Review Article

Research Progress of Nitrite Corrosion Inhibitor in Concrete

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Nitrite inhibitor is a kind of most effective inhibitory corrosion additive used in reinforced concrete. This paper expounded the inhibiting mechanism and physical property of nitrite in concrete. Moreover, the recent progress and application condition at home and abroad were summarized. Meanwhile, corresponding methods for detecting nitrite ion concentration is proposed. Additionally, the inhibition practice on corrosion protection of reinforcing bar in concrete was presented. The long-term inhibiting effectiveness of nitrite ion in concrete when the n(NO\textsuperscript{2-})/n(Cl\textsuperscript{-}) ratios were above the threshold values in concrete was obtained. Finally it is confirmed that critical molar ratio of n(NO\textsuperscript{2-})/n(Cl\textsuperscript{-}) increased with differential nitrite ion concentration, higher cathode, and anode area ratio in steel bar.

1. Introduction

Typically, the hydroxide ions contained in concrete pore solution make the concrete pH above 12.0. In the alkaline environment, the surface of the steel bar is easy to form a passivation film of 20Å to 60Å thick, which acts as a barrier against the intrusion of aggressive species, providing chemical and physical protection to the embedded rebar [1, 2]. Chloride salt and carbonation can easily destroy the passivation film and cause the corrosion of steel bars. Thus, in order to address the issue of steel corrosion in concrete, adding corrosion inhibitors into concrete has been frequently used, which is considered as an effective and economical method to avoid or delay the corrosion of reinforced concrete structures.

Concrete mixed with nitrite corrosion inhibitor is used to protect the steel in concrete. There are plenty of reports of use of this method at home and abroad [3–8]. Nitrite is the best corrosion inhibitor. It is the one used most widely and in the largest quantities. Nitrite corrosion inhibitor can delay the failure time of the passivation film and slow down the corrosion rate of the steel bar in the concrete [9, 10]. After measuring the potential in the reinforced concrete structures, incorporating dozens of steel bar corrosion inhibitors such as phosphate, zinc oxide, gluconate, and nitrite commonly used in engineering, Gonzalez et al. [11] considered that the calcium nitrite has the best corrosion resistance. Berke et al. [12] also agreed that the most widely used corrosion inhibiting admixture is calcium nitrite, due to its excellent inhibitor properties and its benign effect on concrete properties. The corrosion inhibitor with nitrite as the main component has been used in thousands of parking buildings, offshore platforms, and highways in Japan, Europe, and other countries. Chinese “Technical Standard for the Use of Reinforced Concrete Corrosion Preventers” (YB/T9231-98) is also based on calcium nitrite. The RI-1 type inhibitor developed by the National Metallurgical Building Research Institute has been utilized in hundreds of projects around the world. Generally, it can be seen the corrosion inhibitors used in reinforced concrete projects are still dominated by nitrite components.

2. Mechanism of Nitrite Corrosion Inhibitor

As an anodic type steel bar corrosion inhibitor, nitrite forms a dense passivation film by oxidizing the iron atoms on the surface of the steel bar, inhibiting the anodic reaction of the steel bar surface. The mechanism of the corrosion inhibition in reinforced concrete is that the electrochemical reaction between NO\textsuperscript{2-} and Fe\textsuperscript{2+} forms a Fe\textsubscript{2}O\textsubscript{3} passivation film on the surface of the steel which can slow down the steel corrosion by
preventing the loss of electrons after the iron atoms continue to dissolve.

\[
2\text{Fe}^{2+} + 2\text{OH}^- + 2\text{NO}_2^- = 2\text{NO} + \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \tag{1}
\]

\[
\text{Fe}^{2+} + \text{OH}^- + \text{NO}_2^- = \text{NO} + \gamma\text{-FeOOH} \tag{2}
\]

When concrete contains a high concentration of NO\textsubscript{2}\textsuperscript{−}, chemical reactions of (1)/(2) occur to suppress the corrosion reaction and protect the steel bars. When the nitrite ion concentration is low, the surface of the steel bar is unable to form a sufficient passivation film, so the rust inhibiting effect is weakened or disappeared. Nitrite is an anodic passivation film type, which can inhibit the micro-corrosion points in the passivation film into stable pitting. What is more, nitrite does not change the crystal structures and electronic properties of the passivation film; that is, the passivation film is still amorphous n-type semiconductor. The phase film accelerates the growth rate of the film, increases the surface \(\gamma\text{-FeOOH}\) content of the passivation film, improves the surface of the passivation film, makes it more flat, and has a significant inhibitory effect on macro-cell corrosion [13–16].

