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Effects of some ions on ion-selectivity of ferrous sulfide film

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Abstract

The ion-selectivity of ferrous sulfide film formed on a cellulose sheet was determined by measuring the film potentials in neutral chloride solution. The results show that ferrous sulfide film is a bipolar film consisting of an inner cation-selective layer and an outer anion-selective layer. This kind of film structure can accelerate the localized corrosion of steel. The influence of some anions, cations and imidazoline corrosion inhibitor on ion-selectivity of the film was also investigated. The ion-selectivity of the film is altered from bipolar to anion-selective with the adsorption of Ca^{2+}, Mg^{2+} and Ba^{2+} ions, or to cation-selective with the adsorption of MoO_4^{2-}, PO_4^{3-} and imidazoline inhibitor. Potentiodynamic polarization, AC impedance technology, and the weight-loss method were used to understand the relationship between the ion-selectivity and corrosion behaviors of steel in sulfide-containing solution.

Introduction

Steel surfaces exposed to aqueous solutions are frequently covered with a porous precipitate film of corrosion products consisting of insoluble metal salts. It is generally recognized that such a film is usually ion-permeable and exhibits ion-selectivity [1–3]. Because the corrosion behavior of steel is affected by selective ion transport through the precipitate films from the bulk solution to the metal surface and vice versa, the ion-selectivity of the precipitate film, has to be taken into account when considering the corrosion reaction occurring on the metal surface covered with precipitate films.

Many studies have been carried out by Sato and colleagues [4–6] on selective mass transport in a precipitate film. Their results show that the hydrated oxides of iron-group metals are anion-selective in acidic and neutral chloride solutions, while they are cation-selective in basic solution. Ferric hydroxide membranes are anion-selective in neutral chloride solution, but they will change to be cation-selective in the same solution when molybdate anions are adsorbed in their micropores. Corrosion propagation can be accelerated by anion-selective precipitates and retarded by cation-selective precipitates.

According to the membrane theory, the ion-selectivity of a membrane is determined by the immobile electric charge attached to the inner wall of the micropores, which is called the fixed charge. The ion-selectivity can be obtained by measuring the membrane potential E as a function of the concentration ratio of the two solutions.

The membrane potential *(E)* is the potential difference across an ion-exchange membrane separating two solutions of the same electrolyte with different concentrations. For an ideal cation- or anion-selective film, the membrane potential can be expressed by the following equation in dilute NaCl solution [6]:

$$E = -\omega \frac{RT}{F} \log \frac{C_2}{C_1} \tag{1}$$

where ω is the sign of the fixed charge, and C_1, C_2 are the concentrations of NaCl solutions, respectively.

This equation allows estimation of the sign of the fixed charge by measuring the membrane potential in different concentration ratios of the two solutions. If the slope of membrane potential vs $\log(C_2/C_1)$ curve is negative, namely the fixed charge to the micropore is positive, the membrane will be anion-selective, whereas the membrane will be cation-selective if the fixed charge is negative.

Sulfide ions exist in oil recovering and processing industries, and steels used in oil fields and refineries are usually covered with a precipitate film involving ferrous sulfide [7, 8]. However, the ion-selectivity of ferrous sulfide film and its influence are not fully understood. In this work, the ion selectivity of ferrous sulfide products and the effects of some anions, cations, and imidazoline inhibitors were investigated. The corrosion behavior of mild steel with ferrous sulfide film in different solutions was also studied by means of potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and weight-loss methods.

2. Experimental details

Ferrous sulfide was precipitated on a cellulose sheet which was sealed tightly between two plexiglass cells [9, 10]. One cell was filled with 0.1 M $FeCl_2$ solution and the other with 0.1 M Na_2S solution. The former solution was prepared with $FeCl_2{\cdot}4H_2O$, and a small amount of iron powder was added as a reducing agent in order to remove ferric ions from the solution. The latter was prepared with $Na_2S{\cdot}9H_2O$. After immersion for 1 h, the sheet was washed with distilled water. The ferrous sulfide films adsorbing some anions, cations and imidazoline inhibitor were prepared by immersing the film in neutral 3% NaCl solutions containing 0.1 M Ca^{2+}, Mg^{2+}, Ba^{2+}, $MoO_4{}^{2-}$, $PO_4{}^{3-}$ and 0.01 M imidazoline for 5 h, respectively.

