



Article

Cathodic Protection of Carbon Steel in the Tidal Zone: Characterization of the Mineral Layer Formed on the Steel Surface

Clément Genin ^{1,2,†}, Marc Jeannin ¹, Anne-Marie Grolleau ², René Sabot ¹ and Philippe Refait ^{1,*} 

¹ Laboratory of Engineering Sciences for the Environment (LaSIE)—UMR CNRS 7356, La Rochelle University, 17000 La Rochelle, France; clement.genin@cetim.fr (C.G.); mjeannin@univ-lr.fr (M.J.); rene.sabot42@orange.fr (R.S.)

² Naval Group Research, P.O. Box 440, 50104 Cherbourg-Octeville, France; amgcfpc@gmail.com

* Correspondence: prefait@univ-lr.fr

[†] Current address: CETIM, 21 Rue de Chemnitz, 68200 Mulhouse, France.

Abstract

The efficiency of cathodic protection in the tidal zone, in particular in its highest part, remains questionable. To address this problem, experimental vertical structures were designed and set in a commercial seaport. Each structure was composed of 10 cm × 10 cm carbon steel coupons and 50 cm × 10 cm carbon steel strips to obtain a 5.1 m long continuous structure extending all along the tidal zone. Cathodic protection of the structures was carried out with an Al-Zn-In galvanic anode permanently immersed in seawater. The mineral layers formed on the coupons after 32 and 52 months were analyzed by XRD and μ -Raman spectroscopy. The evolution of the mineral layer from the low water zone to the splash zone was due to (i) the decreasing efficiency of the cathodic protection and (ii) the changes in corrosion processes, from those typical of a permanent immersion to those typical of atmospheric corrosion. In particular, brucite $\text{Mg}(\text{OH})_2$ was found up to the high tide zone and, in agreement with the estimated degradation of the coupons, its formation was an indicator of the altitude at which the cathodic protection remained efficient.

Keywords: calcareous deposit; cathodic protection efficiency; corrosion products; XRD; μ -Raman spectroscopy



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1. Introduction

Numerous vertical carbon steel structures are exposed to the marine environment from the immersion zone to the splash zone, e.g., steel sheet piles commonly found in seaports. They are often protected against corrosion via the combination of anticorrosion paint, to protect the emerged part of the structure, and cathodic protection (CP) to protect the immersed part. In the tidal zone, the metal surface is alternately immersed and emerged and the effects of cathodic protection can persist even when the steel surface is not immersed in seawater because a thin electrolyte film may remain on the surface during the emersion period [1,2]. Conversely, delayed application or repair of an organic coating on a constantly wet surface may require complicated and expensive industrial techniques. If CP is efficient in the tidal zone, then even the bare steel areas, created for instance by damage in the protective coating, should be protected against corrosion.

However, because the top of the sheet piles is rarely immersed, CP is not expected to be efficient up to the top of the structure and, for instance, methods based on wrapping

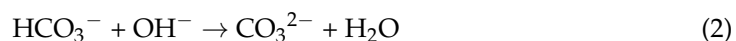
sackcloth and polyethylene rope around steel piles were considered to extend the efficiency of CP up to the splash zone [3]. The study of CP in the tidal zone is therefore of major interest from the industrial point of view. For now, the common practice is to consider that CP is efficient approximately up to the mid-tide zone and that organic coating has to be used above this level. A previous study [1] was performed with coupons set in the mid-tide zone which confirmed the efficiency of CP at that height, in the considered exposure conditions (seaport of Le Havre, in the English Channel, coupons facing south). Further information is however needed to establish a link between position in the tidal zone and CP efficiency, to identify markers of CP efficiency and to specify the electrochemical processes involved. From a practical point of view, the main aim is to evaluate the maximum height of full CP efficiency.

Corrosion processes of continuous vertical structures depend on the considered exposure zone, and involve galvanic coupling, mainly due to differential aeration, between the parts of the metal surface located in different zones [4,5]. One of the well-known consequences is the accelerated corrosion rate in the low water zone, a degradation process that may be accelerated further by microbiological processes and called ALWC (accelerated low water corrosion) [4–7]. Conversely, the galvanic coupling induces a decrease in corrosion rate in the tidal zone [4]. The variability of the corrosion mechanisms influences the composition of the corrosion product layer. In the low water zone, the formation of some phases such as magnetite (Fe_3O_4) and carbonate green rust ($\text{GR}_{\text{CO}_3} = \text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{CO}_3 \cdot 2\text{-}3\text{H}_2\text{O}$) is favoured in the cathodic zones of the underlying metal surface whereas that of the sulfate green rust ($\text{GR}_{\text{SO}_4} = \text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{SO}_4 \cdot 8\text{H}_2\text{O}$) is favoured in anodic zones [8–10]. Cyclic immersion was shown, as observed for atmospheric corrosion [11,12], to favour the formation of magnetite [5]. Akaganeite ($\beta\text{-FeOOH}$) is typical of marine atmospheric corrosion [10,13,14]. In natural environments, the steel surface and the inner part of the corrosion product layer are, after a few months, mostly in anoxic conditions, which favours the development of sulfate-reducing bacteria and induces the formation of iron sulfides on the steel surface [8,10,15–17].

The basic principle of CP is linked to the electrode kinetic theory, which shows that the decrease in the potential of the metal induces a decrease in the anodic reaction rate, i.e., a decrease in the corrosion rate. However, it also induces an increase in the cathodic reaction rate and thus an increase in the interfacial pH, as illustrated by the O_2 reduction reaction, which produces OH^- species:



In seawater, the increase in pH modifies the carbonate/bicarbonate equilibrium, increasing the carbonate concentration:



This increase in interfacial pH and interfacial CO_3^{2-} concentration, induced by CP, leads to the formation of a mineral layer on the steel surface, the so-called calcareous deposit [18–22]. The composition of the calcareous deposit depends in particular on the potential applied to the metal [21]. With the cathodic potential range corresponding to commonly used galvanic anodes, the calcareous deposit is mainly composed of aragonite CaCO_3 , with a small proportion of brucite $\text{Mg}(\text{OH})_2$ [19–22]. Aragonite can form on cathodic zones of an unprotected steel [8,23], i.e., for steel at the open circuit potential (OCP), while brucite forms preferentially at the most cathodic potentials [21]. However, the influence of the applied potential mainly reflects the crucial role of the steel/seawater

interfacial pH. Aragonite can form as soon as pH reaches a value between 7.6 and 8.7 [24], while the formation of brucite requires higher pH values (between 9.3 [25] and 10 [24]).

This analysis of the literature data shows that a thorough detailed characterization of the mineral layer forming on steel surfaces protected by CP in the tidal zone may provide fruitful information about the involved electrochemical processes and CP efficiency. Basically, the relative abundances of compounds resulting from cathodic polarization and compounds resulting from steel corrosion are linked to the efficiency of CP. The aim of the present study is then to describe the evolution with height of the composition of the mineral layer formed on a vertical structure exposed in the tidal zone, from the immersion zone to the splash zone. This structure is composed of numerous steel coupons and steel strips, electrically connected to each other to simulate a continuous structure. Two of these 5.1 m long structures were set in the commercial seaport of La Rochelle, where the maximum tidal range was about 6 m. At the end of the experiments (32 and 52 months), the layer covering each steel coupon was analyzed by X-ray diffraction (XRD) and μ -Raman spectroscopy (μ -RS). The degradation of the coupons was assessed after the 52-month experiment via mass loss measurements.

2. Materials and Methods

2.1. Steel Coupons Immersed in Seawater

A high-density polyethylene (HDPE) mount was first designed, manufactured and fixed on a steel sheet pile wall in La Rochelle commercial seaport (Figure 1). Sample holders were fabricated using rot-resistant red ironwood, with three 1.7 m long sample holders per each column of steel samples. Carbon steel coupons (10 cm $\times$ 10 cm) and carbon steel strips (50 cm $\times$ 10 cm), 10 mm thick, were provided by ArcelorMittal Long Products (Esch-sur-Alzette, Luxembourg). They were composed of the same carbon steel used for steel sheet piles, with the following nominal composition (wt.%): C $\leq$ 0.27, Mn $\leq$ 0.7, Si $\leq$ 0.6, S $\leq$ 0.055, P $\leq$ 0.055, Al $\leq$ 0.02, and Fe for the rest. All coupons and strips were grit-blasted with surface quality Sa 2½.

