THERMODYNAMIC MODEL FOR SOLID IRON IN AQUEOUS SOLUTIONS

Nascimento, L.[1*]; Agostinho, L. C. L.[2]; Cavalcanti, F.B.[3]

[1*]Departamento de Física-*DF/CCEN-UFPB*
Cidade Universitária- Caixa Postal:5008-Cep:58059-900, João Pessoa-PB.
E-mail [1*]: luciano.fisicaufpbccen@gmail.com
[2]Departamento de Química-*DQ/CCT-UEPB*
Rua Juvêncio Arruda,s/n-Bodocongó-Cep:58109-790, Campina Grande-PB.
E-mail [2]:cristina.uepb@gmail.com
[3]Departamento de Hidráulica e Engenharia Civil-*DHEC/CCT-UFCG*
Av. Aprígio Veloso, 882-Bloco CM - 1°Andar - CEP 58.109-970, Campina Grande-PB.
E-mail [3:] bernardete.ufcg@gmail.com

ABSTRACT

Solid iron can be observed at environmental conditions and also as metallic component of quasicrystalline alloys. Its behavior in aqueous solution is analyzed from some particular thermochemical relationships. The model utilizes free Gibbs energy to obtain pH and pε parameters which are related to iron redox reactions. The solid iron system, defined as $Fe_{(s)}$: Fe^{2+} - Fe^{3+} - Fe_2O_3 (hematite) – Fe_3O_4 (magnetite), was modelled by considering a low molar concentration and environmental temperature. In order to obtain pε values, equations relating Gibbs standard free energy and equilibrium constants were applied. A stability diagram such as pε x pH was chosen to depict these thermochemical relationships. Thus, straight line dpε/dpH slopes were obtained for each process step of the solid iron system. In systems relating solid iron to iron species Fe^{2+} and Fe^{3+} the slopes are equal to zero; i.e., a horizontal line shows the iron species dominance in some specific pH range. The negative values obtained show the pH dependence of the iron species investigated. In natural water environment, it is possible to distinguish hematite formation from magnetite formation. However in quasicrystalline AlCuFe alloys the last iron species formed is hematite which ion pairs to copper. Due to the strong pH dependence, it is necessary to measure pH in both environmental condition and quasicrystalline phases formation. Considering that the temperature adopted was 25°C, the results are valid only for this temperature.

Key – words: Iron thermochemical model; Standard free energy; Solid iron species.

INTRODUCTION

Corrosion is the main problem arising with iron in natural waters. Corrosion involves electrochemical reactions between, for instance, the water and the metallic component of the system. As a result, it can be observed pitting, nodule formation, and red water among other problems.

With regard to quasicrystalline alloys, solid iron is used to prepare AlCuFe alloys. These atomic ordered structures exhibit quasiperiodic translational long – range order and were first

reported in 1984 by SCHECHTMAN et al. [1]. Quasicrystals, QC, show forbidden crystallographic symmetries and are prepared by fast cooling techniques [2].

Generally, it is used grinding at high energy for syntherizing metastables and stables QC via reaction of solid state [3]. After this process, chemical treatments are applied during some hours at temperatures above 300ºC in environment or in other medium. Samples are then characterized by using X – ray photoelectron spectroscopy (XPS) and X – ray stimulated Auger electron spectroscopy (XAES) [4].

According to Figure 1 and the second PINHEIRO et al. (1999) [5], pure metals used to form quasicrystalline alloys suffer oxidation under several conditions; i.e., in vacuum, in normal air and after liquid immersion. By using XPS data and XAES spectra obtained in fixed angle, each element of the AlCuFe alloy was studied. They have observed aluminum enrichment on the quasicrystal surface and a decrease in copper and iron.

