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Electrochemical formation of green rusts in deaerated seawater-like solutions

Ph. Refait [a,c,*], D.D. Nguyen [a,d], M. Jeannin [a,c], S. Sable [b,c], M. Langumier [a,b,c], R. Sabot [a,c]

[a] *Laboratoire d'étude des matériaux en milieux agressifs (LEMMA), EA 3167, Université de La Rochelle, Bât. Marie Curie, Av. Michel Crépeau, F-17 042 La Rochelle Cedex 01, France*
[b] *Littoral, Environnement et Société (LiENSs), UMR 6250, CNRS-Univ. La Rochelle, Bât. Marie Curie, Av. Michel Crépeau, F-17 042 La Rochelle Cedex 01, France*
[c] *Féd. de Recherche en Environnement et Développement Durable, FR CNRS 3097, France*
[d] *Hue University's College of Education, Hue, Viet Nam*

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ABSTRACT

Carbon steel electrodes were polarised at a potential ~150 mV higher than the open circuit potential, in a deaerated seawater-like electrolyte (0.5 mol dm^{-3} NaCl, 0.03 mol dm^{-3} Na_2SO_4, 0.003 mol dm^{-3} $NaHCO_3$). X-ray diffraction and μ-Raman analysis demonstrated that a layer mainly composed of GR(SO_4^{2-}) had grown on the steel surface. GR(SO_4^{2-}) was accompanied by traces of GR(CO_3^{2-}). Similar experiments performed in a solution composed of 0.3 mol dm^{-3} of Na_2SO_4 and 0.03 mol dm^{-3} of $NaHCO_3$ led to the same result. The nature of the GR forming on steel is thus mainly linked to the sulphate to carbonate concentration ratio. Finally, carbon steel coupons immersed for 11 years in the harbour of La Rochelle (Atlantic coast) were removed from seawater for analysis. The inner part of the rust layer proved to be mainly composed of magnetite, GR(SO_4^{2-}) and iron sulphide FeS. This definitively confirms that GR(SO_4^{2-}), as Fe_3O_4 and FeS, can form from steel in O_2-depleted environments.

1. Introduction

Marine corrosion of carbon steel involves first the formation of the Fe(II–III) hydroxysulphate also known as sulphated green rust GR(SO_4^{2-}) [1]. Green rusts (GRs) are Fe(II–III) hydroxysalts characterised 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 [2,3]. Several GRs are known, and in 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 $Fe^{II}{}_4Fe^{III}{}_2(OH)_{12}SO_4{\cdot}8H_2O$, [3] sometimes developed as $[Fe^{II}{}_4Fe^{III}{}_2(OH)_{12}]^{2+}$ $[SO_4{\cdot}8H_2O]^{2-}$ to remind that the crystal structure is built on positive hydroxide layers alternating with negative interlayers. In seawater, the $[Cl^-]/[SO_4^{2-}]$ and $[SO_4^{2-}]/[HCO_3^-]$ molar ratios are about 19 and 12, respectively (computed from [4]). Laboratory experiments were devoted to the oxidation by air of aqueous suspensions of $Fe(OH)_2$ in the presence of sulphate and chloride ions [5,6]. It could be demonstrated that GR(SO_4^{2-}) formed instead of GR(Cl^-) even in solutions with large $[Cl^-]/[SO_4^{2-}]$ molar ratios, as the layered structure of GRs presents a strong affinity for divalent anions.

Green rusts are readily oxidised into FeOOH compounds by dissolved O_2. So, at the beginning of the process, the rust layer formed on steel in seawater should be composed of an outer layer of Fe(III) oxyhydroxides and an inner layer of GR(SO_4^{2-}). However, after 6 or 12 months of immersion, GR(SO_4^{2-}) was found systematically associated with iron sulphide FeS and sulphate reducing bacteria (SRB) [1]. This indicated that anoxic conditions were established at the steel/rust layer interface and inside the inner part of the rust layer. The presence of FeS on steel in seawater is a consequence of the metabolic activity of SRB, since in seawater sulphur is only present as sulphate in the absence of bacterial activity. The anoxic conditions are due to the fact that dissolved oxygen is consumed in the outer part of the rust layers by (i) aerobic micro-organisms and (ii) its reaction with GR(SO_4^{2-}) that mainly leads to Fe(III) oxyhydroxides. So, after some time, the kinetics of the corrosion is no more controlled by oxygen transport [7–10]. Since the process is then clearly linked to the activity of micro-organisms, it was for instance proposed that the availability and transport of the nutrients necessary for the micro-organisms could be the limiting step [10].

