



Corrosion behaviour of Q235B carbon steel in sediment water from crude oil



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ABSTRACT

The effects of sediment water from crude oil on Q235B carbon steel corrosion were investigated through electrochemical measurements, surface characterization, mass loss, and mass gain techniques for 11 weeks of immersion. Results showed that the steel surfaces were covered by scale deposits consisting mainly of CaCO_3 . Corrosion pits were initiated under the scale deposits. Moreover, a galvanic corrosion cell was generated under the scale deposits, resulting in localized dissolution. However, the scale deposits blocked the transport of corrosion products into the bulk solution, thereby causing the accumulation of corrosion products under the scale deposits.

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1. Introduction

Atmospheric storage tanks are important in storing and transferring crude oil and other hazardous chemicals. At present, more than 20,000 tanks larger than 5000 m³ are in China, with many atmospheric storage tanks already aging. However, a number of malfunctions caused by storage tank corrosion were detected after a few years' service [1,2]. According to the data from the American Petroleum Institute, approximately 19% of all hydrocarbon product leakage is caused by corrosion damage in storage tanks [2]. Shuai et al. [3] performed a risk comparison between large-scale crude oil tank shell and tank bottom. The results showed that the risk of tank leakage was due to the tank bottom [4].

Most organic compounds in crude oil are not corrosive to metals and alloys. On the contrary, oil film existing on metals or alloys can effectively prevent corrosion [5–11]. However, water-brine in crude oil would settle on the tank bottom under low-velocity or static conditions during long-term storage. Given that at least 200–300-mm-high sediment water is detained on the tank

bottom for a long time [12]. The water mainly comes from the natural geological processes during the crude oil formation, exploration, transportation, and storage. Nevertheless, the water contains large amounts of metals and non-metals ions, which could form inorganic salts and cause high water salinity [13]. Sodium, calcium, magnesium, and chloride ions are the most common ionic forms in crude oil and the main reasons for corrosion and encrustation, along with carbonate and sulfate salts [14,15]. Therefore, the presence of sediment water can lead to severe corrosion of the tank bottom.

Pipeline corrosion has been extensively investigated under different conditions [16–23]. However, the long-term effect of sediment water from crude oil on the localized corrosion of a tank bottom has been rarely demonstrated [24,25]. Cathodic oxygen reduction produces local alkaline surface conditions and forms CaCO_3 and $\text{Mg}(\text{OH})_2$ precipitates in the presence of Ca^{2+} and Mg^{2+} in sediment water [26]. These deposits promote the formation of a physical barrier against oxygen diffusion; thus, the corrosion rate decreases [27]. Hartt et al. [26] investigated the influence of Mg^{2+} on the formation of calcareous deposits on freely corroding low-carbon steel in seawater and found that Mg^{2+} affects the corrosion behaviour of freely corroding steel by causing CaCO_3 to precipitate. Elbeik et al. [28] demonstrated that the preferential formation of CaCO_3 at cathodic sites was caused by its low solubility at high

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local pH. Corrosion rate measurements revealed that a CaCO_3 film on mild steel can lead to a distinct decrease in the corrosion current for an iron oxidation/oxygen reduction couple. However, chloride ions can pass through the defects of a scale deposit film onto a metal surface for large amounts of chloride ions with small radii and strong penetrating power in the sediment water; therefore, localized metal corrosion occurs under the deposited film.

In this work, the natural sediment water from crude oil in a storage tank was selected as a corrosive medium to observe the corrosion of the tank bottom. Wire beam electrode (WBE) was used to investigate the localized corrosion of Q235B carbon steel in sediment water. Other techniques included mass gain/loss, electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) were also applied to explain the mechanism.

2. Experimental

2.1. Sediment water analysis

Sediment water was collected from a South Pars's crude oil storage tank. Dissolved oxygen concentration, electrical conductivity and pH were measured on the spot by using a portable dissolved oxygen meter (JPB-607A, Shanghai instrument scientific instrument co., Ltd., Shanghai, China), a portable conductivity meter (Hach Company, Loveland, CO, USA) and a portable pH meter (Hach Company), respectively.

One end of a rubber tube connected the outfall of the tank bottom and the other end joined a "Y" type shunted connector with adjustable valves to measure dissolved oxygen concentration during sampling. The shunted connector was subsequently connected to an inlet glass tube, which passed through the rubber plug and reached the bottom of the bottle; the water outlet was placed on the rubber plug of the bottle. The dissolved oxygen meter was then inserted into the bottle. All of the joints were sealed with silicone glue. Afterwards, the drain valve of the outfall of the tank bottom was opened and the dissolved oxygen concentration was obtained using the dissolved oxygen meter after the sediment water overflowed the bottle for 10 min. Sediment water was stored in a polyethylene bottle at 4 °C in accordance with standard examination methods for drinking water (GB/T 5750.2-2006) and sent back to the laboratory for experimental and composition analyses on the same day. An ion chromatograph and an inductively coupled plasma optical emission spectrometer were used to analyse the composition and the anion and cation contents of sediment water in accordance with the standard method for drinking natural mineral water examination (GB/T 8538-2008).

