



## RESEARCH ARTICLE

### PREPARATION OF THIOUREA BASED IMIDAZOLINE INHIBITORS

<sup>\*</sup>1Changshan Huang, <sup>1</sup>Jinying Wu, <sup>1</sup>Huiwu Xu, <sup>1</sup>Min Zhang, <sup>1</sup>Min Chen, <sup>1</sup>MianXue,  
<sup>1</sup>Xiaoguang Zhang, <sup>2</sup>Guangxiu Cao and <sup>2</sup>Can Huang

<sup>1</sup>Institute of Energy, Henan Academy of Sciences, Zhengzhou, China, 450008

<sup>2</sup>School of Chemistry & Chemical Engineering, Shangqiu Normal University, Shangqiu, China, 476000

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#### ABSTRACT

Imidazoline quaternary-ammonium-salt corrosion inhibitor and thioureido-imidazoline quaternary-ammonium-salt compound corrosion inhibitor were synthesized using oleic acid, diethylenetriamine, benzyl chloride and thiourea as raw materials. The resulting samples were characterized by static weight-loss method, electrochemical polarization curve, X-ray photoelectron spectrometry (XPS) as well as scanning electron microscope (SEM). The electrochemical characteristics of the inhibitors' inhibition towards carbon dioxide corrosion were investigated, the major constituents of the protective film formed on the surface of A3 carbon steel by thioureido-imidazoline compound corrosion inhibitor were analyzed, and the corrosion inhibiting mechanism for thioureido-imidazoline in hypersaline was explored. The results indicated that thioureido-imidazoline compound corrosion inhibitor had better corrosion inhibiting effect than imidazoline and can efficiently inhibit the corrosion of A3 carbon steel by CO<sub>2</sub>-saturated hypersaline water.

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## INTRODUCTION

Imidazoline and its derivatives, which display strong absorption on steel surfaces due to their electronegative N atoms and unsaturated double bonds, are believed to be excellent corrosion inhibitors for carbon steels in acid solutions and there have been a plenty of reports on their applications as the corrosion inhibitors for carbon steels in circulating cooling water. (ZHANG Jun et al., 2008; MA Tao et al., 2005; LIU Xia and ZHENG Yu-Gui, 2009) Water-soluble imidazoline corrosion inhibitors are widely used in oil fields across the world because of their outstanding corrosion inhibiting performance, irritative odor-free property, good thermal stability and low toxicity. (Burke, 1985; Waard Cde and Millians, 1991; Jovancicevic et al., 1998) However, in recent years, as many of the oil fields enter into the middle and late stage of development, the salinity of the field water increases gradually together with the rising CO<sub>2</sub> content and total water cut, resulting in more severe corrosion perforation of equipments and pipes. In a word, imidazoline alone cannot satisfy the current requirements of carbon steel anticorrosion. Water-soluble imidazoline quaternary-ammonium-salt corrosion inhibitor (HS-1) was synthesized using oleic acid, diethylenetriamine, benzyl chloride as the raw materials, which

was compounded with thiourea (HS-2) to afford the thioureido-imidazoline compound corrosion inhibitor (HS-3). The corrosion inhibiting performance of HS-3 in CO<sub>2</sub>-saturated hypersaline water and the corrosion inhibiting mechanism were studied through static weight-loss method, potentiodynamic polarization curve method, X-ray photoelectron spectrometry, scanning electron microscope, etc.

## MATERIALS AND METHODS

### Instruments and Materials

IS10 Fourier transform infrared spectrometer (Thermo Fisher Scientific Co., USA). AXIS-ULTRA DLD-600W X-ray photoelectron spectrometer (Shimadzu-Kratos Co., Japan). CS2350 electrochemical analysis system (Wuhan Corrtest Instruments Co., Ltd.). JSM-6510 scanning electron microscope (JEOL). Oleic acid (AR), diethylenetriamine (AR), thiourea (AR), benzyl chloride (AR) and xylene (AR).

