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Effects of Sulfate-Reducing Bacterial on Corrosion of 403 Stainless Steel in Soils Containing Chloride Ions

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The effects of sulfate-reducing bacterial (SRB) on the corrosion of the 403 stainless steel in soils containing chloride ions have been studied by weight loss, electrochemical impedance spectroscopy (EIS). The results have showed that the corrosion rate and the maximum pitting depth of 403 stainless steel in soils with SRB are larger than those without SRB, and increase with the chloride ion concentrations increasing, reach a peak at 1.0wt% of chloride ions, and then decrease, which implies that the susceptivity of the pitting is increased under the combined actions of SRB and chloride ions. The results have also indicated that a single capacitive loop is observed before pitting, and double ones after pitting in EIS plot of the steel.

Keywords: SRB, 403 stainless steel, EIS, Corrosion rate, Pitting

1. INTRODUCTION

Sulfate-reducing bacteria (SRB) are commonly found in anaerobic and localized anaerobic environments, such as soil, seawater, sewage [1-10]. In China, SRB can be found in most areas [11]. With the widespread application of the stainless steels, researches on microbiological influenced corrosion (MIC) of the steel become more and more important [12-19]. Since the Chinese soil environment corrosion testing network was built in 1959, large amounts of data, including distributions and types of microbes, environmental factors, etc, have been collected and accumulated [20, 21]. The results have showed that the chloride ions play an important role in the corrosion of buried materials, but studies of the effect of the chloride ions on the MIC have been seldom reported in the soils.

The present work is aimed to determine the effects of chloride ions and SRB on the corrosion of the 403 stainless steel in soils.

2. EXPERIMENTAL

2.1. Material, microbe and soil preparation

Specimens sized 15×15×4mm were cut from a plate of 403 stainless steel with nominal composition (wt%) of 12.62%Cr, 0.1%Ni, 0.31%Mn, 0.061%C, 0.019%P, 0.005%S, 0.38%Si, and balance Fe, then embedded in epoxy resin to prepare test sample with an exposed surface area of 4 cm^2 for electrochemical measurements. The coupons were abraded with a series of grit papers (200, 400, 600, and 800) followed by cleaning in acetone and alcohol and dried.

SRB cultures were inoculated in a medium containing: 0.5 g K_2HPO_4; 1.0 g NH_4Cl; 4.5 g Na_2SO_4; 0.06 g $CaCl_2·H_2O$; 0.004 g $FeSO_4·7H_2O$; 0.04 g $MgSO_4·7H_2O$; 3.5 g sodium lactate; 1.0 g yeast cream; 5.0 g sodium citrate (containing two crystal water); 10ml sodium thioglycollate (1%); 10 ml sodium ascorbate (1%) and 1000ml H_2O which was autoclaved for 30 min. The pH value of the culture solution was between 7.0 and 7.3 [22]. The SRB content was enumerated by the most probable numbers (MPN) techniques [23].

Soils, the chemical compositions of which were given in table 1, taken from Shenyang , China. They were autoclaved at 121 °C for 20 min, and stored for use. The sterilized soils were inoculated with 0.1% (V/V) suspension of SRB that had been incubated for 15 days. The soil moisture content was 23%.

Table 1. Composition of the soil

pH	**Chemical composition (mg/100g·soil)**								**Moisture content (%)**	**Organic content (%)**	**Whole nitrogen content (%)**	**Total salt content (%)**
	NO_3^-	Cl^-	SO_4^{2-}	HCO_3^-	Ca^{2+}	Mg^{2+}	K^+	Na^+				
7.75	0.0046	0.0031	0.0048	0.0234	0.0057	0.0032	0.0002	0.0014	23	2.26	0.091	0.0464

2.2. Weight loss and pitting technique

Rectangular coupons (50×25×3mm) were used for weight loss tests. Before tests, samples were ground down to 800 SiC-paper, degreased in acetone, sterilized and weighed to a precision of 0.1mg. After corrosion test, the sample was extracted, pickled in the solutions, which contained HCl (ρ=1.19 g/ml) 500ml, hexamethylene tetramine_3.5g, distilled water 500ml, for 10 min at 25 °C, cleaned with water, dried at 105 °C for 30 min in a furnace, cooled, then weighted again. Weight-loss measurements were converted into uniform corrosion rates ($g/dm^2·a$). Maximium pit depths were measured by using pitting depth gauges (DDC-2, made in China). Triplicate specimens were used for each experiment to guarantee the reliability of the results.

