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SULFATE REDUCING BACTERIA ON THE CORROSION BEHAVIOUR OF COPPER BASED CONDENSOR TUBE ALLOYS

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In the vast republic of corrosive microbes, sulfate reducing bacteria (SRB) are the most recognised and complicated consortia of anaerobic strains ever known. Some of the strains found in industrial environments are naturally resistant to toxins and also adapt themselves to thrive under high temperatures. The effect of such a strain of *Desulfovibrio*, isolated from a water flow line exposed to temperature fluctuations, on the corrosion behaviour of two copper containing alloys such as cupronickel and brass has been monitored electrochemically, at different time intervals, in 10% Postgate medium (as growth supplement) under static condition. The results support the conventional belief on the antifouling properties of the alloys experimented and also place brass as a prime alloy with greater antifouling properties compared to cupronickel.

Key words: SRB, microfouling, cathodic/anodic polarization, sulphide corrosion, microbicide.

INTRODUCTION

Copper base alloys have a long history of successful application in marine environment [1]. Perhaps case histories of microbial attack of these alloys are poorly documented than for steels or aluminium. This may, in part, be a reflection of the fact that many people have believed copper ions and salts formed by copper alloy corrosion to be lethal to most, if not all, microorganisms [2]. This is now known to be erroneous, as evidences for the copper tolerance of *Thiobacillus thiooxidans* [3] and recently *Desulfovibrio desulfuricans* [4] have been provided.

Copper alloys are frequently used for seawater piping systems and heat exchangers due to good corrosion resistance coupled with mechanical workability, excellent electrical and thermal conductivity as well as their believed antifouling property. Predictions on the paths of microbial attack on copper alloys are available in literature which include differential aeration [5], selective leaching [6], underdeposit corrosion [7], cathodic depolarisation [8], sulfide corrosion [9] and extracellular polymer production [10]. The position of the copper alloys in the antifouling scenario has become quite controversial in the recent past in view of which novel antifouling materials have been proposed [11].

Based on the above, this investigation was specifically devoted to the assessment of fouling and corrosion behaviour of cupronickel and brass exposed to a culture of SRB.

EXPERIMENTAL

The bacterial culture used in the study was isolated from a flow line of a cooling tower, identified as *desulfovibrio* spp by Desulfoviridin test [12] and cultured in postage(B) medium. The strength of the inoculum was 10^5 cells.ml^{-1} after a week. The electrochemical cell employed was as described in our previous work [13]. The electrodes used were brass (Cu 70%, zn 30%) and cupronickel (Cu 70%, Ni 30%) of one square centimeter each.

The influence of SRB on these metals have been studied immediately, after 1 hour, after 24 hours, after 168 hours and after 480 hours of immersion. Control experiments have also been carried our without SRB i.e. in the sterile culture medium. Simultaneously, the quantity of sulfide production, changes in pH and dissolved oxygen in the inoculated cells as well as the population of SRB on the electrode surface have also been monitored. The values of attached bacterial numbers were rounded up to full numbers for easy understanding of the attachment process.

Sand blasted (to accelerate microfouling through increased roughness of the surface) and degreased electrodes have been immersed into the cells with 300 ml of 10% postgate medium. 1 ml of the inoculum from the stock culture has been added to the cells allotted for SRB inoculation, while the control cells received no inocula. Excepting the cells used for instantaneous polarisation studies, others used for long term measurements have been kept in an anaerobic incubator at 303 K.

For all experimental purposes, a Wenking potentiostat POS 73 in conjunction with a potentiostat/galvanostat PAR 173 to get the current values in logarithmic units have been used. A Rikadenki XY recorder has been used to obtain the E vs logi plots. The dissolved oxygen content has been measured with the aid of Orion D.O. meter (Model S4 720) and pH has been monitored using Elico pH meter (Model LI-120). The sulfide produced has been estimated by iodimetric titration.

After measuring the open circuit potentials, the electrodes have been fixed at a cathodic overpotential of 200 mV for 5 minutes to obtain a steady state value. Then the electrodes have been scanned from a cathodic overpotential of 200 mV to an anodic overpotential of 200 mV at a scan rate of 1 mV.s^{-1}. Bacterial counting was done by the conventional scrap count assay coupled with MPN technique [13].

