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# Comparison of Inhibitors MCI and $\text{NaNO}_2$ in Carbonation-Induced Corrosion

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Comparative studies were done on a migrating corrosion inhibitor (MCI) and sodium nitrite ( $\text{NaNO}_2$ ) in carbonation-induced corrosion with and without chloride attack. The corrosion potential and corrosion rate were measured. The results indicate that both corrosion inhibitors can effectively inhibit chloride-free, carbonation-induced corrosion with the minimum dosages of 0.8% for the MCI and 2.0% for  $\text{NaNO}_2$ .  $\text{NaNO}_2$  at dosages up to 4.0% did not prevent corrosion of steel in carbonated concrete under chloride attack; the MCI provided effective corrosion inhibition at dosages of 1.6 and 2.0%.

It is widely recognized that steel in concrete normally is protected by a passive film that is formed as a result of and maintained by the alkali pore solution in contact with the steel. Once the alkalinity is lost, as a result of carbonation, for example, the microenvironment in concrete around

the steel becomes corrosive in the presence of water and oxygen. Carbonation, one of the major causes of steel corrosion in concrete, has led to serious deterioration of concrete structures throughout the world. The processes of carbonation and carbonation-induced corrosion are relatively slow compared to chloride-induced corrosion, however. Nitrite-based corrosion inhibitors have a long-established reputation<sup>1-2</sup> for effectively inhibiting corrosion of steel in concrete. The migrating corrosion inhibitor (MCI), a relatively new type of organic inhibitor, also has been widely studied and applied in the past 2 decades.

MCIs have been used as concrete admixture for new concrete and also as surface treatment for corrosion-damaged concrete, taking advantage of their migrating and penetrating properties in concrete.<sup>3-8</sup> Published studies and practices, however, tend to focus on chloride-induced corrosion. There is a clear need, therefore, to demonstrate whether corrosion inhibitors are effective in preventing carbonation-induced corrosion when used as a concrete admixture and/or surface treatment. This article discusses part of a study program that examined MCI performance in inhibiting carbonation-induced rebar corrosion. The study program compared MCIs with other, more established corrosion inhibitors such as sodium nitrite ( $\text{NaNO}_2$ ).

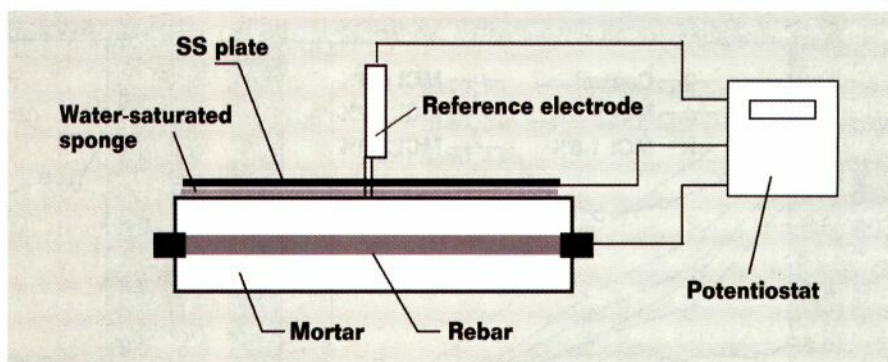
## Experimental Procedures

### SAMPLE PREPARATION

Mortar samples with a water/cement ratio of 0.6 and a sand/cement ratio of 3 were used except when verifying the effect of water saturation on electrical and polarization resistance, in which case a water-cement ratio (w/c ratio) of 0.5 was used for comparison. The mortar mixes contained Portland cement, river sand of fineness modulus 2.6, and tap water.

Two inhibitors with different mechanisms of corrosion inhibition were chosen for the purpose of com-

FIGURE 1



Schematic of the mortar prism with embedded steel bars.

parison: the typical anodic inhibitor  $\text{NaNO}_2$  and a mixed MCI (Cortec MCI 2006<sup>†</sup>) based on amino-carboxylate chemistry. Inhibitor dosages were based on the cement mass.

