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# Effectiveness of corrosion inhibitors in contaminated concrete

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## Abstract

Four types of corrosion inhibitors (calcium nitrite at two dosages, calcium nitrate at three dosages and two organic inhibitors at their recommended dosages) were evaluated at five different levels of contamination, i.e., 0.8% chloride; 0.8% chloride plus 1.5% $SO_3$; seawater; brackish water; and unwashed aggregates. Concrete specimens were used to assess the effect of corrosion inhibitors on the compressive strength of concrete and reinforcement corrosion. The results indicated that the corrosion inhibitors investigated in this study did not adversely affect the compressive strength of concrete. Furthermore, calcium nitrite was efficient in delaying the initiation of reinforcement corrosion in the concrete specimens contaminated with chloride, while both calcium nitrite and calcium nitrate mitigated the corrosive effects of chloride plus sulfate salts or sea water. In the concrete specimens prepared with brackish water or unwashed aggregates, all the inhibitors were effective in reducing the rate of reinforcement corrosion. The type and dosage of corrosion inhibitor were observed to be dependent on the nature and level of contamination.

*Keywords:* Chloride; Concrete; Contamination; Inhibitors; Reinforcement corrosion; Sea water; Sulfate; Unwashed aggregates

## 1. Introduction

Portland cement concrete is the most widely used construction material. Among the many reasons for widespread use and pre-eminence are its economic superiority and its minimal maintenance requirement [1]. It was assumed that concrete produced by mixing of cement, aggregate and water can withstand all the weather and exposure conditions. In fact, concrete was once thought to be a maintenance-free material until durability problems were reported from different parts of the world. Notable among the case histories, where concrete was blamed for poor durability, are the deterioration of the bridge decks in the USA and Europe and the reinforced concrete structures in the Arabian Gulf [2]. Considerable resources have to be diverted towards the repair and rehabilitation of these structures. In the USA, more than $50 billions were spent annually on the repair of inter-state highway systems in late 1980s [3]. In the UK, £20 billions were spent on building repair and maintenance, out of which £500 millions were utilized per annum for concrete repairs by the end of 1980s [4]. While the deterioration of highway structures in the temperate climatic conditions of North America and Europe is attributed to the use of deicer salts, the poor durability of concrete structures in the Arabian Gulf is caused by the following factors [2]: (1) severe climatic and geomorphic conditions, (2) lack of appreciation of the problem, (3) incorrect materials specifications, and (4) inadequate construction practices.

In the aggressive environmental conditions of the Arabian Gulf and worldwide, the predominant modes of concrete deterioration are corrosion of reinforcing steel and sulfate attack. However, there is a unanimous consensus among concrete technologists concerning the fact that corrosion of reinforcing steel is by far the major cause of concrete deterioration worldwide. Corrosion of reinforcing steel is predominantly ascribable to the ability of two aggressive species, namely chloride and carbon dioxide, to reach the steel surface. However, chloride-induced reinforcement corrosion dominates concrete deterioration locally, i.e., along the seaboards of the Arabian Gulf and Red Sea, and worldwide. In these regions, the exposure conditions are very hostile to reinforced concrete structures and the materials used

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in the concrete construction, i.e. coarse aggregate, sand and, sometimes, water, are often contaminated with chloride and sulfate salts [5–7]. These ions may be contributed by either the mix constituents or they may penetrate the hardened concrete from the external environment. The concomitant presence of sulfate and chloride ions is also known to aggravate the corrosive attack on reinforcing steel [5].

In these aggressive exposures, the concrete quality should be specified in terms of durability, in addition to workability and strength [6]. In order to produce a durable concrete, a four-step approach is often recommended [7]. Firstly, the concrete should be designed to be dense and impermeable. Secondly, the reinforcing steel should be protected using an impermeable coating or corrosion inhibitor. Thirdly, the construction practice, in terms of consolidation, curing, etc., should be improved to cope with the aggressivity of the exposure conditions. Fourthly, the concrete should be protected through the application of a suitable protective system.

Though the protection of concrete has been considerably addressed [8–12], the effect of inhibitors, particularly when the concrete is contaminated with chloride and sulfate salts, has not been well investigated. This study was conducted to evaluate the effectiveness of corrosion inhibitors in inhibiting reinforcement corrosion, particularly when chloride and sulfate ions are built in the concrete.

## 2. Use of corrosion inhibitors

ACI 116R-85 defines a corrosion inhibitor as a chemical compound, either liquid or powder, that effectively decreases or slows down reinforcement corrosion in hardened concrete if introduced, usually in very small concentrations, as an admixture [13]. The National Association of Corrosion Engineers (NACE) defines corrosion inhibitors as substances that, when added to an environment, decrease or slow down the rate of attack of the metal. The corrosion inhibiting admixtures should not be viewed as an alternative to the design specifications for durable concrete but as an additional protective measure [14–16]. They are also essential for superior performance or when corrosion inhibiting admixtures or any other type of corrosion protection system are demanded.

The advantages of using inhibitors to provide corrosion protection are that they are uniformly distributed throughout the concrete matrix, protecting the entire steel surface; and that the concrete's low permeability prevents the inhibitor from leaching out. An ideal corrosion inhibitor is a chemical compound that, when added in an adequate amount to concrete, can prevent corrosion of embedded steel and at the same time has no adverse effect on the properties of fresh and hardened concrete [16].

Corrosion inhibitors can be divided into three types: anodic, cathodic, and mixed, depending on whether they interfere with the corrosion reaction preferentially at the anodic or cathodic sites or whether both are involved [17]. Each of these corrosion inhibitor groups may include materials which mitigate reinforcement corrosion by one of the following mechanisms: (a) formation of barrier layers; (b) oxidation by passivation of the surface; and (c) influencing the environment in contact with the metal. To be an effective corrosion inhibitor, the selected chemical or mixture of chemicals should meet the following requirements [17]:

1. The molecules should possess strong electron acceptor or donor properties or both.
2. The solubility should be such that rapid saturation of the corroding surface occurs without being readily leached out.
3. Induce polarization of the respective electrodes at relatively low current values.
4. Be compatible with the intended system so that adverse side effects are not produced.
5. Be effective at the pH and temperature of the environment in which it is to be used.

