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Non-isothermal effects induced by natural illumination and infrared irradiation on cathodically polarized carbon steel electrodes

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ABSTRACT

Experimental–theoretical approach was developed to analyse the heating behavior of carbon steel electrodes cathodically protected in quiescent NaCl 3.5 wt.% solution and exposed to irradiation. Natural and infrared wavelengths induced an increase of electrode surface temperature, enabling to determine oxygen limiting current enhancement. Numerical simulations of laboratory tests performed with infrared wavelength indicated that the Nusselt number ranges between 3.5 and 6, revealing the convective nature of the irradiation depolarization effect. The results obtained in NaCl 3.5 wt.% solution permit us to state that in seawater environment the sunlight depolarizing effect does not affect the current demand for cathodic protection.

1. Introduction

At potentials usually adopted for the protection of steel structures in seawater (ranging between −800 and −1100 mV vs. Ag/AgCl [1]), the main cathodic processes are oxygen and water reduction:

$$O_2 + H_2O + 4e^- \rightarrow 4OH^- \tag{1}$$

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \tag{2}$$

In NaCl 3.5 wt.% quiescent solution, at the oxygen plateau potential the circulating current is limited by the oxygen transport. In real seawater, the current requirement necessary to sustain the protection potential can be modified by variables that influence the oxygen availability at the polarized metal. In this environment, the oxygen transport and availability at the metal surface depend mainly on the forced convection, provided by flowing seawater currents, and on the calcareous deposit growing on cathodically polarized metals.

Due to the alkalinity generated by oxygen and hydrogen discharge (Eqs. (1) and (2)), a mineral layer consisting in $CaCO_3$ and $Mg(OH)_2$ accretes on the polarized metal surface, with $Mg(OH)_2$ prevailing at more cathodic potentials [2]. The calcareous deposit allows a reduction of the current necessary to maintain the protection potential [3,4] making the oxygen transport towards the polarized metal more difficult. On the other hand, until the calcareous deposit is not developed, or is damaged once it is formed, seawater currents increase the oxygen transport inducing depolarization effects.

Among environmental parameters affecting cathodic processes [5–11], it can be asked if the sunlight has some effect for a cathodically protected metal structure vertically developed until a depth of 100 m [12]. Indeed, photosynthetic active radiation (PAR, $400 \leqslant \lambda \leqslant 700$ nm) is attenuated by a factor e^{-1} at a depth of 40.5 m in clear seawater [13].

To the best of our knowledge, only two works exist dealing with sunlight effects on cathodic protection [14,15]. As a matter of fact, from literature it is known that in cathodic protection applications sunlight was exploited as a power source [16–18] and was investigated in non-sacrificial photoanode technology [19–21]. In general, the inhibition of pitting corrosion promoted by UV irradiation [22–25] and natural illumination [26] were investigated.

In Ref. [15], it was shown that 5% of the PAR peaking at noon hour improved the protectiveness of the calcareous deposit on stainless steel protected by coupling with carbon steel. Two hypotheses were proposed. The first, regarding sunlight stimulating stainless steel semiconductive behavior, appears unlikely. Indeed, at the coupling protection potential of about −700 mV vs. SCE the outer part of the passive layer behaves as a conductor [27], and the circulating currents are limited by oxygen transport [15,26,28,29] rather than by activation barrier. The second hypothesis, regarding a better calcification promoted by the photosyn-