It is now demonstrated that SRB can reduce the sulphate ions coming from GR(SO_4^{2-}) [11,12]. This phenomenon induces the transformation of GR(SO_4^{2-}) into various compounds, and in particular iron sulphides such as mackinawite [12]. Therefore it can be expected that GR(SO_4^{2-}) is totally consumed and that after some time, it is totally absent of the rust layers. However, previous

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* Corresponding author at: Laboratoire d'étude des matériaux en milieux agressifs (LEMMA), EA 3167, Université de La Rochelle, Bât. Marie Curie, Av. Michel Crépeau, F-17 042 La Rochelle Cedex 01, France. Tel.: +33 5 46 45 82 27; fax: +33 5 46 45 72 11.
E-mail addresses: prefait@univ-lr.fr, philippe.refait@univ-lr.fr (Ph. Refait).

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works performed in carbonated media indicated that the carbonated green rust, GR(CO_3^{2-}) could be obtained in anoxic or almost anoxic conditions [13–15]. So if GR(SO_4^{2-}) could still form on steel in anoxic conditions it would remain along with FeS one of the components of the rust layer. The aim of this work was then to study the formation of rust on steel in deaerated seawater. In order to focus on the role of anionic species, an electrolyte composed of 0.5 mol dm^{-3} NaCl, 0.03 mol dm^{-3} Na_2SO_4 and 0.003 mol dm^{-3} $NaHCO_3$ was considered as a "seawater-like" solution. The concentration ratios [Cl^-]/[SO_4^{2-}] (=16.6) and [SO_4^{2-}]/[HCO_3^-] (=10) were close to those characteristic of seawater. Electrochemical experiments (voltammetry, chronoamperometry) were performed in anoxic conditions and the components of the electro-generated rust layers were studied by μ-Raman spectroscopy, X-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy dispersive spectrometry (EDS). Finally, rust layers grown during 11 years on steel coupons in seawater were analysed by μ-Raman spectroscopy. The behaviour of the real corrosion system could then be interpreted at the light of the information given by laboratory experiments.

2. Experimental

2.1. Electrochemistry

Electrochemical experiments were carried out in a classical three-electrode glass cell. The working electrodes were carbon steel disks with 2 cm^2 area. The steel approximate composition (in wt%) was: 98.2% Fe, 0.122% C, 0.206% Si, 0.641% Mn, 0.016% P, 0.131% S, 0.118% Cr, 0.02% Mo, 0.105% Ni and 0.451% Cu. The surfaces were polished with silicon carbide (particle size 25 μm), rinsed thoroughly with Milli-Q water and rapidly dried in an air flow. The working electrodes were positioned horizontally with the active surface set upwards. They were set in the electrochemical cell just before the beginning of the experiment. Potentials were measured vs. the saturated calomel electrode (SCE). A large platinum grid was used as counter electrode.

Voltammetric and chronoamperometric (anodic polarisation) experiments were performed with a PGP 201 potentiostat system (Radiometer analytical). For linear voltammetry, the scans were started at −1.20 V/SCE and ended at +0.5 V/SCE, with a scan rate $dE/dt = 1$ mV s^{-1}. Anodic polarisation experiments were performed at −0.60 V/SCE, i.e. approximately 0.15 V above the open circuit potential (OCP). OCP was measured during 30 min at the beginning of each experiment prior to voltammetry or chronoamperometry. It varied around −0.75 V/SCE.