The membrane potential measurement was basically the same as that already described in a previous publication [1]. The concentration of NaCl solution was kept constant at 10^{-2} M in one cell, and ranged from 10^{-4} to 10^{-1} M in another cell. Two saturated calomel electrodes (SCE) and a high input-resistance potentiometer were used to measure the potential difference across the film. The potentials reported were the values of $(E_{0.01} - E_x)$ at 2 min after NaCl solutions were added, $E_{0.01}$ was referred to the potential in solution of 10^{-2} M NaCl, and E_x was the potential in solution of 10^{-4} to 10^{-1} M NaCl.

Potentiodynamic polarization tests were carried out using a 273A Potentiostat/Galvanostat (EG&G Company, USA) in neutral 3% NaCl solutions with and without 0.1 M Ca^{2+}, 0.1 M $MoO_4{}^{2-}$ and 0.01 M imidazoline, respectively. The working electrode was made from mild steel with a chemical composition (wt%): C 0.23, Mn 0.47, Si 0.046, S 0.024, P 0.012, Cu 0.024. Before each test, the working electrode was covered with a film of ferrous sulfide by immersing the electrode in 0.1 M S^{2-} solution for 24 h. The reference electrode was also a SCE, and the counter electrode was Pt plate. The scanning rate was 0.6 mV s^{-1}.

EIS measurements were carried out using a PAR 398 Electrochemical Measurement System comprising a Potentiostat/Galvanastat model 273A and model 5210 lock in amplifier, both manufactured by EG & G Company, USA. The impedance measurements were performed at open circuit potential and used an ac amplitude of 10 mV. The applied frequencies ranged from 10^5 to 10^{-3} Hz using five points/decade.

Corrosion rates of the mild steel were also measured by weight-loss in 3% NaCl + 0.1 M S^{2-} solutions with and without 0.1 M $MoO_4{}^{2-}$ and 0.01 M imidazoline inhibitor, respectively. The immersion period was 240 h.

All the solutions and distilled water were deoxygenated by high purity nitrogen (99.99%) for at least 4 h before use. All the reagents were AnalaR grade except the imidazoline inhibitor, which was developed in our laboratory. All the experiments were carried out at 25 ± 1 °C.

3. Results and discussion

3.1. *Bipolar structure of ferrous sulfide film*

Figure 1 shows the membrane potential curves of cellulose sheet with and without ferrous sulfide film. It can be seen that the membrane potential of cellulose sheet is small enough to be neglected at different concentration ratios of NaCl solution. However, a large potential difference is observed when it is covered with a film of ferrous sulfide. The potential curve slope of the sheet side exposed to $FeCl_2$ solution during the film preparation is positive, while the line slope of the other exposed to Na_2S solution is negative. This indicates that ferrous sulfide film has a bipolar structure with different kinds of fixed charges on either side of the membrane, and each side shows different ion-selectivity. The side of the film, with $FeCl_2$, solution, shows cation-selectivity, and the other side shows anion-selectivity. Accordingly, the ferrous sulfide film formed on steel in S^{2-}-containing solution may be regarded as a bipolar structure with a cation-selective layer on the metal side and an anion-selective layer on the solution side. Figure 2 shows a schematic of the bipolar structure of the ferrous sulfide film. It shows that there is a zone of zero charge between the two sides of the ferrous sulfide film with different electric charge.

According to Equation 1, the slope of membrane potential vs $\log(C_2/C_1)$ is about 59 or −59 mV/decade for an ideal cation- or anion-selective film. The slopes of the two lines in Figure 1 are only 25 and −34 mV/decade, respectively, which implies weak selectivity for anions or cations.

With the cation-selective interior layer of the film, Fe^{2+} ions may migrate into the film easily and react with S^{2-} ions migrating from the bulk solution into the film, and thus promote the anodic reaction. Also, Cl^- ions can transfer to the metal surface easily, which leads to Cl^- enrichment under the precipitate film. Consequently, this kind of film structure can accelerate the localized corrosion of steel [4].

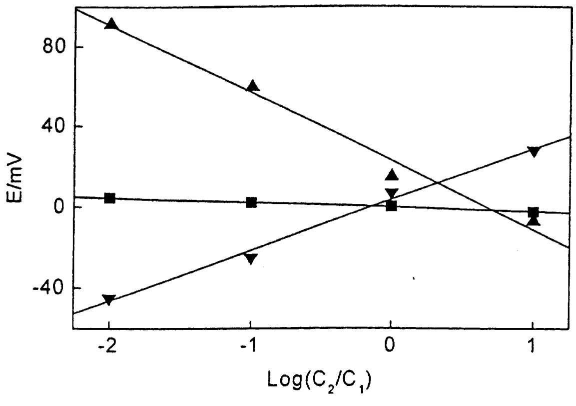

Fig. 1. Membrane potential curves of: ■ Cellulose sheet; ▲The side of ferrous sulfide film exposed to $FeCl_2$ solution during the film preparation; ▼The side of ferrous sulfide film exposed to Na_2S solution during the film preparation.