RESULTS AND DISCUSSION

For the easy understanding and interpretation of the bacterial contribution towards corrosion of the test metals, comparison is first made between bacteria inoculated and sterile systems individually at each time interval studied. At the second stage, comparison is made between the polarization characteristics of a single varibale at all the intervals studied. For e.g. polarization behaviour of copper exposed to SRB instantaneously, at after 124, 168 and 480 hours or polarization behaviour of copper exposed to sterile bacteriological media at the above intervals.

Figures 1 to 5 show the polarization behaviour of brass with and without SRB in Postgate medium polarized instantaneously, after 1 h, after 24 h, after 168 h and after 480 h respectively. In all the cases, excepting 480 h case, cathodic polarization has been observed in the presence of SRB. No immediate effect on anodic dissolution has been noticed till an hour after SRB inoculation; only after 24 h, anodic dissolution has been increased. Enormous anodic dissolution has been noted after 480 h.

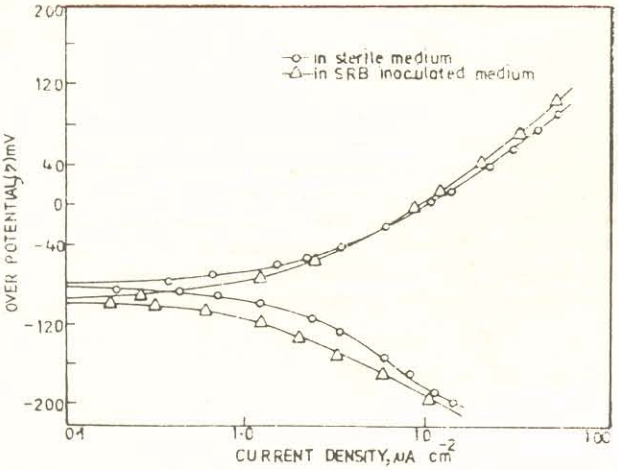

Fig. 1: Steady state polarisation of brass - instantaneous

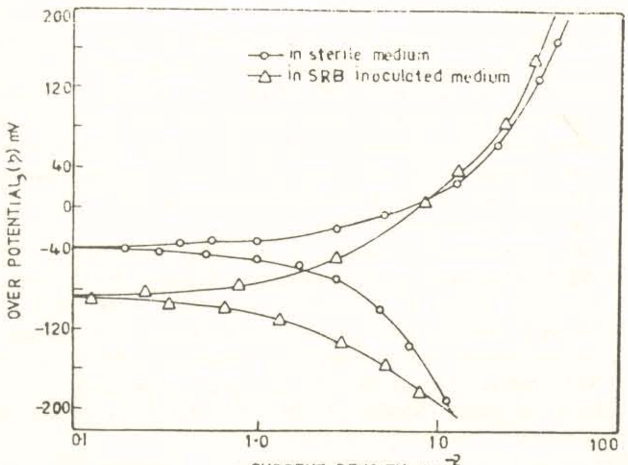

Fig. 2: Steady state polarisation of brass - after 1 h

Figures 6 and 7 compare the time dependency of polarization curves without and with the addition of SRB. With the inoculation of SRB, a decrease in corrosion current is apparent after 1 h. Increased dissolution after 24 h followed by a decrease in dissolution has been noticed after 168 h. Further the dissolution increase with time.

Figures 8 to 12 show the polarization curves of cupronickel in the Postgate medium in the presence and absence of SRB, obtained instantaneously, after 1 h, after 24 h, after 168 h and after 480 h. In this case also, the cathodic depolarization starts only after 168 h. In the initial stages, only polarization effects have been observed on the cathodic current values. Contrary to brass, in cupronickel anodic depolarization has been observed immediately after the inoculation of SRB. All the anodic polarization curves show only depolarization effects, compared to that of the sterile medium.