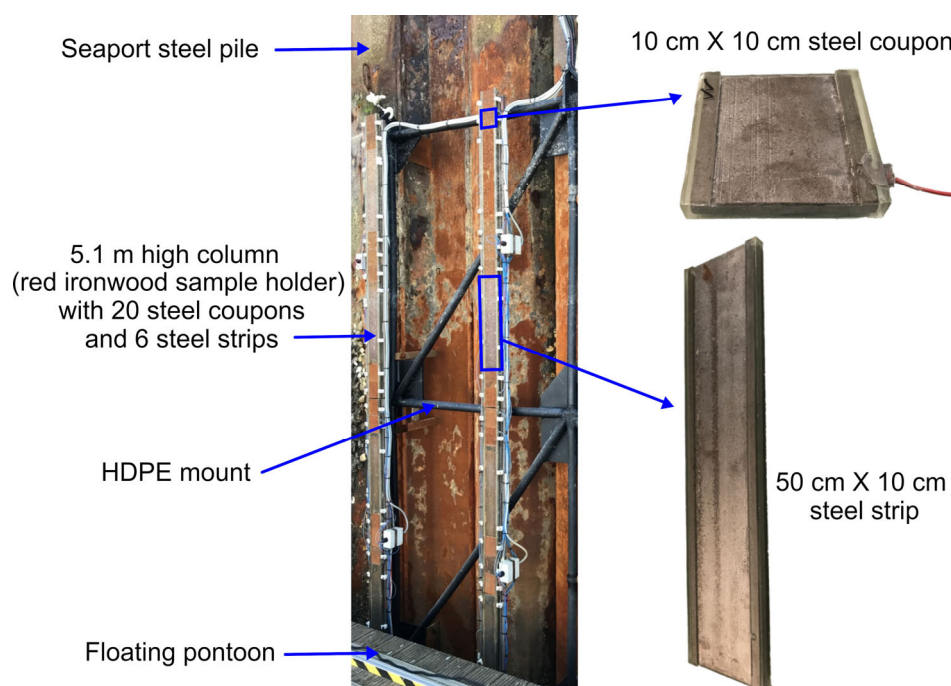


Figure 1. Image of the experimental vertical structures set in the commercial seaport of La Rochelle (France, Atlantic Ocean—photo taken 3 days after the beginning of the experiment), and detailed view of a steel coupon and a steel strip before experiment.

A copper wire was welded on each coupon and each strip for connection to the galvanic anode used for cathodic protection. Each coupon and each strip were embedded in epoxy resin so that only one side was exposed to the marine environment, as displayed in Figure 1. Once prepared, coupons and strips were set in the ironwood sample holders, with coupons denoted as C1 to C20 from top to bottom. The sample holders were finally fixed on a HDPE mount to build two 5.1 m long columns, set vertically so that the lower coupon (C20) was located at the lowest tide level (Figure 2) and the columns ran through the whole tidal range. Blocks of 2 to 4 coupons were set at various representative altitudes (Figure 2), and 1 steel strip was set between two blocks to ensure the continuity of the structure. The surface of all coupons was characterized at the end of the experiment.

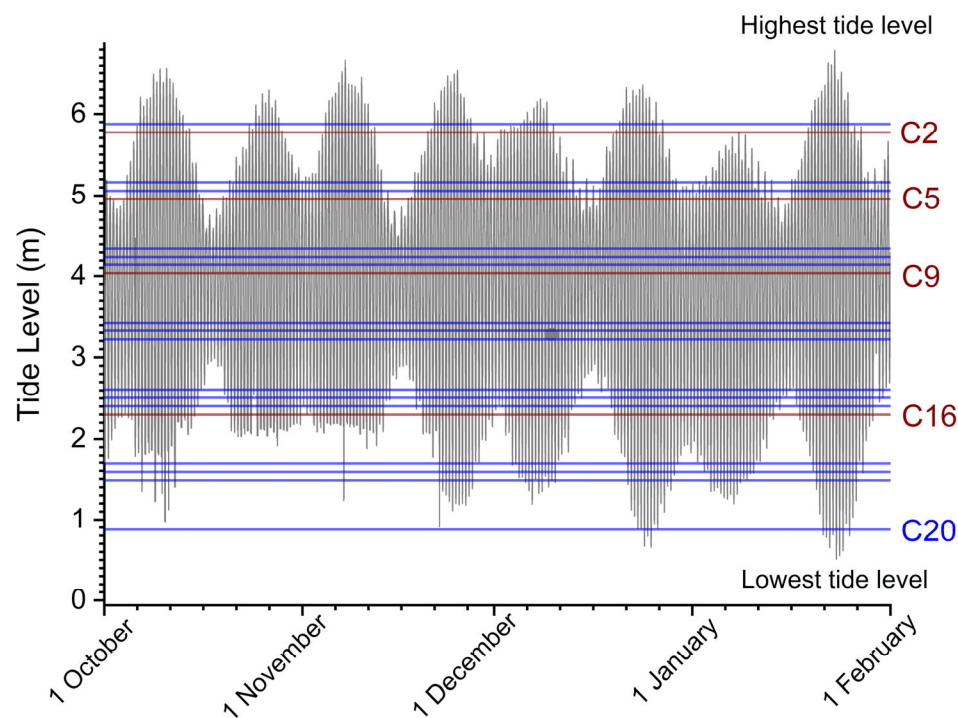


Figure 2. Graphic representation of the tide levels from the SHOM data (1 October to 1 February of the year of experiment) and associated positions of the steel coupons (blue and red-brown lines) in the tidal zone.

Each coupon and each strip were carefully juxtaposed to the previous one and the following one to ensure geometrical continuity. As all edges of coupons and strips were covered with a thin layer of resin, the electrical continuity of the whole structure was achieved via the copper wires welded on the back side of coupons and strips. All these wires ran along the columns up to a connection board set on the quay. Each coupon could be connected or disconnected to the CP system so that measurements of the potential of each coupon could be carried out. However, it proved difficult to carry out electrochemical measurements in situ in the seaport and an alternative methodology had to be developed to estimate corrosion rates (see Section 2.4).

A galvanic anode was fixed on the lower part of the HDPE mount so that it remained immersed even at the lowest tide levels. An Al-Zn-In anode, provided by BAC corrosion control (Voisins-le-Bretonneux, France), was used. Its nominal composition was (wt.%): Zn: 3.5 to 6.5, In: 0.01 to 0.03, Mn $\leq$ 0.01, Fe $\leq$ 0.13, Si $\leq$ 0.10, Cu $\leq$ 0.006, and Al for the rest.

2.2. Exposure Conditions and Immersion Rate

To describe accurately the effects of tide on the steel coupons, an average immersion rate was calculated over a complete year. As the altitude of each sample is precisely known,

if we compare these altitudes with the tide levels, the immersed and emerged times can be determined each tide cycle for all the samples. Then, the accumulated immersed time has been calculated for 365 days and then the percentage of immersion time has been extracted. In other words, this immersion rate is, for a sample at a given altitude, the ratio of the accumulated immersed time over 365 days. The immersion rates of all coupons are given in Table 1.

Table 1. Marine altitude and immersion rate of each coupon.

Block	Coupon	Marine Altitude (m)	Immersion Rate (%)	Block	Coupon	Marine Altitude (m)	Immersion Rate (%)
1	C1	5.88	4.2	4	C10	3.43	66.1
	C2	5.77	5.8		C11	3.32	68.5
2	C3	5.16	19.3		C12	3.22	70.9
	C4	5.06	22.3	5	C13	2.61	84.3
	C5	4.96	25.5		C14	2.51	86.4
3	C6	4.35	44.8		C15	2.40	88.2
	C7	4.24	47.4		C16	2.30	89.9
	C8	4.14	49.9	6	C17	1.69	96.7
	C9	4.04	52.3		C18	1.59	97.4
					C19	1.48	98
				7	C20	0.88	99.5

Atlantic tide-level data come from the SHOM (Service Hydrographique et Océanographique de la Marine) and are consistent with the tide gauge installed in the La Rochelle commercial seaport. Figure 2 shows an extract of these data. The maximum high tide can go up to 6.77 m while the minimal low tide can go down to 0.5 m. The positions of the coupons are indicated by horizontal lines. The highest coupon is C1 and the lowest coupon is C20. It can be seen that C20 is always immersed except at the lowest tides of the year. As a result, the immersion rate was computed at 99.5% for C20 (Table 1). On the contrary, the immersion rates for the highest coupons, C1 and C2, are equal to 4.2% and 5.8%, respectively. The coupons with immersion rates close to 50% are C8 (49.9%) and C9 (52.3%).

A minimum duration of 1 year was required to take into account not only the tide variations but also the seasonal variations that influence many seawater parameters (temperature, O₂ concentration, salinity, pH...). It was considered that averaging over at least 2 years was better, so the minimal duration was chosen as 32 months (a bit less than 3 years). The experiment was then maintained as long as possible, i.e., before technical problems were noted. It was then stopped after 52 months.

In the following, only the immersion rate will be used as the parameter for comparison between each sample (i.e., not the altitude of the coupon). For the sake of clarity, and because the main changes were observed for coupons higher than C9, only the results obtained with blocks 1, 2, 3 and 5, i.e., the blocks of coupons C2, C5, C9 and C16 denoted in brown-red in Figure 2, will be presented.

2.3. Characterization of the Corrosion Product Layers

After 32 months (i.e., 2 years and 8 months) of exposure in the tidal zone, the mineral layers were removed from the coupons of column 1. The column was not dismantled, the coupons remained on site, still protected by the galvanic anode.

