THE TRANSFORMATION OF CHLORIDE-CONTAINING GREEN RUST ONE INTO SULPHATED GREEN RUST TWO BY OXIDATION IN MIXED Cl⁻ AND SO₄²⁻ AQUEOUS MEDIA*

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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 $R = \langle Fe^{2+} \rangle / \langle OH^- \rangle$ and $A = \langle SO_4^{2-} \rangle / \langle Cl^- \rangle$ 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 → green rust 1 → green rust 2 → α and γ 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,[1–7] whereas that of chloride ions was continued[8,9] following the work of Rezel.[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[8,9] and sulphate-containing[1,7] media, which include these compounds.

The compound obtained in the presence of sulphate ions, is green rust 2 (GR2) with formula $4Fe(OH)_2.2FeOOH.FeSO_4.nH_2O$ (n is probably 4). GR2, first observed by Girard,[11] was identified recently as the major product issued from corrosion of steel in marine sediments.[12,13]

The compound obtained in the presence of chloride ions, first observed by Keller[14] and Yoshioka,[15] is green rust 1 (GR1) with the formula $3Fe(OH)_2.Fe(OH)_2Cl.nH_2O$ ($3 \geq n \geq 2$).

In this article, the combined influence of Cl^- and SO_4^{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^- ions for 2.8 g of SO_4^{2-} ions l^{-1}, i.e. 1 SO_4^{2-} ion for 19 Cl^- ions.† In this paper, the chosen medium contains 4 Cl^- ions for 1 SO_4^{2-} ion. Moreover, by means of this study, it is possible to check the results obtained separately in chloride-containing and sulphate-containing

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*Part of the thesis presented at the Université de Nancy I by Ph. Refait.
†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 $\mu°$ of GR2 will be determined with a better accuracy.

EXPERIMENTAL METHOD

The experimental procedure was described recently[9] and discussed elsewhere.[1,5,8] 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 $FeSO_4.7H_2O$ and tetrahydrate ferrous chloride $FeCl_2.4H_2O$ 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 $\langle Fe^{2+}\rangle_{init}/\langle OH^-\rangle_{init} = [\langle FeCl_2\rangle_{init} + \langle FeSO_4\rangle_{init}]/\langle NaOH\rangle_{init}$ and A is the ratio $\langle SO_4^{2-}\rangle_{init}/\langle Cl^-\rangle_{init} = \langle FeSO_4\rangle_{init}/2\langle FeCl_2\rangle_{init}$ where $\langle X\rangle_{init}$ 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_α 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.
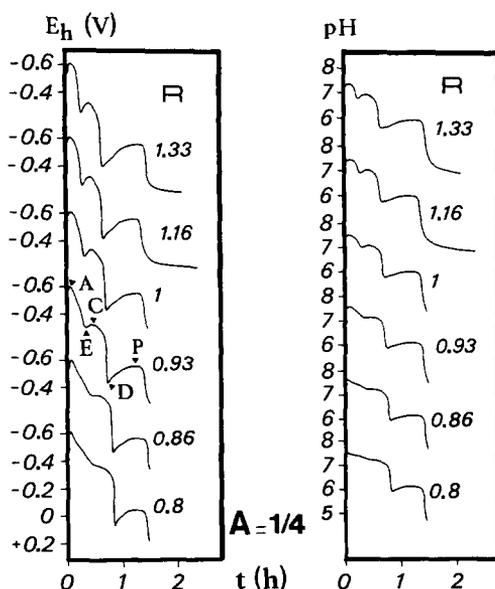

FIG. 1.   Recorded E_h and pH curves with respect to time for the various values of R. Points A, E, C, D and P are equilibrium points. The increasing value for E_h is downward.