They also observed that; (i) aluminum ion oxidizes under all conditions of alloys preparation; (ii) copper and iron are protected from oxidation when the alloy is immersed in water and (iii) this protection is due to the formation of an aluminum passivation layer. Also, they have observed that the 2ρ XPS line falls at 707 eV in pure metal indicating the presence of hematite FeOOH.
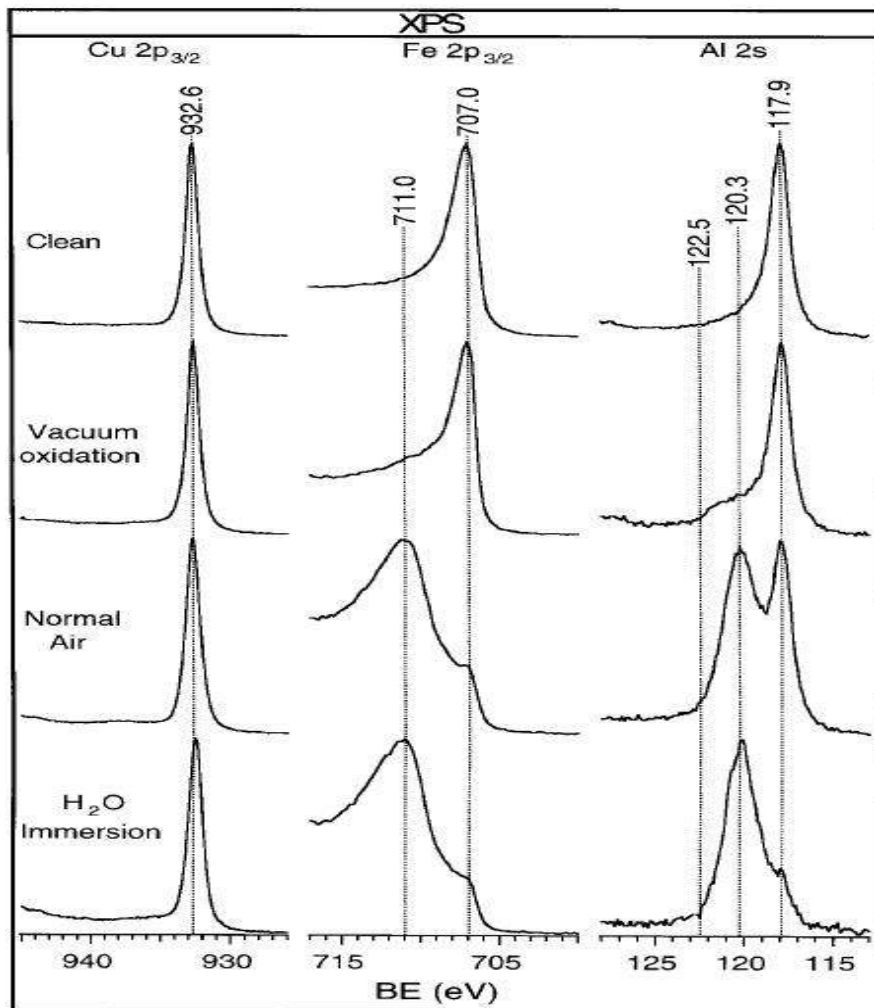

Figure 1. X – ray photoelectron spectroscopy (XPS) of AlCuFe alloy after several treatments according [5].

NASCIMENTO et al (2009) [6] analyzed the oxidation behavior of AlCuFe alloy by applying different conditions of thermal treatment. They have used X – Ray Diffratometry technique and Scanning Electron Microscopy (SEM) to analyze also QC morphology and phases evolution. Regarding solid iron behavior in QC, their work showed similar results as those reported by ROUXEL et al. (2006) [7].

At temperatures above 700ºC in the crystalline phase of AlCuFe, a nodule formation was observed as well as an association of copper with hematite (a solid named cuprospinel, $CuFe_2O_4$), that is the last compound formed until QC reaches its icosahedral phase. Figure 2 below, respectively, shows the result of sample Scanning Electron Microscopy in the sample quasicrystalline alloy AlCuFe, showing the geometric uniformity in the image of the microstructure with the formation of hematite (Fe_2O_3) in the alloy quasicrystalline.
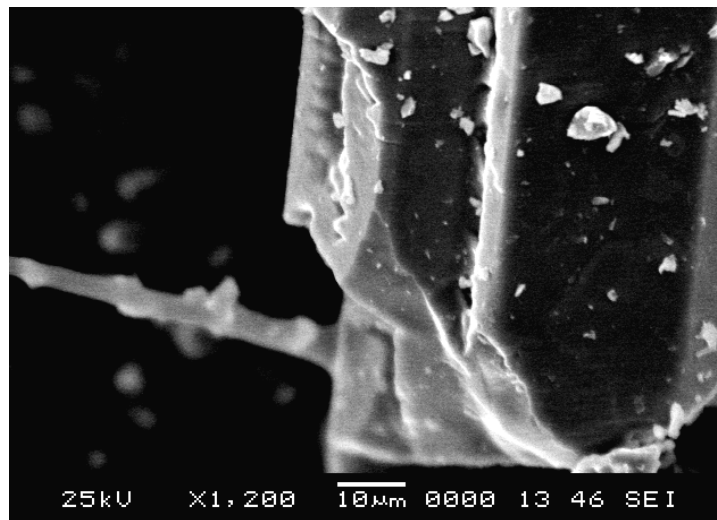

Figure 2. Formation of Fe_2O_3 (hematite) in the alloy quasicrystalline AlCuFe.

