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Corrosion behavior of carbon steel in the presence of sulfate reducing bacteria and iron oxidizing bacteria cultured in oilfield produced water

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ABSTRACT

The corrosion behavior of carbon steel was investigated in the presence of SRB and IOB separately in their respective culture media and in the mixed culture of SRB and IOB in artificially produced water with 4.2 mg/L dissolved oxygen. The results showed that IOB inhibited the growth of planktonic SRB, but promoted the growth of sessile SRB when SRB was cultured together with IOB. The mixture of SRB and IOB had a synergistic effect enhancing the pitting corrosion of the coupons. The limited amount of dissolved oxygen played a key role in the formation of corrosion products.

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1. Introduction

It is well known that microbiologically influenced corrosion (MIC) is a serious issue in the oil and gas industry [1–4]. MIC or biofouling is often caused by a mixture of microorganisms, including anaerobic and aerobic bacteria [4,5]. For example, anaerobic sulfate-reducing bacteria (SRB) and aerobic iron-oxidizing bacteria (IOB) are sometimes found together in the biofilm in the field [6,7]. In an anaerobic environment, SRB used sulphate as electron acceptor and FeS and $Fe(OH)_2$ are often the main corrosion products [8–10]. In the fluid with some dissolved oxygen, anaerobic microorganisms often grow underneath an aerobic biofilm which provides a local anaerobic environment. $Fe(OH)_2$ could continue to be oxidized to form new corrosion products such as FeOOH, Fe_2O_3 and Fe_3O_4 [11]. In an aerobic environment, IOB, the so-called metal-depositing microorganisms, have the capability of depositing iron hydroxides extracellularly [12,13]. Most of them generate energy for growth by oxidizing ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}), and then these ferric ions (Fe^{3+}) precipitates as $Fe(OH)_3$. Several types of iron bacteria are found to biocatalyze this precipitation process [14]. The rate of the oxidation of ferrous ions to ferric ions by IOB can be much faster than the chemical oxidation reaction, which accelerates the dissolution of metal and localized corrosion [12].

Biofilms on metal surfaces are usually composed of sessile cells, extracellular polymeric substances (EPS) and corrosion products [15–17]. Both SRB and IOB can form biofilms on metal surfaces, leading to localized corrosion [4,18–20]. The development of biofilm theory and analytical techniques have allowed a better understanding of the whole process of MIC [19]. Underneath an SRB biofilm, there may be local shortage of organic carbon (electron donor for energy production). Thus, SRB may switch to elemental iron (Fe^0) in carbon steel to harvest electrons for the reduction of sulfate in energy production [21]. However, the oxidation of Fe^0 occurs extracellular, while sulfate reduction occurs intracellular under enzyme catalysis in SRB cytoplasm. This means that SRB biofilm must transport the electrons across SRB cell wall [22]. Thus, SRB biofilm must be an electrogenic biofilm. Castaneda and Benetton [22] also found that SRB-biofilm enhanced corrosion rate and the biofilm affected the diffusion controlled mechanism process. IOB, one of the most troublesome bacteria group, would enhance pitting corrosion of steel [23]. Pipes can be clogged by the formation

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of tubercles in the presence of IOB. SRB may propagate quickly in the locally anaerobic environment beneath the iron rich tubercles produced by IOB [24]. The interaction between SRB and IOB could accelerate the pitting corrosion process of carbon steel [25].

Some oil-water gathering pipeline systems contain a small amount of dissolved oxygen to support the growth of both aerobic IOB and anaerobic SRB [26]. The oil produced water usually contains 1–3 mg/L dissolved oxygen. Unfortunately, there are very few reports about the corrosion behavior of carbon steel in the presence of both SRB and IOB in this condition. The aim of this work is to gain a better understanding of the corrosion process and electrochemical behavior of Q235 carbon steel in the presence of either SRB or IOB separately or SRB and IOB together in an oil-water gathering pipeline system.

2. Experimental

2.1. Metal samples preparation

The corrosion coupons were cut from Q235 carbon steel sheet with the elemental composition (wt%) of 0.3C, 0.01 Si, 0.42 Mn, 0.029 S, 0.01 P, and balance Fe. Coupons were machined into cylindrical shape with a diameter of 10 mm and height of 10 mm. Only one end face (0.785 cm^2) was exposed and the rest was sealed with epoxy resin. A copper wire was soldered to each coupon for electrochemical measurements. Disk shaped coupons with a diameter of 15 mm and thickness of 1.5 mm were used for biofilm growth. For weight loss measurement, coupons with the size of 50 × 13 × 1.5 mm were used. All the coupons were abraded through 600, 800, and 1200-grit silicon carbide metallurgical papers, degreased in acetone, then washed with anhydrous ethanol, finally dried with nitrogen gas and stored in a desiccator until use. All the coupons sanitized under a UV lamp for 30 min before incubation.