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]
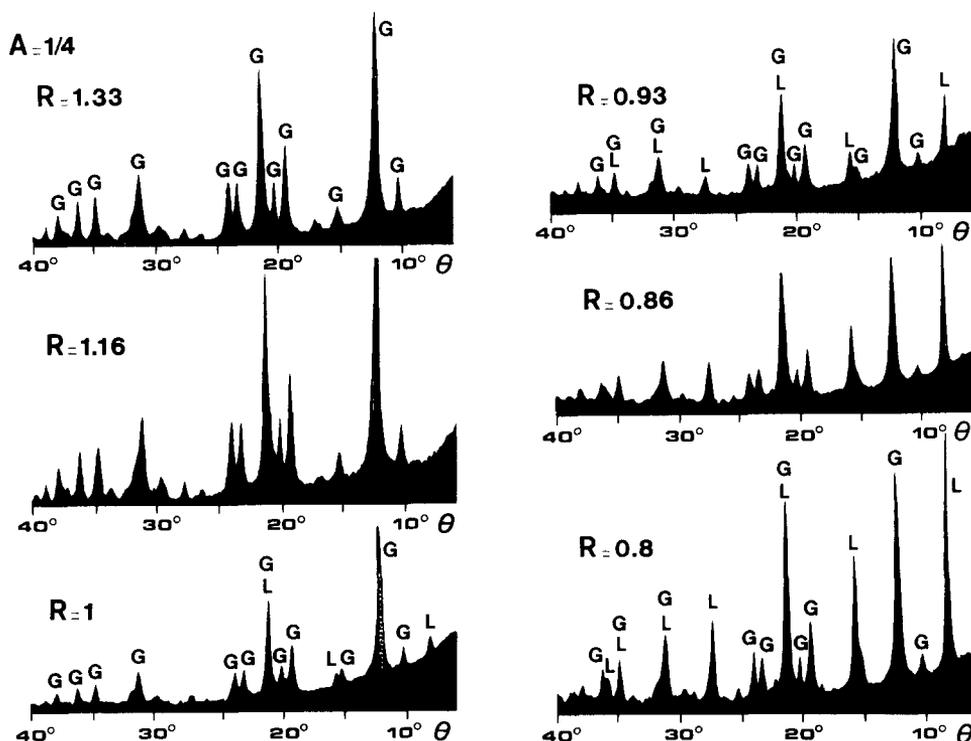

FIG. 2. X-Ray diffraction patterns of the final products obtained at the various values of R. The Co K_α radiation ($\lambda = 1.79$ Å) is used. G = goethite and L = lepidocrocite.
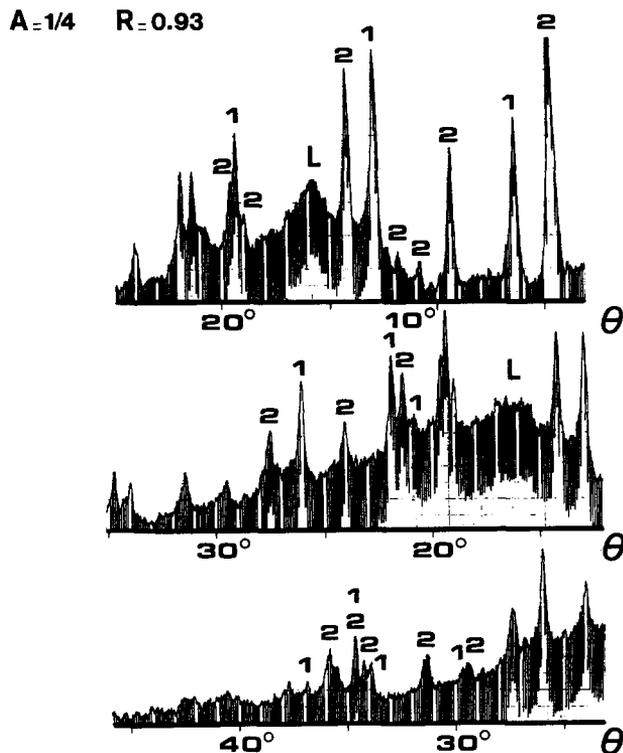
FIG. 3.   X-Ray diffraction patterns of the products obtained at the end of the first stage for
$R = 0.93$. L = lepidocrocite, "1" = GR1 and "2" = GR2.

