Journal of Environmental Science and Engineering A 5 (2016) 383-396
doi:10.17265/2162-5298/2016.08.001

A Consistent Set of Thermodynamic Data for Iron and Reevaluation of Green Rusts and Fougerite Solubilities

Jihaine Ben Nacib[1, 2], Guilhem Bourrié[1], Béchir Ben Thayer[2] and Fabienne Trolard[1]

1. UMR 1114- INRA-University of Avignon, Avignon 84419, France

2. Superior School of Rural Equipment Engineers of Mdjez el Bab, Medjez-el-Bab 9070, Tunisia

Abstract: Over the last ten years, several comprehensive reviews of iron thermodynamics data were published. This work aims to: (i) propose a consistent set of Gibbs free energies (Δ_fG^0) of ferrous hydroxide, $Fe(OH)_{2,cr}$ and of synthetic Green rusts I and II; (ii) check the consistency of the data of these isostructural compounds by means of a correlation obtained with electronegativities of the anions. Experimental data are concentrations in aqueous solutions and pH, and must be processed to obtain ionic activity products (IAP). The model of Specific Interaction Theory (SIT) was used here. Firstly, some complexes whose existences are doubtful were removed from the SIT database. The new modified database is given here. Secondly, experimental data were processed. Thirdly, the following relation of regression between Gibbs free energies of formation of Green rusts and normalized Allred-Rochow electronegativities of anions was obtained as: $\Delta_fG^0 = -488.354 - 353.11\ (\chi/n)$, $r = -0.994$. This relation was then used to assess the Gibbs free energy of formation for GR1-OH, simply written as $Fe_3(OH)_7$.

Key words: Fe, database, Green rusts, ferrous hydroxide, fougerite, Specific Interaction Theory, geochemistry.

1. Introduction

Iron dynamics is of utmost importance in all fields of geochemistry, in soil science and sedimentology. Its abundance and reactivity of iron oxides make it interacts with many metals and metalloids, sometimes impairing phosphate bioavailability. It is considered as a limiting factor for photosynthesis in the ocean [1, 2], as ferredoxin contains Fe. Fe oxidation results in steel corrosion. Both for basic and applied science, a consistent set of thermodynamic data is a need. Obtaining a consistent set of thermodynamic data is however an everlasting challenge as new data must be incorporated. According to Nordström [3], two main methods are used: first, the sequential method starting from the most accurate data on a simple system, $FeO\text{-}H_2O$, then enlarging it progressively $FeO\text{-}Fe_2O_3\text{-}H_2O$, $FeO\text{-}Fe_2O_3\text{-}CO_2\text{-}H_2O$ etc., secondly the simultaneous fit method, optimizing simultaneously a set of experimental data.

For Fe, both methods have been successively used [4]. In addition, experimental data have been usually obtained at medium to large ionic strength and must be extrapolated to “infinite dilution” to obtain “true” thermodynamic data. This implies using some extra thermodynamic assumptions, and different forms of Debye-Hückel laws in order to take into account strong non-ideality of electrolyte solutions, and compute activity coefficients. For sake of consistency, in order to interpret field or experimental data on aqueous solutions, thermodynamic data should preferably be used with the same model as in the previous extrapolation. At present, activity coefficients can be computed: (i) by the simple Debye-Hückel “extended” law; (ii) by the Pitzer’s model [5, 6]; (iii) by the specific interaction theory (SIT) model. The specific interaction theory relies on Brønsted-Scatchard-Guggenheim extension of Debye-Hückel theory [4]. All three models are incorporated in the version 3.0 of Phreeqc code [7]. The selection of the model is implicit in the choice of the database used, respectively phreeqc.dat (default choice), pitzer.dat and sit.dat. Other choices are

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Corresponding author: Guilhem Bourrié, professor, research field: soil science and geochemistry.

variants of phreeqc.dat, differing by the number of elements, complexes or organic molecules taken into account. Pitzer's model has proved to be much better suited in concentrated solutions and brines than Debye-Hückel extended law [6, 8] but parameters are available for a limited number of elements, including Fe, and it appears now as overparameterized [9]. In the recent extensive review of thermodynamic data for Fe [4] SIT model was used to extrapolate experimental data to zero ionic strength. In the following, SIT model will be used with Phreeqc, as recommended by Lemire et al. [4]. Nevertheless, the data selected here may be incorporated in other equilibrium models in dilute solutions when classical Debye-Hückel law holds. Another way to check data consistency is to correlate them with suitable semi-empirical parameters, considering isostructural compounds. The parameter used here is Allred-Rochow electronegativity, following the partial charge model developed by Jolivet [10] as it proved to be successful previously for layered double hydroxides (LDHs) such as green rusts [11], for oxides and oxyhydroxides [12].

2. A Consistent Set of Thermodynamic Data for Fe

Several attempts have been made recently to critically evaluate thermodynamic data for Fe compounds, both in solution and solid state [4, 13, 14]. This was promoted by the need to accurately assess the long-term stability of steel containers used to confine radioactive wastes in repositories (Nuclear Energy Agency of the OECD, Thermochemical Database Project, NEA-TDB). The most extensive review [4] critically evaluates all experimental data from 1857 to 2008. An initial assessment of data was performed by extrapolating them to zero ionic strength, then they were first re-examined to ensure consistency between values from different thermodynamic cycles, and they were ultimately optimized using a weighted least-squares procedure [4]. This work includes data for Fe(0), aqueous species, inorganic complexes of Fe^{2+} and Fe^{3+} with OH^-, halide, sulfur, carbonate and silicon. Auxiliary data are taken from the publication of CODATA Key Values [15]. One must note that for sulfate ion the recent value [3] is -742.628 $kJ\cdot mol^{-1}$, which differs significantly from CODATA set, (-744.004 ± 0.418) $kJ\cdot mol^{-1}$. The review by Lemire et al. [4] includes too many data on Fe minerals: magnetite, goethite, lepidocrocite, feroxyhyte, hematite, maghemite, siderite, Fe sulfides etc.. The main data were incorporated in the sit.dat database. The modified database sit_mod_2016.dat is given in this paper as supplementary material. We will restrict here to complexes with OH^-, Cl^-, SO_4^{2-} and CO_3^{2-}, without considering sulfides, but oxalate complexes are considered too, as this set of data is used to reevaluate thermodynamic properties of green rusts. Indeed, oxalate forms stable green rusts, as sulfate, carbonate and chloride do. The properties of Fe aqueous complexes in STP conditions are given in Table 1.

