SRB ON THE CORROSION BEHAVIOUR OF GALVANIC ANODES SUCH AS Zn-Al AND Mg

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The extent of SRB induced corrosion of magnesium, aluminium and zinc anodes, has been studied with time, in a 10% Postage (B) medium, at 303K. Simultaneously, the magnitude and activity of SRB as well as changes in pH and dissolved oxygen content have also been monitored. The results arrange these metals in terms of susceptibility to SRB-al attack, in the following order: Zn > Mg > Al. Besides, they clearly exemplify that the cathodic depolarization is the initial step for attack by SRB.

Key words: Sulfate reducing bacteria, microfouling, microbial corrosion, corrosion of galvanic anodes

INTRODUCTION

Sulfate reducing bacteria (SRB) are a vast assemblage of anaerobic bacteria, that obtain energy through sulfate reduction. The consortia of these specialised bacteria can induce corrosion directly by the intrusion into electrochemical reactions or indirectly by corrosive metabolites. A wide spectrum of classical research works are available regarding these [1-5].

In general, the cathodic protection of metals by galvanic anodes, involves the usage of aluminium, magnesium or zinc alloys. As these metals seem to be much more susceptible to SRB's attack, the life of the anodes designed would come lesser than the planned life. The present work has been carried out with magnesium, aluminium and zinc to simply exemplify this fact. The influence of zinc, which normally exhibits SRB-cidal property at a concentration of 50 ppm [6], on these sulfidigenic bacteria has also been discussed.

EXPERIMENTAL

The SRB strain has been isolated from a local sewage disposal site and identified to be *Desulfovibrio* sp. using Postgate's technique [4]. The magnitude of the stock culture was 10⁵/ml after a week.

The electrochemical cell and equipments used have been described in an earlier paper [7]. The electrodes of Mg, Al, Zn embedded in teflon have been fabricated with a diameter of 6 mm. The compositions of these metals used are as follows:

Mg (Al-0.0025%; Cu-0.001%; Fe-0.005%; Mn-0.0134% and Si-0.054%)

Al (electrolytic grade) and Zn (electrolytic grade)

The effects of SRB on these metals have been studied instantaneously after 2 hours, after a day, after a week and after twenty days of immersion. Parallel experiments have been carried out without SRB addition in sterile culture medium (control). Simultaneously, the quantity of sulfide production, changes in the pH, dissolved oxygen and the magnitude of SRB in the inoculated cells have also been monitored.

The polished and degreased electrodes have been immersed into the cells with 300 ml of 10% medium. 1 ml of the inoculum from the stock culture has been added to the cells. Excepting the cells used for instantaneous polarisation studies, others used for long

term measurements have been kept in an anaerobic incubator at 303K. After measuring the open circuit potentials, the electrodes have been fixed at a cathodic overpotential of 200mV for 5 minutes to obtain a steady value. The electrodes have been scanned from a cathodic overpotential of 200mV to an anodic overpotential of 200mV at a scan rate of 1 mV \cdot s $^{-1}$

RESULTS AND DISCUSSION

Figure 1 shows the steady state polarisation data for magnesium in sterile medium recorded instantaneously, after 2 hours, after one day, after 7 days and after 20 days. In the absence of SRB, there is a cathodic shift in corrosion potential with time. There is an increase in cathodic polarisation compared to instantaneous values with time.

The effect of SRB addition on the steady state polarisation of magnesium in the above medium taken instantaneously, after 2 hours, after one day, after 7 days and after 20 days is depicted in Fig. 2. A cathodic depolarising action has been noted by the inoculation of SRB throughout the above said period. Excepting the corrosion potential taken after two hours, other values of corrosion potentials are more cathodic than that measured instantaneously. The addition of SRB activates dissolution after 2 hours and brings down dissolution rate after 1 day. The rate increases with time further.

Figure 3 shows the steady state polarisation of aluminium in sterile medium. In this case also, cathodic shift in corrosion potential and increase in cathodic polarisation with time have been observed.

Addition of SRB sterile medium enhances cathodic depolarisation of aluminium, as seen from the steady state polarisation of aluminium in SRB inoculated medium measured instantaneously, after 2 hours, after 1 day, after 7 days and after 20 days (Fig. 4).

After 2 hours, there is a decrease in dissolution rate compared to the instantaneous values. After 20 days, there is an increase in dissolution. Figure 5 shows the steady state polarisation of zinc in sterile medium. In this case also, increased cathodic polarisation over time has been observed. Steady state polarisation of zinc in SRB inoculated medium measured instantaneously, after 2 hours, after 1 day, after 7 days and after 20 days are shown in Fig. 6. Compared to sterile medium, SRB induced medium enhanced cathodic depolarising action on zinc.