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[8,22] and lines denoted by "2" are those of the spectrum of sulphated GR2.[1,23]

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 $R \geqslant 0.80$ 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.[2] showed the existence of a sulphated ferrous
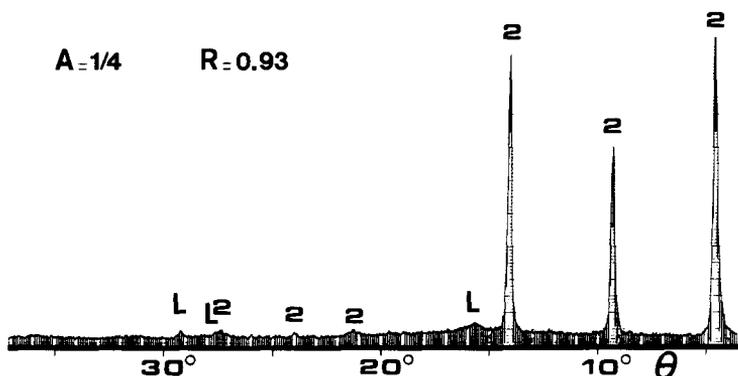
$A = 1/4$ $R = 0.93$

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.

hydroxide (SFH) which was obtained for values of $R \geqslant 0.625$. Its chemical formula is $4Fe(OH)_2.FeSO_4.nH_2O$. For $R = 1$ and $A = \infty$ the initial precipitate is typically made of a mixture of 60% of $Fe(OH)_2$ and 40% of SFH.[1] On the other hand, the work of Rezel[10] demonstrated that in the chloride-containing medium ($A = 0$), the product precipitated at $R = 1$ was constituted of about 55% $Fe(OH)_2$ and 45% of a chlorinated ferrous hydroxide, then called hydroxide 2 (H2). The chemical formula $2Fe(OH)_2.FeOHCl$ was proposed.[24,25]

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 1–green rust 2 (point C)

Introduction. The chemical formula recently proposed[8,9] for GR1 is $3Fe(OH)_2.Fe(OH)_2Cl.nH_2O$ ($3 \geqslant n \geqslant 2$). 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 $4Fe(OH)_2.2FeOOH.FeSO_4.nH_2O$ (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 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:

$$7\,[3Fe(OH)_2.Fe(OH)_2Cl] + 4\,SO_4^{2-} \rightarrow$$

$$4\,[4Fe(OH)_2.2FeOOH.FeSO_4] + 8\,H_2O + 7\,Cl^- + e^-. \quad (1a)$$
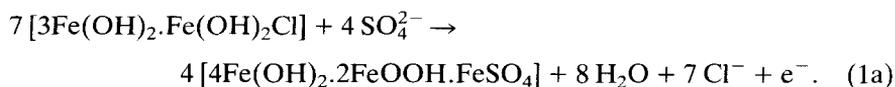
At point C, the electrode potential meets the conditions:

$$E_h = E°(1) + 0.4137\,\log[Cl^-] - 0.2364\,\log[SO_4^{2-}] \quad (1b)$$

where [X] is the activity of ions X in mol l^{-1}. Thus:

$$E°(1) = [4\mu°(GR2^*) + 7\mu°(Cl^-) + 8\mu°(H_2O) - 7\mu°(GR1^*) - 4\mu°(SO_4^{2-})]/23{,}060$$

(1c)

where GR1* and GR2* 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 Cl$^-$ and SO$_4^{2-}$ anions and of the chemical potentials $\mu°$ of green rusts.