Vacuum oxidation is relatively mild, air oxidation is severe and oxidation from liquid immersion is the most severe.

Solubility of iron under different conditions at equilibrium can be conveniently calculated with stability diagrams such as Eh – pH diagram (STUMM & MORGAN, 1990) [8]. These diagrams utilize Nernst equations besides chemical and thermochemical relationships and standard free energies values from literature. Another way to analyze these interrelationships is calculating pε and pH parameters for a particular aqueous system.
In the same way that an acid is able to donate a proton and a base to accept a proton there are substances which have the capacity to donate electrons (reductors) and others to accept electrons (oxidants).

For iron in the ferrous state occurs an oxidation reaction and there is formation of ferric iron species. Similarly, ferric iron as oxidant suffers a reduction reaction producing ferrous iron species. Solid iron $Fe_{(s)}$ used to prepare metallic alloys for the formation of quasicrystals is the most reduced state while ferric ionic species is the most oxidized.

Briefly, the kinetic of oxygenation of iron (II) can be explained as follows: Iron (II) is oxidized by a rate of first order with respect to iron (II) and oxygen and of second order with respect to hydroxide ion (MILLERO et al., 1987) [9]:

$$\frac{\partial \left(Fe^{2+}\right)}{\partial t} = -k\left(Fe^{2+}\right).\left(OH^{-}\right)^{2}.ppO_{2} \tag{1}$$

where, k is a constant equals to $2.\,10^{13}$ $min^{-1}.atm^{-1}.mol^{-3}$ at 25ºC; ( ) indicates active concentration and pp refers to partial pressure. Oxidation of Fe^{2+} is followed by hydrolysis (process that can proceed with water, hydrogen ion and hydroxyl ion) and oxidation to insoluble forms (ferrous oxides and others). This process is, indeed, very fast and is important for several chemical relations. This paper shows the development of a thermochemical model for solid iron system which encompasses the formation of oxidant and reduced iron species besides the formation of hematite and magnetite species. The objective is to show the thermochemical behavior of iron not only at environmental conditions, but also when it is applied in metallic alloys to produce QC after immersion in water.

1. THEORETICAL CONSIDERATIONS

Chemical reactions spontaneously proceed towards an equilibrium state that is energetically most favorable.

The quantitative description of equilibrium conditions is the subject of the field of chemical thermodynamics. In general, the reaction can be written by the following equation ((LANDOLT, 2007) [10] :

$$\sum v_{ox,j}B_{ox,j} + ne = \sum v_{red,j}B_{red,i} \tag{2}$$

In this equation, B_{j} designates the different species that participate in the reaction and v_{i} their stoichiometric coefficient. The subscripts ox and red indicate whether a species j corresponds to the "oxidized" or to the "reduced" state; in other words, whether it stands to the left or to the right of the equality sign of the reduction reaction (2).

$$E_{rev} = E_{0} + \frac{RT}{nF}\ln\frac{\prod a_{OX,J}^{v_{ox,j}}}{\prod a_{red,J}^{v_{red,j}}} \tag{3}$$

Here E_{0} is the standard potential of the electrode reaction and the symbol $\prod$ indicates the multiplication product of the activities of participating species to the power v_{j}; R is the universal gas constant (8,31 $J.mol^{-1}$ K^{-1}), T is the absolute temperature (K) and F is the Faraday constant (96480 Coulomb mol^{-1}). pH is defined as the disponibility of hydrogen ions in solution. In practice, pH is defined according to the equation of Linderstrom – Lang: (In NASCIMENTO et al., 2009) [11].

$$pH = -\log\left(H^{+}\right) = -\log fH^{+}\left[H^{+}\right] = -\log\left[H^{+}\right] \tag{4}$$

The above expression is valid for unity activity coefficient of hydrogen ion.

