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Research Paper

Mechanism of microbiologically influenced corrosion of X52 pipeline steel in a wet soil containing sulfate-reduced bacteria

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ABSTRACT

In this work, corrosion of an X52 pipeline steel was investigated in a field-collected soil containing sulfate-reducing bacteria (SRB) by weight-loss testing, bio-testing, electrochemical measurements and surface analysis techniques. The SRB can grow well in the soil and attach to the steel surface, leading to microbiologically influenced corrosion (MIC) of the steel. The SRB are able to accelerate corrosion of the steel remarkably. Compared to the corrosion rate of 0.0473 mm/y in SRB-absent soil, the corrosion rate of the steel is up to 0.282 mm/y when SRB are contained in the soil. An increase of the water content in the soil favors the growth of SRB, increasing the thickness of the biofilm formed on the steel surface and accelerating the steel MIC. At individual water contents, the presence of CO_2 in the soil accelerates the steel MIC induced by SRB, which is associated with the increasing amount of SRB cells in CO_2-containing soil. The SRB also result in localized corrosion of the steel. This is associated with the unique soil corrosion environment, where the sessile SRB cells and corrosion products do not move freely. The porous structure of the surface film contributes to the initiation of localized corrosion.

1. Introduction

Microbiologically influenced corrosion (MIC) can occur in a wide variety of industry environments [1–7], including oil and gas wells, buried pipelines, sewage water pipes, recirculated cooling systems, marine engineering infrastructure, et al. Particularly, MIC has been the primary mechanism causing perforation and leaking of pipelines buried in soils [8].

In natural environments, there are many types of micro-organisms that cause/accelerate corrosion of metals, such as the anaerobic sulfate-reducing bacteria (SRB) [9]. It was reported that SRB contributed to a half of the MIC events in industry [10]. Li et al. [11] found that the mechanisms of steel corrosion were different in the absence and presence of SRB. The SRB accelerated both uniform and localized corrosion. The SRB induced MIC is an important mechanism for corrosion of buried pipelines. The oxygen content in the soil is usually low, and SO2-4 ions commonly exist in the soil environment [12]. Carbon steel pipelines are attractive for SRB cell colonization because the steel surface can adsorb organics which are utilized by SRB [13]. Moreover, the SRB can directly obtain electrons from Fe in the absence of organic carbon sources [14–16], reducing SO2-4 and promoting the SRB growth. This can provide a proper environment for SRB growth, leading to MIC of underground pipelines.

There are many factors influencing pipeline corrosion in the soil, such as water content, aeration, soil resistivity, pH, redox potential, composition and concentration of chemical species, etc. [17]. In particular, an increase in water content of the soil generally promotes the steel corrosion [18]. Alteration of the factors also influences the SRB activity in the soil, and thus the MIC of pipelines.

Diffusion of chemical species and migration of SRB in soils are usually difficult [19]. SRB cells can reach the steel by gliding and twitching only [20]. While it is realized that the corrosive environment generated in soils is quite different from that in aqueous solutions such as extracted soil solutions, there has been few work conducted in the soil to investigate MIC of pipeline steels. Once the SRB adhere to the steel surface, they can change the local environment quickly and form a biofilm. The MIC is closely related to the biofilm formation [21]. Generally, the biofilm is composed of bacterial cells, extracellular polymeric substance (EPS) secreted by bacteria such as SRB, corrosion products, et al. [22]. While some components can promote the steel corrosion, some have a protective effect for the steel. Actually, SRB induced MIC is a complex process, where the basic contributor to corrosion is sessile SRB cells [23].

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Buried pipelines are always coated by external coatings. After a long time of service in the soil, the coatings would experience degradation such as disbonding, where SRB induced MIC can occur [24]. However, the mechanistic aspect about the SRB induced pipeline corrosion has not been fully understood. In Canada, aged pipelines to be decommissioned and abandoned in soils and their corrosion progression, as well as the resulting structural degradation have become one of top priorities to industry and the country, as evidenced by a series of reports published by Canadian Energy Pipeline Association, Petroleum Technology Alliance of Canada and the National Energy Board [25]. It is expected that MIC is a key contributor to the long-term corrosion progression on the decommissioned/abandoned pipelines. To date, there has been rare research work studying this important topic.

In this work, corrosion of an X52 pipeline steel was investigated in a field-collected soil containing SRB by weight-loss testing, biotesting (i.e., fluorescence images by confocal laser scanning microscope, CLSM), electrochemical measurements (i.e., electrochemical impedance spectroscopy, EIS, and potentiodynamic polarization), and surface analysis techniques including stereoscopic microscopy and scanning electron microscopy (SEM). The effects of water content and the presence of CO_2 in the soil on SRB growth and the resulting MIC were determined. The mechanism of pipeline MIC in the soil with varied conditions was discussed.