### Synthesis of Imidazoline and Thioureido-Imidazoline Corrosion Inhibitors

28.4g (0.1mol) of oleic acid, 12.9g (0.12mol) of diethylenetriamine and 40mL of xylene were added into a three-neck flask under vigorous stirring at room temperature. The resulting mixture was heated at 140-160°C for 2h and then at 190-210°C for another 2h for cyclization reaction. After

\*Corresponding author: Changshan Huang,

Institute of Energy, Henan Academy of Sciences, Zhengzhou, China, 450008.

cooling the system to 90-110°C, 12.65g of benzyl chloride was added slowly and the resulting system was heated at reflux for 3h. Finally, the solvent was evaporated to afford the imidazoline quaternary ammonium salt (HS-1). (YAN Hong-Xia *et al.*, 2003) Half of the obtained HS-1 was reacted with 3.55g (0.05mol) thiourea at 90-110°C for 1.5h to afford the thioureido-imidazoline quaternary ammonium salt (HS-3). HS-1 and HS-3 were purified by recrystallization from a mixture of acetone and toluene. The yields of HS-1 and HS-3 were 92.7% and 91.3%, respectively. The synthetic route was illustrated in Figure 1.

### Evaluating the Corrosion Inhibiting Performances of HS-1 and HS-3 Corrosion Inhibiting System

The corrosion inhibiting performances of HS-1 and HS-3 were evaluated using static weight-loss method and electrochemical method. The corrosive medium employed was CO<sub>2</sub>-saturated simulated mineralized water. The constituents of the mineralized water were listed in Table 1. The static weight-loss experiments were conducted according to the petroleum and natural gas industry standard *Performance Evaluation Methods for Corrosion Inhibitors Used in Oilfield Produced Water* (SY/T5273-2000). The experimental temperature and time were 50°C and 72h, respectively. The corrosion rates and inhibition rates of the standard A3 carbon steel specimens in the above mentioned simulated mineralized water were measured. Electrochemical analysis was conducted on a CS2350 electrochemical analysis system with the reference electrode, auxiliary electrode and working electrode being saturated calomel electrode, platinum electrode and standard A3 carbon steel specimen (area 28.0cm<sup>2</sup>), respectively. In the measurements of the polarization curves, the scanning was conducted in a range of -250~+250mV relative to the free corrosion potentials with the scanning rate being 0.33mV/s. The current densities on the surface of electrodes were recorded to plot the polarization curves. Accordingly, the current density and electrochemical inhibition rate of free corrosion in the corrosion inhibitor system were calculated.

### X-Ray Photoelectron Spectrometry (XPS) Analysis

Surface analysis of the corrosion products was carried out by AXIS-ULTRA DLD-600W X-ray photoelectron spectrometer. The X-ray excitation source was Mg target with the energy, power and pass energy being 1253.6eV, 150W and 10eV, respectively. FRR was tested in moderate resolution with the pressure in the analysis room lower than  $2 \times 10^{-7}$  Pa. The binding energies of all kinds of carbons in the C<sub>1s</sub> spectrum were benchmarked against 284.6eV.

### SEM Analysis

The A3 carbon steel hanging pieces was taken out from the solution after the rotary weight loss test, then cleaned separately and pasted on the sample platform using double sided adhesive tape. Upon spraying, the sample was placed under a JSM-6510 electron scanning microscope to survey the corrosion behavior of the A3 steel surface under different circumstances. The employed accelerating voltage and magnification factor in the tests were 15kV and 5000, respectively.