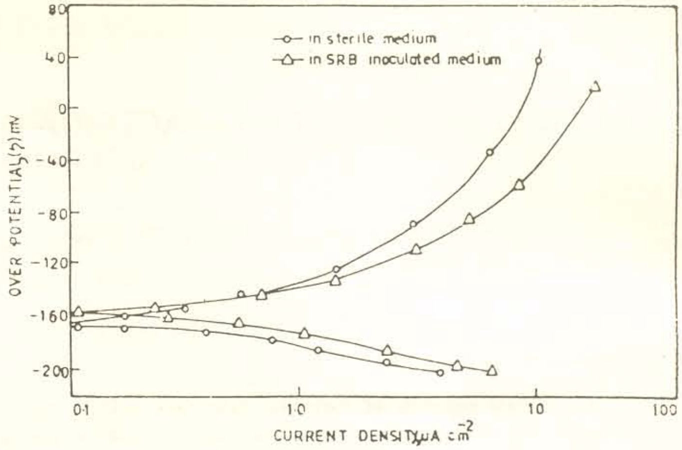

Fig. 3: Steady state polarisation of brass - after 24 h

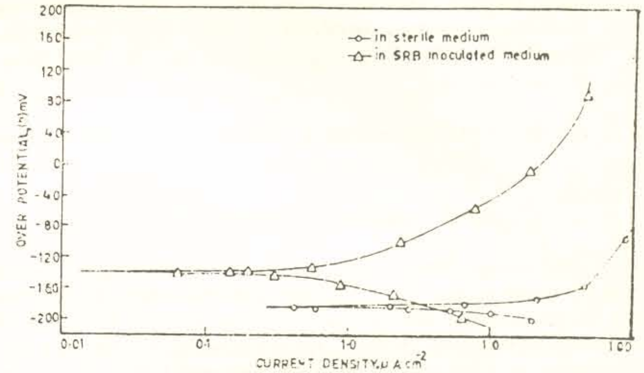

Fig. 4: Steady state polarisation of brass - after 168 h

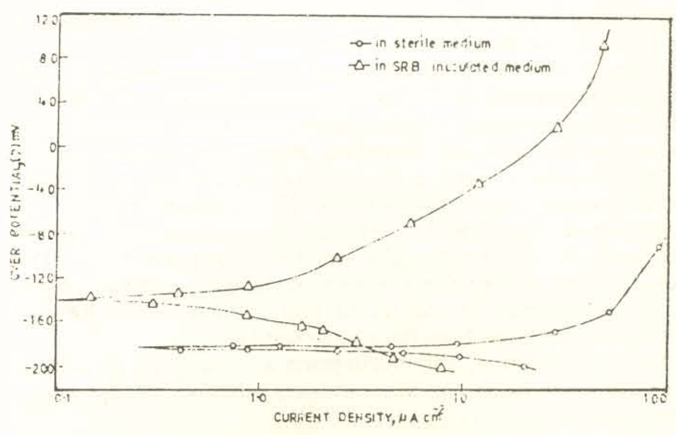

Fig. 5: Steady state polarisation of brass - after 480 h

Figures 13 and 14 explain the comparative behaviour of cupronickel in sterile and SRB inoculated medium with time. Eventhough, there was some initial decrease in the anodic dissolution upto 24 h, the dissolution increased with time thereafter.

Table I indicates the variation in dissolved oxygen in the SRB inoculated medium with time for Brass and Cupronickel. In both the cases, the depletion of oxygen with time apparent. pH variations with time in SRB inoculated cells are given in Table. II. In both the cases, a consistent increase in pH can be noticed. Table. III shows the bacteriogenic sulfide levels in the fertile medium with time. Initially, i.e., upto 24 h, the sulfide produced was in traces and thereafter the sulfide levels increased with time. The sulfide production was greater in the case of cupronickel than

