THERMODYNAMIC ANALYSIS OF IRON SCALE DISSOLUTION IN H_2SO_4 AIMING AT THE PRODUCTION OF IRON (II) SULFATE[1]

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Abstract

Ferrous sulfate heptahydrate, $FeSO_4{\cdot}7(H_2O)$, or *melanterite*, is used as a coagulant in municipal waste-water treatment plants, as a fertilizer additive, animal feed additive, pigment production, and as a raw material for iron oxide based magnetic materials. Aim of this study is to analyze through a computational thermodynamic tool the hydrometallurgical route for the production of ferrous sulfate heptahydrate from mill scale. The use of this raw material in the production of iron (II) sulfate contributes to waste reduction and more efficient use of natural resources. The study involves the use of sulfuric acid to dissolve the mill scale under two conditions: constant oxygen potential and constant sulfuric acid molality in the aqueous solution.

Keywords: Iron (II) sulfate hepta-hidratado; Mill scale; Thermodynamic analysis

ANÁLISE TERMODINÂMICA DA DISSOLUÇÃO DE CAREPA DE FERRO EM H_2SO_4 VISANDO A PRODUÇÃO DE SULFATO FERROSO

RESUMO

Sulfato ferroso hepta-hidratado, $FeSO_4{\cdot}7(H_2O)$, ou *melanterita*, é usado como coagulante em estações municipais de tratamento de águas, como um aditivo de fertilizante, aditivo para alimentação animal, produção de pigmentos e como matéria-prima de materiais magnéticos a base de óxido de ferro. Objetivo deste estudo é analisar através de uma ferramenta termodinâmica computacional uma rota hidrometalúrgica para a produção de sulfato ferroso hepta-hidratado a partir de carepa. O uso desta matéria-prima na produção de sulfato de ferro (II) contribui para a redução de resíduos e o uso mais eficiente dos recursos naturais. O estudo envolve o uso de ácido sulfúrico para dissolver a carepa sob duas condições: potencial de oxigênio constante e molalidade do ácido sulfúrico (inicial) fixa na solução aquosa.

Palavras-chave: Sulfato ferroso hepta-hidratado (II); Carepa; Análise termodinâmica.

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1 INTRODUCTION

Mill scale is the product from the steel oxidation in contact with air when it is handled at elevated temperatures. In steel mills, scale is produced during the operations of continuous casting and rolling, reaching a rate between 10 and 20 kg / ton of steel produced.(1) In integrated mills it is recycled in the process during sintering of iron ore, however, as this possibility does not exist in mini-mills, other disposition must be sought.

Recently, research has shown that, for the non-integrated mills, a possibility exists for recycling the iron content of scale in the EAF, in the form of self reducing briquettes.(2)

Another alternative, which will be addressed in the present study, is the utilization of mill scale as feedstock in the production of crystals of iron (II) sulfate. The use of this raw material in the production of this substance contributes to waste reduction and to a more efficient use of non-renewable natural resources.

Ferrous sulfate heptahydrate, $FeSO_4 \cdot 7(H_2O)$, or *melanterite*, can be obtained commercially from several sources, *e.g.*, the dissolution of iron with sulfuric acid, as a by-product generated through the production of titanium oxide, or, from the waste sulfuric acid used for pickling of steel sheet.(3,4)

This chemical product is used as a coagulant in municipal waste-water treatment plants, as a fertilizer additive, animal feed additive, pigment production, and as a raw material for iron oxide-based magnetic materials.(5)

In order to study this subject matter and prepare future laboratory experiments, several simulations (based on computational thermodynamics) of the production of iron (II) sulfate from steel mill scale were performed in this work.

2 METHODOLOGY

2.1 Theoretical Analysis

Among the several variables that could serve as basis for this theoretical study, two were chosen for the determination of the equilibrium states: (i) oxygen potential (*open* system) and (ii) initially fixed molality of sulfuric acid in aqueous solution. While the first variable is *part* of the state of equilibrium – in fact, it is a state function – the second is just an *initial* condition (or *input*) and will change freely until the equilibrium state is reached. Together they express two interesting *real* situations: (i) use of an acidic solution with a known initial concentration of sulfuric acid and (ii) effect and influence of the ubiquitous oxygen on the aqueous systems.

