Green Rusts and Fougerite; From Mineralogy and Environmental Science to Corrosion

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Why go to Mars when there are so many things to understand under our feet on Earth?

Simulation of chemical potential gradient showing the formation of a redox front between NH$_3$ reducer and (a) a ferrous salt, (b) a Fe(II) Fe(III) mixture and (c) a ferric salt. The medium contains sulphate anions and the GR(SO$_4^{2-}$) forms. Agar gel is used for maintaining the diffusion gradient.

Water table

Hydromorphic soil

Gleysol

Organic Matter

Humic substances

Ferric oxyhydroxides

fougerite
About ¼ of the annual production of iron is destroyed every year by corrosion.

Corrosion is the dissolution of a metal due to its oxidation.

In the case of iron, the sequence is: $Fe^0 \rightarrow Fe^{2+} \rightarrow Fe^{3+}$

Oxidation of iron is
$Fe^0 \Rightarrow Fe^{2+} + 2 \text{e}^-$
$Fe^{2+} \Rightarrow Fe^{3+} + \text{e}^-$

This is due to the reduction of oxidants, e.g.
$O_2 + 4 H^+ + 4 \text{e}^- \Rightarrow 2 H_2O$
$2 H^+ + 2 \text{e}^- \Rightarrow H_2$

$Fe^{2+}_{aq}$ exists in a wide range of pH, whereas $Fe^{3+}_{aq}$ necessitates an acidic solution (pH < 4)

To predict corrosion, one draws the electrode potential $E_h$ versus pH graph

We shall complete the $E_h$-pH Pourbaix diagrams by introducing the intermediate $Fe^{II-III}$ compounds, the green rusts
Layered double hydroxides

Green rusts

\[ [\text{Fe}^{II}_{(1-x)} \text{Fe}^{III}_{x} (\text{OH})_2 ]^{x^+} \quad [(x/n)A^{n-}\cdot(mx/n)\text{H}_2\text{O}]^{x-} \]

Layer
Interlayer

**Anions**

\( \text{Cl}^{-}, \text{CO}_3^{2-}, \text{SO}_4^{2-}, \text{HCOO}^{-}, \text{C}_2\text{O}_4^{2-}, \text{SeO}_4^{2-} \ldots \)

Chloride \[ [\text{Fe}^{II}_{2} \text{Fe}^{III}_{3} (\text{OH})_6]^+ \cdot [\text{Cl}^{-} \cdot 2 \text{H}_2\text{O}]^- \]

Sulphate \[ [\text{Fe}^{II}_{4} \text{Fe}^{III}_{2} (\text{OH})_{12}]^{2+} \cdot [\text{SO}_4^{2-} \cdot 8 \text{H}_2\text{O}]^{2-} \]

Carbonate \[ [\text{Fe}^{II}_{4} \text{Fe}^{III}_{2} (\text{OH})_{12}]^{2+} \cdot [\text{CO}_3^{2-} \cdot 3 \text{H}_2\text{O}]^{2-} \]

Two types of stacking

**XRD pattern of hydroxycarbonate GR1(CO\(_3\)^{2-}).**

**R-3m**

**XRD pattern of hydroxysulphate GR2(SO\(_4\)^{2-}).**
(thesis of Rabha Aïssa 2004).

**P-3m1**
Stacking sequence at scale of the Fe cation layers

(a) $\text{CO}_3^{2-}$ anion interlayers and OH- layers along the 3-fold axis of GR1($\text{CO}_3^{2-}$);

(b) $\text{Cl}^-$ anions and OH- layers of GR1($\text{Cl}^-$);

(c) $\text{SO}_4^{2-}$ anion interlayers and OH- layers along the 3-fold axis of GR2($\text{SO}_4^{2-}$);

A, B, C and a, b, c positions represent the sites in the hexagonal pavement of ions.

\[
\begin{align*}
\text{A} & : \text{Fe}^{n+} \quad \text{B} : \text{OH}^- \\
\text{C} & : \text{OH}^- \\
\text{a} & : \text{Cl}^- \\
\text{b} & : \text{Fe}^{n+} \\
\text{c} & : \text{Fe}^{n+}
\end{align*}
\]
Transmission Mössbauer spectra measured at 78 K of various Green Rusts

2 ferrous doublets \( D_1 \) & \( D_2 \) (large \( \Delta \))

1 ferric doublet \( D_3 \) (small \( \Delta \))