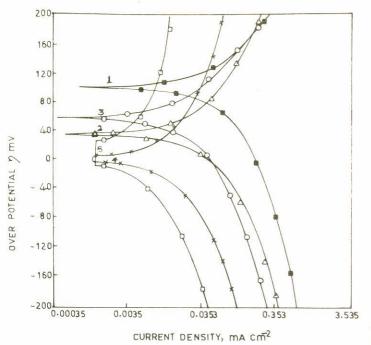


Fig. 1: Steady state polarisation of magnesium in sterile medium (1) Instantaneous polarisation (2) After 2 hours (3) After one day (4) After 7 days (5) After 20 days

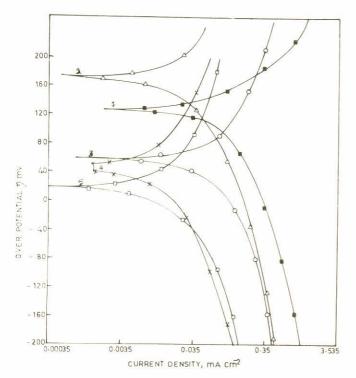


Fig. 2: Steady state polarisation of magnesium in SRB inoculated medium (1) Instantaneous polarisation (2) After 2 hours (3) After one day (4) After 7 days (5) After 20 days

The dissolution rate of zinc is brought down after 2 hours by SRB introduction. The dissolution rate after 7 days and 20 days are lesser than that observed in instantaneous measurement. There is a further increase in dissolution after 20 days compared to the instantaneous value.

The changes in dissolved oxygen content in the SRB inoculated

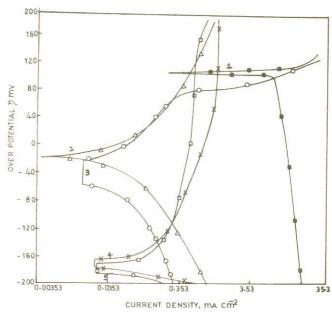


Fig. 3: Steady state polarisation of aluminium in sterile medium (1)Instantaneous polarisation (2) After 2 hours (3) After one day (4) After 7 days (5) After 20 days

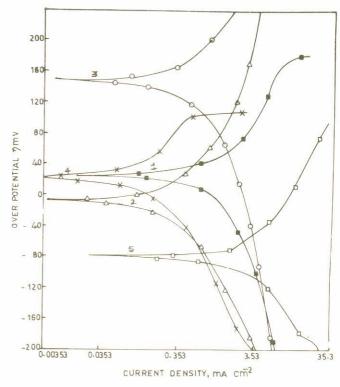


Fig. 4: Steady state polarisation of aluminium in SRB inoculated medium (1) Instantaneous polarisation (2) After 2 hours (3) After one day (4) After 7 days (5) After 20 days

cells are shown in Table I.

Intantaneously all cells introduced with magnesium, aluminium and zinc electrodes show the same value of 0.30 ppm. There is a gradual decrease in oxygen content with time. Maximum amount of depletion of oxygen has been noted in the zinc electrode introduced cell.

pH variation in different metal electrode introduced cells are brought out in Table II.

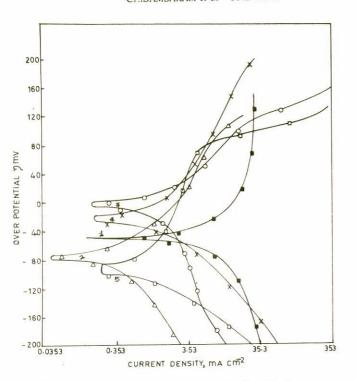


Fig. 5: Steady state polarisation of zinc in sterile medium (1) Instantaneous polarisation (2) After 2 hours (3) After one day (4) After 7 days (5) After 20 days

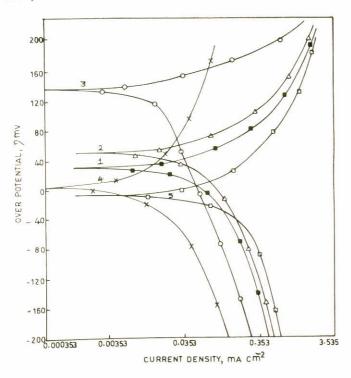


Fig. 6: Steady state polarisation of zinc in SRB inoculated medium (1) Instantaneous polarisation (2) After 2 hours (3) After one day (4) After 7 days (5) After 20 days

All cells showed an initial pH of 7. The pH of the SRB inoculated medium in presence of metal electrodes show an increase with time. Maximum increase in pH is noted in the case of zinc introduced cell followed by magnesium and aluminium.

The sulphide production with time is noted in Table III.

