THE TRANSFORMATION OF CHLORIDE-CONTAINING 
GREEN RUST ONE INTO SULPHATED GREEN RUST 
TWO BY OXIDATION IN MIXED Cl\textsuperscript{-} AND SO\textsubscript{4}\textsuperscript{2-} 
AQUEOUS MEDIA*

PH. REFAIT and J.-M. R. GÉNIN

Laboratoire CNRS Maurice Letort, Groupe de Spectrométrie Mössbauer, Département Sciences des 
Matériaux, Université de Nancy 1, ESSTIN, Parc R. Bentz, F54500 Vandoeuvre-Nancy, France

Abstract—The mechanisms of oxidation of a ferrous hydroxide precipitated by mixing a solution of NaOH 
with a solution containing dissolved ferrous sulphate and chloride depend on the ratios $R = (\text{Fe}^{2+})/(\text{OH}^-)$ 
and $A = (\text{SO}_{4}^{2-})/(\text{Cl}^-)$ of the initial conditions. This study is limited to $A = 1/4$ and $R$ ranging from 0.80 to 
1.33 where the oxidation processes are governed by the formation and transformation of green rusts. The 
overall process is ferrous hydroxide $\rightarrow$ green rust 1 $\rightarrow$ green rust 2 $\rightarrow$ $\alpha$ and $\gamma$ ferric oxyhydroxides. The 
Pourbaix diagram of iron in chloro-sulphated aqueous media is drawn in the case where $A = 1/4$.

INTRODUCTION

The influence of sulphate ions on the oxidation processes of ferrous hydroxide was 
recently presented,\textsuperscript{1-7} whereas that of chloride ions was continued\textsuperscript{8,9} following the 
work of Rezel.\textsuperscript{10} All these studies showed that the oxidation of the initial ferrous 
compounds into ferric compounds displays two stages and the formation of an 
intermediate ferrous-ferric compound takes place before the formation of the end 
rust products. The characteristics of these intermediate compounds, including their 
chemical formulae, were established. It was thus possible to draw the Pourbaix 
diagrams specific to the chloride-containing\textsuperscript{8,9} and sulphate-containing\textsuperscript{1,7} media, 
which include these compounds.

The compound obtained in the presence of sulphate ions, is green rust 2 (GR2) 
with formula $4\text{Fe(OH)}_2.2\text{FeOOH}.\text{FeSO}_4.n\text{H}_2\text{O}$ ($n$ is probably 4). GR2, first ob-
served by Girard,\textsuperscript{11} was identified recently as the major product issued from 
corrosion of steel in marine sediments.\textsuperscript{12,13}

The compound obtained in the presence of chloride ions, first observed 
by Keller\textsuperscript{14} and Yoshioka,\textsuperscript{15} is green rust 1 (GR1) with the formula 
$3\text{Fe(OH)}_2.\text{Fe(OH)}_2\text{Cl}.n\text{H}_2\text{O}$ ($3 \geq n \geq 2$).

In this article, the combined influence of Cl\textsuperscript{-} and SO\textsubscript{4}\textsuperscript{2-} ions is studied in order to 
simulate more closely the phenomena which occur in actual corrosion cases. It is 
obvious that natural media often contain several anions. Seawater, for example, is 
not only a solution of sodium chloride. It contains also a substantial amount of 
sulphate ions. At Brest, Brittany, seawater contains 19.5 g of Cl\textsuperscript{-} ions for 2.8 g of 
SO\textsubscript{4}\textsuperscript{2-} ions 1\textsuperscript{-1}, i.e. 1 SO\textsubscript{4}\textsuperscript{2-} ion for 19 Cl\textsuperscript{-} ions.\textsuperscript{14} In this paper, the chosen medium 
contains 4 Cl\textsuperscript{-} ions for 1 SO\textsubscript{4}\textsuperscript{2-} ion. Moreover, by means of this study, it is possible to 
check the results obtained separately in chloride-containing and sulphate-containing

*Part of the thesis presented at the Université de Nancy I by Ph. Refait.
\textsuperscript{14} Data given by IFREMER, Brest.
Manuscript received 4 February 1993; in amended form 11 May 1993.
media. For instance, the value of the standard chemical potential $\mu^0$ of GR2 will be determined with a better accuracy.