Since the study related mainly to the role of anionic species, a simplified electrolyte prepared with NaCl, Na_2SO_4, and $NaHCO_3$ was used instead of artificial seawater. The sodium salts with 98% min. purity (Aldrich) were dissolved in Milli-Q water (resistivity 18.2 MΩ cm). The concentrations, set as 0.5, 0.03 and 0.003 mol dm^{-3} for NaCl, Na_2SO_4, and $NaHCO_3$ respectively, were close to those typical of seawater. The pH of this electrolyte was measured at the beginning of the experiments at an average value of 7.95. Note that the pH of ASTM D1141 artificial seawater is 8.2.

Two procedures were considered for deaeration. First, experiments were achieved in the electrochemical cell under an argon flow. The solutions were deaerated by the argon flow during 45 min before the beginning of each experiment and the argon flow was maintained till the end. Secondly, experiments were performed in an electrochemical cell set inside a glove box (Jacomex P[box]-T4) filled with Argon. In this case, the atmosphere inside the box contained a residual oxygen content ≤1 ppm.

The electrolyte was not stirred during the experiments. However, the argon flow induced by itself a stirring of the electrolyte through its permanent bubbling. In contrast, during the experiments performed in the glove box, the electrolyte was really stagnant.

Additional experiments were performed in a second electrolyte, composed of Na_2SO_4 (0.3 mol dm^{-3}) and $NaHCO_3$ (0.03 mol dm^{-3}). It kept the sulphate to carbonate concentration ratio of 10 of the seawater-like electrolyte but the concentrations were ten times larger. The experimental procedure was strictly identical to that used in the seawater-like electrolyte.

2.2. Steel coupons immersed in seawater

In 1999, a series of carbon steel coupons (70 mm × 70 mm × 6 mm) were immersed in one the harbours of La Rochelle (Atlantic coast, France) in the frame of a PhD work. Most of the coupons were used at that time but it was decided to leave a few of them in place for future works. One of these coupons was removed for analysis in 2010. It was made of the carbon steel used for laboratory experiments (see Section 2.1) and was permanently immersed at a constant depth of 1 m during those 11 years. For μ-Raman spectroscopy analysis, the coupons were frozen at −80 °C. This freezing procedure was necessary to preserve the reactive Fe(II) compounds from the oxidizing action of O_2. Moreover, the rust layers are easier to handle in this hardened frozen state than in their wet and slurry room temperature state. Slices of the corrosion products layer could then be easily extracted and their stratification could be investigated.

2.3. Characterisation of the rust layers

Micro-Raman analyses were performed on a Jobin Yvon High Resolution Raman spectrometer (LabRAM HR) equipped with a microscope (Olympus BX 41) and a Peltier-based cooled charge coupled device (CCD) detector. The zones analysed through a 50× objective had a diameter of ~6 μm. Spectra were recorded with the acquisition LabSpec software at room temperature with a resolution of ~0.1 cm^{-1}. Excitation was provided by a He–Ne laser (632.8 nm). Its power was 0.9 mW, that is 10% of the maximal power, in order to prevent an excessive heating that could have induced the transformation of the analysed sample into hematite α-Fe_2O_3. The acquisition time was variable, around an average value of 1 min, and was chosen for each analysis so as to optimise the signal to noise ratio.

XRD experiments were carried out with a classical powder diffractometer (Brucker AXS® D8-Advance), using Cu-Kα wavelength ($\lambda = 0.15406$ nm) in Bragg–Brentano geometry. The electrodes were removed from the electrochemical cell just before analysis. Since the expected Fe(II) compounds were sensitive to the oxidising action of air, the electrodes were immediately placed on the sample holder and the rust layer was coated with glycerol before the analysis. This procedure limits the oxidation of the Fe(II) compounds during the acquisition of the pattern.

Finally, the morphology of the electrochemically generated rust layers was observed using scanning electron microscopy (SEM) with a PHILIPS FEI Quanta 200F apparatus. The composition of the main component of the rust layers was estimated by energy dispersive spectroscopy (EDS) coupled to SEM (acceleration voltage: 15 kV). The samples to be analysed were carried from the laboratory to the SEM apparatus inside a bag filled with argon. They were exposed to atmosphere when they were removed from the cell before to be set in the bag and when they were removed from the bag before to be set in the SEM apparatus.