2.3. Electrochemical technique

The soil redox potential, being considered indicative of the risk of bacterial corrosion, was measured by a multimeter, 5 Pt electrode and a saturated calomel electrode (SCE). The redox potential was calculated by the following relationship:

$$E_h = E_m + 250 + 60 \times (pH - 7)$$

where E_h=redox potential at pH=7 (mV, standard hydrogen scale); E_m=mean of the potential measured from the five platinum electrode (mV) [24].

A classical three electrode cell was used with platinum foil as counter electrode, saturated calomel electrode, SCE, (0.242V vs. SHE) as reference electrode, and the samples as working electrode. Electrochemical impedance spectroscopy (EIS) measurements were performed using an electrochemical measurement system from EG＆G, which comprised an M273 potentiostat, an M5210 lock-in amplifier and M398 software. An alternating current signal with a frequency range from 100kHz to 0.01Hz and amplitude of 10mV (rms) was applied to the working electrode at the corrosion potential. Before each group of experiment, the working electrode was buried in the test soil for 24 hours to reach steady state.

2.4. Morphological and element analytical technique

Microscope, transmission electron microscope and Scanning electron microscopy (SEM) in the combination with energy-dispersive X-ray analysis (EDXA) (Philips XL30) was used to observe and analyze SRB and the specimens.

3. RESULTS AND DISCUSSION

3.1 Growth of SRB in the soil containing chloride ions

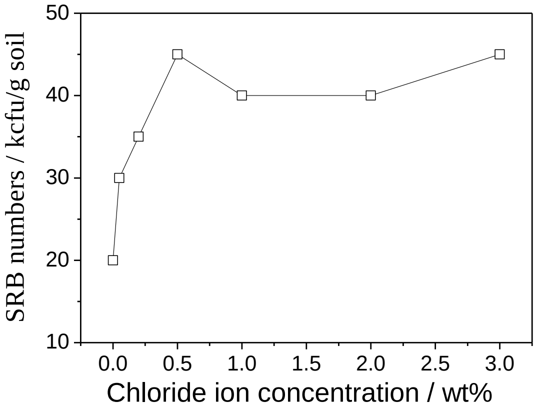

Figure 1. Growth of SRB with chloride ion concentration in soils

The effects of chloride ions on the growth of SRB in soils are given in Fig. 1. The amounts of SRB range from 20 to 45 kcfu/g soil. The amounts of SRB sharply increase with chloride ion concentrations increasing in soils with SRB when the chloride ion concentrations are less than 0.5wt%, which is agreement with the result by Fang et al [25]. They have concluded that suitable amounts of chloride ions are beneficial to the growth of SRB, and lower concentrations will inhibit them. When the chloride ions exceed 0.5wt%, the amounts of SRB remained stable with chloride ion concentrations increasing, which indicates that the higher addition of chloride ions have little influence on the SRB growth.

3.2 Corrosion potential with chloride ion concentration

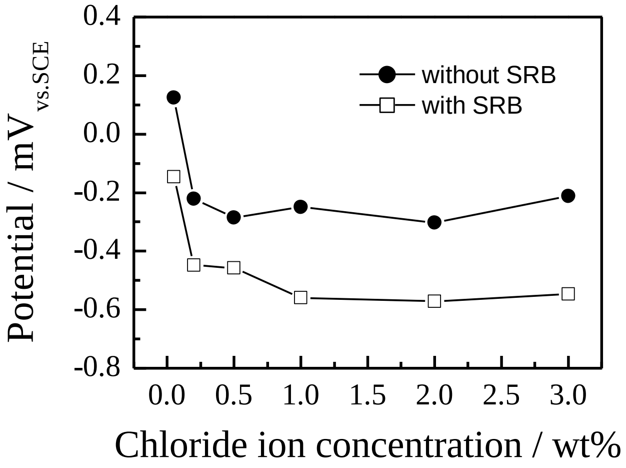

Figure 2. Corrosion potential of 403 stainless steel with chloride ions in soils

Figure 2 shows the relationship between the corrosion potential and the chloride ion concentration in soils with and without SRB. The corrosion potentials of the stainless steel decrease with chloride ion concentrations increasing, and the potentials are more negative in soils with SRB than those without SRB, which indicates that the presence of SRB increases the corrosive tendency of the stainless steel. The above results are due to the forming of metabolic sulfide by SRB, e.g. hydrogen sulfide, which accelerate the corrosion of the steel in the presence of SRB.