The surface of the coupons was covered with a variable amount of macrofouling. The largest shells, mainly oysters, were removed from the coupons before the mineral layer was scraped from the steel surface. Smallest animals, such as barnacles that adhered strongly to the surface, were not removed to avoid damaging the mineral layer. It is then important to note that the diffraction peaks of calcite, very intense in some X-ray diffractograms,

must be attributed to the shells of these animals, and are not linked to any electrochemical process (these shells, mainly barnacles, were analyzed alone and were confirmed to be only composed of calcite). For each coupon, the obtained sample (mineral layer and part of macrofouling) was stored in a freezer ($-18\text{ }^{\circ}\text{C}$) to prevent any further oxidation of Fe(II)-containing compounds. After 52 months (i.e., 4 years and 4 months), column 2 was dismantled so that both the mineral layer and coupon surface could be analyzed. Each coupon was then carried to the lab in a tank filled with seawater then stored frozen at $-18\text{ }^{\circ}\text{C}$ to prevent any further corrosion or corrosion product oxidation. Note that, as for column 1, the largest shells were removed from the coupon surface.

μ -Raman spectroscopy (μ -RS) analysis was then carried out on a small fragment of each mineral layer. The rest, i.e., the main part, of the layer was analyzed by XRD.

XRD analysis was carried out with Co- K_{α} radiation ($\lambda = 0.17903\text{ nm}$) using a Thermo Scientific ARL-INEL EQUINOX 6000 diffractometer equipped with a CPS-590 curved detector (Thermo Fisher Scientific, Waltham, MA, USA). This 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 (7°) during 45 min. Each sample was rapidly (less than 15 s) crushed with a mortar to obtain a wet paste still containing coarse particles. Glycerol was then added to prevent the oxidation of Fe(II)-containing compounds during further steps of preparation and during XRD analysis, a procedure used in previous works, e.g., [8,9,23]. The samples were crushed again to obtain smaller grains until a homogenous paste was obtained.

μ -RS analysis was carried out at room temperature with a Horiba High Resolution Raman spectrometer (LabRam HR evo, Horiba, Tokyo, Japan) equipped with a confocal microscope and a Peltier-based cooled charge coupled device (CCD) detector. For each sample, 20 zones ($\sim 5\text{ }\mu\text{m}$ diameter) were analyzed through the $\times 50$ objective. Spectra were recorded at room temperature with a resolution of $\sim 0.1\text{ cm}^{-1}$. The power of the incident laser beam, provided by a green laser diode (533 nm), was reduced to 2.5% of the maximum ($\sim 0.5\text{ mW}$) in order to prevent any excessive heating able to induce the transformation of Fe compounds into $\alpha\text{-Fe}_2\text{O}_3$ (hematite) [26]. In some cases, it had to be reduced to 1% of the maximum, thus requiring an acquisition time larger than those usually considered [27,28], and set at 60 s for all recorded spectra.

2.4. Estimation of Corrosion Damage

It was initially planned to perform in situ electrochemical measurements (e.g., linear polarization resistance measurements and electrochemical impedance spectroscopy) on individual coupons but, for reasons that are still under discussion, these measurements proved unreliable. Actually, the only measurements that could be performed correctly were measurements of the potential of the immersed coupons. These results only confirmed that the connections with the anode were still effective, because all potential values (about $-1.0\text{ V}_{\text{Ag-AgCl-seawater}}$ in any case) were close to that of the anode.

As the initial mass of the coupons, embedded in resin and welded to a copper wire, was not measured, it was necessary to develop an unusual methodology to estimate the degradation of the steel coupons (52 months exposure only).

First, both resin and weld could be removed easily as the ageing of the resin turned it brittle and poorly adherent. Then, the last traces of the mineral layers remaining on the surface were removed by dissolution in a mixture of HCl and ethylenediaminetetraacetic acid (EDTA). The final mass of the cleaned coupons, denoted as m_f , could then be measured. The coupons were initially cut from the same plate so that their thickness was identical and their initial mass only differed because of slight differences in other dimensions, i.e., in the surface S ($\sim 100\text{ cm}^2$) of each coupon. The parameter finally used to estimate the degradation

was then m_f/S , with S being the actual (i.e., measured) surface of the coupon. The final volume of the coupon, V_f , is equal to $S \times e_f$, where e_f is the residual thickness of the coupon, and m_f/V_f is equal to the specific mass of steel, ρ . Consequently, $m_f/S = \rho \times e_f$, i.e., m_f/S is actually proportional to the residual thickness e_f of the coupon.

The results given by this method are only discussed qualitatively and are not translated in corrosion rates. Moreover, when problems (e.g., removal of very adherent corrosion products, unwanted degradation due to infiltration of seawater at the back or at the sides of a coupon, etc.) were encountered, the corresponding coupons were discarded. Thus, data about coupons C1, C13 and C16 are not given in the corresponding Section 3.3.

3. Results

First, the analysis of the layers sampled after 32 months and 52 months gave similar results, i.e., the same trends were observed. To be as concise and synthetic as possible, only the XRD results obtained after 32 months and the μ -RS results obtained after 52 months are presented. The evolution of the composition of the mineral layers is restricted to qualitative comparison between data obtained at different altitudes.

3.1. XRD Analysis of the Mineral Layers Formed on Steel Coupons After 32 Months of CP in the Tidal Zone

Figure 3 gathers the XRD patterns obtained for the mineral layers of coupons C16 and C13, representative of block 5 (immersion rates between 89.9% and 84.3%). The most intense peak of both diffractograms is the main diffraction peak (C104) of calcite (CaCO_3), a compound mainly coming from the shells that have been crushed with the mineral layer before XRD analysis (see Section 2.3). Numerous diffraction peaks are also associated with minerals coming from the marine environment. This is the case with quartz (SiO_2), i.e., sand, and halite (NaCl). This is also the case with kaolinite and illite, clay minerals present in marine sediments [29].

Another important compound, as revealed by the strong intensity of its diffraction peaks, is aragonite, another CaCO_3 polymorph. At the CP potential considered here, i.e., the potential of the coupons due to the coupling with the Al-Zn-In galvanic anode, aragonite is known to be the main component of the calcareous deposit [19–22]. The presence of aragonite on the coupons is then directly linked to CP. Finally, magnetite (Fe_3O_4) is also identified. It results from the residual corrosion process that occurs, at a very low rate, even when CP is efficient [1,30]. In conclusion, the characteristics of this mineral layer are those expected for a steel surface effectively protected by CP, in agreement with the high immersion rate of the coupons.

Figure 4 shows typical XRD patterns obtained with coupons of block 3, namely C9 (immersion rate of 52.3%) and C7 (immersion rate of 47.4%). The main diffraction peak is still the main peak of calcite, but its relative intensity is smaller than for C13 and C16. Similarly, it can be seen that the relative intensity of the diffraction peaks of quartz and kaolinite is smaller for C7 than for C9. This is consistent with visual observation, which showed that the amount of fouling decreased with the altitude of the coupons. In both cases, aragonite is the other important identified compound, which suggests that CP was efficient most of the time. In agreement, brucite ($\text{Mg}(\text{OH})_2$), the other (minor) component of calcareous deposits due to CP [19–22], is also clearly identified. As for coupons C13 and C16, magnetite is the only identified corrosion product. The formation of magnetite is favoured by an increase in pH [8,9] which may explain why it is the main compound resulting from the “residual” corrosion process occurring when CP is applied.

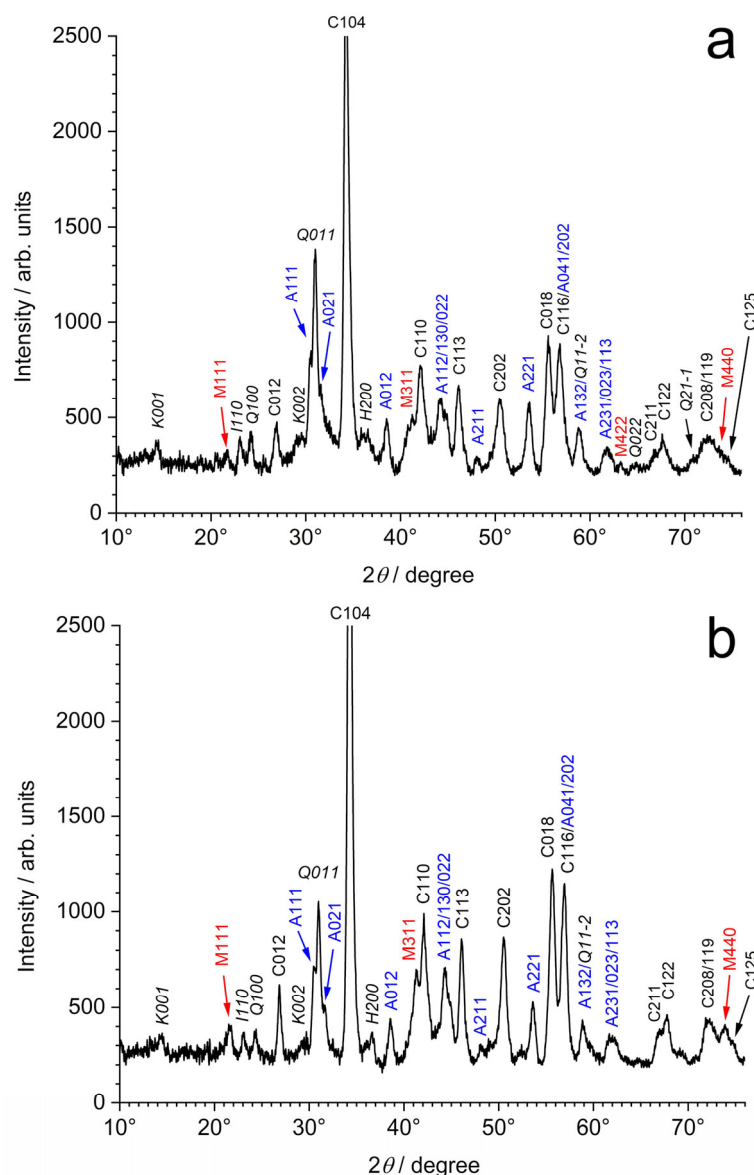


Figure 3. X-ray diffraction patterns of the layers covering coupons C16 (a) and C13 (b) of block 5. A = aragonite, C = calcite, H = halite, I = illite, K = kaolinite, M = magnetite, Q = quartz, with corresponding Miller index.