\( x = \text{Fe}^{III} / \text{Fe}_{\text{total}} \) is obtained directly from the spectrum (\( RA \) of \( D_3 \))

Experimentally

\( 0.25 < x < 0.33 \)
The Fe$^{II}$-Fe$^{III}$ hydroxycarbonate can be prepared by coprecipitation of a mixture of ferrous and ferric salts in the presence of carbonate ions when adding NaOH solution. Mössbauer spectra measured at 78 K demonstrate that the range of composition for $x = [\text{Fe}^{III}]/[\text{Fe}_{\text{total}}]$ is limited to $[1/4, 1/3]$ since for $x > 1/3$ there exists two phases, the Green rust at $x = 1/3$, GR(CO$_3^{2-}$), and another phase, $\alpha$-FeOOH.

The spectrum of GR(CO$_3^{2-}$) consists of 2 ferrous doublets $D_1$ and $D_2$ with large quadrupole splitting $\Delta$ and one ferric doublet $D_3$ with small splitting.

Fe$^{II}$-Fe$^{III}$ ions coprecipitation giving for $x > 1/3$ a mixture of phases: GR(CO$_3^{2-}$) and goethite

Fe$^{II}_{(1-y)}$Fe$^{III}_y$(OH)$_2$($y/2$)CO$_3$ with $1/4 < y < 1/3$
Projections perpendicular to the c axis of the GR structure of, from left to right, GR1(Cl\(^-\)), GR1(CO\(_3\)^{2-}\)) and GR2(SO\(_4\)^{2-}\)). OH\(^-\) ion layers are not taken into account; (a) one anion interlayer, (b) a Fe layer and (c) the next interlayer; (d) superimposition of (a), (b), (c) where only one Fe layer in the way between two interlayers is represented; (e) three adjacent interlayers in GR1s.
Structure of GR(CO$_3^{2-}$) Fe$^{II}$-Fe$^{III}$ hydroxycarbonate at $x = (1/3)$; (a) Three-dimensional view of the stacking of brucite-like layers. OH$^-$ ions lie at the apices of the octahedrons surrounding the Fe cations. CO$_3^{2-}$ ions in interlayers.

(b) Projections along the $c$ axis of the CO$_3^{2-}$ anions for three interlayers constituting a repeat.

Génin, J.-M. R.; Aïssa, R.; Géhin, A.; Abdelmoula, M.; Benali, O.; Ernstsen, V.; Ona-Nguema, G.; Upadhyay, C.; Ruby, C. Fougerite and Fe$^{II}$-Fe$^{III}$ hydroxicarbonate green rust; ordering, deprotonation and/or cation substitution; structure of hydroxotalcite-like compounds and mythic ferrosic hydroxide Fe(OH)$_{2+3x}$ (2005) 545-572.
The *usual* oxidation of green rusts by dissolution and precipitation

- Most of the time the corrosion of iron ends into a ferric oxyhydroxide that is the result of the oxidation of the green rust by dissolution and precipitation
End products of the aerial oxidation of Fe(OH)$_2$, in the chloride containing medium with respect to the initial ratio $R' = \{[\text{Cl}^-] / [\text{OH}^-]\} = 2 / R$.

$R = [\text{Fe}^{III}][\text{Fe}_{\text{total}}]$  

D. Rézel 1986

- $M$ : magnetite,  
- $G$ : goethite,  
- $L$ : lepidocrocite,  
- $A$ : akaganeite
Sulphate containing medium

(a) Zero-current potential $E_h$ (SHE) and pH vs. time curves recorded during the oxidation of an aerated suspension of ferrous hydroxide in a sulphate containing medium for initial ratio $R = [[\text{OH}^-]/[\text{Fe}_{\text{total}}]] = R_g = 1.67$. Three stages A, B and C illustrated by plateaus when $E_h$ and pH stay constant correspond to three equilibrium reactions. At $t_g$, 100% of GR2(SO$_4^{2-}$) forms and at $t_f$ there exist only one solid phase, lepidocrocite $\gamma$-FeOOH with Fe$^{II}$ ions within solution. Points (a)–(g) indicate the times at which the precipitates analysed by Mössbauer spectroscopy were sampled [6].

(b) Transmission electron micrograph of sample of GR2(SO$_4^{2-}$) at $t_g$ [6].