Mortar prisms were cast with centrally embedded steel bars. The size of the prism was 30 by 30 by 90 mm. The steel bars measured 7 mm in diameter and 100 mm in length and had an exposure area of  $19.5 \text{ cm}^2$  (Figure 1). Mortar prisms of each mix were cast with and without steel bars. The former were used for the purpose of examining the carbonation process. The samples were cured at  $20 \pm 2^\circ\text{C}$  and relative humidity (RH)  $>95\%$ . After 14 days' curing, the samples were dried in an oven at  $40^\circ\text{C}$  for 2 days and then cooled to room temperature in 24 h. The samples then were placed in the carbonation chamber.

#### DETERMINATION OF CARBONATION STATE

The samples in the carbonation chamber were conditioned at  $18 \pm 3^\circ\text{C}$ , RH  $\sim 75\%$ , and 50 to 80% carbon dioxide ( $\text{CO}_2$ ). To ensure that the samples with embedded steel bars were carbonated completely, the same mortar

prisms—but without embedded steel—were treated in parallel under the same conditions. Plain mortar samples were split from one end each week to see the depth of carbonation with the help of phenolphthalein [ $(\text{C}_6\text{H}_4\text{OH})_2\text{COC}_6\text{H}_4\text{CO}$ ] indicator until there was no sign of red color in the center of the cross section. Samples with embedded steel were considered completely carbonated and were ready for corrosion measurement.

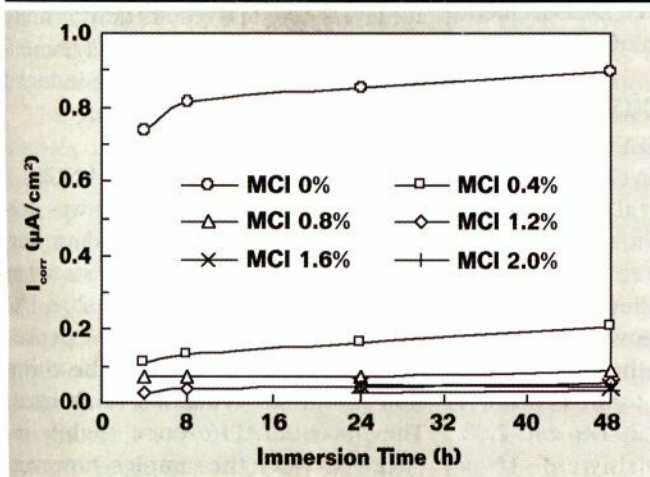
#### DETERMINATION OF CORROSION CONDITION

After carbonation, the protective cover lost its alkalinity, and the passive film on the steel no longer could be maintained in the pore solution with a

pH value  $<10$ . The steel corrosion would not proceed significantly, however, unless there were sufficient water and oxygen in the cover mortar.<sup>9</sup> This favorable condition was achieved by immersing the samples in water of  $20^\circ\text{C}$  for at least 4 h. The electrical resistance between the steel bar in the mortar and the stainless steel (SS) plate on the mortar surface, which was used as a counter-electrode in the linear polarization resistance (LPR) test, was continuously monitored until the stable lowest value was established, indicating saturation. Polarization resistance measurements also were made to confirm the observation.