3.3 Influence of SRB and Chloride on corrosion of the steel

Figure 3 and 4 show the variation of the average corrosion rate and maximum pit depth of the 403 stainless steel with chloride ion concentration in soils. The average corrosion rates are bigger in soils with SRB than those without SRB, which indicates that the presence of SRB increase the corrosion rate of the stainless steel in soils. The above result is due to the reason that hydrogenase in SRB can utilize hydrogen as an electron donor to obtain energy and thus removed molecular hydrogen from the cathode, which leads to cathodic depolarization of the metal surface and increasing of the corrosion rate of the stainless steel [26, 27]. The average corrosion rate and maximum pit depth increase with chloride ion concentration increasing, reach a peak at chloride ion concentrations of 1.0wt%, and then decreased.

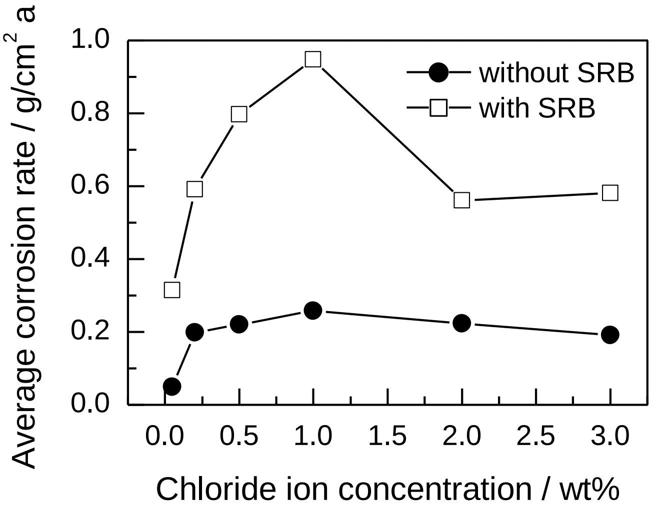

Figure 3. Variable relationship between the average corrosion rate of 403 stainless steel and Cl^- ion concentration

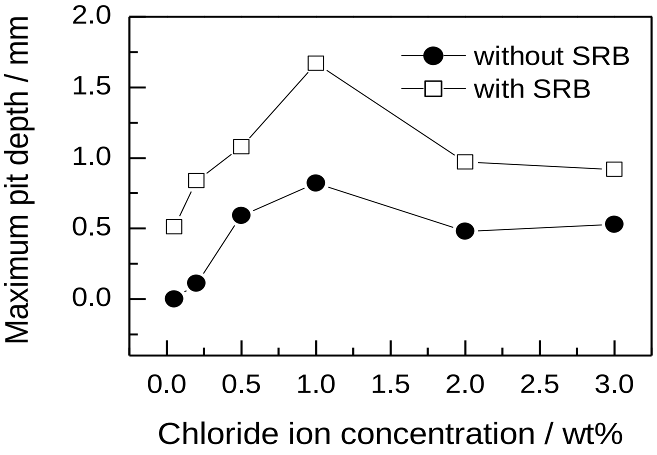

Figure 4. Variable relationship between the maximum pit depth of 403 stainless steel and Cl^- ion concentration

The peak appeared in the moderate chloride ion concentration because lower or higher concentrations inhibited the activity of SRB [25, 28]. The increasing of chloride ion concentrations can enhance the pit susceptibility of the steel. The pitting occurs in soils with SRB and no pitting was observed without SRB, which indicates SRB increase the pitting tendency of the steel in soils containing chloride ions.

The heterogeneity of the soil grains, such as the soil granularity, enhances the inhomogeneity of the medium, which changes the area ratios between the metal surface with oxygen contents and without oxygen contents [29]. The surfaces in contact with the soil grains are exposed to lower oxygen concentrations than those not in contact with the soil grains, which generates an oxygen concentration cell. Furthermore, low oxygen concentrations are beneficial to the growth of SRB. In an anaerobic environment, SRB use sulfates as an electron acceptor and reduce them to the sulfides, such as H_2S and FeS, which deposit on the local surface of the steel. A new corrosion cell is formed, in which the sulfides accumulated act as a cathode, and the base of the stainless steel as anode. The pitting corrosion occurs in the anodic regions. In addition, chloride ions are one of the most important factors for the pitting of the stainless steel and can destroy the stability of the passivating film, which leads to the occurrence of the pitting under the combined effects of chloride ions and SRB.

