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Electrochemical Behavior of Cast Iron in the Presence of Bacteria in Water Distribution Systems

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Electrochemical behavior and corrosion of cast iron were investigated in the presence of sulfate-reducing bacteria and iron bacteria (SRB) and iron bacteria isolated from water distribution system using electrochemical techniques, scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) analysis. The results of corrosion potentials showed that corrosion occurred on the surface of specimens were decelerated by the presence of SRB and iron bacteria, SRB presented the higher corrosion rate than iron bacteria. SEM morphologies indicated that cast iron revealed no signs of pitting corrosion in sterile water whereas pitting holes were observed in other mediums. Passive films attached on the specimens that immersed in the combination of SRB and iron bacteria were maintained partly leading to a lower corrosion rate.

Keywords: SRB, iron bacteria, corrosion rate, water distribution system

1. INTRODUCTION

The urban water distribution systems are susceptible to corrosion causing hydraulic and water quality problems including water leaks, water quality deterioration and corrosion products build up [1]. For instance, corrosion is able to release iron into the bulk water that re-precipitate iron hydroxides which lead to the occurence of “red water” [2]. Corrosion in distribution systems leads to the formation of so-called “tubercles” which consists of biofilms, scales and corrosion products [3]. The corrosion products are the mixture of iron oxyhydroxides including lepidocrocite and goethite, magnetite, green rusts, hematite, ferrous hydroxide, ferric hydroxide and siderite [1]. The increase in turbidity, Fe concentration and rapid deacy of residual disinfectant is possibly attributable to corrosion scales or products [4, 5]. The most serious corrosion is observed mainly in steel and iron pipelines which hold a large proportion, e.g. 56.6% in USA, 53% in Poland and 67.2% in Italy [1, 6]. Iron pipes are commonly used in drinking water distribution systems [7].The study reported in this paper is limited to such materials.

In 1934, Kühr etc. firstly proposed that the graphitizing phenomenon of cast iron was actually an electrochemical process with participating of microorganisms in anaerobic situation. Biofilms which are attributable to microorganisms and their metabolic activities affect the kinetics of cathode and anode reactions leading to considerable variation of compositions in protective layers, thus accelerating or inhibiting the corrosion process [8]. The formed tubercles from the same distribution system are heterogeneous and usually appear with pores; therefore the rough inner surface of pipes provided an appropriate environment for bacteria to affect the corrosion process [9]. Various corrosion damages caused by microorganisms have been observed in the past years and sulfate-reducing bacteria (SRB) and iron bacteria are regarded as the most troublesome bacteria [8, 10]. Most of iron bacteria oxide ferrous ions into ferric ions which precipitate as $Fe(OH)_3$ to obtain energy for growth [11]. The rust deposits caused by iron bacteria may form an oxygen concentration area and initial crevice corrosion on iron pipes [10]. The passive layers produced by corrosion scales accumulated on the inner surface of pipes can protect the substrate (e.g. iron) from further corrosion. However, the low oxygen concentration area which turns anodic compared to the large surrounding cathode results in a high corrosion rate underneath the hard external layer [12, 13]. Iron bacteria do not cause health problems in people but a series of problems are produced such as turbidity, unpleasant odors and taste [14]. Sulfate-reducing bacteria (SRB) are commonly undesired because their metabolic activity combined with iron material causes the formation of aggressive corrosion products (e.g. hydrogen sulfide H_2S) [15]. They are mainly found beneath tubercles which are anaerobic conditions or low dissolved oxygen concentration environments [16, 17]. Iron sulfide films produced when iron pipes are exposed to SRB surroundings are unstable and easy to brush away since the formation process is in the absence of oxygen [18]. SRB obtain energy for growth and cell synthesis by oxidizing the organic compounds or molecular hydrogen (anode) and reducing sulfate to sulfide (cathode) [29].

