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EVALUATION OF PH IN REDUCING THE CONTENT OF IRON IN THE LEACHING OF PHOSPHORUS IN IRON[1]

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Abstract

The phosphorus element is found in sensitive contents on steels, as a result of contamination of raw material, in which is usually an undesirable impurity. It is harmful to the quality of steel especially because it reinforces the tendency to the segregation, increasing the hardness of the ferrite phase and the tendency to fragility of the steels. The leaching process is the most promising process for the reaction of iron ore dephosphorization given the formation of phosphoric acid after the leaching process the present study aims to study the effect of pH variation in the reduction of phosphorus content in iron ore. Through the process of X-ray diffraction using the Rietveld method it was demonstrated that the sample is formed by 72.89% Hematite; kaolinite 4.64%; Quartz 12.5; Gibbsite 3.18% and Goethite 7.25%. Diagrams of speciation shows the salt formation $FePO_4.2H_2O$ and its precipitation in the pH around 5. It is also demonstrated that at concentrations from 0.1 M there is loss of phosphorus content in the sample of iron ore and Pourbaix diagram shows the way of the element Fe passivated as Fe_2O_3 and Fe_3O_4 value of from pH 3.

Key words: Reduction of phosphorus; Iron ore; Phosphoric acid.

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1 INTRODUCTION

Iron is one of the most abundant elements in Earth's crust is well distributed geographically because it is found in all geological epochs[1]. However depending on the location where you extracted the ore it can produce various types of contaminants. One of the elements is phosphorus, the presence of high levels of phosphorus in the steel becomes brittle and fractures, which influences the market price of iron ore. However, the form found to reduce the content of phosphorus element on the iron ore batch leaching with high speed. Was observed the use of sulfuric acid as the leaching agent the most promising way to reduce the phosphorus element in iron ore because its offers offering better yield properties to the dephosphorization. The acid concentration which provides a higher yield of phosphorus removal in iron ore was found to be 0.2 M. According to Gooden, Walker and Allen[2] has been reported that the concentration of sulfuric acid for removal of phosphorus ore was 0.2 M, but according to Cheng, Misra and Clough[3] an economic point of view, 0.1 M sulfuric acid solution is the best choice to obtain a reasonable phosphorus extraction with a minimum cost of acid intake.

However during the process of acid lixiviation addition to the extraction of the element phosphorus in the iron ore is also loss of the element iron to the acidic solution thereby decreasing the contents thereof in the ore and causing formation of salts those will interfere in the diffusion of H^+ ions to the inside of the particles of iron ore. One way of controlling the loss of iron in the leaching solution and thereby avoid the formation of iron salts is the use of pH-EH diagram which shows diagrammatically the variation of the pH of in solution and changes in electrochemical potentials which the same must forward the a metal ion condition or an inactive state in aqueous solution. Considering the goal of non-transfer of iron ions to the aqueous solution during the leaching of phosphorus element should be evaluated the EH-pH diagram with the objective to find the pH value where there is immunity of the element iron during the leaching process.

2 MATERIALS AND METHODS

The samples of iron ore are from the region of the Iron Quadrangle in Minas Gerais, Brazil. All samples were comminuted and then classified in granulometric sizes of 28, 35, 48, 150 and 200 micrometers, as shown in Table 1.

Table 1. The particle size distribution of samples of iron ore.

Mesh	Free Opening (cm)	Wire diameter (in)	Mass (g)
28	0,0589	0,0125	815,86
35	0,0417	0,0122	404,58
48	0,0295	0,0092	788,59
150	0,0104	0,0026	1651,62
200	0,0074	0,0021	1336,87

The chemical analysis performed by the method of optical emission spectrometry performed inductively coupled plasma in CETEM (MCTI) indicated that the phosphorus content of the ore sample was 0.0453%. The standard of X-ray diffraction of the sample ore is shown in Picture 1, indicating that the ore is mainly composed by kaolinite 4.64%, gibbsite 3.18%, goethite 7.25%, hematite 72.89% and Quartz12.05% as shown in Table 2. The phosphorus occurs in the structure of the goethite forming a stable complex. In the Figure 1 is demonstrated the spectrum by x-ray diffraction of the sample of iron ore.

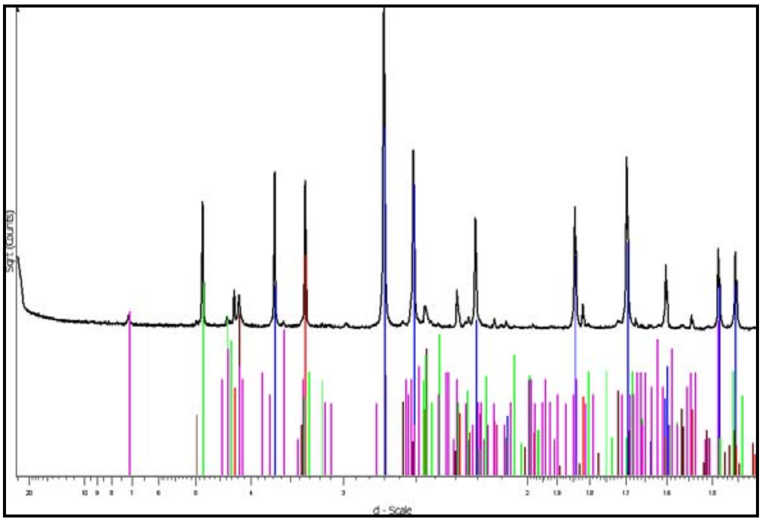

Figure 1. Diffraction standard of X - ray of the sample of iron ore.