The latter topic will be discussed briefly here. Any amount of *dissolved* oxygen in water can be related to an oxygen partial pressure in the gas phase according to:

$$O_2(g) = O_2(aq.) \qquad (1)$$

The oxygen partial pressure of the superficial water layer in contact with the gas phase is, naturally, equal to 0.21 [atm]. The abundance of oxygen in the atmosphere is of paramount significance, however, at the bottom of lakes or places where oxygen is consumed by chemical or biochemical reactions and no satisfactory renewal takes place, its ‘partial pressure’ can be very low.

Another factor which is important for systems containing the aqueous phase is the activity of hydronium or oxonium ion (H_3O^+, H^+) – according to the nomenclature suggested by IUPAC.(6) Here, closely related to the initial amount of sulfuric acid in solution.

One can relate these two factors through the stoichiometric reaction:

$$4\ H^+ + O_2(aq.) + 4\ e^- = 2\ H_2O \qquad (2)$$

The application of the *Nernst* equation in this reaction provides the following equation, which serves to determine the electrochemical potential of the aqueous system from the known pH and pO_2 values:(7)

$$E_h\ [V] = 1.229 + 0.015 \cdot \log(pO_2) - 0.0591 \cdot pH$$

Together, E_h and pH values define a *point* in the 'Pourbaix diagram' – which maps out possible stable (equilibrium) phases of an aqueous electrochemical system.

For the sake of completeness, it must be informed that in this analysis, the electrochemical potential ranged from $\log(pO_2) = -25$ to -50 (with pressure given in atmospheres). On the other hand, the input of sulfuric acid concentration or molality $m\ H_2SO_4$ = varied from 0.1 up to 5.

2.2 Software and Database

The equilibrium state for every simulation of the present work was determined by the Gibbs energy minimization method using the *Equilib* module of the FactSage software (version 6.2) – the software is described elsewhere by Bale et al.(8)

The following database was employed: FACT53 – Fact 5.3 compound database [2009]; data for aqueous and gaseous phases are included in this data file.

For the sake of simplicity, the analysis was restricted to the temperature of 25ºC but O_2 partial pressure varied greatly.

3 RESULTS AND DISCUSSION

For the two conditions surveyed – as stated in the methodology, two main parameters (that characterize the state of thermodynamic equilibrium in the aqueous phase) were determined: pH and electrochemical potential. When displaying these electrochemical potentials as a function of pH values in a diagram (Figure 1) is obtained. Note that the two conditions naturally intersect at the common point: (initial) $m\ H_2SO_4 = 3$ and $\log(pO_2) = -45$.

In the same diagram, for reference, a line was drawn indicating where the concentration of ferrous ion in aqueous solution is equal to 1 mol/kg H_2O (Fe^{2+} molality = 1).

Consequently, it is easy to see that both the effect of lowering the potential of oxygen as well as the effect of increasing the molality of sulfuric acid is: to increase the concentration of ferrous ion in solution. With respect to pH, however, those same actions produce the opposite results.

For the two conditions studied (considering only the solid phases of iron oxides are free to participate in the equilibrium state) the single stable solid phase is hematite, Fe_2O_3.

