

# Research on the inhibiting effect of nitrite on steel corrosion

## 1. Introduction

A new self-repairing coating for the protection of steel exposed to aggressive environment is being developed by concrete laboratory of KIT. This new coating has two layers, the inner layer is a composite system composing of nitrite, cement and polymer, and the outer layer is epoxy resin. When this coating is slightly damaged, the nitrite in the inner coating can be released to react with ferrous ions to form a stable and compact passive film, thus inhibit the corrosion of steel. Some preliminary experiments have proved this self-repairing coating has a larger value for development. As this research is still at the primary stage, there are many problems to be solved. The purpose of this thesis is to make sure the inhibiting effect of nitrite and the influence of alkaline environment on this inhibiting effect.

## 2. Experiment

### 2.1 Specimens

Steel sheets with a dimension of 60mm×60mm×1mm were used in the experiments. At one corner of the steel sheet, 4mm diameter hole was drilled by drilling machine, and M4×10mm screw was used to fix the lead wire to the steel plate. To avoid the reaction between the exposed copper wire and water, a barrier coating of PS resin was applied to seal this connection area. The exposed area of the steel was 67.7cm<sup>2</sup>. Before the experiments, steel sheets, in turn, were polished by grinder with grade of 180 and sandpaper with grade of 400, at last cleaned with acetone.

### 2.2 Experimental design

The inhibiting effect of nitrite was investigated in chloride-induced corrosion environment and sulfate-induced corrosion environment, respectively. Three pH solutions related to pH12.6, pH10.3 and distilled water were selected to evaluate the influence of pH values on the inhibiting effect of nitrite. Detailed information was presented in Table1 and Table2.

### 2.3 Experimental methods

#### (1) Half-cell potential

Half-cell potential was mainly used in these experiments. The reference electrode used here was copper sulfate electrode (CSE). Two specimens were performed for each case at the same time. Half-cell potential was measured everyday until the potential kept a constant value.

#### (2) Visual examination

At the end of the experiments, specimens were taken out from the solutions and examined for the formation of any corrosion product on its surface. For each case, whether corrosion or not was judged according to Table 3.

Table 1 Experimental design in chloride environment

pH environments	Nitrite mol/L	Ratio of nitrite to chloride						
		0.1	0.2	0.5	1	2	4	8
Distilled Water pH10.3±0.3 pH12.6±0.3	0			0.4	0.2	0.1	0.05	
	0.053	0.53	0.265	0.106	0.053	0.027		
	0.2		1	0.4	0.2	0.1	0.05	
	0.53			1.06	0.53	0.265	0.133	0.066

Table 2 Experimental design in sulfate environment

pH environments	Nitrite mol/L	Ratio of nitrite to sulfate						
		0.1	0.2	0.5	1	2	4	8
Distilled Water pH10.3±0.3 pH12.6±0.3	0				0.2	0.1	0.05	0.025
	0.02	0.2	0.1	0.04	0.02	0.01		
	0.053		0.265	0.106	0.053	0.027	0.013	
	0.2			0.4	0.2	0.1	0.05	0.025

