

## Cathodic behaviour of stainless steel in coastal Indian seawater: calcareous deposits overwhelm biofilms

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Type-316 stainless steel (SS) was investigated as the cathode in galvanic couples in full-strength seawater from the Gulf of Mannar on the southeast coast of India. Tests were devised to examine the impact of SS cathodes on anode materials with or without the accrual of marine biofilms. Biofilmed SS cathodes significantly enhanced the rate of corrosion of nickel, causing noble shifts in the couple potentials. With mild steel and zinc as the anodes, calcareous deposits developed quite rapidly on the SS cathodes and led to a significant reduction of bacterial numbers. The calcareous deposits also caused substantial reduction of galvanic corrosion rates for mild steel, whereas there was no difference for zinc. The deposits were identified by XRD as essentially carbonates, oxides and hydroxides of calcium and magnesium. Potentiodynamic polarization performed on the actual couples after disconnection and equilibration provided reasonable interpretations of the galvanic corrosion trends. Data from this work suggest that a potential of about  $-0.70$  V vs. saturated calomel electrode (SCE) should provide optimum protection of SS in warmer, full-strength seawater that supports the precipitation of calcareous deposits. The criterion commonly recommended for temperate conditions of lower water temperature and estuarine waters of lower alkalinity is  $-1.0$  V (SCE).

**Keywords:** stainless steel; seawater; biofilms; galvanic couples; cathodic protection; calcareous deposit; protective potential

### Introduction

Biofilms are known to inflict significant effects on the electrochemical behaviour of stainless steels (SSs) and alloys in seawater. Little and Lee (2007) and Mansfeld (2007) have recently reviewed the literature in this subject area. It is well established that natural biofilms lead to an ennobling of the open-circuit potentials for stainless alloys by a few hundreds to several hundreds of millivolts (Mollica and Trevis 1976; Motoda et al. 1990; Dexter and Zhang 1991; Little and Mansfeld 1994; Eashwar and Maruthamuthu 1995; Dickinson et al. 1996; Scotto and Lai 1998; Baker et al. 2003; Wang et al. 2004; Mattila et al. 2007). At the same time, biofilms modify the cathodic properties of these alloys in a major way. Enhanced cathodic kinetics favours the initiation and propagation of crevice attack on the less corrosion-resistant SSs (eg Zhang and Dexter 1995). The process also leads to greater current demand for cathodic protection of SSs in natural seawater (Johnsen and Bardal 1985; Holthe et al. 1987; Little et al. 1988). In addition, the increased cathodic currents are capable of accelerating as well as sustaining the rate of corrosion of anode members in

galvanic couples (Dexter and LaFontaine 1998; Ruppel et al. 2001).

Over the years, a number of investigators (eg Scotto et al. 1985; Mollica 1992; Dexter 1995) have proposed hypothetical polarization diagrams suggesting an enhanced rate of corrosion of anodic members coupled to biofilmed SSs and alloys. The first experimental evidence to this premise came from Dexter and La Fontaine (1998) who measured galvanic corrosion rates for copper, carbon steel, aluminium and zinc coupled to AL-6XN alloy with and without the development of natural biofilms from lower Delaware Bay waters. The investigators found that biofilm accrual on the AL-6XN cathodes significantly increased the rate of corrosion of all anodic members except zinc. Following up, Ruppel et al. (2001) discussed possible mechanisms by which cathodic currents could increase. The most favoured mechanism is that biofilms act as a sink for manganese redox reactions (Dickinson et al. 1996; Olesen et al. 2000) leading to biological manganese cycling that can sustain large galvanic currents over long time periods.

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Results from the studies by Dexter and La Fontaine (1998) substantiated the widespread idea that biofilms are capable of both increasing and sustaining cathodic currents up to potentials as negative as  $-0.9$  V vs. saturated calomel electrode (SCE). In consequence, Dexter's data reinforced the  $-1.0$  V (SCE) criterion for optimal cathodic protection of SS under marine conditions. Without exception, all the above reports have come from temperate ocean conditions of relatively lower water temperatures, or from estuarine waters of lower salinity and alkalinity. In what manner biofilms influence the cathodic properties of SS and the galvanic corrosion process in tropical Indian conditions appeared a worthy topic to investigate. In this work, the effect of biofilms on the cathodic behaviour of type-316 SS during galvanic coupling with nickel, mild steel and zinc in natural seawater taken from the Gulf of Mannar on the southeast coast of India was examined.

## Method

### Study site

The present study was conducted in Mandapam on the southeast coast of India. Mandapam lies in the Gulf of Mannar region ( $9^{\circ} 16'$  North;  $79^{\circ} 9'$  East), which is presently nurtured as a national marine park. The coastal seawater in Mandapam is relatively unpolluted and the water characteristics are fairly stable except during the northeast monsoon period (October through December) when rainfall lowers salinity and alkalinity to some extent. The tidal amplitude is rather small (0.5 m or lower) and the water characteristics vary little with the tidal cycle. The period of the present study, viz. March 2006 to August 2006 and January 2007 to May 2007, corresponded to generally dry weather.

### Alloys investigated

Type-316 SS was considered as the cathode material in this work in view of its prevalent application in tropical marine conditions. The choice of anode materials, viz. nickel-200, mild steel and zinc, was based on both relevance to marine conditions and the wide range of couple potentials that seemed desirable.

Metal samples were of commercial grade, purchased from Lawrence Metal Suppliers, Chennai (India). Sheets (1 or 1.2 mm thick) were cut into coupons of desired sizes, pickled in appropriate solutions (Champion 1952), polished on motor wheels to a mirror finish, degreased in acetone, rinsed in ethanol, weighed to an accuracy of 0.1 mg and stored in desiccators until use. The nominal compositions of the alloys are given in Table 1.