Finally, pyroaurite ($\text{Mg}^{\text{II}}_6\text{Fe}^{\text{III}}_2(\text{OH})_{16}\text{CO}_3 \cdot 4\text{H}_2\text{O}$) [31] is also observed. This compound has already been reported on coupons subjected to CP in seawater and its formation was attributed, as that of aragonite and brucite, to the increase in interfacial pH [1]. As it contains Fe atoms, it may be considered as a corrosion product, but it does not form at OCP and is characteristic of the “residual” corrosion process of the metal subjected to CP. It must be noted that pyroaurite and carbonate green rust, GR_{CO_3} , are structurally identical. GR_{CO_3} only contains Fe(II) cations, and its chemical formula is $\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{CO}_3 \cdot 2\text{-}3\text{H}_2\text{O}$ [32,33], while pyroaurite contains only Mg(II) ions. However, intermediate compounds, containing both Fe(II) and Mg(II) cations, may form [34]. It is difficult, with only XRD analysis, to state whether the compound detected here is pyroaurite *sensu stricto*, or a Mg(II)-Fe(II)-Fe(III) hydroxycarbonate. This compound is then denoted as “pyroaurite” hereafter.

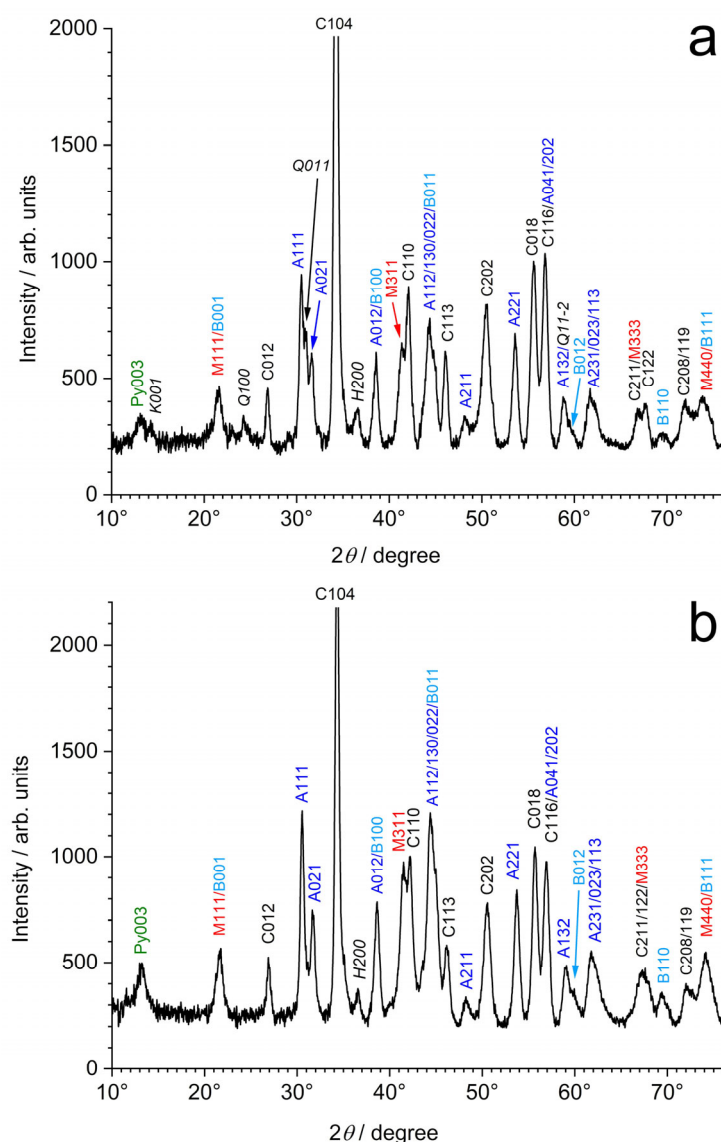


Figure 4. X-ray diffraction patterns of the layers covering coupons C9 (a) and C7 (b) of block 3. A = aragonite, B = Brucite, C = calcite, H = halite, K = kaolinite, M = magnetite, Py = pyroaurite, Q = quartz, with corresponding Miller index.

The XRD patterns displayed in Figure 5 are those of coupons with lower immersion rates, i.e., C4 (block 2, immersion rate of 22.3%) and C2 (block 1, immersion rate of 5.8%). Calcite is still present for C4 (Figure 5a) but the intensity of the main peak of magnetite (M311) is now similar to that of the main peak of calcite (C104). Magnetite is accompanied by other corrosion products, mainly goethite α -FeOOH, with traces of lepidocrocite γ -FeOOH and akaganeite β -FeOOH. Aragonite, brucite and pyroaurite are still clearly observed. However, while the main peak of aragonite (A111) was more intense than the main peak of magnetite (M311) for the previous coupons (see for instance Figure 4b for C7), the main peak of magnetite is much more intense than the main peak of aragonite for C4. This result, and the presence of other corrosion products, demonstrate that the corrosion process was more active for C4, i.e., CP could not be efficient all the time at that altitude.

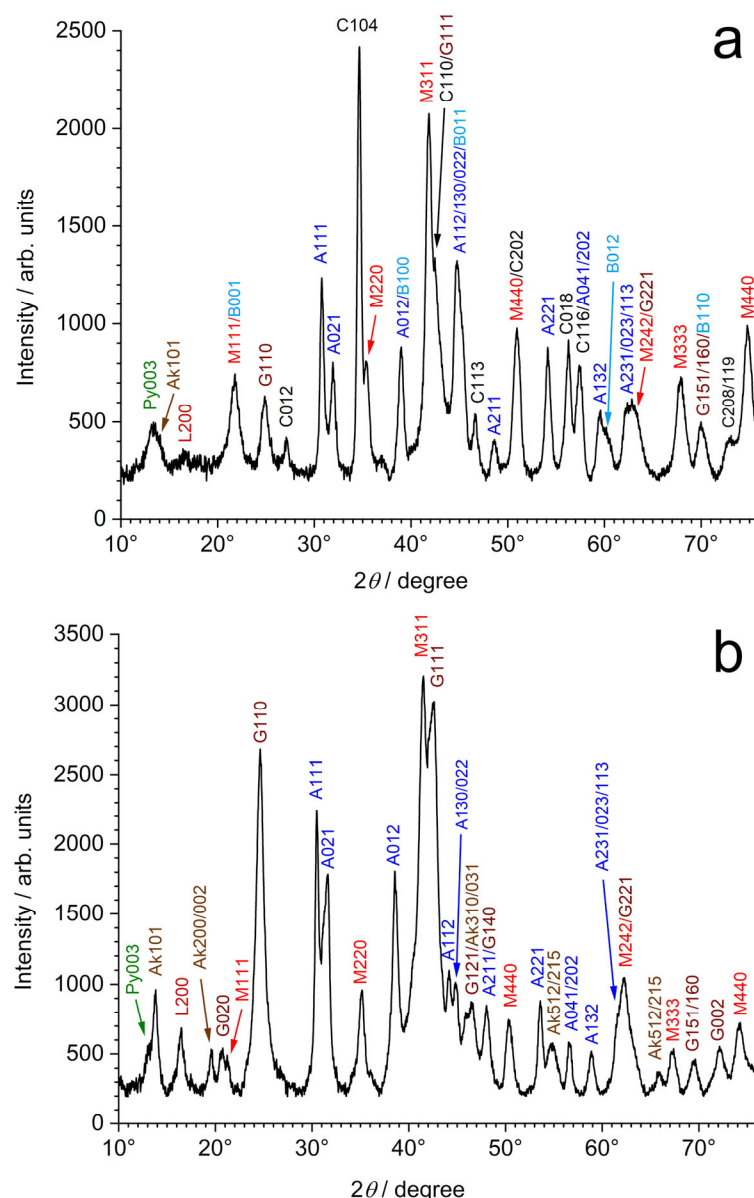


Figure 5. X-ray diffraction patterns of the layers covering coupons C4 of block 2 (a) and C2 (b) of block 1. A = aragonite, Ak = akaganeite, B = Brucite, C = calcite, G = goethite, L = lepidocrocite, M = magnetite, Py = pyroaurite, with corresponding Miller index.