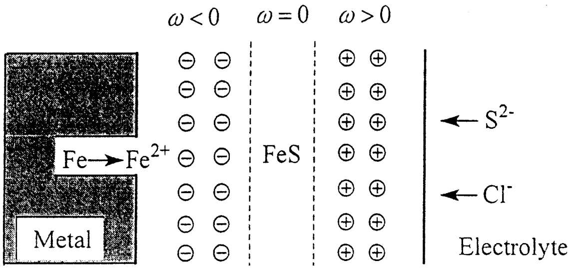

Fig. 2. Schematic of bipolar structure of ferrous sulfide film.

3.2. *Effect of some cations on ion-selectivity*

The negative slopes of membrane potential vs log(C_2/C_1) curves, as shown in Figure 3, indicate that adsorption of Ca^{2+}, Mg^{2+} and Ba^{2+} ions can change the ion-selectivity of ferrous sulfide film from a bipolar structure to anion-selective. The reason is that these cations accumulate on the film and result in net positive charges. This kind of film structure also allows the migration of aggressive ions such as S^{2-} and Cl^- through the film. Therefore, it has little protective effect against corrosion. The slopes of the three lines for ferrous sulfide film adsorbing Ca^{2+}, Mg^{2+} or Ba^{2+} ions are −10.6, −11.7, −9.61 mV/decade, respectively. There is no obvious difference in these line slopes.

3.3. *Effect of some oxyanions and imidazoline on ion-selectivity*

The positive slopes of membrane potential vs log(C_2/C_1) curves shown in Figure 4 mean that the moving ions are cations, and hence the ferrous sulfide films adsorbing MoO_4^{2-}, PO_4^{3-} and imidazoline derivative exhibit cation-selective properties. It also indicates that the adsorption of these inhibitors can change the ion selectivity of the film from bipolar to cation-selective. The slopes of three lines for ferrous sulfide film adsorbing MoO_4^{2-}, PO_4^{3-} and imidazoline are 12.0, 12.4, and 15.4 mV/decade, respectively. The film adsorbing imidazoline shows the greatest slope, so it has the strongest cation-selectivity in the present study.

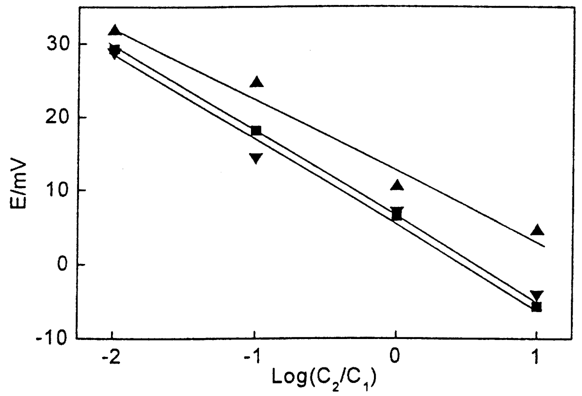

Fig. 3. Membrane potential curves of ferrous sulfide film after: ▼immersed in 0.1 M Ca^{2+} for 5 h; ■immersed in 0.1 M Mg^{2+} for 5 h; ▲immersed in 0.1 M Ba^{2+} for 5 h.

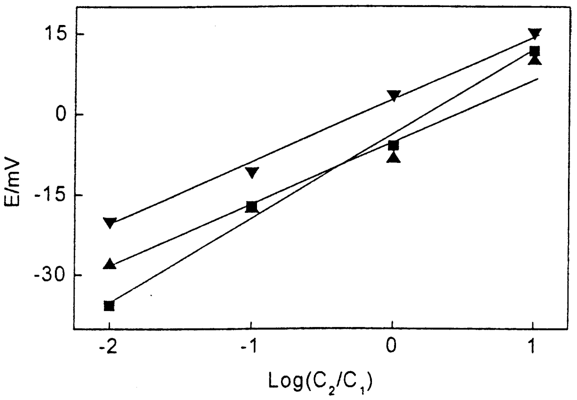

Fig. 4. Membrane potential curves of ferrous sulfide film after: ▼immersed in 0.1 M PO_4^{3-} for 5 h; ▲immersed in 0.1 M MoO_4^{2-} for 5 h; ■immersed in 0.01 M imidazoline solution for 5 h.