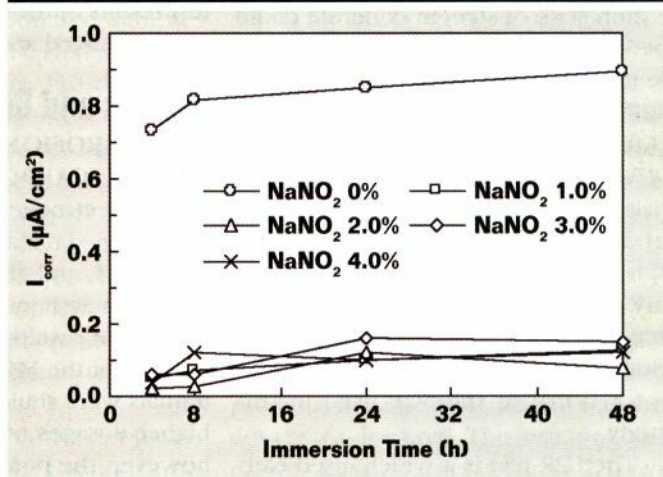
Aside from obtaining a low, stable LPR value, there are other benefits to

FIGURE 2



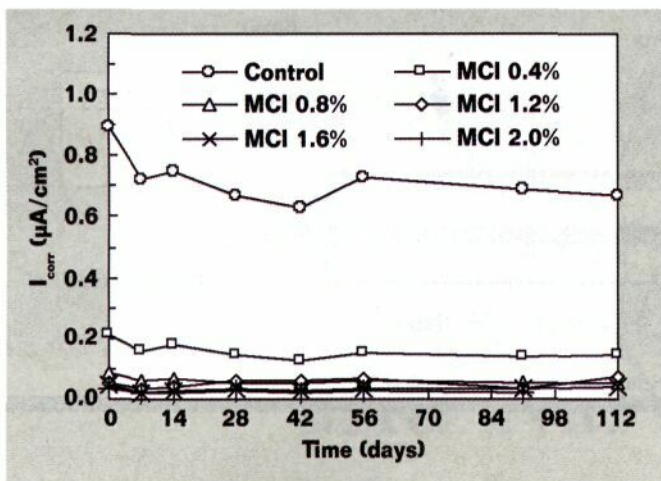
Corrosion rate as a function of immersion time after carbonation for samples with and without MCI.

FIGURE 3



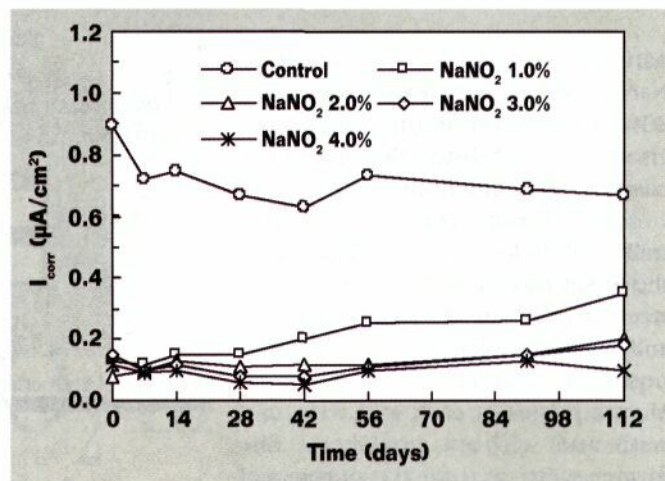
Corrosion rate as a function of immersion time after carbonation for samples with and without  $\text{NaNO}_2$ .

FIGURE 4



Comparison of corrosion rate vs time for MCI-containing and control samples.

FIGURES



Comparison of corrosion rate vs time for NaNO<sub>2</sub>-containing and control samples.

having the samples saturated before the tests. For example, the electrochemical readings were stable during the tests and the IR-drop was reduced to the lowest possible level; this reduced the error when the LPR measurements were undertaken with a device without the ohm-drop compensation function.

### CORROSION MONITORING

The electrochemical experiments were performed using model ZF-3 potentiostat with CorrTest software. A saturated calomel electrode (SCE) was used as the reference. According to the standard ASTM C 876,<sup>10</sup> the corrosion state of steel in concrete could be identified according to half-cell potentials. Potentials more positive than -270 mV to a copper/copper sulfate (Cu/CuSO<sub>4</sub>) electrode (CSE) indicate a 90% probability of passive state; potentials more negative than -350 mV (CSE) present a >90% likelihood of corrosion. When the potentials are between -270 mV and -350 mV (CSE), the corrosion state is uncertain. The potential criterion of -350 mV (CSE) corresponds to ~ -270 mV to the SCE used in this study.