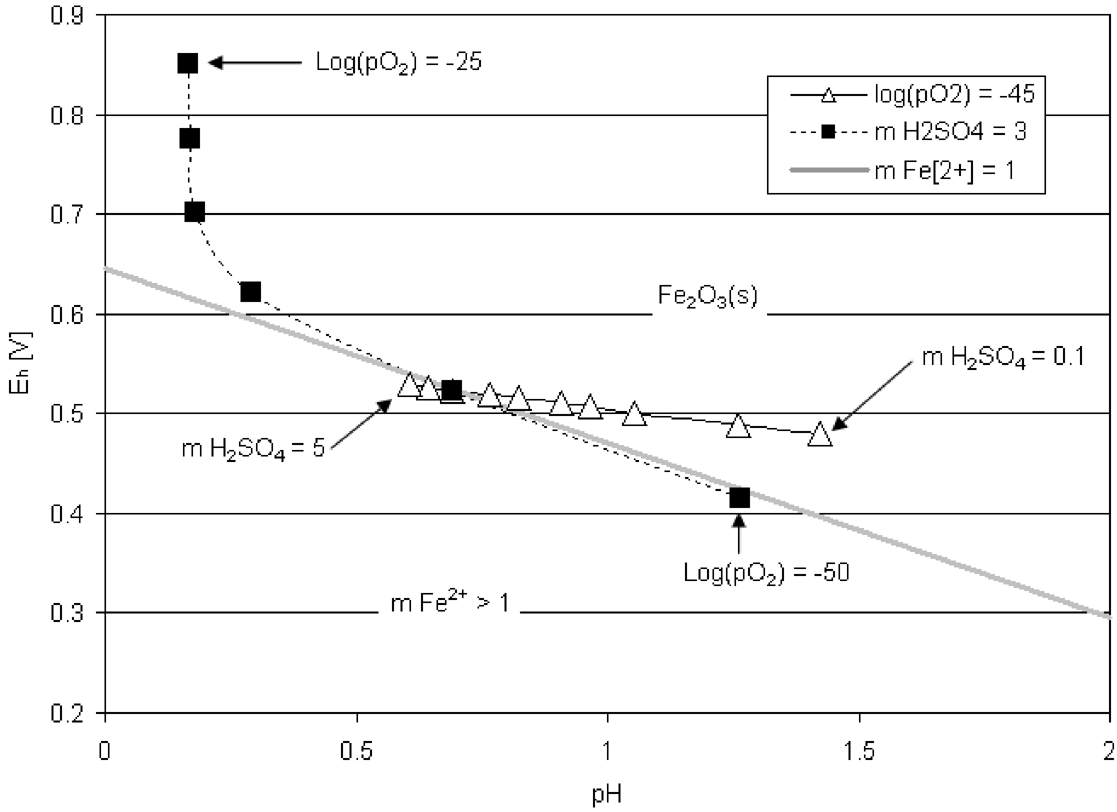

Figure 1. Diagram displaying E_h and pH result values from all simulations (black squares: fixed (initial) H_2SO_4 molatity m = 3; white triangles: constant oxygen potential).

3.1 Constant Oxygen Potential

Results of simulations under the condition of constant oxygen pressure of $1x10^{-45}$ atm (open system) show that the activity of all ions in aqueous solution increases, the extent of increasing the molality of sulfuric acid (Figure 2).

It is easy to see from this Figure, the most abundant ions throughout the range are: HSO_4^- and Fe^{2+}. However, it is also interesting to note the increasing value of the monovalent cation $FeSO_4^+$ activity, to the extent that more sulfuric acid is added to water. On the other hand, also the scarcity of Fe^{3+} ion all the way through the scale is noticeable.

The determination of the logarithm of the equilibrium constant for this reaction:

$$Fe^{3+}(aq) + SO_4^{2-}(aq) = FeSO_4^+(aq) \qquad (3)$$

made through the activities found all over the entire range of sulfuric acid molalities has resulted in the value 4.19 – which correlates well with the value 4.05 listed in MINTEQA2 database.(9) Thus, one can say that an increase in the concentration of $FeSO_4^+$ cation also means, ultimately, an increase in the concentration of *ferric* ion in aqueous solution.

Based on this logic, a determination was made of the *overall* mass ratio Fe^{2+} / Fe^{3+} by computing the amount of iron associated with each of the ions carrying this element in solution (considering the iron valence). As expected from the information already presented, there was a marked decrease in the value of the ratio, the extent of increasing the molality of sulfuric acid (Figure 3).

