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Cathodic protection of carbon steel in natural seawater: Effect of sunlight radiation

Alessandro Benedetti[a,*], Luca Magagnin[b], Francesca Passaretti[c], Elisabetta Chelossi[d], Marco Faimali[d], Giampiero Montesperelli[e]

[a] *Istituto per l'Energetica e le Interfasi, IENI – CNR, Milano, via Roberto Cozzi 53 20125 Milano, Italy*
[b] *Dip. Chimica, Materiali e Ing. Chimica G. Natta, Politecnico di Milano, via Mancinelli 7, 20131 Milano, Italy*
[c] *Istituto per l'Energetica e le Interfasi IENI – CNR, Lecco, c.so Promessi Sposi 29, 23900 Lecco, Italy*
[d] *Istituto di Scienze Marine, ISMAR– CNR - Via De Marini 6, 16149, Genova, Italy*
[e] *Università di Roma – Tor Vergata, Dipartimento di Scienze e Tecnologie Chimiche, Via della Ricerca Scientifica 00133, Roma, Italy*

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ABSTRACT

Cathodic protection of metals in seawater is known to be influenced by chemical–physical parameters affecting cathodic processes (oxygen discharge, hydrogen evolution and calcareous deposit precipitation). In shallow seawater, these parameters are influenced by sunlight photoperiod and photosynthetic activity. The results presented here represent the first step in studies dedicated to cathodic protection in shallow photic seawater. This paper reports on carbon steel protected at −850 mV *vs.* Ag/AgCl (oxygen limiting current regime) in the presence of sunlight radiation but in the absence of biological and photosynthetic activity, the role of which deserves future research. Comparison of results obtained by exposing electrochemical cells to daylight cycles in both biologically inactivated natural seawater and in NaCl 3.5 wt.% solutions showed that sunlight affects current densities and that calcareous deposit interfere with light-currents effects. Sunlight radiation and induced heating of the solution have been separated, highlighting results not otherwise obvious: (1) observed current waves concomitant with sunlight radiation depend fundamentally on solar radiation, (2) solar radiation can determine current enhancements from early to late phases of aragonite crystal growth, (3) a three-day-old $CaCO_3$ layer reduces but does not eliminate the amplitude of the current waves. Theoretical calculations for oxygen limiting currents and additional field tests showed that sunlight, rather than bulk solution heating, is the main cause of daily current enhancements. This was confirmed by polarizations performed at −850 and −1000 mV *vs.* Ag/AgCl (constant bulk temperature), during which the electrode was irradiated with artificial lighting. This test also confirmed O_2 discharge to be the cathodic process involved. A mechanism of radiation conversion to heat in the oxygen diffusion layer region is proposed.

1. Introduction

The protection of metals in seawater is obtained by making the structure work as a cathode with impressed current or by coupling to a less noble metal. The second method is preferentially used in seawater, with sacrificial anodes of aluminum-, zinc- or magnesium-based alloys.

Recently, protection techniques involving nontraditional approaches such as photo-electrochemistry [1,2] and marine sediments [3] have been studied. Whatever the source of electrons, the current requirement for the protection of metallic structures in aerobic environments is controlled by oxygen coming into contact with the surfaces [4]. The oxygen discharge occurs *via* a two-electron mechanism with the formation of H_2O_2 as an intermediate until about −900 mV *vs.* SCE; for higher cathodic potentials, it occurs *via* a four-electron mechanism to form OH^- directly [5]. At lower cathodic potentials, a four-electron reduction mechanism was obtained along with H_2O_2 residual formation with a pre-reducing cathodic polarization [6].

The increase of OH^- in seawater as a result of cathodic polarization shifts the $HCO_3{}^-/CO_3{}^{2-}$ equilibrium towards the formation of $CO_3{}^{2-}$, inducing the precipitation of $CaCO_3$ [7]. Furthermore, if the pH value of 9.5 is reached through more cathodic polarization, $Mg(OH)_2$ starts to precipitate [8].

Calcareous deposit growth reduces oxygen diffusion towards the metal. As a consequence, the lower current requirement necessary for sustaining the protection potential represents an economic advantage.

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[*] Corresponding author. Tel.: +39 3336196808; fax: +39 2 66173321.
E-mail address: alessandro.benedetti@cnr.it (A. Benedetti).

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The most protective deposits are obtained at more cathodic potentials [8–10] until the hydrogen evolution starts to mechanically compromise the deposited minerals to the point of mechanical failure [11].

Even if the $CaCO_3$ is supersaturated in seawater [12], various substances are a kinetic hindrance preventing $CaCO_3$ spontaneous precipitation: this process requires energy.

From an electrochemical point of view, the kinetic roles of PO_4^{3-}, organic compounds, Mg^{2+} [8] and SO_4^{2-} [13] were investigated. Magnesium ions are able to block the precipitation of calcite (the most stable $CaCO_3$ phase) [14] by inducing morphological variations in its crystal geometry [15]. Concerning aragonite, Mg^{2+} inhibits nucleation but not the following crystal growth [16]. Investigations have been carried out to better understand the precipitation of Ca and Mg salts on cathodically protected metals [17,18,19].

The protective characteristics of calcareous deposits depend on how the precipitation mechanism interacts with surrounding conditions.