Mössbauer spectra measured at 15 K

A. Olowe
Ph. Refait
Mass balance diagram comprising stoichiometric Fe$^{II-III}$ hydroxysulphate green rust GR2(SO$_4^{2-}$) at $x = 1/3$. The path followed during the aerial oxidation of Fe(OH)$_2$ with an excess of Fe$^{2+}_{aq}$ is stressed displaying the 3 stages, AB, BC, CD, as observed in $E_h$ or pH versus time curves (inset). The final ferric oxyhydroxide is lepidocrocite at point C (stage 2) that transforms slowly into goethite (stage 3) from C to D in acidic conditions providing some Fe$^{III}$ ions into solution.

$$R = \frac{n_{\text{OH}^-}}{[n_{\text{Fe(II)}} + n_{\text{Fe(III)}}]}$$

$$x_{\text{Fe(III)}} = \frac{n_{\text{Fe(III)}}}{[n_{\text{Fe(II)}} + n_{\text{Fe(III)}}]}$$

A. Géhin 2004
Carbonate containing medium

$D_1, D_2, D_3 : GR1(CO_3^{2-})$ doublets

$S_1 :$ ferrihydrite sextet

$S_2, S_3 :$ goethite sextets

$D_4 :$ ferrihydrite doublet

$t_g : GR1(CO_3^{2-})$ alone

$t_1 : GR1(CO_3^{2-}) +$ some ferrihydrite

$t_2 : GR1(CO_3^{2-}) +$ goethite + ferrihydrite

$t_3 :$ goethite + ferrihydrite

After $t_1 :$ goethite alone

O. Benali
\[ R = \left\{ \frac{n_{\text{OH}^-}}{n_{\text{Fe(II)}} + n_{\text{Fe(III)}}} \right\} \]

**Dissolution-precipitation of** \( \text{GR(CO}_3^{2-}) \)

- **A**: \( \text{Fe(OH)}_2 + \text{Fe}^{II} \)
- **B**: \( \text{Fe}^{II}_4 \text{Fe}^{III}_2(\text{OH})_{12} \text{CO}_3 \)
- **G**: \( \text{Fe(OH)}_2 \)
- **H**: Magnetite \( \text{Fe}_3 \text{O}_4 \)
- **E**: Goethite \( \alpha \text{FeOOH} \)
- **K**: \( (5/3) \text{Fe}_3 \text{O}_4 + \text{Fe}^{2+} \)
- **L**: \( 5 \text{FeOOH} + \text{Fe}^{2+} \)

**Mass balance diagram of iron compounds**

\[ x_{\text{Fe(III)}} = \left\{ \frac{n_{\text{Fe(III)}}}{n_{\text{Fe(II)}} + n_{\text{Fe(III)}}} \right\} \]
Oxidation of GR2($\text{SO}_4^{2-}$) and GR1($\text{CO}_3^{2-}$)  
Lepidocrocite *versus* ferrihydrite & goethite

**Stage A**

\[
5 \text{Fe}^{\text{II}}(\text{OH})_2 + \text{SO}_4^{2-} + \text{Fe}^{2+}_{\text{aq}} + (1/2)\text{O}_2 + \text{H}_2\text{O} \iff \text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{SO}_4 \\
5 \text{Fe}^{\text{II}}(\text{OH})_2 + \text{CO}_3^{2-} + \text{Fe}^{2+}_{\text{aq}} + (1/2)\text{O}_2 + \text{H}_2\text{O} \iff \text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{CO}_3
\]

**Stage B**

\[
\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{SO}_4 + (3/4)\text{O}_2 \iff 5\gamma\text{-Fe}^{\text{III}}\text{OOH} + \text{SO}_4^{2-} + \text{Fe}^{2+}_{\text{aq}} + (7/2)\text{H}_2\text{O} \\
\text{Fe}^{\text{II}}_4\text{Fe}^{\text{III}}_2(\text{OH})_{12}\text{CO}_3 + (3/4)\text{O}_2 \iff 5\text{Fe}^{\text{III}}\text{OOH} + \text{CO}_3^{2-} + \text{Fe}^{2+}_{\text{aq}} + (7/2)\text{H}_2\text{O}
\]

**Stage C**

\[
3 \text{Fe}^{2+}_{\text{aq}} + (1/4)\text{O}_2 + (3/2)\text{H}_2\text{O} \iff \alpha\text{-Fe}^{\text{III}}\text{OOH} + 2\text{Fe}^{3+} + \text{H}_2 \\
\text{Fe}^{2+}_{\text{aq}} + (1/4)\text{O}_2 + 2\text{OH}^- \iff \alpha\text{-Fe}^{\text{III}}\text{OOH} + (1/2)\text{H}_2\text{O}
\]