### Galvanic corrosion set-up

All studies reported in this article were performed in the laboratory under low light conditions. The light level in the laboratory was approximately 50 lux as measured on a Kyoritsu Model 5200 illuminometer. Fluorescent lamps were turned on for brief periods during water renewal and electrochemical measurements. A gravity feed and overflow system was designed in which freshly sampled coastal seawater from the shoreline behind CECRI laboratory in Mandapam was continually fed from a reservoir tank (100 l) into the experimental tanks (65 l). The rate of flow was about  $10 \text{ l h}^{-1}$  which ensured complete replenishment of the water in the experimental tanks almost 4 times a day. The water was taken in arrays of 20 and 50 l jerry cans and brought to the laboratory periodically. All jerry cans, tanks, flow tubes and flow regulators had been seasoned for at least 3 months before the commencement of the experiments.

Two series of tests were conducted with a constant cathode-to-anode ratio of 8:1 and identical experimental conditions, including flow rate. In the first series of tests, galvanic corrosion rates were determined in terms of weight loss. Galvanic corrosion tests for nickel (Ni), mild steel (MS) and zinc (Zn) coupled to 316 SS were performed in separate series of tanks. The SS cathodes had exposed areas of  $10 \text{ cm} \times 10 \text{ cm}$  with  $5 \text{ cm} \times 2.5 \text{ cm}$  flags, whereas the anodes had  $10 \text{ cm} \times 2.5 \text{ cm}$  exposed areas with  $5 \text{ cm} \times 1.25 \text{ cm}$  flags. The flag portions remained above the waterline allowing room for electrical leads with copper wire and 5-mm drills for fastening. The cathodes and anodes were secured firmly onto independent wooden frames using brass bolts and nuts. Thus, each wooden frame housed three cathodes or anodes. The copper lead

Table 1. Nominal compositions of the alloys tested in the present work.

Alloys	Cr	Ni	Mo	Fe	C	Zn	Cu	Pb	Mn	P	S
316 SS	17.0	7.0	2.1	Bal.	0.07	—	—	—	—	—	—
Mild steel	—	—	—	Bal.	0.1	—	—	—	0.46	0.07	0.03
Nickel	—	Bal.	—	—	0.15	—	0.25	—	—	—	—
Zinc	—	—	—	—	—	Bal.	—	0.09	—	—	—

junctions and the bimetallic junctions with the brass bolts were coated with marine epoxy to avoid galvanic action from moisture. Figure 1a provides a schematic illustration of the sample exposure method used in the galvanic corrosion tests and, in particular, indicates the location of the air/seawater interface on the samples. The wooden frames were placed across the tank such that the cathode-to-anode separation was 7.5 cm and the samples were aligned edge-on to the flow. Couples were established using alligator clip connections as soon as the samples were immersed in the test tanks.

An effect of biofilms on galvanic corrosion was assessed in a manner similar to that employed by Dexter and LaFontaine (1998) and Ruppel et al. (2001). One set of galvanic couples remained connected throughout the exposure allowing biofilm development. In the other, cathodes were changed every 24 h. A wooden frame holding three fresh cathodes was placed adjacent to the anodes and the samples allowed to equilibrate for 45 to 60 min. The new cathodes were then connected to the anodes and the old cathodes removed at once. The removed cathodes were pickled again and stored in desiccators for subsequent use. This procedure ensured minimal development of biofilms on the set of cathodes that served as the controls. An additional set of SS samples was exposed, which remained uncoupled throughout the immersion period. The potentials of the uncoupled SS samples together with the mixed potentials of the different couples were measured on a daily basis using a high impedance voltmeter (Tektronix, Model DMM155) in conjunction with a SCE. The SCEs (type PE-77) were purchased from Protech Anode and Alloy Engineers, SIDCO Industrial Estate, Karaikudi (India), and have demonstrable precision. The SCEs were standardized by several ways such as measuring the potentials across

a series of similar SCEs (up to 5), Ag/AgCl electrodes and also by periodically measuring the open-circuit potential of zinc sheet in natural seawater as recommended by LaQue (1975).

After immersion in the seawater flow system for 64 days, the couples were disconnected. The anodes were removed, cleaned in respective solutions and reweighed for the estimation of weight loss. Corrosion rates were calculated from weight loss and surface area data in triplicate. One-way analysis of variance (ANOVA) was performed on Microcal Origin-50 software to test the significance of variations in corrosion rates between the control and biofilmed conditions at a significance level of 0.01 (calculated as statistical *p* values).

In the second series of tests, smaller samples were used wherein the cathodes and anodes had immersed areas of 25 mm × 100 mm and 12.5 mm × 25 mm, respectively. The portions of coupons above the waterline (25 mm × 25 mm and 12.5 × 12.5 mm flags, respectively) provided room for copper electrical leads with alligator clips. The samples were suspended from wooden frames with the support of the electrical leads, which fitted firmly on to grooves on the sides of the wooden frames (Figure 1b). Couples of SS with Ni, MS and Zn were immersed in separate sets of the seawater flow tanks as previously described. Here, the couples remained connected throughout the exposure. Uncoupled SS samples, in addition, were also exposed to the flow system as added controls. Ten samples of each category were used in this exposure. Potentials were not recorded everyday, but measurements were made periodically to ascertain that the smaller samples behaved in a manner similar to those in the first series of experiments. The uncoupled SS samples as well as the cathodes were used for bacterial enumeration and characterization and potentiodynamic polarization studies after exposure to the flow system for 65 days.

