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Short Communication

Investigation on Effect of Different Inhibitors on Corrosion Behavior of 45# Steel in Simulated Concrete Pore Solution

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Different inhibitors are added into the simulated concrete pore solution to inhibit the corrosion process of 45# steel. The effect of different inhibitors on surface morphology, roughness, corrosion inhibition efficiency, and corrosion behavior of 45# steel in simulated concrete pore solution is studied. The corrosion inhibition efficiency of sodium molybdate is about 30%, and that of sodium silicate is about 50%. However, the inhibition efficiency of sodium molybdate mixed with sodium silicate is approximate 75%. It is found that sodium silicate and sodium molybdate in the solution will react with Fe^{2+} to generate $FeMoO_4$, Fe_2SiO_4 and Fe_7SiO_{10} that further inhibit the corrosion process resulting in denser corrosion products and smaller surface roughness. According to the potentiodynamic polarization curves, the corrosion current density of 45# steel immersed in the simulated concrete pore solution mixed with sodium silicate and sodium molybdate for 6 days is about 15.93 μA/cm^2.

Keywords: Corrosion inhibitor; Simulated concrete pore solution; Potentiodynamic polarization curves;

1. INTRODUCTION

Steel is considered as a kind of common construction materials because of its low price and excellent mechanical property. It is known that many parts used in the construction field are made of steel, such as bearings, bolts, holders and so on. Especially, steel is widely used in the concrete environment because of its better comprehensive mechanical property [1-5]. However, there are a large number of chloride ions, hydroxide ions, calcium ions and other substances in the concrete environment which will corrode the steel to greatly reduce its service life [6-9]. Therefore, it is essential to improve corrosion resistance of the steel used in the concrete environment. For example, some scholars use electrodeposition technology to prepare alloy coatings with excellent corrosion resistance on the surface of steel to extremely improve its service life in the concrete environment [10-11]. Except for electrodeposition method, it is reported that alloy coatings can also be fabricated by electroless deposition on the surface of steel to improve corrosion resistance [12-14]. Moreover, some researchers prepare passivation film on the surface of steel to improve its corrosion resistance in harsh environment [15-19]. Although surface treatment can effectively improve the corrosion resistance of steel, the surface treatment process is complex and the cost is high.

In recent years, it has been found that adding corrosion inhibitors can effectively inhibit the corrosion process of steel in the concrete environment. The addition of corrosion inhibitors has been widely concerned by scholars because of its low cost, simple process and remarkable effect [20-21]. It is found that the corrosion inhibitor can inhibit the cathode or anode reaction between steel and concrete pore solution to protect steel. Although common corrosion inhibitors such as chromate and nitrite have good corrosion inhibition effect, chromate and nitrite is harmful and unfriendly to the environment. Silicate is considered as a kind of environmental-friendly corrosion inhibitor. It has been found that adding silicate in the corrosion process of steel will generate silicate and metal hydroxide which can effectively inhibit the corrosion of steel [22-23]. Molybdate is a kind of corrosion inhibitor with low toxicity and almost no pollution to the environment. However, when molybdate is used alone, the corrosion inhibition effect is general and the dosage is large. Compared with single inhibitor, the combination of multiple inhibitors has better corrosion inhibition effect. Therefore, in the paper, silicate and molybdate is mixed as the corrosion inhibitor to investigate its corrosion inhibition effect on steel in simulated concrete pore solution which is significant and innovative.

2. EXPERIMENTAL

2.1 Materials and experimental process

The 45# steel as the construction material used in the concrete environment is chosen as the substrate in the experiment. The surface area of the each 45# steel sheet is 2 cm×2 cm. The detailed chemical composition of 45# steel is listed in Table 1.