The standard free energy for the formation of 1 mol of substance from pure elements is defined as the standard free energy of formulation. Its equation for a particular reaction is given by [12]:

$$\Delta G°_r \ = \ \sum \Delta G°f_{(products)} \ - \ \sum \Delta G°f_{(reactants)} \tag{5}$$

$\Delta G°f$ values for almost all chemical substances of interest are well defined in literature at 25°C temperature.

In turn, the relationship between the equilibrium constant k' of, for instance, a monoprotic weak acid/base and the standard free energy change of reaction is given by:

$$\Delta G°_r = - R.T. \ln k'a \ = -2, 303. R.T. \log k'a \tag{6}$$

For the values of R (gas constant) and absolute temperature at 25°C (T = 298,13K):

$$pk'a \ = \ - \log k'a \ = \ \frac{\Delta G°_r}{1,364} \tag{7}$$

$p\varepsilon$ is related to the standard free energy by the equation:

$$p\varepsilon = \frac{\Delta G°_r}{2,303.n.R.T} \tag{8}$$

$p\varepsilon$ is also related to the electrode potential E as follows (CAVALCANTI,1995) [12]:

$$p\varepsilon \ = \ \frac{F.E}{2,303.R.T} \tag{9}$$

$$E \ = \ \frac{E° \ + \ 2,303RT}{n.F \ .\log \left(\frac{[ox]}{[red]} \right)} \tag{10}$$

where, E° is the standard electrode potential; "red","ox" refer to reductant and oxidant, respectively. Values for standard potentials of redox process are listed in literature. In all thermochemical studies the standard free energy of formation of hydrogen ion from $\frac{1}{2}H_2O$ is $\Delta G°f$ of hydrogen elements equal to zero.

2. THESI MODEL DEVELOPMENT

2.1 – Initial Considerations

Thesi Model (**The**rmodynamic on **S**olid **I**ron) is based on equations for k', $\Delta G°_r$, pH and pε as given above. The model is applied to solid iron which forms the system $Fe_{(s)} = Fe^{3+} - Fe^{2+} - Fe_2O_3 - Fe_3O_4$; i.e., iron in ferric and ferrous state as well as hematite and magnetite. In the

present study it was considered for total solid iron a molar concentration of 10^{-6} mol/L which means a solution with 0, 06 mg/L of iron.

The main dissociation reactions of the system are as follows:

$$Fe_{(s)} \leftrightarrow Fe^{2+} + 2e^- \text{ (oxidation)} \tag{11}$$

$$Fe_{(s)} \leftrightarrow Fe^{3+} + 3e^- \text{ (reduction)} \tag{12}$$

$$2Fe_{(s)} + 3H_2O \leftrightarrow Fe_2O_3 + 6H^+ + 6e^- \tag{13}$$

$$3Fe_{(s)} + 4H_2O \leftrightarrow Fe_3O_4 + 8H^+ + 8e^- \tag{14}$$

2.2 – Analysis of the Iron Redox Systems

Each equation of the solid iron system is analyzed "per se" in order to determine values for the chemical equilibrium constant k' and for pε and pH parameters from Gibbs standard free energy of formation. For constructing a stability diagram such as pε x pH, the slope represented by $\dfrac{dp\varepsilon}{dpH}$ is obtained from each particular reaction of the system.

Table 1 shows the selected values of Gibbs standard free energy of formation for iron species at 25°C and one atmosphere of pressure.

Table 1. Values of Gibbs standard free energy of formation for iron species at 25°C and one atmosphere of pressure [10].

Chemical species	Standard free energy of formation in kg cal/mol
H_2O	- 56,69
FeO	- 59,38
Fe_2O_3	- 179,10
Fe_3O_4	- 242,30
Fe^{2+}	- 20,30
Fe^{3+}	-2,52

Briefly, the main analysis of the iron system is:

(1) $Fe_{(s)}$: Ferrous Iron System.
    Equilibrium Constant for unity activity and pε value is given by:

$$k' = \left(Fe^{2+}\right).\left(e^{-}\right)^{2}; p\varepsilon = -\frac{1}{2}\log k' + \frac{1}{2}\log\left(Fe^{2+}\right)$$

Gibbs free energy for reaction of equation (11):

$$\Delta G°_{r} = \Delta G°f\left(Fe^{2+}\right) = -20,3 \text{ kg .cal. mol}^{-1}$$

Hence:

log k´= -15. For $[Fe^{2+}] = 10^{-6}M$ and k' value, $p\varepsilon = -10, 5$.