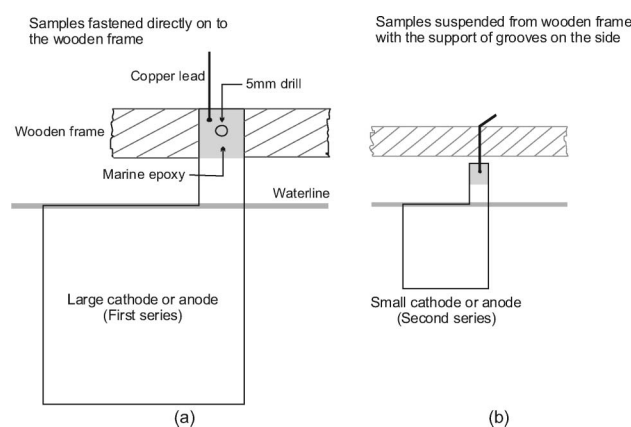


Figure 1. Schematic illustration showing sample exposure details for the first and second series of galvanic corrosion tests in seawater (a,b, respectively). Samples are not to scale in view of the size differences between cathodes and anodes.

### Seawater analysis

The physicochemical characteristics of Mandapam seawater were determined in accordance with the recommended procedures (Strickland and Parsons 1978; Grasshoff et al. 1983). Temperature was read on a standard mercury thermometer (0°C–50°C range; 0.1°C resolution), and pH readings were taken on a Hanna (Model PH211) digital pH meter. These readings were taken around noon everyday, whereas salinity and dissolved oxygen estimations were limited to fortnightly intervals. The analyses of other parameters relevant for studies of marine corrosion were made twice during the study period, one each during 2006 and 2007. In addition, the variations in temperature between ambient seawater (at the seawater sampling site) and the water in the experimental tanks

were recorded thrice everyday between 2 January 2007 and 26 March 2007. These measurements were made in the morning (9:30 h), afternoon (14:00 h) and evening periods (17:30 h). The purpose of these measurements was to ascertain the deviation in the laboratory seawater temperature from the ambient.

### **Biofilm analysis**

The biofilm material from one side of the SS samples (with the accrued calcareous deposit in the case of cathodes) was scrap-removed using a sterile nylon brush. The material was diluted with sterile seawater (0.22  $\mu\text{m}$  millipore filtration) and homogenized. Appropriate dilutions were plated on Zobelle's 2216 marine agar (Hi Media, Mumbai) in triplicate. Plates were incubated at 29°C and colony forming units (CFUs) enumerated after 72 h. ANOVA was again used for CFU comparisons among control and coupled SS samples.

Conspicuous and morphologically different colonies were picked and transferred to the same medium. This procedure was repeated until the isolates were obtained in pure culture. The isolates were stored on agar slants and characterized on the basis of a series of standard biochemical tests that comprised colony morphology, pigmentation, Gram staining, motility (hanging drop method), fermentation of lactose, sucrose and dextrose, indole-, methyl red- and VP-tests, citrate-, catalase- and oxidase-tests, and starch hydrolysis and penicillin sensitivity tests (Cappuccino and Sherman 1996).

### **Potentiodynamic polarization**

Polarization tests were made on the small cathode and anode samples after disconnection and equilibration. The uncoupled-and-biofilmed SS samples, in addition to unexposed (bare) controls, were also scanned. Potentiodynamic polarization was performed on an AUTOLAB Electrochemistry System (Model: PG Stat 30; Eco Chemie, Utrecht) at a scan rate 0.16  $\text{mV s}^{-1}$ . A conventional three-electrode system was used with platinum as the counter electrode and SCE as reference. The electrochemical cell had a volume of 1 l, and freshly collected seawater was used as the electrolyte after 0.22  $\mu\text{m}$  millipore filtration. The SS samples were polarized cathodically from their equilibrium potential to about  $-1.2$  V (SCE), whereas anode samples were anodically polarized by 300 mV.

### **Calcareous deposit analyses and scanning electron microscopy**

A further series of tests was conducted to examine the character of the calcareous deposits and their

association with the biofilm. Calcareous deposits were formed on small SS samples (exposed in triplicate) that were potentiostatically polarized at  $-0.7$  V (SCE) for 96 h in the gravity feed and overflow seawater system in the laboratory. Control SS samples in open-circuit (in triplicate) were also immersed in the system for 96 h. The calcareous deposits were analyzed on an X-ray Diffractometer (JEOL, Model JDX 8030) employing search match technique based on standard analytical references (JCPDS). The search was made for the presence of calcium and magnesium compounds at a step size of 0.017 ( $^{\circ}2\theta$ ) and a step time of 16 s.

Samples for scanning electron microscope (SEM) observations were first fixed in 5% glutaraldehyde (5% v/v 0.1 M phosphate buffer, pH 7.4) for 4 h, rinsed thrice in 0.1 M phosphate buffer, then post-fixed in a mixture of 2% glutaraldehyde and 3% formaldehyde solution (v/v 0.1 M phosphate buffer) for 1 h. The samples were then rinsed thrice with the phosphate buffer and dehydrated for 20 min each in 30, 50, 70, 90 (v/v 0.1 M phosphate buffer) and 100% acetone. The samples were sputter coated with gold and then viewed immediately on a JEOL Model JSM 35-CF SEM.

Quantitative estimations of calcium and magnesium in the deposits were performed on the large cathodes (first series of tests) after the deposits were scraped and finely powdered with a mortar and pestle. Here, the ethylene diamine tetra acetic acid titrimetric method with murexide and erichrome black-T indicators was used (APHA 1981). The thickness of the calcareous deposit formed on the small cathodes (with the accrued biofilm; second series of tests) was measured using a Minitest Thickness Detector supported by a 600 F/N probe (Elektrophysik, Model FN2, Hamburg). This device measures the distance between the bold surface of the base metal and the uppermost portion of any dry material present. On each SS sample, thickness was detected at 10 random points and averaged. The resolution of the thickness measurement was  $\pm 2$   $\mu\text{m}$ .