Activities. All the experiments concern solutions with ionic strengths ranging from 0.3 to 1.0 mol l^{-1}, close to that of seawater which is about 0.7 mol kg^{-1}.[26,27] It is thus legitimate to consider that the activity coefficients γ of anions are constant over the studied domain and equal to those used in seawater, i.e. $\gamma(Cl^-) = 0.64$ and $\gamma(SO_4^{2-}) = 0.12$.[26,27]

Standard chemical potentials. The chemical potential $\mu°$ of GR1* was recently estimated:[8,9]

$$\mu°[3Fe(OH)_2 . Fe(OH)_2Cl] = -509{,}500 \pm 500 \text{ cal mol}^{-1}.$$

The chemical potential $\mu°$ of GR2* was previously estimated by Olowe:[1,7]

$$\mu°[4Fe(OH)_2 . 2FeOOH . FeSO_4] = -902{,}890 \text{ cal mol}^{-1}.$$

This last estimation was done from the experimental values of E_h at the equilibrium between Fe(OH)$_2$ and GR2, observed for $A = \infty$, i.e. from equations:

$$7 Fe(OH)_2 + SO_4^{2-} \rightarrow 4Fe(OH)_2 . 2FeOOH . FeSO_4 + 2H_2O + 2 e^- \quad (2a)$$

$$E_h = E°(2) - 0.02955 \log[SO_4^{2-}] \quad (2b)$$

$$E°(2) = [\mu°(GR2^*) + 2\mu°(H_2O) - 7\mu°(Fe(OH)_2) - \mu°(SO_4^{2-})]/46{,}120. \quad (2c)$$

These computations were made assuming an activity [SO$_4^{2-}$] equal to the concentration $\langle SO_4^{2-}\rangle$. In conditions of ionic strength which are close to those used here, the activity coefficient $\gamma(SO_4^{2-})$ is of the order of 0.10–0.15. It is therefore necessary to determine more accurately the standard chemical potential of GR2. The values of E_h and pH at the equilibrium Fe(OH)$_2$/GR2 observed by Olowe[1,7] are gathered in Table 1. From these values and equations (2), $E°(2)$ and $\mu°(GR2^*)$ (Table 1) were computed again, by taking an activity of sulphate ions equal to [SO$_4^{2-}$] $= \gamma\langle SO_4^{2-}\rangle = 0.12 \times 2 \times R \times 0.1$. The values of the considered chemical potentials are those of Table 2.

From all this $\mu°(GR2^*) = -904{,}100 \pm 350$ cal mol^{-1} is obtained instead of $-902{,}890$ as computed previously.

Comments. The actual formula of GR1 is 3Fe(OH)$_2$.Fe(OH)$_2$Cl.nH$_2$O but the value of n, between 2 and 3, is not fully ascertained. The actual value of $\mu°$(GR1) is then exactly: $\mu°$(GR1) $= \mu°$(GR1*) $+ n\mu°$(H$_2$O).

It must be noticed that by using the 3Fe(OH)$_2$.Fe(OH)$_2$Cl formula and its

TABLE 1. E_h AND pH AT THE EQUILIBRIUM $Fe(OH)_2/GR2$ OBSERVED IN SULPHATED AQUEOUS MEDIA ($A = \infty$) AND COMPUTATIONS OF $E°(2)$ AND $\mu°(GR2^*)$

R	E_h (mV)*	pH*	$[SO_4^{2-}]$ (mol l^{-1})	$E°(2)$ (mV)	$\mu°$ (cal mol^{-1})
0.52	−497	9.93	0.012	−553	−904,194
0.56	−494	9.82	0.013	−549	−904,010
0.5625	−493	8.54	0.0135	−548	−903,964
0.564	−502	8.40	0.014	−557	−904,379
0.565	−488	8.19	0.014	−543	−903,733
0.569	−494	8.12	0.014	−549	−904,010
0.5714	−495	8.19	0.014	−550	−904,056
0.58	−495	8.17	0.014	−550	−904,056
0.5833	−497	8.07	0.014	−552	−904,148
0.60	−496	8.09	0.014	−550	−904,056
0.625	−495	7.82	0.015	−549	−904,010