## RESULTS AND DISCUSSION

### Characterization for the Compound Corrosion Inhibitor HS-3: FT-IR spectrum of the thioureido-imidazoline

quaternary ammonium salt HS-3 was shown in Figure 2. The results indicated that the peak at 3420.21cm<sup>-1</sup> which corresponds to the symmetrical stretching vibration of secondary amine (V<sub>N-H</sub>) and the peaks at 2925.21 and 2853.73cm<sup>-1</sup> correspond to the symmetrical stretching vibrations of methyl and methylene groups (V<sub>C-H</sub>), respectively. The characteristic peak of alkene double bond stretching vibration (V<sub>C=C</sub>) is located at 1653.78cm<sup>-1</sup>, while the characteristic peak of imidazoline ring stretching vibration (V<sub>C=N</sub>) is located at 1606.73cm<sup>-1</sup>.<sup>(8-10)</sup> These peaks at 1465.45cm<sup>-1</sup>, 1302.43 cm<sup>-1</sup>, 1159.98 cm<sup>-1</sup>, 722.31 cm<sup>-1</sup> are assigned to the in-plane bending vibrations of methyl and methylene groups, the stretching vibration of amine (V<sub>C-N</sub>), the stretching vibration of thioketone (V<sub>C=S</sub>) and the out-plane bending vibration of alkene protons (δ<sub>C-H</sub>), respectively. The major locations of peaks are consistent with the structure of the target compound, indicating that the main constituent in the product is thioureido-imidazoline quaternary ammonium salt.

### Performance Evaluation of the Imidazoline Corrosion Inhibitor

The average corrosion rates are obtained from the results of the static weight-loss experiments. The corrosion behavior with various concentrations of inhibitor HS-1 in CO<sub>2</sub>-saturated simulated saline water was investigated using static weight-loss method and the result is shown in Figure 3. As can be seen in Figure 3, the corrosion rate of A3 steel sheet decreases gradually with increasing of the adding amount of HS-1, while the inhibition rate increases gradually. When the concentration of inhibitor reaches 20mg/L, the corrosion rate and inhibition efficiency are 0.065mm/a and 92.12%, respectively, i.e. the inhibiting effect is not significant at this concentration. When the concentration of inhibitor arrives at 30mg/L, the corrosion rate and inhibition efficiency are 0.057mm/a and 93.26% respectively, which are slightly better than the requirements suggested in SY/T5273-2000 *Performance Evaluation Methods for Corrosion Inhibitors Used in Oilfield Produced Water* (corrosion rate < 0.076mm/a, inhibition efficiency > 85.0%). When the concentration of inhibitor becomes higher than 30mg/L, the inhibition efficiency declines slightly. As a result, HS-1 needs to be compounded with other inhibitors to achieve better inhibiting effect and better satisfy the field needs. In this work, thiourea HS-2, a commonly used corrosion inhibitor which is a small molecule containing two amino groups and S element, was chosen. Thiourea has strongly electronegative N and S atoms as well as unsaturated C=S double bond. The lone pair electrons of S and N elements in the molecule can bind to the empty orbital of Fe element covalently, thus resulting in its strong affinity for metal substrates and film forming property on the surfaces.

### Performance Evaluation for Thioureido-Imidazoline Corrosion Inhibitor

#### Static Weight-Loss Experiment

The corrosion rate and inhibition efficiency for A3 steel sheet using HS-3 inhibitor were investigated also through static weight-loss method and the result was presented in Figure 4. As can be seen in Figure 4, the best inhibiting effect is obtained when the concentration of the compound inhibitor is 20mg/L with the inhibition efficiency being as high as 98.5%, which has been confirmed by repeated experiments. The corrosion rate of A3 steel in the presence of the compound inhibitor is