## **Results**

### **Water characteristics**

Seawater temperature in the test tanks varied between 27.8°C and 31.7°C during the 2006 experiments. The more systematic measurements during 2007 established that the average ambient seawater temperature under natural conditions (29.7°C  $\pm$  1.02°C) and the average water temperature in the laboratory (30.9°C  $\pm$  1.76°C) were within 1.5°C. In Table 2, some major characteristics of Mandapam coastal seawater pertinent to electrochemical reactions are presented. Notably, Mandapam seawater showed salinity variations between 32.3 and 34.7 ppt and pH ranges from 7.95 to 8.33.



### Open circuit- and couple-potentials

Figure 2 presents the open-circuit potential (OCP) trends for the control SS samples together with the mixed potentials for the various couples. Uncoupled control SS samples exhibited typical ennobling of OCP, reaching steady values between +270 and +288 mV (SCE) after immersion for 1 week all the way through the entire experimental period of 64 days. The SS-Ni couples showed considerable variation in corrosion potential trends depending on whether or not the cathode member accrued natural marine biofilms. Thus, the couple potentials stayed almost unchanged in the absence of biofilms (controls), whereas biofilm development produced noble shifts in the couple potentials. The case was different for the SS couples with MS and Zn. Here, although the couple potentials fluctuated with time, they remained the same with immersion time regardless of biofilm development on the cathode SS surfaces.

Table 2. Characteristics of Mandapam seawater during the period of this study.

Parameter	Minimum	Maximum	Average
Salinity (ppt)	32.3	34.3	33.9
pH	7.95	8.33	8.21
Dissolved oxygen (mg l <sup>-1</sup> )	5.2	6.0	5.7
Calcium (mg l <sup>-1</sup> )	426	440	432
Magnesium (mg l <sup>-1</sup> )	1195	1222	1209
Carbonate (mg l <sup>-1</sup> )	14.8	16.2	15.5
Bicarbonate (mg l <sup>-1</sup> )	166	180	172
Sulphate (mg l <sup>-1</sup> )	2180	2320	2250

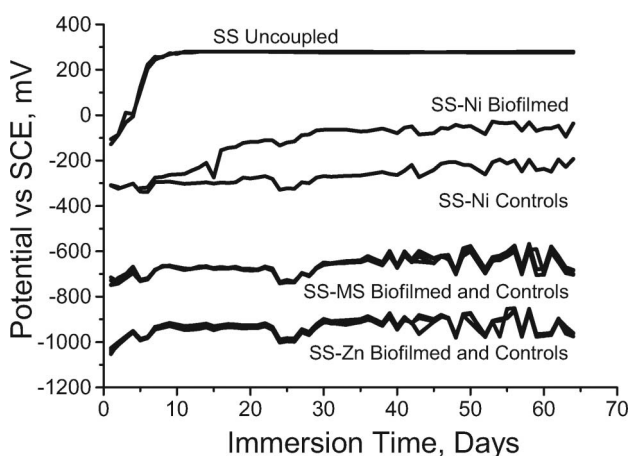


Figure 2. Open circuit potentials for uncoupled SS samples and mixed potentials for the SS couples with Ni, MS and Zn as function of immersion time in seawater.

### Corrosion rates and patterns

The condition of the test samples was carefully monitored by visual inspection throughout the exposure tests. No instances of crevice corrosion were observed at or near the air/seawater interface. The corrosion pattern on the Ni anodes was essentially in the form of pits that were distributed evenly on the samples whereas it was almost uniform on MS and Zn anodes. The rates of corrosion of the anode members in the couples with and without biofilm development on the cathode surfaces are presented in Figure 3. Predictably, the biofilmed SS cathodes led to significant increases in the corrosion rate of Ni when compared to the controls ( $p < 0.01$ ). In sharp contrast, the control anodes in the SS-MS couples suffered significantly higher corrosion rates than the biofilmed anodes ( $p < 0.01$ ). There was no significant variation in the corrosion rate of Zn anodes between the controls and the biofilmed ( $p = 0.58$ ). Calcareous deposits developed quite rapidly in the couples with MS and Zn. At times, these deposits were conspicuous even on the control cathodes at the end of 24 h when a new cathode was replaced. The deposits on the aged ('biofilmed') cathodes were particularly conspicuous, appearing much thicker on the cathodes coupled to Zn than on those coupled to MS.

### Biofilm characteristics

In Figure 4, the total culturable bacteria, ie colony-forming units (CFUs cm<sup>-2</sup>) on the uncoupled SS and the SS coupled to various anodes, are presented. The bacterial density on the uncoupled SS was of the order of 10<sup>4</sup> cells cm<sup>-2</sup>. It could be inferred from the data that the coupling with Ni produced little variation in

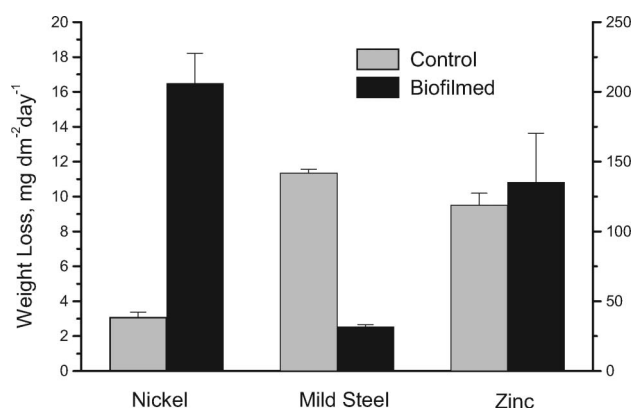


Figure 3. Rates of corrosion of anode members coupled to SS with or without biofilm development. The Y axis on the left denotes corrosion rate of Ni, and the axis on the right stands for MS and Zn. Error bars are based on triplicate samples.

the biofilm density on the cathode surface *versus* the control ( $p = 0.89$ ). The data indicate, however, that the SS surfaces in the couples with MS and Zn accrued significantly lower bacterial numbers ( $p < 0.01$  in both cases) than the control SS. These results suggest that the cathodic polarization during the coupling of the SS cathode with either MS or Zn was strong enough to discourage biofilm accumulation.