**As a whole**

\[
5 \text{Fe}^{\text{II}}(\text{OH})_2 + \text{Fe}^{2+}_{\text{aq}} + (4/3)\text{O}_2 \iff (16/3)\alpha\text{-Fe}^{\text{III}}\text{OOH} + (2/3)\text{Fe}^{3+} + 2\text{H}_2\text{O} + (1/3)\text{H}_2 \\
5 \text{Fe}^{\text{II}}(\text{OH})_2 + \text{Fe}^{2+}_{\text{aq}} + (3/2)\text{O}_2 + 2\text{OH}^- \iff 6\alpha\text{-Fe}^{\text{III}}\text{OOH} + 3\text{H}_2\text{O}
\]
The *in situ* oxidation of green rusts by deprotonation

Use a strong oxidant such as $\text{H}_2\text{O}_2$, Dry the green rust and oxide in the air,

Violent air oxidation, Oxide in a basic medium...
The oxidation is in situ and does not destroy the crystals.
XRD patterns of the Fe$^{II-III}$ oxyhydroxycarbonate with respect to $x = \text{Fe}^{III}/\text{Fe}_{\text{total}}$

G. Ona N’Guema

$\text{Fe}^{II}_{6(1-x)} \text{Fe}^{III}_{6x} \text{O}_{12} \text{H}_{2(7-3x)} \text{CO}_3$

Lines of ferric GR$^*$ ($x=1$) are very weak; this explains why its existence was not discovered sooner
The oxidation or reduction of GR(CO$_3^{2-}$) gives rise to GR(CO$_3^{2-}$)* or GR(CO$_3^{2-}$)$^\delta$, i.e. $\text{Fe}^{II}_{6(1-x)} \text{Fe}^{III}_{6x} \text{O}_{12} \text{H}_{2(7-3x)} \text{CO}_3$ where $x \in [0, 1]$; the fougerite mineral is limited to the range $[1/3, 2/3]$. 

$$R = \frac{n_{\text{OH}^-}}{n_{\text{Fe(II)}} + n_{\text{Fe(III)}}}$$
Comparative Mössbauer spectra for
(b) 50 mg ferric green rust in graphite
(b) 100 mg ferric green rust in graphite
(c) thin film of ferric green rust on gold
(d) Reference ferric green rust

\[
\begin{align*}
\text{Fe}^{II}_{6(1-x)} \text{Fe}^{III}_{6x} \text{O}_{12} \text{H}_{2(7-3x)} \text{CO}_3
\end{align*}
\]

\[x \in [0 - 1]\]
SEM image of the orange ferric compound resulting from the oxidation by air of electrochemically formed GR1(CO$_3^{2-}$)* after ageing at 30 °C for 50 days.

Three sublattices

1$^{st}$ lattice
2$^{nd}$ lattice
3$^{rd}$ lattice
H₂O         OH⁻         O₂⁻
in upper layer

H₂O         OH⁻         O₂⁻
in lower layer

1st sublattice
Fe^{II} Fe^{II} (CO₃²⁻)
Fe^{II} (H₂O)

2nd sublattice
3rd sublattice

Fe^{II-III} oxyhydroxycarbonate

Protonation and deprotonation of OH- ions
Evolution of Mössbauer spectra with measurement temperature displaying the ferrimagnetic behaviour of stoichiometric GR(CO$_3^{2-}$) between 1.4 and 12 K.

Mössbauer spectra of GR(CO$_3^{2-}$) sample oxidised violently by H$_2$O$_2$ and named ferric [GR(CO$_3^{2-}$)]. Measurement temperatures are (a) 16 K, (c) 50 K, (d) 60 K and (e) 78 K. (b) and (f) are the hyperfine field distribution of (a) and quadrupole splitting distribution of (e) using a Voigt profile analysis, respectively.
Hexagonal pavements of Fe$^{II}$ and Fe$^{III}$ cations in the layers of (a) Fe(OH)$_2$, (b) stoichiometric GR(CO$_3^{2-}$) at $x = 1/3$, (c) GR(CO$_3^{2-}$)$^*$ with $1/3 < x < 2/3$, (d) GR(CO$_3^{2-}$)$^*$ at $x = 2/3$, (e) GR(CO$_3^{2-}$)$^*$ with $2/3 < x < 1$ and (f) fully ferric GR(CO$_3^{2-}$)$^*$ at $x = 1$. Long range order is displayed showing magnetic domains.
Aqueous corrosion of iron