Table 1. Chemical composition of 45# steel

Chemical composition	Percentage (%)
C	0.42~0.50
Cr	≤0.25
Mn	0.50~0.80
Ni	≤0.25
P	≤0.035
S	≤0.035
Si	0.17~0.37

Firstly, the 45# steel is polished and cleaned by pure water. Secondly, the substrate is immersed in an alkaline solution containing 30 g/L NaOH at 60 ℃ for 10 minutes to remove oil. Thirdly, 10%

dilute hydrochloric acid solution is used to clean the surface of the substrate at room temperature for 5 minutes. Finally, the pretreated 45# steel is cleaned and dried. The pretreated substrate is immersed in a 100 ml simulated concrete pore solution (3 g/L KOH saturated calcium hydroxide and 3 g/L NaCl), a 100 ml simulated concrete pore solution with 0.1 g/L Na_2SiO_3, a 100 ml simulated concrete pore solution with 1 g/L Na_2MoO_4, and a 100 ml simulated concrete pore solution mixed with 0.1 g/L Na_2SiO_3 and 1 g/L Na_2MoO_4 respectively for 2 days, 4 days and 6 days. The surface morphology, roughness, potentiodynamic polarization curve, and weight loss of 45# steel in the simulated concrete pore solution with different corrosion inhibitors for different days are characterized and tested to investigate the corrosion behavior.

2.2 Testing

The high precision electronic balance (LICHEN ES2085A) is used to calculate the weight loss of 45# steel immersed in the simulated concrete pore solution with different corrosion inhibitors for different days. The weight loss is calculated based on the equation (1).

$$v = \frac{m_1 - m_2}{s} \qquad (1)$$

According to equation (1), m_1 is the mass of 45# steel before immersion, m_2 is the mass of 45# steel after immersion in the simulated concrete pore solution with different corrosion inhibitors for different days, s is the area of the substrate. The potentiodynamic polarization curves of 45# steel immersed in the simulated concrete pore solution with different corrosion inhibitors for different days are tested by electrochemical station (CHI660E). Meanwhile, the 45# steel of 1 cm×1 cm is as the cathode, the pure platinum sheet is the anode and the reference electrode is the saturated calomel electrode at the scan rate of 1 mV/s. The effect of different corrosion inhibitors on corrosion inhibition efficiency of 45# steel in simulated concrete pore solution is calculated based on the equation (2).

$$\eta = \frac{J_{corr} - J'_{corr}}{J_{corr}} \times 100\% \qquad (2)$$

The J'_{corr} and J_{corr} represent respectively the corrosion current density of 45# steel in simulated concrete pore solution with and without corrosion inhibitor.

The surface roughness of 45# steel after corrosion is tested by probe type surface profiler (KLAP7). The scan length is from 0 μm to 2000 μm at the scan rate of 5 μm/s. Metalloscope is used to observe the surface morphology of 45# steel before and after corrosion with the 100 times magnification.

3. RESTULS AND DISCUSSION

3.1 Effect of corrosion inhibitors on weight loss of 45# steel

The effect of different corrosion inhibitors on the weight loss of 45# steel immersed in simulated concrete pore solution for different days is shown in Figure 1. According to the data of weight loss, it can be found that the corrosion degree of 45# steel in the simulated pore solution without corrosion inhibitor is more serious. With the increase of immersion time, the weight loss gradually increases. The weight loss of 45# steel in the simulated pore solution without corrosion inhibitor reaches 1.67 mg/cm^2 after immersing for 6 days. When the corrosion inhibitor is added into the simulated concrete pore solution, the weight loss also gradually increases, but the increase rate is relatively slower than that of without corrosion inhibitor. The weight loss of 45# steel in simulated concrete pore solution with Na_2MoO_4 for 6 days is 1.17 mg/cm^2 while the weight loss of 45# steel in simulated concrete pore solution with Na_2SiO_3 for 6 days is only 0.92 mg/cm^2. It means that the corrosion inhibition effect of Na_2SiO_3 is better than that of Na_2MoO_4 for 45# steel in simulated concrete pore solution. However, the weight loss of 45# steel immersed in the simulated concrete pore solution mixed with sodium molybdate and sodium silicate for 6 days is the lowest which is equal to 0.66 mg/cm^2, indicating that sodium molybdate combined with sodium silicate as the corrosion inhibitor has the best corrosion inhibition effect for 45# steel in the simulated concrete pore solution.

