**In situ** oxidation of green rusts by deprotonation; wet corrosion and passivation of weathering steels

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**Abstract.** Intermediate compounds that belong to the layered double hydroxide family and bear the common name of green rusts (GR) get oxidized through two modes determining material wearing for steel corrosion: either the classical aerial mode where the GR gets dissolved before precipitating into several types of orange ferric oxyhydroxides FeOOH rusts, or the *in situ* deprotonation of OH⁻ ions within the GR. Hydroxycarbonate, GR(CO₃²⁻), [Fe₄II₃III(II)₂(OH)₁₂]²⁺ · [CO₃²⁻ · 3H₂O]²⁻, produced e.g. in carbonated medium, becomes [Fe₆III₃II₄(OH)₁₂(CO₃)₈], which is an oxyhydroxycarbonate where ferric molar ratio x = [Fe₃II / Fe₃III] belongs to the [0, 1] interval; it ends into the “ferric green rust”, GR(CO₃²⁻)ₙ, [Fe₆III₃II₄H₃]ₙ⁺ · [CO₃²⁻ · 3H₂O]ₙ⁺, which is in fact orange. These two modes of oxidation of GR that depend upon the flux of oxygen that is used give rise to two different corrosion behaviors. The first one corrodes the material since the GR layer covering the steel surface gets dissolved before precipitating ferric oxyhydroxide. The second mode occurs within the GR layer without destruction; thus, the metal is passivated as for weathering steels.

1. Introduction

Wet corrosion of steels corresponds to the presence of intermediate Fe^{II,III} compounds commonly named green rusts (GR) because of their colour [1, 2]; they belong to the family of layered double hydroxides (LDH) where di- and trivalent cations are Fe^{II} and Fe^{III} ions, respectively [3]. They form during iron oxidation from the ferrous state, i.e. Fe(OH)₂, and transform into ferric oxyhydroxides of general formula Fe^{III}OOH [4-6]. The type of GR depends upon the anion species dissolved in the water solution and the most studied GRs incorporate Cl⁻, SO₄²⁻ and CO₃²⁻ anions [4-6, 7-11]. They are constituted of brucite-type layers [Fe^{II}(1-x)Fe^{III}x(OH)₂]ₓ⁺ that are electrostatically balanced by interlayers [(x/ₙ)Aⁿ⁺ · (m/ₙ)H₂O]ⁿ⁻, where Aⁿ⁺ are intercalated anions. For instance, GR(CO₃²⁻), the Fe^{II,III} hydroxycarbonate Fe₄ІІІ₃ІІІ(II)₂(OH)₁₂CO₃ at x = 0.33, displays a long range order for cations and anions as determined by XRD and Mössbauer spectroscopy, which is very suitable for assessing the ferric molar ratio x = [Fe^{III}]/[Fe^{total}] [12, 13]. Spectra display in the paramagnetic state at 78 K three doublets, D₁ and D₂ with quadrupole splitting Δ of 2.97 and 2.55 mm s⁻¹ and isomer shift δ both of 1.28 mm s⁻¹ attributed to Fe^{II}, and D₃ with Δ and δ of 0.43 and 0.47 mm s⁻¹ attributed to Fe^{III}.

Using Mössbauer spectroscopy for monitoring the speciation of iron, it was possible to follow the oxidation of GRs in usual conditions and simulate the wet corrosion of steel [4, 7-11]. We consider the carbonated medium, the most important for practical purposes and for which the EₚH Pourbaix diagram of GR(CO₃²⁻) has been established [9]. Let us recall that a GR layer forms on the surface of an
iron-based material before transforming into Fe$^{III}$OOH as observed when stirring a solution of GR(CO$_2$$^2$) in the air [Top left [Figure 1], from [14]]. This is the usual mode of corrosion of steel when intermediate GR(CO$_2$$^2$)$^*$ disappears into solution before forming a brownish orange ferric rust Fe$^{III}$OOH.

In this paper, we shall show that another mode of oxidation may occur and that GR(CO$_2$$^2$)$^*$ may get oxidized in situ by deprotonation up to a ferric GR(CO$_2$$^2$)$^*$*, which is reddish orange [15].

2. Influence of oxygen rate on the oxidation mode of GR(CO$_2$$^2$)$^*$

2.1. Synthesis of initial Fe$^{II-III}$ hydroxycarbonate
An initial GR(CO$_2$$^2$)$^*$ precipitate was prepared in a gas tight reactor through which a continuous flux of nitrogen bubbled. A 600 mL salt mixture, which was composed of dissolved Fe(SO$_4$$^2$)$^*$7H$_2$O and Fe$_2$(SO$_4$$^3$)$^*$5H$_2$O, was progressively neutralised with 37 mL of Na$_2$CO$_3$ solution ([Fe$^{III}$] = 2.2 × 10$^{-2}$ M, [Fe$^{III}$] = 1.2 × 10$^{-2}$ M, [Na$_2$CO$_3$] = 1.1 M) [17]. The suspension was homogenised by stirring with a magnetic rod. Once the basic solution completely added, the pH was about 9.3.