For coupon C2, calcite is not detected (Figure 5b), in agreement with visual observations that revealed the complete absence of fouling. This is of course the consequence of the very low immersion rate of this coupon. Moreover, the main peaks of goethite and magnetite are now the most intense peaks of the diffractogram, and the diffraction peaks of lepidocrocite and akaganeite are now clearly seen. Clearly, CP is not really efficient in this case. Accordingly, brucite is not detected and “pyroaurite” is hardly seen. However, the peaks of aragonite remain rather intense, which suggests that CP was efficient for a longer time than that corresponding to the immersion rate of C2, i.e., more than 5.8% of the year. This could of course be due to the persistence of a thin seawater film connecting the coupon to bulk seawater even when the coupon was not immersed itself.

3.2. μ RS Analysis of the Mineral Layers Formed on Steel Coupons After 52 Months of CP in the Tidal Zone

The results obtained with μ RS are presented in this section using the same structure as for XRD analysis. Raman spectra of compounds coming from seawater, e.g., calcite, are not presented.

First, Figure 6 gathers the results obtained for coupon C14 of block 5 (immersion rate of 86.4%). Three phases could be identified, aragonite and magnetite, in agreement with XRD analysis, and mackinawite FeS.

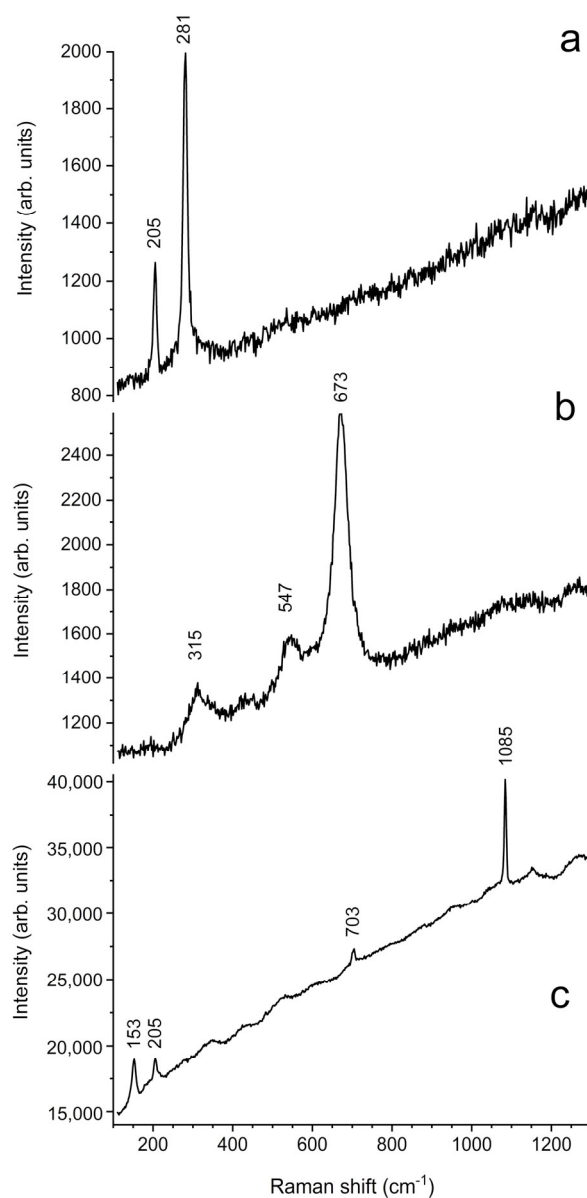


Figure 6. Typical Raman spectra obtained during the analysis of the layer covering coupon C14 of block 5: (a) nanocrystalline mackinawite, (b) magnetite and (c) aragonite.

Figure 6a shows the typical Raman spectrum of nanocrystalline mackinawite with an intense peak at 281 cm^{-1} and a smaller one at 205 cm^{-1} [35]. Due to its nanocrystalline state that persists in alkaline conditions [35], mackinawite is usually not detected via XRD [8–10,16]. This compound is a common corrosion product of steel permanently immersed in natural seawater and is formed once sulfate-reducing bacteria (SRB) can develop at the vicinity of the steel surface [36]. The growth of SRB requires anoxic conditions,

which are met once the thickness of the corrosion product layer is sufficient to prevent the transport of dissolved O_2 from seawater to steel surface [15]. O_2 is consumed in the corrosion product layer by aerobic micro-organisms and via its reaction with Fe(II)-containing corrosion products. Moreover, dissolved O_2 can be reduced far from the steel surface on particles of conductive corrosion products, i.e., FeS and Fe_3O_4 , provided that these particles are interconnected and connected to the metal surface [8–10]. For coupons of block 5, the only identified corrosion products are indeed FeS and Fe_3O_4 , so that dissolved O_2 can readily be reduced at the outer surface of the corrosion product layer. It does not diffuse inside this layer, and anoxic conditions then prevail. The growth of SRB and the subsequent formation of FeS show that at least the most inner part of the corrosion product layer remained permanently wet, which ensured that CP could be efficient all the time. Note also that, for coupons under CP, the calcareous layer further hinders the diffusion of O_2 towards the metal surface.

Figure 6b shows the typical spectrum of magnetite, with one main peak at 673 cm^{-1} and two smaller peaks at 315 cm^{-1} and 547 cm^{-1} [26]. Figure 6c shows the typical spectrum of aragonite, with an intense sharp peak at 1085 cm^{-1} , and three small peaks at 153 cm^{-1} , 205 cm^{-1} and 703 cm^{-1} [37]. Note that the peak at 703 cm^{-1} is actually a doublet of peaks at 701 cm^{-1} and 705 cm^{-1} , which cannot be distinguished at the scale of the figure. It can also be noted that in each case the baseline of the spectrum is not horizontal. This effect is more important in the case of the aragonite spectrum (Figure 6c) that is moreover characterized by a very high intensity. Both effects are due to the fluorescence signal of organic matter, i.e., the biofouling covering the coupons. They are more intense for aragonite because it forms the outer stratum (seawater side) of the mineral layer, while the corrosion products form an inner stratum, close to the metal.

Figure 7 gathers typical spectra obtained for coupon C7 of block 3 (immersion rate of 47.4%). Four compounds could be identified, including nanocrystalline FeS as shown in Figure 7a. In this spectrum, nanocrystalline mackinawite (peaks at 205 cm^{-1} and 281 cm^{-1}) is found together with magnetite (peaks at 310 cm^{-1} , 546 cm^{-1} and 673 cm^{-1}). A small peak appears at 254 cm^{-1} . It may be attributed to FeS [35,38] but could also correspond to the main Raman peak of lepidocrocite $\gamma\text{-FeOOH}$ [26]. The spectrum of Figure 7b is typical of magnetite while that of Figure 7c is a spectrum of aragonite. Finally, in agreement with XRD analysis, brucite was identified (Figure 7d). This compound, i.e., $Mg(OH)_2$, is more adequately identified in the O-H stretching spectral region, and thus the displayed spectrum (in blue) relates to the $3000\text{--}4000\text{ cm}^{-1}$ wavenumber range. Brucite is clearly identified with its sharp peak located at 3650 cm^{-1} [39].

Finally, Figures 8 and 9 display the typical spectra of the 8 phases identified on the surface of coupon C5 of block 2 (immersion rate of 25.5%). Figure 8 gathers the Raman spectra of the corrosion products. As previously, magnetite was identified. Its three Raman peaks at 312 cm^{-1} , 544 cm^{-1} and 671 cm^{-1} are accompanied in Figure 8a with two small peaks at 433 cm^{-1} and 515 cm^{-1} typical of a GR compound [8,16,29,30,36]. The Raman spectra of GR_{CO_3} and GR_{SO_4} are similar, so μRS is not a suitable method to distinguish both GR [30]. Goethite is identified in Figure 8b with its main peak at 387 cm^{-1} and smaller peaks at 247 cm^{-1} , 298 cm^{-1} , 482 cm^{-1} and 550 cm^{-1} [40]. The peaks seen at 415 cm^{-1} , 682 cm^{-1} and 996 cm^{-1} can also be attributed to goethite [41–43], though the peak at 682 cm^{-1} may also be due to magnetite [43]. The third spectrum (Figure 8c) is typical of lepidocrocite [8,26,36] while the fourth one (Figure 8d) is that of akaganeite [26,41].