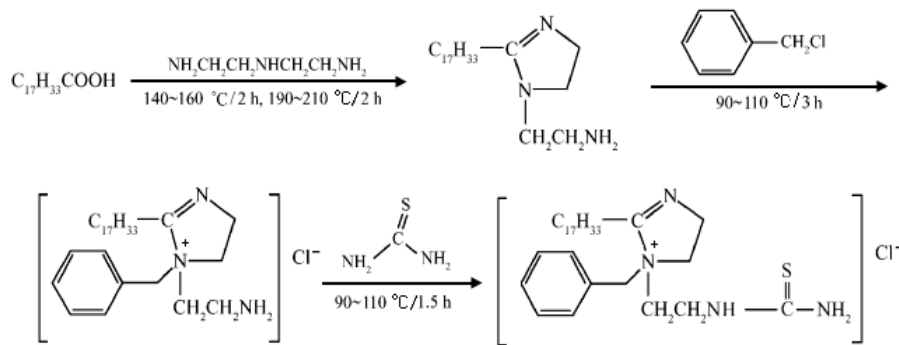


Figure 1. The synthetic routes of HS-1 and HS-3

Table 1. The Constituents of the Simulated Hypersaline Water

Constituent	NaCl	MgCl <sub>2</sub> ·6H <sub>2</sub> O	Na <sub>2</sub> SO <sub>4</sub> ·10H <sub>2</sub> O	NaHCO <sub>3</sub>	CaCl <sub>2</sub>
concentration g/L	70	1.4	1.2	1.2	1.5

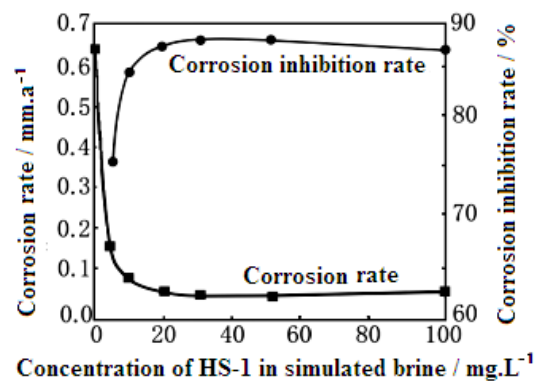
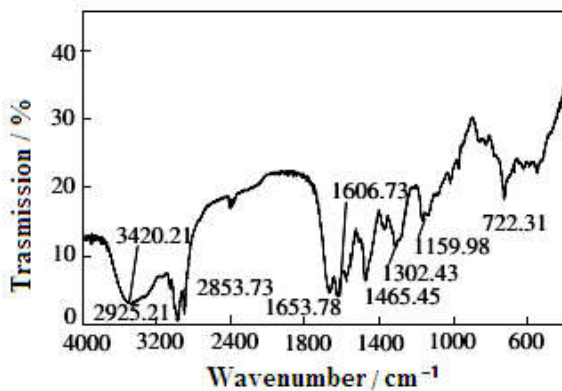


