

Formation and transformation of Fe(II-III) hydroxysalts (GRs) in marine environments

P. REFAIT^{1*}, M. JEANNIN¹, R. SABOT¹,
C. REMAZEILLES¹, AND A.-M. GROLLEAU²

¹ LaSIE, UMR 7356 CNRS, Univ. La Rochelle, Bât. Marie Curie, Av. Michel Crépeau, 17042 La Rochelle, France
(*correspondence: prefait@univ-lr.fr, mjeannin@univ-lr.fr, rsabot@univ-lr.fr, celine.remazeilles@univ-lr.fr)

² DCNS Research, BP 440, 50104 Cherbourg-Octeville, France (anne-marie.grolleau@dcsngroup.com)

The Fe(II-III) hydroxysulfate green rust $\text{GR}(\text{SO}_4^{2-})$ is one of the main corrosion products of carbon steel in marine environments [1, 2]. It is typical of the abiotic (i.e. purely electrochemical) process as demonstrated by laboratory experiments [3] in aerated and anoxic conditions as well. Even though the Cl^- to SO_4^{2-} concentration ratio is equal to 19 in seawater, $\text{GR}(\text{SO}_4^{2-})$ forms preferentially to the hydroxychloride $\text{GR}(\text{Cl}^-)$ because divalent anions gave to the layered structure of GRs a greater stability than monovalent anions. However, variations of seawater parameters such as pH, carbonate concentration or organic matter content can induce the transformation of $\text{GR}(\text{SO}_4^{2-})$ into other Fe(II-III) bearing minerals such as hydroxycarbonate $\text{GR}(\text{CO}_3^{2-})$, magnetite Fe_3O_4 or even other GRs built on organic anions. For instance, an increase of pH, leading to an increase of the CO_3^{2-} to HCO_3^- concentration ratio, may lead to the transformation of $\text{GR}(\text{SO}_4^{2-})$ into $\text{GR}(\text{CO}_3^{2-})$ [4]. The respective proportions of $\text{GR}(\text{SO}_4^{2-})$ and $\text{GR}(\text{CO}_3^{2-})$ in marine environments are mainly governed by the SO_4^{2-} to CO_3^{2-} concentration ratio [3]. On the other hand, the accumulation of bacterial cells and their lysis can induce the formation of unexpected GRs, e.g. $\text{GR}(\text{C}_2\text{O}_4^{2-})$, as for instance observed on steel immersed in marine sediments.

It is suspected that a partial substitution of Fe^{2+} by Mg^{2+} occurs in the GR structure at low corrosion rates, i.e. for low dissolved Fe(II) species concentrations. This was also observed for the naturally occurring fougérite mineral GR [5]. The presence of Mg(II) in the hydroxide layer of GRs should enhance the redox flexibility of GR minerals, hence improving their well-known ability to reduce oxidized pollutants such as nitrite, selenate, chromate, etc..

[1] Pineau *et al.* (2008) *Corros. Sci.* 50, 1099-1111. [2] Refait *et al.* (2016) *Corros. Sci.* 111, 583-595. [3] Refait *et al.* (2011) *Electrochim. Acta* 56, 6481-6488. [4] Refait *et al.* (2013) *Corros. Sci.* 71, 32-36. [5] Refait *et al.* (2001) *Amer. Min.* 86, 731-739.