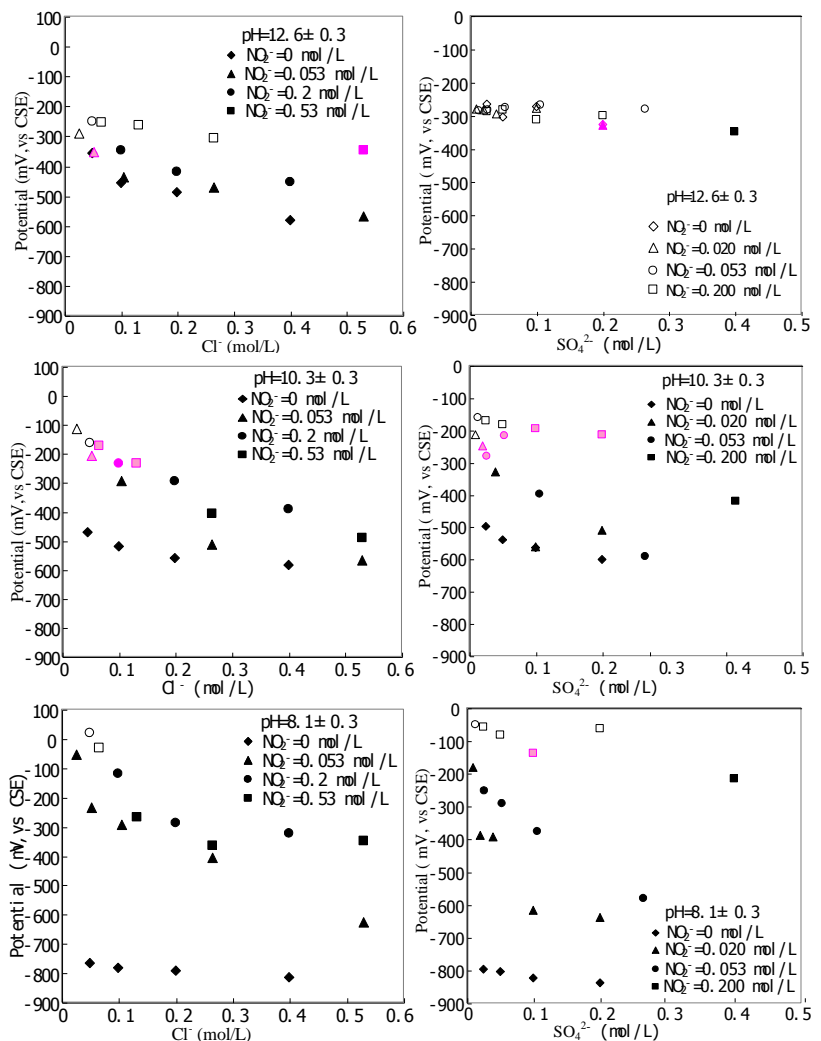
Note: pH 12.6±0.3 solution is made by 25g/L LiOH and 12.5g/L H<sub>3</sub>BO<sub>3</sub>;

pH 10.3±0.3 solution is made by 2g/L LiOH and 3.1g/L H<sub>3</sub>BO<sub>3</sub>;

With the addition of nitrite, the pH of distilled water changes to 8.1±0.3

Table 3 Corrosion judgement

Specimen 1	Specimen 2	Judgement
Corrosion	Corrosion	Corrosion
Corrosion	Nocorrosion	Uncertain
Nocorrosion	Corrosion	Uncertain
Nocorrosion	Nocorrosion	No Corrosion



(1) In chloride environment (2) In sulfate environment

◇△□ No Corrosion ◆▲■ Uncertain ♦●■ Corrosion

Fig 1 Effect of nitrite on self-potential

### 3. Results

#### 3.1 Effect of nitrite on steel self-potential

(1) In chloride environment (Fig1-1)

The results shown in Fig1-1 confirmed the beneficial action of nitrite. The self-potential of steel obviously increased with the addition of nitrite for all pH environments, especially for low pH environment. The increment of potential in pH8.1 was greater than that in pH12.6. So with the decreasing of pH, nitrite became more effective to increase the self-potential, but not helpful to inhibit the corrosion. This was because the corrosion potential was -344mV vs. CSE for pH 12.6, -199 mV vs. CSE for pH 10.3 and -60 mV vs. CSE for pH 8.1, increased with the decreasing of pH. If the self-potential was greater than corrosion potential, the steel would be passivated; otherwise, the steel was corroded.

The concentrations of nitrite had an influence on steel self-potential. For highly alkaline environment with pH12.6, the self-potential increased with the increasing of nitrite concentration, and this increment was more evident in higher chloride content. However, for the conditions of pH10.3 and pH8.1, when nitrite was increased from 0.2mol/L to 0.53mol/L, the increment of potential was not obvious. The self-potential with 0.53 mol/L nitrite was equal to or even lower than that with 0.2 mol/L nitrite.

(2) In sulfate environment (Fig1-2)

The self-potential of steel increased with the addition of nitrite in pH10.3 and pH8.1 environments. The lower the pH value is, the higher the increment of potential. However, in pH12.6 environment, the increment of potential was negligible.

The concentrations of nitrite had an influence on steel potential. For highly alkaline environment with pH12.6, with the increasing of nitrite concentration, the increment of potential was not obvious, even the decrease of potential can be found according to the experimental results. However, for the conditions of pH10.3 and pH8.1, the potential increased significantly with the raising of nitrite content, and this increment was more evident when sulfate content was high.