The LPR test is a widely used electrochemical method for measuring in-

stantaneous corrosion rates. The ratio of E/I represents polarization resistance ( $R_p$ ) and may relate to the instantaneous corrosion rate ( $I_{corr}$ ) by means of the expression:

$$I_{corr} = B / R_p \cdot A \quad (1)$$

where A is the area of the steel bar surface polarized and B is a constant that may vary from 13 to 52 mV. In this study, B = 52 mV is used for the passive state and B = 26 mV for the active corrosion state.<sup>9</sup> The measurements were conducted by scanning from +10 to -10 mV at the rate of 10 mV/min. Three samples from each group were tested at the specified time, and the test results of the three measurements were averaged and plotted.

## Results and Discussion

### CORROSION STATE AFTER CARBONATION

The electrochemical measurements were carried out at the specified times of 4, 8, 24, and 48 h to determine the corrosion activity induced by carbonation. The results show that at lower dosages of the MCI, the corrosion potentials were similar to the control. At higher dosages of 1.2, 1.6, and 2.0%, however, the potentials were ~150 to 300 mV more positive. The results indicate that the MCI used may consist of different inhibiting components that

provide mixed corrosion inhibition at lower dosage but anodic inhibition dominants at higher dosages. For samples with NaNO<sub>2</sub>, the corrosion potentials moved significantly positive as expected.

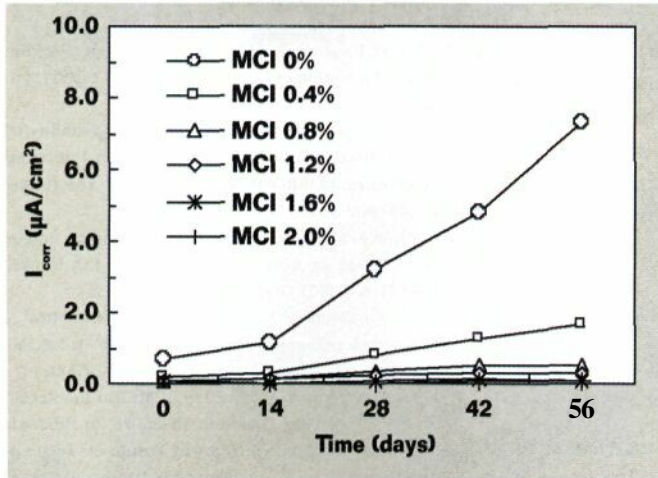
Figures 2 and 3 display the effects of the two corrosion inhibitors on corrosion rate. The steel bar in the carbonated mortar was in an active corrosion state with a corrosion rate as high as 0.9 μA/cm<sup>2</sup>. The use of the MCI at all the dosages dramatically reduced the corrosion activity to a very low level. Similarly, the corrosion rates for samples with NaNO<sub>2</sub> significantly reduced corrosion activity at all the dosage levels. The test results demonstrate that both the MCI and NaNO<sub>2</sub> can effectively inhibit carbonation-induced corrosion of steel in concrete.

### LONG-TERM PERFORMANCE

The corrosion monitoring was performed over a period of 112 days, during which the samples were stored in a curing room conditioned at 20 ± 1 °C and RH > 90%. Throughout the period, the distribution pattern of the corrosion potentials remained unchanged. The potential difference slightly reduced between the samples, however, indicating that the MCI functioned effectively and that corrosion states that had initially been achieved were main-

