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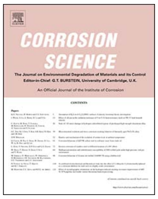

Corrosion of mild steel at the seawater/sediments interface: Mechanisms and kinetics

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ABSTRACT

Corrosion product layers formed on mild steel coupons after 6 years of permanent immersion at shallow depth in marine sediments were characterized by X-ray diffraction and µ-Raman spectroscopy. They proved mainly composed of FeS which testifies for an intense sulfate-reducing bacteria activity. Other identified compounds were siderite $FeCO_3$ and four varieties of green rust associated with local variations of composition of the environment. The corrosion rates determined by residual thickness measurements were higher on the lower half of the coupons (average 40 µm/yr, local maximum 140 µm/yr) and smaller on the upper half, suggesting that differential aeration effects took place.

1. Introduction

Few studies were recently devoted to the behavior of mild steel in marine sediments as it is generally admitted that the corrosion rates are low in the mud zone. In the absence of microbiologically influenced phenomena, corrosion rates after 89 days of immersion in various types of sediments (clay or sand) were for instance measured around 10 µm yr^{-1} [1,2]. They are smaller of 1–2 orders of magnitude than those generally observed in other exposure zones, e.g. around 200–400 µm yr^{-1} in the immersion zone or 100–300 µm yr^{-1} in the tidal zone for 12–18 months of exposure in various area of the Australian coasts [3]. The smaller corrosion rates were found in clay sediments that have the smaller grain size [1]. Oxygen transport, and more generally transport of matter, is less hindered in sediments with large average grain size, i.e. large average pore diameters. Corrosion rate thus increases with sediment grain size [1]. However, marine sediments are depleted in oxygen and even in sandy sediments with large particle size the corrosion rate is kept low.

Consequently, the main corrosion risk in the mud zone is associated with bacterial activity. Due to the low oxygen content, marine sediments favor the growth of anaerobe micro-organisms such as sulfate-reducing bacteria (SRB) that are well known to influence the corrosion processes of mild steel in marine media [e.g. 4–10]. The immersion of mild steel coupons in clay sediments containing variable SRB concentrations (5×10^2–5×10^4 bact/100 g of sediments) led to corrosion rates ranging from 2 µm yr^{-1} for low SRB concentration to 20 µm yr^{-1} for high SRB concentration [2]. In the presence of SRB, the corrosion rate is then increased by one order of magnitude though it can be noted that the corrosion rates remain low. The situation drastically worsens in the presence of electroactive SRB [11,12] as a three month immersion in marine sediments led to corrosion rates as high as 260 µm yr^{-1} [11]. Consequently, the risk associated with microbiologically influenced corrosion (MIC) cannot be discarded in marine sediments.

A particular case is that of the mud zone/seawater interface. In this case, a differential aeration effect can be expected, because the aerated zones of the metal located around this interface may act as cathode with respect to the metal immersed more deeply in the mud. A recent study showed that the presence of aerated/deaerated zones acting as cathode and anode respectively could induce a heterogeneity of the corrosion product layer that favors the persistence of the differential aeration cell [13]. In other words, the galvanic effects are self-sustaining via their influence on the corrosion products. These mechanisms were brought to light by a thorough characterization of corrosion product layers. Typically, it was found that the formation of magnetite Fe_3O_4 was favored in the cathodic zones which in turn favored the persistence of these zones as magnetite is an electronic conductor that can act as cathode. In contrast, the sulfated green rust $GR(SO_4^{2-})$ was favored in the anodic zones. Green rusts (GRs) are Fe(II–III) hydroxysalts characterized by a crystal structure that consists of the stacking of $Fe(OH)_2$-like layers carrying a positive charge due to the presence of Fe(III), and interlayers constituted of water molecules and anions that restore the electrical neutrality of the crystal [14,15]. Several GRs are known, and in