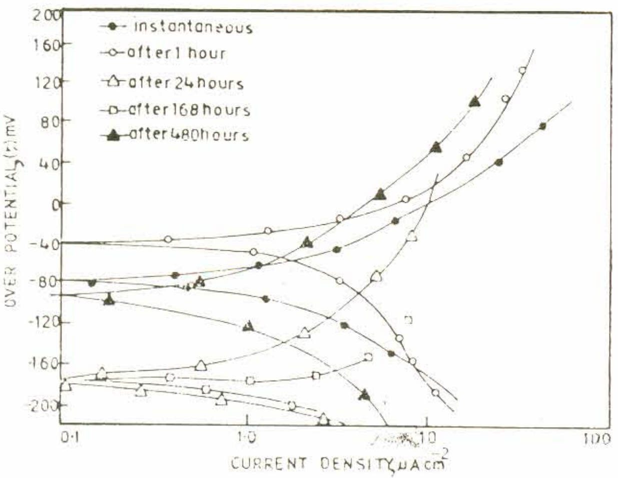

Fig. 6: Steady state polarisation of brass in sterile medium with time

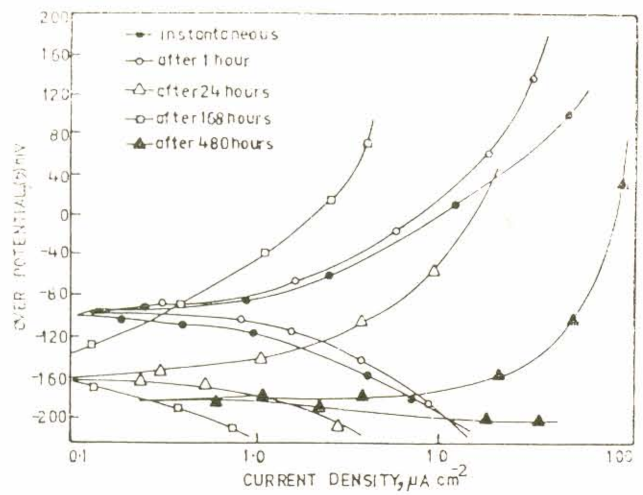

Fig. 7: Steady state polarisation of brass in SRB inoculated medium with time

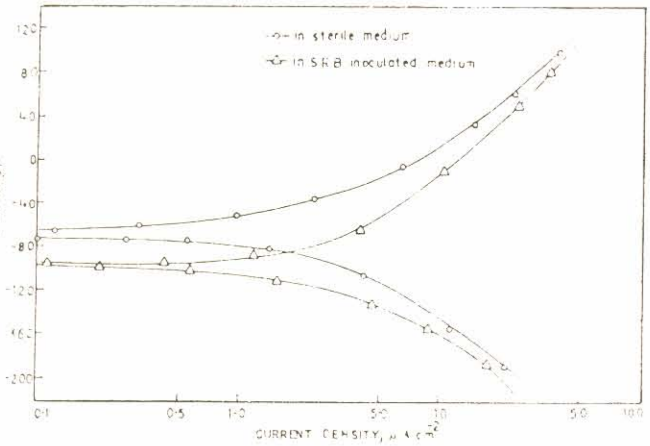

Fig. 8: Steady state polarisation of cupronickel-instantaneous

brass. The population of bacteria with time is given in Table. IV. On cupronickel, a slight increase in bacterial attachment with time is noticeable at the end of experimentation compared to brass.

The generalized type of attack by SRB has been proposed by Von Wolzogen Kuhr and Van der Vlugt [14]. The