2.2. Water sample

Oilfield produced water was collected from the three-phase separator outlet of an oil production plant in Sinopec oilfield in China. The water samples were taken using a sterile plastic container and then immediately transported to a laboratory for further analysis. The water chemistry data were presented in Table 1. In this study, artificially produced water, which was prepared based on the water chemistry data of oilfield produced water, was used. Its chemical composition was also presented in Table 1. Before experiment, the artificially produced water was autoclaved at 121 °C for 20 min.

2.3. Microbe cultivation and inoculation

In this study, both SRB and IOB were isolated from the sludge in Sinopec oilfield, China and identified by polymerase chain reaction (PCR) amplification of 16S rDNA [14,27]. The 16S rDNA sequence was compared with sequences in the GenBank database with BLAST program. SRB and IOB belong to *Desulfotomaculum nigrificans* (*D. nigrificans*) and *Pseudomonas* sp., respectively. SRB and IOB seed cultures were cultivated separately in different medium. The SRB culture medium composition was (g/L): K_2HPO_4 0.01, $MgSO_4{\cdot}7H_2O$ 0.2, $(NH)_2Fe(SO_4)_2$ 0.2, NaCl 10, yeast extract 1.0, vitamin C 0.1, in addition to 4.0 ml/L sodium lactate (pH 7.2). The IOB culture medium contained (g/L): K_2HPO_4 0.5, $NaNO_3$ 0.5, $CaCl_2$ 0.2, $MgSO_4{\cdot}7H_2O$ 0.5, $(NH_4)_2SO_4$ 0.5 and ammonium iron citrate 10.0 (pH 6.5). Both SRB and IOB were incubated at 37 °C. The artificially produced water was used to culture the SRB alone, IOB alone, and a mixture culture of SRB and IOB. Each 520 mL culture vial which contained 440 mL medium was sealed by silicon rubber. The culture media were autoclaved at 121 °C for 20 min. The initial concentration of dissolved oxygen (DO) in the media was 4.2 mg/L, which was measured by a dissolved oxygen meter (DO200, YSI) after autoclaving. Vials were inoculated with 40 mL seed culture and 40 mL sterile culture, and then incubated at 37 °C. For the mixed SRB and IOB culture, 40 mL SRB seed culture and 40 mL IOB seed culture were used for inoculation. SRB seed culture and IOB seed culture were obtained after 1 day of incubation. The initial concentration of SRB and IOB inoculum were shown in Table 2. Although the artificially produced water lacked organic carbon and other nutrients, the inoculum provided some nutrients to each vial. Planktonic SRB (N_{SRB}) and IOB (N_{IOB}) and sessile SRB (N_{SRB}) and IOB (N_{IOB}) were enumerated using the most probable number (MPN) method [28] using culture medium according to the American Society of Testing Materials (ASTM) Standard D4412-84.

2.4. Weight loss measurement

After the corrosion test for 21 days at 37 °C, the coupons were taken out and the corrosion products were stripped using a pickling solution containing corrosion inhibitor (imidazoline derivative) for several minutes. The exposed coupon surface was finally rinsed with distilled water, cleaned in absolute ethanol, and dried under a nitrogen gas stream. The corrosion rates of carbon steel were assessed from the specific weight loss based on the exposed the coupon surface area.

2.5. Characterization of biofilm, corrosion surface morphology, and corrosion products

Prior to observation of the surface morphology, the coupons were taken out of the culture medium, rinsed in a pickling solution containing corrosion inhibitor (imidazoline derivative) to remove corrosion products, followed by rinsing with acetone and sterile deionized water, and then dried with a nitrogen gas stream. Three-dimensional stereoscopic microscope (VHX-10000) was used to observe the surface morphology of coupon. Before SEM observation and EDS analysis of the biofilm and corrosion products, the coupons were pretreated by being soaked in a phosphate buffer solution containing 2.5% (w/w) glutaraldehyde for 8 h [29]. The coupons were then dehydrated using ethanol. Afterwards, all the coupons were dried with a nitrogen gas stream and placed in desiccators. The composition of corrosion products on the coupon was analyzed by X-ray diffraction (XRD). XRD patterns were recorded by a diffractometer with Cu Kα radiation (PANalytical X'pert PRO-DY2198, Holland).

2.6. Electrochemical measurements

The open circuit potential (OCP), electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves were performed using a ChenHua Electrochemical Workstation (ChenHua, China). A saturated calomel electrode (SCE) and a platinum plate were used as the reference and counter electrodes, respectively. EIS were obtained at OCP by applying a sinusoidal voltage signal of 10 mV in a frequency range of 10^{-2} to 10^5 Hz. The EIS data were analyzed using Zview2 software (Scribner Inc.) with a suitable equivalent circuit model. Potentiodynamic polarization curves were measured by scanning the potential from −200 mV to +300 mV vs. OCP at a sweep rate of 0.5 mV/s. And the polarization curves were analyzed using CVIEW2 software (Scribner Inc.). In this study, the volume ratio of bacteria seed culture, culture medium and the air in the head space was 1:10:2, and all culture vials was sealed. All the experiments were repeated at least three times.

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