Iron, Steels

Ferrous hydroxide

Agressive anions (Cl\(^{-}\), CO\(_{3}\)\(^{2-}\), SO\(_{4}\)\(^{2-}\))

Green rusts

Dissolution-precipitation

In situ deprotonation

Common rusts

Goethite
Lepidocrocite
\(\delta\)-FeOOH

Magnetite
Akaganeite
Ferroxyhite

Ferric green green rust

Including anions

The secret of passivation of steel is understood
POURBAIX diagrams of iron and water

Possibility of oxidation of iron by dissolved $\text{O}_2$ and by water mainly in acidic medium

$\text{Fe}^{3+}$

$\text{O}_2$

$\text{H}_2\text{O}$

$\text{Fe}^{2+}$

$\text{H}_2$

Immunity

Fe(s)

$E_h(V)$

1.23 V

3.7

9.5

-0.6 V

$\text{O}_2 + 4\text{H}^+ + 4 \text{e}^- \Rightarrow 2 \text{H}_2\text{O}$

pH

$\text{Fe}^0 \Rightarrow \text{Fe}^{2+} + 2 \text{e}^-$

$2 \text{H}^+ + 2 \text{e}^- \Rightarrow \text{H}_2$
How to complete the Pourbaix diagram of iron with the domains of green rusts?
Pourbaix diagram of the Fe - H₂O - Cl⁻ system at 25 °C for a [Cl⁻] activity of 0.55 and in situ Mössbauer spectra of corrosion products of corrosion of an α-iron foil obtained at \( E_h = -0.55 \) V and -0.35 V at pH = 9 in an electrochemical cell.

\( \oplus \) experimental conditions.

\( D_1, D_2 \) and \( D_3 \) are doublets of green rusts, \( FH \) is that of Fe(OH)_2 and \( S_1, S_2 \) et \( S_3 \) are sextets due to magnetite and goethite.

• The first step of corrosion: the green rust layer

CEMS spectrum at room temperature of a steel disk dipped 24 hours in a 0.1 M NaHCO₃ solution.
• • • : experimental curve, - - - : global computed curve. ____ : components of the spectra.
The new rust
*In situ* deprotonation of GR1(CO$_3$$^{2-}$)

GR$^*$($x+dx$) + $dx$ H$^+$ + $dx$ e$^-$ → GR$^*$($x$)

Fe$_{6[1-(x+dx)]}^{II}$ Fe$_{6(x+dx)}^{III}$ O$_{12}$ H$_{2[7-3(x+dx)]}^{2-}$ CO$_3$ + (6$\times$dx) H$^+$ + (6$\times$dx) e$^-$ → Fe$_{6(1-x)}^{II}$ Fe$_{6x}^{III}$ O$_{12}$ H$_{2(7-3x)}^{2-}$ CO$_3$
[Fe$^{2+}$] is 10^{-6} M

Dissolution and Precipitation

CORROSION

In situ deprotonation of GR1(CO$_3^{2-}$)

PASSIVATION

$E_h$ (V)

pH

$H_2CO_3$

$HCO_3^-$

$CO_3^{2-}$

Fe(OH)$_2^+$

FeOH$^+$

FeOOH$^-$

α-FeOOH

GR(CO$_3^{2-}$)

Fe$^{++}$

Fe

Fe(OH)$_2$

[Fe$^{2+}$] is 10^{-6} M
Oxidation by oxygen

(a) & (b) Dissolution-precipitation

- \( \text{Fe}^{II}\text{Fe}^{III}(\text{OH})_{12} \text{CO}_3 + 3/4 \text{O}_2 \rightarrow 5 \text{Fe}^{III}\text{OOH} + \text{CO}_3^{2-} + \text{Fe}^{2+} + 7/2 \text{H}_2\text{O} \)

(2) \( \text{Fe}^{II}\text{Fe}^{III}(\text{OH})_{12} \text{CO}_3 + 1/3 \text{O}_2 \rightarrow 5/3 \text{Fe}^{II}\text{Fe}^{III}_2 \text{O}_4 + \text{CO}_3^{2-} + \text{Fe}^{2+} + 6 \text{H}_2\text{O} \)

(c) \text{In situ} deprotonation

(3) \( \text{Fe}^{II}\text{Fe}^{III}(\text{OH})_{12}\text{CO}_3 + \text{O}_2 \rightarrow \text{Fe}^{III}_6\text{O}_{12}\text{H}_8\text{CO}_3 + 2 \text{H}_2\text{O} \)

\( \alpha\)-FeOOH

\( \text{GR}^* \)

A. Renard
Production of Fe(II) and consumption of methanoate during culture of *Shewanella putrefaciens* in presence of lepidocrocite. The initial amount of Fe$^{III}$ (as lepidocrocite) and of methanoate were respectively 80 mM and 43 mM.