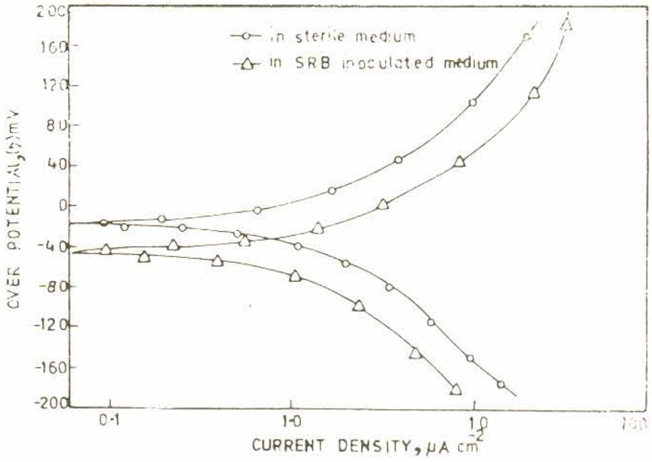

Fig. 9: Steady state polarisation of cupronickel - after 1 hour

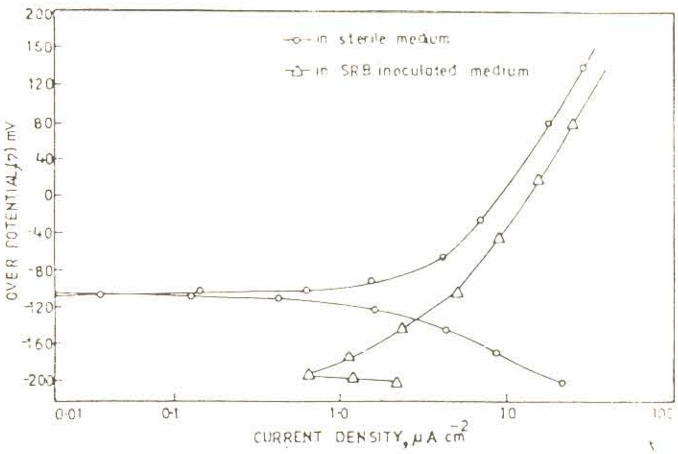

Fig. 10: Steady state polarisation of cupronickel - after 24 h

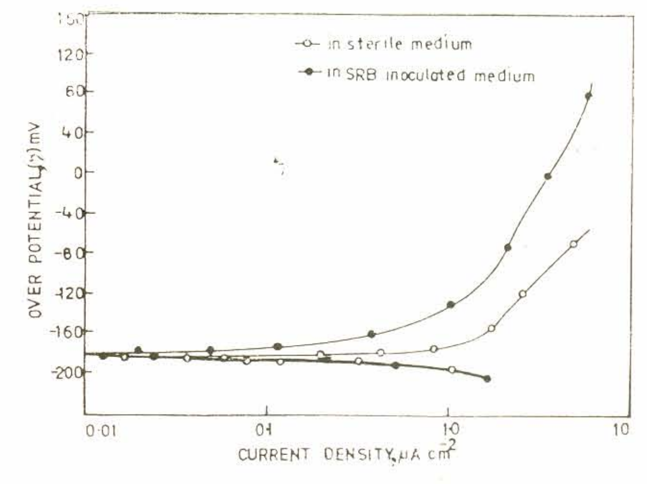

Fig. 11: Steady state polarisation of cupronickel - after 168 h

cathodic depolarization effect generally starts immediately after the inoculation of SRB in iron, magnesium, zinc and aluminium [13]. In the case of brass and cupronickel, upto 168 h only the cathodic polarization has been observed. Although the microbial attack varies from metal to metal, or alloy to alloy, this prolonged period taken for microfouling has never been reported earlier.

Probably, this might have been due to the antifouling properties of these alloys: even after reducing the culture medium