The slope of the straight line for constructing a stability diagram is obtained from:

$\frac{dp\varepsilon}{dpH} = 0$; i.e. in the stability diagram this line is horizontal at $p\varepsilon = -10, 5$.

(2) $Fe_{(s)}$: Ferric Iron System.

Equilibrium Constant for unity activity is given by:

$$k' = \left(Fe^{3+}\right).\left(e^{-}\right)^{3}; p\varepsilon = -2,6$$

Gibbs free energy for reaction of equation (12):

$$\Delta G°_{r} = \Delta G°f\left(Fe^{3+}\right) = -2,5 \text{ kg cal mol}^{-1}$$

Hence, the equilibrium constant k' is given by:

log k´= 1,85

Slope given by: $\frac{dp\varepsilon}{dpH} = 0$; i.e., line representing ferric ion is horizontal at $p\varepsilon = -2, 6$.

(3) $Fe_{(s)}$: Fe_2O_3 System.

Equilibrium Constant for unity activity and pε value are given by:

$$k' = \frac{1}{\left(H^{+}\right)^{6}\left(e^{-}\right)^{6}} =; p\varepsilon = \frac{1}{6}\log k' - pH$$

Gibbs free energy for reaction of equation (13):

$$\Delta G°_{r} = 3\Delta G°f\left(H_2O\right) - \Delta G°f\left(Fe_2O_3\right) = 9,03 \text{ kg cal mol}^{-1}$$

log k´= - 6,6 and $p\varepsilon = -pH - 1,1$.

Slope given by: $\frac{dp\varepsilon}{dpH} = -1$. For pH = 0, then $p\varepsilon = -1,1$.

(4) $Fe_{(s)}$: Fe_3O_4 System.

Equilibrium Constant for unity activity and pε value given by:

$$k' = \frac{1}{\left(H^{+}\right)^{8}\left(e^{-}\right)^{8}}; p\varepsilon = -pH -1,43$$

Gibbs free energy for reaction of equation (14):

$$\Delta G°_{r} = 4\Delta G°f\left(H_2O\right) - \Delta G°f\left(Fe_3O_4\right) = -15,54 \text{ kg cal mol}^{-1}$$

Results obtained are:

log k′= - 11,4; Slope is given by: $\dfrac{dp\varepsilon}{dpH} = -1$. For pH = 0 then pε = -1,4.

(5) Fe^{3+}: Fe^{2+} System.

Initial equation for the system is given by:

$$Fe^{2+} \leftrightarrow Fe^{3+} + 1e^- \tag{15}$$

Equilibrium constant k' defined in terms of activity is given by:

$$k' = \dfrac{\left(Fe^{3+}\right)\left(e^-\right)}{\left(Fe^{2+}\right)}; \text{ i.e, } p\varepsilon = pk' + \log\dfrac{\left[Fe^{3+}\right]}{\left[Fe^{2+}\right]}$$

Gibbs free energy for reaction of equation (14):

$$\Delta G^\circ_r = \Delta G^\circ f\left(Fe^{3+}\right) - \Delta G^\circ f\left(Fe^{2+}\right) = 17,78 \text{ kg cal mol}^{-1}$$

Results for pε and slope of the straight line for stability diagram are given by:

pε = - log k' = 13 and slope : $\dfrac{dp\varepsilon}{dpH} = 0$

(6) Fe_2O_3: Fe_3O_4 System

Equilibrium reaction for this system is given by:

$$3Fe_2O_3 + 2H^+ + 2e^- \leftrightarrow 2\,Fe_3O_4 + H_2O \tag{16}$$

Equilibrium Constant for unity activity and pε value are given by:

$$k' = \dfrac{\left(Fe_3O_4\right)}{\left(Fe_2O_3\right)\left(H^+\right)^2\left(e^-\right)^2} = \dfrac{1}{\left(H^+\right)^2\left(e^-\right)^2} \quad \text{; i.e., activities of hematite and magnetite}$$

are equal to unity. Thus,

$$p\varepsilon = \dfrac{1}{2}\log k' - pH$$

Gibbs free energy for reaction of equation (16):

$$\Delta G^\circ_r = 2\Delta G^\circ f\left(Fe_3O_4\right) + \Delta G^\circ f\left(H_2O\right) - 3\,\Delta G^\circ f\left(Fe_2O_3\right) = -4,0 \text{ kg cal mol}^{-1}$$

Results given by:

pε = 1,45 – pH; slope : $\dfrac{dp\varepsilon}{dpH} = -1$. For pH = 0, then pε = 1,45.

