12.0. Only ACI has been used for testing of corrosion prevention and concrete setting time, while other tests (compressive strength and permeability) used all three inhibitors.

2.1. Testing for strength and setting time

Compressive strength of concrete containing corrosion inhibitors was tested on cylindrical concrete specimens (200 mm in the length and 100 mm in the diameter). Mix proportion for manufacturing specimens is 370 kg/m^3 OPC, 787 kg/m^3 fine aggregate (density: 2.61), 1055 kg/m^3 10 mm coarse aggregate (density: 2.71). The free water/cement ratio was 0.5, after taking the water content in corrosion inhibitor into consideration. This concrete mix was also used for testing of setting time and ion permeability. The dosage of corrosion inhibitors was 0, 3, 6 or 12 l/m^3. After demoulding, the specimens were cured in a 95% humidity chamber at 20 °C. The compressive strength was measured at 7, 28, 60 and 900 days.

Setting time was determined by penetration resistance. A mortar was obtained by removing coarse aggregate from fresh concrete using a sieve. The initial set was defined as the time for the penetration resistance to reach 35 kg/cm^2 and the final set to 280 kg/cm^2.

2.2. Testing for ion permeability

Rapid chloride permeability tests were used to assess the permeability of concrete mixed with corrosion inhibitors. This test is based on the standard test method of ASTM C 1202 [14]. A concrete disc 50 mm in the thickness and 100 mm in the diameter was connected to two chambers: one is filled with 3% sodium chloride solution and the other with 0.1 M sodium hydroxide to form electrodes. An electric charge of 60 V was applied to the electrodes for 6 h. The current flowing through concrete specimen and the temperature of solution in the chamber were monitored every 30 min. Then, the total charge passed through the cell was calculated to determine the penetrability. The higher level of charge passed represents the higher permeability of concrete. The detail for the test procedure is well described in Ref. [14].

2.3. Testing for corrosion

The present study employed a polarisation method to determine the corrosion rate of embedded steel in mortar. Mortar specimens with a centrally located 9.5 mm diameter

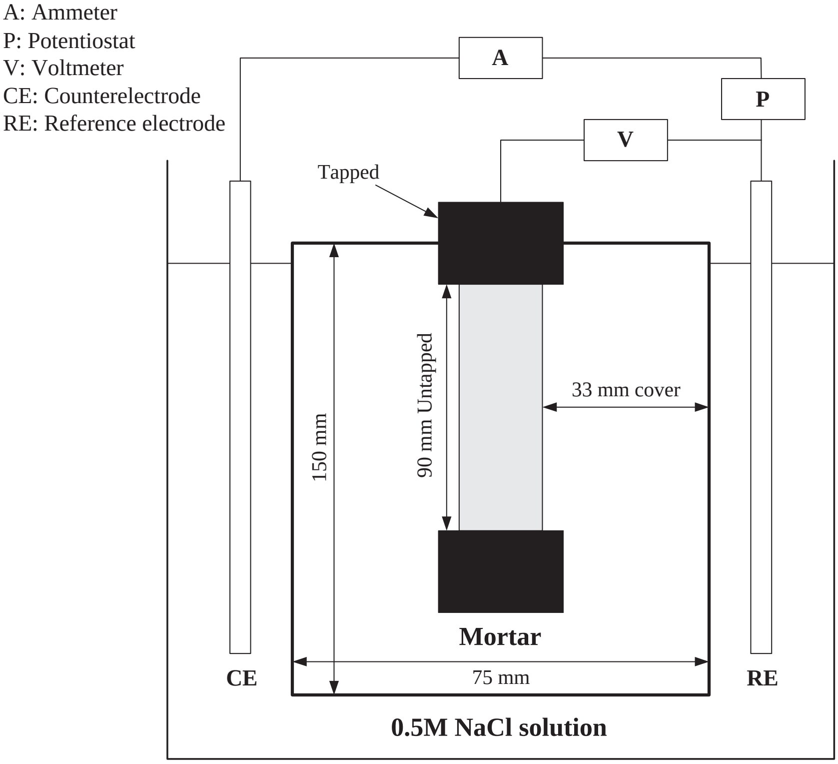

Fig. 1. Experimental set-up for testing of the corrosion rate in the use of various dosage of corrosion inhibitor.