Lewandowski et al. [20] reported the importance of aerobic manganese-oxidizing bacteria and SRB on steel corrosion, Pi et al. [21] showed that mixed colonies composed of micrococcus and SRB decelerated the corrosion process of carbon steel, David et al. indicated the strong acceleration in pitting corrosion process induced by the iron bacteria due to an increase in both cathodic and anodic reaction rates [10]. However, the role of SRB and iron bacteria combination in cast iron pipes in water distribution systems is still unknown. In the present study, the corrosion process of cast iron pipes were investigated to obtain better understanding of the influence SRB and iron bacteria combination isolated from water distribution system. Compositions of corrosion products formed on the inner surface of pipelines were measured by SEM-EDS and electrochemical behaviors of cast iron were measured using potentiodynamic scanning technique.

2. EXPERIMENTAL

2.1 Metal samples preparation

Sections of cast iron pipes were removed from local water distribution systems. In order to fit the reactor of electrochemical workstation, the specimens were processed into square shape with the size of 20mm×20mm×10mm. To create working electrodes, an electrical contact to each specimen were applied by a copper wire connect with the back of coupons mounted in an epoxy resin. All coupons were cleaned in distilled water then kept in loft drier after removing oil by acetone. The surface for measurements was wet polished on 400, 800 and 1200 mesh carborundum papers.

2.2 Microbiological cultivation

Tests were conducted using a nutrient-rich medium and except the blank group. Sealed flasks applied for microorganism cultivation were autoclaved at 120℃ for 25 min and stored at room temperature. The main composition of culture medium was shown below (g/l): (NH4)2SO4 0.5, NaNO3 0.5, K2HPO4, MgSO4•7H2O 0.5, CaCl2•6H2O 0.5 and Ferric ammonium citrate 10.0. Experimental SRB and iron bacteria were isolated from sections of cast iron pipes in water distribution system, and the chemical composition of water is shown in Table 1. The chromaticity was 15 and turbidity was 0.47NTU. Enrichment cultures were used as the corrosion cell inoculum and incubated at 30℃. Most probable number (MPN) method was adopted to evaluate the growth situation of bacteria according to the American Society of Testing Materials (ASTM) standard D4412-84 [22, 23].

Table 1. Analytical results of tap water sample from water distribution systems (mg/L).

Total hardness ($CaCO_3$)	Alkalinity ($CaCO_3$)	TOC	NH_3-N	Residual chlorine	Total iron	Dissolved oxygen
32.35	27.50	1.341	<0.025	0.02	0.094	7.94

2.3 Electrochemical measurements

Electrochemical tests were carried out in a cell with classic three-electrode system using 2273 electrochemical system driven by the software-package POWESUIT. Working electrode potentials were referred to a saturated silver/silver chloride (Ag/AgCl 3 M KCl) electrode and the counter electrode was a platinum plate. Polarization curves were determined potentiodynamically with a scan rate of 0.5mV/s. All the experiments were performed at room temperature (26±2℃).

2.4 Surface analysis

Scanning electron microscopy (SEM) and energy dispersive spectrometer (EDS) analysis were carried out on the surface of cast iron specimens after 7days of exposure to different solutions. The morphology and chemical compositions of corroded specimens were studied by SEM and EDS. Prior to the observations, specimens were washed in sterile distilled water. For SEM test, the edges and back of the specimen were painted with silver electrodag, and subsequently carbon coated.

3. RESILTS AND DISCUSSION

3.1 Electrochemical measurement

The corrosion potential (E_{corr}) of new sample is -0.845V which shows that the exposed iron sample surface is easy to suffer from corrosion. The sample that has been in service for over 20 years appeares a potential of -0.545V indicating that the compact passive layer has already formed and the material substrate effectively protected.

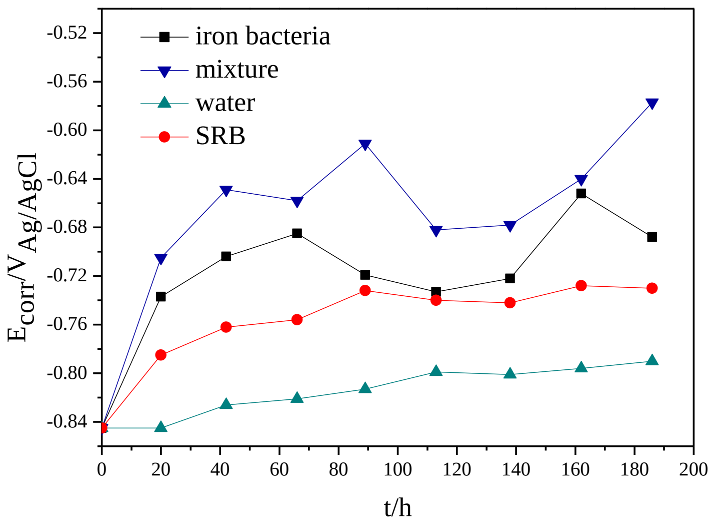


Figure 1. Ecorr (vs Ag/AgCI)~t curves of samples immersed in different solutions.