2.2. Oxidation of Fe$^{II-III}$ hydroxycarbonate GR(CO$_2$$^2$)$^*$ by O$_2$ bubbling.
GR(CO$_2$$^2$)$^*$ got oxidized with relative oxygen concentrations X(O$_2$) = [p(O$_2$) / p$_{total}$] at 2.7, 6.7, 13.3 and 20% from a mixture of synthetic air and nitrogen with a magnetic rod rotation of 375 rpm. Electrode potential $E_t$(V) and pH were recorded continuously with time [Figure 1]. Gas flow F(O$_2$) varied from 0.4 to 2.9 moles per day [Table 1]. Oxidation efficiency, i.e. the ratio between the O$_2$ mole number reacting with Fe$^{II}$ species and O$_2$ mole number introduced in the solution, was approximately 1%, a value independent of F(O$_2$); pH did not vary significantly ~9, due to the buffering effect of carbonate.

Curves (β-δ) display two plateaus separated by equivalent point E. Around E, the initial dark-blue colour of the suspension became rapidly yellow-brown. Point E is attributed to the end of oxidation; its abscissa t$_f$ shifts towards longer periods when X(O$_2$) decreases. Curve (α) exhibits one more plateau separated by point P before reaching point E for the lowest X(O$_2$) value at 2.7%. A hook H is distinguished on all curves at the beginning of oxidation process and its height increases with X(O$_2$) [Figure 1]. Mean oxidation velocity V(O$_2$) = [n(O$_2$)/t$_f$] is evaluated where n(O$_2$) is the consumed oxygen mole; it corresponds to Fe$^{II}$ species present in the initial GR(CO$_2$$^2$)$^*$ [Table 1]. Oxidation efficiency is computed from [V(O$_2$) / F(O$_2$)] and stays practically constant at a low value around 1%.

Solid characterisation carried out by XRD and Mössbauer reflection at ambient under continuous inert N$_2$ gas flow in a glove box showed that goethite formed for X(O$_2$) values of 20, 13.3 and 6.7% [Figure 1b], whereas it led to a mixture of magnetite and goethite for X(O$_2$) = 2.7% [Figure 1a] [16]. Mössbauer spectrum measured at ambient confirmed that off-stoichiometric magnetite formed [17] and that only 12% of Fe atoms were present into α-FeOOH [Figure 1a] [Table 2]. According to XRD patterns, doublet D in the central part is attributed to Fe$^{III}$ species present in superparamagnetic goethite crystals of low size (< ~100 nm) [Figure 1a]. Similar behaviour was observed for goethite forming alone at higher X(O$_2$) where doublet D became a magnetic sextet due to increasing crystal size [Figure 1b].

2.3. Air oxidation of Fe$^{II-III}$ hydroxycarbonate GR(CO$_2$$^2$)$^*$
N$_2$ bubbling was stopped and the reactor was exposed to the air. A vigorous magnetic stirring was set at 750 rpm in order to accelerate the oxidation process. The final pH at the end of the co-precipitation experiments decreased slightly from 9.3 to 9. In a second experiment, the final pH obtained at the end of the GR(CO$_2$$^2$)$^*$ co-precipitation, i.e. pH = 9.3, was adjusted with a concentrated HCl solution at a value of 7 ± 0.2. The same air oxidation experiment was performed by maintaining a constant pH of 7.

The evolution of redox potential $E_h$ for pH values of 9 and 7 was recorded [curve (ε) for pH 9]. The trend was significantly different if compared to the previous {O$_2$ + N$_2$} bubbling experiments [curves (α–δ)]; (i) a gradual increase of $E_h$ was observed along with the absence of equivalent points, (ii) the kinetics of oxidation was much faster and the final $E_h$ plateau situated between +300 and +400 mV was reached between 2 and 8 times more rapidly. In contrast, the pH did not influence the kinetics.
Table 1. Experimental conditions and nature of the final oxidation products; \( X(O_2) \% \) is the percentage of oxygen present in the gas flow. The oxidation velocity is determined by using the oxidation time \( t_f \) at the equivalent point of Figure 1. The efficiency of the oxidation is determined by the ratio \( V(O_2) / F(O_2) \) where \( F(O_2) \) is the flow of \( O_2 \) bubbled into the solution.