The use of corrosion inhibitors in concrete has been reviewed by Treadaway and Russell [18], Craig and Wood [19], Griffin [20], Slater [21], and most recently by Berke [22]. Early studies looked at numerous inhibitors with the most attention focused on sodium nitrite, potassium chromate, sodium benzoate, stannous chloride, dinitrobenzoic acid, sodium molybdate and sodium florophosphite ($Na_2PO_3F$) [16,23,24].

The beneficial effect of calcium nitrite is reported in the literature [16], though not being researched well. Sodium nitrite, however, suffers two disadvantages, one pertinent to reduction in strength [18,19] and the other being the risk of the alkali–aggregate reaction which may be aggravated by the addition of sodium salts [25]. El-Jazairi et al. [23] concluded that, for effective performance of calcium nitrite exposed to aggressive environments, it is essential to use good quality concrete with the following limits:

1. The water-to-cement ratio should not be more than 0.5, preferably 0.4.
2. The minimum cement content should be 300 kg/m$^3$, preferably 350 kg/m$^3$.
3. The minimum cover to reinforcement should be 30 mm, preferably 38 or greater than the maximum aggregate size plus 18 mm.

Calcium nitrite has been used in concrete in Europe and the United States for long time [26]. Extensive testing shows that:

(a) it protects the steel against chloride-induced corrosion,
(b) its efficiency increases as the concrete quality improves,
(c) it improves the compressive strength,
(d) it lowers the corrosion rate once corrosion begins, and
(e) it works in the presence of cracks.

Several organic-based inhibitors have been patented for different applications, including the protection of reinforcing steel in concrete. Their advantages include the following [27]:

1. they provide corrosion inhibition in the presence of varying amounts of chlorides,
2. they can diffuse through concrete thereby providing both cathodic and anodic protection,
3. they are organic in nature and environmentally safe, and
4. they are non-toxic.

During the past 15 years, corrosion inhibitors have been increasingly used worldwide for long-term protection of reinforced concrete structures in many applications, such as parking garages, highway bridges, and marine structures, etc. In the Arabian Gulf, according to Matta and Berke [28], more than 100,000 $m^3$ of concrete containing calcium nitrite has been used in the United Arab Emirates to build sea walls, swimming pools, power stations and other residential structures. The significance of using corrosion inhibitors in these aggressive exposures is ascribable to the fact that data are lacking on the performance of reinforced concrete that is contaminated with both chloride and sulfate salts. Further, the usefulness of these chemical admixtures in inhibiting reinforcement corrosion in concrete prepared with brackish water, sea water and unwashed aggregates, as frequently used in the Arabian Gulf, was not fully addressed in the literature [16]. Moreover, experience with calcium nitrate [$Ca(NO)_3$] is mostly limited to few studies conducted in Europe where concrete is free of chloride and sulfate contamination [29,30].

This investigation was conducted to evaluate the effectiveness of four different types of corrosion inhibitors in reducing reinforcement corrosion in contaminated concrete. The performance of the selected inhibitors in reducing reinforcement corrosion was evaluated by measuring corrosion potentials and corrosion current density.

## 3. Experimental program

### 3.1. Materials

To achieve the objectives of this investigation, plain and reinforced concrete cylindrical specimens, 75 mm in diameter and 150 mm high, were prepared using ASTM C 150 Type V Portland cement. Table 1 presents the chemical and mineralogical composition of the cement. All the concrete mixtures were proportioned for an effective water to cement ratio of 0.45 and a cement content of 350 kg/$m^3$. A coarse to fine aggregate ratio of 1.63 by weight was kept invariant in all the concrete mixtures.

Table 1
Chemical composition of cement

| Composition | % by weight |
|---|---|
| Silicone dioxide ($SiO_2$) | 22.3 |
| Aluminum oxide ($Al_2O_3$) | 3.55 |
| Ferric oxide ($Fe_2O_3$) | 3.63 |
| Magnesium oxide (MgO) | 2.10 |
| Sulfur trioxide ($SO_3$) | 1.93 |
| Calcium oxide (CaO) | 64.6 |
| Sodium oxide ($Na_2O$) | 0.10 |
| Potassium oxide ($K_2O$) | 0.21 |
| Titanium dioxide ($TiO_2$) | 0.29 |
| Loss on ignition | 1.22 |
| Insoluble residue | 0.59 |
| *Bogue composition* | |
| Tricalcium aluminate ($C_3A$) | 3.27 |
| Tetracalcium aluminoferrite ($C_4AF$) | 11.05 |
| Tricalcium silicate ($C_3S$) | 58.96 |

Crushed limestone with a maximum size of 12.5 mm was used as coarse aggregate. The coarse aggregates were first sieved into different sizes and mixed to obtain a grading within the limits of size #7 of ASTM C 33. They were washed with potable water to remove the dust and salt contamination. The concentration of water-soluble contamination in the coarse aggregates is shown in Table 2. The bulk specific gravity and water absorption of the coarse aggregates were 2.46 g/$cm^3$ and 2.9%, respectively. Dune sand with a bulk specific gravity of 2.64 g/$cm^3$ and water absorption of 0.57% was used as the fine aggregate.