Figure 1 shows the potential distributions with exposure time for cast iron coupons in sterile water, SRB, iron bacteria and the combination of SRB and iron bacteria. It indicates that the presence of SRB and iron bacteria influences the corrosion process occurred on the iron coupon surfaces. An iron electrode was activated by cathode reduction of the initial surface oxide showing an initial potential of -0.845V. No significant changes of E_{corr} are observed in sterile water and the curve gradually ascends. There was no obvious corrosion appeared on the electrode surface indicating the specimen was in a passive state in sterile water [24]. The corrosion potential increased gradually after exposure indicating the passivation of cast iron coupons [10]. E_{corr} of coupons immersed in iron bacteria ranged from -0.785V to -0.728V whereas in SRB solutions, it varied between -0.733V and -0.652V versus Ag/AgCl. It demonstrated that iron bacteria produced the lowest corrosion rate since the metabolism of iron bacteria is low [25]. The potential drop was more pronounced in the presence of SRB indicating an activation of the initially passive films. In the later period, the activated specimen repassivated and passive films formed again so that E_{corr} shifted to positive direction [24]. The higher corrosion rate of SRB is attributable to the aggressive corrosion with iron specimens under anaerobic circumstance in which SRB are ubiquitous in water distribution system, and they generate hydrogen sulfide which can react with iron coupons [26]. In solutions with SRB and iron bacteria, corrosion potentials were distributed above the other curves indicating the repassivation occurred more rapidly and the high stability of passive layers accounted for the higher potentials [10]. Moreover, potential decreases were observed in SRB medium and the combination of SRB and iron bacterial. The potential decrease is mainly attributed to the dissolution of nature oxide films. There are two factors influencing the variation of potential: the formation of biofilms and the dissolution of oxide films. The potential decrease when the forming rate of biofilms is faster than those of dissolving oxide films.

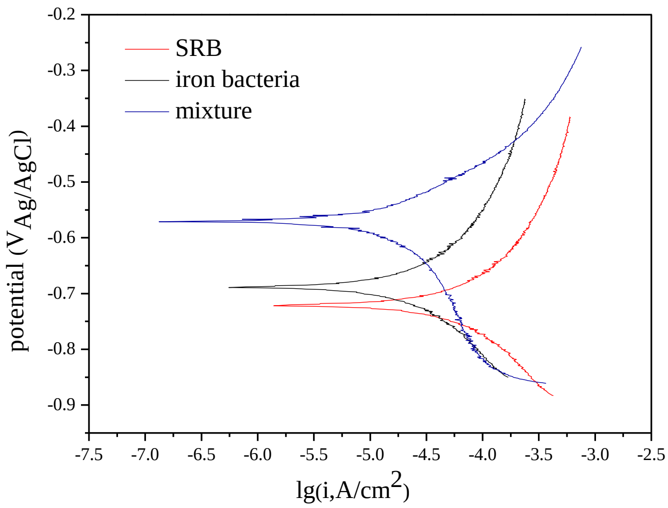


Figure 2. Potential dynamic curves for cast iron coupons in different mediums after 195h exposure.

Figure 2 shows the polarization curves of cast iron after exposure to different solutions for 195 h. It illustrates that the shapes of poentialdynamic polarization curve are not essentially different in three biological solutions indicating that the mechanisms of anode and cathode process are not modified in essential [22].

It was specified that the coexistence of SRB and iron bacteria had the advantage of inhibiting corrosion [21]. The results of E_{corr} indicated that within the mixture of bacterial, the corrosion process was less possible to occur. There was fluctuation in the potential dynamic curves pointing out that in the initial phase, the formative biofilm was not stable enough to attach on the sample surface [27]. Coupling with the breaking off of the passive layer, the sample surface was exposed to the surrounding again, hence the potential dropped sharply. As a result, there were some points dropped again during the test period.