The bacterial genera that contributed to the biofilms belonged predominantly to the Gram-negative types. Thus, 65 among the 79 isolates obtained from the biofilms were Gram-negative. These comprised the rod-shaped, penicillin-sensitive and non-fermentative *Pseudomonas* spp., the coccid, pigmented and penicillin-resistant groups of *Flavobacterium* and *Cytophaga*, and the non-pigmented and penicillin-resistant rods, *Achromobacter* spp. The Gram-positive representatives were the non-motile and non-spore forming *Corynebacterium* spp. and the coccid, *Micrococcus* spp. The compositions of bacterial flora on the control and cathode SS samples were fairly similar, with *Pseudomonas* spp. contributing 55% or more in all cases.

#### Calcareous deposits and SEM

The character of the calcareous deposits as analysed by XRD is given in Figure 5. The compounds were identified as  $\text{CaCO}_3$  (calcite, aragonite and vaterite),  $\text{MgCO}_3$  (magnesite),  $\text{Mg(OH)}_2$  (brucite) and  $\text{MgO}$  (brucite). With particular reference to  $\text{CaCO}_3$ , more aragonite phases were recorded than either calcite or vaterite. The MTD data revealed the average thickness of the calcareous deposit to be  $470 \mu\text{m}$  on the SS cathodes coupled to Zn and  $290 \mu\text{m}$  on those coupled to MS after immersion for 65 days. Quantitative analytical estimates of the amounts of calcium and magnesium in the

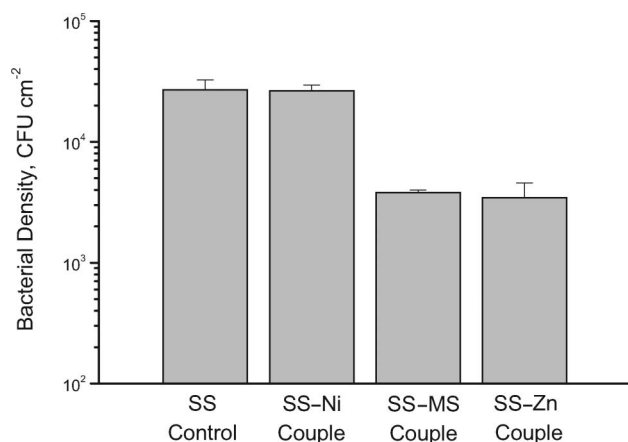


Figure 4. Biofilm bacterial densities on uncoupled (control) SS and SS cathodes with Ni, MS and Zn. Error bars are based on triplicate samples.

deposits are shown in Figure 6. Calcium occurred in markedly much higher proportions than magnesium on both cathode surfaces, although the deposition of magnesium was relatively higher on the cathode SS surfaces coupled to Zn. The level of adherence, as judged during removal of the deposits from the large cathodes, was quite good in both cases.

SEM images of biofilms and calcareous deposits on the control and cathode SS samples after 96 h immersion in seawater are shown in Figure 7a,b, respectively. The control SS sample (Figure 7a) showed aggregates of bacteria and isolated diatom cells, despite the low light conditions in the experimental set-up. The diatoms belonged to the genera *Diploneis*, *Navicula* and *Climacosphenia*. The cathode SS surface polarized to  $-0.7 \text{ V (SCE)}$  was covered with calcareous scales in

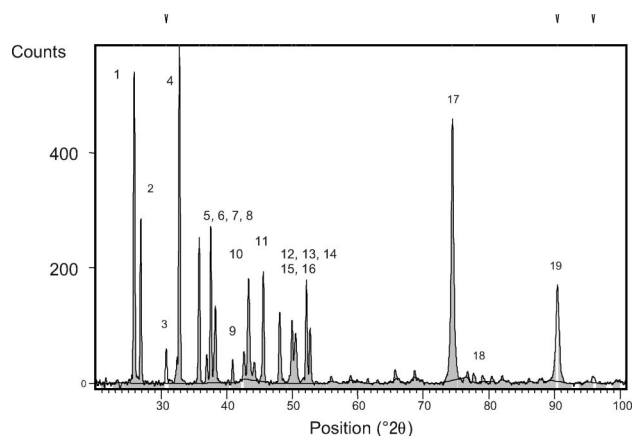


Figure 5. XRD results for small SS sample polarized to  $-0.70 \text{ V (SCE)}$  for 96 h in natural seawater revealing the forms of calcium and magnesium compounds in the calcareous deposit. The list of compounds is as follows: 1, 7, 8, 11, 12, 13, 15, 16 and 18: aragonite; 2 and 9: vaterite; 3, 5 and 10: calcite (all  $\text{CaCO}_3$ ); 4: magnesite ( $\text{MgCO}_3$ ); 6, 14 and 19: brucite [ $\text{Mg(OH)}_2$ ]; 17: brucite ( $\text{MgO}$ ).

