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Corrosion and cathodic protection of carbon steel in the tidal zone: Products, mechanisms and kinetics

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ABSTRACT

Carbon steel coupons were set in the tidal zone of a French seaport for 7 years with or without cathodic protection. The average corrosion rates decreased from 90 μm yr^{-1} to 9 μm yr^{-1} under cathodic protection. The corrosion product layers covering the unprotected coupons, characterized by Raman spectroscopy and X-ray diffraction, were mainly made up of magnetite and Fe(III) oxyhydroxides, with magnetite being clearly predominant. The products of the residual corrosion process under cathodic protection, similar to those observed at open circuit potential, formed a thin layer on the steel surface under the calcareous deposit.

1. Introduction

In most cases, carbon steel seaport structures, sheets and other pilings are not initially protected against corrosion. To increase the lifetime and preserve existing structures that have reached a critical age the decision to apply a cathodic protection (CP) is often considered. CP would then be applied on already strongly corroded steel surfaces and it is questionable whether the polarization could induce harmful effects on the corrosion system. Similarly, if for any reason the cathodic protection is interrupted for a long time, peculiar corrosion processes could develop. The effects and magnitude of such corrosion resumption are also still questionable. For instance, CP induces the precipitation of $CaCO_3$ and/or $Mg(OH)_2$ [1–4] on the steel surface, and the corrosion resumption phenomena could be influenced by the mineral deposits previously formed under CP. More generally, information about the behavior of strongly rusted carbon steel under CP is required to optimize the design of the CP system.

To address these questions, carbon steel coupons were exposed to seawater for 7 years in two French harbors in various conditions of CP, i.e. without protection, with a permanent protection, or with a temporary protection applied only for the first six years or for the last year. The results obtained with coupons permanently immersed in the low water zone were published earlier [5]. It was in particular demonstrated that CP could induce important transformations in the pre-existing corrosion product layers. For instance, one of the main corrosion product of steel in seawater, the sulfated green rust $GR(SO_4^{2-})$ (i.e. the Fe(II–III) hydroxysulfate $Fe^{II}_4Fe^{III}_2(OH)_{12}SO_4{\cdot}8H_2O$), was entirely transformed into carbonated green rust $GR(CO_3^{2-})$ (i.e. the Fe(II–III) hydroxycarbonate $Fe^{II}_4Fe^{III}_2(OH)_{12}CO_3{\cdot}2H_2O$) by the cathodic polarization. The present article deals with coupons placed in the tidal zone, i.e. coupons alternatively immersed in seawater and exposed to atmosphere.

It must be recalled that the corrosion processes of continuous vertical steel strips in contact with both immersion and tidal zones differ from those of isolated steel coupons in contact with only one of these zones. The earliest results [6,7] and various studies afterwards [8–11], showed that for continuous vertical strips the corrosion rate was highest in the low water zone and slowest in the mid tide zone. The origin of this phenomenon was attributed to differential aeration. In contrast, the corrosion rate of isolated coupons was the highest in the mid tide zone and it was proposed [12] that the corrosion mechanisms in the tidal zone, characterized by wet/dry cycle conditions, were similar to those of atmospheric corrosion [13–15]. These mechanisms involve Fe(III) oxyhydroxides that act as oxidizers and thus accelerate the corrosion of the metal.

The present article describes results obtained in the seaport of Le Havre (English Channel) where the tidal range is about 8 meters. The coupons were located in the mid tide zone, facing south, and were not electrically connected to the carbon steel seaport structure. In order to study the corrosion mechanisms of steel in the

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tidal zone, the corrosion product layers of unprotected coupons were analyzed after 6, 12 months and 7 years of exposure. The other coupons, permanently or temporary protected by cathodic polarization, were only analyzed at the end of the 7 year exposure. Note that in the tidal zone, environmental factors (sunlight irradiation, rainfall washes, etc.) are likely to play a role on the corrosion and protection processes. However it can be considered that a 7 year exposure is sufficiently long to give an average view of the phenomenon, i.e. of the impact of the environmental factors.

The characterization of the corrosion product layers was achieved by means of X-ray diffraction and μ-Raman spectroscopy. The average corrosion rates were estimated by measurements of the residual thickness of the coupons.

2. Experimental

2.1. Steel coupons immersed in seawater

In situ experimentations were conducted in the harbor of Le Havre (English Channel) with AISI 1010 (C10, 1.0301) carbon steel coupons. The coupons (50 × 60 × 4 mm) had a weight percent composition of 0.380 Mn, 0.120 C, 0.037 Al, 0.023 Ni, 0.017 Cr, 0.010 P, 0.007 Si, 0.007 Cu, 0.004 S, 0.001 Mo, and Fe for the rest. Their surface was shot blasted to obtain a roughness value of 50–70 μm, degreased with acetone and dried. The coupons were immersed shortly after the shot-blasting and so it was really bare steel, free of any rust layer, that was exposed to the tidal zone. They were disposed in a Teflon holder as described in Fig. 1. The electrical connection was maintained by weld point between each coupon. To prevent any crevice corrosion phenomenon in the sliding channel of the Teflon holder, the right and left sides of the coupons were protected with polyurethane painting. The test units (18 or 20) were set on a carbon steel holder fixed to the quay structure. The experimental mounts were set in the tidal zone, at mid-height between the average low water zone and the average high water zone. The coupons were facing south and were not sheltered from daylight. The hydrodynamic regime was typical of the tidal zone and involved mainly the vertical flow of water due to tide. It must finally be noted that the coupons were isolated from the carbon steel seaport structure, i.e. not electrically connected to steel permanently immersed in seawater.

