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The influence of temperature on the corrosion resistance of 10# carbon steel for refinery heat exchanger tubes

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ABSTRACT

Based on the corrosion problem of refinery heat exchanger tubes (10# carbon steel) in the course of using, the corrosion and electrochemical behaviors of 10# carbon steel in saline wastewater were investigated by means of autoclave test and electrochemical methods, respectively. The experiment results explained the formation mechanism of corrosion products film and indicated that the corrosion process of 10# steel in the corrosion medium with different temperature was divided into two parts: one was the formation of corrosion products below 50 °C, the other was the formation and dissolution of corrosion products film. The corrosion rate reached the maximum of 0.195 mm/a when the medium temperature was 60 °C.

1. Introduction

At present, the corrosion problem of refinery heat-exchangers tubes especially the heat-exchanger for electric desalting [1–3] in petroleum industry becomes more and more serious following the trends of the lower quality of crude oil. The corrosion perforation and scaling of tubes are the main reasons for this kind of heat-exchanger failure due to the existence of plenty of Ca^{2+}, Mg^{2+} and Cl^- in the shell side medium [4–7]. A lot of methods are adopted to inhibit the corrosion of equipments, such as the preparation of protective coating [8–10], the addition of corrosion inhibitor [11,12] and the material upgrading [13,14] and so on. However, the corrosion rate of heat-exchanger tubes every year is still very considerable.

Most researches at home and aboard are focused on the external protection methods including on-line monitoring methods, corrosion inhibitors and various coatings [11–14]. Deep researches about the corrosion behavior and mechanism of refinery heat-exchangers tubes in this environment have been seldom discussed but which are beneficial to the choosing of reliable protective methods. Especially, the medium temperature as an important parameter has great influence on the corrosion of heat-exchangers tubes.

Taking the shell side medium of atmospheric-vacuum refinery heat-exchanger E502 used for electric desalting as the corrosion medium and typical 10# carbon steel as the research object in this paper, the corrosion mechanism and electrochemical behaviors of 10# carbon steel in corrosion medium with different temperature were discussed carefully. The results can provide guidance in choosing a suitable method to improve the corrosion resistance property of refinery heat-exchanger.

2. Experimental details

2.1. Materials and corrosion medium

10# carbon steel with size of 50 mm × 10 mm × 5 mm was used as substrate whose chemical compositions were shown in Table 1.

According to atmospheric-vacuum refinery heat-exchanger E502 environment in Lanzhou Petrochemical Company, the shell side medium of heat-exchanger was saline wastewater (corrosion medium) and its contents were displayed in Table 2. The inlet and outlet temperatures of saline wastewater were 40 °C and 65 °C respectively and the operation pressure was maintained about 1.4 MPa. All commercial chemicals were employed without further pre-treatment in this research.

2.2. Experiments

The corrosion rate tests were carried out using a 5 L autoclave made by Corrtest Company. The samples were immersed in the corrosion medium for 7 days at 30 °C, 40 °C, 50 °C, 60 °C and 70 °C, respectively. The total pressure was maintained about 1.4 MPa in process of the testing. Before the test, the samples surfaces were

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Table 1
Chemical compositions of 10# carbon steel.

Elements	C	Si	Mn	P	S	Cr	Ni	Mo	Cu
wt.%	0.09–0.12	0.20–0.26	0.44	≤0.02	≤0.01	≤0.05	≤0.01	≤0.01	≤0.025

degreased with acetone and rinsed with absolute ethanol, weighted using a precision of 0.0001 g. And after the test, one group corrosion samples were rinsed with deionized for surface analysis. Another group specimen were descaled, rinsed with water and absolute alcohol, dried in nature state and weighted again. The corrosion rate v (mm/a) was calculated according to Eq. (1) [15].

$$v = \frac{8.76(m_0 - m_1)}{S \cdot t \cdot \rho} \quad (1)$$

where m_0 and m_1 represent the weight of samples before and after the test respectively (g), S is the surface area of specimen (m^2), t refers to the corrosion time (h) and ρ is the metal density (g/cm^3).

2.3. Characterization

The surface photograph of corrosion products was characterized by scanning electron microscopy (INCA-350, 20 kV) and the elemental composition was determined by energy dispersion spectrometry (EDS, Oxford Link Isis). The compositions of corrosion products were analyzed by X-ray diffraction spectrometer (XRD-6000, 40 kV, 40 mA) with Cu Kα radiation at a scan rate of 6°/min.