The Na_2MoO_4 in the simulated concrete pore solution will react with the Fe^{2+} to generate $FeMoO_4$ which inhibits the corrosion of 45# steel [24-25]. Studies have shown that sodium silicate in solution can hydrolyze to generate colloids adsorbed on the metal surface, so as to achieve corrosion inhibition [26-28].

$$Na_2SiO_3 + 2H_2O = \mathrm{NaH_3SiO_4} + \mathrm{NaOH} \quad (3)$$

$$2NaH_3SiO_4 = Na_2H_4Si_2O_7 + H_2O \quad (4)$$

According to the equation (3) and (4), sodium silicate in the solution hydrolyzes to generate NaH_3SiO_4 and $Na_2H_4Si_2O_7$ adsorbed on the metal surface can effectively isolate the corrosive medium and inhibit the corrosion process to a certain extent.

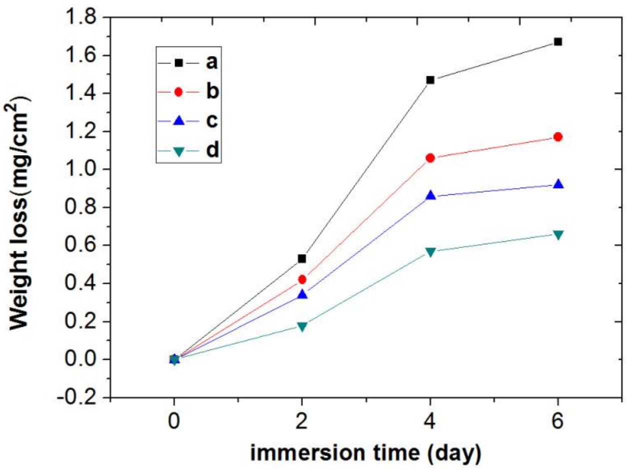

Figure 1. Effect of different corrosion inhibitor on weight loss of 45# steel immersed in simulated concrete pore solution for different days: (a) without corrosion inhibitor; (b) Na_2MoO_4; (c) Na_2SiO_3; (d) Na_2MoO_4 and Na_2SiO_3;

Moreover, sodium silicate can react with Fe^{2+} in an alkaline environment to generate Fe_2SiO_4 and Fe_7SiO_{10} with better corrosion resistance that contributes to the inhibition of corrosion. When sodium silicate and sodium molybdate are mixed together as corrosion inhibitor, on the one hand, silicate generated by sodium silicate hydrolysis can be adsorbed on the surface of the substrate, which inhibits the corrosion process to a certain extent. On the other hand, sodium silicate and sodium molybdate react with Fe^{2+} to generate $FeMoO_4$, Fe_2SiO_4 and Fe_7SiO_{10} that further inhibit the corrosion process.

3.2 Effect of corrosion inhibitors on potentiodynamic polarization curves of 45# steel

Effect of different corrosion inhibitors on potentiodynamic polarization curves of 45# steel in simulated concrete pore solution for different days is shown in Figure 2 and Table 2. It is obvious that the corrosion potential and corrosion current density of 45# steel immersed in concrete pore solution containing different corrosion inhibitors for various days is totally different. With the increase of immersion time, the corrosion potential of 45# steel in simulated concrete pore solution without corrosion inhibitor moves to negative position while the corrosion current density increases gradually. After 6 days of immersion, because no corrosion inhibitor is added, the corrosion of 45# steel in simulated concrete pore solution is serious with 62.76 μAcm^{-2} current density. The corrosion behavior of steel in simulated concrete pore is studied by some researchers as well [29-32].