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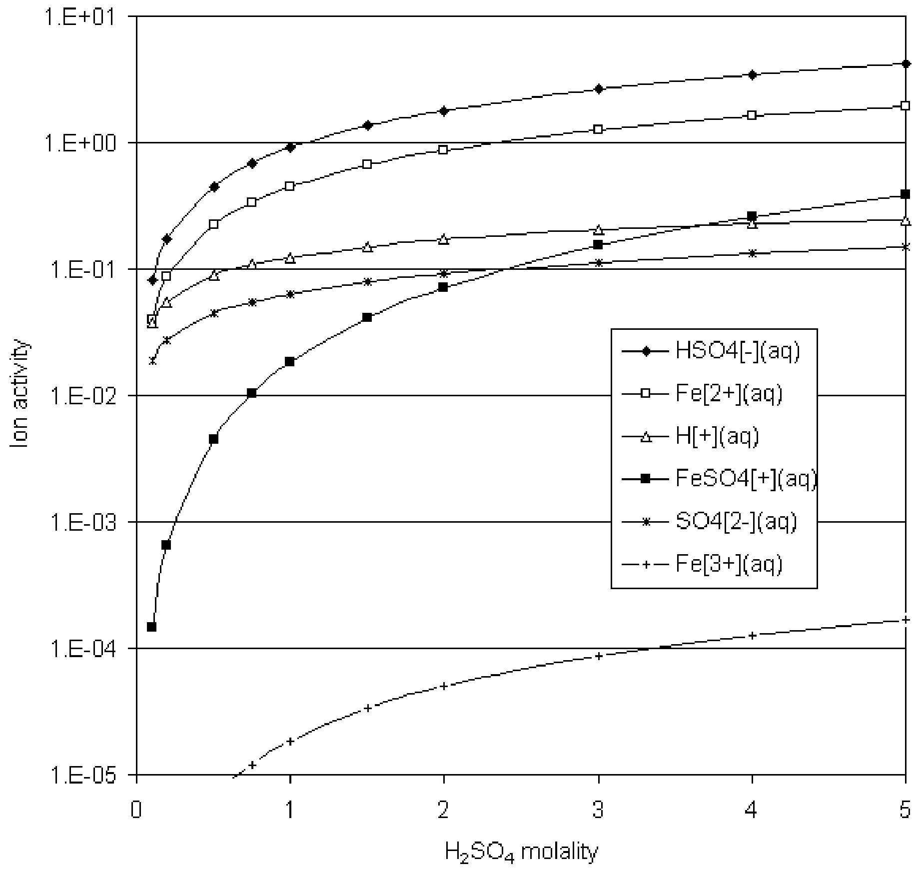

Figure 2. Aqueous ion activities as a function of H_2SO_4 fixed (initial) molality.