(b) X-ray pattern of the solid phase of incubation experiments with *S. putrefaciens*: mixture of green rust (GR1) and siderite (S) obtained after 15 days of incubation.

(c) TEM observations and (d) optical micrograph of GR crystals obtained by reduction of lepidocrocite by *S. putrefaciens*; One sees the bacteria that respirate GR$^*$. 

Georges Ona-Nguema

Asfaw Zegeye
Mass balance diagram of iron compounds

\[ R = \{ n_{\text{OH}} - (n_{\text{Fe(II)}} + n_{\text{Fe(III)}}) \} \]

**Bacterial reduction of FeOOH**

8Fe\text{III}OOH + Fe\text{2+} + CO\text{3}\text{2-} \rightarrow Fe\text{II}Fe\text{III}2O_4 + Fe\text{III}6O_{12}H_8CO_3

**Stoichiometric**

- **A**: Fe\text{II}_6O_{12}H_{14}CO_3
- **B**: Fe\text{II}_4Fe\text{III}_2(OH)_{12}CO_3
- **C**: Fe\text{II}_2Fe\text{III}_4O_{12}H_{10}CO_3
- **D**: Fe\text{III}_6O_{12}H_8CO_3
- **AD**: Fe\text{II}_{6(1-x)}Fe\text{III}_6xO_{12}H_{2(7-3x)}CO_3
- **G**: Fe(OH)\text{2}
- **H**: Fe\text{3}O_4
- **E**: FeOOH
- **N**: Fe\text{3}O_4 + GR*
- **P**: Fe\text{II}Fe\text{III}_5O_{12}H_9CO_3

**Fe(OH)_2**

\[ x_{\text{Fe(III)}} = \{ n_{\text{Fe(III)}} / (n_{\text{Fe(II)}} + n_{\text{Fe(III)}}) \} \]
Microbially Influenced Corrosion and Marine Corrosion

A field study: Steel sheet piles in harbours
(With Laboratoire Central des Ponts et Chaussées, Dr A. Raharinaivo)

The harbour: Boulogne sur Mer (late eighties)

Wharf, half a mile long, built on big piles supporting cranes, trains and many heavy materials.
Piles were 15 m high, made from 1 cm thick plain carbon steel sheets surrounding heavy stone blocks, gravel and sand. The external steel sheets displayed huge holes under the fouling crust, 10 cm thick, at a very specific level, that of the lowest tide (solstices), after only some years of service whereas they were planned for at least half a century.

The corrosion diagnosis was MIC and Mössbauer spectroscopy revealed that the rust, above the hole level, was essentially constituted of sulphated green rust and magnetite.

Some years later, the Coal and Steel European Community committed a contract to study the disorders about similar phenomena observed in other harbours. Involved companies were British Steel, Usinor (Unimétal), Hoescht, Arbed, i.e. makers of thick sheets. The disorders were found in harbours of the Atlantic Ocean, English Channel, North Sea and Baltic Sea. Curiously, there was no major problem in the Mediterranean Sea.

Anoxic conditions for long periods \(\rightarrow\) MIC.
Strains of bacteria?
Level and specificity of pollution?
Eddy currents and redox potential?
No definite answer was then proposed, except that it was most probably MIC.
How do we explain today all these features?
Marine corrosion of steel

GR2(SO$_4^{2-}$)

(a) SEM micrograph showing hexagonal shaped crystals of GR(SO$_4^{2-}$) upon corroded steel sheet left 25 years in seawater, (b) sequence of the rust layers: metal–magnetite–lepidocrocite–GR(SO$_4^{2-}$), (c) Raman spectrum of the outer part of the marine corroded layer.