**EXPERIMENTAL METHOD**

The experimental procedure was described recently and discussed elsewhere. The starting ferrous hydroxide is precipitated from a solution of caustic soda NaOH and a solution containing a mixture of ferrous sulphate and ferrous chloride. Melanterite FeSO$_4$.7H$_2$O and tetrahydrate ferrous chloride FeCl$_2$.4H$_2$O were used. All solutions were kept at 25°C and the initial concentration of NaOH was fixed at 0.2 mol l$^{-1}$. Two parameters determine the initial quantities of reactants: $R$ is the ratio $(\text{Fe}^{2+})_{\text{init}}/(\text{OH}^-)_{\text{init}} = [(\text{FeCl}_2)_{\text{init}} + (\text{FeSO}_4)_{\text{init}}]/(\text{NaOH})_{\text{init}}$ and $A$ is the ratio $(\text{SO}_4^{2-})_{\text{init}}/(\text{Cl}^-)_{\text{init}} = (\text{FeSO}_4)_{\text{init}}/2(\text{FeCl}_2)_{\text{init}}$ where $(X)_{\text{init}}$ designates the initial concentration of species $X$ before precipitation.

All results presented in this article relate to $A = 1/4$ and to values of $R$ ranging from 0.80 to 1.33. The mechanisms of oxidation relative to GR1 and GR2 are then predominant. The variations of electrode potential, measured by means of a platinum electrode and a saturated calomel electrode, and pH of the solution were recorded. The intermediate and final products were analysed by X-ray diffraction using Co $K_{\alpha}$ radiation. In the case where the final products are stable with respect to the oxidizing action of oxygen, the precipitate is immediately filtered at the end of the reaction and dried in the open air. In the case where the products are those of an intermediate stage, the reaction is stopped at the corresponding stage and stored, sheltered from air, during one week at room temperature. The precipitate is then filtered and analysed within minutes. It is in the open air during the accumulation of the spectrum and oxidized at the surface.

**EXPERIMENTAL RESULTS**

*Electrode potential $E_h$/time and pH/time experimental curves*

The electrode potential and pH of the solution are recorded during the course of the oxidation reactions. Though a saturated calomel electrode is used for the potential measurements all data are given with respect to the standard hydrogen electrode (SHE). The curves are presented in Fig. 1. Increasing values of $E_h$ are drawn downward to facilitate a comparison with the pH curve.

![Fig. 1. Recorded $E_h$ and pH curves with respect to time for the various values of $R$. Points A, E, C, D and P are equilibrium points. The increasing value for $E_h$ is downward.](image-url)
On the $E_h(t)$ curve obtained for $R = 0.93$, particular points are noted to designate electrochemical equilibria. Point A corresponds to the first stage, points E and C correspond to a second stage and points D and P to the last stage. The existence of an overall oxidation reaction made of three stages departs from what is observed when dealing with the chloride-containing or with the sulphated media. In these cases, there exist only two stages, the first corresponding to the oxidation of the initial ferrous hydroxide into green rust and a second corresponding to the oxidation of the green rust into the final product.

**The final products**

The final products which are formed for various values of ratio $R$ are analysed by X-ray diffraction. The patterns are displayed in Fig. 2. The only lines of diffraction are those of lepidocrocite$^{16}$ and goethite$^{17}$ denoted by L and G respectively. The proportion of goethite increases when the ratio $R$ increases: the final product is made of 50% of goethite and 50% of lepidocrocite for $R = 0.80$ and reaches 100% of goethite for $R = 1.16$ and $R = 1.33$. In the sulphated medium ($A = \infty$), the results are quite similar. For $R = 0.7$ and $R = 3$, Olowe *et al.*$^{5}$ found that the final products were constituted of a mixture of 50% of goethite and 50% of lepidocrocite and a mixture of 92% of goethite and 8% of lepidocrocite respectively. These results are to be connected to the increase of excess Fe$^{2+}$ ions in solution, a fact which is known to favour the formation of goethite.$^{18-21}$

![Fig. 2. X-Ray diffraction patterns of the final products obtained at the various values of $R$. The Co $K_\alpha$ radiation ($\lambda = 1.79$ Å) is used. G = goethite and L = lepidocrocite.](image)
The products of the first stage

The products obtained after the first stage of oxidation, i.e. just before point E, are analysed by X-ray diffraction in the case where $R = 0.93$. Patterns are displayed in Fig. 3. Besides the main line of lepidocrocite denoted by L which results from the oxidation of the sample surface, two types of lines appear: lines denoted by “1” are those of the spectrum of chloride-containing GR1 and lines denoted by “2” are those of the spectrum of sulphated GR2.

The products of the second stage

The products obtained after the second stage, i.e. just before point D, are also analysed by X-ray diffraction. The pattern displayed in Fig. 4 is essentially constituted of the three main lines (001), (002) and (003) of sulphated GR2. Some lines of lepidocrocite and faint lines of GR2 of other indices than (00m) are also seen. The abnormal intensity of lines (00m) is due to preferential orientation of GR2 microcrystallites.