*References Olowe et al.[1,7]

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

$$7\,[3Fe(OH)_2.Fe(OH)_2Cl.nH_2O] + 4\,SO_4^{2-} \rightarrow$$

$$4\,[Fe(OH)_2.2FeOOH.FeSO_4.mH_2O] + (8 - 4m + 7n)\,H_2O + 7\,Cl^- + e^-. \quad (1'a)$$
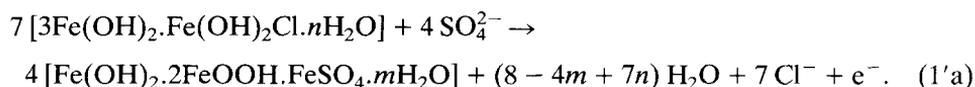
Equation (1b) becomes:

$$E_h = E°(1') + 0.4137\,\log[Cl^-] - 0.2364\,\log[SO_4^{2-}] \quad (1'b)$$

with:

$$E°(1') = [4\mu°(GR2) + 7\mu°(Cl^-) + (8 - 4m + 7n)\mu°(H_2O) - 7\mu°(GR1)$$

$$- 4\mu°(SO_4^{2-})]/23,060 \quad (1'c)$$

TABLE 2. OXIDATION STATES AND CHEMICAL POTENTIALS OF THE COMPOUNDS CONSIDERED

Species	Oxid. no.	$\mu°$ (cal mol^{-1})	Refs
Fe	0	0	
$Fe(OH)_2$	+2	−116,300	28
$3Fe(OH)_2.Fe(OH)_2Cl$	+2,25	−509,500	8, 9
$4Fe(OH)_2.2FeOOH.FeSO_4$	+2,29	−904,272	This work
$\gamma FeOOH$	+3	−111,985	1
H_2O		−56,690	28
Cl^-	−1	−31,350	29
SO_4^{2-}	+6 (S)	−177,970	28
Fe^{2+}	+2	−20,300	29
$FeOH^+$	+2	−66,300	30
$HFeO_2^-$	+2	−90,627	31
$Fe(OH)_2^+$	+3	−106,200	29

TABLE 3. E_h AND pH AT THE EQUILIBRIUM GR1/GR2 OBSERVED AT POINT C AND
COMPUTATIONS OF $E°(1)$ AND $\mu°(GR2*)$

R	E_h (mV)	pH	$E°(1)$ (mV)	$\mu°(GR2*)$ (cal mol^{-1})
1.33	−312	6.89	−515	−904,321
1.16	−314	7.00	−508	−904,281
1.0	−327	7.03	−509	−904,287
0.93	−319	7.13	−496	−904,211
0.86	−324	7.18	−495	−904,206
0.80	−350	7.24	−516	−904,327

i.e.

$$E°(1') = \{4[\mu°(GR2) - m\mu°(H_2O)] + 7\mu°(Cl^-)$$

$$+ 8\mu°(H_2O) - 7[\mu°(GR1) - n\mu°(H_2O)] - 4\mu°(SO_4^{2-})\}/23,060.$$

As $\mu°(GR1) = \mu°(GR1*) + n\mu°(H_2O)$ and $\mu°(GR2) = \mu°(GR2*) + m\mu°(H_2O)$ we have $E°(1') = E°(1)$ and thus equation (1b') = 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 $E°(1)$ is computed from (1b) and the chemical potential of GR2 from (1c). The results are gathered in Table 3. The activities $[Cl^-]$ and $[SO_4^{2-}]$ are computed as follows:

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

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

$$[SO_4^{2-}] = \gamma\langle SO_4^{2-}\rangle = 0.12\langle SO_4^{2-}\rangle$$

with

$$\langle SO_4^{2-}\rangle = [(0.4\,RA)/(2A + 1)] - 0.0167/2 \text{ and } A = 1/4.$$

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

The mean value $\mu°(GR2*) = -904,272 \pm 70$ cal mol^{-1} is obtained. It is consistent with $\mu°(GR2*) = -904,100 \pm 350$ 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 $\langle SO_4^{2-}\rangle/\langle Cl^-\rangle = 1/4$ corresponds to a transformation of the type:
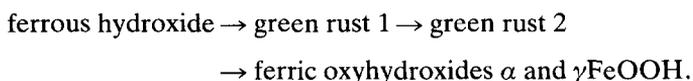
ferrous hydroxide → green rust 1 → green rust 2

→ ferric oxyhydroxides α and γFeOOH.

TABLE 4. EQUILIBRIUM EQUATIONS

(a)	$H_2 = 2\,H^+ + 2\,e^-$
	$E_h = 0.000 - 0.0591\,pH$

(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)	$Fe^{2+} + 2\,H_2O = Fe(OH)_2^+ + 2\,H^+ + e^-$
	$E_h = 1.192 - 0.1182\,pH + 0.0591\,log([Fe(OH)_2^+]/[Fe^{2+}])$
(4)	$FeOH^+ + H_2O = Fe(OH)_2^+ + H^+ + e^-$
	$E_h = 0.728 - 0.0591\,pH + 0.0591\,log([Fe(OH)_2^+]/[FeOH^+])$
(5)	$HFeO_2^- + H^+ = Fe(OH)_2^+ + e^-$
	$E_h = -0.675 + 0.0591\,pH + 0.0591\,log([Fe(OH)_2^+]/[HFeO_2^-])$
(6)	$Fe + 2\,H_2O = Fe(OH)_2 + 2\,H^+ + 2\,e^-$
	$E_h = -0.0633 - 0.0591\,pH$
(7)	$4\,Fe(OH)_2 + Cl^- = Fe_4(OH)_8Cl + e^-$
	$E_h = -0.562 - 0.0591\,log[Cl^-]$
(8)	$4\,Fe + Cl^- + 8\,H_2O = Fe_4(OH)_8Cl + 8\,H^+ + 9\,e^-$
	$E_h = -0.119 - 0.0525\,pH - 0.0066\,log[Cl^-]$
(9)	$7\,Fe_4(OH)_8Cl + 4\,SO_4^{2-} = 4\,[4Fe(OH)_2.2FeOOH.FeSO_4] + 7\,Cl^- + 8\,H_2O + e^-$
	$E_h = -0.507 + 0.4137\,log[Cl^-] - 0.2364\,log[SO_4^{2-}]$
(10)	$Fe(OH)_2 = \gamma FeOOH + H^+ + e^-$
	$E_h = 0.1871 - 0.0591\,pH$
(11)	$Fe_4(OH)_8Cl = 4\,\gamma FeOOH + Cl^- + 4\,H^+ + 3\,e^-$
	$E_h = 0.437 - 0.0788\,pH + 0.0197\,log[Cl^-]$
(12)	$4Fe(OH)_2.2FeOOH.FeSO_4 + 2\,H_2O = 7\,\gamma FeOOH + SO_4^{2-} + 7\,H^+ + 5\,e^-$
	$E_h = 0.484 - 0.08274\,pH + 0.01182\,log[SO_4^{2-}]$
(13)	$Fe = Fe^{2+} + 2\,e^-$
	$E_h = -0.440 + 0.02955\,log[Fe^{2+}]$