3.2 Surface analysis

Figure 3 shows the micrograph appearance of cast iron samples after exposure to different solutions. SEM observation confirmed the formation of biofilms on the surface of coupons immersed in pure SRB solution. The biofilms formed in the medium of SRB were relatively loose and porous, with a pitting structure that was destructive in corrosion process. The deposits contained spongy and needle-shaped aggregates. Iron oxides can be dissolved reductively by biogenic hydrogen sulfide and iron sulfides consequently produced [8, 28]. EDS analysis (Figure 4) shows the higher concentration of sulfur (3.08 wt %) and iron (95.13 wt %). The proliferation and metabolism of SRB result in the generation of iron sulfide which has poor protective properties changing the thickness and density of passive layers [28]. After 7 days, the numerous annular damages showed up on the inner surface as sites of localized corrosion and became distributed over the whole surface indicating pitting initiated.

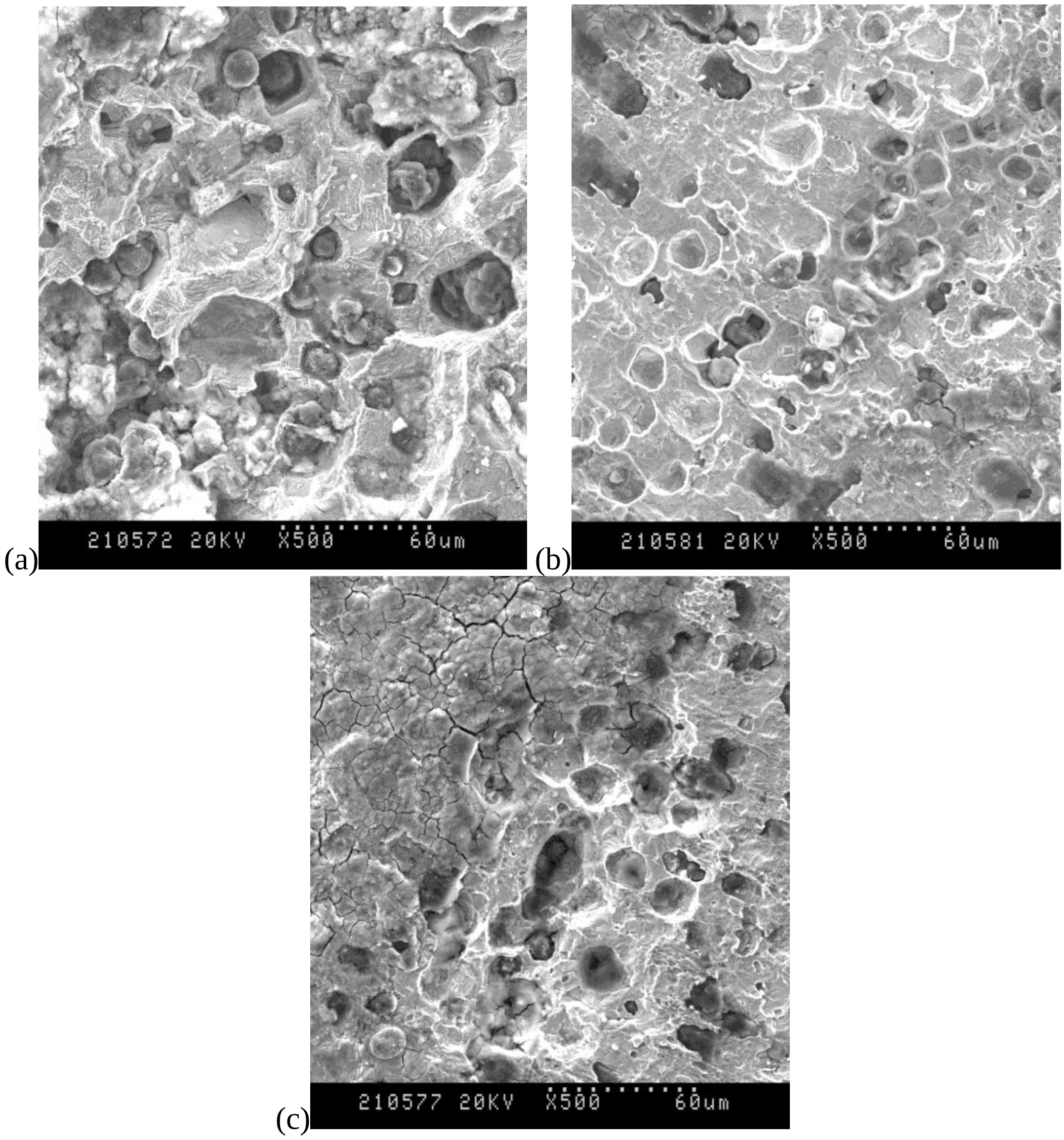
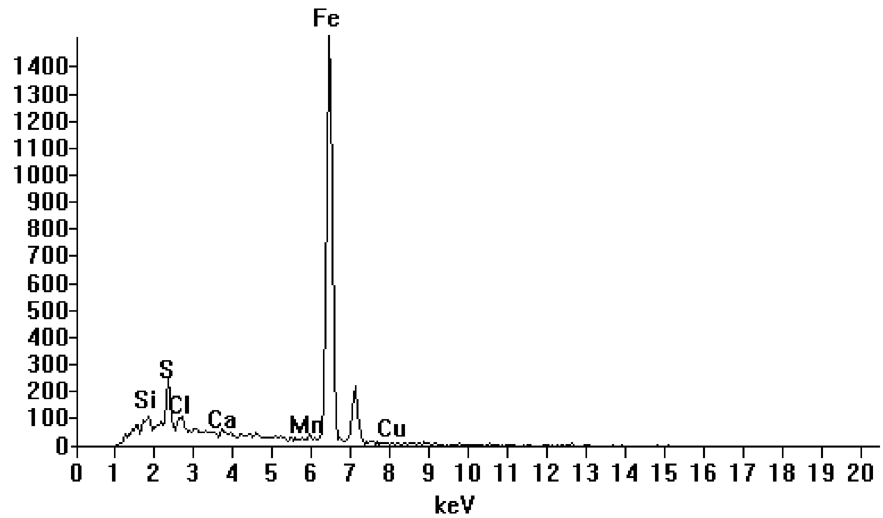