- The reactions of formation of Fe aqueous complexes, with the values of log K and enthalpies of reaction, used to modify the sit.dat database are given in Table 2 for Fe(II) and Fe(III). By comparison with other databases, phreeqc.dat, it appears that some complexes are no more considered:
- for Fe(II): $Fe(OH)_4^{2-}$, $FeHSO_4^+$, $FeCO_3OH^-$, $FeHCO_3^+$;
- for Fe(III): $Fe(OH)_{3,aq}$, $Fe(OH)_4^-$ and $Fe_3(OH)_4^{5+}$.

These complexes are no more considered because their existence is doubtful and the rationale has been detailed by Lemire et al. [4]. For example, the existence of $Fe(OH)_{3,aq}$ and $Fe(OH)_4^-$ is doubtful because of the dimerisation of $Fe(OH)_2^+$. Accordingly, they are removed from the sit_mod_2016.dat database, simply by "commenting" the corresponding lines in the database. As the process of revision and optimisation included the two methods, namely stepwise revision and global optimisation, there are some differences between the values in the synthesis [4] and the detailed values retained in the following chapters V to XI [4]. For sake of consistency, we chose the values from Table 3, with the auxiliary data from Table 4 [4]. But some values lack, especially enthalpies of reactions necessary to compute at temperatures different from the reference temperature. In some cases, Lemire et al. [4] provided data, not formally retained in the TDB project, but proposed for incorporating provisionally in the models to this end. We selected those values of enthalpies for $Fe(OH)^+$, $Fe(OH)_{2,aq}$ and $Fe(OH)_3^-$, as regards Fe(II) species [4]; in the same way, we selected the value of 26 $kJ·mol^{-1}$ for the enthalpy of reaction of formation of $FeSO_4^+$; there seems to occur a change of coordination at temperatures larger than 328.15 K with a doubling of the enthalpy [4]. We selected here the value suited for lower temperatures.

Table 1 Standard thermodynamic properties at 29,815 K, $1*10^5$ Pa of Fe aqueous complexes considered by Lemire et al. [4] and values of the specific interaction factor for SIT theory.

Species	$\Delta_fG°$ (T°) ($kJ·mol^{-1}$)	$\Delta_fH°$ (T°) ($kJ·mol^{-1}$)	S° (T°) species ($J·mol^{-1}·K^{-1}$)	Cp°. m ($J·mol^{-1}·K^{-1}$)	ε (Cat., Cl^-) ($kg·mol^{-1}$)	ε (Cat., ClO_4^-) ($kg·mol^{-1}$)	Ref.
	Aqueous Fe(II) species						
Fe^{2+}	-90.719	-90.295	-102.171	-23.000	0.17	0.37	1
$FeOH^+$	-275.916	-343.000	-88.000				1
$Fe(OH)_2$	-446.000	-547.000	22.000				1
$Fe(OH)_3^-$	-608.000	-784.000	6.000				1
FeF^+	-381.946					0.34	1
$FeCl^+$	-216.228	-235.824			0.16		1
$FeSO_4$	-848.651	-991.235	-8.785				1
$Fe(CO_3)$	-648.677	-752.609	95.537				1
$Fe(CO3)_2^{2-}$	-1,186.670						1
Fe(Ox*)	-741.583						2
$Fe(Ox)_2^{2-}$	-1,403.862						2
$Fe(Ox)_3^{4-}$	-2,083.723						2
	Aqueous Fe(III) species						
Fe^{3+}	-16.226	-50.056	-282.404	-108.000	0.76	0.73	1
$Fe(OH)^{2+}$	-241.094	-299.886	-132.871			0.46	1
$Fe(OH)_2^+$	-463.107	-550.170				0.37	1
$Fe_2(OH)_2^{4+}$	-490.635	-627.773	-331.321			1.04	1
$FeCl^{2+}$	-156.119	-194.656	-121.309		0.64	0.62	1
$FeCl_2^+$	-291.332	-352.226	-19.410			0.52	1
$FeCl_3$	-415.700						1
$FeCl_4^-$	-535.501						1
$FeSO_4^+$	-784.488	-933.396				0.4	1
$Fe(SO4)_2^-$	-1,539.738	-1,849.488					1, 3
$FeHSO_4^{2+}$	-795.800					0.58	1
$Fe(CO_3)_3^{3-}$	-1,736.918						1
$FeCO_3(OH)$	-842.342				10		1
$Fe(HOx)^{2+}$	-743.577						2
$Fe(Ox)^+$	-744.890						2
$Fe(Ox)_2^-$	-1,454.661						2
$Fe(Ox)_3^{3-}$	-2,154.328						2

*Ox = oxalate.

1. [4];

2. Data for oxalate complexes are not reviewed by Lemire, et al. [4], the values in the sit-database are from Akram et al. [16];

3. ε ($Fe(SO_4)_2^-$, Na^+) = 0.24 from Lemire et al. [4]. Data are given with 3 decimals only to avoid propagation of errors due to rounding.

Table 2 Reactions of formation of Fe aqueous complexes, with the values of log K and enthalpies of reaction, used to modify the sit.dat database.