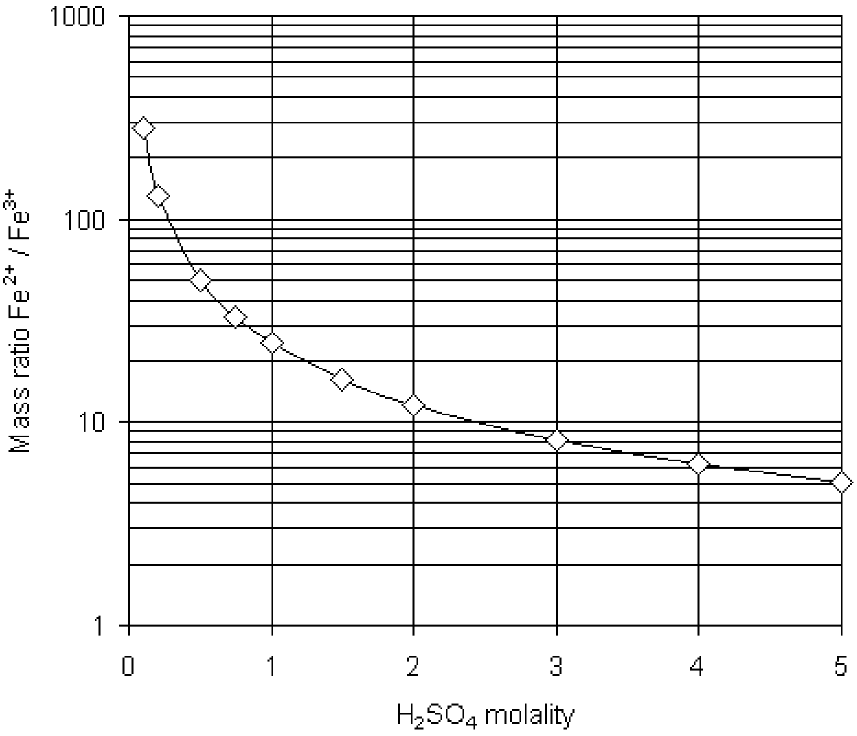

Figure 3. Fe^{2+} / Fe^{3+} mass ratio as a function of H_2SO_4 fixed (initial) molality.

On the other side, the ratio between the activities of *plain* ferrous and ferric ions, Fe^{2+} / Fe^{3+}, can be related to the stoichiometric reaction:

$$Fe^{3+}(aq) + e^{-} = Fe^{2+}(aq) \quad . \qquad (3)$$

This reaction is strongly associated with consumption of electrons in the system and can replace the reaction (1) in this function, especially when there is a shortage of oxygen in the aqueous phase.(10)

The electrochemical potential can be determined by applying the Nernst equation:

$$E_h[V] = 0.771 - \frac{RT}{F} \cdot \ln\left(\frac{Fe^{2+}}{Fe^{3+}}\right) \, .$$

The electrochemical potential values computed using this equation coincide – as one would expect – with the values plotted in Figure 1.