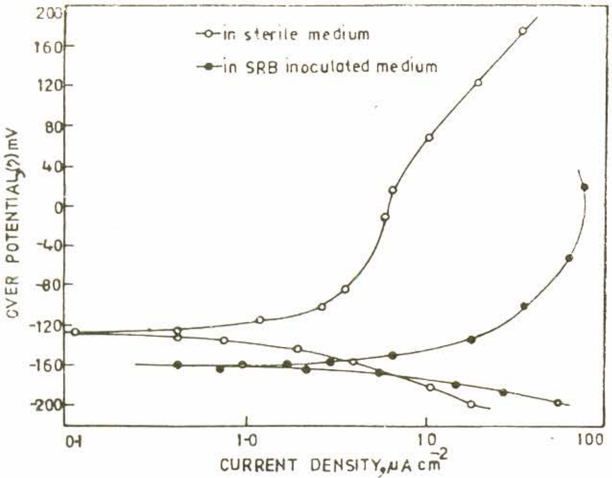

Fig. 12: Steady state polarisation of cupronickel - after 480 h

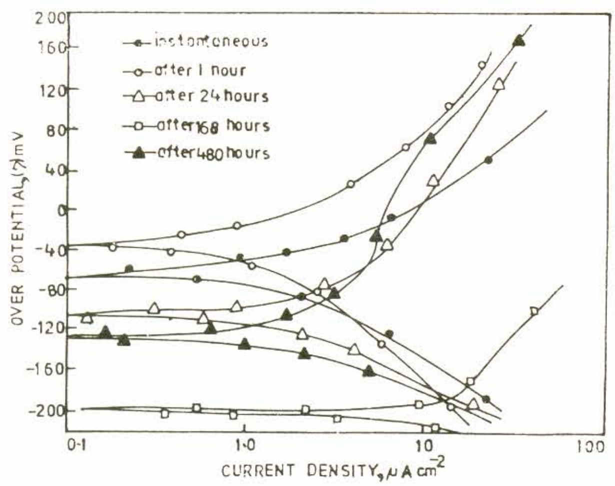

Fig. 13: Steady state polarisation of cupronickel in sterile medium with time

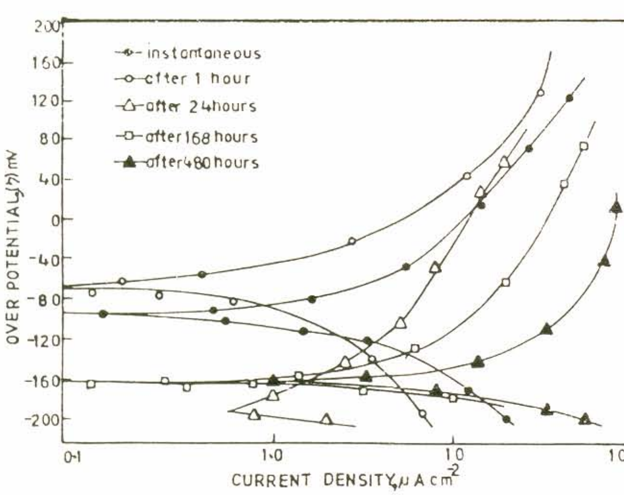

Fig. 14: Steady state polarisation of cupronickel in SRB inoculated medium with time

concentration and thereby reducing the nutrient status of the environment and also by making the metals rough by sand blasting and thereby creating the favourable conditions for microfouling, the SRB foul on the metals in significant numbers only after a week. This has been confirmed by the periodical scrap count of the electrodes (Table. IV). This point also stands for the antifouling properties of these alloys. It should be noted that in generally natural aquatic environments, the nutrient availability is limited [15]. The initial cathodic polarization can be due to the depletion of dissolved oxygen in the medium. After 168 h, the production of hydrogen sulfide, and the depolarization of cathodic hydrogen film occur and consequently the biological corrosion starts to dominate.

Brass shows more reluctance than cupronickel, towards SRB attack. In the case of cupronickel, the anodic depolarization starts immediately after the inoculation of SRB. In most of the

Table-I:Variations in dissolved oxygen content (D.O) in the SRB inoculated medium with time (ppm)

Duration	Cupronickel (70:30)	Brass (70:30)
instantaneous	0.30	0.30
after 1 h	0.30	0.30
after 24 h	0.28	0.28
after 168 h	0.22	0.21
after 480 h	0.18	0.18

Table-II:Variations in pH with time in SRB inoculated medium

Duration	Cupronickel (70:30)	Brass (70:30)
instantaneous	7.0	7.0
after 1 hour	7.0	7.0
after 24 hours	7.1	7.1
after 168 hours	7.3	7.3
after 480 hours	7.9	7.8

Table-III: Magnitude of bacteria with time (Cells.cm^2)

Duration	Cupronickel (70:30)	Brass (70:30)
instantaneous	—	—
after 1 h	—	—
after 24 h	5	5
after 168 h	101	78
after 480 h	128	103

Table-IV:Magnitude of bacteria with time (Cells.cm^2)

Duration	Cupronickel (70:30)	Brass (70:30)
instantaneous	10^2	10^2
after 1 h	10^2	10^2
after 24 h	10^3	10^2
after 168 h	10^3	10^4
after 480 h	10^7	10^6

cases SRB attack by stealing the atomic hydrogen and depolarizing the cathode. The mysterious behaviour of SRB i.e., anodic depolarization, on brass contradicts some of the previous reports [14]. The resistance shown by brass to bacterial attack can be explained in the following manner. Copper as sulfate or oxide, is a well known bactericide and also zinc at 50 ppm acts as a bactericide [16]. Hence due to a temporary, synergistic, bactericidal effect brought about by copper and zinc together, significant microfouling on brass may take place after some reasonable time, i.e., after developing resistance over that minimal bactericidal action. On the other hand, the role of nickel in this phenomenon which is equally toxic to zinc needs further study.

The SRB attack from the beginning progresses constantly with time, the dissolution of brass is observed to increase after 24 h and shows the least attack after 268 h. Again the dissolution tries to increase at 480 h. The lowering of current at 168 h would probably have occurred due to the temporary protection offered by the corrosion products on the surface of the metal.

CONCLUSION

The conventional belief on the copper alloys, regarding their antifouling nature is very true to certain extent. This fact is well exemplified by the reluctance shown by SRB to foul on these metals upto one week, even after reducing the culture medium concentration and providing other essential conditions for fouling like the creation of rough surface, etc.

Brass shows more reluctance than cupronickel, in terms of microfouling.

In cupronickel, SRB depolarizes the anode immediately after inoculation instead of depolarizing the cathode and thereby causing the anodic depolarization, contrast to the generalized mechanism proposed in the classical theory.

The activity of SRB shifts the pH towards alkaline side. Depletion of oxygen and thereby creation of anaerobic condition by SRB themselves in which these oxyphobic bacteria can thrive, is also noticeable.

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