mild steel bar were cast in a cylinder mould to create a 33 mm cover depth. The mix proportion for the cement : water : sand mixture was 1.00 : 0.50 : 2.13, (which equates to 611, 306 and 1301 kg/m^3, respectively in weight). Five levels of chloride and four levels of corrosion inhibitor were added in the mixing water. The ends of the steel bars were masked using cementitious materials, which was then covered with heat shrink insulation to avoid corrosion under the masking. The specimens were demoulded 1 day after casting and then cured in a chamber of 95% humidity at 20 °C for 28 days. Prior to measuring the corrosion rate, the mortar specimen and probes were immersed in 0.5 M sodium chloride solution for 24 h to ensure chemical stability, but the top of specimen was kept aerated for the supply of oxygen. To measure the corrosion rate, the potential was initially set 30 mV below the corrosion potential and then swept at a low scan rate of about 0.1 mV/s to a potential of 30 mV above the corrosion potential. Then, the corrosion rate was calculated by extrapolating Tafel's curves that determine the cathodic and anodic slopes as given in Eq. (1). The electrical resistance of concrete (i.e., IR drop) was automatically compensated by using a current interruption technique. An experimental set-up for measuring the corrosion rate is given in Fig. 1.

$$I_{\mathrm{corr}} = \frac{\beta_{\mathrm{a}}\beta_{\mathrm{c}}}{2.3R_{\mathrm{p}}(\beta_{\mathrm{a}} + \beta_{\mathrm{c}})} \tag{1}$$

where,

I_{corr} = corrosion rate
β_{a} = anodic Tafel slope
β_{c} = cathodic Tafel slope
R_{p} = polarisation resistance.

3. Results

3.1. Concrete properties

The development of compressive strength with corrosion inhibitor is given in Fig. 2 showing the strength for 3 l/m^3 at 7, 28, 60 and 900 days. Statistical tests (*T*-test) showed that the compressive strength did not depend on the dosage of corrosion inhibitor (calcium nitrite content), but was dependent on whether or not corrosion inhibitor was present in concrete. Hence, this study provides only the results of compressive strength for 3 l/m^3 corrosion inhibitor. The compressive strength for all specimens increased with the time to 60 days regardless of type of corrosion inhibitor. The range of strength for corrosion inhibitor varied from 311 to 368 kg/cm^2 at 7 days, from 386 to 403 kg/cm^2 at 28 days and from 410 to 416 kg/cm^2 at 60 days, respectively, while control specimen produced the strength of 302 kg/cm^2 at 7 days 377 kg/cm^2 at 28 and 396 kg/cm^2 at 60 days, respectively.

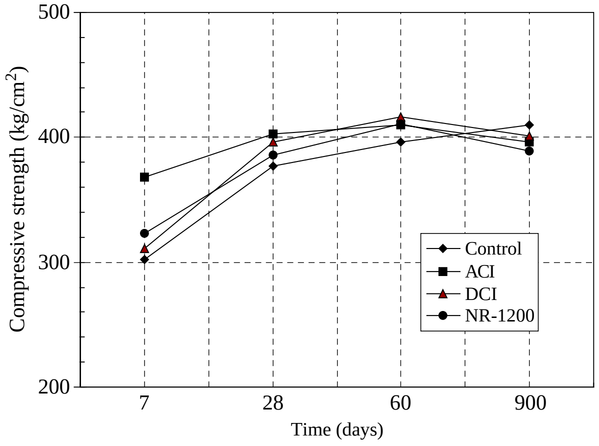

Fig. 2. Development of compressive strength at 7, 28, 60 and 900 days for addition of 3 type corrosion inhibitors at 3 l/m^3.