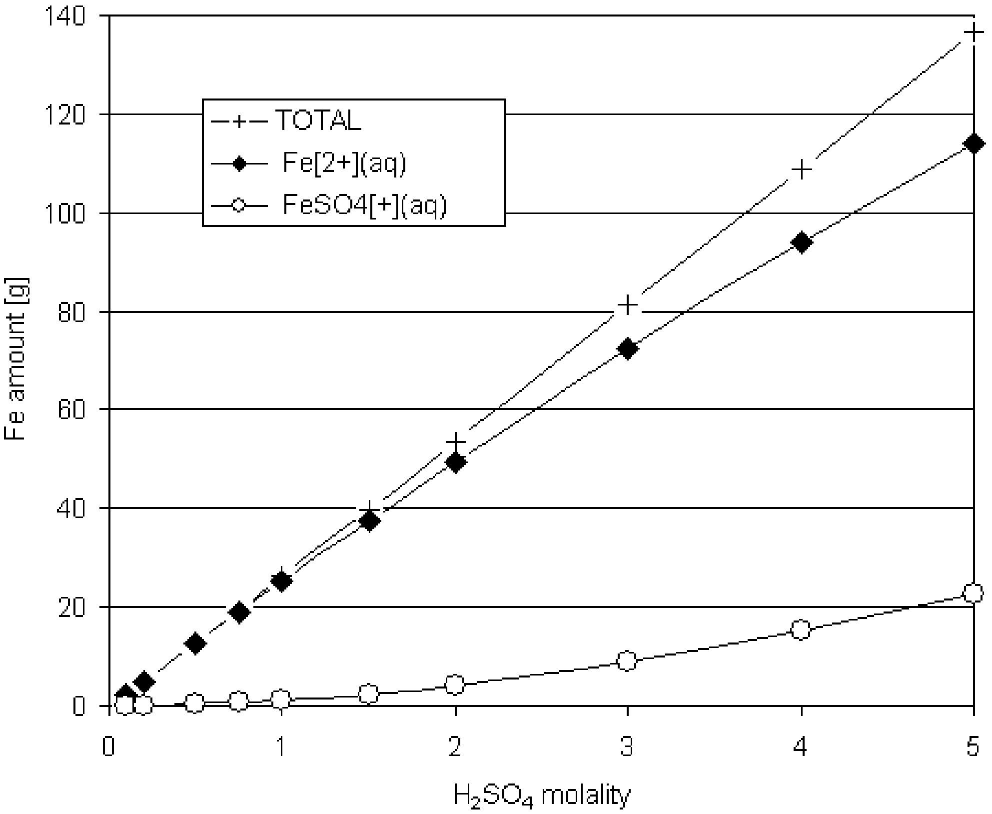

Figure 4. Iron amount in solution as a function of H_2SO_4 fixed (initial) molality.

The *total* amount of iron dissolved in the aqueous solution of sulfuric acid (Figure 4), is strongly related to the particular amounts associated with each of the two more abundant (iron-bearing) cations earlier mentioned – as could be predicted from the examination of ion activities.

Also clearly noticeable (within this anoxic condition), is the fact that strongly acidic solutions are needed for a high dissolved amount of mill scale.

To complete the study, melanterite precipitation was simulated. The amount of ferrous sulfate precipitated in each of the equilibrium states of this constant oxygen potential condition is such that it consumes almost all the mass of iron dissolved in the solution – even considering the increasing fraction of ferric iron in the system to more acidic solutions. In practice, however, there may be obstacles – of kinetic nature – that hinder the achievement of the predicted values in the simulation.

3.2 Fixed Initial H_2SO_4 Molality

Simulation results, now under the condition of constant molality, m H_2SO_4 = 3 show that – except for the ferrous and ferric ions – the activity of ions tends to a constant value to the extent that the chemical potential of oxygen in the system grows (Figure 5). The behavior of the ferric and $FeSO_4^+$ ion activities inside the solution is completely different: while one increases the other decreases. The activity of the ferrous ion is – as expected – favored in anoxic conditions.

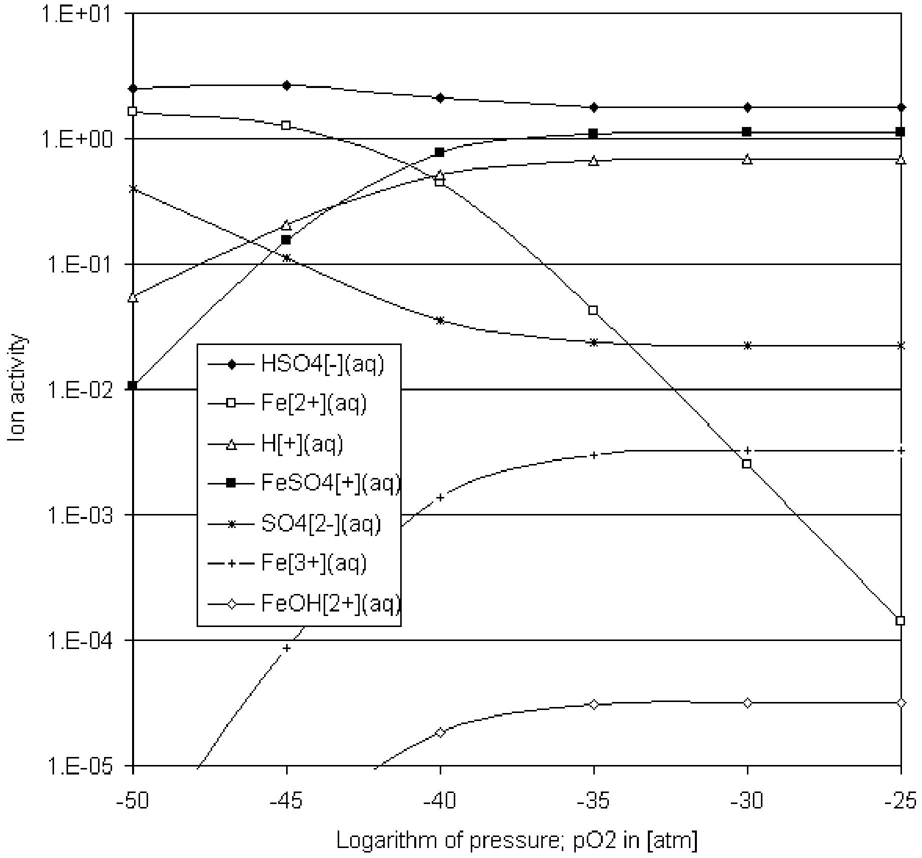

Figure 5. Aqueous ion activities as a function of the oxygen potential in the system