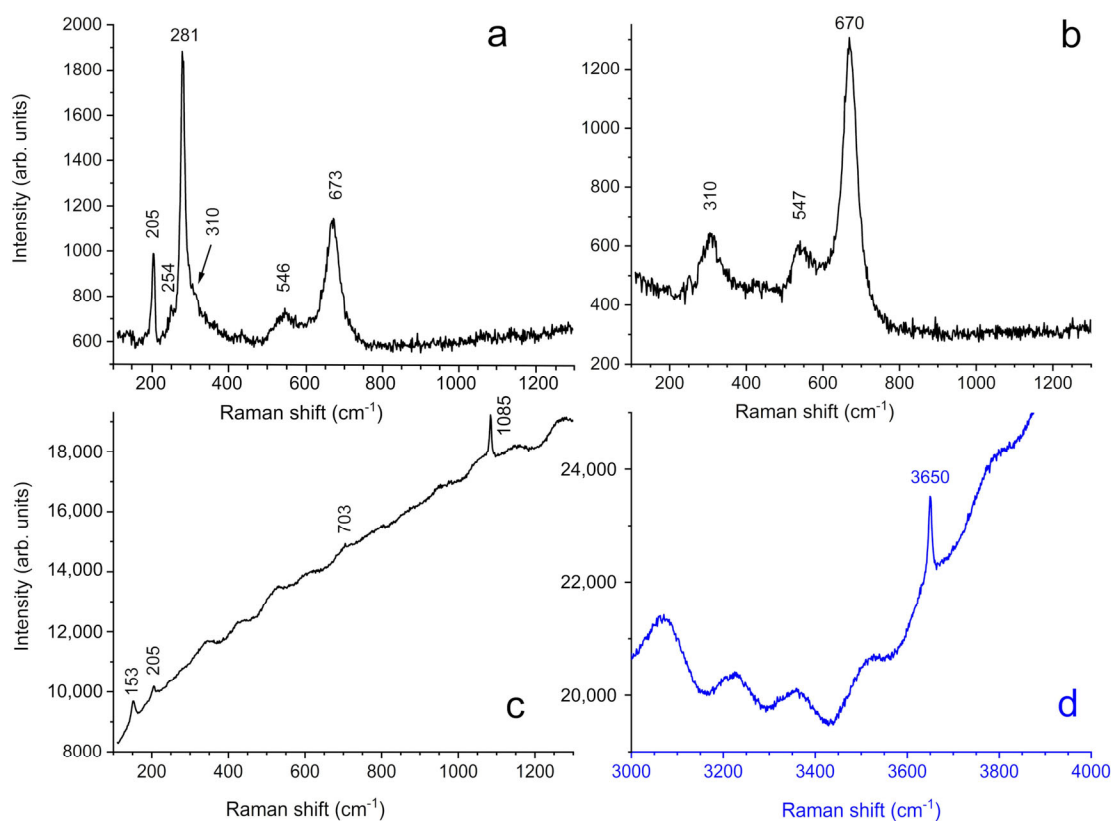


Figure 7. Typical Raman spectra obtained during the analysis of the layer covering coupon C7 of block 3: (a) nanocrystalline mackinawite and magnetite, (b) magnetite, (c) aragonite and (d) brucite (O-H stretching spectral region).

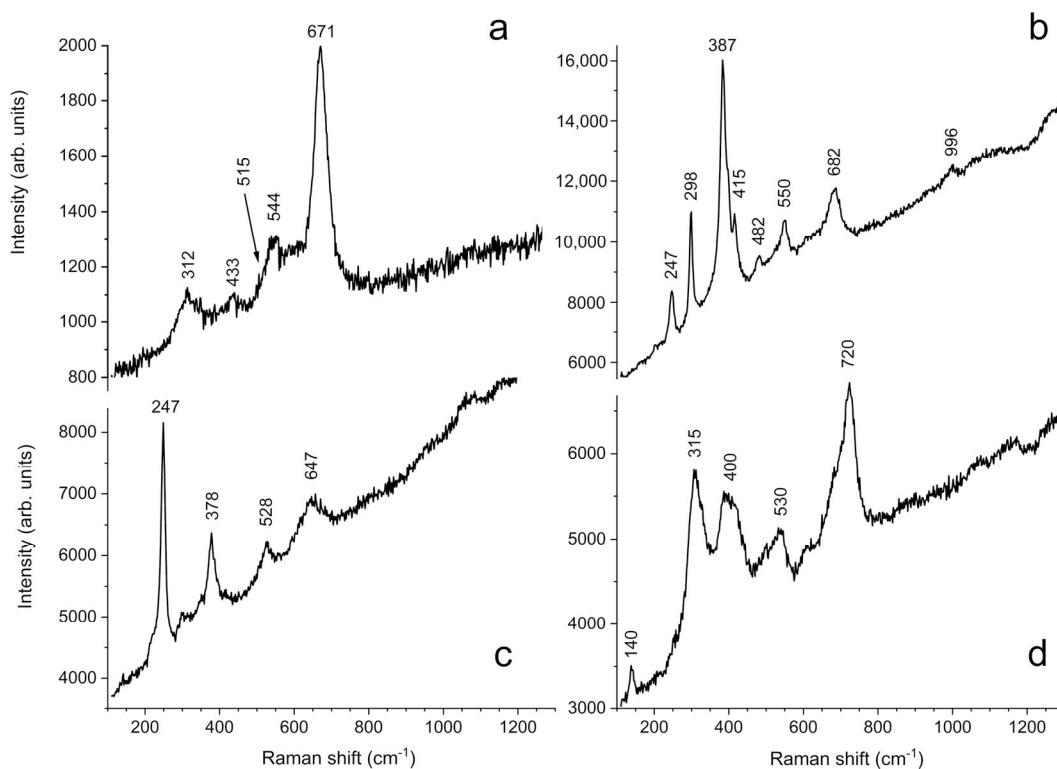


Figure 8. Typical Raman spectra obtained during the analysis of the layer covering coupon C5 of block 2—corrosion products: (a) magnetite and green rust, (b) goethite, (c) lepidocrocite and (d) akaganeite.

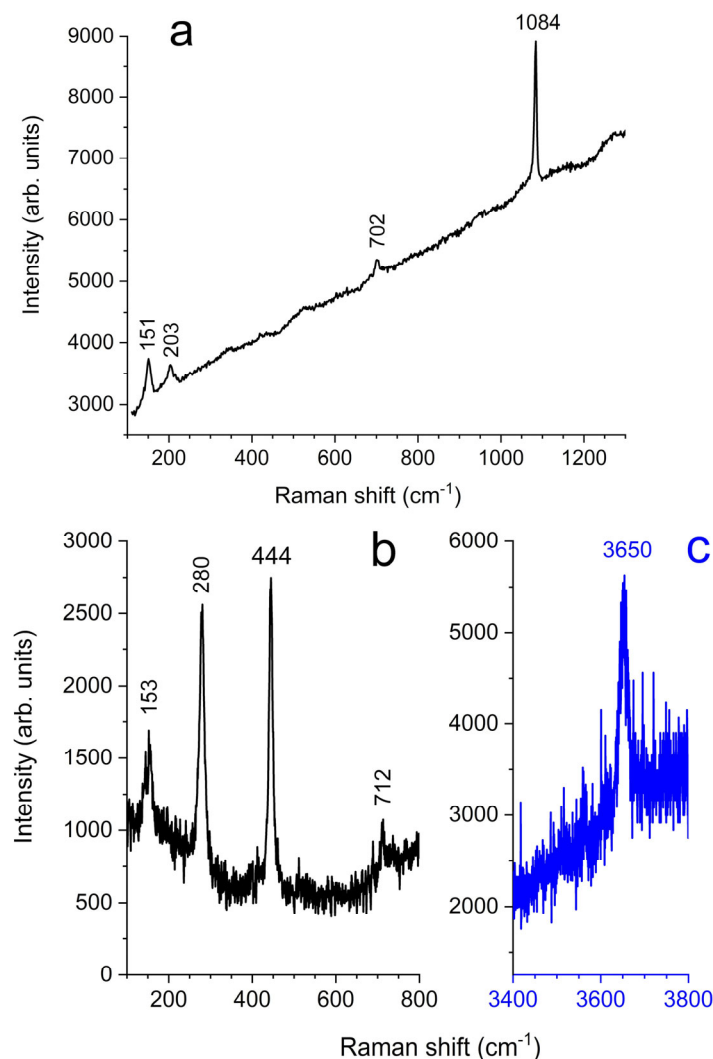


Figure 9. Typical Raman spectra obtained during the analysis of the layer covering coupon C5 of block 2—calcareous deposit: (a) aragonite, (b) brucite and calcite, (c) brucite (O-H stretching spectral region).

Figure 9 displays the typical spectrum of aragonite (Figure 9a) and two parts of a spectrum that demonstrates the presence of brucite. In Figure 9b, a typical peak of brucite at 444 cm^{-1} [39] is seen together with pics at 153 cm^{-1} and 712 cm^{-1} , which can be attributed to calcite [37]. The fourth Raman peak, at 280 cm^{-1} is due to both brucite and calcite [37,39]. In the spectral region corresponding to the OH-stretching modes (Figure 9c), the characteristic peak of brucite is seen at 3650 cm^{-1} [39]. In conclusion, the Raman analysis of coupon C5 is fully consistent with the results obtained via the XRD analysis of coupon C4, except for “pyroaurite”, only detected with XRD. It must also be noted that FeS could not be detected. This indicates that the immersion rate (25.5% for C5) was not sufficient to avoid the drying of the surface and to prevent O_2 from reaching the inner part of the corrosion product layer. This result is consistent with the presence of akaganeite, which requires very high concentrations of both Fe^{2+} and Cl^- [44]. Akaganeite was demonstrated to form after a coupon removed from seawater was exposed to air and dried [10].