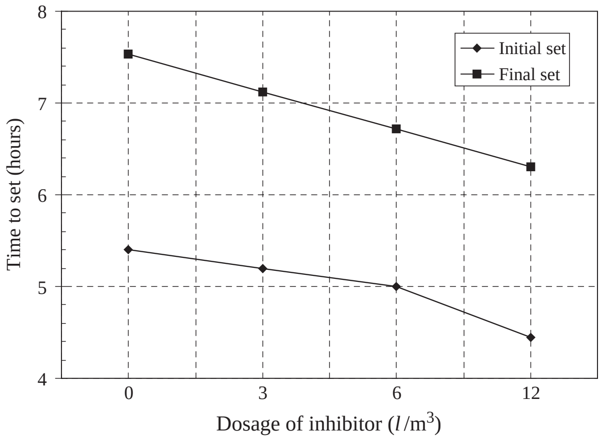

Fig. 3. Setting time for 0, 3, 6 and 12 l/m^3 of corrosion inhibitor (ACI).

The strength for concrete containing corrosion inhibitor was about 10% higher than for inhibitor-free specimens. It appears that calcium nitrite enhanced the concrete strength at early ages, which suggests that there is no adverse effect, at least, in the early development of compressive strength. However, the strength after 900 days produced different trends, depending on whether or not corrosion inhibitor was added. The compressive strength for the control concrete was slightly increased at 900 days, compared to those at 60 days, whereas concretes containing corrosion inhibitor showed a decrease in strength; compressive strength ranged from 386 to 401 kg/cm^2, (equivalent to the values at 28 days). This is an important finding that may challenge previous studies [4,6], since the use of calcium nitrite-based corrosion inhibitor may be detrimental to the strength development in a long term.

The present study obtained the setting time with various content of one corrosion inhibitor (ACI). The dosage of corrosion inhibitor were 0, 3, 6 and 12 l/m^3. As shown in Fig. 3, the setting time was remarkably reduced as the dosage of corrosion inhibitor increased. For the control concrete, the initial set time was 5.4 h and the final set time was 7.53 h. For the concrete with an addition of 12 l/m^3 of corrosion inhibitor, the initial set time was 4.45 h and final set time 6.30 h. The decrease in the setting time may imply the increase in the heat generation in the process of hydrating cement matrix as well as the decreased time for site work.

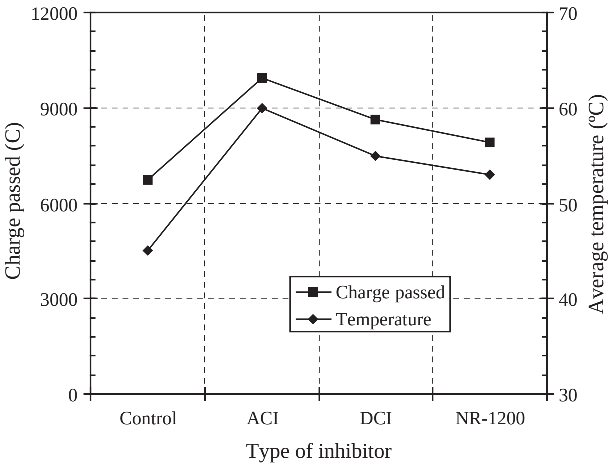

Fig. 4. Temperature of chambers and total charge passed through concrete specimens containing corrosion inhibitors in a rapid test of ion penetration (ASTM C 1202).

3.2. Permeability

Results of the rapid ion penetration test are given in Fig. 4; showing the total charge passed through concrete specimen for 6 h. It was seen that corrosion inhibitor increased the total charge, compared to the control specimen. The values of the charge passed for 3 l/m^3 corrosion inhibitor varied from 7905 to 9946 C, while the control specimen produced 6722 C. It was also observed that the temperature in chambers of each cell increased proportionally with the total charge. This is primarily because a direct current (DC) of 60 V induced heat, which in turn accelerates the flowing speed of ions [15]. The temperature strongly affects the mobility of ions.