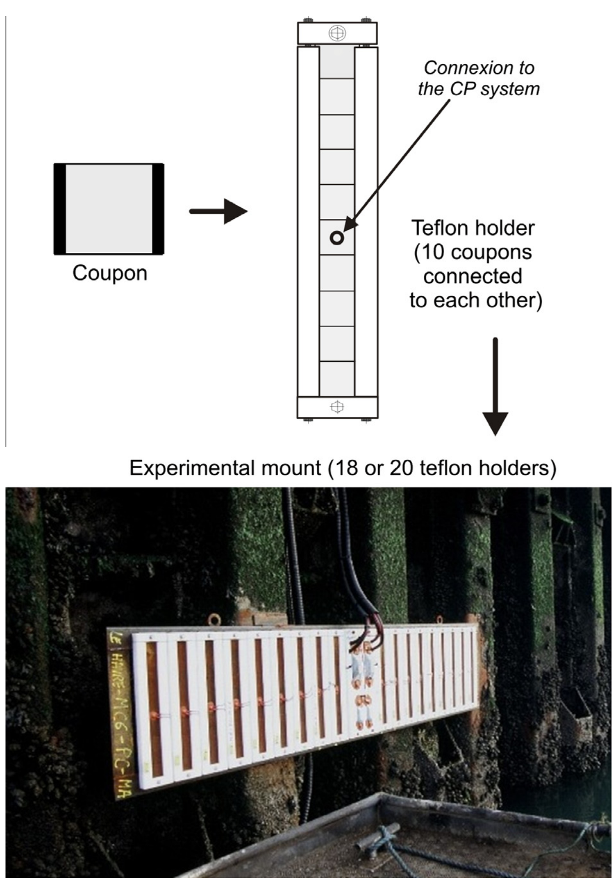

Fig. 1. Principle of the experimental sampling mount based on three steps of modularity (coupon(s) – holder(s) – mount), with photograph of an experimental mount after installation.

CP was achieved by a galvanic coupling between the coupons and zinc-based anodes. The potential of the coupons was measured every 3 months during four years and monitored continuously for the last three years (1 measurement every 30 min). These measurements testified that CP was correctly applied. A zinc-based electrode was used as a pseudo-reference but all potentials are given in the manuscript with respect to the Ag/AgCl/seawater reference electrode (+0.250 V/SHE). The pseudo-electrode reference was set in the lower part of the experimental mount and so it emerged from seawater with the lowest coupons. Its potential was checked every 6 months. No significant variation was observed.

Various conditions of protection were considered:

a. No cathodic protection (NCP): the coupons were never subjected to CP.
b. Permanent cathodic protection (PCP): CP was applied all along the 7 year exposure.
c. Delayed cathodic protection (DCP): the coupons were left unprotected during 6 years before CP was applied during 6–12 months.
d. Interrupted cathodic protection (ICP): CP was applied during 6 years and interrupted afterwards. The coupons were then left unprotected during 15 months.

2.2. Corrosion rates

Corrosion rates were estimated after the 7 year exposure by measurements of the residual thickness of the coupons. The corrosion product layers were removed from the steel surface according to the NF-ISO 8407:2010 standard [16]. The thickness of the coupons was determined via 25 measurements performed with a micrometer (1 μm resolution) each 10 mm. Four coupons were considered for each condition of CP, which corresponds to 100 measurements per experimental condition (NCP, PCP, DCP and ICP).

The corrosion process proved only approximately uniform and the residual thickness varied. The average of the 25 measurements performed on a coupon was used to determine the average corrosion rate. Similarly, the standard deviation for the corrosion rate was derived from the dispersion of the 25 thickness measurements performed on a coupon. For instance, the thickness loss of one of the unprotected coupons varied around an average of 630 μm with a standard deviation of 280 μm. The exposure time is 7 years and so the average corrosion rate is 90 μm/year with a standard deviation of 40 μm/yr. In this case, the standard deviation is not related to the accuracy of the method. It measures the difference between the real corrosion process and a perfectly uniform corrosion process.

With this approach, the standard deviation was about 40 μm/yr for unprotected (NCP) and mainly unprotected (DCP) coupons, and about 4 μm/yr for coupons permanently (PCP) or most of the time (ICP) under CP.