TABLE-I: Variation of dissolved oxygen in the SRB inoculated medium with time

Sl.No.	Duration	Dissolved oxygen(ppm)		
		Zn	Al	Mg
1.	Instantaneous	0.30	0.30	0.30
2.	After 2 hours	0.29	0.30	0.30
3.	After one day	0.25	0.29	0.27
4.	After 7 days	0.21	0.22	0.23
5.	After 20 days	0.15	0.18	0.17

TABLE-II: Variation in pH with time in SRB inoculated medium

		pH variation		
Sl.No.	Duration	Zn	Al	Mg
1	Instantaneous	7.0	7.0	7.0
2.	After 2 hours	7.1	7.0	7.0
3.	After one day	7.1	7.0	7.0
4.	After 7 days	7.4	6.9	6.9
5.	After 20 days	8.1	7.4	7.9

TABLE-III: Production of sulfide with time

	AT HIS PLANT OF THE PARTY		Sulphide lev	el(ppm)	
Sl.No.	Duration	Zn	Al	Mg	
1.	Instantaneous	100	-	-	
2.	After 2 hours		(<u>1744)</u> ()		
2. 3.	After one day	13	-	5	
4	After 7 days	106	83	90	
5.	After 20 days	124	92	110	

In sterile medium, no appreciable changes in the above variables were noticed.

Even though there is a general increase in sulphide production with time, the cell with zinc electrode generates more sulphide than with others.

The magnitude of bacterial activity with time in the cells with magnesium, aluminium and zinc electrodes are focussed in Table IV. Here also the cell with zinc electrode shows the maximum.

TABLE-IV: Increase in the magnitude of bacteria with time

SI.No.	Duration	Magnitude of bacteria (Cells.ml ⁻¹		
		Zn	Al	Mg
1	Instantaneous	102	10 ²	102
2.	After 2 hours	10^{2}	10^{2}	10^{2}
3.	After one day	10^{4}	10^{3}	10^{3}
4.	After 7 days	10^{5}	10^{4}	104
5.	After 20 days	10^{7}	10^{6}	106

The generalised reaction scheme for a bacteria induced corrosion of iron, proposed by the Von Wolzogen Kuhr etal, is,

$$\begin{array}{lll} \mbox{4Fe} \longrightarrow \mbox{4Fe}^{2+} + \mbox{8e}^{-} & (1) & \mbox{Anodic reaction} \\ \mbox{8H}_2\mbox{O} \longrightarrow \mbox{8H}^+ + \mbox{8OH}^- & (2) & \mbox{Dissociation of water} \\ \mbox{8H}^+ + \mbox{e}^- \longrightarrow \mbox{8H} & (3) & \mbox{Cathodic reaction} \\ \mbox{SO}_4^{2-} + \mbox{8H} \longrightarrow \mbox{S}^{2-} + \mbox{H}_2) & (4) & \mbox{Cathodic depolarisation} \\ \mbox{by bacteria} \end{array}$$

$$Fe^{2+} + S^{2-} \longrightarrow FeS$$
 Corrosion product (5)
 $3Fe^{2+} + 6OH^{-} \longrightarrow 3Fe(OH)_{2}$ Corrosion product (6)

$$4Fe + SO_4^{2-} + 4H_2O \longrightarrow 3Fe(OH)_2 + FeS + 2OH^-$$
 (7)

Overall reaction

In the present study, the addition of SRB enhances cathodic depolarisation of all metals. This indicates that the initial step for the attack by SRB induced corrosion in cathodic depolarisation.

Magnesium does not show any instantaneous attack by SRB. There is some inhibitive action by SRB that persists for one day. SRB induced attack has been observed after 7 days of incubation. After that, the corrosion products stifle further attack.

Aluminium shows instantaneous attack by already generated sulphide. The protective action by SRB remains for a smaller period on aluminium. SRB attack is increasing after one day to a maximum and after 7 days there is a reduction sulphide attack.

Zinc is highly prone to SRB attack. Excepting the value after two hours, which shows inhibition to sulphide attack, the rate of dissolution increases with time and comes to a steady value after 20 days. The deep pits observed visually also support this.

Magnesium alone exhibits resistance to SRB attack for more than a day. The exact time of attack requires further study.

All the data reveal that the SRB induced attack has been initiated through cathodic depolarisation. The depletion of dissolved oxygen content indicates the prevailing anaerobic conditions. The pH rise has been accompanied by the generation of OH⁻ ions at the end of the reaction.

Even though zinc is supposed to behave like SRB-cide, it is more prone to attack by SRB than magnesium and aluminium. Aluminium exhibits more resistance than the other metals.

CONCLUSION

(i) SRB induced corrosion of magnesium, aluminium and zinc is caused by initial cathodic depolarisation (ii) SRB inoculation initially inhibits corrosion of metals for some time. The inhibitive action persists on magnesium for more than a day (iii) Zinc is more prone to attack by SRB than other metals while aluminium is showing the highest resistance (iv) The rise in pH and depletion of oxygen are associated with the generation of alkali and creation of anaerobic conditions respectively (v) The order of susceptibility to SRB induced corrosion is Zn > Mg > Al.

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