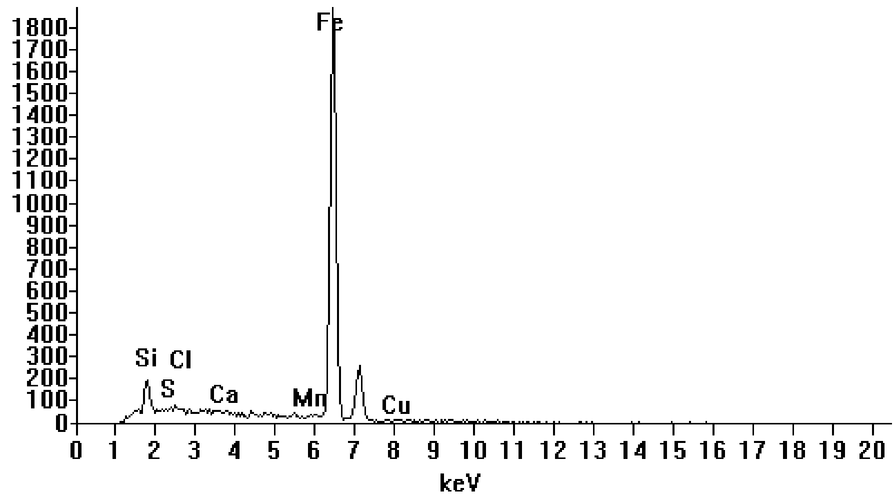
Figure 3. SEM images showing biofilms formed on cast iron surfaces after 170 h exposure, with the presence of SRB (a), iron bacteria (b) and the combination of SRB and iron bacteria (c).