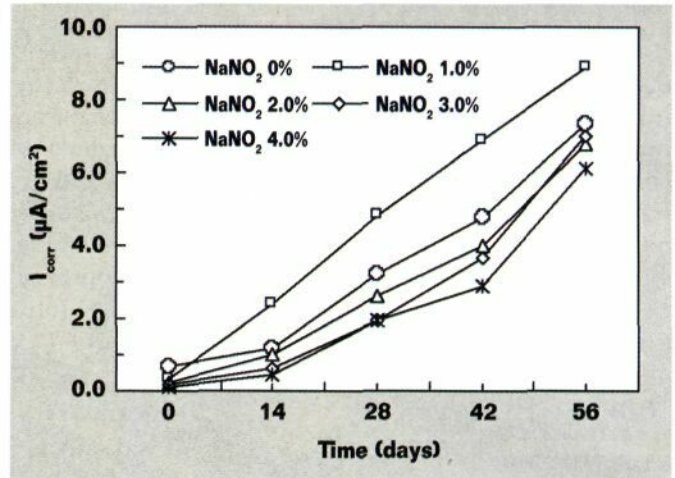
<sup>†</sup>Trade name.

FIGURES



Evolutions of corrosion rates after immersion in 3% NaCl solution for samples with and without MCI.

FIGURE 7



Evolutions of corrosion rates after immersion in 3% NaCl solution for samples with and without NaNO₂.

tained over the time period studied. This does not necessarily imply, however, that the tested inhibitors will remain effective for many decades.

The corrosion rates displayed in Figure 4 support the judgments from the potential measurements. The high corrosion rate of the control sample changed very little during the long testing period. The corroding states of the MCI-containing samples did not change. The fact that the corrosion rates for samples with the MCI dosages of 0.8% or higher were lower than 0.1  $\mu\text{A}/\text{cm}^2$  indicates that the minimum dosage of the MCI may be  $\sim 0.8\%$ . These results bolster the case for using MCIs to combat carbonation-induced corrosion of steel in concrete under normal conditions.

The long-term behavior of the samples containing  $\text{NaNO}_2$  led to a different conclusion. Over time, the corrosion potentials of all of the inhibitor-containing samples became more negative—in contrast to the control sample, which became more positive. This situation is coincident with the corrosion rate measurements in Figure 5. The increase in corrosion rate for samples with 1.0%  $\text{NaNO}_2$  is clear: it gradually reached a value of  $\sim 0.35 \mu\text{A}/\text{cm}^2$  at 112 days, although other samples with higher  $\text{NaNO}_2$  dosages still were in low-corrosion states. The

phenomenon confirms that the anodic inhibitor should be used at a high enough dosage level to ensure long-term effectiveness. Under such conditions, the minimum dosage of  $\text{NaNO}_2$  should be 2%. Note, however, that the higher  $\text{NaNO}_2$  dosages would be harmful to concrete properties.

INFLUENCE OF CHLORIDES

In this study, the chlorides were externally introduced into concrete by immersing carbonated samples with and without inhibitors MCI and  $\text{NaNO}_2$  into 3% sodium chloride ( $\text{NaCl}$ ) solution (the chloride concentration at the depth of the steel was not measured, however). The carbonated samples were those cured and tested under the standard condition for 112 days. The corrosion potentials and corrosion rates at the time were used as the initial data for the immersion test; for the immersion tests, the samples first were cured in the standard curing condition for 13 days and then subjected to 1 day of immersion in the chloride solution before the corrosion behavior was measured. The immersion tests were cycled every 2 weeks.

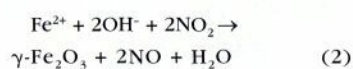
The results of the corrosion potentials show that the MCI samples became more negative with time but without changes in the order (i.e., the higher the dosage of the MCI, the more

positive the potential was). The changes in corrosion rates presented in Figure 6 show that the corrosion rate of the control sample sharply increased with time—higher than  $7.0 \mu\text{A}/\text{cm}^2$  at 56 days after 4 cycles. The changes for the MCI samples were 0.15 to  $1.65 \mu\text{A}/\text{cm}^2$  for MCI 0.4%, 0.06 to  $0.54 \mu\text{A}/\text{cm}^2$  for MCI 0.8%, and 0.07 to  $0.54 \mu\text{A}/\text{cm}^2$  for MCI 1.2%. The samples with 1.6 and 2.0% MCI changed little, however, and were still in a passive state with a corrosion rate lower than  $0.1 \text{ mA}/\text{cm}^2$ .