Reaction of formation	log K(T°)	log K(T°)	log K(T°)	$Delta_fH^0_m$ (kJ·mol^{-1})
	phreeqC.dat	sit.dat	[4]	[4]
Aqueous Fe(II) species				
$Fe = Fe^{2+} + 2 e$			15.893	-90.295
$Fe^{2+} + H_2O = FeOH^+ + H^+$	-9.5	-9.5	-9.1	33.125
$Fe^{2+} + 2 H_2O = Fe(OH)_2 + 2 H^+$	-20.57	-20.6	-20.848	114.955
$Fe^{2+} + 3 H_2O = Fe(OH)_3^- + 3H^+$	-31	-31.9	-34.011	123.546
$Fe^{2+} + 4 H_2O = Fe(OH)_4^{2-} + 4H^+$		-46		
$Fe^{2+} + Cl^- = FeCl^+$	0.14	0.14	-1.0	21.551
$Fe^{2+} + SO_4^{2-} = FeSO_4$	2.25	2.2	-2.44	8.4
$Fe^{2+} + HSO_4^- = FeHSO_4^+$	1.08	1.082		
$Fe^{2+} + CO_3^{2-} = Fe(CO_3)$	4.38	5.69	5.266	12.916
$Fe^{2+} + CO_3^{2-} + H_2O = FeCO_3OH^- + H^+$		-4.03		
$Fe^{2+} + HCO_3^- = FeHCO_3^+$	2	1.44		
$Fe^{2+} + 2CO_3^{2-} = Fe(CO_3)_2^{2-}$		7.45	7.034	
$Fe^{2+} + (Ox)^{2-} = Fe(Ox)$		4.1		
$Fe^{2+} + 2(Ox)^{2-} = Fe(Ox)_2^{2-}$		6.2		
$Fe^{2+} + 3(Ox)^{2-} = Fe(Ox)_3^{4-}$		5.22		
Aqueous Fe(III) species				
$Fe = Fe^{3+} + 3 e$			2.843	-50.056
$Fe^{2+} = Fe^{3+} + e$	-13.02	-13.01	-13.051	40.239
$Fe^{3+} + H_2O = Fe(OH)^{2+} + H^+$	-2.19	-2.19	-2.15	36.0
$Fe^{3+} + 2 H_2O = Fe(OH)_2^+ + 2H^+$	-5.67	-5.67	-4.8	71.546
$Fe^{3+} + 3 H_2O = Fe (OH)_3 + 3H^+$	-12.56	-12.56		
$Fe^{3+} + 4 H_2O = Fe (OH)_4^- + 4H^+$	-21.6	-21.6		
$2Fe^{3+} + 2 H_2O = Fe_2(OH)_2^{4+}$	-2.95	-2.95	-2.82	43.999
$3Fe^{3+} + 4 H_2O = Fe_3(OH)_4^{2+}$	-6.3	-6.3		
$Fe^{3}+ + Cl_{-} = FeCl^{2+}$	1.48	1.4	1.52	22.48
$Fe^{3+} + 2Cl^- = FeCl_2^+$	2.13	2.1	2.22	31.99
$Fe^{3+} + 3 Cl^- = FeCl_3$	1.13	1.13	1.02	
$Fe^{3+} + 4 Cl^- = FeCl_4^-$		-0.79	-0.87	
$Fe^{3+} + SO_4^{2-} = FeSO_4^+$	4.04	4.1	4.25	26.0
$Fe^{3+} + 2 SO_4^{2-} = Fe(SO_4)_2^-$	5.38	5.4	6.22	19.248
$Fe^{3+} + H^+ + SO_4^{2+} = FeHSO_4^{2+}$	4.468	4.47	6.232	
$Fe^{3+} + 3 CO_3^{2-} = Fe(CO_3)_3^{3-}$		24.24	24	
$Fe^{3+} + CO_3^{2-} + H_2O = FeCO_3OH + H^+$		10.76	10.7	
$Fe^{3+} + H^+ + (Ox)^{2-} = Fe(HOx)^{2+}$		9.3		
$Fe^{3+} + (Ox)^{2-} = Fe(Ox)^+$		9.53		
$Fe^{3+} + 2(Ox)^{2-} = Fe(Ox)_2^-$		15.57		
$Fe^{3+} + 3(Ox)^{2-} = Fe(Ox)_3^{3-}$		20.2		

- Data of oxalate complexes are not reviewed by Lemire et al. [4], the values in the sit.dat database are from Akram et al. [16].

In order to be consistent, the specific interaction theory must be used to compute non-ideality interactions between ions. Throughout their study, Lemire, et al. [4] provides values for the specific interaction coefficients of several cations with Cl^- and ClO_4^-, and one value for the interaction between the anion $Fe(SO)_4^{2-}$ and Na^+ (Table 1). These values were incorporated in the sit_mod_2016.dat database, with now 17 ε values for cations against only 3 previously: 4 for Fe(II) (none before) and 13 for Fe(III) (3 before). The coefficient ε

Table 3 Standard thermodynamic properties at 29,815 K, 10^5 Pa of some Fe minerals.

Mineral	$\Delta_fG°$ (T°) ($kJ \cdot mol^{-1}$)	$\Delta_fH°$ (T°) ($kJ \cdot mol^{-1}$)	S° (T°) ($J \cdot mol^{-1} \cdot K^{-1}$)	Cp°.m ($J \cdot mol^{-1} \cdot K^{-1}$)	Ref.
Fe	0.000	0.000	27.085	25.084	[4]
FeOOH goethite	-489.537	-560.460	59.700	74.360	[4]
FeOOH lepidocrocite	-479.881	-549.200	65.080	69.140	[4]
Fe_2O_3 hematite	-744.448	-826.290	87.400	103.930	[4]
Fe_2O_3 maghemite	-727.830	-807.990	93.040	104.690	[4]
Fe_2O_3 magnetite	-1,012.719	-1,115.780	145.890	150.780	[4]
$FeSO_4 \cdot 7H_2O$ melanterite	-2,507.710	-3,012.512	409.118	100.780	[4]
$FeCO_3$ siderite	-679.557	-752.609	95.537	82.450	[4]
$Fe(OH)_2$ ferroushydroxide	-490.035				e
GR2-SO_4 sulfate green rust (a)	-5,688.347				e
GR1-Cl chloride green rust (b)	-2,619.250				e
GR1-CO_3 carbonate green rust (c)	-4,066.242				e
GR1-O_x oxalate green rust (d)	-5,414.168				e
Fougerite	-676.740				e

GR2-SO_4 = $[Fe^{II}_4Fe^{III}_2(OH)_{12}][SO_4 \cdot 8H_2O]$; (b) GR1-C1 = $[Fe^{II}_3Fe^{III}(OH)_8][Cl \cdot 8H_2O]$;
(c) GR1-CO_3 = $[Fe^{II}_4Fe^{III}_2(OH)_{12}][CO_3 \cdot nH_2O]$; (d) GR1-$O_x$ = $[Fe^{II}_6Fe^{III}_2(OH)_{16}][C_2O_4 \cdot 4H_2O]$;
e: This study: the value for fougerite is relative to 1 Fe atom in the mole formula $Fe(OH)_{7/3}$.

(Fe^{3+}, ClO_4^-) is changed from 0.5 $kg \cdot mol^{-1}$ to 0.73 $kg \cdot mol^{-1}$. The previous value ε ($FeOH^{2+}$, Cl^-) = 0.186 $kg \cdot mol^{-1}$ was kept, as no new value was found but it is significantly different from the value ε ($FeOH^{2+}$, ClO_4^-) = 0.46 $kg \cdot mol^{-1}$, while all coefficients of interaction of a given cation with Cl^- and ClO_4^- are quite similar. For minerals, the values selected by Lemire, et al. [4] were incorporated too in sit_mod_2016.dat. Data for goethite, lepidocrocite, hematite, maghemite (ord.), magnetite, melanterite and siderite are given in Table 3.