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particular those based on the main anions found in seawater, that is GR (Cl^-), GR(CO_3^{2-}) and GR(SO_4^{2-}). The chemical composition of GR (SO_4^{2-}) is for instance $Fe_4^{II}Fe_2^{III}(OH)_{12}SO_4 \cdot 8H_2O$ [14]. The methodology used in [13] was then envisioned so as to precise the mechanisms and kinetics of corrosion of mild steel at the mud zone/seawater interface. Various coupons were immersed at low depths in natural marine sediments for 6 months and 6 years. The resulting corrosion product layers were characterized by µ-Raman spectroscopy and X-ray diffraction whereas corrosion rates were determined on various zones of the coupons by residual thickness measurements.

2. Experimental

2.1. Materials

Twelve coupons were used, 6 for a 6 year experiment and 6 for a 6 month experiment. In each case, the 6 coupons remained in the sediments until the end of the experiment. The coupons were made of S355NL carbon steel and had an initial thickness of 5 mm. The steel composition, as given by the manufacturer Arcelor-Mittal, was (in wt. %): 0.17% C; 1.4% Mn, 0.015% P, 0.005% S, 0.21% Si, 0.02% Al, 0.02% Cr, 0.01% Cu, 0.02% Ni and Fe for the rest. All the coupons had the shape of a flag, i.e. were made of a 10 cm × 10 cm square plate (the "flag") and a 5 mm wide and 5 cm long "pole" in one corner. Their surface was shot blasted (Sa 2.5, angular shot) which led to a roughness value of 50–70 µm, degreased with acetone and dried. An electrical connection was achieved by welding a copper wire at the tip of the "pole" of the coupon and the weld was isolated from the aggressive environment by a thick layer of epoxy resin. The pole itself was painted. Observations of the coupons at the end of the 6 year experiment showed that the painted "pole" did not suffer corrosion and that the painted/unpainted junction of the coupon did not suffer particular damage such as crevice corrosion.

The immersion experiments were performed at the DCNS Research marine corrosion department in Cherbourg (France). Natural seawater was pumped directly from the English Channel to flow continuously at a rate of 100 L/h through a large tank before being rejected back to sea. A glass vessel was filled with the marine sediments that have accumulated within the tank. It was set inside the tank at low depth, i.e. with only 5 cm of seawater above the mud. Six steel coupons were then immersed vertically in the sediments as shown in Fig. 1. Their square part was entirely dipped in the sediments with the upper edge set approximately at the sediment/seawater interface. The results presented here relate to the two sides A and B of coupon C6, located at the right side of the glass vessel. The side of coupon C6 denoted A is the one facing the neighboring coupon C5. Note that the photograph in Fig. 1 was taken at the end of the 6-year experiment.

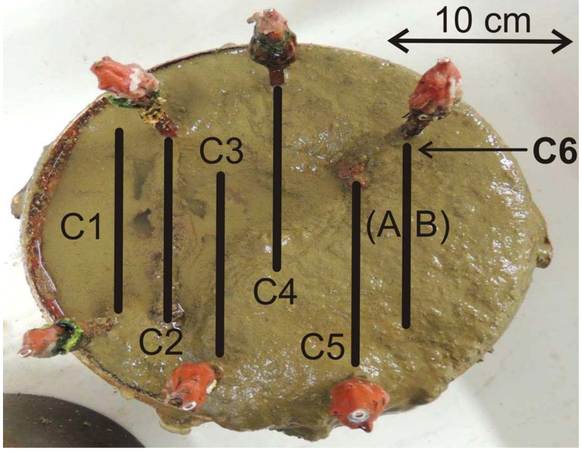

Fig. 1. Photograph of the glass vessel containing the 6 mild steel coupons immersed in marine sediments during 6 years. The black lines show the location of the coupons.