3.4 Electrochemical impedance

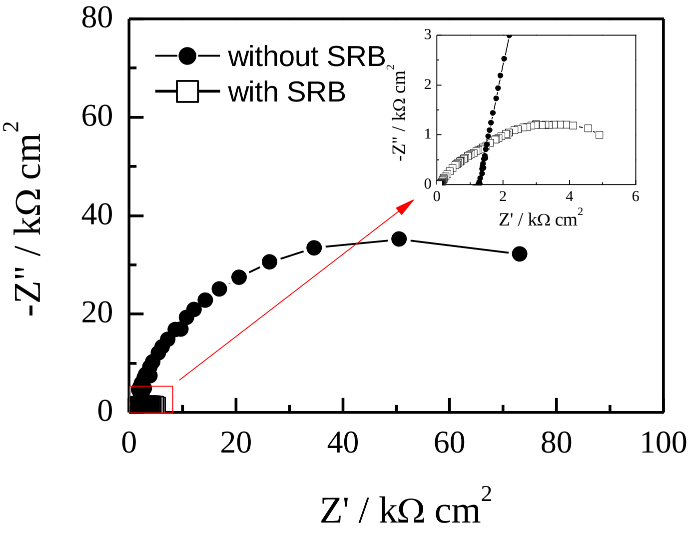

Figure 5. EIS plot of 403 stainless steel in soils containing 0.2wt% chloride ions after burying for 8 days

Table 2. Fitting results of EIS for figure 5

SRB condition	R_s Ω cm^2	Y_f mS sec^n/ cm^2	n_f	R_f kΩ cm^2
with	188.3	0.2177	0.4524	6.476
without	1165	0.0718	0.8207	98.1

Figure 5 shows EIS plot of the 403 stainless steel in soils containing 0.2% chloride ions and with and without SRB after 8 days, fitting results are give in table 2, and the equivalent circuit is given in Fig. 8. In both cases, a single capacitive loop is observed, which indicates that the passivating films of the steel are stable in soils containing lower chloride ion concentrations in the initial stage. The radius of the capacitive loop is much smaller in the soil with SRB than that without SRB, which also indicates that SRB increase the pitting susceptibility of the steel in the soils.

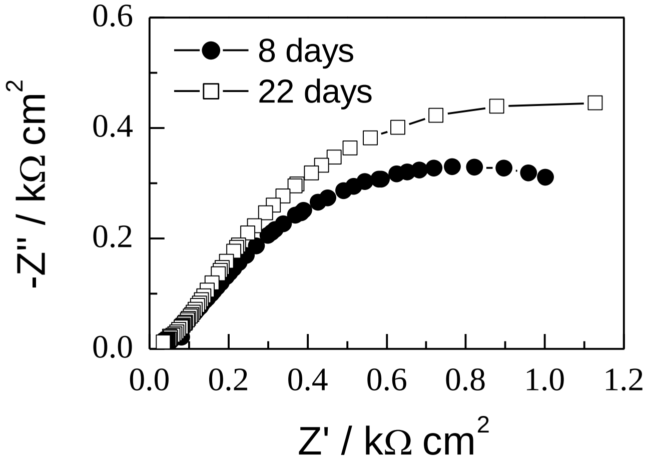

Figure 6. EIS of stainless steel in the soil containing 2.0wt% chloride ions with SRB

EIS plot of the steel with time in the soil containing 2.0wt% chloride ions and with SRB is given in Fig. 6, and fitting results are given in table 3. There is one capacitive loop after 8 days, and two loops are observed after 22 days which the radius of the capacitive loop is much small in the high frequency region. It indicates that the protective ability of the passivating film decreases with time.

Table 3. Fitting results of EIS for figure 6

Time days	R_s $\Omega\cdot cm^2$	Y_f $mS\cdot sec^n/cm^2$	n_f	R_f $\Omega\cdot cm^2$	Y_{dl} $mS\cdot sec^n/cm^2$	n_t	R_t $k\Omega\cdot cm^2$
8	39.68	1.47	0.4912	1679			
22	25.71	1.374	0.4806	92.59	1.267	0.6978	1.854

Table 4. Fitting results of EIS for figure 7

Time days	R_s $\Omega\cdot cm^2$	Y_f $mS\cdot sec^n/cm^2$	n_f	R_f $\Omega\cdot cm^2$	Y_{dl} $mS\cdot sec^n/cm^2$	n_t	R_t $k\Omega\cdot cm^2$
22	14.35	0.5622	0.7015	7065			
44	3.178	0.0138	0.8725	141.2	3.428	0.6554	1.876

Figure 7 shows EIS plot of the steel with time in soils containing 2.0wt% chloride ions and without SRB, and fitting results are given in table 4. After 22 days, there is only one capacitive loop in the EIS plot. Two distinctive capacitive semicircles are observed after 44 days, which indicates that pitting corrosion is occurred on the surface of the steel [30, 31].