Consequently, it is obvious that chloride-containing GR1 transforms into sulphated GR2.

Nature of the initial precipitate

It was shown that for values of $R \geq 0.80$ the initial product is not the common simple Fe(OH)$_2$ ferrous hydroxide. For instance, the studies relative to the sulphated medium ($A = \infty$) by Olowe et al. showed the existence of a sulphated ferrous
Transformation of GR1 into sulphated GR2

Fig. 4. X-Ray diffraction pattern of the products obtained at the end of the second stage for \( R = 0.93 \). L = lepidocrocite and “2” = GR2.

The presence of these compounds besides Fe(OH)$_2$ in the chloride-containing and sulphate-containing medium as well, comes from the fact that for those values of \( R \), the precipitation takes place in the presence of an important excess of ferrous salts, FeCl$_2$ or FeSO$_4$. It is clearly the same for \( A = 1/4 \): Fe(OH)$_2$ is not the only product of precipitation; the reaction must lead to the obtention of one or several compounds which are ferrous hydroxides incorporating a part of the excess anions.

DISCUSSION

The electrochemical equilibrium green rust I–green rust 2 (point C)

Introduction. The chemical formula recently proposed$^8,9$ for GR1 is 3Fe(OH)$_2$.Fe(OH)$_2$.Cl.nH$_2$O (3 \( \approx n \approx 2 \)). It corresponds to an oxidation number of +2.25 (3 Fe$^{2+}$ ions for 1 Fe$^{3+}$ ion). The formula proposed by Olowe et al.$^1,2,5$ for GR2 is 4Fe(OH)$_2$.2FeOOH.FeSO$_4$.nH$_2$O (n is probably 4) and corresponds to an oxidation number of +2.29 (5 Fe$^{2+}$ ions for 2 Fe$^{3+}$ ions). The transformation of GR1 into GR2 reported here is therefore a good confirmation that the oxidation number of GR2 is higher than that of GR1. The particular point in the \( E_h(t) \) and \( \text{pH}(t) \) curves which corresponds to the electrochemical equilibrium between GR1 and GR2 is point C (Fig. 1) and the equilibrium is, without taking into account the water molecules incorporated to the GRs:

\[
7 [3\text{Fe(OH)}_2.\text{Fe(OH)}_2\text{Cl}] + 4 \text{SO}_4^{2-} \rightarrow \\
4 [4\text{Fe(OH)}_2.2\text{FeOOH.FeSO}_4] + 8 \text{H}_2\text{O} + 7 \text{Cl}^- + e^-.
\]  

At point C, the electrode potential meets the conditions:

\[
E_h = E^0(1) + 0.4137 \log[\text{Cl}^-] - 0.2364 \log[\text{SO}_4^{2-}]
\]
where \([X]\) is the activity of ions \(X\) in \(\text{mol} \cdot \text{L}^{-1}\). Thus:

\[
E^\circ(1) = \frac{\left[4\mu^\circ(\text{GR}^2\star) + 7\mu^\circ(\text{Cl}^-) + 8\mu^\circ(\text{H}_2\text{O}) - 7\mu^\circ(\text{GR}^1\star) - 4\mu^\circ(\text{SO}_4^{2-})\right]}{23,060}
\]  

(1c)

where \(\text{GR}^1\star\) and \(\text{GR}^2\star\) designate the corresponding compound without water molecules.

First it is necessary to check that the electrode potentials \(E_h\) which were experimentally observed at point C fulfil condition (1b). To do that, it is necessary to know or estimate the value of the activities of \(\text{Cl}^-\) and \(\text{SO}_4^{2-}\) anions and of the chemical potentials \(\mu^\circ\) of green rusts.

**Activities.** All the experiments concern solutions with ionic strengths ranging from 0.3 to 1.0 \(\text{mol} \cdot \text{L}^{-1}\), close to that of seawater which is about 0.7 \(\text{mol} \cdot \text{kg}^{-1}\).26,27 It is thus legitimate to consider that the activity coefficients \(\gamma\) of anions are constant over the studied domain and equal to those used in seawater, i.e. \(\gamma(\text{Cl}^-) = 0.64\) and \(\gamma(\text{SO}_4^{2-}) = 0.12\).26,27

**Standard chemical potentials.** The chemical potential \(\mu^\circ\) of \(\text{GR}^1\star\) was recently estimated:8,9

\[
\mu^\circ[3\text{Fe(OH)}_2.\text{Fe(OH)}_2\text{Cl}] = -509,500 \pm 500 \text{ cal mol}^{-1}.
\]

