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The effect of magneticfield on biomineralization and corrosion behavior of carbon steel induced by iron-oxidizing bacteria

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ABSTRACT

In this paper, the effect of a magneticfield (MF) on biomineralization and corrosion behavior of Q235 carbon steel were studied using surface analysis, weight loss and electrochemical measurements. Experimental results showed that MF inhibited the growth of iron-oxidizing bacteria (IOB) and the corrosion of Q235 carbon steel. MF reduced the largest pit depth by half, while it reduced pit population density from 50 pits cm^{-2} to 10 pits cm^{-2}. MF also altered the morphology of biomineralization film, leading to the formation of a more compact biomineralization film which contributed to the lower corrosion rate.

1. Introduction

The corrosion of metal materials is a major issue due to huge economy losses associated with it [1–3]. About 20% of all corrosion losses was attributed to microbiologically influenced corrosion (MIC) and 50% of corrosion pipeline failures involved MIC [4]. Microbial attachment and subsequent biofilm formation on metal surfaces are responsible for MIC [5–8]. A significant portion of MIC involves iron-oxidizing bacteria (IOB) which are frequently found in natural environments, including storage tanks and pipelines [4]. In an aerobic environment, IOB, known to be metal-depositing microorganisms, has the capability to deposit iron hydroxides extracellularly [9,10]. They generate energy for growth by oxidizing ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}) with oxygen as the terminal electron acceptor [11]. Under biocatalysis by IOB, the rate of the oxidation of ferrous ions to ferric ions can be much faster than the abiotic chemical oxidation reaction. Thus, IOB accelerate the dissolution of metal and localized corrosion [10,12,13].

IOB not only influence the corrosion process of metals, but also contribute to the formation of iron biominerals by bio-oxidation of ferrous ions at neutral pH [14]. Biomineralization is a term used to describe the formation of minerals induced by microorganisms [15]. Most microbial biomineralization follows a two-step process. Initially, metals are electrostatically bound to anionic cell wall surfaces and surrounding extracellular polymers (EPS) and act as nucleation sites for crystal growth [16,17]. Iron minerals precipitate partly within the IOB cell periplasm and partly in the surrounding EPS, promoting the nucleation of iron minerals out the cells [18]. The iron minerals include α-FeOOH and Fe_2O_3, among which α-FeOOH is dominant [19,20].

The effects of static magnetic fields (MF) on the metal corrosion process have been studied for the past few years [21–23]. Sueptitz et al. [24] found that the effect of MF on steel corrosion is related to the pH value of test solution, and high magnetic flux densities and high gradients of the magnetic flux density could inhibit the mass transfer resulting in a low material loss. Depending on magnetohydrodynamic theory, MF could closely influence the electrochemical corrosion process and the process of mass transfer [25]. And, MF also could change the metal material properties, promote the oxygen activation and enhance the growth of ferromagnetic Fe_3O_4 oxide [26].

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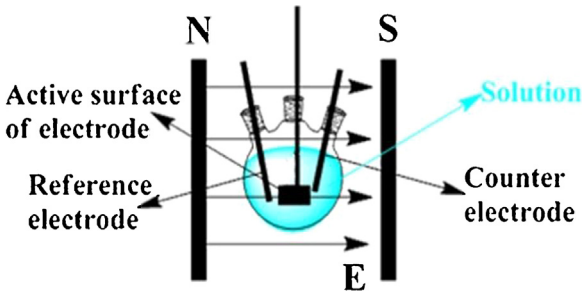

Fig. 1. Experimental setup.

However, the effects of MF on the MIC attracted less attention [27]. MF could influence MIC due to its effect on living microorganisms [28]. A previous study indicated that a low magnetic field intensity (2–4 mT) inhibited the growth of planktonic sulfate reducing bacteria (SRB) and delayed the biofilm formation on the 304SS surfaces and reduced the pitting corrosion [27]. MF not only influences microbial metabolism [29], but also the electrochemical corrosion process and mass transfer of MIC. Li et al. [30] found that MF with the intensity of 2–4 mT could inhibit the uniform corrosion of carbon steel. However, MF effects are strain-dependent [31]. MF could also contribute to the formation of crystal morphology. Antiscale magnetic treatment has been applied to the waste water purification by changing the crystal morphology of the scale [32].

In this work, MF was applied to inhibit MIC by IOB for the first time. It aimed to determine the effects of MF on the corrosion process and electrochemical behavior of steel and biomineralized iron minerals. Surface analysis, weight loss and electrochemical measurements were used to probe the corrosion process and the corrosion inhibition by MF.