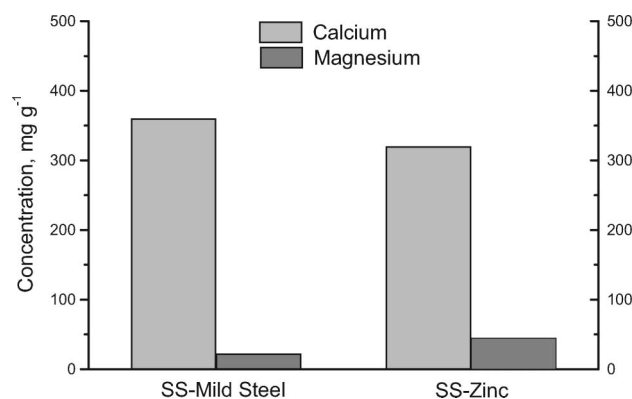
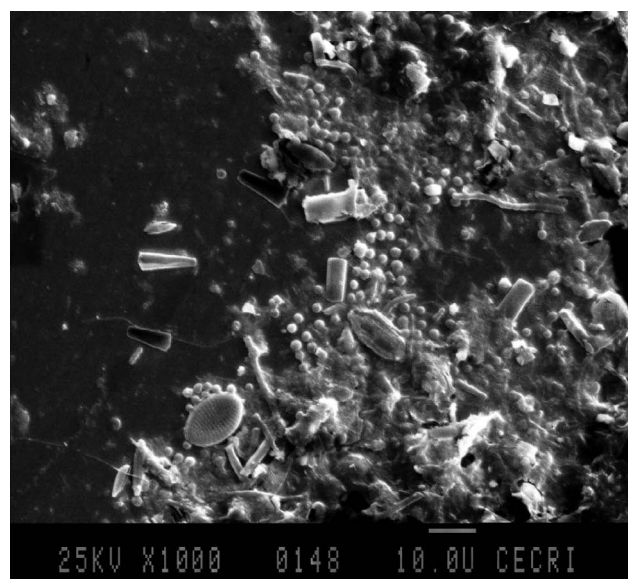


Figure 6. Relative concentrations of calcium and magnesium in the calcareous deposit formed on the SS cathodes with MS and Zn as the anodes.

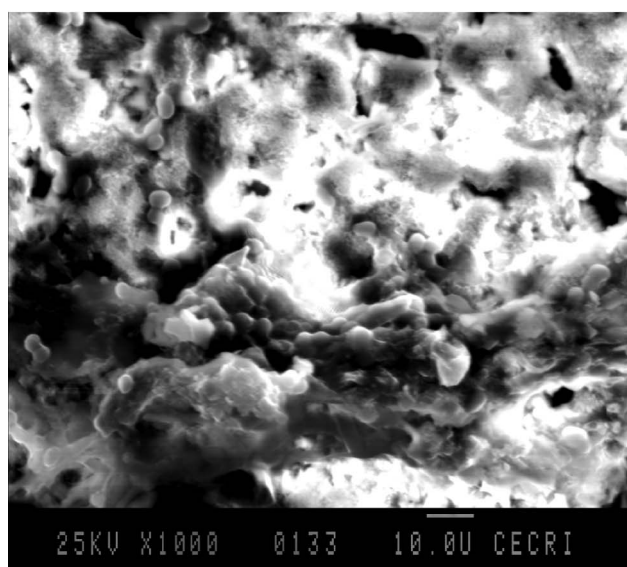
combination with scattered bacteria and diatoms (Figure 7b). Direct counts of biofilm microorganisms were not made, but the SEM observations essentially revealed that the cathode SS surface had significantly lower numbers of bacteria and diatoms than the control.

### Polarization characteristics

Figure 8a through 8d illustrates the polarization characteristics of the SS samples exposed to the



(a)



(b)

Figure 7. SEM images of uncoupled SS in open-circuit (a) and cathodically polarized SS (b) after 96 h immersion in seawater. Scale bar = 10  $\mu\text{m}$  on both images.

seawater flow system under various conditions. The polarization behaviour of bare, unexposed samples (controls) is shown in Figure 8a, accompanied by scans for biofilmed SS samples that remained uncoupled throughout the exposure. The shapes and positions of the curves indicate a noticeable increase in cathodic currents for the biofilmed samples when compared to the bare controls in the entire potential range down to about  $-1.0$  V (SCE). In Figure 8b, an additional set of polarization curves is added to the ones in Figure 8a. This set of curves (in grey) represents the SS samples that were disconnected from the couples with MS. These curves begin from more negative potentials. It must be stated here that disconnection of the galvanic couples after 65 days of seawater immersion led to potential variations in the cathode SS samples in different ways. With Ni as the anode, disconnected SS cathodes reached potentials corresponding to those of the uncoupled SS samples [about  $+280$  mV (SCE)] instantaneously. The recovery of potentials to positive values was quite slow for the SS samples coupled to MS. The most positive potentials to which these SS samples stabilized in 48 h were about  $-0.1$  V (SCE). Polarization runs were performed beginning at those stable potentials after 48 h of disconnection since further time lag would change the surface character of the samples. These curves looked different from those for the uncoupled SS samples, with much smaller currents in the region between  $0.0$  V and  $-0.4$  V (SCE). At further negative potentials, where anodic scans for MS intersected the cathodic curves, ie  $-0.6$  to  $-0.7$  V (SCE), the current densities very nearly overlapped those of the controls (Figure 8c). Polarization runs were not performed on the SS cathodes coupled to Zn as these samples did not equilibrate even