The major ionic compositions of the water sample are shown in Table 1. The samples were analyzed for component cations, including K^+ , Na^+ , Ca^{2+} , and Mg^{2+} , and anions, such as Cl^- , NO_3^- , SO_4^{2-} and HCO_3^- . The concentrations of other ions were much lower than those of Cl^- and Na^+ , which were 23,059 mg L^{-1} and 3425 mg L^{-1} , respectively. By contrast, sediment water exhibited a high conductivity of 36.6 mS cm^{-1} , and the oxygen concentration was 0.3 ppm. The sediment water was a neutral medium with pH 7.12 ± 0.08 . Moreover, there were suspended solids and some organics in sediment water.

2.2. Materials

WBE consisted of a 10×10 electrode matrix with 100 Q235B carbon steel wire (mass%: 0.15% C, 0.30% Si, 0.42% Mn, 0.045% P, 0.050% S and Fe balance; 1.5 mm diameter) sensors. Fig. 1 shows the electrode array image. First, all wire sensors were embedded in

Table 1

The analysis of the sediment water: ionic composition, organics concentration, suspended solid concentration, conductivity, pH, and dissolved oxygen concentration.

Content		
Ionic concentration (mg L^{-1})	Cl^-	23059
	NO_3^-	1348
	SO_4^{2-}	1664
	HCO_3^-	458
	Na^+	3425
	K^+	170
	Ca^{2+}	1396
Organics concentration (mg L^{-1})	n-Hexane	76
	Trichloromethane	112
	Ethyl benzoate	345
Suspended solid concentration (mg L^{-1})		287
Conductivity (mS cm^{-1})		36.6
pH		7.12 ± 0.08
Dissolved oxygen concentration (ppm)		0.3

epoxy resin with 1 mm interval. The total working area of the array electrode was approximately 1.76 cm^2 .

Rectangular coupons (30 mm \times 15 mm \times 2 mm) were cut from Q235B carbon steel plates and used for mass loss assay, as well as surface and component analyses. The end and the middle of the coupons were bored with circular holes (2 mm diameter).

Prior to the experiments, the exposed surfaces of samples, including coupons and WBE, were ground to 400#, 800#, and 1200# using SiC paper. The samples were then rinsed with deionized water and degreased with acetone for 2 min before drying under cool air. Afterwards, all samples were placed in a desiccator for 24 h. Subsequently, the coupon weights were measured.

2.3. Electrochemical experiments

Given that the WBE uses coordinates on the x–y plane, any wire electrode on the WBE can be expressed using (x, y), where x is any line number on the x-axis and y is the row number on the y-axis, as shown in Fig. 1a. The measurements of potential and galvanic current distributions on WBE were reported using a multichannel zero-resistance ammeter (CST520, Corrtest) [29]. A total of 100 local potentials were measured in a period of approximately 6 s, and the interval between two channels was 2 s in current measurements. Data were saved automatically to a Microsoft Excel file towards the end of the measurement. The current and potential maps were graphed using Surfer 11.0 software.

Electrochemical experiments were conducted with a three-electrode system using a Gamry Reference 600 workstation (Gamry Instruments, Inc., Philadelphia, PA, USA). WBE, platinum gauze, and Ag/AgCl (saturated KCl) were used as working, counter, and reference electrodes, respectively. All the wire sensors were connected together once WBE was placed in the test chamber. Thus, the entire electrode array was taken as an integrated electrode, with electrons moving freely among the wire sensors. EIS measurements were conducted with frequencies ranging from 100 kHz to 10 mHz at open circuit potential (OCP) with a potential perturbation of ± 5 mV. Three repeated measurements were performed to determine reproducibility.

Prior to the test, the solution was purged with N_2 gas (500 mL min^{-1}) for 1 h to reduce the dissolved oxygen concentration. The N_2 gas flow was maintained throughout the test while the flow velocity of the N_2 gas in the solution was 100 mL min^{-1} during the measurements. The dissolved oxygen concentration in the solution was constant at approximately 0.2 ± 0.1 ppm, as measured by the portable dissolved oxygen meter (JPB-607A, Shanghai Scientific Instrument Co., Ltd). Fig. 1b shows that the coupons and

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