3. General Characteristics of Nitrite Corrosion Inhibitor

Nitrite species have a great impact on the setting time of cement paste, therefore, limiting the application of some nitrite corrosion inhibitors in concrete engineering. The results show the cement paste with a water-cement ratio of 0.3 will produce rapid setting when the content of calcium nitrite or magnesium nitrite is 4%; rapid setting will occur when the amount of potassium nitrite is 2%; lithium nitrite, sodium nitrite, and bismuth nitrite can reach 10% [17]. On the other hand, sodium nitrite accelerates the occurrence of alkali-aggregate reaction by increasing alkali content in concrete pore solution; lithium nitrite not only has good rust resistance, but also inhibits the occurrence of alkali-aggregate reaction [18, 19]. Calcium nitrite has low price and excellent rust resistance effect and has a certain early strength effect, but it shortens the setting time and increases the shrinkage deformation. [20].

4. Corrosion Inhibition of Nitrite Corrosion Inhibitor

4.1. Corrosion Inhibition in Chloride-Containing Concrete. Recently, nitrite corrosion inhibitors are often used in chloride-containing concrete. “The Technical Specification for the Application of Concrete Admixture” (GB50119-2013) stipulates that only when the molar ratio of nitrite to chloride is higher than a certain proportion can the effect of steel bar corrosion inhibition be guaranteed. The following factors will affect the critical molar ratio of \(n(\text{NO}_2^-)/n(\text{Cl}^-)\), such as chloride and nitrite species in concrete, curing conditions and period, corrosion environment, and evaluation methods. Liu et al [21] conduct accelerated steel corrosion test steel of reinforced concrete containing various quantities of calcium chloride and calcium nitrite and determine the critical molar

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Ca(NO\textsubscript{3})\textsubscript{2}/L/m\textsuperscript{3}</th>
</tr>
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<tbody>
<tr>
<td>Time/d</td>
<td>70  125  190  235</td>
</tr>
<tr>
<td>NaCl Concentration/%</td>
<td>0.14  0.26  0.38  0.46</td>
</tr>
</tbody>
</table>

ratio of \(n(\text{NO}_2^-)/n(\text{Cl}^-)\) by visual observations, anodic polarization, half-cell potentials, mass loss, and corroded area. It can be seen from Figures 1 and 2 that when the chloride ion concentration is constant, the corrosion effect of steel bars is more obvious with the increase of \(n(\text{NO}_2^-)/n(\text{Cl}^-)\); the higher the chloride ion concentration in concrete, the more severe the corrosion of the steel. The inhibiting effect of nitrite from reinforcement corrosion is not obvious and sometimes speeds up the macro-cell corrosion when critical value of \(n(\text{NO}_2^-)/n(\text{Cl}^-)\) in reinforced concrete is less than 0.4. However, when the molar ratio reaches 0.8, the pit erosion is basically eliminated, but it is not enough to completely inhibit the corrosion of the steel bar; when the molar ratio of \(n(\text{NO}_2^-)/n(\text{Cl}^-)\) is more than 1.2, the corrosion of the steel bar can be completely suppressed.

Meanwhile, Berke et al. [12] presented a methodology for predicting an increased threshold for chloride induced corrosion, which can then be utilized with models that address the issue of chloride ingress into concrete over time, to predict service life extension through the use of calcium nitrite. And he found that calcium nitrite does not increase corrosion rates after chloride protection values are surpassed and in contrast often lowers them.