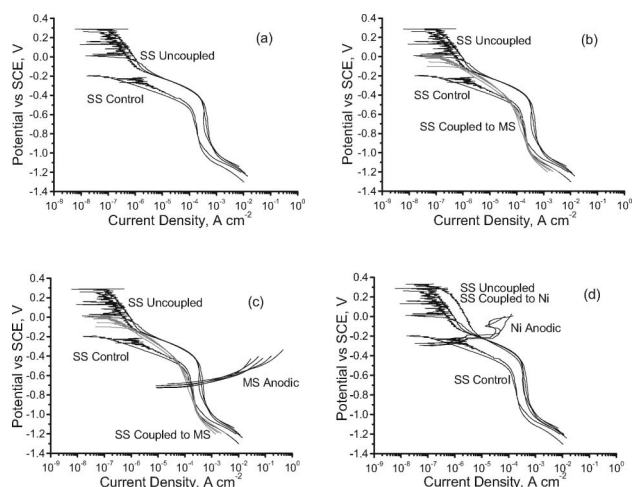


Figure 8. Potentiodynamic cathodic polarization curves for SS exposed to Mandapam seawater under various conditions and anodic polarization curves for Ni and MS.

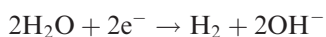
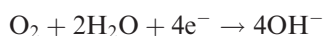
after 48 h of disconnection. This fact is an adequate indication of the potency of cathodic polarization in the present study. It is presumed that the polarization behaviour of SS (after disconnection with MS) did not truly reflect the corrosion rate measurement by weight loss because the 'driving force' of the cathodic polarization would have been different before and after disconnection.

Cathodic curves for the coupled-and-disconnected SS cathodes with Ni looked similar to the uncoupled SS samples (Figure 8d). As a result, the anodic curves for Ni intersected the two sets of cathodic curves in the same potential and current density regimes. These current densities were higher than those for the bare controls by several fold, providing faithful reproduction of the weight loss data in Figure 3.

### Discussion

The present data are consistent with the observations by many authors (eg Scotto et al. 1985; Motoda et al. 1990; Dickinson et al. 1996) that biofilms increase the cathodic kinetics of SS in seawater. Accordingly, the rate of corrosion of Ni was significantly much higher due to biofilm development when compared to 'control' conditions. However, results in this work are at variance with published information concerning the influence of biofilms at more negative potentials. The inability of cathodic biofilms to enhance the rate of corrosion of MS at potentials as positive as  $-0.7$  V (SCE) (which was the mixed potential region for the SS-MS couples in the present work) is linked to the development of calcareous deposits on the cathode surface.

For most cathodic surfaces in aerated waters such as seawater, the principal cathodic reactions are:



In either case, the production of hydroxyl ions results in an increase of pH at the metal/electrolyte interface, regardless of the presence of surface films (eg Lewandowski et al. 1989; Dexter and Lin 1992). This leads to the precipitation of calcium and magnesium according to the following reactions:



It has been well established that these deposits, once developed, offer significant protection to the

cathodic surface and serve to bring down current density requirements for cathodic protection (eg Wolfson and Hartt 1981; Hartt et al. 1984). The deposits also protect cathodic surfaces from corrosion during interruption of protective currents. The deposits are usually composed mainly of carbonates, oxides and hydroxides of calcium and magnesium as also noted in the present study (Figure 5).

The literature on the interrelationship between cathodic polarization and biofilms, as stated by Little et al. (1999) is rather confusing. Some authors (eg Guezennec 1991; Nekoksa and Gutherman 1991) have reported more bacterial settlement on cathodically protected metals than unpolarized ones, whereas others (eg Videla et al. 1993; Miyanaga et al. 2007) have reported the reverse. Maxwell (1986) did not find variations in biofilm bacterial numbers, but measured reduction of metabolic activity during cathodic polarization. Likewise, Bhosle et al. (1993) noticed that cathodic polarization negatively affected carbohydrate metabolism in a marine diatom. Little et al. (1999) have attributed such unpredictability to variations in experimental conditions such as field vs. laboratory. An added factor could be the extent of polarization employed in the different studies and the accompanying calcareous deposit formation that can vary in relation to environmental factors. Further, the morphological structure and composition of calcareous deposits can also vary depending on the type of alloy in question (eg titanium vs. SS, as illustrated by Mansfeld and Little 1991).

Under natural seawater conditions, biofilms and calcareous deposit formation occur simultaneously over cathodically protected surfaces (eg Edyvean 1984; Mansfeld et al. 1990; Little and Wagner 1993). In the present study, calcareous deposits (both calcium and magnesium compounds) formed copiously when SS was polarized to just about  $-0.7$  V (SCE). According to Hartt (2006), the near-surface pH for cathodically protected surfaces under steady-state conditions would be about 9.5 and that this pH would be sufficient for the precipitation of  $\text{Mg}(\text{OH})_2$ . This interfacial pH seems also high enough to discourage biofilm accumulation and activity since both culture techniques and direct microscopic observations in this work pointed to significant reduction of bacterial numbers on cathodic SS surfaces polarized to about  $-0.7$  V (SCE).

The potential at which calcareous deposits develop on cathodic SS surfaces in seawater and the chemistry of the water that affects the precipitation of these deposits are probably two key factors that require detailed inspection. As reviewed by Hartt et al. (1984), McGrath et al. (1987) and more recently by Johnsen (2006), salinity, pH, temperature and organic matter



are the major water quality parameters that affect calcareous deposit formation on cathodic surfaces in seawater. LaQue (1975) states 'there is reason to believe that the lower content of protective scale-forming compounds in brackish estuarine waters, often accompanied by a decrease in alkalinity, can offset the effects of a lower chloride ion concentration'. In the context of the subject under discussion, this statement is suggestive that the sharp divergence from Dexter's data was due to the radical difference in water chemistry between coastal seawater and estuarine waters. Working in estuarine waters, Dexter and LaFontaine (1998) do not mention calcareous deposit formation on cathode surfaces even at potentials as negative as  $-1.0$  V (SCE). In low saline waters, cathodic protection current densities are nearly twice that in coastal ocean waters, because calcareous deposit formation is relatively low (eg Aromaa et al. 2006). The concentrations of calcium and magnesium are also significantly altered by salinity. For instance, Palanichamy et al. (1989) found a sharp decrease in the levels of calcium and magnesium corresponding to salinity reduction in the different zones within a tropical estuary in southern India. Sen and Naik (1981) have recorded similar variations in the Zuari and Mandovi estuaries on the west coast of India.