Figure 2. FT-IR spectrum of the compound corrosion inhibitor HS-3

Figure 3. The result of static weight-loss experiments in the presence of HS-1

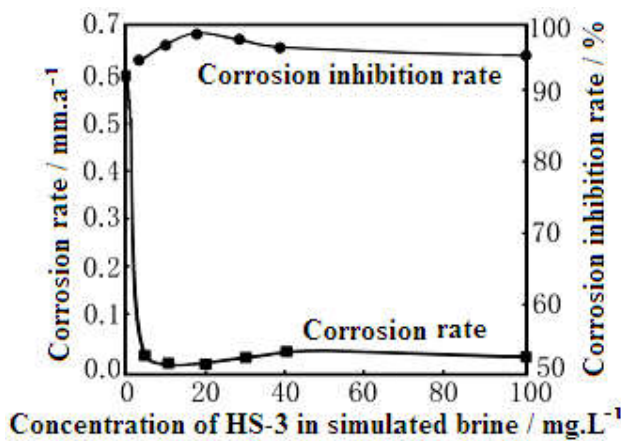


Figure 4. The results of static weight-loss experiments in the presence of HS-3

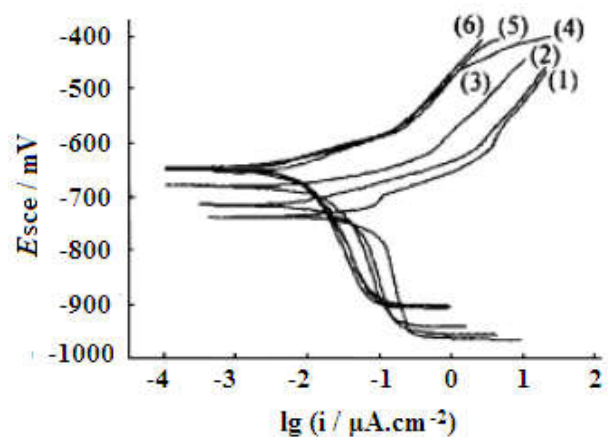
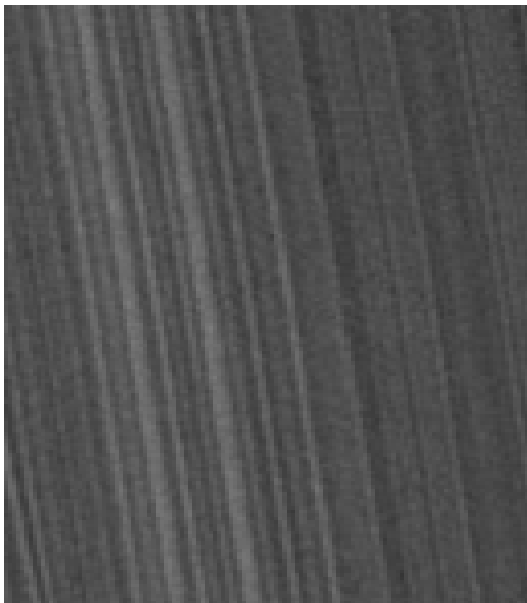


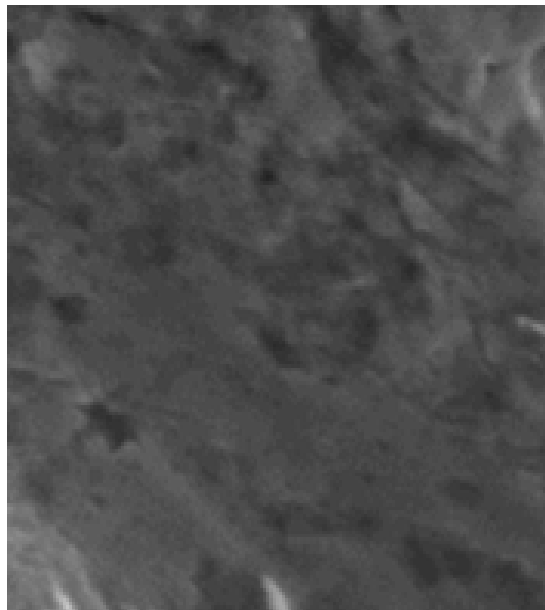
Figure 5. The polarization curves with various concentrations of HS-3: (1) blank, (2) 5mg/L, (3) 10mg/L, (4) 20mg/L, (5) 40mg/L, (6) 100mg/L

Table 2. The Electrochemical Parameters of Corrosion in the Presence of HS-3

Mass concentration, mg/L	Self-corrosion potential $E_{corr}$ , mV	Corrosion current density $i_{corr}$ , A/cm <sup>2</sup>	$\eta$ , %
0	-718		99.16
5	-714	10.59	88.45
10	-713	5.44	94.51
20	-679	3.90	98.45
40	-677	4.61	95.35
100	-674	4.88	95.08



**Figure 6. SEM image of the corroded steel specimen in the presence of HS-3**



**Figure 7. SEM image of the corroded steel specimen in the presence of HS-1**

0.0091mm/a, far lower than the value (0.076mm/a) suggested in SY/T5273-2000 *Performance Evaluation Methods for Corrosion Inhibitors Used in Oilfield Produced Water*. Therefore, thioureido-imidazoline quaternary-ammonium-salt corrosion inhibitor HS-3 displays excellent inhibiting effect for A3 steel in CO<sub>2</sub>-saturated hypersaline water and can be considered a compound corrosion inhibitor of outstanding performance.