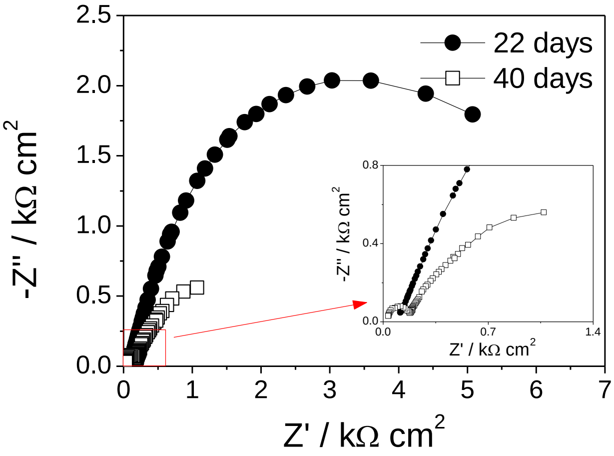

Figure 7. EIS plot of stainless steel in the soil containing 2.0wt% chloride ions and without SRB

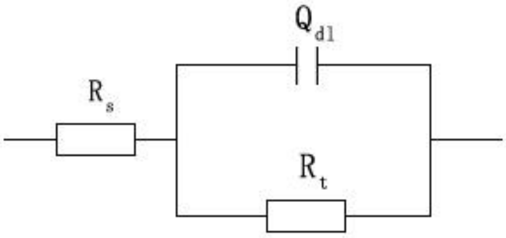

Figure 8. Equivalent circuit for 403 stainless steel stainless steel (single-layer model)

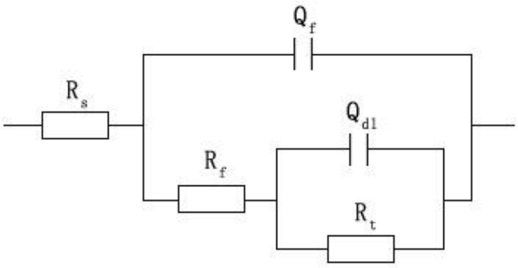

Figure 9. Equivalent circuit for 403 stainless steel stainless steel (double-layer model)

Pitting is generated in soils without SRB, which is due to the reason that chloride ions can destroy the stability of the passivating film formed on the surface of the steel. However, in inoculated soils, SRB can use the sulfates as the electron acceptors and reduce them to the sulfides, such as H_2S and FeS, which accelerate the process of cathodic depolarization. The pitting corrosion easily occurs as a result of the actions of chloride and metabolic sulfide ions. According to the electrochemical mechanism of the pitting formation, two different reaction regions exist on the surface of the electrodes: one, anode, is on the surface of the metal in the pits, the other, cathode, is outside the pits. Because the potential of the former is much more negative than that of the latter, when both are coupled, anodic dissolution occurs in the pits. The areas of the anodic regions are much smaller than those of the cathodic regions, the anodic current density is much bigger, and the ohmic resistance of the solution in the pits can not be neglected. The corresponding admittance was negligible because of the large reactive resistance on the passive surface. The equivalent circuit of the pitting expansion of the stainless steel in soils with SRB is shown in Fig. 9. R_s represents the soil electrolyte resistance, Q_f represents the capacitance of the passive film, R_f represents the soil electrolyte resistance in the pitting. R_t and Q_{dl} represent the charge transfer resistance and the double layer capacitance, respectively. There are two time constants for the equivalent circuit. A gap between two time constants and the value of R_f are essential elements whether two distinguishable capacitive loops can be observed in the EIS plots. After the forming of the pitting, R_f is much smaller, and it is difficult to observe a capacitive loop in the high frequency region of the Nyquist plots.

4. CONCLUSIONS

1. The amounts of SRB in the soil containing chloride ions are more than those without chloride ions, but the amounts of chloride ions have no significant effects on the growth of SRB.
2. The corrosion potentials shift towards the negative direction with chloride ion contents increasing, and the corrosion potentials in the soil with SRB are more negative than those without SRB.
3. The corrosion rates are faster in the soils with SRB than those without SRB. The corrosion rate and maximum pit depth increase with chloride ion concentration increasing, reach the peak at 1.0wt% chloride ions, and then decrease.

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