The cation-selectivity of ferrous sulfide film inhibits anodic metal dissolution due to reduction in the adsorption and migration of S^{2-} and Cl^- ions. As a result, the enrichment of Cl^- and the hydrolysis of metal chloride under the precipitate film would be more difficult. Instead, hydrogen ions in the occluded solution can diffuse through the film to the bulk solution, which prevents the local pH value from decreasing during the corrosion reaction. Therefore, corrosion will be retarded under the ferrous sulfide film with adsorption of MoO_4^{2-}, PO_4^{3-} and imidazoline derivate.

3.4. *Polarization curves of mild steel with ferrous sulfide film in different solutions*

Figure 5 shows the polarization curves of mild steel with ferrous sulfide film in different solutions. It is seen that the anodic polarization curve of steel shows weak passivation in 3% NaCl solution. In 3% NaCl solution containing 0.1 M Ca^{2+}, the cathodic branch of the curve

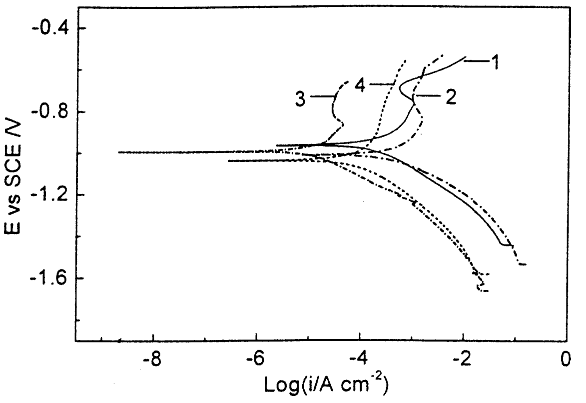

Fig. 5. Polarization curves of mild steel with ferrous sulfide film: 1–in 3% NaCl solution; 2–in 3% NaCl solution containing 0.1 M Ca^{2+}; 3–in 3% NaCl solution containing 0.1 M MoO_4^{2-}; 4– in 3% NaCl solution containing 0.01 M imidazoline

shows almost no change, while the anodic branch moves in the direction of higher current density, which implies that Ca^{2+} ions exert a weak acceleration effect on anodic metal dissolution. As comparison, the polarization curves in solutions containing MoO_4^{2-} or imidazoline compound all move in the direction of lower current density, indicating that both the anodic and cathodic processes have been reduced. Relatively the electrode in MoO_4^{2-}-containing solution shows the best passivation, which may be attributed to molybdate ions being adsorbed on the film more easily than imidazoline compound during polarization.

The different polarization behaviors mentioned above may be explained by different ion selectivity of the films. The ferrous sulfide film adsorbing Ca^{2+} ions shows an anion-selective property, which still allows the migration of aggressive ions through the film, so it has little protective effect on metal corrosion. However the adsorption of MoO_4^{2-} and imidazoline can change ferrous sulfide film to cation-selective; hence the migration of aggressive anions from solution to metal surface is retarded and corrosion is inhibited.

3.5. *EIS of mild steel with ferrous sulfide film in different solutions*

To confirm the effects of different ions on the protective properties of the sulfide films on mild steel, electrochemical impedance tests for mild steel with ferrous sulfide film were conducted in different solutions. It can be seen from Figure 6a that each impedance spectra displays a capacitive arc. The equivalent circuit can be simply regarded as a parallel combination of a pure capacitor and a resistor, as shown in Figure 6b. Table 1 shows the parameters fitted by Zview software. The charge transfer resistance, R_t, decreases after Ca^{2+} is added to 3% NaCl solution, and increases after molybdate or imidazoline inhibitor is added, while capacitance C_d changes in the opposite direction to R_t. These results indicate that corrosion of the steel is accelerated by Ca^{2+} ions, and retarded by molybdate and imidazoline inhibitors.