(7) Fe^{2+}: Fe_2O_3 System.

Equilibrium reaction of the system is defined as follows:

$$2Fe^{2+} + 3H_2O \leftrightarrow Fe_2O_3 + 6H^+ + 2e^- \tag{17}$$

$$k' = \dfrac{\left(Fe_2O_3\right).\left(H^+\right)^6.\left(e^-\right)^2}{Fe^{2+}} \quad ;k' = \dfrac{1}{\left(H^+\right)^6.(e^-)^2} \quad \text{for activities of hematite and ferrous}$$

species equal to unity.
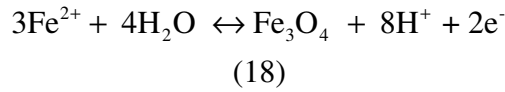
Gibbs free energy for reaction of equation (16):

$$\Delta G^\circ_r = \Delta G^\circ f\left(Fe_2O_3\right) - 2\,\Delta G^\circ f\left(Fe^{2+}\right) - 3\Delta G^\circ f\left(H_2O\right) = 32 \text{ kg cal mol}^{-1}$$

The results are given by:

log k´= - 23,5 e pε = - 3pH + 17,6 and slope : $\dfrac{d p\varepsilon}{dpH} = -3$. For pH = 0 then pε = 18.

(8) Fe^{2+}: Fe_3O_4 System.

Equilibrium reaction given by:

$$3Fe^{2+} + 4H_2O \leftrightarrow Fe_3O_4 + 8H^+ + 2e^-$$

$$(18)$$

k' = $1/(H^+)^{8}(e^-)^2/(Fe^{2+})^3$

Gibbs free energy for reaction of equation (14):

$$\Delta G^\circ_r = \Delta G^\circ f\left(Fe_3O_4\right) - 3\,\Delta G^\circ f\left(Fe^{2+}\right) - 4\,\Delta G^\circ f\left(H_2O\right) = 45,4 \text{ kg cal mol}^{-1}$$
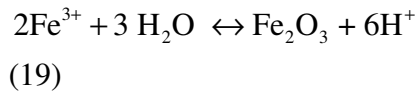
Results for k' and pε :

log k' = - 33,25 ; pε = - 4pH + 25,6.

Slope is given by: $\dfrac{d p\varepsilon}{dpH} = -4$. For pH = 0 then pε = 25,6

(9) Fe^{3+}: Fe_2O_3 System:

This system is not a redox reaction but a weak acid reaction, the chemical equation is defined as follows:

$2Fe^{3+} + 3\,H_2O \leftrightarrow Fe_2O_3 + 6H^+$

(19)

Equilibrium constant for unity activity is given by:

$$k' = \frac{\left(H^+\right)^6}{\left(Fe^{3+}\right)^2}$$

Gibbs free energy for reaction of equation (19):

$$\Delta G^\circ_r = \Delta G^\circ f\left(Fe_2O_3\right) - 2\,\Delta G^\circ f\left(Fe^{3+}\right) - 3\,\Delta G^\circ f\left(H_2O\right) = 4 \text{ kg cal mol}^{-1}$$

Results for k' and pH:

log k´= 2,9 and pH equation is now given by:

$$pH = 2 - \frac{1}{6}\log k';\ pH = 1,5 \text{ indicating a very weak acid solution.}$$

In stage (5) of the model it was necessary to verify if $Fe_{(s)}$ is limited by ferrous species or by ferric species and also by Fe_2O_3 and Fe_3O_4.

Table 2 shows all data determined for pk', pε, pH and slope for all the stages of the model here developed.

Table 2. Results obtained from the study on the $Fe_{(s)} = Fe^{2+} - Fe^{3+} - Fe_2O_3 - Fe_3O_4$
system with data of Gibbs free energy from literature at temperature of 25°C.

