Calcareous deposit precipitation on cathodically polarized carbon steel in natural seawater exposed to daylight cycles

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ABSTRACT

This paper deals with calcareous deposit precipitation occurring on cathodically protected carbon steel in natural seawater. Daylight cycles related effects were here investigated. Being O₂ both cathodic reactant and key molecule of aerobic environments, a potential involving oxygen limiting current without hydrogen evolution (~–850 mV vs. Ag/AgCl) was employed. Comparison of natural seawater with NaCl 3.5% wt. solution data showed that sunlight radiation plays a primary role with respect to temperature in affecting cathodic currents even in presence of electro-accreted aragonite. Calcareous deposit morphology and composition was investigated through SEM, highlighting properties and peculiarities.

KEYWORDS: cathodic protection; calcareous deposit; oxygen; sunlight radiation; temperature; natural seawater.

NOMENCLATURE

EDS: Energy Dispersive Spectroscopy
SEM: Scanning Electron Microscopy
iₓO₂: oxygen limiting current

INTRODUCTION

Cathodic protection is a widely employed technique which allows the oxidative power of environment affecting metals to be controlled. This can be achieved making the structure working as a cathode, where the reducing power necessary for the onset of cathodic processes can be supplied by impressed current or coupling to a less noble metal. This second way is preferably used in seawater where the metallic structure is protected with sacrificial anodes of aluminum, zinc or magnesium based alloys.

In aerobic environments, current requirement for completely protect the structure is reached when the oxygen that comes in contact with the metallic surface is reduced (Foster et al. 1986). Hence, all the factors that control oxygen diffusion towards the surface also control the cathodic current behavior.

As a result of the cathodic polarization is the alkalization at the metal/solution interface, where the increase of OH⁻ shifts the carbon dioxide system equilibrium towards the formation of carbonate and allowing the precipitation of CaCO₃ to take place (Barchiche et al. 2003).

The commonly called calcareous deposit is not formed only by CaCO₃; if the alkalinity is enhanced with further cathodic polarization, when pH value of 9.5 is reached Mg(OH)₂ starts to precipitate (Hartt et al. 1984).

Calcareous deposit growth at metal/electrolyte interface is of importance because it controls the oxygen diffusion towards metal admitted by coating protective characteristics (porosity, thickness, adhesion), whose final properties depend on how the intrinsic precipitation mechanisms are conditioned by environmental factors.

It is known that the most protective deposits are generally obtained at more electronegative potentials (Hartt et al. 1984, Mao et al. 1985, Luo et al. 1991) until the hydrogen evolution starts to mechanically damage till disbonding the deposit (Salvago et al. 2003). Therefore, an important role is played by hydrogen since its evolution starts at cathodic potentials comprised in the range of potentials employed in cathodic protection, from ~–800 mV to ~–1200 mV vs. Ag/AgCl (DNV-RP-B401, 2005).

Even if thermodynamically allowed, calcium carbonate precipitation does not spontaneously takes place in seawater because of kinetic hindrance performed by sulfates (Barchiche et al. 2004), PO₄³⁻, various organic compounds and Mg²⁺ (Hartt et al. 1984).

Among the listed factors, a special role is played by Mg²⁺. Investigations were performed in order to better understand the precipitation phenomena on cathodically protected metals considering the role of Ca and Mg ions with the separation (Deslouis et al. 1998, Deslouis et al. 2000) and combination (Barchiche et al. 2003) of their contributes to calcareous deposit formation.

Besides chemistry of the solution being able to affect the calcareous deposit growth, important physical parameters like temperature (Barchiche et al. 2004, Lin et al. 1988) and hydrodynamic regime (Lee et al. 1986, Mantel et al. 1992) were investigated.

In natural environments, a particular role is of course played by biology. In absence of an external potential applied, the biofilm is known to strongly affect electrochemical behavior of metals; large