#### 3.2 Effect of nitrite on chloride threshold level

The effect of nitrite on chloride threshold level (CTL) was shown in Fig 2. As can be seen from the figure, in pH12.6 environment, the CTL increased markedly when the concentration of nitrite increased from 0.053mol/L to 0.53mol/L. The relevant CTL was 0.045mol/L for 0.053mol/L nitrite, 0.124mol/L for 0.2mol/L nitrite and 0.507mol/L for 0.53mol/L nitrite. In pH10.3 and pH8.1 environments, when the concentration of nitrite was less than 0.2mol/L, the CTL had an increasing trend with the nitrite content increasing. While the nitrite content was higher than 0.2mol/L, there was almost no increase in the CTL, even the decrease can be found according to the experimental results.

#### 3.3 Effect of nitrite on sulfate threshold level

The effect of nitrite on sulfate threshold level (STL) was presented in Fig 3. Seeing from the figure, irrespective of the pH values, with the increasing of nitrite concentration, the STL increased significantly. In pH12.6 environment, the STL was 0.1mol/L for 0.02mol/L nitrite, 0.265mol/L for 0.053mol/L nitrite and 0.305mol/L for 0.2mol/L nitrite. In pH10.3 environment, it was 0.011mol/L for 0.02mol/L nitrite, 0.022mol/L for 0.053mol/L nitrite and 0.076mol/L for 0.2mol/L nitrite. In pH8.1 environment, it was 0.005mol/L for 0.02mol/L nitrite, 0.016mol/L for 0.053mol/L nitrite and 0.086mol/L for 0.2mol/L nitrite. For the same nitrite content, the STL in pH12.6 was greater than that in pH10.3 and pH8.1. So the highly alkaline environment played an important role in inhibiting sulfate-induced corrosion.

### 4. Conclusions

- (1) With the presence of nitrite, irrespective of chloride-induced corrosion or sulfate-induced corrosion, steel potential increased significantly, the increment of potential was affected by pH and with the order of pH8.1 > pH10.3 > pH12.6.
- (2) For chloride-induced corrosion, the influence of nitrite concentration on self-potential was more obvious in pH12.6 than that in pH10.3 and pH8.1. However, for sulfate-induced corrosion, the influence of nitrite concentration on self-potential was more obvious in pH8.1 and pH10.3 environments than that in pH12.6 environment.
- (3) Chloride threshold level obviously increased with the increasing of nitrite concentration in pH12.6. However, in pH10.3 and pH8.1, the increment of CTL was not obvious and lower than that in pH12.6.
- (4) Sulfate threshold level increased significantly with the nitrite content increasing in all pH environments. Highly alkaline environment played an important role in assisting nitrite to inhibit both chloride-induced corrosion and sulfate-induced corrosion.

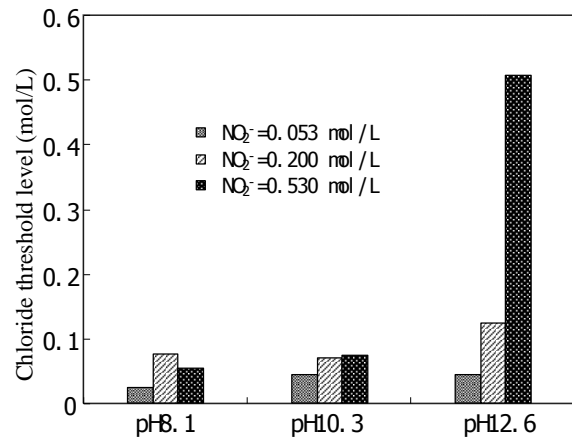


Fig 2 Effect of nitrite on chloride threshold level

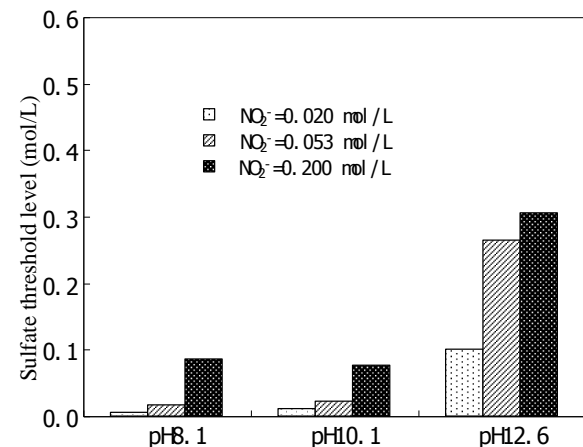


Fig 3 Effect of nitrite on sulfate threshold level