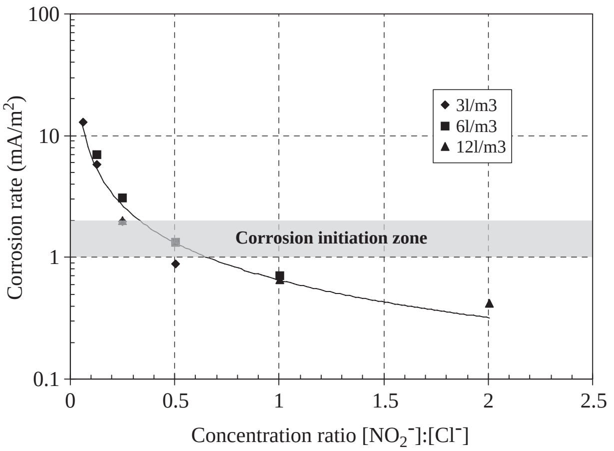

Fig. 5. Relationship between the concentration ratio of $[NO_2^-]:[Cl^-]$ and the corrosion rate.

3.3. Effect of corrosion inhibitor

The results for corrosion test using corrosion inhibitor (ACI) are given in Table 1, which shows the corrosion rate for various levels of corrosion inhibitor and chlorides. Also, the chloride threshold level for corrosion was calculated by fitting the relationship, in the quadratic form, between the corrosion rate and chloride contents for each dosage of corrosion inhibitor, assuming that the corrosion rate ranges 1–2 mA/m^2 at corrosion initiation [16]. It was seen that an increase in the chloride contents increased the corrosion rate irrespective of the dosage of corrosion inhibitor and, however, an increase in the dosage of corrosion inhibitor, at a given chloride content, resulted in a decrease in the corrosion rate. Corrosion inhibitor increased the chloride threshold level. For the control

Table 1
Measurements of the corrosion rate and chloride threshold level in the use of calcium nitrite-based corrosion inhibitor

Inhibitor (l/m^3)	Chloride		$[NO_2^-]:[Cl^-]$	Corrosion rate (mA/m^2)	Chloride threshold level (%, cement)
	(kg/m^3)	(%, cement)			
0	0	0	N/A	0.36	$Y=0.175X^2+0.558X-0.006$ (0.18 – 0.33)
	1.5	0.25	N/A	1.02	
	3.0	0.49	N/A	2.69	
	6.0	0.98	N/A	7.59	
	12.0	1.96	N/A	17.54	
3	0	0	N/A	0.35	$Y=0.121X^2+0.421X+0.003$ (0.22 – 0.42)
	1.5	0.25	0.50	0.89	
	3.0	0.49	0.25	1.95	
	6.0	0.98	0.13	5.75	
	12.0	1.96	0.06	12.89	
6	0	0	N/A	0.35	$Y=0.066X^2+0.213X+0.024$ (0.33 – 0.68)
	1.5	0.25	1.00	0.71	
	3.0	0.49	0.50	1.32	
	6.0	0.98	0.25	3.09	
	12.0	1.96	0.13	6.92	
12	0	0	N/A	0.19	$Y=0.018X^2+0.130X+0.014$ (0.73 – 1.95)
	1.5	0.25	2.00	0.42	
	3.0	0.49	1.00	0.66	
	6.0	0.98	0.50	1.32	
	12.0	1.96	0.25	1.99	

*: the value in the bracket is the calculated chloride threshold level from each fitting equation.

specimen, the chloride threshold level ranged from 0.18% to 0.33% by weight of cement, while the values for corrosion inhibitor ranged from 0.22% to 0.42% for 3 l/m^3, from 0.33% to 0.68% for 6 l/m^3 and from 0.73% to 1.95% for 12 l/m^3, respectively. This suggests that calcium nitrite-based corrosion inhibitors are effective in resisting against the chloride-induced corrosion in concrete, thereby being likely to increase the corrosion-free service life. Fig. 5 gives the relationship between the corrosion rate and the concentration ratio of $[NO_2^-]:[Cl^-]$. The curve was fitted to the form of $y=ax^b$. The corrosion rate was decreased by an increase in the concentration ratio of $[NO_2^-]:[Cl^-]$ which indicates the required nitrite content to prevent corrosion. This ensures that a large content of nitrite relatively to chlorides is more likely to passivate the steel surface from corrosion. The threshold ratio of $[NO_2^-]:[Cl^-]$ to prevent corrosion ranges from 0.34 to 0.66, which is slightly lower than from previous studies suggesting the values from 0.5 to 1.0.

