CORROSION OF MILD STEEL BY SRB IN THE ABSENCE OF SULPHATE

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ABSTRACT

A sulphate-reducing bacteria (SRB) that is able to use nitrate as a final electron acceptor (*Desulfovibrio desulfuricans* ATCC 27774) was grown in lactate-nitrate medium. Weight loss and open circuit potential measurements, cyclic voltammetry and unidirectional polarisation were performed, both in sterile media as well as in the culture, using a mild steel electrode.

These results were compared with previous ones obtained with the same bacteria grown in lactate-sulphate medium, thus allowing testing biocorrosion mechanism where either sulphide acumulates and cathodic depolarisation occurs or when only the last mechanism occurs.

INTRODUCTION

Sulphate reducing bacteria (SRB) are a wide group of bacteria with the common feature of being able to conduct dissimilatory sulphate reduction, i.e., using sulphate as a final electron acceptor, thus reducing it to sulphide, a process also known as "sulphate respiration". *Desulfovibrio desulfuricans* ATCC 27774 (*Dd* 27774) is a sulphate-reducer with the ability of using either sulphate or nitrate as the final electron acceptor.

Microbial influenced corrosion (MIC) is a process of increasing importance, both economically and scientifically. Among the most important microbes involved in MIC are the SRB, namely the genus *Desulfovibrio*.

The influence of sulphate reducing bacteria (SRB) on the corrosion of mild steel is reported to be due to its ability to catalyse the cathodic reaction via hydrogenase enzyme [1], to create conditions favourable to the cathodic reaction (formation of FeS) [2, 3] or even due to the production of H_2S[4]. Recently it has been recognised an

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increasing importance of the biofilm formation, altering the interface, trapping FeS and creating concentration cells [5].

We have used *Dd* 27774 grown in lactate/nitrate to evaluate the anaerobic corrosion of mild steel in the absence of sulphate.

EXPERIMENTAL

The bacteria used was *Desulfovibrio desulfuricans* ATCC 27774, grown in a lactate/nitrate medium with the composition as given in Table 1. pH was adjusted to 7.2 after deaeration with nitrogen, then sterilised at 120 °C for 30 minutes. 20 hours after a 10% (v:v) inoculation a steady-state population of *Dd* 27774 is reached with about 5 x 10^6 cells/ml.

Table 1: Nitrate/lactate medium composition/ 1 dm^3

Compound	Quantity
NH_4Cl	2.00 g
$MgCl_2.6H_2O$	2.00 g
K_2HPO_4	0.50 g
$FeCl_2.4H_2O$	0.007 g
$CaCl_2$	0.20 g
$NaNO_3$	2.40 g
mineral complement	10 cm^3
Sodium lactate 60% (w:w)	11.5 cm^3
yeast extract	1.0 g
cystein-HCl	0.25 g

Mineral Complement /1 dm^3: 12,8 g nitriloacetic acid. pH adjusted to 6.5 by KOH, then: 0.21 g $FeCl_2.4H_2O$ + 0.10 g $MnCl_2.4H_2O$ + 0.17 g $CaCl_2.6H_2O$ + 0.1 g $ZnCl_2$

Steel samples (working electrodes) were made from steel with the following nominal composition: C 0.71, S 0.015, Si 0.30, Mn 0.50, P 0.020 and balance Fe. The steel electrode was polished with alumina up to 0.05 µm, degreased with ethanol in an ultrasonic bath and dried in cool air before each experiment.

Weight loss measurements (coupons (5 *x* 1 *x* 0.1) cm) were setup for 1, 7, 14, 21 and 28 days of exposure.

Open circuit potential was followed for about 50 hours.

Potentiodynamic curves were run with a PARC potentiostat model 178 coupled to a PARC waveform generator model 173 with a current follower PARC model 176. The cyclic voltammograms and the quasi-steady-state polarisation curves were recorded on a X-Y recorder from Phillips, model PM 8120.