### Electrochemical Evaluation

The corrosion parameters obtained in electrochemical measurements in the presence of HS-3 were listed in Table 2 and the polarization curve is presented in Figure 5. As can be seen from Table 2, the corrosion current decreases evidently after adding HS-3, indicating its excellent inhibiting effect towards corrosion by CO<sub>2</sub>-saturated hypersaline water. As can be seen in Figure 5, strong inhibiting effect towards the cathodic process of corrosion is observed when the concentration of the inhibitor is low. The self-corrosion potential of the system shifts negatively and cathodic process inhibition is mainly involved. As the concentration of HS-3 increases, the self-corrosion potential positive shift positively, exhibiting strong inhibiting effect towards the anodic process of corrosion. The corrosion inhibiting effect transforms into anodic type. Thus the corrosion inhibition displayed by HS-3 is a mixed type. When the concentration of HS-3 is 20mg/L, the self-corrosion current density of the system decreases from 99.16μA/cm<sup>2</sup> to 3.90μA/cm<sup>2</sup> with the inhibition efficiency exceeding 96.0%, making it clear that HS-3 has excellent inhibiting effect towards corrosion of A3 steel in CO<sub>2</sub>-saturated hypersaline water, which is consistent with the results of the static weight-loss experiments.

### XPS Analysis of the A3 Steel Surface in the Compound Corrosion Inhibitor System

HS-3 can form firm protective films on the surface of metals, which separates the metal matrix from the corrosive medium to play a protective role. The corrosion products on the surface of

the corroded steel sheets were analyzed using XPS. Table 3 listed the experimental results and standard values of the binding energies for Fe<sub>2p</sub>, O<sub>1s</sub> and S<sub>2p</sub> elements in the corrosion products on A3 steel corroded in CO<sub>2</sub>-saturated 5% saline water with the content of HS-3 being 20mg/L.

### Analysis of the Outer Products in the Corrosion Film

By comparing the experimental and standard values of binding energies, the outermost products on A3 steel surface (before corrosion) can be understood: the binding energy of Fe<sub>2p</sub> is 711.1eV, approaching that in Fe<sub>2</sub>O<sub>3</sub> and FeS; the binding energies of O<sub>1s</sub> are 530.0eV and 530.8eV, which is close to that in Fe<sub>2</sub>O<sub>3</sub>; the binding energy of S<sub>2p</sub> is 163.0eV, similar to that in FeS. It is clear that the outer products contain Fe<sub>2</sub>O<sub>3</sub> and FeS, indicating that both Fe<sub>2</sub>O<sub>3</sub> and FeS protective films formed on the outer layer of A3 steel in the HS-3 compound corrosion inhibitor system.

### Analysis of the Mid-Layer Products in the Protective Film

Analysis of the A3 mid-layer (corroded for 45min) by comparing the experimental and standard values of binding energies (same method as in the case of outer layer) manifests that: FeO, FeS and Fe<sub>3</sub>O<sub>4</sub> exist in the mid-layer products, indicating the formation of FeS and Fe<sub>3</sub>O<sub>4</sub> corrosion films in the mid-layer through combination between HS-3 and A3 steel.

### Analysis of the Inner Products in the Protective Film

As can be known from Table 3, a protective layer of Fe<sub>2</sub>O<sub>3</sub> and FeS forms in the inner layer of A3 steel surface (corroded for 90min), which is extremely compact and binds tightly to the metal matrix. From the above we can see that, in the HS-3 system, the products formed on A3 steel surface can be divided into three layers (inner layer, mid-layer and outer layer); the inner and outer layer are composed of Fe<sub>2</sub>O<sub>3</sub> and FeS, while the mid-layer consists FeO, FeS, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>.

## SEM Analysis of the Corroded Metal

SEM photographs of A3 steel specimens demonstrate that: in the HS-3 corrosion inhibiting system, a relatively intact metal matrix surface is observed with unobvious evidence of corrosion (Figure 6); however, in the HS-1 system, relatively rough surface is observed with corrosion pits appearing on the surface of the specimens (Figure 7).