Finally, it can be noted that the only differences observed between the two columns were identifications of minor phases in one case and not in the other. Only two couples of coupons were concerned, coupons C2 where traces of brucite were observed after 52 months but not after 32 months, and coupons C16 where traces of a green rust compound were

observed after 32 months, but not after 52 months. In both cases, these were minor phases that may have been present on the other column but not detected because they were present in a too small amount.

3.3. Evolution of the Final m_f/S Ratio with Immersion Rate

Figure 10 displays the evolution of the m_f/S ratio with the immersion rate. As explained in Section 2.4, the m_f/S ratio is proportional to the residual thickness of the coupons and thus the lowest its value, the largest the corrosion damage. In Figure 10, the black crosses correspond to the m_f/S values determined for each considered coupon. The red points are the average values of this ratio for each block of coupons, with the standard deviation represented by the solid red lines. The dash red rectangles highlight the range of m_f/S values for each block. Finally, the dash blue line shows the average m/S value measured on coupons of the same steel with the same dimensions never exposed in corrosive conditions.

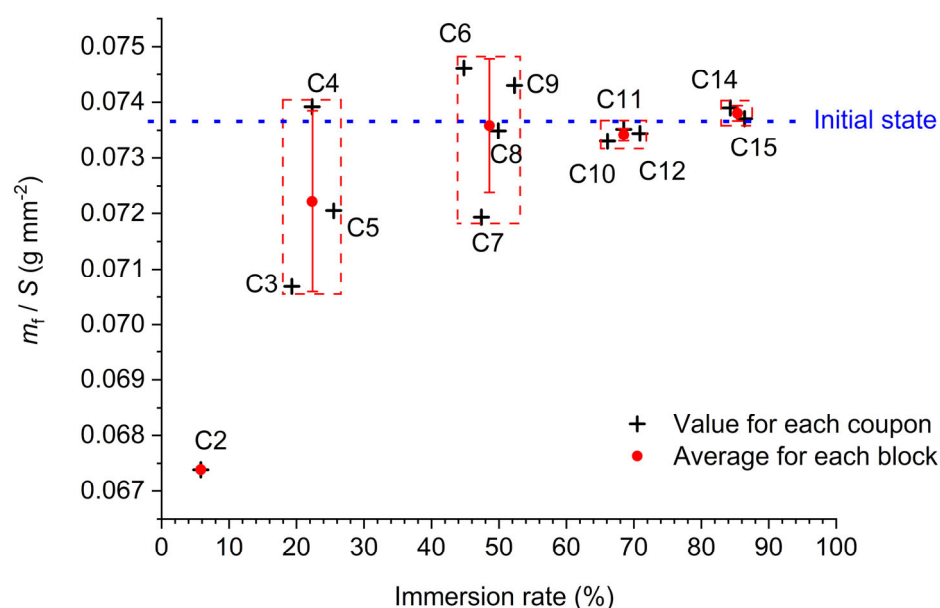


Figure 10. Evolution of the m_f/S ratio with the immersion rate of the steel coupons (back cross) gathered in blocks (red dotted rectangles). The blue dotted line corresponds to uncorroded coupons.

The average m_f/S values obtained for blocks 4 and 5 (C10, C11, C12 and C14, C15) are similar to the value obtained for uncorroded coupons. Moreover, the standard deviation is low, i.e., the determined ratio does not vary significantly from one coupon to another. This indicates that CP is fully effective for the largest immersion rates, i.e., $\geq 66.1\%$ (C10). For block 3 (C6, C7, C8, C9), the average m_f/S value is still comparable with that of uncorroded coupons but the scattering of measured values is important. This indicates that CP may not be fully efficient in this region of the tidal zone. Actually, the values obtained for C8 and C9 are the closest to the average while that of C7 is the lowest, suggesting that the full efficiency of CP may not be guaranteed for coupons higher than C8, i.e., for immersion rates lower than 50%. In agreement, the average m_f/S value decreased for block 2 (C3, C4, C5) and reached a minimum for block 1 (C2).

4. Discussion

The composition of the mineral layers and its evolution with altitude is schematically displayed in Figure 11, from block 5 (Figure 11a) to block 1 (Figure 11d). Brucite and akaganeite are assumed to form locally, as they both require specific conditions (high pH

for brucite [24,25], high Fe^{2+} and Cl^- concentrations for akaganeite [44]) that may not be met all over the steel surface.

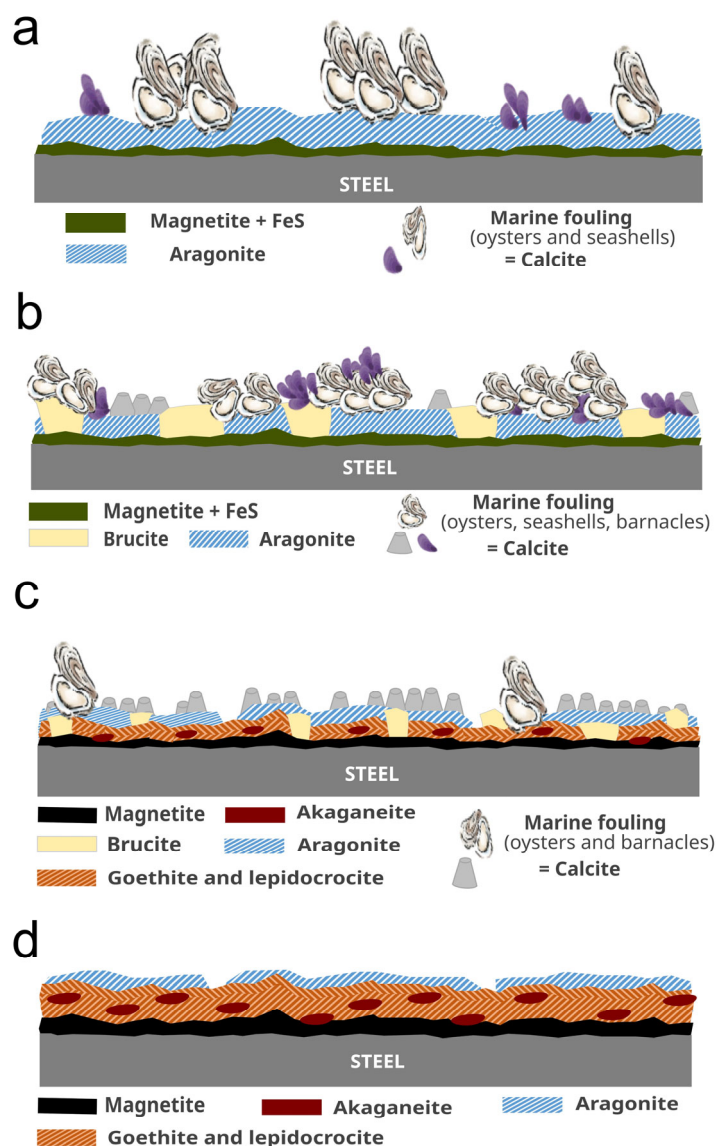


Figure 11. Tentative schematic representation of the composition of the mineral layer covering the coupons as a function of altitude: (a) block 5, e.g., C13, (b) block 3, e.g., C7, (c) block 2, e.g., C4, (d) block 1, e.g., C2. Minor phases such as “pyroaurite” and GR are omitted.

In the low part of the tidal zone (up to coupon C10, immersion rate of 66.1%), both estimation of corrosion damage and analysis of the mineral layer covering the steel surface indicated that CP was fully efficient. Apart from the phases corresponding to fouling and macro-organisms covering the coupons, XRD and μRS analysis only revealed the presence of aragonite, the main constituent of the calcareous deposit induced by CP, and a minor amount of corrosion products, resulting from the “residual” corrosion process occurring even when CP is fully efficient [30,45]. Two corrosion products, magnetite and nano-crystalline mackinawite, were identified on coupons C13, C14 and C16. Only traces of GR compounds could be found, though GR_{SO_4} is one of the main corrosion product forming at OCP [8,10,16,36]. It was however demonstrated that an anodic polarization favoured the formation of GR_{SO_4} while, conversely, a cathodic polarization favoured magnetite [8–10], because of the increased interfacial pH. The quasi-absence of GR_{SO_4} on coupons C13, C14 and C16 is then consistent with the assumption of a fully efficient CP. The presence of

nano-crystalline mackinawite FeS shows that SRB could colonize the steel surface, grow and be active to produce sulphide species. SRB are anaerobe microorganisms and thus the formation of FeS indicates that anoxic conditions were met at the steel surface and in the inner part of the mineral layer covering the coupons. This shows that the coupon surface remained permanently wet, even at low tide. Both magnetite and mackinawite are electronic conductors so that the reduction in dissolved O_2 associated with CP can take place at the surface of the inner layer composed of FeS and Fe_3O_4 . Aragonite, i.e., the calcareous deposit, can then grow on top of this inner layer of “residual” corrosion products (Figure 11a).