4.2. Corrosion Inhibition in Chloride Salt Erosion Concrete. When the chloride ions penetrate into concrete due to deicing salt, sea breeze, waves, etc., the preincorporation of nitrite can also effectively protect the steel bars. The concrete specimen containing calcium nitrite is immersed in a 3% aqueous solution of sodium chloride with the circulating environment of high temperature and high humidity (60°C, 90%), low temperature, and low humidity (20°C, 40%). Figure 3 shows measurement results of the chloride ion concentration in concrete and the potential of steel bar. Referring to Figure 3, calcium nitrite can effectively slow down the decline of potential and reduce the degree of corrosion. Table 1 shows that the greater the amount of calcium nitrite incorporation, the higher the NaCl concentration associated with initial corrosion. Be seen, when the chloride salt is infiltrated into the concrete from the external environment, the preincorporation nitrite corrosion inhibitor can prolong the corrosion start time of the steel bar and prolong the life of the reinforced concrete structure [22, 23].
accelerate the formation of hydration products and reduce the porosity of capillary pores, in order to increase density of specimen and benefits to the raise of the carbonation resistance of specimens. The carbonation depth of mixed NaNO\(_2\) specimen is minimum under the dosage of 1.0%; the carbonation depth of concrete is obviously bigger than the carbonation depth of cement mortar for NaNO\(_2\).

Secondly, it can be seen in the research [25] that a new hydrated crystallization phase NO\(_2\)-AFm is produced after the hydration of nitrite-containing cement paste and is evenly distributed. During the carbonation process, NO\(_2\)-AFm redissolves and generates nitrite ions, diffusing to noncarbonated area. This resulted in a decrease of NO\(_2^-\) concentration in carbonated area and an increase in noncarbonated area.

As can be seen from Figure 4 under carbonation, the nitrite ions uniformly distribute in the cement paste diffuse to the uncarbonated zone due to the migration and concentration of the N element.

Furthermore, nitrite can effectively inhibit the corrosion of steel bars caused by carbonation. The steel bar with a diameter of 10 mm and a length of 150 mm is embedded in a 40 mm × 40 mm × 160 mm nitrite-containing mortar, which carbonated in a solution of 20°C, 60% RH, and 10% CO\(_2\) until the phenolphthalein ethanol solution is confirmed to be completely carbonated at a high temperature and accelerated corrosion of steel bars under dry and wet cycling conditions. The results show the higher the NO\(_2^-\) concentration in the mortar, the better the antirust effect of steel bar. When the NO\(_2^-\) concentration in the mortar is about 1.66% of cement mass, the steel corrosion caused by carbonation is totally inhibited. The critical molar ratio of n(NO\(_2^-\))/n(Cl\(^-\)) under the combined action of chloride and carbonation is about 3 times that of concrete containing only chloride salt [26, 27].

4.4. Corrosion Inhibition in Existing Reinforced Concrete Structures. Newly built reinforced concrete structures can improve the rust resistance by increasing the compactness and incorporating corrosion inhibitors when formulating concrete [28–30]. As for existing reinforced concrete structures that are corroding or in corrosive environment, the commonly used method is to treat the protective layer on the concrete surface with large cracks or high chloride salt concentration and fill the mortar containing nitrite components [30–33]. Ann et al. [8] treated the rusted steel bar with mortar containing adsorbent and achieved a certain corrosion-resisting effect. This adsorbent is capable of adsorbing chloride ions in the concrete surrounding the steel bar and releasing nitrite ions. After the treatment, the potential of the repair site increases from -400mV to -450mV to about -200mV (Cu/CuSO\(_4\) electrode) in the
Figure 2: Corrosion grade of steel bar at 30 cycles.