2. Experimental

2.1. Materials and specimens

All specimens used in this work were cut from an X52 pipeline steel sheet, with a chemical composition (wt. %) 0.24C, 1.4 Mn, 0.45 Si, 0.025 P, 0.015 S, 0.10 V, 0.05 Nb, 0.04 Ti and Fe balance. The specimens used for electrochemical measurements had a dimension of 10 mm × 10 mm × 5 mm, and were sealed in epoxy, leaving a work area of 100 mm^2. The specimens of 30 mm × 10 mm × 2 mm in dimension were used for weight-loss testing. The work face of the specimens was ground by 400, 600, 800 and 1200 grit silicon carbide papers, degreased by acetone and anhydrous ethanol, and was then dried in high-purity N_2 (99.999%). Prior to testing, all specimens were sanitized for 30 mins using an ultraviolet (UV) lamp.

2.2. Soil

The Regina clay soil obtained from Saskatchewan, Canada was used in this work. The chemical composition of the soil contained (g/L): $NaHCO_3$ 0.0760, NaCl 0.0089, $NaNO_3$ 0.0014, Na_2SO_4 0.0773, K_2SO_4 0.0619, $CaSO_4{\cdot}2H_2O$ 0.8823 and $MgSO_4{\cdot}7H_2O$ 0.3226. The soil particles were smaller than 0.4 mm in diameter. Prior to testing, the soil was dried and sterilized at 100 °C for 4 h.

2.3. Bacterial culturing and inoculation

SRB seeds (ATCC 13541) isolated from the soil were used in this work. A modified Baar's medium was used as the SRB culturing medium, with the chemical composition (g/L): K_2HPO_4 0.5, $(NH_4)_2SO_4$ 0.5, $(NH_2)Fe(SO_4)_2$ 0.2, $MgCl_2$, 0.3, sodium citrate 5.0, yeast extract 1.0 and sodium lactate 3.5 (pH 7.2). The medium was autoclaved at 121 °C for 20 min, and then deoxygenated using high-purity N_2 for 2 h. The amount of remaining dissolved oxygen was below 0.3 mg/L, which was measured using a dissolved oxygen meter (ExStik DO600). The SRB were incubated at 30 °C, i.e., the optimal temperature for SRB growth, in the culturing medium [26,27].

2.4. Soil conditions for corrosion testing

A diluted Na_2SO_4 solution (1 g/L, pH 7.1) was made of distilled water and analytical grade chemical (i.e., Na_2SO_4 powders) to adjust the water content of the soil. The addition of SRB in the soil was made by adding 10 wt.% SRB-containing culturing medium, as prepared above, in the Na_2SO_4 solution, with a pH of 7.2. The oxygen amount in the wet soil environment was controlled carefully, where the dried and sterilized soil mentioned above was wetted to achieve varied water contents with the prepared Na_2SO_4 solution containing 10 wt.% SRB-containing culturing medium in an anaerobic glove chamber. During testing, the soil testing chamber was continuously purged with high-purity N_2 to reduce the oxygen content below 0.3 mg/L, as measured.

To investigate the effect of CO_2 on MIC of the steel, the prepared Na_2SO_4 solution was deoxygenated by purging with 5% CO_2 balanced with N_2 for 2 h until the amount of dissolved oxygen was below 0.3 mg/L. The 10 wt.% SRB-containing culturing medium was then added in the solution (the pH of the CO_2-purged mixture was 6.4), which was used to adjust the water content of the soil. During testing, the soil chamber was continuously purged with 5% CO_2/N_2 to control the oxygen content below 0.3 mg/L, as measured.

2.5. Weight-loss testing

The steel specimens were taken out after 21 days of testing in the SRB-containing soil with varied conditions. Five parallel specimens were tested under each condition to ensure the reproducibility of the results. Generally, the bacterial growth and biofilm formation on metal surface in SRB-containing environments are time dependent. The authors' previous work showed that the time period of 21 days was sufficient to achieve a stable bacterial growth and attachment [6,9]. Thus, the testing time of 21 days was selected in this work to ensure the stable metabolism of SRB and, at the same time, to avoid lengthy testing period. The soil left on the specimen surface was removed by washing with distilled water. Corrosion products were removed using a pickling solution containing corrosion inhibitor of imidazoline derivative (10^{-3} M) for 5 min. The specimens were then rinsed with distilled water immediately, cleaned in absolute ethanol, and dried using high-purity N_2. The corrosion rate (CR) of the steel (mm/y) was calculated by:

$$CR = \frac{8.76 \times 10^4 \times \Delta m}{\rho A t} \quad (1)$$

where Δm, ρ, A and t were weight-loss (g), density (g/cm^3), area (cm^2) and time (h), respectively.

2.6. Characterization of biofilm and corrosion morphology

The steel specimens used in weight-loss testing, i.e., five parallel specimens under each testing condition, were taken out, cleaned by distilled water to remove soil, and then immersed into a phosphate buffered saline (PBS) solution containing 2.5% (w/w) glutaraldehyde for 8 h in order to immobilize sessile SRB cells [9]. The specimens were then immersed into ethanol solutions with various concentrations (30%, 50%, 70%, 90% and 100% for 15 min each) to dehydrate sequentially. Finally, the specimens were dried using high-purity N_2. Prior to SEM observation, a thin gold film of 0.5 μm in thickness was coated on the specimen surface to improve the electrical conductivity.

Moreover, a Zeta 3D stereoscopic microscope was used to characterize the topographic profile of the corroded steel specimens after the corrosion products were removed. The contrast between the corrosion area on the steel specimen and the epoxy