Reproducible conditions were obtained by exposure of the steel electrode to the medium for 10 minutes at open circuit, followed by 3 minutes of cathodic polarisation at -1.5 V *vs.* SCE, and finally the polarisation curve was recorded.

Cyclic voltammograms were recorded at two sweep rates, namely of 20 mV s^{-1} and 1 mV s^{-1}, quasi-steady-state conditions.

All experiments were performed at 37 °C (optimum temperature for the growth of this strain) and in an anaerobic environment. 1 day-old bacterial cultures were used in the polarisation experiments.

RESULTS AND DISCUSSION

Table 2. Average corrosion rate, v_c, (mg dm^{-2} day^{-1})for mild steel exposed to: Lactate-nitrate medium (Lact/NO_3^-); *Dd* 27774 grown in lactate-nitrate medium (*Dd*-NO_3^-); lactate-sulphate medium (Lact/SO_4^{2-}); *Dd* 27774 grown in lactate-sulphate medium (*Dd*-SO_4^{2-}).

time (days)	Medium			
	Lact/NO_3^-	*Dd*-NO_3^-	Lact/SO_4^{2-}	*Dd*-SO_4^{2-}
1	28.3	25.6	60.3	103.8
7	10.2	4.1	15.2	11.0
14	9.5	4.2	8.7	7.2
21	4.6	1.3	7.4	4.7
28	10.9	2.1	8.2	3.5

The left side of Table 2 shows the weight loss obtained with this systems (both sterile and inoculated). The right side of the table gives the results [6, 7] obtained for the same system using lactate/sulphate medium.

One can see in Table 2 that the sterile and the inoculated lactate/nitrate media produce a similar v_c *vs.* time curve, the culture being less aggressive than the sterile medium. This may be due to the formation of the biofilm which introduces barriers at the interface, protecting the coupon, in terms of weight loss. The lactate/sulphate systems have a similar behaviour for the observations made at 7, 14, 21 and 28 days, but during the first day of exposure the average corrosion rate is much higher, which will have to be interpreted in terms of the contact of the metal with the medium, before the formation of the biofilm. The medium now is poisoned with hydrogen sulphide, as a consequence for the bacterial growth.

Fig. 1 shows a set of open circuit potential curves obtained for the systems under study.

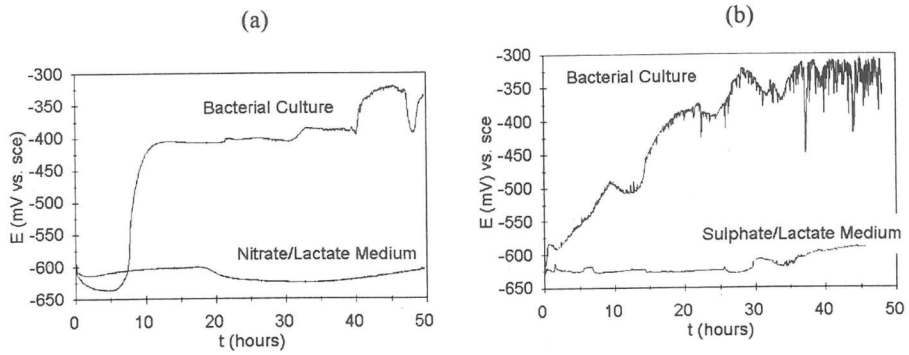

Figure 1: Open circuit potential (OCP) of mild steel immersed in the sterile media and in an *Dd* 27774 culture (inoculated at t = 0).(a): lactate-nitrate system; (b): lactate-sulphate system.

It can be seen that, as the bacterial growth takes place, the corrosion potential shifts from -600 mV *vs.* SCE (average value for both sterile media) to about - 320 mV *vs.* SCE, thus enabling to predict the protection of the steel against iron dissolution. However in the lactate-sulphate system systematic oscillations are observed towards the

negative direction, indicative of localised corrosion: the breakdown and repassivation of the protective film. Such oscillations were not observed in the lactate-nitrate culture.