System	Conditions	pk'	pε	pH	Slope
$Fe_{(s)}: Fe^{2+}$	$[Fe^{2+}] = 10^{-6}$ mol. L^{-1}	15	-10,5	-	0
$Fe_{(s)}: Fe^{3+}$	$[Fe^{3+}] = 10^{-6}$ mol. L^{-1}	- 1,9	-2,6	-	0
$Fe_{(s)}: Fe_2O_3$	$[Fe_2O_3] = 10^{-6}$ mol. L^{-1}	6,6	-1,1	0	-1
$Fe_{(s)}: Fe_3O_4$	$[Fe_3O_4] = 10^{-6}$ mol. L^{-1}	11,4	-1,4	0	-1
$Fe^{3+}: Fe^{2+}$	$[Fe^{3+}] = [Fe^{2+}]$	13	13	-	0
$Fe_2O_3: Fe_3O_4$	$[Fe_2O_3] = [Fe_3O_4] = 1$	-2,9	1,5	0	-1
$Fe^{2+}: Fe_2O_3$	$[Fe^{2+}] = [Fe_2O_3] = 1$	23,2	17,6	0	-3
$Fe^{2+}: Fe_3O_4$	$[Fe^{2+}] = [Fe_3O_4] = 1$	33,3	25,6	0	-4
$Fe^{3+}: Fe_2O_3$	$[Fe^{3+}] = 10^{-6}$ mol. L^{-1}	-2,9	-*	1,5	-

(*) Weak acid reaction.

3. DISCUSSION AND CONCLUSIONS

This model shows the solubility of solid iron under a particular condition at equilibrium
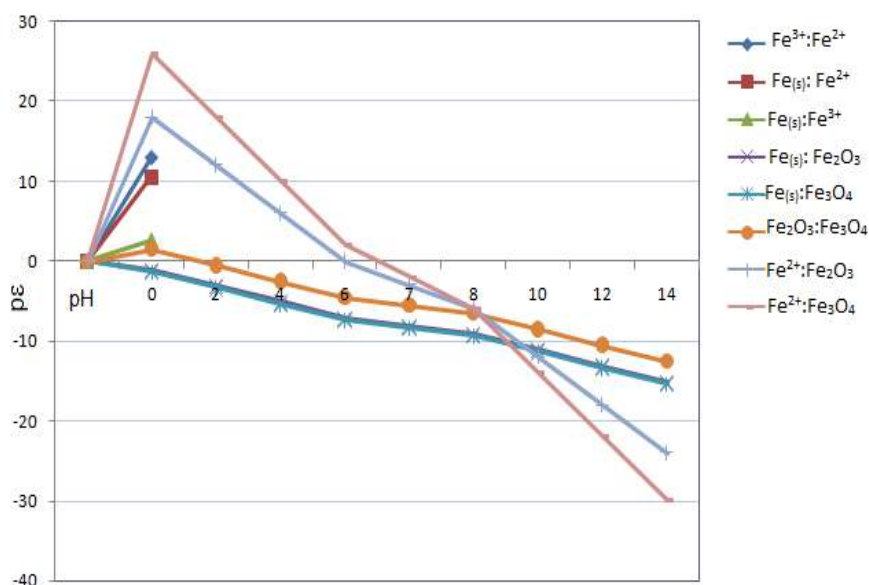Results are shown graphically by means of pε versus pH stability diagram in Figure 3.

Figure 3. Stability diagram for solid iron in aqueous solution.

This diagram was prepared by using the Nernst equation and some thermodynamically relationships and data. For natural waters, it was not considered the influence of dissolved carbon dioxide, CO_2, and species which are generally involved in precipitation of some solid forms of iron. In this figure it can be seen a strong dependence of the oxidation rate on pH. The hydrolyzed Fe^{2+} and reacts more rapidly with O_2 than nonhydrolized Fe^{2+}. In the stability diagram, it seems that hydrolyzed Fe^{3+} species are not dominant, only in saline environment. Regarding the calculations, in stage (6) it can be seen that for $\frac{dp\varepsilon}{dpH} = 0$, Fe^{3+}-$Fe_{(s)}$ line falls away in the diagram. In stages (7) to (8) it was studied the lines surrounding Fe^{2+} others than Fe^{3+} and $Fe_{(s)}$. In stage (10) it can be seen that the reaction is not a redox reaction but a weak acid reaction. Thus, in the stability diagram it will get a straight line separating Fe^{3+} and Fe_2O_3. An intermediate region of high solubility exists between the domains of pyrite and $Fe(OH)_2$. This can be verified by means of Eh – pH diagrams in which Eh refers to the activity of electrons.

Concerning solubility of iron species, the well – crystallized form as hematite and FeOOH are less soluble. Reoxidation of Fe^{2+} produces a solid ferric hydroxide as a colloid or on a surface.

The following conclusions can be made:

❖ The interrelationship between chemical and redox equations represented by pk', pH and pε reflect the net effect of chemical and thermodynamic processes in oxidation analysis of solid iron.