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Nomenclature

A	electrode cross sectional area
c	specific heat
C_E	excess of charge made to be exchanged by sunlight illumination
D	oxygen diffusion coefficient
d	electrode diameter
h	convection heat transfer coefficient
K	electrode thermal conductivity
K_s	thermal conductivity of the solution
I_0	radiant power effectively absorbed at the electrode surface
i_L	oxygen limiting current
$i_{L,diff}$	oxygen limiting current where the mass transport is limited by diffusion only
I_{PAR}	irradiation power of the photosynthetic active radiation (PAR, $400 \leqslant \lambda \leqslant 700$ nm)
L	characteristic length
N_u	Nusselt number
r_{cs}	carbon steel surface reflectivity
r_s	reflectivity of the NaCl 3.5 wt.% solution
S	sample perimeter
s_b	depth of the seawater column
T_{bulk}	temperature of the bulk of the solution
$T_{bulk,s}$	temperature of the bulk of the solution when enhanced by sunlight illumination
$T_{bulk,d}$	temperature of the bulk of the solution in the dark (absence of sunlight illumination)
t_f	temporal duration of the illuminated part of a natural photoperiod
T_1	thermocouple placed 0.7 mm beneath the irradiated surface of the electrode
T_2	thermocouple placed at a distance of 1.5 mm from the electrode lateral surface for the measure of T_w
T_{el}	temperature of the irradiated electrode surface
T_w	temperature of the solution at a distance of 1.5 mm from the electrode lateral surface
W_a	part of W_t sent to the power meter
W_b	part of W_t impinging the surface of the NaCl solution
W_t	laser power ($\lambda = 980$ nm) emitted by a laser diode system (LW-30250)
x	distance from the electrode surface irradiated by the laser beam
x_0	electrode surface irradiated by the laser beam
x_e	electrode surface opposite to the irradiated one
δ_{diff}	diffusion boundary layer
δ_{eff}	effective mass transport boundary layer
ε	electrode surface emissivity
$\Delta i_{L,conv}$	difference between i_L under irradiation and i_L in the dark (when T_{bulk} = cost)
$\Delta i_{L,diff}$	enhancement of i_L depending on T_{bulk} increase (when I_0=0)
ΔT_{el}	difference between T_{el} and T_{bulk}
ΔT_w	difference between T_w and T_{bulk}
ϑ	I_{PAR} fraction due to attenuation along the seawater column
ρ	electrode density (carbon steel)
τ_s	transmission coefficient of the NaCl 3.5 wt.% solution

thetic activity of colonizing microorganisms appears more credible.

The presenting authors performed initial investigations concerning sunlight effects on cathodic protection [14]. Larger currents were observed in presence of natural illumination (carbon steel, quiescent NaCl 3.5 wt.% solution). A modification of the oxygen transport at the irradiated electrode interface was proposed as the governing mechanism.

Improvements adopted here with respect to [14] consisted in the collection of polarization data at a higher acquisition rate (10^{-1} Hz vs. 4×10^{-3} Hz in [14]), and in monitoring PAR and bulk temperature data as well. The phenomena observed during field tests were reproduced in the laboratory by using infrared radiation as heating source. Numerical simulations of the electrode heating behavior were performed, revealing the convective nature of the depolarization effect in presence of both natural and artificial irradiation. Hence, once the irradiation effect was highlighted in NaCl 3.5 wt.% solution, the direct influence of the sunlight illumination on cathodic protection in a real seawater condition was verified accounting for differences between the NaCl and the seawater environments.

2. Experimental method

2.1. Electrochemical setup

The configuration of the electrochemical cell, used for both field and laboratory experiments, is described as follows. The polarization tests were performed in a 10 l glass recipient filled with quiescent NaCl 3.5 wt.% solution (NaCl solution, throughout the text). The working electrode was made of carbon steel (14 mm diameter, 5 mm thickness), and was positioned maintaining horizontal the irradiated surface. The electrode sides as well as the electrical contacts were isolated with epoxy resin. The anode was a platinum wire and the reference was a saturated Ag/AgCl electrode. The amperometric curves were obtained imposing −850 mV vs. Ag/AgCl with AMEL mod. 2051 potentiostat. Details concerning the acquisition systems and procedures for the different experiments are successively provided.

2.2. Field tests

Polarizations were performed in the MARECO IENI-CNR marine station in Bonassola (44°11′00″N, 9°35′00″E), on the Ligurian Coast of the Mediterranean Sea, exposing the electrochemical cell to a natural photoperiod in mid season. The power of visible wavelengths, I_{PAR} (W m^{-2}), and the temperature of the bulk, T_{bulk} (°C), were collected during polarization tests with underwater spherical quantum sensor Licor Li-193 and a thermometer probe, both connected to a Campbell Scientific data logging device. The probes and the electrode were placed 5 cm below the NaCl solution surface. I_{PAR} and T_{bulk} data, as well as amperometric data, were acquired at the frequency of 0.1 Hz.

In order to evaluate sunlight influences, two polarization tests were performed around noon hour. In the first test, the electrochemical cell was exposed to the sunlight and was covered 3 times. In the second test, the cell worked covered and was illuminated for 4 times. Obscuration as well as illumination periods in the first and the second test respectively lasted 10 min. The time separating illumination and obscuration periods in both tests was 20 min. The dark performed with a box hindering the sunlight illumination was guaranteed assuring that $0.1 < I_{PAR} < 1$ W m^{-2}.

2.3. Laboratory tests

In order to design the configuration of the experimental apparatus, the knowledge of the most effective parameters featuring the