To determine the corrosion behavior of 10# steel in refinery exchanger environment, the electrochemical measurements including the polarization behavior and electrochemical impedance spectroscopy (EIS) experiments were performed in corrosion medium solution at different temperatures. A CS370 electrochemical workstation manufactured by Wuhan CorrTest Instrument Co. Ltd. was used to test electrochemical behaviors and the data were recorded by a three-electrode mode. The sample with 1.0 cm^2 exposure area was used as working electrode. The saturated calomel electrode (SCE) was used as a reference electrode, and pare kryptol pole was used as an auxiliary electrode. The range of potential was from −1.1 V to −0.3 V at a constant scan rate of 0.5 mV/s. All electrochemical measurements were carried out in open air without stirring.

3. Results and discussion

3.1. The influence of medium temperature on the corrosion rate

Fig. 1 shows the corrosion rates of refinery exchanger tubes at different corrosion solution temperature for 7 days. It can be seen that the corrosion rate of 10# steel increases obviously at the beginning stage and then decreases slightly with the increasing temperature. It is because that higher temperature can promote the ions transport and then accelerate the corrosion. When a corrosion products film forms on the substrate, the corrosion rate of 10# carbon steel will be suspend and even decrease. According to the NACE standard RP-0775-2005, all the corrosion rates of refinery exchanger tubes at different corrosion solution temperatures are serious corrosion. Especially, the value of corrosion rate at 60 °C reaches 0.195 mm/a.

Table 2
Contents of the corrosion medium of refinery exchanger tube (mg/l).

Cl^-	Na^+	Ca^{2+}	SO_4^{2-}	Mg^{2+}	HCO_3^-	pH
242.66	550	112.3	240.24	200.15	455.5	8.16

The SEM images of refinery exchanger tubes at different corrosion solution temperature for 7 days are presented in Fig. 2. As seen, plenty of corrosion pits appear on the substrate surfaces at the corrosion medium temperature of 30 °C and 40 °C and there is no corrosion product formed (Fig. 2a and b). When the solution temperature is over 50 °C, corrosion products films form on 10# steel surface obviously (Fig. 2c–e). The EDS analysis of the corrosion products (inset of Fig. 2e) reveals strong O, Ca, Si and C signals, which are the main elements of corrosion product. When the corrosion products are removed, a lot of corrosion pits reveals on the substrate surface (Fig. 2f). It is because that the chloride ions in the test solution can damage the corrosion product film and accumulate the pit corrosion. Additional, the potential difference between the internal and external film can also result in the electrochemical corrosion.

Fig. 3 displays the compositions of corrosion products. As observed in Fig. 3, the main composition of corrosion products are $CaCO_3$, SiO_2 and Fe_3O_4, which indicates that the corrosion of substrate is mainly caused by the under scale corrosion and the electrochemical corrosion of dissolve oxygen in corrosion medium.

3.2. The formation mechanism of the corrosion products film

When the corrosion product appears on the substrate surface, the substrate under corrosion product is in active state and its potential is more negative, which is in contrast to the metal surface around the corrosion product. As a result, an electrochemical corrosion with the large cathode and small anode is formed, which causes the fast corrosion of the substrate under corrosion product. Fig. 4 depicts the electrochemical corrosion and corrosion products film formation process of 10# carbon steel in corrosion medium. As seen, the corrosion pit occurs on the metal surface following the dissolution of Fe. Meanwhile, H^+ and Cl^- in the corrosion medium can penetrate the corrosion product to accumulate the pit corrosion and then the main corrosion product Fe_3O_4 deposits around the original corrosion product. This cycle will be repeated again and again, until the corrosion products film forms on the whole metal surface.

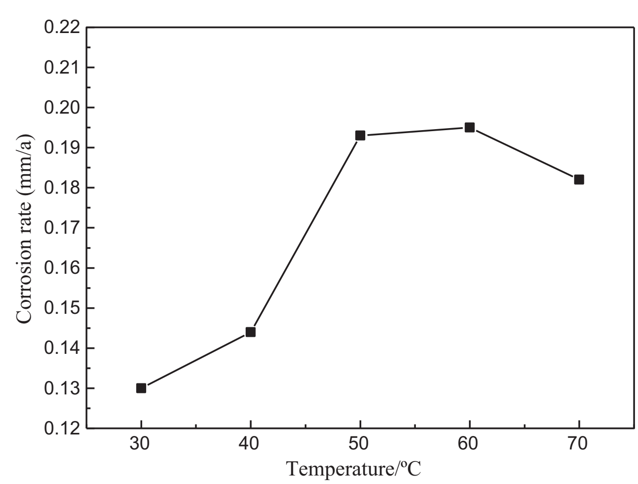

Fig. 1. The corrosion rates of 10# carbon steel at different temperature.