| Type of oxidation | Controlled O\(_2\) bubbling | Controlled O\(_2\) bubbling | Controlled O\(_2\) bubbling | Controlled O\(_2\) bubbling | Air oxidation |
|------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|--------------|
| Curve name       | (\( \alpha \))              | (\( \beta \))               | (\( \gamma \))              | (\( \delta \))              | (\( \epsilon \)) |
| \( X(O_2) \% \) | 2.7 ± 0.1                   | 6.7 ± 0.1                   | 13.3 ± 0.2                  | 20 ± 0.2                    | -            |
| magnetic stirring (rpm) | 375                          | 375                          | 375                         | 375                         | 750          |
| oxidation time \( t_f \) (min) | 700 ± 10                      | 440 ± 10                     | 290 ± 5                     | 170 ± 5                     | 80 ± 2       |
| Oxidation velocity (Mole per day) | 0.005                         | 0.011                        | 0.016                       | 0.028                       | 0.06         |
| \( F(O_2) \) Flow of \( O_2 \) (Mole per day) | 0.4                           | 1                            | 1.9                         | 2.9                         | -            |
| Efficiency       | 1.2                          | 1.1                          | 0.9                         | 1                           | -            |
| \([V(O_2) / F(O_2)] \%\) | Black                         | Yellow-brown                 | Yellow-brown               | Yellow-brown                | Orange-brown |
| Colour of the final product | Magnetite + Goethite          | Goethite                     | Goethite                    | Goethite                    | GR*          |

Figure 1. Top left. The first step of corrosion: the GR layer observed by CEMS spectrum at ambient of a steel disk dipped 24 hours in a 0.1 M NaHCO\(_3\) solution [14]. Top right. Electrode potential during oxidation of GR(CO\(_3\)\(^{2-}\)) with rate of O\(_2\); Bottom: XRD patterns and Mössbauer spectra at 293 K of end products: dissolution-precipitation (a-b) [curves (\( \alpha-\delta \))] or in situ deprotonation (c) [curve (\( \epsilon \))].
since a constant value for $E_h$ was reached after $\sim 80$ minutes in both experiments (pH = 7 and 9). End product of oxidation as shown by XRD was now GR(CO$_3^{2-}$)*, ferric oxyhydroxycarbonate, which was characterized by two (00.3) and (01.2) main lines, in good agreement with literature [Figure 1c].

Similarly, a paramagnetic doublet characteristic of GR(CO$_3^{2-}$)* was observed for these samples in the Mössbauer spectra for both experiments performed at pH = 9 or 7 [Figure 1c] [18].

### 3. Conclusion

A first stage of aqueous corrosion of iron corresponds to the formation of Fe(OH)$_2$ followed by that of a GR layer at the metal surface depending on the nature of the dissolved anions. For instance, a GR(CO$_3^{2-}$) rust layer was identified by CEMS at ambient on a steel disk dipped 24 hours in a 0.1 M NaHCO$_3$ solution (upper part [Figure 1]) [14]. Once a GR layer is formed, oxidation proceeds. Two modes may occur depending on the conditions: slow or fast oxidation i.e. dissolution-precipitation or in situ deprotonation [Figure 2]. This last mode is responsible for the passivation of weathering steels.

### References

[1] Girard A and Chaudron G 1935 C.-R. Acad. Sci. Paris **200** 127
[2] Feitknecht W and Keller G 1950 Z. Anorg. Allg. Chem. **262** 61
[3] Hansen H C B 2001 Environmental chemistry of iron(II)-iron(III) LDHs (green rusts) *Layered double hydroxides: present and future* Nova Science publishers p. 469
[4] Génin J-M R, Bauer Ph, Olowe A and Rézel D 1986 *Hyperfine Interact.* **29** 1355
[5] Olowe A, Génin J-M R and Bauer Ph 1987 *Hyperfine Interact.* **41** 501
[6] Drissi S H, Refait Ph and Génin J-M R 1994 *Hyperfine Interact.* **90** 395
[7] Refait Ph and Génin J-M R 1993 *Corros. Sci.* **34** 797
[8] Génin J-M R, Olowe A A, Refait Ph and Simon L 1996 *Corros. Sci.* **38** 1751
[9] Drissi S H, Refait Ph, Abdelmoula M and Génin J-M R 1995 *Corros. Sci.* **37** 2025
[10] Génin J-M R, Refait Ph, Simon L and Drissi S H 1998 *Hyperfine Interact.* **111** 313
[11] Génin J-M R, Ruby C, Génin A and Refait Ph 2006 *C.-R. Geoscience* **338** 433
[12] Génin J-M R and Ruby C 2004 *Solid State Sci.* **6** 705
[13] Génin J-M R and Ruby C 2008 *Solid State Sci.* **10** 244
[14] Abdelmoula M, Refait Ph, Drissi S H, Mihé J P and Génin J-M R 1996 *Corros. Sci.* **38** 623
[15] Génin J-M R, Aïssa R, Génin A, Abdelmoula M, Benali O, Ernstsen V, Ona-Nguema G, Upadhyay C and Ruby C 2005 *Solid State Sci.* **7** 545
[16] Benali O, Abdelmoula M, Refait Ph and Génin J-M R 2001 *Geochim. Cosmochim. Acta* **65** 1715
[17] Vanderberghe R E, Barrero C A, Da Costa G M, Van San E and De Grave E 2000 *Hyperfine Interact.* **126** 247
[18] Génin J-M R, Ruby C and Upadhyay C 2006 *Solid State Sci.* **8** 1330