The following four types of corrosion inhibitors were used in this study: (i) calcium nitrite; (ii) calcium nitrate; (iii) CI1 (commercial inhibitor); and (iv) CI2 (commercial inhibitor). Calcium nitrite was in a liquid form and the solid content was 30% by weight and it was mixed in the mixing-water at two dosages of 2% and 4%, by

Table 2
Water-soluble ions in the coarse aggregates

| Ion | Concentration, % by weight of the coarse aggregates |
|---|---|
| Chloride ($Cl^-$) | 0.424 |
| Sulfate ($SO_4^{2-}$) | 0.110 |
| Sodium ($Na^+$) | 0.112 |
| Calcium ($Ca^{2+}$) | 0.072 |
| Magnesium ($Mg^{2+}$) | 0.008 |
| Potassium ($K^+$) | 0.006 |

weight of cement. Analar grade calcium nitrate was used in the mixing water at dosages of 2%, 3% and 4% by weight of cement. The commercially available, proprietary organic inhibitors CI1 and CI2 were mixed in the mixing-water at a dosage of 5 l/m$^3$ and 1.2 kg/m$^3$ of concrete, respectively, as recommended by their manufacturers.

The reinforced concrete specimens were prepared with the following contaminations: (i) 0.8% chloride, (ii) 0.8% chloride plus 1.5% $SO_3$, (iii) sea water and (iv) brackish water. Another batch of concrete specimens was prepared with unwashed aggregates. Tables 3 and 4 show the chemical analysis of seawater and brackish water, respectively.

### 3.2. Mixing and casting

The concrete constituents were mixed in a revolving drum type mixer for approximately 3–5 min till a uniform consistency was achieved. The molds were filled with concrete in two equal layers and vibrated for consolidation using a small laboratory-vibrating table.

After casting, the specimens were covered with wet burlap for 24 h. Thereafter, they were demolded and cured by covering them with wet burlap and plastic sheets for two weeks. The burlaps were wetted twice daily. Following curing, the specimens were placed in the various exposure conditions.

Table 3
Composition of the seawater

| Ion | Concentration (ppm) |
|---|---|
| Chloride ($Cl^-$) | 24,408 |
| Sulfate ($SO_4^{2-}$) | 4211 |
| Bicarbonate ($HCO_3^-$) | 114 |
| Alkalinity as $CaCO_3$ | 128 |
| Sodium ($Na^+$) | 14,400 |
| Calcium ($Ca^{2+}$) | 642 |
| Magnesium ($Mg^{2+}$) | 1570 |
| Potassium ($K^+$) | 937 |
| Iron ($Fe^{2+}$) | 60 |
| Total dissolved solids | 46,324 |
| pH | 7.6 |

Table 4
Composition of the brackish water

| Ions | Concentration (ppm) |
|---|---|
| Chloride ($Cl^-$) | 893 |
| Sulfate ($SO_4^{2-}$) | 630 |
| Alkalinity as $CaCO_3$ | 216 |
| Sodium ($Na^+$) | 459 |
| Total dissolved solids | 3270 |
| Turbidity as NTU | 1.5 |
| Total hardness as $CaCO_3$ | 1155 |
| pH | 7.78 |

### 3.3. Exposure conditions

The concrete specimens contaminated with 0.8% chloride and sea water were immersed in 5% sodium chloride solution while those contaminated with 0.8% chloride plus 1.5% $SO_3$ were partially immersed in 5% sodium chloride plus 3.11% sodium sulfate solution. The specimens contaminated with brackish water and unwashed aggregates were immersed in brackish water. The specimens were partially immersed (76 mm) to the selected exposure solutions. The objective of partially immersing the concrete specimens was to provide moisture required for reinforcement corrosion. The chloride or sulfate concentrations of the exposure solutions were selected to avoid leaching of these ions built into concrete as contamination. Further, the exposure conditions selected in this study present worst-case scenario where chloride or chloride plus sulfate salts are present both within and outside concrete.

### 3.4. Test methods

The average compressive strength of three concrete cylinders was determined according to ASTM C 39, using a hydraulically operated digital compression machine of ±0.1 kN accuracy.

Concrete specimens, 75 mm in diameter and 150 mm high, reinforced with a 12 mm diameter steel bar embedded at the center and with an effective cover of 25 mm at the bottom, were used for the corrosion studies. Reinforcement corrosion was monitored by measuring the corrosion potentials and corrosion current density at periodic intervals.

## 4. Results and discussion

### 4.1. Compressive strength

Fig. 1 depicts the average compressive strength of the control concrete specimens and those incorporating the corrosion inhibitors. The compressive strength was determined after 28 days of wet-burlap curing. The compressive strength of all the specimens incorporating the corrosion inhibitors was more than that of the control specimens. The increase in strength varied from 4% in the concrete specimens contaminated with the CI1 organic inhibitor to 14.5% in those with 4% calcium nitrate. Further, the compressive strength of the concrete specimens incorporating calcium nitrate increased with increasing dosage of this corrosion inhibitor. In summary, the data in Fig. 1 indicate that the corrosion inhibitors investigated in this study did not adversely affect the compressive strength of concrete.

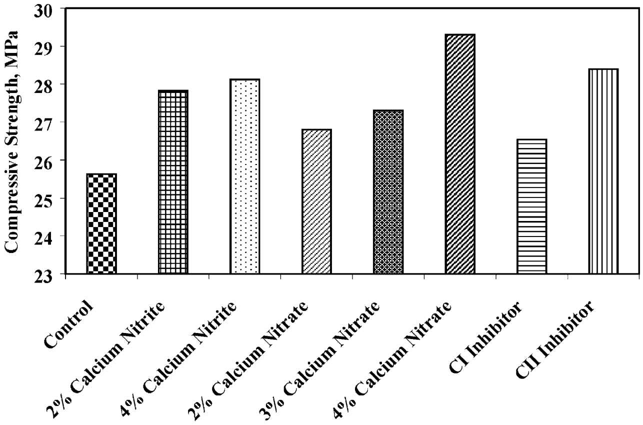

Fig. 1. Compressive strength of concrete specimens incorporating corrosion inhibitors (after 28 days of curing).