(14)	$4\,Fe^{2+} + 8\,H_2O + Cl^- = Fe_4(OH)_8Cl + 8\,H^+ + e^-$
	$E_h = 2.453 - 0.4728\,pH - 0.0591\,log[Cl^-] - 0.2364\,log[Fe^{2+}]$
(15)	$7\,Fe^{2+} + SO_4^{2-} + 12\,H_2O = 4Fe(OH)_2.2FeOOH.FeSO_4 + 14\,H^+ + 2\,e^-$
	$E_h = 2.083 - 0.4137pH - 0.02955\,log[SO_4^{2-}] - 0.2069\,log[Fe^{2+}]$
(16)	$Fe^{2+} + 2\,H_2O = \gamma FeOOH + 3\,H^+ + e^-$
	$E_h = 0.941 - 0.1773\,pH - 0.0591\,log[Fe^{2+}]$
(17)	$Fe + H_2O = FeOH^+ + H^+ + 2\,e^-$
	$E_h = -0.208 - 0.02955\,pH + 0.02955\,log[FeOH^+]$
(18)	$FeOH^+ + H_2O = Fe(OH)_2 + H^+$
	$4.91 = pH + log[FeOH^+]$
(19)	$4\,FeOH^+ + 4\,H_2O + Cl^- = Fe_4(OH)_8Cl + 4\,H^+ + e^-$
	$E_h = 0.600 - 0.2364\,pH - 0.2364\,log[FeOH^+] - 0.0591\,log[Cl^-]$
(20)	$FeOH^+ + H_2O = \gamma FeOOH + 2\,H^+ + e^-$
	$E_h = 0.477 - 0.1182\,pH - 0.0591\,log[FeOH^+]$
(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 $\langle Cl^- \rangle = 0.55\,mol\,l^{-1}$ (about seawater) and $\langle SO_4^{2-} \rangle = 0.1375\,mol\,l^{-1}$, the corresponding activities which intervene in the equilibrium equations are $[Cl^-] = 0.64\,\langle Cl^- \rangle = 0.35\,mol\,l^{-1}$ and $[SO_4^{2-}] = 0.12\,\langle SO_4^{2-} \rangle = 0.0165\,mol\,l^{-1}$.
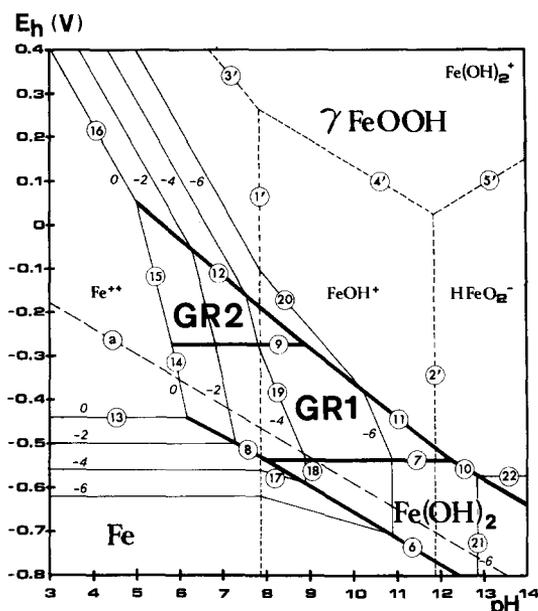
FIG. 5. E_h–pH equilibrium diagram at 25°C for the system Fe–H_2O–Cl^-–SO_4^{2-}–GR1–
    GR2–γFeOOH where $A = 1/4$. $[Cl^-] = 0.35$ mol l^{-1} and $[SO_4^{2-}] = 0.0165$ mol l^{-1}.

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 $\mu°$ of Table 2. The compact formula $Fe_4(OH)_8Cl$ 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}.[9] 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,[8,9] related to GR1, and those obtained in the sulphated medium[1–7] related to GR2. They confirm that the chemical formula of GR1 is $3Fe(OH)_2.Fe(OH)_2Cl$ for a chemical potential $\mu° = -509,500 \pm 500$ cal mol^{-1} and that of GR2 is $4Fe(OH)_2.2FeOOH.FeSO_4$ for

a chemical potential $\mu° = -904,100 \pm 350$ 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 Cl$^-$ ions and that related to SO$_4^{2-}$ ions can be extended to other anions in any natural environment.