3. Reevaluation of Thermodynamic Data of Green Rusts

Green rusts are a group of synthetic iron compounds that belong to the larger group of layered double hydroxides (LDHs). These compounds play a major role as intermediates in steel corrosion. They were extensively studied and synthesized in order to better understand corrosion processes. Their structure is well known: they consist of a simple octahedral layer made of a compact stacking of OH^- ions, with divalent and trivalent cations in the octahedral sites. For purely M(II) end members, such as $Mg(OH)_2$ brucite and $Fe(OH)_2$ white rust, the layer is neutral. When trivalent cations M(III) partly substitute for divalent cations, an excess positive charge appears; the layers pull apart and hydrate, while anions enter the inter layer to compensate the electric charge. There exist natural LDHs minerals, such as pyroaurite $[Mg_6Fe^{III}_2(OH)_{16}][CO_3 \cdot 4H_2O]$ and hydrotalcite $[Mg_6Al_2(OH)_{16}][CO_3 \cdot 4H_2O]$, in which M(II) is Mg, and M(III) are Fe(III) and Al. The specificity of green rusts is that M(II) is Fe(II) and M(III) is Fe(III). Electrons can thus be exchanged between adjacent Fe ions, leading to an ordering of cations in the octahedral layers. For the OH of the structure to be stable, every Fe(III) must be surrounded by divalent cations, which limits the mole ratio $Fe^{III}/(Fe^{II}+Fe^{III})$ to less than 1/3 [11]; larger oxidation leads to oxolation forming Fe-O-Fe bonds that are not compatible with the LDHs' structure; this is a step towards formation of proto-lepidocrocite or proto-hematite. If instead, this mole ratio is smaller than 1/4, the mineral dissolves, as $Fe(OH)_2$ is very soluble; combining the structural constraint and the geochemical constraint, it appears that the range of composition of green rusts is very narrow, with a mole ratio $¼ \leq Fe^{III}/(Fe^{II}+Fe^{III}) \leq 1/3$. Green rusts are thus a family of isostructural compounds with limited range of variation of the electric charge. There are two types of structure, GR1 and GR2, with different XRD patterns [17]. GR1 forms with planar or spherical anions: carbonate, chloride and oxalate, and there is only one layer of water molecules in the interlayer; GR2 forms with tetrahedral anions such as sulfate and selenate, and there are two layers of waterin the interlayer [17]. The GR1s present a stacking sequence similar to that of pyroaurite, AcBiBaCjCbAk, where A, B, C are planes of OH^- ions, a, b, c, planes of Fe atoms and i, j, k, the interlayers. The lattice is rhombohedral and the space groupis R $\bar{3}$ m. The general following formula could be proposed for GR1s:

$[Fe^{II}_{(1-x)}Fe^{III}_x(OH)_2]^{+x}[x/nA^{-n}\cdot m/nH_2O]^{-x}$, where 1/4 < x < 1/3. The GR2s present a stacking sequence similar to the crystal structure of $Fe(OH)_2$, AcBiA, with the same notations as above. The lattice is trigonal and the space group is P $\bar{3}$ m1. Thus the following formula could be proposed: $[Fe^{II}_4Fe^{III}_2(OH)_{12}][A^{2-}\cdot 8H_2O]$, where A^{2-} is one of the three-dimensional divalent anions cited above [19, 20]. During their synthesis, first $Fe(OH)_2$ is obtained by neutralizing with NaOH, an iron salt, then the precipitate is allowed to oxidize in solution as O_2 from the ambient air dissolves, while oxido-reduction potential E and pH are continuously monitored [21]. A plateau with quasi-constant E and pH is obtained during which progressively $Fe(OH)_2$ transforms into GRs. At specific points, the solution is in equilibrium both with $Fe(OH)_2$ and Green rust; when oxidation proceeds further, GRs transform into lepidocrocite or magnetite and at specific points, solution is in equilibrium with both GR and lepidocrocite or magnetite. GRs are thus compounds whose standard state is well defined with knowledge both on the solid, by XRD and transmission Mössbauer spectroscopy, and on the aqueous solution, thus well fitted to be revised according to the consistent set of data above.

3.1 Ferrous Hydroxide White Rust

The chemical composition of the solution at equilibrium with $Fe(OH)_2$ before the beginning of formation of GR2-SO_4 is given in Table 4.

This corresponds to point (a) [22]. Using our modified database (sit_mod_2016.dat), the equilibrium constant obtained (log K = 13.133) is slightly different from reported previously as log K = 13.32 ± 0.18. Reprocessing of data leads here to $\Delta_fG^0_m$ = -490.035 ± 1 kJ·mol^{-1}, instead of -489 ± 1.0 kJ·mol^{-1} [22].

3.2 Sulfate Green Rust

Due to the instability of the initial product melanterite, the previous formula with a mole ratio $Fe^{\{III\}}/Fe_{\{total\}}$= 2/7 was demonstrated as erroneous [23]. The structural formula of GR2-SO_4 used in this paper is:

GR2-SO_4=$[Fe^{II}_4Fe^{III}_2(OH)_{12}][SO_4\cdot 8H_2O]\}$

Accordingly, the equilibrium reaction is:

GR2-SO_4 = 2 Fe^{2+} + 4 Fe^{3+} + 12 OH^- + SO_4^{2-} + 8 H_2O, hence log K = 4 log $\{Fe^{2+}\}$ + 2 log $\{Fe^{3+}\}$ + 12 log $\{OH^-\}$ + log $\{SO_4^{2-}\}$ +8 log $\{H_2O\}$. The chemical composition of the solution both at equilibrium with $Fe(OH)_2$ and GR2-SO_4 is given in Table 5.

Brackets {}designate activities. This leads to log K_{sp} = -134.067, and results in $\Delta_fG^0_m$ = -5,688.347 ± 6 kJ·mol^{-1} for the complete formula and in $\Delta_fG^0_m$ = -3,791.227 ± 6 kJ·mol^{-1} for the anhydrous formula, instead of $\Delta_fG^0_m$ = -3,790 ±10 kJ·mol^{-1} from [22].

Table 4 Chemical composition of the solution in equilibrium with $Fe(OH)_2$ at (25 ± 0.5 °C) from Refait, et al. [22].