The chemical potential \(\mu^\circ\) of \(\text{GR}^2\star\) was previously estimated by Olowe:1,7

\[
\mu^\circ[4\text{Fe(OH)}_2.2\text{FeOOH}.\text{FeSO}_4] = -902,890 \text{ cal mol}^{-1}.
\]

This last estimation was done from the experimental values of \(E_h\) at the equilibrium between \(\text{Fe(OH)}_2\) and \(\text{GR}^2\), observed for \(A = \infty\), i.e. from equations:

\[
7\text{Fe(OH)}_2 + \text{SO}_4^{2-} \rightarrow 4\text{Fe(OH)}_2.2\text{FeOOH}.\text{FeSO}_4 + 2\text{H}_2\text{O} + 2e^- \tag{2a}
\]

\[
E_h = E^\circ(2) - 0.02955 \log[\text{SO}_4^{2-}] \tag{2b}
\]

\[
E^\circ(2) = \frac{\left[\mu^\circ(\text{GR}^2\star) + 2\mu^\circ(\text{H}_2\text{O}) - 7\mu^\circ(\text{Fe(OH)}_2) - \mu^\circ(\text{SO}_4^{2-})\right]}{46,120}. \tag{2c}
\]

These computations were made assuming an activity \([\text{SO}_4^{2-}]\) equal to the concentration \((\text{SO}_4^{2-})\). In conditions of ionic strength which are close to those used here, the activity coefficient \(\gamma(\text{SO}_4^{2-})\) is of the order of 0.10–0.15. It is therefore necessary to determine more accurately the standard chemical potential of \(\text{GR}^2\). The values of \(E_h\) and \(p\text{H}\) at the equilibrium \(\text{Fe(OH)}_2/\text{GR}^2\) observed by Olowe1,7 are gathered in Table 1. From these values and equations (2), \(E^\circ(2)\) and \(\mu^\circ(\text{GR}^2\star)\) (Table 1) were computed again, by taking an activity of sulphate ions equal to \([\text{SO}_4^{2-}] = \gamma(\text{SO}_4^{2-}) = 0.12 \times 2 \times R \times 0.1\). The values of the considered chemical potentials are those of Table 2.

From all this \(\mu^\circ(\text{GR}^2\star) = -904,100 \pm 350 \text{ cal mol}^{-1}\) is obtained instead of \(-902,890\) as computed previously.

**Comments.** The actual formula of \(\text{GR}^1\) is \(3\text{Fe(OH)}_2.\text{Fe(OH)}_2\text{Cl}.n\text{H}_2\text{O}\) but the value of \(n\), between 2 and 3, is not fully ascertained. The actual value of \(\mu^\circ(\text{GR}^1)\) is then exactly:

\[
\mu^\circ(\text{GR}^1) = \mu^\circ(\text{GR}^1\star) + n\mu^\circ(\text{H}_2\text{O}).
\]

It must be noticed that by using the \(3\text{Fe(OH)}_2.\text{Fe(OH)}_2\text{Cl}\) formula and its
Transformation of GR1 into sulphated GR2

<table>
<thead>
<tr>
<th>$R$</th>
<th>$E_h$ (mV)*</th>
<th>pH*</th>
<th>[SO$_4^{2-}$] (mol$^{-1}$)</th>
<th>$E^\circ(2)$ (mV)</th>
<th>$\mu^\circ$ (cal mol$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.52</td>
<td>−497</td>
<td>9.93</td>
<td>0.012</td>
<td>−553</td>
<td>−904,194</td>
</tr>
<tr>
<td>0.56</td>
<td>−494</td>
<td>9.82</td>
<td>0.013</td>
<td>−549</td>
<td>−904,010</td>
</tr>
<tr>
<td>0.5625</td>
<td>−493</td>
<td>8.54</td>
<td>0.0135</td>
<td>−548</td>
<td>−903,964</td>
</tr>
<tr>
<td>0.564</td>
<td>−502</td>
<td>8.40</td>
<td>0.014</td>
<td>−557</td>
<td>−904,379</td>
</tr>
<tr>
<td>0.565</td>
<td>−488</td>
<td>8.19</td>
<td>0.014</td>
<td>−543</td>
<td>−903,733</td>
</tr>
<tr>
<td>0.569</td>
<td>−494</td>
<td>8.12</td>
<td>0.014</td>
<td>−549</td>
<td>−904,010</td>
</tr>
<tr>
<td>0.5714</td>
<td>−495</td>
<td>8.19</td>
<td>0.014</td>
<td>−550</td>
<td>−904,056</td>
</tr>
<tr>
<td>0.58</td>
<td>−495</td>
<td>8.17</td>
<td>0.014</td>
<td>−550</td>
<td>−904,056</td>
</tr>
<tr>
<td>0.5833</td>
<td>−497</td>
<td>8.07</td>
<td>0.014</td>
<td>−552</td>
<td>−904,148</td>
</tr>
<tr>
<td>0.60</td>
<td>−496</td>
<td>8.09</td>
<td>0.014</td>
<td>−550</td>
<td>−904,056</td>
</tr>
<tr>
<td>0.625</td>
<td>−495</td>
<td>7.82</td>
<td>0.015</td>
<td>−549</td>
<td>−904,010</td>
</tr>
</tbody>
</table>