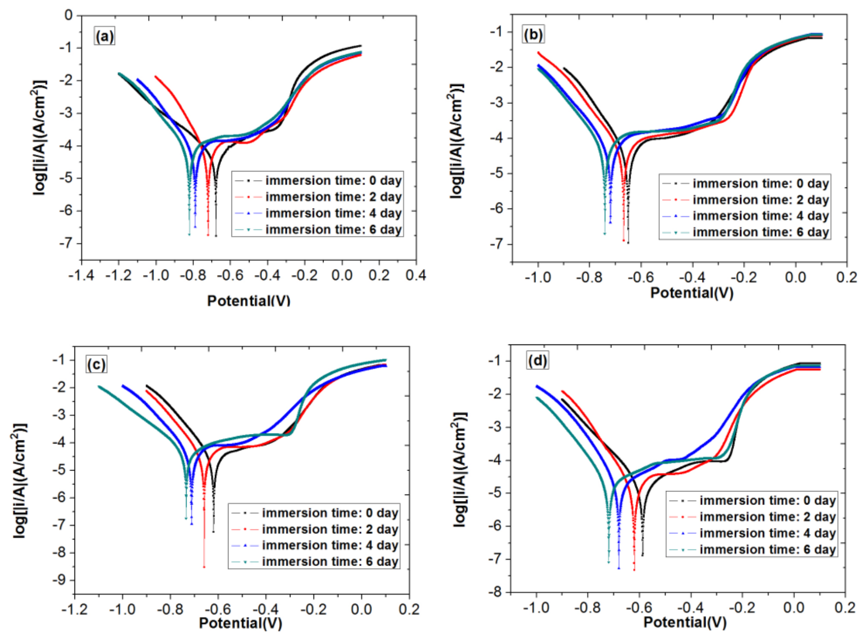

Figure 2. Effect of different corrosion inhibitors on potentiodynamic polarization curves of 45# steel immersed in simulated concrete pore solution for different days: (a) without corrosion inhibitor; (b) Na_2MoO_4; (c) Na_2SiO_3; (d) Na_2MoO_4 and Na_2SiO_3; The immersion time is from 0 day to 6 days; The scan rate is 1 mV/s;

When the corrosion inhibitor is added, the growth rate of corrosion current is slow during two days immersion. According to the previous analysis, corrosion inhibitors such as sodium silicate and sodium molybdate can react with Fe^{2+} to generate silicate and molybdate adsorbed on the substrate surface, which to a certain extent inhibits the corrosion process. With the increase of immersion time, the substrate is gradually destroyed, and the corrosion current increases gradually. When the immersion time increases to 6 days, the corrosion process is inhibited to a certain extent, because the substrate surface is covered with a large number of corrosion products, which make the corrosion current density be stable. According to the corrosion current density, the corrosion inhibition efficiency of different corrosion inhibitors can be calculated, as shown in Figure 3.

Table 2. E_{corr} and J_{corr} of 45# steel in simulated concrete pore solution with and without corrosion inhibitors for different days: (b) Na_2MoO_4; (c) Na_2SiO_3; (d) Na_2MoO_4 and Na_2SiO_3;

Corrosion inhibitor	Immersion 0 day		Immersion 2 day		Immersion 4 day		Immersion 6 day	
	E_{corr}/ V	J_{corr}/ μAcm^{-2}	E_{corr}/ V	J_{corr}/ μAcm^{-2}	E_{corr}/ V	J_{corr}/ μAcm^{-2}	E_{corr}/ V	J_{corr}/ μAcm^{-2}
/	-0.683	38.52	-0.721	46.56	-0.792	58.72	-0.821	62.76
b	-0.652	31.23	-0.673	36.23	-0.723	43.70	-0.747	45.69
c	-0.623	19.68	-0.663	23.49	-0.713	29.49	-0.732	31.89
d	-0.592	9.82	-0.628	11.72	-0.681	14.39	-0.722	15.93

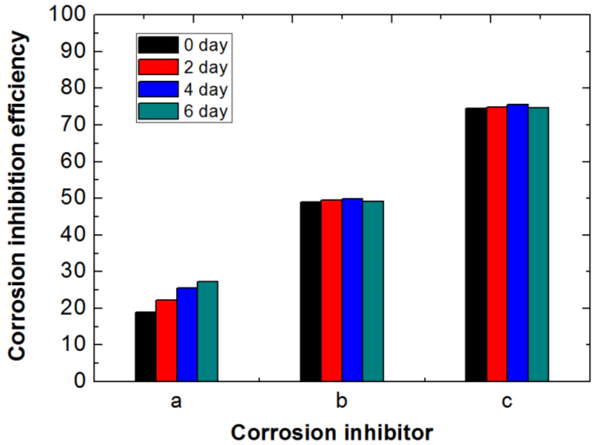

Figure 3. Corrosion inhibition efficiency of different corrosion inhibitors for 45# steel in simulated concrete pore solution: (a) sodium molybdate; (b) sodium silicate; (c) sodium silicate mixed with sodium molybdate;