2. Experimental

2.1. Corrosion device

The experimental setup is illustrated in Fig. 1. The flux intensity of MF in the center where the working electrode located was 76 mT. The corrosion coupons were cut from a Q235 carbon steel sheet with the elemental composition (wt%) of 0.3C, 0.01Si, 0.42Mn, 0.029S, 0.01P, and balance Fe. Coupons were machined into cylindrical shape with the diameter of 10 mm length (a surface area of 0.785 cm^2) and sealed with epoxy resin with only the end disk-shaped face (area 0.785 cm^2) exposed to the solution. A copper wire was soldered to each electrode.

Disk-shaped coupons with a diameter of 15 mm and thickness of 1.5 mm were used for biofilm observation and weight loss measurement. All the coupons were abraded through 600, 800 and 1200-grit silicon carbide metallurgical papers, degreased with acetone, washed with anhydrous ethanol, then ethanol, dried with nitrogen gas and stored in a desiccator before use. All the coupons were sterilized using a UV lamp for 30 min before experiment.

2.2. Microbial inoculation and cultivation

The IOB were isolated from a Sinopec oil field in China. The 16S rDNA sequences were compared with the sequences in the GenBank database with the BLAST software. The results showed that the IOB belonged to *Pseudomonas* sp. The IOB culture was grown aerobically in a medium with the following composition (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). This medium was autoclaved at 121 °C for 20 min. The IOB culture was incubated at 37 °C. The growth curves in the presence and absence of MF were determined using optical density (OD) with a UV–vis Spectrophotometer (Specord 50, Analytic Jena, Germany) at 600 nm. The dissolved oxygen (DO) was measured by a dissolved oxygen meter (DO200, YSI).

2.3. Characterizations of biofilm and corrosion morphology

Before the SEM observation of the biofilm and corrosion products, the coupons were soaked in a 2.5% (v/v) glutaraldehyde-containing phosphate buffer solution for 8 h to fix the biofilm [33]. The coupons were then dehydrated using serial dilution of ethanol (10%, 30%, 50%, 70%, 90%, 95% and 100% in v/v), each for 10 min except the final step for 30 min. After that, all the coupons were dried using nitrogen and placed in desiccators. The composition of corrosion products on a coupon was analyzed by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). A digital 3D microscope (VHX-1000E, Japan) was also used to observe the surface morphology of coupons. Prior to the observation, coupons were removed from the culture medium, brushed using a soft brush to remove corrosion products, followed by rinsing with acetone and sterile deionized water. They were finally dried with a nitrogen gas stream.

2.4. Electrochemical measurements

The potentiodynamic polarization curves and electrochemical impedance spectroscopy (EIS) were performed using a CS350 electrochemical workstation (Corrtest, China). A glass cell with three electrodes was constructed with the Q235 carbon steel electrode as the working electrode (WE). A saturated calomel electrode (SCE) with a Luggin capillary filled with KCl containing agar and a platinum plate served as the reference and counter electrodes, respectively. Electrochemical impedance spectroscopy (EIS) measurements were obtained at the open circuit potential (OCP) by applying a sinusoidal voltage signal of 10 mV in the frequency range of 10^{-2}–10^5 Hz. EIS data were fitted by Zview2 software (Scribner Inc.) with an equivalent circuit. Potentiodynamic polarization curves were measured by scanning the potential from −200 mV to +200 mV *versus* OCP at a sweep rate of 0.5 mV s^{-1}. All the potentials in this work were based on SCE, unless otherwise indicated.

3. Results

3.1. Planktonic IOB growth curves

The initial DO of test solution is 3.12 mg L^{-1}. And after 21-day incubation, the DO decrease with concentration of 2.82 mg L^{-1}. DO is a key factor, contributing to the growth of IOB. Fig. 2a shows the corresponding relationship between absorbance and the amount of IOB (N_{IOB}). It indicates that the linear relationship between absorbance and N_{IOB} is very good and the correlation coefficient value (R^2) is 0.9994. Fig. 2b shows the growth curves of planktonic IOB. It can be seen that IOB propagated quickly in the logarithmic stage after inoculation. Moreover, there is no lag phase, consistent with a previous report [9]. In the presence of MF, the logarithmic phase is shortened and the peak broth optical density (OD) value is considerably lower than that in the absence of MF.

3.2. Biofilm analysis

SEM and EDS analyses are conducted to study the morphology and composition of the IOB biofilm on a coupon surface. As shown in Fig. 3a, the coupon surface is only partially covered by a biofilm. Some IOB cells and sphere-shaped corrosion products are observed. The EDS analysis in Fig. 3a-1 suggests that the main components of the biofilm are organics and some corrosion products (iron oxides)