* References Olowe et al.$^1,7$

Table 1. $E_h$ and pH at the equilibrium Fe(OH)$_2$/GR2 observed in sulphated aqueous media ($A = \infty$) and computations of $E^\circ(2)$ and $\mu^\circ$(GR2$^+$)

Corresponding value for $\mu^\circ$, there is no influence on the equilibrium conditions of the reactions. The equation (1a) with the actual formulae of the green rusts is:

$$7 \ [3\text{Fe(OH)}_2,\text{Fe(OH)}_2\text{Cl},n\text{H}_2\text{O}] + 4 \ \text{SO}_4^{2-} \rightarrow$$

$$4 \ [\text{Fe(OH)}_2,2\text{FeOOH},\text{FeSO}_4,m\text{H}_2\text{O}] + (8 - 4m + 7n) \ \text{H}_2\text{O} + 7 \ \text{Cl}^- + e^- \quad (1'a)$$

Equation (1b) becomes:

$$E_h = E^\circ(1') + 0.4137 \log[\text{Cl}^-] - 0.2364 \log[\text{SO}_4^{2-}] \quad (1'b)$$

with:

$$E^\circ(1') = [4\mu^\circ(\text{GR2}) + 7\mu^\circ(\text{Cl}^-) + (8 - 4m + 7n)\mu^\circ(\text{H}_2\text{O}) - 7\mu^\circ(\text{GR1})$$

$$- 4\mu^\circ(\text{SO}_4^{2-})]/23,060 \quad (1'c)$$

Table 2. Oxidation states and chemical potentials of the compounds considered

<table>
<thead>
<tr>
<th>Species</th>
<th>Oxid. no.</th>
<th>$\mu^\circ$ (cal mol$^{-1}$)</th>
<th>Refs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>Fe(OH)$_2$</td>
<td>+2</td>
<td>−116,300</td>
<td>28</td>
</tr>
<tr>
<td>3Fe(OH)$_2$.Fe(OH)$_2$Cl</td>
<td>+2.25</td>
<td>−509,500</td>
<td>8, 9</td>
</tr>
<tr>
<td>4Fe(OH)$_2$.2FeOOH.FeSO$_4$</td>
<td>+2.29</td>
<td>−904,272</td>
<td>This work</td>
</tr>
<tr>
<td>γFeOOH, yFe(OH)$_2$</td>
<td>+3</td>
<td>−111,985</td>
<td>1</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>−1</td>
<td>−56,690</td>
<td>28</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>−1</td>
<td>−31,350</td>
<td>29</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>+6 (S)</td>
<td>−177,970</td>
<td>28</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>+2</td>
<td>−20,300</td>
<td>29</td>
</tr>
<tr>
<td>FeOH$^+$</td>
<td>+2</td>
<td>−66,300</td>
<td>30</td>
</tr>
<tr>
<td>HFeO$_3^+$</td>
<td>+2</td>
<td>−90,627</td>
<td>31</td>
</tr>
<tr>
<td>Fe(OH)$_2^+$</td>
<td>+3</td>
<td>−106,200</td>
<td>29</td>
</tr>
</tbody>
</table>
TABLE 3. \( E_h \) AND pH AT THE EQUILIBRIUM GR1/GR2 OBSERVED AT POINT C AND COMPUTATIONS OF \( E^\circ(1) \) AND \( \mu^\circ(\text{GR2}^*) \)