In contrast, the pitting hole was not clearly observed after exposure to iron bacteria medium. The surface was covered with deposits which had a layered structure, EDS analysis indicated high concentration of iron (97.19 wt%) and there were small quantities of silicon, manganese and sulfur at 2.26, 0.31 and 0.10 wt% respectively. SEM revealed that the presence of floccules (ferric oxide) with a heterogeneous distribution of different compounds attached to cast iron surface. The upper layer of deposits contained spherical granules in which iron was the predominant species according to EDS analysis [23]. Small cracks were observed although pitting holes were not distinct. However, the initiation of cracks related to pits which resulted from discontinuities in the biofilm. The structure of biofilm was non-uniform, consisting of biological (e.g. iron bacteria) and non-biological substances (e.g. corrosion products). Electrochemical cells arising therefrom brought about pitting [13].

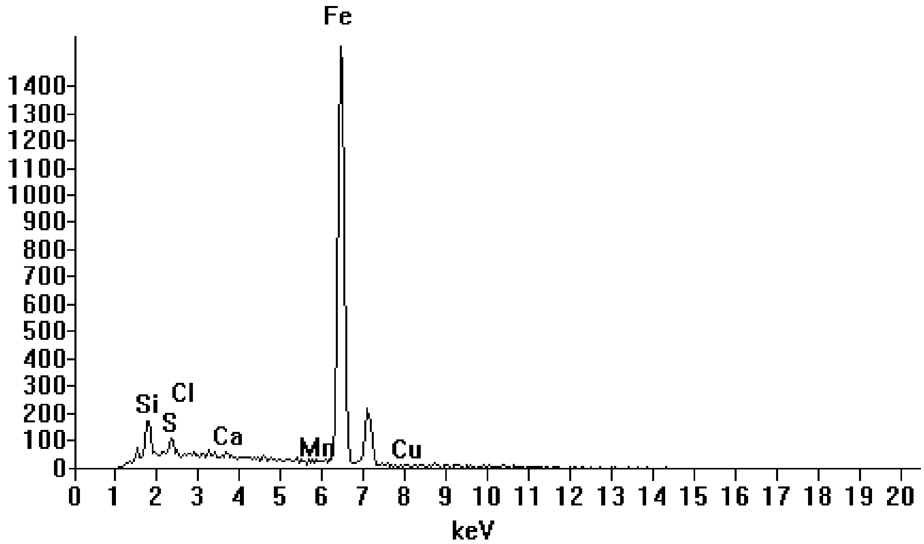
In the solution of SRB and iron bacteria combination, cast iron coupons were covered with thick substances, EDS analysis indicated high concentration of iron (96.29 wt%), sulfur (1.08 wt%), and a small quantity of silicon.



(a)



(b)



(c)

Figure 4. EDS spectrums of biofilms formed on cast iron surfaces after 170 h exposure, with the presence of SRB (a), iron bacteria (b) and the combination of SRB and iron bacteria (c).

The upper layer of deposits contained spherical granules in which iron was the predominant species but also some sulfur based compounds were found at the surface. The biofilms exhibited a loose and homogeneous structure without obvious cracks or pits explaining the lowest corrosion rate in the medium of SRB and iron bacteria combination [21, 23]. In general, the pitting corrosion damage of cast iron in SRB solution was the most sever, it took the second place in iron bacteria and it was the least in SRB and iron bacteria combination.

4. CONCLUSIONS

The corrosion process of cast iron in water distribution system was affected by the presence of SRB and iron bacteria, and SRB demonstrated the high corrosion rate than iron bacteria. At the beginning of the experiment, E_{corr} inclined clearly due to the formation of passive layer or biofilms. During the later period, E_{corr} dropped quickly ascribed to the biofilms or corrosion scales which were brushed off from the substrate. E_{corr} of the combination of SRB and iron bacteria was higher than that of SRB and iron bacteria indicating the corrosion of cast iron was decelerated due to the diversity of bacteria.

The morphologies of specimens indicated the formation of biofilms on working surfaces in the presence of microorganisms. Iron coupons revealed no signs of pitting attack in the sterile medium whereas micrometer-scale pitting corrosion appeared in biological solutions, but the protective layers partially remained when iron specimens were exposed to the combination of SRB and iron bacteria. In accordance with electrochemical results, in the presence of SRB, the highest corrosion rate was obtained, coupons immersed in SRB and iron bacteria combination showed the lowest corrosion rate.

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