### 4.2. Reinforcement corrosion

#### 4.2.1. Corrosion potentials

The corrosion potentials were measured using a saturated calomel referenced electrode (SCE) and a high impedance voltmeter. According to ASTM C 876 [31], potentials more negative than −270 mV, with respect to SCE, indicate greater than 90% probability of active reinforcement corrosion. Values less negative than −120 mV SCE indicate a probability of corrosion below 5%, while those falling between −270 and −120 mV SCE indicate uncertainty of corrosion.

The corrosion potentials on steel in the concrete specimens contaminated with 0.8% chloride and incorporating calcium nitrite are shown in Fig. 2. The corrosion potentials on steel in the concrete specimens prepared with 2% and 4% calcium nitrite were more negative than the ASTM C 876 threshold value of −270 mV SCE, after 28 days of exposure. In the concrete specimens without corrosion inhibitor, the corrosion potentials were more negative than −270 mV SCE right from the initial stages of exposure. The corrosion potentials on steel in the concrete specimens prepared with 0%, 2% and 4% calcium nitrite were −691, −583 and −580 mV SCE, respectively, after about 170 days of exposure.

Fig. 3 depicts the corrosion potentials on steel in the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate and incorporating calcium nitrite. The corrosion potentials on steel in the concrete specimens containing 2% and 4% calcium nitrite crossed the threshold potential value of −270 mV SCE, after 34 and 38 days of exposure, respectively. In the concrete specimens with no inhibitor, the corrosion potentials were less than −270 mV SCE right from the beginning of exposure. The corrosion potentials on steel in the concrete specimens admixed with 0%, 2% and 4% calcium nitrite were −673, −481 and −510 mV SCE, respectively, after 170 days of exposure.

The corrosion potentials on steel in the concrete specimens prepared with sea water and incorporating calcium nitrite are depicted in Fig. 4. The corrosion potentials on steel in the concrete specimens incorporating 2% and 4% calcium nitrite were more or less similar and they were more negative than −270 mV SCE, after about 30 and 35 days of exposure, respectively. In the concrete specimens without inhibitor, the corrosion potentials were less than −270 mV SCE from the initial stages. After about 170 days of exposure, the corrosion potentials on steel in the concrete specimens with 0%, 2% and 4% calcium nitrite were −715, −563 and −572 mV SCE, respectively.

Fig. 5 shows the corrosion potentials on steel in the concrete specimens admixed with brackish water (chloride = 893 mg/l and sulfate = 630 mg/l) and calcium nitrite. The corrosion potentials on steel in the concrete specimens incorporating 2% and 4% calcium nitrite were more than −270 mV SCE, indicating the

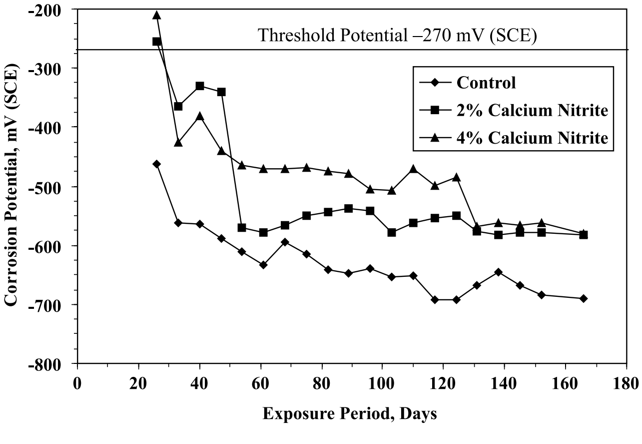

Fig. 2. Corrosion potentials on steel in the concrete specimens contaminated with 0.8% chloride and incorporating calcium nitrite.

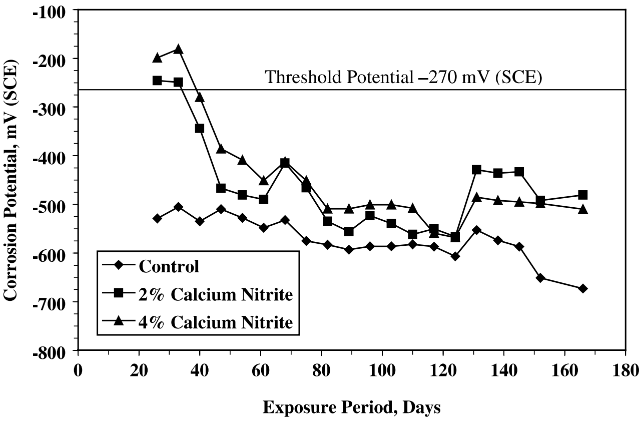

Fig. 3. Corrosion potentials on steel in the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate and incorporating calcium nitrite.

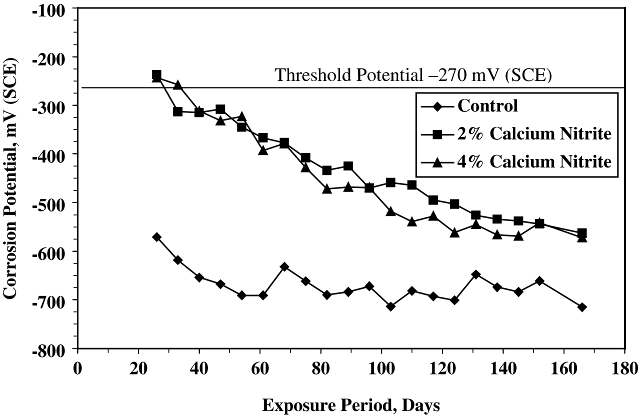

Fig. 4. Corrosion potentials on steel in the concrete specimens prepared with seawater and incorporating calcium nitrite.