REFERENCES

1. A. A. OLOWE, Thesis, Nancy (1988).
2. A. A. OLOWE, J. M. R. GÉNIN and PH. BAUER, *Hyp. Int.* **41**, 501–504 (1988).
3. A. A. OLOWE and J. M. R. GÉNIN, *Hyp. Int.* **46**, 445–452 (1989).
4. A. A. OLOWE and J. M. R. GÉNIN, *Hyp. Int.* **57**, 2029–2036 (1990).
5. A. A. OLOWE and J. M. R. GÉNIN, *Corros. Sci.* **32**, 965–984 (1991).
6. A. A. OLOWE, B. PAURON and J. M. R. GÉNIN, *Corros. Sci.* **32**, 985–1001 (1991).
7. A. A. OLOWE and J. M. R. GÉNIN, *Proc. Int. Symp. Corros. Sci. Engng*, CEBELCOR RT297, 363–380 (1989).
8. PH. REFAIT, Thesis, Nancy (1991).
9. PH. REFAIT and J. M. R. GÉNIN, *Corros. Sci.* **34**, 797–819 (1993).
10. D. REZEL, Thesis, Nancy (1988).
11. A. GIRARD, Thesis, Lille (1935).
12. A. A. OLOWE, PH. BAUER, J. M. R. GÉNIN and J. GUÉZENNEC, *NACE Corrosion* **45**, 229–235 (1989).
13. A. A. OLOWE, N. ROLLET, J. M. R. GÉNIN, D. PRIEUR, M. CONFENTE and B. RESIAK, *C.r. Acad. Sci.* **314**, II, 1157–1163 (1992).
14. G. KELLER, Thesis, Berne (1948).
15. H. YOSHIOKA, *Kagaku* **18**, 413 (1948).
16. ASTM card 8-98 (γFeOOH).
17. ASTM card 29-713 (αFeOOH).
18. P. SCHINDLER, W. MICHAELIS and W. FEITKNECHT, *Helv. Chim. Acta* **46**, 444–449 (1963).
19. G. W. VAN OOSTERHOUT, *J. Inorg. Nucl. Chem.* **29**, 1235–1238 (1967).
20. M. FRANÇOIS and J. P. MARTINY, Institut de Chim. Ind., ULB, Rapport interne (1972).
21. J. DETOURNAY, M. GHODSI and R. DERIE, *Ind. Chim. Belg.* **39**, 695–701 (1974).
22. ASTM card 13-88 (GR1).
23. ASTM card 13-92 (GR2).
24. J. M. R. GÉNIN, PH. BAUER, A. A. OLOWE and D. RÉZEL, *Hyp. Int.* **29**, 1355–1360 (1986).
25. D. RÉZEL, PH. BAUER and J. M. R. GÉNIN, *Hyp. Int.* **42**, 1075–1078 (1988).
26. R. M. GARRELS and M. E. THOMPSON, *Am. J. Sci.* **260**, 57–66 (1962).
27. R. M. GARRELS and C. L. CHRIST, *Equilibres des minéraux et de leurs solutions aqueuses*. Gauthier-Villars, Paris (1967).
28. *Handbook of Chemistry and Physics*, 68th edn (ed. R. C. WEST). CRC Press, Boca Raton, FL (1987–1988).
29. W. M. LATIMER, *The Oxidation States of the Elements and their Potentials in Aqueous Solutions*, 2nd edn. Prentice-Hall, New York (1952); *Recent references to thermodynamic data*. University of California (1954).
30. N.B.S. technical note 270–4, Selected values of thermodynamic properties (1973).
31. M. POURBAIX, *Atlas d'équilibres électrochimiques à 25°C*. Gauthier-Villars, Paris (1963).