Differences in test procedures may also contribute to variability in results. In the present work, biofilms were formed on the SS cathodes concurrently with the start of the galvanic corrosion process and this was based on the reckoning that cathodic protection generally commences once a material is put to service. On the other hand, Dexter and LaFontaine (1998) grew biofilms on the cathode samples for about a month before galvanic coupling. If the experimental conditions were reversed in the two studies being addressed, the calcareous deposits or the biofilms would still have played respective key roles, although the rate at which they functioned could have been altered (lowered) to some extent. The above statement is supported by contrasting cathodic polarization behaviour in the two investigations, which almost certainly was because of the presence or absence of calcareous deposition on cathode surfaces. Thus, it is presumed that a difference in test procedure would have had an effect only on the rapidity of the processes rather than their trends.

The relatively lower temperatures in the temperate coastal ocean waters could also affect calcareous deposit formation. For instance, Holthe et al. (1987) noticed only scattered calcareous deposits mixed with the biofilm layer at potentials as negative as  $-0.8$  V (SCE). Only at potentials  $-1.0$  V (SCE) or more negative did these investigators observe copious deposition. Holthe et al. (1987) also noticed that only the deposits

that formed at  $-1.0$  V (SCE) offered the best protection. In the present work, the calcareous deposition that occurred at potentials around  $-0.7$  V (SCE) was enough to offer good protection, although that which formed at about  $-1.0$  V (SCE) was much thicker.

It would be worth considering the optimum temperature for a discernible biological influence on cathodic kinetics and the ceiling up to which such an effect would continue to exist. From tests with Norwegian coastal waters, Holthe et al. (1987) suggested that the maximal biological influence was at temperatures around  $25^{\circ}\text{C}$  and that the effect vanished at about  $30^{\circ}\text{C}$ . On the basis of experiments in relatively warmer waters from the Mediterranean, Mollica et al. (1989) noticed a maximal effect from biofilms at a water temperature of about  $30^{\circ}\text{C}$  and that biofilms were still capable of producing conspicuous effects at  $35^{\circ}\text{C}$ . From a water temperature point of view, the amount of deviation from the ambient is probably more critical than the absolute temperature itself. From this perception, it is believed that the average ambient seawater temperature under natural conditions ( $29.7^{\circ}\text{C} \pm 1.02^{\circ}\text{C}$ ) and the average water temperature in the laboratory ( $30.9^{\circ}\text{C} \pm 1.76^{\circ}\text{C}$ ), which were within  $1.5^{\circ}\text{C}$ , warrant a good level of demonstrability in the present data. Perhaps, a difference of about  $5^{\circ}\text{C}$  would have rendered the data somewhat disputable.

Collectively, the data in this work suggest that potentials close to  $-0.7$  V (SCE) should be adequate for the optimal protection of SS in warmer, full-strength seawater that supports the precipitation of calcareous scales. This potential seems adequate to offset biological effects, against the  $-1.0$  V (SCE) criterion normally recommended for temperate ocean conditions of lower water temperatures and estuarine waters of lower alkalinity. This recommendation is based on tests performed for a little over 2 months with reference to conditions of microbial biofilm formation and would thus be relevant for situations where macrofouling is excluded. In general, microbial biofilms are acknowledged to play a more critical role in cathodic protection than macroorganisms. The suggested protection criterion sounds reasonable in terms of current density requirements and the economics of cathodic protection for the reason that more than a 4-fold reduction in anode consumption rate was noted for MS with calcareous deposition on the cathode SS surface than without it (Figure 3). Further, the higher Ca:Mg ratio of the deposit in the couple with MS rather than with Zn (Figure 6) is suggestive of its better 'scale quality' and protective nature (Hartt et al. 1984; Okstad et al. 2007) that would provide the lower current density requirement for cathodic protection. The minor deviation in corrosion rates for zinc with or

without a calcareous deposit on the cathode SS surface provides added significance to the suggested protection criterion. The effect of macrofouling on current density requirements and the stability of calcareous deposits remains to be investigated. Thus, the long-term prediction would require further studies under conditions of natural immersion in the sea.

### Conclusions

Galvanic corrosion rates for Ni, MS and Zn coupled to 316 SS were measured with and without the accrual of marine biofilms in the coastal waters of Mandapam on the southeast coast of India. Biofilms caused significant acceleration of galvanic corrosion rate for Ni. With MS and Zn as the anodes, calcareous deposits developed rapidly on the SS cathodes and led to significant reduction of biofilm density. The calcareous deposits, which were identified as chiefly  $\text{CaCO}_3$  and  $\text{Mg}(\text{OH})_2$ , also caused a substantial reduction of galvanic corrosion rates for MS, whereas there was no difference for Zn.

Potentiodynamic polarization curves provided sufficient corroboration of the weight loss data. It is concluded that in the relatively warmer coastal waters of India, the criterion for cathodic protection of SS could be reduced to about  $-0.7$  V (SCE) from the  $-1.0$  V (SCE) required for temperate ocean water conditions.

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