It can be seen from Figure 3 that sodium silicate and sodium molybdate have a certain inhibition effect on the corrosion process of 45# steel in simulated concrete pore solution. The corrosion inhibition efficiency of sodium molybdate is about 30%, and that of sodium silicate is about 50%. However, the corrosion inhibition efficiency of sodium molybdate mixed with sodium silicate is approximate 75%. Therefore, the corrosion inhibition efficiency of sodium molybdate mixed with sodium silicate is the best. This is because silicate generated by sodium silicate hydrolysis can be adsorbed on the surface of the substrate to inhibit the corrosion process. In addition, sodium silicate and sodium molybdate in the solution will react with Fe^{2+} to generate $FeMoO_4$, Fe_2SiO_4 and Fe_7SiO_{10} that further inhibit the corrosion process.

3.3 Effect of corrosion inhibitors on roughness and surface morphology of 45# steel

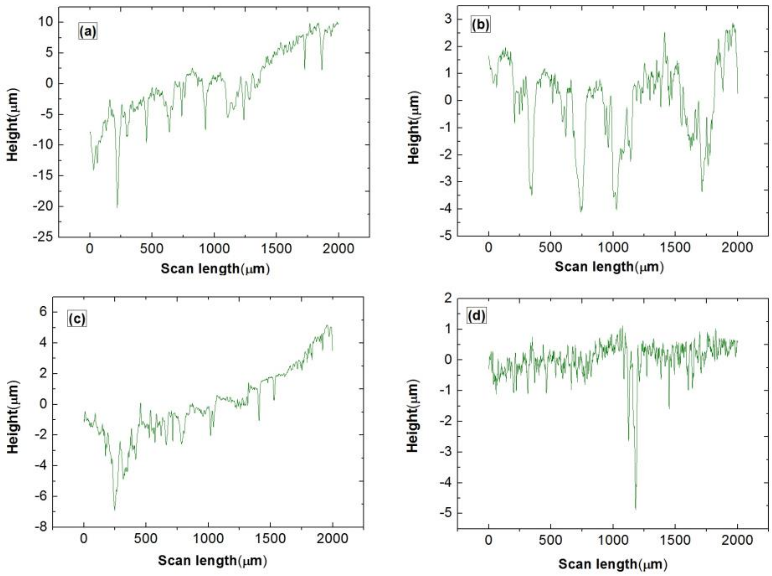

Figure 4. Effect of different corrosion inhibitors on surface roughness of 45# steel immersed in simulated concrete pore solution for 6 days: (a) without corrosion inhibitor; (b) Na_2MoO_4; (c) Na_2SiO_3; (d) Na_2MoO_4 and Na_2SiO_3; The maximum scan length is 2000 μm at the scan rate of 5 μm/s;