Figure 3: Variation of NaCl concentration and potential.
Figure 4: Distribution of N elements after carbonation.
29th month after treatment, but the unrepaired other parts produce different degrees of macro cell corrosion. This is because the corrosive environment of the steel surface after repairing is different; the unrepaired area tends to become the anode of the reinforced magnetic battery and accelerates the corrosion of the macro battery, which does not achieve the expected effect. In addition, if the above method is used, the damage caused to the concrete structures in which the surface of the concrete is not rusted and expanded is too severe. Therefore, the most effective method is to take certain measures to form a blunt environment around the steel bar without destroying the concrete protective layer, so as to achieve the purpose of preventing rust. At present, MCI migration type corrosion inhibitors have appeared at home and abroad, the main components of such corrosion inhibitors are amines, esters, fatty acids, alcohols, and other organic substances; those have certain characteristics of permeation and volatilization and can penetrate into concrete to protect them by adsorption and film formation. This type of corrosion inhibitor is generally harmless to human body, but its effect is not satisfactory, mainly because the rust prevention effect is not obvious. In addition, MCI’s long-term effectiveness, testing methods, etc. are also issues for future research, mainly because there are still some different understandings in terms of penetration depth, test indicators, volatilization, and retention time [34–38]. Liang et al. [39] considered that nitrite has better diffusion effects than other inorganic salts such as sodium benzoate, stannous chloride, chromium salt borate, molybdate, and phosphate. In particular, calcium nitrite not only has a strong diffusion capacity, but also has no obvious adverse effect on concrete and the possibility of causing alkali-aggregate reaction. For concrete corrosion caused by seawater, chloride salt admixture or deicing salt, and other external chloride ions, Liu et al. [40] who used Fick’s law to predict the concentration distribution of NO$_2^-$ in concrete applied a certain concentration of calcium nitrite aqueous solution on concrete surface, and the nitrite ions diffused from the outer surface of the concrete to the inside to make the nitrite ion concentration around the steel bar reach the critical n(NO$_2^-$)/n(Cl$^-$) molar ratio of corrosion inhibition. When 35% high concentration aqueous calcium nitrite is applied to the concrete surface at 250 g/m$^2$, 500 g/m$^2$, 1000 g/m$^2$, and 1500 g/m$^2$, nitrite is infiltrated into the concrete after 6 months and the ion osmotic concentration is shown in Figure 5, where M is the measured value and T is the theoretical value, which fully demonstrates that the nitrite ion has excellent diffusion properties. The higher the concentration of the aqueous solution of calcium nitrite, the greater the amount of concrete surface coating, and the greater the concentration of nitrite ions permeating the concrete, which can effectively protect the steel. It is worth noting that when the concentration of nitrite ions diffused to the surface of the steel bar after repair is not uniform, the uneven concentration of the surface of the steel bar and the ratio of the area of the anode and the cathode have a great influence on the corrosion of the steel bar. The research results show that the larger the difference of the concentration of nitrite ions in the surface of the steel in the concrete, the greater the ratio of the area of the anode and the cathode, the more serious the corrosion of the steel.

**4.5. Long-Term Corrosion Inhibition Effect of Nitrite Corrosion Inhibitor.** In the concrete setting and hardening stage, C$_3$A will react with Cl$^-$ which accounts for 0.4% of the cement mass to form Friedel’s salt. At the same time, part of Cl$^-$ participates in the electrochemical corrosion reaction of steel bars, which changes the concentration of chloride ions in the pore solution. Similarly, some of the NO$_2^-$ will be consumed by the reaction with the corrosion products during the electrochemical corrosion process of the steel bars, and part of NO$_2^-$ will adsorb on the surface of the cement product, causing the concentration of NO$_2^-$ in the pore solution to change. The changes in the concentration of...
these two ions will affect corrosion inhibition effect of nitrite corrosion inhibitor. The higher the concentration of nitrite, the more obvious the effect of inhibiting corrosion. When the concentration of nitrite is low, the $\mathrm{NO}_2^-$ is totally consumed during the reaction of formula (1), so the corrosion inhibition effect on the steel bar is lost. Therefore, it is necessary to further clarify the changes of free nitrite ion and chloride ion concentration in concrete during corrosion reaction. In addition, the concentration of free chloride and nitrite ions in chloride and nitrite-containing concrete changes greatly during the 28 days of hydration and stabilizes in the later stage, indicating that as long as sufficient critical $n(\mathrm{NO}_2^-)/n(\mathrm{Cl}^-)$ molar ratio is incorporated into the concrete, the nitrite concentration can ensure the long-term rust inhibition effect of reinforced concrete. The American Concrete Institute ACI also confirmed that it is a long-term effective measure to prevent corrosion of steel bars [41–44].