3.6. *Corrosion rates of mild steel in different solutions*

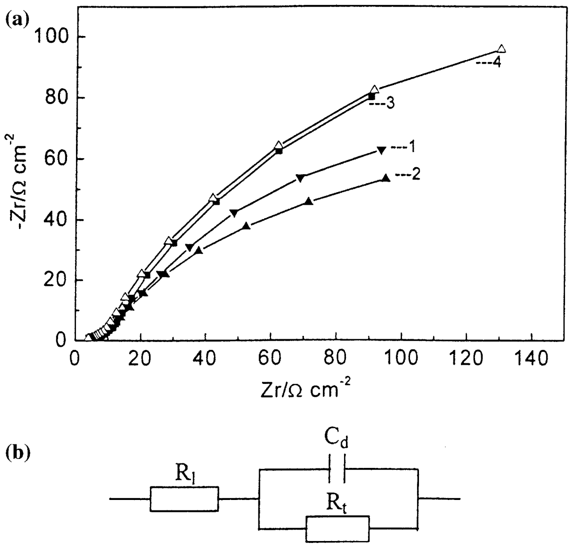

Fig. 6. (a) Nyquist impedance diagrams for mild steel with ferrous sulfide film: 1–in 3% NaCl solution; 2–in 3% NaCl solution containing 0.1 M Ca^{2+}; 3–in 3% NaCl solution containing 0.1 M MoO_4^{2-}; 4– in 3% NaCl solution containing 0.01 M imidazoline; (b) Equivalent circuit for the electrode, R_l is the solution resistance, R_t the charge transfer resistance, and C_d the capacitance.

Table 2 shows corrosion rates of mild steel in four solutions. Severe pitting corrosion took place on the surfaces of the steel specimen immersed in 0.1 M Na_2S + 3% NaCl and 0.1 M Na_2S + 3% NaCl + 0.1 M $CaCl_2$ solutions, while relatively slight corrosion was observed in 0.1 M Na_2S + 3% NaCl + 0.1 M Na_2MoO_4 and 0.1 M Na_2S + 3% NaCl + 0.01 M imidazoline solutions, especially in the latter solution. These results agree well with those mentioned above. The accelerating effect of calcium ions on the corrosion of mild steel was also reported by Xu et al. [11], and was attributed to the formation of calcium carbonate on the steel surface.

Therefore, the fixed charge and ion-selectivity of ferrous sulfide film can be changed by altering the solution composition, and hence the protective property of the film against corrosion will be changed. This result is useful for the control of corrosion of carbon steel in S^{2-}-containing solution. Corrosion may be reduced by adding inhibitors which can adsorb, replace or react on membrane surface and change the properties of the films.

4. Conclusions

(1) Ferrous sulfide film on steel surface shows bipolar behavior with a cation-selective layer on the metal side and an anion-selective layer on the solution side. It may promote anodic dissolution and accelerate local corrosion under the precipitate film.

(2) The adsorption of Ca^{2+}, Mg^{2+}, Ba^{2+} ions on ferrous sulfide film may change the ion-selectivity from

Table 1. Values of the capacitance and charge transfer resistance for mild steel in tested solutions

Solutions	R_l/Ω cm^2	R_t/Ω cm^2	C_d/F cm^{-2}
0.1 M Na_2S + 3% NaCl	4.9	239.8	0.180
0.1 M Na_2S + 3% NaCl + 0.1 M $CaCl_2$	5.4	171.4	0.190
0.1 M Na_2S + 3% NaCl + 0.1 M Na_2MoO_4	5.9	295.0	0.163
0.1 M Na_2S + 3% NaCl + 0.01 M imidazoline	4.3	310.0	0.155

Table 2. Corrosion rates of mild steel in test solutions

Solution	Corrosion rate/mm a^{-1}
0.1 M Na_2S + 3% NaCl	0.3677
0.1 M Na_2S + 3% NaCl + 0.1 M $CaCl_2$	0.4536
0.1 M Na_2S + 3% NaCl + 0.1 M Na_2MoO_4	0.1208
0.1 M Na_2S + 3% NaCl + 0.1 M imidazoline	0.0372

bipolar to anion-selective. The reason is that these cations accumulate on the film and result in the addition of positive charges. This kind of film structure also allows migration of aggressive ions such as S^{2-} and Cl^{-}.

(3) The adsorption of MoO_4^{2-}, PO_4^{3-} ions and imidazoline derivative may alter the ion-selectivity of ferrous sulfide films from bipolar to cation-selectivity. Such films can reduce migration of S^{2-} and Cl^{-} ions to the metal surface. Therefore, corrosion may be reduced under the cation-selective precipitate film.

(4) Ca^{2+} ions accelerate corrosion of steel in sulfide solution, while MoO_4^{2-} and imidazoline derivate show inhibition effects on both anodic and cathodic processes.

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