Experimental data				
pH	E (V)	Fe(II)	SO_4^{2-} (mmol/L)	Na^+(mmol/L)
8.0 ± 0.1	-0.497 ± 0.007	15 ± 1	113 ± 3	120
Processed data				
pH	log $\{Fe^{2+}\}$	log a_w	log K	
8.0 ± 0.1	-2.863	-0.002	13.133	

Table 5 Chemical composition of the solution in equilibrium with $Fe(OH)_2$ at (25 ± 0.5 °C) from Refait et al. [22].

Experimental data					
pH	E (V)	Fe(II)	SO_4^{2-} (mmol/L)	Na^+ (mmol/L)	
8.0 + -0.1	-0.497	15	113	120	
Processed data					
log $[Fe^{2+}]$	log $\{Fe^{3+}\}$	log $\{OH^-\}$	log $\{SO_4^{2-}\}$	log a_w	log K
-2.921	-24.371	-6.002	-1.601	-0.002	-134.067

3.3 Chloride Green Rust

The structural formula of GR1-Cl is: GR1-Cl = $[Fe^{II}_3Fe^{III}(OH)_8][Cl \cdot 8H_2O]$. The experimental data correspond to equilibrium between ferrous hydroxide and GR1-Cl [21]. On their experimental bases (Table 6), the authors assumed that chloride concentration was identical to its initial value, neglecting the amount of Cl^- precipitated and considering only the formation of $FeOH^+$ and not chloride complexes of Fe^{2+}.

As a consequence, the activity of chloride was slightly overestimated. Indeed our results provide an indication of the errors that may occur when the solution was not analysed for chloride concentration at equilibrium. The average value of log K is: log K_{sp}= -81.922 ± 0.11, which results in $\Delta_fG^0_m$ = -2,619.250 ± 0.6 $kJ \cdot mol^{-1}$ for the complete formula and in $\Delta_fG^0_m$ = -2,144.970 ± 0.6 $kJ \cdot mol^{-1}$ for the anhydrous formula, instead of $\Delta_fG^0_m$ = -2,131 ± 10 $kJ \cdot mol^{-1}$ from Refait et al. [21]. These results corroborate those selected by Refait et al. [21] with E^0 = 0.5536 ± 0.0058 V as

Table 6 Chemical compositions of the solution in equilibrium with $Fe(OH)_2$ and GR1-Cl at (25 ± 0.5) °C from Refait et al. [21] and processed data with PhreeqC using SIT model and sit_mod2016.dat database (see text).

Experimental data						Processed data	
pH	E (V)	Fe(II)	Na^+ (mmol/L)	Cl^-(mmol/L)	log $[Cl^-]$	E° (V)	log K
9.15	-0.527	0.2053	0.40	0.4105	-0.5724	-0.5609	-81.97
8.67	-0.52	0.2055	0.40	0.4110	-0.5719	-0.5538	-81.83
8.24	-0.51	0.2060	0.40	0.4120	-0.5709	-0.5438	-81.68
7.71	-0.526	0.2100	0.40	0.4200	-0.5625	-0.5593	-81.95
7.89	-0.51	0.2134	0.40	0.4268	-0.5555	-0.5429	-81.67
7.73	-0.524	0.2160	0.40	0.4320	-0.5503	-0.5566	-81.92
7.78	-0.514	0.2190	0.40	0.4380	-0.5443	-0.5462	-81.74
7.69	-0.53	0.2200	0.40	0.4400	-0.5423	-0.5621	-82.02
7.72	-0.522	0.2220	0.40	0.4440	-0.5384	-0.5538	-81.88
7.67	-0.527	0.2240	0.40	0.4480	-0.5345	-0.5586	-81.97
7.67	-0.527	0.2260	0.40	0.4520	-0.5306	-0.5584	-81.96
7.60	-0.522	0.2280	0.40	0.4560	-0.5268	-0.5532	-81.87
7.51	-0.528	0.2320	0.40	0.4640	-0.5192	-0.5587	-81.97
7.64	-0.522	0.2400	0.40	0.4800	-0.5045	-0.5518	-81.87
7.48	-0.526	0.2520	0.40	0.5040	-0.4833	-0.5546	-81.94
7.49	-0.534	0.2600	0.40	0.5200	-0.4697	-0.5618	-82.10
7.47	-0.53	0.2660	0.40	0.5320	-0.4598	-0.5572	-82.02
7.42	-0.53	0.2800	0.40	0.5600	-0.4376	-0.5559	-82.02
7.41	-0.53	0.3000	0.40	0.6000	-0.4076	-0.5541	-82.03
7.36	-0.526	0.3100	0.40	0.6200	-0.3934	-0.5493	-81.95
7.36	-0.526	0.3200	0.40	0.6400	-0.3796	-0.5485	-81.95
7.33	-0.525	0.3340	0.40	0.6680	-0.3610	-0.5464	-81.94
7.31	-0.526	0.3500	0.40	0.7000	-0.3407	-0.5462	-81.95

Fe(II) and Cl^- are the initial total concentrations in mmol/L; log $\{Cl^-\}$ is the logarithm of activity of Cl^-; $E^0 = E + S \log \{Cl^-\}$, where S = 0.0591597 $V \cdot mol^{-1}$; log K is for the reaction: $Fe_4(OH)_8Cl(H_2O)_2 = Fe^{3+} + 3Fe^{2+} + 8OH^- + Cl^- + 2H_2O$.

Table 7 Values of pH and E at equilibrium with $Fe(OH)_2$ and GR1-CO_3 (point B) at (25 ± 0.5) °C from Drissi et al. [24] (Table 2) and processed data.