❖ It was observed a strong pH influence in all equations developed in the study especially in the oxi – reduction equation of solid iron $Fe_{(s)}$ and ferrous ion, Fe^{2+}. In the system defined by ferrous iron and hematite, pH appears to be on the acid side. For pH values above 8,0 iron precipitation is very fast. The dominance of ferrous iron is stronger than that of ferric iron.

❖ The influence of temperature was not analyzed. However it is very important for all stages of the model. Some researches have showed that during formation of AlCuFe metallic alloys at high temperatures and further immersion in water only iron is oxidized. The cooling process and leaching into acid solutions can create a severe oxidation state.

❖ Due to the strong pH dependence, it is necessary to measure pH and temperature increase and verify iron species formation after liquid immersion in both environmental condition and QC phases formation.

NOTATION

( ), [ ] or C = active and molar concentration (mol. L^{-1}), respectively.

CT = total concentration of species for iron system in solution, mol. L^{-1}.

$e^{-} = \varepsilon$ = electron.

E = electrode potential.

F = Faraday constant.

fH^{+} = activity coefficient for the hydrogen ion, H^{+} in the molar scale.

$\Delta G°_r$ = total free standard energy or Gibbs free energy of reaction, kg cal mol^{-1}.

$\Delta G°f$ = free energy of formation, kg cal.mol^{-1}.

k' = dissociation Constant for a monoprotic weak acid/base.

R = universal gas constant= 1, 987 cal mol^{-1}kg.

T = absolute temperature = T($°C$) + 273,15 (K).

ACKNOLEDGEMENTS

REFERENCES

[1]. SCHECHTMAN, D.; BLECH, I.; GRATIAS, D.; CAHN, J. V. "Metallic phase with long-range orientational order and no translational symmetry", Phys. Rev. Lett. 53, 1951-1953,1984.

[2]. LIFSHITZ, RON. "Quasicrystals: a matter of definition. Foudations of Physics", Vol..33, n.12, p.1703-1711, 2003.

[3].BARUA, P., "Nanostructured icosahedral phase formation in $Al_{70}Cu_{20}Fe_{10}$: Comprehensive study". Journal of Applied Physics, vol.91, p. 5353 – 5359, 2002.

[4].HUTTUNEN-SAARIVIRTA,E. "Microstructure, fabrication and properties of quasicrystalline AlCuFe alloys". Journal of Alloys and Compounds, v.363, p. 150-174, 2004.

[5].PINHEIRO, P. J. et al. "Surface oxidation of AlCuFe alloys: a comparison of quasicrystalline and crystalline phases". Philosophical Magazine B, 79 (1); 91 – 110, 1999.

[6].NASCIMENTO, L; AGOSTINHO, C.L.L., CAVALCANTI, F.B., "Comportamento da Oxida ão na Fase Icosaedral do Quiasicristal $Al_{62,2}Cu_{25,3}Fe_{12,5}$", Acta Microscopica, 18 (3); 294 – 296, 2009.

[7].ROUXEL, D., PIGEAT, P. "Surface oxidation and thin film preparation of AlCuFe quasicrystals". Progress in Surface Science: Review. 81; 488–514, 2006.

[8].STUMM, W.; MORGAN, J.J. "Aquatic chemistry: an introduction emphasizing chemical equilibrium in natural watery". New York: Wiley-Interscience, 1990.

[9].MILLERO, F. J., "Thermodynamic models from the nstate of metal ions in seawater". The Sea, E.D. Goldberg et al., Eds, Vol.6, Wiley – Interscience, N.Y., p. 653 – 692, 1987.

[10].LANDOLT, D., "Electrochemical and materials aspects of tribocorrosion systems", J. Physics D: Appl. Phys. Vol.39, p.1-7, 2006.

[11].NASCIMENTO, L; AGOSTINHO, C.L.L., CAVALCANTI, F.B., "Modelagem Termoquímica Da Desinfecção Por Cloro Gasoso. Tecno-Lógica", Santa Cruz do Sul, v. 13, n. 2, p. 86-92, jul./dez. 2009.

[12].CAVALCANTI, B.F.; A "Thermodynamical Model for Predicting Nitrification and Denitrification in Activated Sludge". Achieving High Performance at Low Cost in Environmental and Sanitation Control Systems, International Symposium on Technology Transfer, Salvador, Ba, p.1 – 11, 1995.