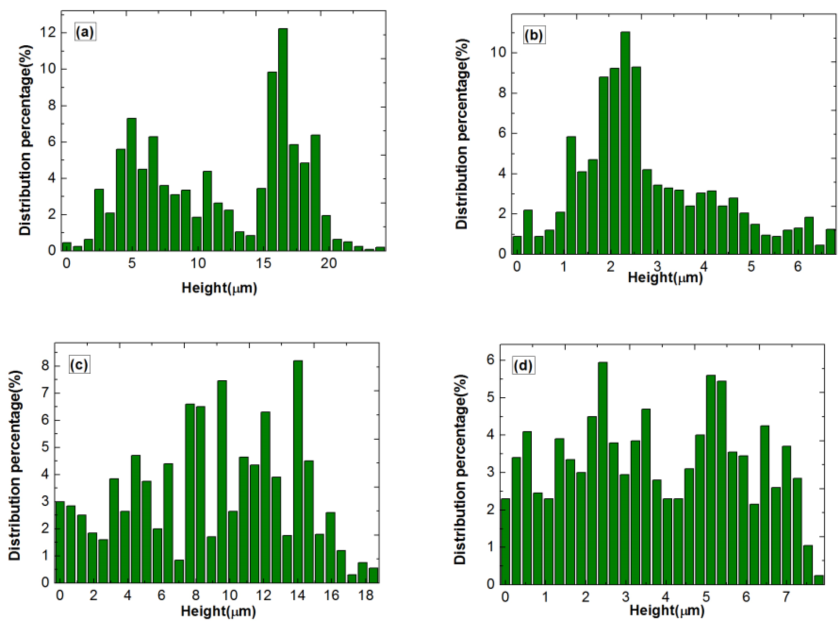

Figure 5. Surface height distribution of 45# steel immersed in simulated concrete pore solution with and without corrosion inhibitors for 6 days: (a) without corrosion inhibitor; (b) Na_2MoO_4; (c) Na_2SiO_3; (d) Na_2MoO_4 and Na_2SiO_3; The maximum scan length is 2000 μm at the scan rate of 5 μm/s;

Table 3. Surface roughness of 45# steel immersed in simulated concrete pore solution with and without corrosion inhibitors for 6 days: (b) Na_2MoO_4; (c) Na_2SiO_3; (d) Na_2MoO_4 and Na_2SiO_3; Roughness R_a is the arithmetic mean deviation of surface profile; Roughness Rq is the root mean square value of surface profile;

Corrosion inhibitor	Roughness R_a (μm)	Roughness R_q (μm)
/	1.53	1.91
b	0.93	1.15
c	0.42	0.57
d	0.39	0.48

The surface roughness R_a and R_q of 45# steel immersed in simulated concrete pore solution containing different corrosion inhibitors for 6 days is shown in Figure 4 and Figure 5. Table 3 lists the specific roughness data calculated based on the Figure 4 and Figure 5. It is obvious that, after immersing in the simulated concrete pore solution without corrosion inhibitor for 6 days, the surface roughness of 45# steel is the largest.

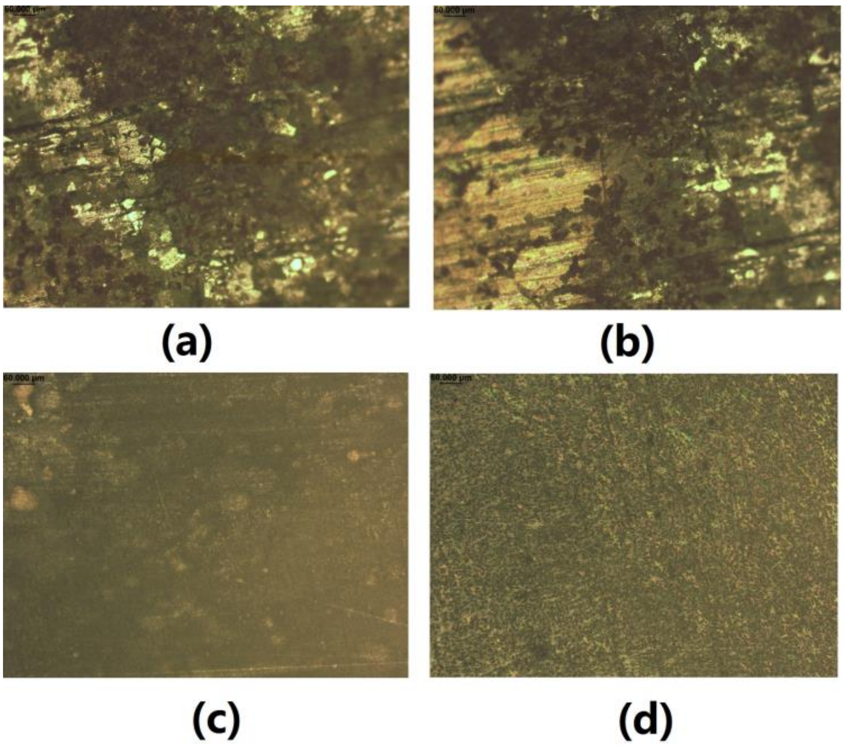

Figure 6. Surface morphology of 45# steel immersed in simulated concrete pore solution with different corrosion inhibitors for 6 days: (a) without corrosion inhibitor; (b) Na_2MoO_4; (c) Na_2SiO_3; (d) Na_2MoO_4 and Na_2SiO_3;