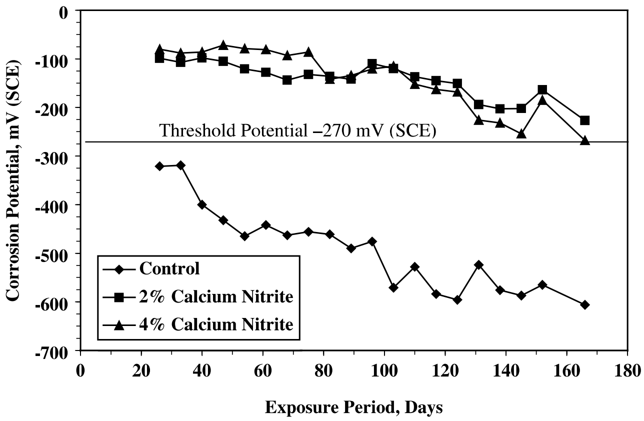

Fig. 6. Corrosion potentials on steel in the concrete specimens prepared with unwashed aggregates and incorporating calcium nitrite.

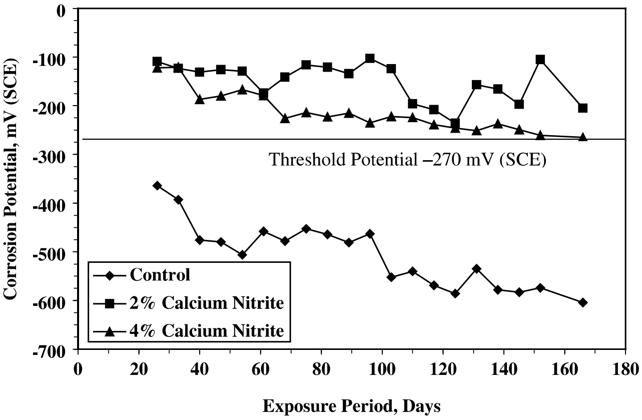

Fig. 5. Corrosion potentials on steel in the concrete specimens prepared with brackish water and incorporating calcium nitrite.

passivity of reinforcing steel even after about 170 days of exposure. However, the potentials in the concrete specimens incorporating 4% calcium nitrite were unexpectedly more negative than those incorporating 2% calcium nitrite. In the concrete specimens without inhibitor, the potential values were less than −270 mV SCE right from the beginning. The corrosion potentials on steel in the concrete specimens with 0%, 2% and 4% calcium nitrite were −604, −205 and −260 mV SCE, respectively, after 170 days of exposure.

The corrosion potentials on steel in the concrete specimens prepared with unwashed aggregates and incorporating calcium nitrite are shown in Fig. 6. The corrosion potentials on steel in the concrete specimens admixed with 2% and 4% calcium nitrite were more or less similar. The corrosion potentials on steel in the concrete specimens prepared with unwashed aggregates were more negative than the threshold value of −270 mV SCE, right from the beginning, while in the concrete specimens incorporating 2% and 4% calcium nitrite, the steel bars were in a passive state of corrosion. The corrosion potentials on steel in the concrete specimens incorporating 0%, 2% and 4% calcium nitrite were −606, −227 and −268 mV SCE, respectively, after about 170 days of exposure.

Corrosion potentials on steel bars in the concrete specimens incorporating calcium nitrate (i.e., 2%, 3% and 4%) and the two organic inhibitors (i.e., CI1 and CI2) and other contaminations were also measured. The corrosion potential–time curves were analyzed to assess the time to initiation of reinforcement corrosion based on the ASTM C 876 criterion of −270 mV SCE. A summary of the data on the time to initiation of reinforcement corrosion in the concrete specimens incorporating the selected corrosion inhibitors and the five contaminations is presented in Table 5. These data indicate that calcium nitrite was efficient in delaying reinforcement corrosion in the concrete specimens contaminated with chloride, chloride plus sulfate and seawater.

In the concrete specimens prepared with brackish water or unwashed aggregates, all the inhibitors were generally effective in delaying reinforcement corrosion within the 170 day duration of this investigation.

Table 6 summarizes the corrosion potentials after 170 days of exposure. Except for the specimens contaminated with brackish water and unwashed aggregates, the corrosion potentials on steel in all the concrete specimens were more negative than the threshold value of −270 mV SCE. However, no definite trend with regard to the types of contamination and the inhibitors could be observed. Further, the corrosion potentials on steel in the concrete specimens prepared with brackish water and unwashed aggregates and incorporating all the selected corrosion inhibitors, were less than the threshold value indicating the passivity of the reinforcing steel.

Table 5
Time to initiation of reinforcement corrosion based on ASTM C 876 criterion

| Contamination | Time to initiation of reinforcement corrosion (days) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Control | Calcium nitrite | | Calcium nitrate | | | CI1 | CI2 |
| | | 2% | 4% | 2% | 3% | 4% | | |
| Chloride | –[a] | 28 | 28 | –[a] | –[a] | –[a] | –[a] | –[a] |
| Chloride plus sulfate | –[a] | 34 | 38 | –[a] | –[a] | –[a] | –[a] | –[a] |
| Seawater | –[a] | 30 | 35 | –[a] | –[a] | –[a] | –[a] | –[a] |
| Brackish water | –[a] | –[b] | –[b] | –[b] | –[b] | –[b] | –[b] | –[b] |
| Unwashed Aggregates | –[a] | –[b] | –[b] | –[b] | –[b] | –[b] | –[b] | –[b] |

[a] Potentials were more negative than −270 mV SCE.

[b] Potentials were less negative than −270 mV SCE, even after 170 days of exposure.