Experimental data				Processed data			
pH	E (V)	Na^+_t (mmol/L)	$SO_4^{2-}{}_t$ (mmol/L)	Fe_t (mmol/L)	Alk	log $\{CO_3^{2-}\}$	log Q
10.32	-0.572	660	180	0.157	300.3	-2.0668	-136.74
10.28	-0.573	660	180	0.189	300.3	-2.068	-136.76
10.32	-0.575	660	180	0.157	300.3	-2.0658	-136.84
10.45	-0.578	660	180	0.09	300.3	-2.0598	-136.46
10.47	-0.578	660	180	0.082	300.17	-2.0592	-136.9
10.48	-0.579	660	180	0.079	300.15	-2.0588	-136.94
10.61	-0.586	660	180	0.044	300.08	-2.0546	-137.18
10.68	-0.585	660	180	0.032	300.06	-2.0529	-137.12
10.7	-0.581	660	180	0.03	300.05	-2.0525	-136.98
10.76	-0.587	660	180	0.023	300.04	-2.0513	-137.19
10.76	-0.589	660	180	0.023	300.04	-2.0513	-137.27
10.81	-0.588	660	180	0.018	300.03	-2.0506	-137.24
10.86	-0.588	660	180	0.014	300.02	-2.0499	-137.22
10.87	-0.581	660	180	0.013	300.02	-2.0498	-137.02
10.96	-0.585	660	180	0.009	300.01	-2.0489	-137.12
11	-0.585	660	180	0.007	300.01	-2.0486	-137.17
10.95	-0.587	660	180	0.009	300.01	-2.049	-137.18
10.96	-0.586	660	180	0.009	300.01	-2.0489	-137.16
11.01	-0.563	660	180	0.007	300.01	-2.0486	-136.39

Fe_t is the value leading to the equilibrium with $Fe(OH)_{2,cr}$ and Alkalinity is computed from eq.1.

compared to $E^0 = 0.554 \pm 0.001$ V from Refait et al. [21]. This small difference is due to the fact that chloride complexes with Fe^{2+} are very weak and suggest that $FeCl^+$ is of the same order of magnitude as $FeOH^+$ and amounts to only 1% of Fe^{2+}.

3.4 Carbonate Green Rust

Carbonate-green rust is not obtained directly, as siderite is not soluble enough. Instead, it is obtained by precipitation of $Fe(OH)_2$, by mixing NaOH and $FeSO_4$ in presence of Na_2CO_3. Carbonate-green rust 1 forms instead of sulfate green rust 2. The structural formula of GR1-CO_3 is: GR1CO_3 = $[Fe^{II}_4Fe^{III}_2(OH)_{12}][CO_3{\cdot}2H_2O]$. In the original paper [24], the activity of CO_3^{2-} was derived from the total concentration of carbonate and the equilibrium constant for reaction $HCO_3^- = CO_3^{2-} + H^+$. Carbonato-complexes are thus neglected, and the amount of carbonate precipitated in the solid phase is neglected too. Instead, the starting point is here the equation of alkalinity written as:

$$Alk = [Na^+]_t + 2\,[Fe^{2+}]_t - 2[SO_4^{2-}]_t \quad (1)$$

As $[Na^+]_t$ and $[SO_4^{2-}]_t$ are kept constant, alkalinity is simply proportional to $[Fe^{2+}]_t$. The experimental data are given in Table 7.

The solutions are both at equilibrium with ferrous hydroxide and GR1-CO_3. Accordingly, the equilibrium constant is obtained directly by taking the average value of log Q (Table 7). The values are very close from each other, with $\log K_s = -137.017 \pm 0.224$, which results in $\Delta_fG^0_m = -4{,}066.242 \pm 1.300$ kJ·mol^{-1} for the complete formula instead of $\Delta_fG^0_m = -4{,}042.79$ kJ·mol^{-1} (-966.250 kcal·mol^{-1}) from Drissi et al. [24], and in $\Delta_fG^0_m = -3{,}591.967$ kJ·mol^{-1} for the anhydrous formula. The dominant Fe(II) aqueous species is $Fe(CO_3)_2^{2-}$, in a solution at pH = 10.32 in equilibrium both with $Fe(OH)_{2,cr}$ and with GR1-CO_3. It amounts to 99.4% of total aqueous Fe(II). The complexation of Fe^{2+} by carbonate is thus a major term.

3.5 Oxalate Green Rust

The structural formula of GR1-O_x is:

GR1-O_x = $[Fe^{II}_6Fe^{III}_2(OH)_{16}][C_2O_4 \cdot 4H_2O]$. Basic experimental data are from Refait et al. [25], Fe complexation by oxalate was neglected, and activity coefficient of $C_2O_4^{2-}$ was calculated as 0.23 by using Davies equation. As shown in Table 2, it is not possible to neglect the complexation of Fe^{2+} by oxalate. Indeed, there are four complexes (Table 2). The starting point is here the equation of alkalinity, related to weak diprotic acid character of oxalic acid, and the expression of Alk_{ox} at the proton condition [26, 27] can be written as:

$$Alk_{ox} = 2[O_x^{2-}] + 2[FeO_x^0] + 4[Fe(O_x)_2^{2-}] + 6[Fe(O_x)_3^{3-}] + 2[NaO_x^-] + [HO_x^-] + [OH^-] - [H^+] \quad (2)$$

where Alk_{ox} is oxalate-alkalinity. While only Fe(II)-oxalate complexes are explicitly written in equation above, Fe(III)-oxalate complexes are automatically considered too in the computation using Phreeqc. Eq. (2) can be combined with the balance equation for oxalate:

$$[Ox_t] = [O_x^{2-}] + [FeO_x^0] + 2[Fe(O_x)_2^{2-}] + 3[Fe(O_x)_3^{3-}] + [NaO_x^-] + [HO_x^-] + [H_2O_x] \quad (3)$$

to give a new expression of Alk_{ox}:

$$Alk_{ox} = 2[Ox_t] - [HO_x^-] - 2[H_2O_x] + [OH^-] - [H+] \quad (4)$$

Considering the experimental conditions of GR1-Oxalate formation (Table 8), the total concentration of oxalate is the largely dominant term of the right hand side member.

$$Alk_{ox} = 2[Ox_t] = [Na^+]_t + 2\,[Fe^{2+}]_t \quad (5)$$

As the solution is in equilibrium with ferrous hydroxide, the activity of Fe^{2+} is fixed by the value of pH, so that $\log\{Fe^{2+}\} = -4.467$. On the second hand, it is noticeable in Table 8 that though the dominant oxalate species is O_x^{2-}, nearly 40% of oxalate is complexed with Fe(II). This is in striking contrast with the hypothesis that all oxalate present was free [25]. From the newly processed data and writing at equilibrium between ferrous hydroxide and oxalate-GR:

$$\log K = -2pe - 3\log a_w - \log\{O_x^{2-}\}, \quad (6)$$

The value obtained is log K = 18.997, hence $\Delta_f G^0_m$ = -5,414.168 ± 8 kJ·mol^{-1} for the complete formula instead of $\Delta_f G^0_m$ = -5,383 ± 3 kJ·mol^{-1} from Refait et al. [25], and $\Delta_f G^0_m$= -4,702.745 kJ·mol^{-1} for the anhydrous formula. The reevaluated values for the hydrated minerals are given in Table 3, while the values for the ‘anhydrous’ minerals are presented in Table 11 along with previous values and more recent values from Bourdoiseau et al. [28].