In spite of the fact that the amount of iron associated with each of the ions Fe^{2+} and $FeSO_4^+$ follows the pattern of their activities, the *total* amount of dissolved iron in solution is always high – though it decreases slightly with increasing oxygen potential (Figures 6 and 7).

For reference, a line was drawn in the diagram indicating where the amount of iron in aqueous solution is equal to 1 mol (Figure 6 (doted line).

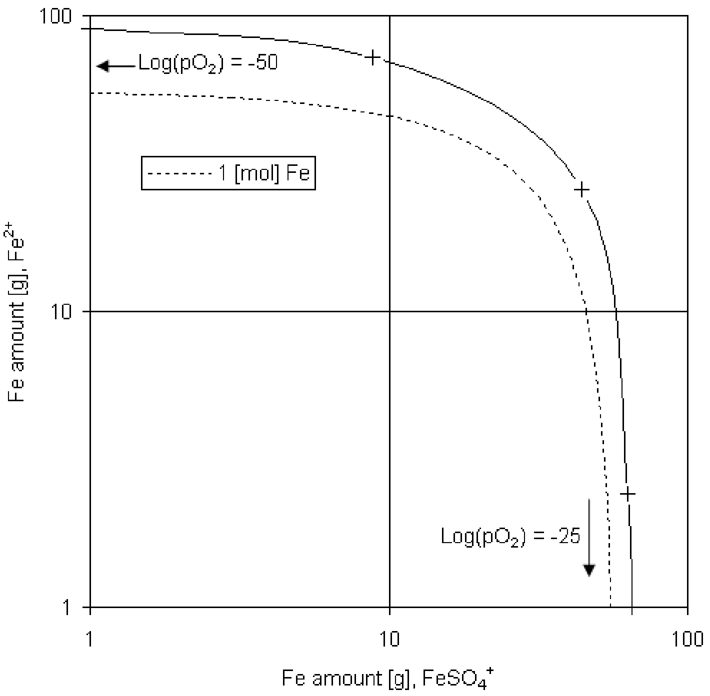

Figure 6. Fe^{2+} and Fe^{3+} relationship as a function of the oxygen potential.