Table 6
Corrosion potentials after 170 days of exposure

| Contamination | Corrosion potential (mV (SCE)) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Control | Calcium nitrite | | Calcium nitrate | | | CI1 | CI2 |
| | | 2% | 4% | 2% | 3% | 4% | | |
| Chloride | −691 | −583 | −580 | −598 | −575 | −580 | −542 | −655 |
| Chloride plus sulfate | −673 | −481 | −510 | −523 | −564 | −505 | −521 | −614 |
| Seawater | −715 | −563 | −572 | −601 | −548 | −568 | −566 | −653 |
| Brackish water | −604 | −205 | −260 | −260 | −228 | −253 | −250 | −201 |
| Unwashed aggregates | −606 | −227 | −268 | −261 | −243 | −257 | −267 | −259 |

### 4.2.2. Corrosion current density

The corrosion current density was measured using the DC linear polarization resistance method. The resistance to polarization ($R_p$) was determined by conducting a linear polarization scan in the range of ±10 mV of the open circuit potential and the corrosion current density ($I_{corr}$) was then calculated using the Stern–Geary formula [32]: $I_{corr} = B/R_p$, where $B$ is a constant based on the anodic and cathodic Tafel constants ($\beta_a$ and $\beta_c$) [32]. Values of $B$ equal to 52 mV for steel in a passive condition and equal to 26 mV in an active condition are frequently used [33]. Lambert et al. [34] have indicated a good correlation between the corrosion current density determined by the linear polarization resistance method and gravimetric weight loss using these values. In this investigation, a potentiostat/galvanostat was used to polarize the steel at a rate of 0.1 mV/s. The Ohmic drop between the working and the reference electrode was compensated by using a positive feed back technique. Tafel constants of 120 mV/decade were utilized in the calculation of the corrosion current density.

The linear polarization resistance method has been considered to be a relatively simple and reliable technique to assess the rate of reinforcement corrosion in concrete [33,35]. An $I_{corr}$ value of less than 0.1 μA/cm$^2$ indicates negligible corrosion, while a value greater than 0.3 μA/cm$^2$ indicates active corrosion [36,37]. Therefore, in this investigation, an $I_{corr}$ value of 0.3 μA/cm$^2$ was considered as the threshold criterion for corrosion initiation.

The $I_{corr}$ on steel in the concrete specimens contaminated with 0.8% chloride and incorporating calcium nitrite is plotted against the period of exposure in Fig. 7. The $I_{corr}$ on steel in the concrete specimens without inhibitor crossed the threshold value of 0.3 μA/cm$^2$ after 53 days of exposure, whereas the $I_{corr}$ on steel in the concrete specimens with 2% and 4% calcium nitrite was much less than the threshold value. After 122 days of exposure, the $I_{corr}$ on steel in the concrete specimens admixed with 0%, 2% and 4% calcium nitrite was 0.52, 0.060 and 0.057 μA/cm$^2$, respectively.

Fig. 8 depicts the $I_{corr}$ on steel in the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate

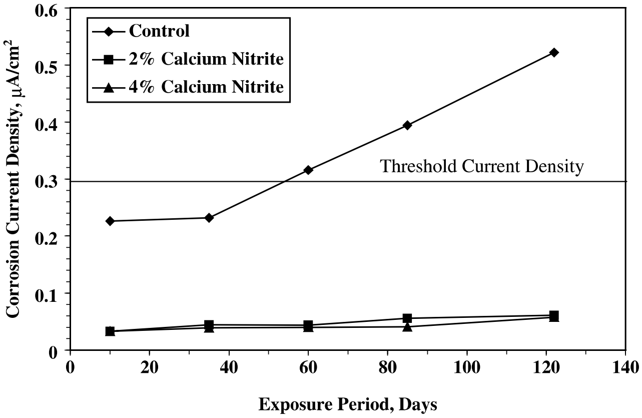

Fig. 7. Corrosion current density on steel in the concrete specimens contaminated with 0.8% chloride and incorporating calcium nitrite.

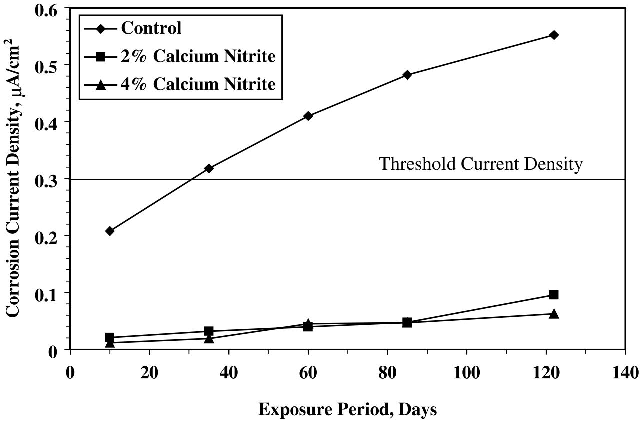

Fig. 8. Corrosion current density on steel in the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate and incorporating calcium nitrite.

and incorporating calcium nitrite. The $I_{\mathrm{corr}}$ on steel in the concrete specimens without inhibitor crossed the threshold value after 31 days, whereas the $I_{\mathrm{corr}}$ on steel in the concrete specimens with calcium nitrite was less than the threshold value. The $I_{\mathrm{corr}}$ on steel in the concrete specimens admixed with 0%, 2% and 4% calcium nitrite was 0.55, 0.095 and 0.062 μA/cm$^2$, respectively, after 122 days of exposure.

The $I_{\mathrm{corr}}$ on steel in the concrete specimens prepared with sea water and incorporating calcium nitrite is plotted in Fig. 9. The $I_{\mathrm{corr}}$ on steel in the concrete specimens admixed with 2% and 4% calcium nitrite was more or less similar, while it crossed the threshold value in the concrete specimens without inhibitor after 98 days of exposure. The $I_{\mathrm{corr}}$ on steel in the concrete specimens with 0%, 2% and 4% calcium nitrite was 0.54, 0.044 and 0.042 μA/cm$^2$, respectively, after 122 days of exposure.

Fig. 10 shows the variation of $I_{\mathrm{corr}}$ on steel in the concrete specimens prepared with brackish water and incorporating calcium nitrite. The $I_{\mathrm{corr}}$ values in all the concrete specimens with and without calcium nitrite were less than the threshold value, even after 122 days of exposure. The $I_{\mathrm{corr}}$ on steel in the concrete specimens with 0%, 2% and 4% calcium nitrite was 0.28, 0.033 and 0.033 μA/cm$^2$, respectively, after 122 days of exposure.