<table>
<thead>
<tr>
<th>( R )</th>
<th>( E_h ) (mV)</th>
<th>pH</th>
<th>( E^\circ(1) ) (mV)</th>
<th>( \mu^\circ(\text{GR2}^*) ) (cal mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.33</td>
<td>-312</td>
<td>6.89</td>
<td>-515</td>
<td>-904,321</td>
</tr>
<tr>
<td>1.16</td>
<td>-314</td>
<td>7.00</td>
<td>-508</td>
<td>-904,281</td>
</tr>
<tr>
<td>1.0</td>
<td>-327</td>
<td>7.03</td>
<td>-509</td>
<td>-904,287</td>
</tr>
<tr>
<td>0.93</td>
<td>-319</td>
<td>7.13</td>
<td>-496</td>
<td>-904,211</td>
</tr>
<tr>
<td>0.86</td>
<td>-324</td>
<td>7.18</td>
<td>-495</td>
<td>-904,206</td>
</tr>
<tr>
<td>0.80</td>
<td>-350</td>
<td>7.24</td>
<td>-516</td>
<td>-904,327</td>
</tr>
</tbody>
</table>

\[ E^\circ(1') = \{4[\mu^\circ(\text{GR2}) - m\mu^\circ(\text{H}_2\text{O})] + 7\mu^\circ(\text{Cl}^-) \]
\[ + 8\mu^\circ(\text{H}_2\text{O}) - 7[\mu^\circ(\text{GR1}) - n\mu^\circ(\text{H}_2\text{O})] - 4\mu^\circ(\text{SO}_2^-)/23,060. \]

As \( \mu^\circ(\text{GR1}) = \mu^\circ(\text{GR1}^*) + n\mu^\circ(\text{H}_2\text{O}) \) and \( \mu^\circ(\text{GR2}) = \mu^\circ(\text{GR2}^*) + m\mu^\circ(\text{H}_2\text{O}) \) we have \( E^\circ(1') = E^\circ(1) \) and thus equation \((1b') = \text{equation (1b)}, \) i.e. the equilibrium conditions are conserved.

The equilibrium GR1/GR2. From the experimental \( E_h \) values observed at point C, the standard potential \( E^\circ(1) \) is computed from \((1b) \) and the chemical potential of GR2 from \((1c) \). The results are gathered in Table 3. The activities \([\text{Cl}^-]\) and \([\text{SO}_2^-]\) are computed as follows:

\[ [\text{Cl}^-] = \gamma(\text{Cl}^-) = 0.64 \langle \text{Cl}^- \rangle \text{ with } \langle \text{Cl}^- \rangle = [(0.4R)/(2A + 1)] - 0.0286/2 \text{ and } \gamma = 1/4. \]

The last term \((-0.0286/2)\) takes into account the \text{Cl}^- \) ions which are not in solution but in GR1, where an equilibrium of 50% GR1/50% GR2 is assumed.

\[ \langle \text{SO}_2^- \rangle = 0.12 \langle \text{SO}_2^- \rangle \]

with

\[ \langle \text{SO}_2^- \rangle = [(0.4 RA)/(2A + 1)] - 0.0167/2 \text{ and } \gamma = 1/4. \]

The values of the considered chemical potentials are those of Table 2. The value of \( E^\circ(1) \) is constant, independent of \( R \), around a mean value \( E^\circ(1) = -0.507 \pm 0.010 \) V. The experimental \( E_h \) value meets therefore the conditions of equilibrium GR1/GR2. The chemical potential \( \mu^\circ(\text{GR2}^*) \) can be computed from \( E^\circ(1) \).

The mean value \( \mu^\circ(\text{GR2}^*) = -904,272 \pm 70 \text{ cal mol}^{-1} \) is obtained. It is consistent with \( \mu^\circ(\text{GR2}^*) = -904,100 \pm 350 \text{ cal mol}^{-1} \) as determined from the solely sulphated medium.

Pourbaix diagram of iron in chloro-sulphated aqueous medium

The oxidation process of a ferrous hydroxide precipitate in a chloro-sulphated medium such that \( \langle \text{SO}_2^- \rangle/\langle \text{Cl}^- \rangle = 1/4 \) corresponds to a transformation of the type:

ferrous hydroxide \( \rightarrow \) green rust 1 \( \rightarrow \) green rust 2

\( \rightarrow \) ferric oxyhydroxides \( \alpha \) and \( \gamma \text{FeOOH} \).
TABLE 4. EQUILIBRIUM EQUATIONS

(a) \[ H_2 = 2 H^+ + 2 e^- \]
\[ E_h = 0.000 - 0.0591 \text{pH} \]

(1) \[ Fe^{2+} + H_2O = FeOH^+ + H^+ \]
\[ 7.84 = pH - \log[FeOH^+] + \log[Fe^{2+}] \]