5. Methods for Detecting Nitrite Ion Concentration

5.1. Direct Titration. The 28-day cement mortar specie is cut into pieces with a cutter at intervals of 20 mm. After cleaning the cutting surface, spraying resorcinol and zirconium oxide ion developer, potassium iodide, and starch solution developer on the surface, ion concentration can be judged by observing the color change of different sodium nitrite concentration.

5.2. Semiquantitative Determination of Color Difference. The 28-day cement mortar specie is cut into pieces with a cutter at intervals of 20 mm, and the cut surface is cleaned as a sample of the spray display agent. Mixing 4,4-diphenylmethane disiocyanate with toluene in a ratio of 1:10 by volume is to uniformly prepare isocyanate display solution. After preparing the sample and the display liquid, spraying the isocyanate display solution on the cut sample at a dosage of 80 g/m², the sample is dried for 2 hours and then measured with a color difference meter. Compare the color difference between the product under test and the sample plate and output three sets of data of brightness $L$, chromaticity $a$, chromaticity $b$, and color difference $\Delta E$.

5.3. Spectrophotometric Quantitative Determination. According to the “Cement Chemical Analysis Method” (GB/T176-2008), after 7 days of standardization, the cement paste specimen is crushed with a steel mill, so place the small pieces in a standard square sieve with a hole diameter of 0.6 mm, 0.3 mm, and 0.15 mm, and then the powder after the 0.15 mm filter hole is taken out and dried in a dry box. 10 g of each cement paste dry powder is placed in an Erlenmeyer flask containing 100 ml of water, and the Erlenmeyer flask is placed in a 60 °C water bath and heated with a glass rod for 10 minutes, after which the Erlenmeyer flask is placed in a shaker and shaken for 10 minutes. Then 10 ml of the solution which is sufficiently heated and shaken separated is extracted and diluted 1000 times, and each diluted solution is placed in a test tube to a designated mark; at last measurement is performed by a spectrophotometer.

The nitrite ion mass concentration in concrete can be measured semiquantitatively, qualitatively, and quantitatively by direct titration, color display, and spectrophotometry, respectively. Li et al. [45] found that the nitrite ion mass concentration measured by spectrophotometry is lower than the actual mixed value, only takes up 30%–60% of actual value. Direct titration method is simple, direct, and obvious. The concentration of nitrite in concrete is directly determined by observing, but more influential factors, and cannot be quantitative analysis. Color display method is also more convenient to operate, but only semi-quantitative analysis. As for spectrophotometry quantitative analysis, the sensitivity of the method is too high, thus the detection error is unavoidable. All in all, these methods provide a theoretical basis for the effective method to evaluate nitrite ion concentration in concrete.

6. Environmental Concerns about Nitrite Corrosion Inhibitor

Nitrite corrosion inhibitor is the earliest, most used, and most effective steel bar corrosion inhibitor. However, at present, there are some environmental concerns in China. In fact, nitrite does not have skin permeability and volatility, and nitrite poisoning can only occur through ingestion. As an industrial product, its production and use are not related to food. As long as necessary protective measures are taken at every link, the probability of poisoning in the human body is very small. Nitrite has been used as a steel bar corrosion inhibitor for more than 60 years, but no news on the poisoning of nitrite corrosion inhibitor has been reported. Studies have shown that the dissolution rate of nitrite-containing concrete after soaking in water for 10 months is only 0.0041%. It found, what concerns the application does not affect the environmental corrosion inhibitor nitrite in a reinforced concrete structure [46].

7. Conclusions

(1) Nitrite is a long-term effective steel bar corrosion inhibitor. Regardless of whether it is carbonation or chloride salt, the corrosion inhibition effect of nitrites in the common steel bar is the most obvious. The reasonable corrosion resistance method should be selected according to the corrosive environment and engineering characteristics.

(2) The greater the content of nitrite in concrete, the more effective the inhibition of steel corrosion. The methods of direct titration, color display, and spectrophotometry can effectively measure the nitrite ion mass concentration in concrete.

(3) The greater the concentration difference of nitrite ions on the surface of the steel in concrete, the greater the ratio of the area of the anode to the cathode, the more severe the corrosion. Due to the toxicity of nitrite, it should be restricted to some extent in some special projects.
Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

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