The results demonstrate the MCI's effectiveness in the case of carbonation together with chloride attack—one of the most corrosive environments for steel corrosion in concrete. The results also indicate that the mechanism of the corrosion inhibition may be related to the competitive adsorption onto the steel surface between the MCI molecules and chloride ions.<sup>7</sup> A proper reservation in specifying the dosage of the MCI inhibitor is necessary in the case of chloride attack.

In the case of  $\text{NaNO}_2$ , the potentials became more negative with time: the potential became more negative as the dosage was lowered. The results of corrosion rates displayed in Figure 7, however, show that the corrosion rates of all the  $\text{NaNO}_2$  samples increased sharply with time. In particular, the

corrosion rate of the sample with 1.0% dosage had exceeded that of the control samples; this observation confirms that the anodic inhibitor may promote corrosion in the case "where its concentration becomes lower than what is needed compared to the concentration of corrosive species. One may better understand the observation by referring to the widely accepted mechanism of the passive film formation:<sup>1,7</sup>



As the mechanism shows, the hydroxyl ions play a role as important as that of nitrite ions in passivating steel bar in concrete. Literature analyzing the effectiveness and mechanism of nitrite-based corrosion inhibitors often ignores this fact, however. The observation that the inhibiting power of  $\text{NaNO}_2$  in the carbonated concrete was reduced in comparison with noncarbonated concrete may well be explained by the reduction of the concentration of hydroxyl ions in the neutralized pore solution. Similar experimental observations can also be found in some published studies.<sup>11-14</sup> Such explanations do not appear to be the case for the MCI used because it relies on a different inhibiting mechanism. The MCI molecules form a protective molecular layer on the steel surface through competitive adsorption with chloride ions. The mechanism has been experimentally verified by the surface microstructure analysis, which shows that the MCI molecules are more powerful in the competitive adsorption.<sup>3</sup>

The long-term results indicate that, in the case of carbonation-induced corrosion, both MCI and  $\text{NaNO}_2$  are effective inhibitors as long as sufficient concentration is available in the concrete. The fact that  $\text{NaNO}_2$  at dosage levels up to 4.0% did not protect the rebar from corrosion (in the case of carbonation together with chloride attack) implies that the inhibitors based on nitrites may be unsuitable for this ap-

plication—at least at dosage levels 4%—because they have similar inhibiting mechanisms. Note that the MCI used remained stable and effective for the entire test period, despite its thin cover and less-dense mortar. Nevertheless, the minimum dosage for effecting corrosion prevention should increase as chloride ions accumulate in the concrete.

## Conclusions

Based on the experimental results in this study, the following conclusions can be drawn:

- After the concrete carbonates, the reinforcing steel bar is in an active corrosion state and could have a high corrosion rate under favorable corrosion conditions.
- MCI and  $\text{NaNO}_2$  inhibitors can effectively inhibit chloride-free carbonation-induced corrosion of steel in concrete with enough dosages. The minimum recommended dosages are 0.8% for MCIs and 2.0% for  $\text{NaNO}_2$ .
- $\text{NaNO}_2$  at dosages up to 4.0% did not prevent corrosion. At the dosages tested,  $\text{NaNO}_2$  may not be a proper choice as an effective corrosion inhibitor in the case of carbonation together with chloride attack from the environment.
- The MCI at dosages of 1.6 and 2.0% provided effective corrosion inhibition for carbonation together with chloride attack. The minimum dosage should be increased in comparison to that of carbonation-induced corrosion in relation to chloride concentration.

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