Formation of the Fe(II)-Fe(III) hydroxysulphate green rust during marine corrosion of steel, Ph. REFAIT, J.B. MEMET, C. BON, R. SABOT and J.-M. R. GÉNIN Corrosion Science 2003, 45, 833-845
Formation of GR2(SO$_4^{2-}$) during the reduction of γ-FeOOH by a dissimilatory iron-respiring bacterium, *Shewanella putrefaciens*. Reduction was performed in a non-buffered medium without any organic compounds and with 25 mM of sulphate and with a range of lepidocrocite concentrations with H$_2$ as the electron donor under nongrowth conditions.

The resulting biogenic solids, after iron-respiring activity, were characterized by X-ray diffraction (XRD), transmission Mössbauer spectroscopy (TMS) and electron microscopy (SEM and TEM). The sulphate has been identified as the intercalated anion by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS). In addition, the structure of this sulphate anion was discussed. Our experimental study demonstrated that, under H$_2$ atmosphere, the biogenic solid was a GR2(SO$_4^{2-}$), as the sole iron(II-III) bearing mineral, whatever the initial lepidocrocite concentration. The crystals of the biotically formed GR2(SO$_4^{2-}$) are significantly larger than those observed for GR2(SO$_4^{2-}$) obtained through abiotic preparation, < 15 µm diameter as against 0.5-4 µm, respectively.
Green Rust Sulfate precipitates

(a) Exp. n° 2, with 25 mM of sulfate and $R = 1.15$

(b) Exp. n° 4, with 75 mM of sulfate and $R = 0.17$

$R = \text{HCO}_3^- / \text{SO}_4^{2-}$

Asfaw Zegeye
Marine corrosion of steel

The competition between GR1(Cl\(^-\)) & GR2(SO\(_4^{2-}\))

\[ \frac{[\text{Fe}^{2+}]}{[\text{OH}^-]} = 0.58 \]
\[ \frac{[\text{Fe}^{2+}]}{[\text{OH}^-]} = 1 \]

ESHE (V vs SHE) and pH vs. time curves obtained during the oxidation of aqueous suspensions of Fe(II)-containing precipitates in the presence of Cl\(^-\) and SO\(_4^{2-}\) ions.

[Cl\(^-\)]/[SO\(_4^{2-}\)] = 12. (a) [Fe\(^{2+}\)]/[OH\(^-\)] = 0.58; (b) [Fe\(^{2+}\)]/[OH\(^-\)] = 1
Ferric oxyhydroxides are reduced by dissimilatory iron-reducing bacteria, e.g. forming GR2(SO$_4^{2-}$) in sea water.

Then, GR2(SO$_4^{2-}$) is reduced into FeS by sulphate reducing bacteria.
The morphology of gley soils, first described in 1905 by G. N. Vysostskii\(^1\), remained a mystery up till recently when Mössbauer spectroscopy has been the determining tool to identify the iron containing compound that lies in a horizon formed under waterlogged conditions in an anaerobic environment, which encourages the reduction of iron compounds by microorganisms and often causes mottling of soil into a patchwork of greenish-blue-grey and rust colors. This finding is of utmost practical importance since there exists a correlation between the concentration of some pollutants and that of Fe\(^{II}\) ions that are dissolved in the water table. For instance, nitrates disappear where Fe\(^{II}\) appear in the anaerobic zone by following the water level in equilibrium with a mineral, which has been given the name of fougerite (IMA 2003-05). It occurs to be the Fe\(^{II-III}\) oxyhydroxycarbonate of formula \(\text{Fe}^{II}_{6(1-x)}\text{Fe}^{III}_{6x}\text{O}_{12}\text{H}_{2(7-3x)}\text{CO}_3\) where the domain of \(x\) is limited to [0.33-0.67].

Originally studied for explaining the corrosion of iron-based materials, Fe\(^{II-III}\) hydroxysalts belong to the family of layered double hydroxides (LDH) and are constituted of layers, \([\text{Fe}^{II}_{(1-x)}\text{Fe}^{III}_x\text{(OH)}_2]^{x^+}\), and interlayers, \([(x/n)\text{A}^{-}\bullet(mx/n)\text{H}_2\text{O}]^x\). Here, we shall consider only the case where the anion is \(\text{CO}_3^{2-}\).