4. Discussion

4.1. Content of corrosion inhibitor

The present study showed that an increase in the dosage of corrosion inhibitor lowered the corrosion rate at every level of chloride in mortar. The chloride threshold level was also raised by corrosion inhibitor. This can be explained by the fact that the increased resistance to corrosion is strongly associated with the role of nitrite ions in reacting with ferrous ions on the surface of steel to form an oxide, which protects the steel from corrosion [17]. Calcium nitrite modifies the electrochemistry of the steel surface to reinforce the passive film against corrosion [18]. Because both nitrite and chloride ions (anions) tend to react with ferrous ions (cations), the amount of nitrite ions can be a key factor in being effective in inhibiting corrosion. This implies that a higher amount of nitrite would be more likely to passivate and protect the embedded steel against chloride attack. This may lead to the concept of the ratio of $[NO_2^-]:[Cl^-]$ for expressing the appropriate dosage of corrosion inhibitor.

However, an increase in dosage of corrosion inhibitor may not guarantee the properties of concrete. As shown in Figs. 2 and 3, for addition of corrosion inhibitor, while the strength at early ages was higher than for control compressive strength, the long term strength was lowered. The cause of the reduction in compressive strength is not well known. Furthermore, decreased setting time may have an important implication for a higher level of heat generation in hydrating cement, which may lead to cracking concrete. Hence, set retarders may be necessary when large dosage of corrosion inhibitor are used.

4.2. Prediction of corrosion-free life

The time to chloride-induced corrosion initiation can be calculated from the chloride transport and chloride threshold level. The present study dealt with a testing of rapid ion penetration, showing that calcium nitrite-based corrosion inhibitor increased the charge passed through concrete specimens. The high level of passed charge may reflect the lower concrete resistivity, which is associated with a high diffusivity of chloride ions. This postulation has been supported by experiment work [19] showing that an increase in the total charge resulted in decreased compressive strength and increased chloride diffusion coefficient. Also, it was observed in experimental works [20,21] that calcium nitrite accelerated the chloride ingress at the depth of the steel when concrete was externally exposed to a chloride environment. It suggests that the beneficial effect of corrosion inhibitor in raising the chloride threshold level may be offset by an increase in the chloride transport. However, the method of rapid chloride penetration testing (ASTM C 1202) is often inconclusive because it generates heat, which will in turn affect the results and can lead to an erroneous assessment.

Notwithstanding, lower concrete resistivity can help corrosion propagate more rapidly after the onset of corrosion, because chloride ions as well as oxygen and water would become more accessible to the depth of the embedded steel in concrete. For corrosion inhibitor to be fully effective, it has been advised to add silica fume to concrete mix [11,12], which allows the concrete pore structure to be denser, thereby being more resistant to chloride penetration. However, little has been reported about the influence of calcium nitrite on the chloride transport altogether with the chloride threshold level, considering the corrosion-free service life, which requires to extensively investigate the chloride transport in concrete containing corrosion inhibitor.

5. Conclusion

The present study used calcium nitrite-based corrosion inhibitors to investigate their inhibition effect and the influence on the chloride transport, compressive strength and setting of concrete. The conclusion obtained are as follows.

The inhibition effect of calcium nitrite-based corrosion inhibitor was remarkable. The corrosion rate was reduced by addition of corrosion inhibitor at all levels of chloride ions in mortar and the chloride threshold level was raised by an increase in the dosage of corrosion inhibitor, ranging from 0.22% to 1.95% by weight of cement, while nitrite-free specimen produced the values ranging from 0.18% to 0.33%. It was also observed that the threshold mole ratio of $[NO_2^-]:[Cl^-]$ ranged from 0.34 to 0.66 for preventing corrosion.

However, addition of corrosion inhibitor resulted in an increase in the total charge passed in the test of rapid ion penetration using a 60 V DC, which may imply the increased chloride transport and thus offset the beneficial effect in increasing the chloride threshold level.

For corrosion inhibitor, the compressive strength at early ages was higher than for control. However, at 900 days, the strength for corrosion inhibitor was slightly reduced, while control specimen produced a bit higher strength, compared to the strength at early ages. In addition, an increase in the dosage of corrosion inhibitor resulted in decreased concrete setting by about 1 h, when 12 l/m^3 inhibitor was added.

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