## The Corrosion Mechanism of the Thioureido-Imidazoline Compound Corrosion Inhibitor

The compound corrosion inhibitor HS-3 is made up of corrosion inhibitor HS-1 and thiourea HS-2. As can be seen from Figure 3 and Figure 4, compared with that in the case of using HS-1 alone, the inhibition efficiency can be greatly uplifted when employing HS-3 as the compound corrosion inhibitor, which can form a continuous and compact protective film on the surface of A3 steel matrix to prevent further corrosion. Due to reasons such as the oxygen concentration, the sites of the protective film at various distances from the metal matrix fall into outer layer, mid-layer and inner layer which are different in constituents. Moreover, the protective film is compact and binds tightly to the A3 steel matrix, which endows HS-3 with better corrosion inhibiting performance than that of HS-1. The mechanism involved in the formation of protective film on the surface of A3 steel in the presence of HS-3 lies in the lone pairs and abundant  $\pi$  electrons in its molecules. The synergy effects of N atoms, polar groups and especially strongly electronegative structures such as S atoms<sup>(11)</sup>, unsaturated double bonds and N-containing five-membered ring result in the formation of an adsorption film, which covers the metal surface to form an adsorption film reticular layer. Within the adsorption film reticular layer, the S elements in HS-3 molecules bind to the empty orbital of Fe elements on the metal surface through lone pair electrons to generate a protective layer of iron sulfides in various forms, which is adsorbed on the metal surface within the reticular layer in the forms of both physical adsorption and chemical adsorption. The protective film combined with the metal matrix constitutes a firm adsorption film. As part of the metal matrix has dissolved in the process of the protective film formation, and a small amount of oxygen presents in the aqueous solution, oxygen-consuming corrosion still exists in the cathodic process of corrosion, which explains the fact that there are many iron oxides in the corrosion products. As can be seen in the SEM photographs, A3 steel specimens in the presence of HS-3 display more smooth surfaces without conspicuous corrosion pits than those in the presence of HS-1, indicating a better anti-corrosion protection acquired by the A3 steel matrix.

## Conclusion

- Water-soluble imidazoline quaternary-ammonium-salt corrosion inhibitor was synthesized using oleic acid, diethylenetriamine, benzyl chloride as the starting materials, which was compounded with thiourea to

afford the thioureido-imidazoline compound corrosion inhibitor. FT-IR spectrum confirmed that the product obtained was thioureido-imidazoline quaternary ammonium salt.

- Static weight-loss experiments demonstrated that, when the concentration of the compound inhibitor is 20mg/L, the corrosion rate of A3 steel was 0.0091mm/a with the inhibition efficiency being as high as 98.5%, far outperforming the standards suggested in SY/T5273-2000 *Performance Evaluation Methods for Corrosion Inhibitors Used in Oilfield Produced Water* (corrosion rate <0.076mm/a, inhibition efficiency >85.0%). SEM analysis showed that A3 steel specimens in the presence of HS-3 display more smooth surfaces without conspicuous corrosion pits than those in the presence of HS-1, proving that the corrosion inhibiting effect of the thioureido-imidazoline quaternary-ammonium-salt compound corrosion inhibitor was superior to that of the imidazoline corrosion inhibitor in a similar type.
- The electrochemical experiments indicated that the synergy effects of strongly electronegative structures in the molecules of the compound corrosion inhibitor such as S atoms, unsaturated double bonds and N-containing five-membered ring resulted in the formation of a compact and firm chemical adsorption film on the surface of the A3 steel matrix. XPS analysis manifested that the adsorption film was divided into three layers, the inner and outer layer were composed of Fe<sub>2</sub>O<sub>3</sub> and FeS, while the mid-layer consisted FeO, FeS, Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>2</sub>O<sub>3</sub>, which efficiently prevented the corrosion of A3 steel in CO<sub>2</sub>-saturated hypersaline water.

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