4. Discussion

The present reexamination of previous results was divided in five broad parts, first on “white rust”, then on GRs according to the nature of intercalated anion (SO_4^{2-}, Cl^-, CO_3^{2-} and oxalate). The starting points are the experimental original data of previous studies, in which solutions are in equilibrium both with the specific Green rust and $Fe(OH)_{2,cr}$. New values of $\Delta_f G^0_m$ and log K are then determined with PhreeqC and the new database sit_mod_2016.dat. The value used here for $Fe(OH)_{2,cr}$ is quasi-identical to the values used in the previous studies.

4.1 Influence of Complexation of Fe by Anions

In every case, neglecting complexation of Fe by the specific anion leads to large errors. For GR2-SO_4 complexation was taken into account, so the difference is 1.2 kJ/mol, *i.e.* mainly due to the difference for $Fe(OH)_{2,(cr)}$.. For GR1-Cl, GR1-Oxalate

Table 8 Values of pH and E at equilibrium with $Fe(OH)_2$ and GR1-oxalate (point B) at (25 ± 0.5) °C from Refait et al. [25] and processed data.

Experimental data [25]							
pH	E (V)	Na^+ (mmol/L)	Ox_t (mmol/L)				
8.8	-0.505	300	150				
Processed data [this study]							
$[O_x^{2-}]$	$[FeO_x^0]$	$[Fe(O_x)_2^{2-}]$	$[Fe^{2+}]$	$[Fe_t]$	$\log\{O_x^{2-}\}$	$\log a_w$	log K
62.25	5.26	41.23	7.031	53.52	-1.916	-0.003	18.997

and GR1-CO_3, differences are respectively 14, 31 and 24 kJ/mol. When normalized to 1 atom of Fe per mole formula (Table 11), these differences are respectively 3.5, 3.8 and 4 kJ/mol: they increase with the complexing capacity of anions: chloride < oxalate < carbonate: chloride complex $FeCl^+$ amounts to less than 1% of aqueous Fe(II), but $Fe(O_x)_2^{2-}$ amounts to 87% of aqueous Fe(II), and $Fe(CO_3)_2^{2-}$ amounts to 99% of aqueous Fe(II).

The reevaluated data are in quasi-complete agreement with data reevaluated independently [28], with the same value for $Fe(OH)_{2,(cr)}$: -5,687 ± 10 kJ/mol (-5,688.347 ± 6 here) for GR2-SO_4; -2,620 ± 15 kJ/mol for GR1-Cl (-2,619.250 ± 0.6 here); -4,064 ± 10 (-4,066.242 ± 6 here) for GR1-CO_3. An additional source of experimental error identified by Bourdoiseau et al. [28] is the fact that measured potentials can be slightly overestimated due to the influence of (O_2/H_2O) redox couple when solutions are not deaerated (Table 4). The agreement is only good for GR1-Oxalate -5,424 ± 10 kJ/mol [28] against -5,414.168 ± 8 here, but the authors did not consider Fe complexation with oxalate, so it appears that our value is slightly better.

4.2 Stoichiometry of GR2-SO_4

A large discrepancy exists between the formulae and values proposed for GR2-SO_4 by many authors [29-32], more specifically on the mole ratios of Fe^{III}/Fe_{tot} and Fe^{III}/SO_4, and on the presence of Na^+ in the interlayer [29]. The classical formula of green rust is $[Fe^{II}_{(1-x)}Fe^{III}_x(OH)_2]^{+x}[x/nA^{-n}\cdot yH_2O]^{-x}$ where A is a n-valent anion, y is the number of intercalated water molecules per formula unit and x is the ratio (Fe^{III}/Fe_{tot}); x is in between 1/4 and 1/3 [22, 23, 33-36]. However, compounds with Fe^{II}/Fe^{III} ratio ranging between 0.5 and 1.34 were obtained [32], which leads to a Fe^{III}/Fe_{tot} mole ratio in between 3/7 and 2/3. This ratio implies the phenomenon of oxolation [10] resulting from the loss of a proton H^+ during the formation of the green rust, thereby rewriting the formula of green rust as follows: $[Fe^{II}(1-x)Fe^{III}_x(OH)_{(2+x-2y)}][(A^{m-}_{y/m}\cdot yH_2O]$. This formula, applicable when x is larger than 1/3, was explained as the effect of the substitution of hydroxyl groups by O^{2-} [32, 37]. Although measurements by Mössbauer spectrometry have well confirmed the GR-0.5 (Fe^{II}/Fe^{III}= 0.5) [32], the other levels of the Fe^{II}/Fe^{III} mole ratio are still doubtful. Indeed, assuming a ratio larger than 0.5, this gives a mole ratio Fe^{III}/S different from 2. Calorimetry demonstrated that there is no thermodynamic preference for any Fe^{II}/Fe^{III} mole ratio [32]. In addition, there is no significant statistical difference for GR2-SO_4 whether Na^+ is considered in the interlayer or not [29], so the classical structural formula for GR2-SO_4 is used here. In addition, values obtained here are based upon the most recent critically evaluated database for Fe [4], incorporated in sit_mod_2016.dat, and on SIT theory for computation of activity coefficients while many previous studies relied on compilations outdated and not traceable to the original works [38, 39].

4.3 Relation with Electronegativity and Partial Charges Model

Since the interaction between the layer and the anion is mainly of electrostatic origin, a relationship was investigated with a suitable electrostatic parameter, namely electronegativity, as in earlier studies [11, 12, 20]. The model of partial charges [10] allows for computation of the electronegativity χ of any molecule or ion as:

$$\chi=\frac{\sum\sqrt{\chi^*}+1.36Z}{\sum\frac{1}{\sqrt{\chi^*}}} \tag{7}$$

where χ^* is the electronegativity of the element taken on the Allred-Rochow scale and Z is the overall charge of the ion. Electronegativities of the interlayered anions considered here χ are given in Table 10, along with the electronegativities of the elements, which they are composed of, χ^*. As earlier, Gibbs free energies of formation of GRs considered here are Gibbs free