(2) \[ FeOH^+ + H_2O = HFeO_2^+ + 2 H^+ \]
\[ 11.87 = pH - 1/2 \log[HFeO_2^+] + 1/2 \log[FeOH^+] \]

(3) \[ Fe^{2+} + 2H_2O = Fe(OH)_2^+ + 2 H^+ + e^- \]
\[ E_h = 1.192 - 0.1182 pH + 0.0591 \log[(Fe(OH)_2^+) / [Fe^{2+}]] \]

(4) \[ FeOH^+ + H_2O = Fe(OH)_2^+ + H^+ + e^- \]
\[ E_h = 0.728 - 0.0591 pH + 0.0591 \log[(Fe(OH)_2^+) / [FeOH^+]] \]

(5) \[ HFeO_2^- + H^+ = Fe(OH)_2^+ + e^- \]
\[ E_h = -0.675 + 0.0591 pH + 0.0591 \log[(FeOH)_2^+] / [HFeO_2^-] \]

(6) \[ Fe + 2H_2O = Fe(OH)_2^- + 2H^+ + 2 e^- \]
\[ E_h = -0.0633 - 0.0591 pH \]

(7) \[ 4 Fe(OH)_2^- + Cl^- = Fe_d(OH)_2^- Cl + e^- \]
\[ E_h = -0.562 - 0.0591 \log[Cl^-] \]

(8) \[ Fe^{2+} + 8H_2O = Fe_d(OH)_2^- Cl + 8H^+ + 9 e^- \]
\[ E_h = -0.119 - 0.0525 pH - 0.0066 \log[Cl^-] \]

(9) \[ 7 Fe_d(OH)_2^- Cl + 4 SO_4^{2-} = 4[4Fe(OH)_2^- 2FeOOH.FeSO_4] + 7 Cl^- + 8H_2O + e^- \]
\[ E_h = -0.507 + 0.4137 \log[Cl^-] - 0.2364 \log[SO_4^{2-}] \]

(10) \[ Fe(OH)_2^- = \gamma FeOOH + H^+ + e^- \]
\[ E_h = 0.1871 - 0.0591 pH \]

(11) \[ Fe_d(OH)_2^- Cl + 4 SO_4^{2-} = 4 Fe_d(OH)_2^- Cl + 4H^+ + 3 e^- \]
\[ E_h = -0.437 - 0.0788 pH + 0.0197 \log[Cl^-] \]

(12) \[ 4Fe(OH)_2^- 2FeOOH.FeSO_4 + 2H_2O = 7 \gamma FeOOH + SO_4^{2-} + 7H^+ + 5 e^- \]
\[ E_h = -0.484 - 0.08274 pH + 0.01182 \log[SO_4^{2-}] \]

(13) \[ Fe^{2+} + 2H_2O = \gamma FeOOH + 3H^+ + e^- \]
\[ E_h = 0.487 - 0.1182 pH - 0.0591 \log[Fe^{2+}] \]

(14) \[ 4 Fe^{2+} + 8 H_2O + Cl^- = Fe_d(OH)_2^- Cl + 8H^+ + 3 e^- \]
\[ E_h = 2.453 - 0.4728 pH - 0.0591 \log[Cl^-] - 0.2364 \log[Fe^{2+}] \]

(15) \[ 7 Fe^{2+} + SO_4^{2-} + 12 H_2O = 4Fe(OH)_2^- 2FeOOH.FeSO_4 + 14H^+ + 2 e^- \]
\[ E_h = 2.083 - 0.4137 pH - 0.02955 \log[SO_4^{2-}] - 0.2069 \log[Fe^{2+}] \]

(16) \[ Fe^{2+} + 2 H_2O = \gamma FeOOH + 3H^+ + e^- \]
\[ E_h = 0.941 - 0.1773 pH - 0.0591 \log[Fe^{2+}] \]

(17) \[ Fe + H_2O = FeOH^+ + H^+ + 2 e^- \]
\[ E_h = -0.208 - 0.02955 pH + 0.02955 \log[FeOH^+] \]

(18) \[ FeOH^+ + H_2O = Fe(OH)_2^- + H^+ \]
\[ 4.911 = pH + \log[FeOH^+] \]

(19) \[ 4 FeOH^+ + 4 H_2O + Cl^- = Fe_d(OH)_2^- Cl + 4H^+ + e^- \]
\[ E_h = 0.600 - 0.2364 pH - 0.2364 \log[FeOH^+] - 0.0591 \log[Cl^-] \]

(20) \[ FeOH^+ + H_2O = \gamma FeOOH + 2H^+ + e^- \]
\[ E_h = 0.477 - 0.1182 pH - 0.0591 \log[FeOH^+] \]