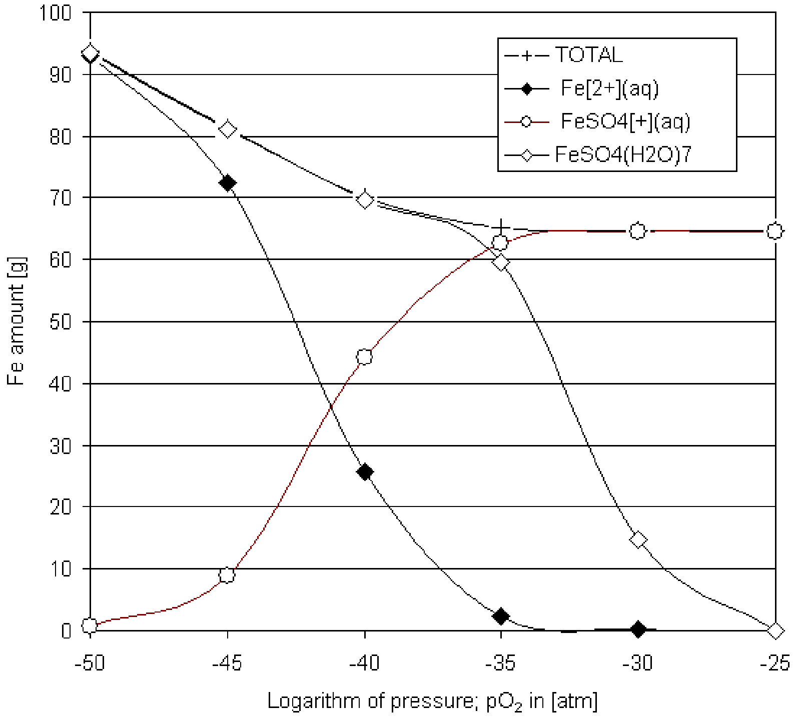

Figure 7. Iron amount in solution as a function of the oxygen potential and iron amount precipitated in iron (ii) sulfate (melanterite), $FeSO_4{\cdot}7(H_2O)$.

In Figure 7 one can also deduce – from the amount of iron – the maximum amount of melanterite that can be precipitated from the solution – not considering here any kind of resistance of kinetic nature.

For the lower oxygen potential it corresponds exactly to the content of ferrous iron in solution. To the extent that the oxygen potential increases, it follows precipitating faithfully all the iron in the acid solution – even though the fraction of ferrous ion decays rapidly. In the end, when the ferric ion becomes absolute in the solution, the maximum possible amount to be precipitated decreases and ultimately vanishes.

4 CONCLUSIONS

From the simulation results can be concluded that, based on thermodynamics, the pH value (within the range of simulation) is not the central factor. Three points with pH ~0.17 and two with pH ~1.26 – but with different oxygen potential – *confirm* that, in both cases, Fe dissolves more intensely under *anoxic* conditions.

In practice, anoxic conditions can be obtained, for example, by adding *iron scrap* together with the mill scale; this, however, can raise the solution pH.

Regarding the oxygen potential, the amount of ferrous sulfate precipitated is strongly associated with the sector of high Fe^{2+} concentration – as would be expected – though, it goes beyond this region, still continuing, for a time, in the transition segment, where the ferric ion concentration gradually exceeds that of ferrous ions.

REFERENCES

1 TAKANO, C.; DEODORO, J.T.C.; NASCIMENTO, R.C.; MOURÃO, M.B.; LENZ, G.; MARTINS, D.S. A reciclagem de resíduos siderúrgicos sólidos. In *Proc.*: Seminário Nacional sobre Reuso/reciclagem de Resíduos Sólidos Industriais, 2000, São Paulo. São Paulo: Departamento de Engenharia Metalúrgica e de Materiais, Escola Politécnica da USP, 2000

2 BUZIN, P. J. W. K. Desenvolvimento de briquetes autorredutores a partir de carepas de processamento siderúrgico para a utilização em forno elétrico a arco. *Dissertação de mestrado*, PPGEM, Universidade Federal do Rio Grande do Sul, Porto Alegre, 136 p., 2009

3 PETERSON, M. Produção de Sulfato Ferroso a Partir da Pirita: Desenvolvimento Sustentável. *Tese de Doutorado*, Universidade Federal de Santa Catarina, Florianópolis, 127 p., 2008

4 ANONYMOUS. *Recovery of spent sulfuric acid from steel pickling operations*.US EPA, EPA-625/2-78-01

5 METCALF & EDDY, INC. *Wastewater engineering: treatment and reuse*. Boston, McGraw-Hill, 1819 p., 2003

6 ANONYMOUS.http://goldbook.iupac.org/O04378.htm

7 JACKSON, E. *Hydrometallurgical extraction and reclamation*. Ellis Horwood, Chichester. 266 p., 1986

8 BALE, C. W. *et al.* FactSage Termochemical Software and Databases. *Calphad*, Vol. 26, No. 2, 2002, p. 189-228

9 Allison, J.D.; et al. ‘MINTEQA2/PRODEFA2, A Geochemical Assessment Model for Environmental Systems: User Manual Supplement for Version 4.0, 1999

10 HAYES, P.C. *Process selection in extractive metallurgy*. Hayes Publishing, Brisbane, 1985