In the mid-tide zone (immersion time around 50%), where the coupons of block 3 were exposed, CP can be considered efficient, with a full efficiency for immersion rates higher than 50% (coupon C8). XRD and μ RS analysis of the mineral layers covering the coupons revealed that brucite was formed together with aragonite in this case, and not present as traces but as an important component of the calcareous deposit, unambiguously identified with both XRD and μ RS methods. Laboratory studies demonstrated that applied potentials lower than or equal to -1.2 V/SCE were required to obtain calcareous deposits containing important proportions of brucite [21]. Actually, the formation of $Mg(OH)_2$ requires an interfacial pH higher than a value estimated between 9.3 [25] and 10 [24], which can only be reached, for steel electrodes permanently immersed in seawater, if water reduction is active. Formation of brucite, however, could be favoured at the beginning of the cathodic polarization, due to an initial “pulse” of pH increase, as suggested by Yan et al. [20]. In a previous study, carbon steel coupons were exposed in the mid-tide zone, and after 6 years of CP, the mineral layers were observed to contain a high proportion of brucite [1]. The present study then confirms that the formation of brucite is favoured in the mid-tide zone, if compared to the immersion zone or the lower part of the tide zone, as discussed above.

More precisely, this result demonstrates that brucite, in the mid-tide zone, does not form when the steel surface is immersed, but when it is out of seawater. This can be explained by the concept of persistent humidity: after a few days of exposure in the mid-tide zone, the steel surface is necessarily covered with a porous mineral layer, composed of a mixture of corrosion products, aragonite and brucite. Because of capillary action, the pores of this layer facilitate the persistence of water on the steel surface at low tide. Therefore, as the structure is geometrically continuous and entirely covered with a porous mineral layer, CP remains efficient and O_2 reduction active, with a diffusion pathway restricted to the electrolyte trapped in the pores of the mineral layer. The key point here is that the OH^- ions produced at the steel surface can only accumulate in this thin layer of electrolyte and cannot go away from the interface because of the small layer thickness. Consequently, even if the applied potential is about -1.0 V/Ag-AgCl-seawater (or even higher due to the ohmic drop in the thin electrolyte layer, see thereafter), the pH reaches a sufficiently high value to lead to brucite formation.

The “residual” corrosion products are, as for the coupons exposed in the low part of the tidal zone, magnetite and nano-crystalline mackinawite (Figure 11b). This result confirms that most of the steel surface remained permanently wet with an increased interfacial pH, as explained above. Another Fe-containing phase was however observed as a minor component of the mineral layer. It is similar to pyroaurite, the $Mg(II)$ - $Fe(III)$ hydroxycarbonate isomorphous to GR_{CO_3} , but may contain $Fe(II)$, i.e., may be an intermediate between pyroaurite and GR_{CO_3} . Anyway, this result also illustrates that the residual corrosion process took place at a pH higher than that of seawater. At the pH of seawater, and at lower pH values, GR_{SO_4} is obtained, whereas if the pH is increased, GR_{CO_3} is favoured [23]. It was even observed that a layer of GR_{SO_4} formed on a steel coupon immersed in seawater at OCP could be transformed to a layer of GR_{CO_3} when CP was applied [30].

For the coupons immersed in the higher part of the tidal zone, the results proved different. First, the efficiency of CP was only partial, i.e., a significant degradation of the metal was observed. The results obtained for coupons C3 to C5 (block 2, immersion rate between 19.3% and 25.5%), schematized in Figure 11c, indicate that CP was efficient, at least partially, when the coupons were out of seawater. The estimated degradation was intermediate between that of coupon C2 and that of coupons C6–C9 (Figure 10). Similarly, the mineral layers (Figure 5, XRD for C4 and Figures 8 and 9, μ RS for C5), contain phases such as goethite, lepidocrocite and akaganeite, also detected on coupon C2, and brucite, also detected on coupons C6–C9. A key point is that FeS could not be identified. This shows that the coupons, at that altitude, were repeatedly sufficiently dried so that anaerobic microorganisms could not develop and produce the sulphide species required for FeS formation. It can be forwarded that this drying led to the breaking of the electrolytical connection between coupons and the anode so that CP was not effective when the coupons were emerged, at least for part of the emersion time.

The degradation was finally the most severe for the highest coupons (block 1, Figure 10). For coupon C2 (immersion rate of 5.8%), the mineral layer formed on the steel surface was mainly composed of corrosion products (Figure 11d). XRD analysis revealed that goethite and magnetite were predominant and accompanied by lepidocrocite and akaganeite (Figure 5b). Pyroaurite and aragonite were observed too, indicating that CP was partially efficient, at least when the coupon was immersed. However, brucite was not detected, which indicates that CP was rarely efficient when the coupon was out of the water. Two assumptions, which do not exclude each other, can be forwarded. The first one is that the continuity of the electrolytic pathway required for the current to flow from the steel coupon to the anode was rarely achieved. The second assumption is linked to the ohmic drop. For coupon C2, set 5 m above the low-tide level, even if persistent humidity is sufficient to connect the coupon surface to the seawater level, the ohmic drop may be so important that only a slightly cathodic polarization would be achieved. To take an example and to simplify, we can consider that persistent humidity corresponds to a 2 mm-thick layer of pure seawater electrolyte. Its width would be that of the coupons, i.e., 10 cm, then the electrolyte section S would be 2 cm^2 . The resistance R of an electrolytic pathway of length L and section S is given by:

$$R = \frac{\rho L}{S} \quad (3)$$

In this equation, ρ is the resistivity of the electrolyte, i.e., ρ is about $25 \text{ } \Omega \text{ cm}$ for seawater. Then, if $L = 5 \text{ m}$, $R = 625 \text{ } \Omega$. According to the relevant CP standard [46], the recommended protection current density for unpainted steel structures in the tidal zone is $|j_{\text{CP}}| = 45 \text{ mA m}^{-2}$. For 100 cm^2 , i.e., the surface of a coupon in the present study, the cathodic current (in absolute value) is then $I_{\text{CP}} = 0.45 \text{ mA}$. The corresponding ohmic drop, $R \times I_{\text{CP}}$, is then equal to 281 mV . With this example, considering the cathodic potential measured when steel was immersed ($-1.0 \text{ V}_{/\text{Ag-AgCl-seawater}}$), the potential of coupon C2 would be equal to $-719 \text{ mV}_{/\text{Ag-AgCl-seawater}}$ at low tide if the electrolytical pathway is maintained. Such a potential may be too low for a fully efficient CP, too low for brucite to form even if the electrolyte thickness is small, but sufficiently low for aragonite to form [23]. In contrast, for coupon C8 set 2 m lower, R would be equal to $375 \text{ } \Omega$, the ohmic drop then equal to 169 mV and the potential of the coupon to $-831 \text{ mV}_{/\text{Ag-AgCl-seawater}}$ at low tide, i.e., in the worst case. Such a potential is lower than the recommended threshold value of $-800 \text{ mV}_{/\text{Ag-AgCl-seawater}}$ for steel in an aerobic environment [46]. This simplified computation, only given as an example, illustrates the role of the ohmic drop. It demonstrates that, even if humidity could persist all along the steel surface, with seawater

trapped in the pores of the mineral layer, CP may be fully efficient at mid-tide but not (or much less) in the highest part of the tidal zone.

5. Conclusions

The composition of the mineral layer formed on vertical steel structures under CP varied all along the tidal zone:

In the lowest part of the tidal zone, the composition proved similar to that observed for permanently immersed steel, i.e., mainly composed of aragonite, with magnetite and FeS as minor components associated with the “residual” corrosion process [30].

In the mid-tide zone, a transition between full and partial efficiency of CP was observed. In the specific conditions of this study, the transition took place around an immersion rate of 50% (coupon C8). In the mid-tide zone, the mineral layer proved enriched in brucite (and “pyroaurite”), a typical feature that can be associated with the persistence of humidity on the steel surface even when it is emerged. Steel is covered with fouling and a porous mineral layer. Seawater is then trapped in the pores of this mineral layer, leading to “persistent humidity”, which can be considered, for simplification, as a thin persistent electrolyte film. The OH^- ions produced by the reduction of O_2 accumulate in this thin electrolyte film, leading to the high pH values required for $\text{Mg}(\text{OH})_2$ to form.

In the highest part of the tidal zone (blocks 1 and 2, immersion rates $\leq 25\%$), CP efficiency was only partial and decreased with the altitude of the coupon. The mineral layer included corrosion products typical of aerated marine environments such as akaganeite and goethite.

Finally, it must be recalled that these results were obtained in a given seaport, with a given orientation (coupons facing north). The general trends observed here should not vary significantly from one seaport to another, as the proposed mechanisms may take place similarly everywhere, but the altitude where CP efficiency remains maximal may vary from one seaport to another and even in a given seaport, depending on the orientation with respect to sun, wind, etc.

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