Fig. 2 shows typical cyclic voltammograms for the media under study.

The lactate-nitrate systems show a similar behaviour, with the exception of very anodic potentials (higher than -0.4 V *vs.* SCE) in which the sterile medium shows higher susceptibility to corrosion. Both of the voltammograms show current crossing. The lactate-sulphate systems show, however, a very different behaviour: the currents are always much higher in the culture, the anodic peaks are not visible and there is no current crossing, even if the polarisation is extended into more anodic potentials.

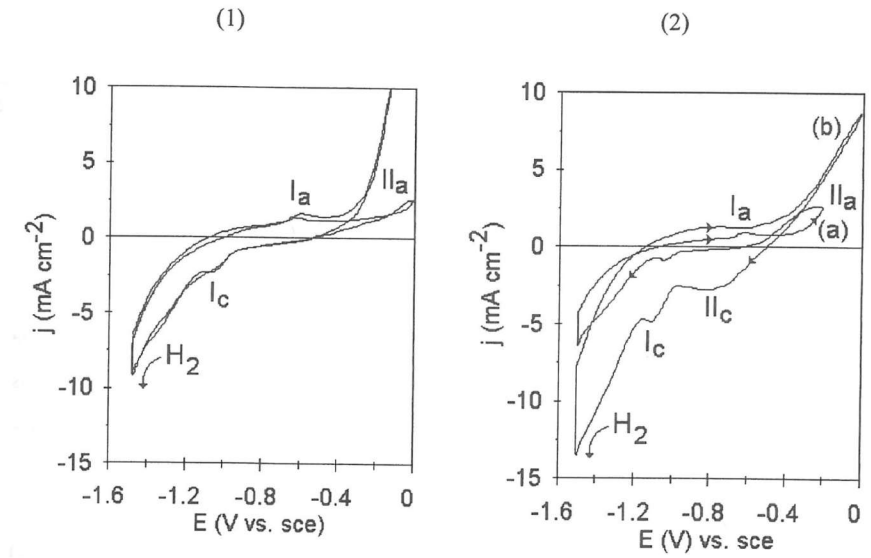

Figure 2: Typical CV´s of mild steel in (1):(a) lactate-nitrate medium and (b) Desulfovibrio desulfuricans ATCC 27774 grown in lactate-nitrate medium; (2):(a) lactate-sulphate medium and (b) Desulfovibrio desulfuricans ATCC 27774 grown in lactate-sulphate medium;

Fig. 3 shows Log j *vs.* E plots from typical anodic polarisation curves obtained at 1 mV s^{-1}. Table 3 shows parameters obtained by Tafel analysis and resistance polarisation technique. Cathodic depolarisation is put in evidence in Fig. 3a, for the lactate-nitrate

technique. Cathodic depolarisation is put in evidence in Fig. 3a, for the lactate-nitrate system. The anodic branches are, however, similar. For the lactate-sulphate systems (Fig. 3b) one can observe a great difference in both the anodic and cathodic branches, which is also clear in Table 3:

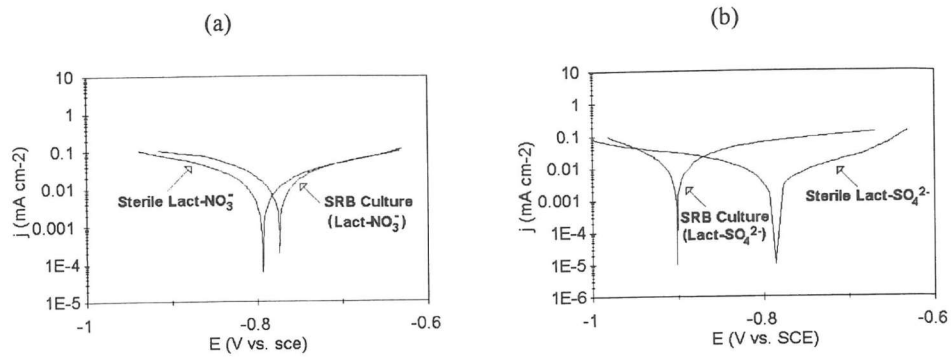

Figure 3.: Log j *vs.* E plots. Data from polarisation curves recorded at 1 mV s^{-1} (a) lactate-nitrate systems; (b) lactate-sulphate systems.