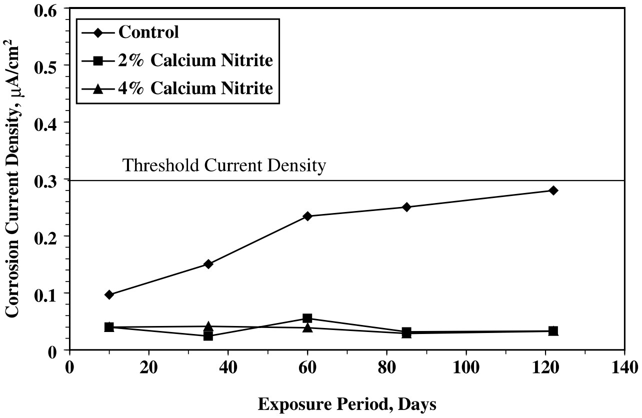

Fig. 10. Corrosion current density on steel in the concrete specimens prepared with brackish water and incorporating calcium nitrite.

The $I_{\mathrm{corr}}$ on steel in the concrete specimens prepared with unwashed aggregates and incorporating calcium nitrite is plotted in Fig. 11. The $I_{\mathrm{corr}}$ values on steel in the concrete specimens with and without calcium nitrite were less than the threshold value. The $I_{\mathrm{corr}}$ on steel in the concrete specimens admixed with 0%, 2% and 4% calcium nitrite was 0.24, 0.075 and 0.064 μA/cm$^2$, respectively, after 122 days of exposure.

Data on corrosion current density were developed for the concrete specimens admixed with the other corrosion inhibitors. A summary of the $I_{\mathrm{corr}}$ values on steel in the concrete specimens with and without corrosion inhibitors, after an exposure period of 122 days, is presented in Table 7, whereas Table 8 shows the time to initiation of reinforcement corrosion as determined

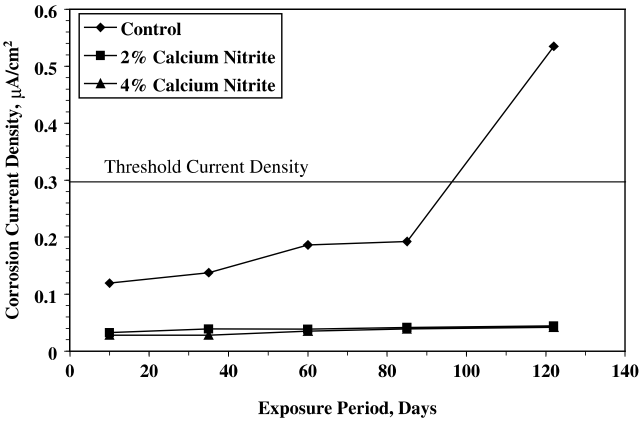

Fig. 9. Corrosion current density on steel in the concrete specimens prepared with seawater and incorporating calcium nitrite.

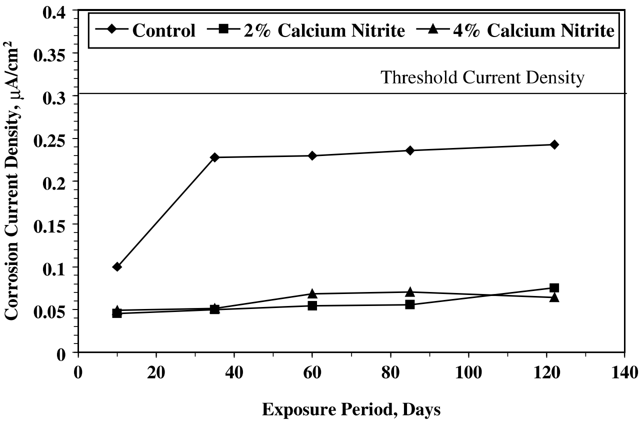

Fig. 11. Corrosion current density on steel in the concrete specimens prepared with unwashed aggregate and incorporating calcium nitrite.

Table 7
Corrosion current density after 122 days of exposure

| Contamination | Corrosion current density ($\mu A/cm^2$) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Control | Calcium nitrite | | Calcium nitrate | | | CI1 | CI2 |
| | | 2% | 4% | 2% | 3% | 4% | | |
| Chloride | 0.52 | 0.060 | 0.057 | 0.064 | 0.061 | 0.060 | 0.073 | 0.082 |
| Chloride plus sulfate | 0.55 | 0.095 | 0.062 | 0.072 | 0.063 | 0.068 | 0.077 | 0.076 |
| Sea water | 0.54 | 0.044 | 0.042 | 0.059 | 0.061 | 0.060 | 0.087 | 0.11 |
| Brackish water | 0.28 | 0.033 | 0.033 | 0.064 | 0.056 | 0.047 | 0.052 | 0.12 |
| Unwashed aggregates | 0.24 | 0.075 | 0.064 | 0.062 | 0.059 | 0.057 | 0.11 | 0.14 |

Table 8
Time to initiation of reinforcement corrosion based on corrosion current density

| Contamination | Time to initiation of reinforcement corrosion (days) | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Control | Calcium nitrite | | Calcium nitrate | | | CI1 | CI2 |
| | | 2% | 4% | 2% | 3% | 4% | | |
| Chloride | 53 | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] |
| Chloride plus sulfate | 31 | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] |
| Sea water | 98 | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] |
| Brackish water | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] |
| Unwashed aggregates | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] | –[a] |

[a] $I_{corr}$ on steel was less than the threshold value of 0.3 $\mu A/cm^2$ after 122 days of exposure.

from the corrosion current density results, i.e., the time required to attain the threshold $I_{corr}$ of 0.30 $\mu A/cm^2$. Based on the data presented in Tables 7 and 8, it is vividly clear that the steel bars in the control specimens were in an active state of corrosion when they were contaminated with chloride, chloride plus sulfate, and sea water. However, in the specimens contaminated with brackish water and unwashed aggregates, the steel bars were in a passive state of corrosion.