The open circuit potential (OCP) of the coupons was measured with a PHM210 Radiometer millivoltmeter. A saturated calomel electrode (SCE) was used as reference electrode ($E = +244$ mV/SHE at 20 °C). The average concentrations of the main ionic species present in the pumped seawater were determined at: $[Cl^-] = 19\ g\ kg^{-1}$, $[SO_4^{2-}] = 2.7\ g\ kg^{-1}$, $[HCO_3^-] = 0.14\ g\ kg^{-1}$, $[Na^+] = 10\ g\ kg^{-1}$, $[Mg^{2+}] = 1.3\ g\ kg^{-1}$, $[Ca^{2+}] = 0.41\ g\ kg^{-1}$ and $[K^+] = 0.4\ g\ kg^{-1}$. The pH was measured between 8.0 and 8.2. The temperature varied between 5 °C and 18 °C and the oxygen concentration between 5 mg/L and 10 mg/L.

2.2. Characterization of the corrosion product layers

The obtained corrosion product layers were analyzed by X-ray diffraction (XRD) and µ-Raman spectroscopy. This analysis requires that the samples, containing Fe(II)-based phases in most cases, are preserved from oxidation by air. Consequently, the glass vessel containing the coupons and the marine sediments was removed from seawater and immediately set in a freezer at −24 °C. Two days later, a part of the frozen block of sediments was separated from the rest with a saw, set in carbon ice (−79 °C) and carried away for analysis at LaSIE laboratory in La Rochelle, France. This block contained two coupons (C5 and C6) as shown in Fig. 2. Once received, it was kept in a freezer (−24 °C), a simple procedure that hinders the resumption of the corrosion processes and the oxidation of the Fe(II)-based corrosion products that are highly reactive towards oxygen. As it can be seen in Fig. 2b, the steel surface was in any case covered by a black layer that did not show particular local features. Samplings were then performed at random on various spots of the steel surface, two on the upper half and two on the lower half of each side of the coupon. Samples were also extracted from the block of frozen sediments at various distances from the steel surface (side B only). Sampling operations were achieved with a stainless steel spatula.

The Raman analysis was performed at room temperature on a Jobin Yvon High Resolution Raman spectrometer (LabRAM HR Evolution) equipped with a confocal microscope, a Peltier-based cooled charge coupled device (CCD) detector and a solid-state diode pumped green laser (532 nm). The laser power was reduced between 25% and 1% of the maximum (i.e. between 1.94 and 0.07 mW) so as to prevent the transformation of the analyzed compounds into hematite α-Fe_2O_3 that can take place due to an excessive heating. The investigations were performed without specific protection from air. The acquisition time was then generally small (60 s) to minimize the risk of transformation of the analyzed compound as a result of both oxidation and heating. As a consequence, the signal-to-noise ratio was not optimized in most cases. For each steel coupon, 16 zones (diameter of ~4 µm) of the corrosion product layer were analyzed through a 50× objective, with a resolution estimated at ~0.4 cm^1.

X-ray diffraction (XRD) analysis was performed with an Inel EQUINOX 6000 diffractometer, using a curved detector (CPS 590), with the Co-Kα radiation ($\lambda = 0.17903$ nm). The curved detector is designed for the simultaneous detection of the diffracted photons on a 2θ range of 90°. Acquisition was made with a constant angle of incidence (5°) during 45 min. To prevent the oxidation of Fe(II)-based compounds during preparation and analysis, the samples were scraped from the coupon still frozen and immediately mixed with a few drops of glycerol in a mortar. They were then crushed until a homogenous oily paste was obtained. With this procedure the various particles that constitute the sample are coated with glycerol and sheltered from the oxidizing action of O_2.

The various phases were identified via the ICDD-JCPDS database. The considered files were 01-086-1560 (quartz), 00-002-0056 (illite, i.e. clay), 01-078-2110 (kaolinite, another type of clay), 00-005-0586 (calcite), 01-075-2230 (aragonite), 01-086-0389 (mackinawite), 00-029-0696 (siderite) and 00-050-1380 (carbonate green rust). The