The anodic Tafel slopes, E_{corr} and i_{corr} are similar in the sterile lactate-nitrate medium and in the lactate-nitrate culture. In the lactate-sulphate systems the situation is very different, both Tafel slopes are smaller, E_{corr} is more negative in the culture and i_{corr} is higher in the culture.

Table 3: Parameters obtained by Tafel analysis and resistance polarisation from polarisation curves of mild steel in sterile and inoculated media.

	Tafel Analysis				R_p
Medium	β_a (V/dec.)	β_c (V/dec.)	E_{corr} (V *vs.* sce)	i_{corr} (μA cm^{-2})	i_{corr} (μA cm^{-2})
Lact-NO_3^-	0.208	0.107	-0.782	19	20
Dd-NO_3^-	0.219	0.128	-0.786	20	21
Lact-SO_4^{2-}	0.140	0.125	-0.781	9	11
Dd-SO_4^{2-}	0.107	0.094	-0.899	30	23

CONCLUDING REMARKS

The conclusions of this work can be summarised as follows:

In the first moments of exposure the corrosion induced by SRB in Lactate/Sulphate is much more severe than in Lactate/Nitrate.

Most probably a pure SRB biofilm inhibits the corrosion rate (in weight loss) over a period of 28 days.

The formation of a biofilm shifts the corrosion potential to more positive values but introduces oscillations, indicative of pitting corrosion;

Potential oscillations are particularly important on samples exposed to SRB grown in Lactate/Sulphate.

The presence of bacteria shifts the pitting potential to more positive values;

SRB grown in Lactate/Nitrate seems to affect only the cathodic process (cathodic depolarisation), whereas SRB grown in Lactate/Sulphate affect both the kinetics and the mechanism of mild steel corrosion as well as the cathodic depolarisation process;

SRB grown in Lactate/Sulphate shifts the corrosion potential by about 100 mV in the negative direction, whereas SRB grown in Lactate/Nitrate seem to have little effect on this parameter;

The instantaneous corrosion current density is enhanced by SRB in the Lactate/Sulphate medium, but it's presence does not affect this parameter in the Lactate/Nitrate medium;

Thus:

Without Sulphate the results in the sterile medium and in the SRB culture are similar: The reduction of SO_4^{2-} to S^{2-} is a key process in the SRB Induced Corrosion.

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Study of the stability of SnO_2 doped anodes

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INTRODUCTION

Wastewater containing organic pollutants, which can not be easily treated by biological action, has to be treated by chemical oxidation. Chemical oxidation allows, in general, complete elimination of the organic pollutants but complete removal of total organic carbon (TOC) is more difficult [1,2]. Using the electrochemical oxidation the TOC removal is higher than that obtained by chemical oxidation [3, 4, 5]. This higher TOC removal using electrochemical oxidation has been attributed to the oxidation of adsorbed organic compounds to CO_2.

A good electrode for the elimination of organic pollutants has to have high oxygen overpotential and a good stability in the anodic work conditions. The electrode of SnO_2 doped satisfies these requeriments.

In this work, the stability of SnO_2 electrodes doped only with antimony or antimony and platinum have been studied.

EXPERIMENTAL

The SnO_2 film electrodes doped with antimony were prepared on titanium base metal by the standard spray pirolysis method. Preparation details are given in [6]. The electrolyte was 0.5M sulphuric acid (Merck suprapur) solution and the water used for its preparation was from a Millipore-Milli Q system. A counter electrode was a