It is evident from the data in Tables 7 and 8 that the steel bars in the concrete specimens incorporating all the corrosion inhibitors investigated in this study were in a passive state of corrosion, after an exposure period of 122 days. This proves the efficiency of all inhibitors in retarding the corrosion of reinforcing steel. However, in the long run, different types of inhibitors may exhibit different degrees of protection in terms of: (i) the type of inhibitor and its dosage, and (ii) level of chloride and sulfate contamination.

The lowest $I_{corr}$ of 0.057 $\mu A/cm^2$ was recorded in the concrete specimens contaminated with 0.8% chloride and incorporating 4% calcium nitrite, whereas the $I_{corr}$ values in the concrete specimens incorporating inhibitors CI1 and CI2 were 0.073 and 0.082 $\mu A/cm^2$, respectively. This indicates that in a chloride-contaminated concrete, almost all the inhibitors were suitable, however, the selection of an appropriate inhibitor will depend on the cost of the selected inhibitor and, of course, its long-term performance.

In the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate, the $I_{corr}$ values were 0.062 and 0.063 $\mu A/cm^2$ in the concrete specimens incorporating 4% calcium nitrite and 3% calcium nitrate, respectively. The $I_{corr}$ values in the concrete specimens with all the other inhibitors and dosages were in the range of 0.062–0.077 $\mu A/cm^2$. However, the $I_{corr}$ on steel in the concrete specimens admixed with 2% calcium nitrite inhibitor was 0.095 $\mu A/cm^2$.

In the concrete specimens prepared with seawater, the usage of 2% and 4% calcium nitrite was relatively more effective in minimizing reinforcement corrosion as compared to the other inhibitors. Similarly, calcium nitrate displayed better performance compared to the organic inhibitors investigated in this study. All the inhibitors were efficient in retarding reinforcement corrosion in the concrete specimens contaminated with brackish water and unwashed aggregates. In normal conditions, the inhibitor either forms a protective layer on the steel surface or inhibits the corrosion reaction. However, once corrosion is initiated, the inhibitor may also mitigate the rate of reinforcement corrosion by increasing the electrolytic resistance [26]. Such retardation of reinforcement corrosion was noted in the $I_{corr}$ data summarized in Table 7.

Based on the corrosion current density measurements and within the time frame of this study, the preferred corrosion inhibitors for the various contaminations are outlined in Table 9. Calcium nitrite or nitrate appear to

Table 9
Preferred corrosion inhibitors for different contaminations

| Contamination | Preferred corrosion inhibitors |
|---|---|
| Chloride | 4% calcium nitrite or 4% calcium nitrate |
| Chloride and sulfate | 4% calcium nitrite or 3% calcium nitrate |
| Sea water | 4% calcium nitrite |
| Brackish water | 2% calcium nitrite |
| Unwashed aggregate | 4% calcium nitrate |

be the preferred corrosion inhibitors and the dosage should be between 3% and 4%.

The corrosion potentials data in Table 5 indicate corrosion initiation in all the concrete specimens contaminated with chloride, chloride plus sulfate and sea water, with and without all the corrosion inhibitors. However, the $I_{corr}$ data, summarized in Table 7, indicate corrosion activation only in the control concrete specimens, i.e., those without inhibitor. Since the DC linear polarization technique has proven to be more accurate and reliable, and correlates well with the gravimetric weight loss measurements [33,34], the inconsistency between the data in Tables 5 and 8 indicates the unsuitability of the ASTM C 876 criterion to assess reinforcement corrosion in concrete. In fact, several researchers have expressed a similar concern [33,36,37]. Further, it may not be out of place to state that, while the corrosion potentials provide a qualitative and probable indication of reinforcement corrosion, quantitative and reliable information on reinforcement corrosion can only be obtained by measuring the corrosion current density.

## 5. Conclusions

This investigation was conducted to assess the effectiveness of corrosion inhibitors in mitigating reinforcement corrosion in the concrete specimens prepared with various types of contaminations. Based on the results obtained within the time frame of this study, the following conclusions can be drawn:

(1) The compressive strength of the concrete specimens incorporating all the inhibitors investigated in this study was more than that of the control specimens. The increase in strength varied from 4% in the specimens incorporating an organic inhibitor CI1 to 14.5% in the concrete specimens admixed with 4% calcium nitrate. This indicates that the corrosion inhibitors investigated in this study did not adversely affect the compressive strength of concrete.

(2) Although all the four corrosion inhibitors investigated were effective in delaying the initiation of reinforcement corrosion, calcium nitrite was distinctly efficient in the concrete specimens contaminated with chloride, chloride plus sulfate and sea water.

(3) The $I_{corr}$ data indicated that the steel bars in the concrete specimens incorporating all the corrosion inhibitors investigated in this study were in a passive state, even after 122 days of exposure. However, corrosion activation was indicated on the steel bars in all the concrete specimens without inhibitors after 31–98 days of exposure.

(4) All the corrosion inhibitors investigated in this study were generally equally effective in retarding the rate of reinforcement corrosion in the chloride-contaminated concrete specimens. However, other types and dosages of inhibitors displayed better performance with some contaminations. Typically, in the concrete specimens contaminated with 0.8% chloride plus 1.5% sulfate, the minimum $I_{corr}$ values were noted on the steel in the concrete specimens incorporating 4% calcium nitrite and 3% calcium nitrate. In the concrete specimens prepared with sea water, 2% calcium nitrite was more effective in retarding reinforcement corrosion than the other inhibitors. In the concrete specimens prepared with brackish water and unwashed aggregates, all the inhibitors were efficient in mitigating reinforcement corrosion. In the concrete specimens prepared with brackish water, calcium nitrite inhibitor was superior while calcium nitrate inhibitor was more useful in maintaining the passivity on steel bars in the concrete specimens prepared with unwashed aggregates.

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