(21) \[ Fe(OH)_2^- = HFeO_2^- + H^+ \]
\[ 18.84 = pH - \log[HFeO_2^-] \]

(22) \[ HFeO_2^- = \gamma FeOOH + e^- \]
\[ E_h = -0.926 - 0.0591 \log[HFeO_2^-] \]

The Pourbaix diagram of iron in such a medium is specific to this medium since it includes both GR1 and GR2. Taking the example of \( A = 1/4 \) with \( \langle Cl^- \rangle = 0.55 \text{ mol l}^{-1} \) (about seawater) and \( \langle SO_4^{2-} \rangle = 0.1375 \text{ mol l}^{-1} \), the corresponding activities which intervene in the equilibrium equations are \( \langle Cl^- \rangle = 0.64 \text{ mol l}^{-1} \) and \( \langle SO_4^{2-} \rangle = 0.12 \text{ mol l}^{-1} \).
0.3, 0.12

0.4

Fe(OH)$_2^+$

7 FeOOH

\( \gamma \)FeOOH

\( \alpha \)FeOOH

Fe$^{2+}$

GR2

GR1

Fe

Fe(OH)$_2$

\( \gamma \)FeOOH

\( \alpha \)FeOOH

3 Fe(OH)$_2$.Fe(OH)$_2$.Cl

4 Fe(OH)$_2$.2 FeOOH.FeSO$_4$

Fig. 5. \( E_h \)-pH equilibrium diagram at 25°C for the system Fe-H$_2$O-Cl$^-$.SO$_4^{2-}$--GR1--GR2-\( \gamma \)FeOOH where \( A = 1/4 \). [Cl$^-\] = 0.35 mol l$^{-1}$ and [SO$_4^{2-}\] = 0.0165 mol l$^{-1}$.

The considered compounds. A list of the compounds in solid or liquid state, and of the ions which are taken into account is presented in Table 2. The oxidation numbers and the standard chemical potentials are given.

Chloride-containing hydroxides and basic sulphates are not considered.

Equilibrium equations. The equations describing the considered equilibria and gathered in Table 4 are established by using the values of chemical potentials \( \mu^o \) of Table 2. The compact formula Fe$_4$(OH)$_8$.Cl is used to designate GR1.

The diagram is shown in Fig. 5. The lower part of the diagram, i.e. for \( E_h \) potentials smaller than that of GR1/GR2 equilibrium (line 9), is the same as the lower part of the Pourbaix diagram drawn for a chloride-containing medium with the same activity [Cl$^-\] = 0.35 mol l$^{-1}$. The upper part of the diagram is also the same as the upper part drawn for a sulphated medium with the same activity [SO$_4^{2-}\] = 0.0165 mol l$^{-1}$.

CONCLUSION

The existence of an oxidation reaction which transforms chloride-containing green rust (GR1) into sulphated green rust 2 (GR2) is a direct experimental proof that these two compounds are characterized by different mean oxidation numbers, +2.25 and +2.29 for GR1 and GR2 respectively. The study of the electrochemical equilibrium which involves these two compounds gave results consistent with those obtained previously in the chloride-containing medium, related to GR1, and those obtained in the sulphated medium related to GR2. They confirm that the chemical formula of GR1 is 3Fe(OH)$_2$.Fe(OH)$_2$.Cl for a chemical potential \( \mu^o = -509,500 \pm 500 \text{ cal mol}^{-1} \) and that of GR2 is 4Fe(OH)$_2$.2FeOOH.FeSO$_4$ for
a chemical potential $\mu^o = -904,100 \pm 350 \text{ cal mol}^{-1}$ where water molecules are not taken into account.

By departing from solutions containing only one anion species, one makes a step towards the understanding of the mechanisms in actual corrosion. For instance, it is known that the observation of GR2 at the surface of corroded steel does not mean necessarily that sulphate ions are the main actors of corrosion, since GR2 can be obtained from a previous chloride-containing compound, i.e. GR1. It is very likely that this interaction or synergy which was observed between the mechanism related to $\text{Cl}^-\text{ ions}$ and that related to $\text{SO}_4^{2-}\text{ ions}$ can be extended to other anions in any natural environment.

REFERENCES

15. H. YUSHIPOKA, Kagaku 18, 413 (1948).
16. ASTM card 8-98 ($\gamma$FeOOH).
17. ASTM card 29-713 (cFeOOH).
22. ASTM card 13-88 (GR1).
23. ASTM card 13-92 (GR2).