The main reason is that after 45# steel is immersed in alkaline simulated concrete pore solution containing hydroxide ion and chloride ion for a long time, the surface is corroded seriously to generate loose corrosion products, such as ferrous hydroxide, ferric hydroxide and ferroferric oxide covered on the surface, which greatly increases the surface roughness. The corrosion products of steel in simulated concrete pore solution have been reported in some papers in detail [33-35].

According to the previous analysis, the Na_2MoO_4 in the simulated concrete pore solution will react with the Fe^{2+} to generate $FeMoO_4$ which inhibits the corrosion of 45# steel. Moreover, sodium silicate in the solution can hydrolyze to generate NaH_3SiO_4 and $Na_2H_4Si_2O_7$ adsorbed on the substrate to isolate the corrosive medium and further inhibit the corrosion process to a certain extent. Therefore, the surface roughness of 45# steel decreases when the corrosion inhibiter is added. It is found that the surface roughness of 45# steel is the smallest due to the generation of dense corrosion products under the action of sodium silicate combined with sodium molybdate.

The surface morphology of 45# steel immersed in simulated concrete pore solution with different corrosion inhibitors for 6 days is shown in Figure 6. It can be seen from Figure 6 that different corrosion inhibitors have a significant influence on the corrosion morphology of 45# steel. The corrosion phenomenon of 45# steel is very serious in the simulated pore solution without corrosion inhibitor. There are large number corrosion products such as loose iron oxides and iron hydroxide covered on the surface which protrudes obviously and the roughness is very large. Some people find that the pitting corrosion is dominant when steel is immersed in the simulated concrete pore solution [36-37]. However, when sodium molybdate corrosion inhibitor is added to the corrosion solution, the molybdate ions react with Fe^{2+} to generate $FeMoO_4$ as relatively dense corrosion products. Moreover, sodium silicate can react with Fe^{2+} in an alkaline environment to generate Fe_2SiO_4 and Fe_7SiO_{10} with better corrosion resistance that contributes to dense surface and the inhibition of corrosion. However, when sodium silicate and sodium molybdate are mixed together as corrosion inhibitor, silicate generated by sodium silicate hydrolysis can be adsorbed on the surface of the substrate, which inhibits the corrosion process to a certain extent. Moreover, sodium silicate and sodium molybdate react with Fe^{2+} to generate $FeMoO_4$, Fe_2SiO_4 and Fe_7SiO_{10} that further inhibit the corrosion process resulting in denser corrosion products and smaller surface roughness.

4. CONCLUSIONS

Influence of different inhibitors on the corrosion inhibition effect of 45# steel in simulated concrete pore solution is investigated in the paper. The results are as follows.

(1) With the increase of immersion time, the weight loss of 45# steel in the simulated pore solution gradually increases. When the corrosion inhibitor is added into the simulated concrete pore solution, the weight loss also gradually increases, but the increase rate is relatively slower than that of without corrosion inhibitor. Corrosion inhibitors such as sodium silicate and sodium molybdate can react with Fe^{2+} to generate silicate and molybdate adsorbed on the substrate surface, which to a certain extent inhibits the corrosion process.

(2) The corrosion inhibition efficiency of sodium molybdate is about 30%, and that of sodium silicate is about 50%. However, the corrosion inhibition efficiency of sodium molybdate mixed with sodium silicate is approximate 75%. This is because silicate generated by sodium silicate hydrolysis can be adsorbed on the surface of the substrate to inhibit the corrosion process. In addition, sodium

silicate and sodium molybdate in the solution will react with Fe^{2+} to generate $FeMoO_4$, Fe_2SiO_4 and Fe_7SiO_{10} that further inhibit the corrosion process resulting in dense corrosion products and smaller surface roughness.

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