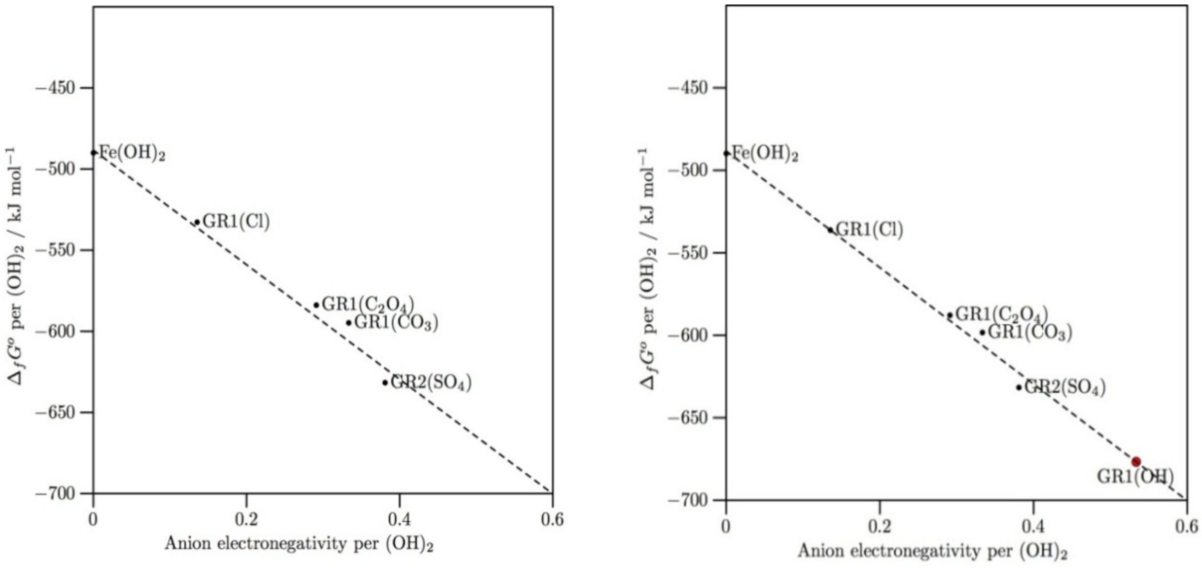
Table 10 Electronegativities of the elements and of interlayered anions, following the partial charges model [10].

Element	H	C	O	S	Cl
χ^*	2.1	2.5	3.5	2.48	2.83
Anion	Cl^-	OH^-	CO_3^{2-}	SO_4^{2-}	$C_2O_4^{2-}$
χ	0.5421	1.6005	2.0007	2.2856	2.329

Table 11 Values of GRs (anhydrous formulae) and electronegativities of anions.

Mineral	Previous studies		This study				
	$\Delta_fG^0_m$ (kJ·mol^{-1})	Ref.	$\Delta_fG^0_m$ (kJ·mol^{-1})	n	χ	$\Delta_fG^0_m/n$	χ/n
$Fe(OH)_2$	-489	[22]	-490.035	1	0	-490.035	0
GR2-SO_4	-3790	[22]	-3,791.227	6	2.2856	-631.872	0.3809
GR1-Cl	-2131	[21]	-2,144.970	4	0.5421	-536.243	0.136625
GR1-CO_3	-3568	[24]	-3,591.967	6	2.0007	-598.661	0.3345
GR1-O_x	-4672	[25]	-4,702.745	8	2.329	-587.873	0.291125

n is the number of $(OH)_2$ groups in the mole formula, *i.e.* in the layer, excluding OH^- in the interlayer.



A. Previous study [20]

B. This study

Fig.1 Correlation between Gibbs free energies of formation of synthetic Green rusts and electronegativities of interlayered anions.

energies of formation for the ‘anhydrous’ minerals, *i.e.* by subtracting y (-237.14) kJ/mol, where y is the number of moles of water in the GR and -237.14 stands for the Gibbs free energy of liquid water in STP. This is justified as calorimetric study [32] demonstrated that interlayered water is less tightly bound than in hydrotalcites with indeed slightly positive entropy. Gibbs free energies are correlated with electronegativities of the interlayered anions, both being normalized to 2 structural OH per mole formula (Table 11, Fig. 1).

A highly significant correlation is obtained as earlier [11, 12, 20], and it is slightly improved (Fig. 1B) as compared to the previous ones (Fig. 1A).

The sum of residuals decrease from 237 kJ^2·mol^{-2} to 150 kJ^2·mol^{-2}; when weighing the experimental data above, the standard deviation of the linear regression is obtained as 1 kJ·mol^{-1}.

The regression line obtained is: y= -488.354 -353.11(χ/n), r = -0.994, where n is the number of $(OH)_2$ per mole formula used to normalize the values.

From this equation, and the electronegativity of OH^-,

χ = 1.6005, the Gibbs free energy of formation of GR1-OH (fougerite) is obtained as: $\Delta_f G^0_m$ = -676.74 kJ·mol^{-1} instead of $\Delta_f G^0_m$ = -678.19 kJ·mol^{-1} and a mole formula $1/3[Fe^{II}_2Fe^{III}(OH)_6][OH] \equiv Fe(OH)_{7/3}$. All selected values are reported in Table 3.

5. Conclusion

The thermodynamic data carefully selected on Fe compounds [4] were used here for sake of consistency with the Specific Interaction Theory to compute activity coefficients in aqueous solutions. Doubtful aqueous species were discarded. Those data and the parameters for SIT theory relative to Fe compounds were incorporated in a new sit database associated with PhreeqC geochemical model: this is the sit_mod_2016.dat database. The free energies of formation of ferrous hydroxide and different synthetic green rusts were then recalculated from the original experimental data. The reevaluated data for this group of isostructural compounds are very well correlated with the electronegativity of the interlayered anion, taken on the Allred-Rochow scale, and following the partial charges model [10], which confirms the robustness of the model. A better confidence interval is obtained from this correlation, which demonstrates that the contribution of the layer to Gibbs free energy is quasi-constant, once normalized to 2 structural OH per mole formula. All experimental data are largely based upon equilibria between GRs and ferrous hydroxide, hence on the value of the solubility product of ferrous hydroxide that Lemire et al. [4] discussed but did not retain, as data on this compound are scarce and ancient. Better experimental data on this compound will thus be welcome.

Acknowledgements

The Universitéd'Avignonet des Pays de Vaucluse (UAPV) is gratefully acknowledged for a Agricol Perdiguier grant to Mrs. Jihaine Ben Nacib. The support of Inra and of the EcoleSupérieured'Ingénieurs de l'Equipement Rural at Medjez-el-Bab (Tunisia) and of her Director Pr. HassenKharroubi is gratefully acknowledged too.

Supplementary Material

The modified database, sit_mod_2016.dat, is available as supplementary material.

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