The effects of hydrodynamic regime [20,21], temperature [13,16] and pressure [22,23] have been investigated. In natural environments, a particular role is played by biology. At least since the mid-seventies [24], it has been known that if no polarization is imposed, the presence of biofilm strongly affects the electrochemical behavior of metals, inducing the ennoblement of active–passive alloys. The underlying mechanism of OCP ennoblement has still not been fully explained. Consequently, the matter has been the object of many investigations because of its significance in microbiologically induced corrosion (MIC) [25–31]. Recently, Faimali et al. [32] found a correlation among depolarization phenomena, bacterial colony growth and different applied potentials.

If a cathodic potential is applied, the interactions among cathodic currents, calcareous deposits and biofilms are highly complex. Important results have been achieved by highlighting bacterial interactions with cathodically protected pre-fouled metal [33] and with cathodically polarized naked metals [34,35].

To the best of our knowledge, cathodic protection in the environment of photic shallow seawater has not yet been studied. Sunlight radiation induces daily and seasonal cyclic modifications of physical and chemical parameters characterizing shallow seawater. How do cathodic processes depending on sunlight radiation itself behave? How do they behave in relation to induced thermal excursions? The photoperiod induces biologically mediated variation of O_2, pH, Mg^{2+}, PO_4^{3-}, and SO_4^{2-}, i.e., parameters affecting cathodic processes at the metal-seawater interface. Furthermore, biofilm, whose activity can be influenced by sunlight [36], is able to transform vertical profiles of current velocity and dissolved oxygen saturation [37].

How do the main cathodic processes behave under these conditions, considering that what happens on a metal surface in the presence of calcareous deposits can be mediated by biological layers once they colonize the calcareous deposits?

The off-shore oil industry is a very important field concerning the application of cathodic protection techniques. Cathodic protection in irradiated shallow seawater appears not to be a relevant topic for this field due to the negligible quantitative importance of the photic zone with respect to the whole vertical development of extractive plants. Nevertheless, in light of the limited information on the photic zone effects, it would be interesting to characterize this area and to evaluate its real contribution to CP. In shallow irradiated seawater, the parameters affecting cathodic processes can be influenced by (1) daily and seasonal radiation and induced heating cycles alone and (2) radiation and induced heating along with the mediation of photobiology. Sunlight and temperature can affect the rate of cathodic reactions, while biofouling can modify the oxygen balance at the electrode surface. In this case, the biolayer can play both passive functions (a mere mechanical shield of O_2 diffusing from the bulk) and active functions (local O_2 balance modifications through photosynthetic activity).

This paper presents field tests in which electrochemical cells are exposed to daylight cycles utilizing biologically inactivated natural seawater. In this way, control conditions for CP in photic seawater are investigated by focusing on how sunlight radiation affects cathodic seawater electrochemistry, under conditions where photosynthetic processes would normally be stimulated but in the absence of biological contributions. The role of biofouling will be investigated with further experiments.

Particular attention was paid to oxygen, since O_2 is simultaneously the main cathodic reactant at the potential considered and a key molecule in the aerobic environment. Focusing on oxygen discharge is important in order to determine reference conditions because (1) hydrogen evolution as the dominant cathodic process cannot be excluded *a priori* in the range of CP potentials [38] and 2) physical-chemical parameters affect in different ways the involved cathodic processes.

2. Experimental

Electrochemical tests were performed at the MARECO IENI-CNR marine station, located in Bonassola, on the Ligurian Coast of the Mediterranean Sea. Far from harbors and close to the national Marine Protected Area of "Cinque Terre," the sea laboratory provides natural seawater feeding tanks placed both inside the laboratory and on the roof. Here, photosynthetic biology is allowed to develop due to the tanks' exposure to the natural photoperiod.

Cathodic polarizations were performed on samples cut from $\phi = 10$ mm commercial carbon steel bars, with an exposed area of $0.785\,cm^2$. Surface finishing was performed with 120 grit paper. The anode was a platinum wire, and the reference was an Ag/AgCl electrode.

Field polarization tests were performed imposing for 70 h the potential of −850 mV *vs.* Ag/AgCl for oxygen limiting discharge currents (i_L) as individuated in a dynamic scan (room temperature, 1000 mV/h scan rate, explored potential range OCP/−1200 mV *vs.* Ag/AgCl), as shown in Fig. 7.

The apparatus for electrochemical investigations consisted of AMEL mod. 2051 potentiostats connected to personal computer with digital interfaces AMEL mod. 7800.

The experiments were performed in a 60 L tank filled with natural seawater and in a 5 L cell containing NaCl 3.5 wt.%. Both tanks were placed on the laboratory roof and exposed to the photoperiod. All polarizations were performed in quiescent conditions.

The working electrode was placed at an immersion depth of about 15 cm, and its surface was turned in order to allow it to receive the most intense sunlight at the zenith hour. The plane electrode resulted in a 45° angle with respect to the water plane. In order to make the heating caused by the illumination over the NaCl 3.5 wt.% 5 L cell comparable to that in the other tank, this cell was placed in a 60 L tank filled with seawater (thermostatic function). Direct sunlight started around 8.00 a.m. and lasted until early afternoon (around 2.30 p.m.), ending because of the disappearance of the sun behind a hill.

The natural seawater was biologically inactivated with an isothiazolin-based additive after the tank was filled, and no filtration was made. The treatment is the same as that employed for corrosion resistance tests in seawater by Gusmano et al. [39]. Following the supplier's (Nalco Italiana) instructions, a concentration of 5 ppm was used to guarantee a biocide effect. The absence of electrochemical effects induced by the biocide at the potential investigated here was ascertained by statically polarizing a carbon steel electrode at −850 mV *vs.* Ag/AgCl in NaCl 3.5% solution (acquisition rate 2 points/s). The test was performed as follows: once the