\(^1\)G. N. Vysostskii, Gley, Pochvovedeniye, 4 (1905) 291-327.
Comparison between field experiments and laboratory assays

The similarity between the original spectrum obtained in 1996\(^1\) (a) and that of the deprotonated oxyhydroxycarbonate\(^2\) (b) is striking. More recently, field experiments were done in Fougères using back-scattering miniaturized Mössbauer spectrometer MIMOS\(^3\) (c) to follow the value of ratio \(x\) with time and depth \textit{in situ} within the gley soil. (d) The fougerite mineral is able to reduce pollutants within the water table such as nitrates. Dissimilatory iron reducing bacteria regenerate the fougerite active mineral\(^4\).


Nitrate reduction and
In situ oxidation of GR(CO$_3^{2-}$)*

Typical time of half reaction is one week

$\text{Fe}^{\text{II}}_6[1-(x+d)x] \text{Fe}^{\text{III}}_6(x+dx) \text{O}_{12} \text{H}_2[7-3(x+dx)] \text{CO}_3 + (6 \times dx) \text{H}^+ + (6 \times dx) \text{e}^- \rightarrow \text{Fe}^{\text{II}}_6(1-x) \text{Fe}^{\text{III}}_6x \text{O}_{12} \text{H}_2(7-3x) \text{CO}_3$

or

$\text{GR}^*(x+dx) + dx \text{H}^+ + dx \text{e}^- \rightarrow \text{GR}^*(x)$

<table>
<thead>
<tr>
<th>$x$</th>
<th>$\text{GR}^*(\text{CO}_3^{2-})$ at 0.33</th>
<th>$\text{GR}^*(\text{CO}_3^{2-})$ at 0.38</th>
<th>$\text{GR}^*(\text{CO}_3^{2-})$ at 0.58</th>
<th>$\text{GR}^*(\text{CO}_3^{2-})$ 1.00 and magnetite (d)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\text{GR}^*(\text{CO}_3^{2-})$ at 0.33</td>
<td>$\text{GR}^*(\text{CO}_3^{2-})$ at 0.38</td>
<td>$\text{GR}^*(\text{CO}_3^{2-})$ at 0.58</td>
<td>$\text{GR}^*(\text{CO}_3^{2-})$ 1.00 and magnetite (d)</td>
</tr>
<tr>
<td>$D_{1+2}$</td>
<td>$1.12$</td>
<td>$0.98$</td>
<td>$1.03$</td>
<td>$0.4$</td>
</tr>
<tr>
<td>$D_3$</td>
<td>$0.41$</td>
<td>$0.37$</td>
<td>$0.31$</td>
<td>$0.4$</td>
</tr>
<tr>
<td>$S_1$</td>
<td>$0.27$</td>
<td>$463$</td>
<td>$39$</td>
<td></td>
</tr>
<tr>
<td>$S_2$</td>
<td>$0.67$</td>
<td>$440$</td>
<td>$41$</td>
<td></td>
</tr>
</tbody>
</table>

$\delta$, isomer shift in mm s$^{-1}$ (metallic iron as reference at room temperature); $\Delta$ quadrupole splitting in mm s$^{-1}$; $RA$ in %: relative abundance. Half widths at half maximum are 0.3, 0.35, 0.4 and 0.6 mm s$^{-1}$. 

Fig T

Initial

$\text{GR}^*(\text{CO}_3^{2-})$ ($a$) $x = 0.33$

300 K, one day

$\text{GR}^*(\text{CO}_3^{2-})$ ($b$) $x = 0.38$

300 K, one month

$\text{GR}^*(\text{CO}_3^{2-})$ ($c$) $x = 0.58$

300 K initial

$\text{GR}^*(\text{CO}_3^{2-})$ ($d$) $x = 1$

$\text{GR}^*(x+dx) + dx \text{H}^+ + dx \text{e}^- \rightarrow \text{GR}^*(x)$
Fougerite is the active mineral that is mixed with clay minerals and responsible for the natural reduction of nitrates in gley soils within the water table.

Hyperfine parameters of Mössbauer spectra measured at 78 K of samples extracted in Denmark at different depths of 2 m, 2.50 m, 3 m out of hydric soils from (a) an oxidised zone to (c) a reduced zone. A mixture of fougerite, ferric oxyhydroxides and clay minerals is observed. $H$: hyperfine field (kOe); $\delta$: isomer shift (mm s$^{-1}$) with respect to $\alpha$ Fe at room temperature; $\Delta$ or $\epsilon$: quadrupole splitting or shift (mm s$^{-1}$); $\Gamma$: half-width at half maximum (mm s$^{-1}$); RA: relative abundance (%).

In red: thesis about 
Green rusts or fougerite
Viele Danke