Table 2. Chemical composition of the sample of iron ore (% of the mass fractions)

MINERAL	MASS FRACTION,%
HEMATITE (Fe_2O_3)	72,89
KAOLINITE [$Al_2Si_2O_5(OH)_4$.]	4,64
QUARTZ (SiO_2)	12,05
GIBBSITE [$Al(OH)_3$]	3,18
GOETHITE [FeO(OH)]	7,25

In this study, the sulfuric acid was used for preparing solutions of leaching because of many advantages over the other acids such as hydrochloric acid and nitric acid[4]. In shaping for the elements Fe, P and S were obtained from several species including H_3PO_4 and salts $FePO_4$, $2H_2O$, and $FeHSO_4^{2-}$,$FeH_2PO_4^{2+}$.

By varying of pH values (1-10), were modeled the dissociation species phosphoric acid and sulfuric acid, all at a room temperature. Next, the effects of the conditions in precipitation of species $FePO_4{:}2H_2O$ were calculated. Leaching tests were carried out using a mechanical stirrer with digital display RW20 model, where the the stirring was maintained at a velocity of 605rpm. In order to assess the loss of the element iron in solution was added to a becher volume 1,000 ml contains 50g of sulfuric acid in which the iron ore had its average particle size by mixing 50% of the ore sample to 200 micrometers. The leachate was filtered on a vacuum filter and the leach liquor was separated thus creating a sample of iron ore leachate. The amount of 250 ml of leach liquor was separated and its pH was changed to the value 10. Was observed at pH 5 an apparent change of color and formation of a precipitate however the pH value was raised to the 10 in order to precipitate the maximum possible of the metal ions on the hydroxide form in which the value occurred at pH 8. The precipitate was separated by filtration through a membrane filter of 0.45 micrometers opening. The amount of iron removed was calculated from the reduction of the iron concentration in the sample of iron ore leachate. The quantification of iron content on the ore sample was performed by the Chemical Analysis Laboratory located in Mineral Technology Center maintained by the Ministry of Science and Technology CETEM / MCT) was used the technique of optical emission spectroscopy with inductively coupled plasma (ICP-OES).

The calculation of the percentage of removal is then:

$$\% = \frac{C_0 - C_f}{C_o} .100 \qquad (1)$$

In which C_0 is the initial concentration of the phosphorus element before the leaching process and C_f is the final concentration of phosphorus element after the leaching process. At the end of procedure, the ore was leachate and it was filtered and dried a temperature of 40^0C over 20 min for later chemical analysis.

2.1Calculation of Eh-pH Diagram for Fe-H_2O System

For the construction of the EH-pH diagram activity factors for aqueous species have been neglected and, similarly the water activity was adjusted to a unit and is therefore in accordance with the supposition frequently used in the elaboration and use of chemical balances diagrams. However, this approach cannot be used in concentrated solutions, for example solutions with pH values too low or too high. The activity coefficient of these solutions are probably larges and changes rapidly with the variation of pH and the concentration ratios may deviate strongly from the corresponding activity obtained from the thermodynamic equations. For this reason, lines chemical equilibrium diagrams based on the ratio of the activity might require significant when the lines are less than the pH1 and beyond the value of pH13. Lines in these regions should be traced and have been included in this work for reasons of construction.
Taking the information of E_0 and K is possible to calculate the equilibrium diagram in relation to electrochemical potentials and pH values for the system Fe_2O using the equations:

Equilíbrium Fe/ Fe^{2+}

$Fe + 2e \Leftrightarrow Fe^{2+}$

$$E_{Fe/Fe^{2+}} = E^0 + RT/2F \, Log[Fe^{2+}] \qquad (2)$$

Equilíbrium Fe^{2+}/Fe^{3+}

$Fe^{2+} + e \Leftrightarrow Fe^{3+}$

$$E_{Fe^{2+}/Fe^{3+}} = E^0 + RT/F \, Log[Fe^{2+}]/[Fe^{3+}] \qquad (3)$$

Equilíbrium Fe/Fe_3O_4

$3Fe + 4H_2O \Leftrightarrow Fe_3O_4 + 8H^+ + 8e$

$$E_{Fe/Fe3O4} = E^0 +(0,059/8)Log[Fe_3O_4] + (0,059/8)Log[H^+]^8$$

$$E_{Fe/Fe3O4} = E^0 + (0,059/8)Log[Fe_3O_4] - (0,059pH) \qquad (4)$$

Equilíbrium Fe^{2+}/Fe_3O_4

$3Fe^{2+} + 4H_2O \Leftrightarrow Fe_3O_4 + 8H^+$

$\text{Log } K = 8\log[H^+] - 3\log[Fe^{2+}] = -8pH - 3\text{Log }[Fe^{2+}]$

$pH = (-\log K/8) + 8/3(\log[Fe^{2+}])$ (5)

Equilíbrium Fe^{3+}/Fe_2O_3

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

$\text{Log } K = 6\log[H^+] - \log[Fe^{3+}] = -6pH - 2\text{Log }[Fe^{3+}]$

$pH = (-\log K/6) + (\log[Fe^{3+}]/3)$ (6)

Equilíbrium Fe^{2+}/Fe_2O_3

$2Fe^{2+} + 3H_2O \Leftrightarrow Fe_2O_3 + 6H^+ + 2e$

$E_{Fe^{2+}/Fe2O3} = E^0 + (0{,}059/2)\text{Log}[Fe_2O_3] + (0{,}059/2)\text{Log}[H+]^6$

$E_{Fe^{2+}/Fe2O3} = E^0 + (0{,}059/2)\log[Fe_2O_3] - 3(0{,}059pH)$ (7)

Equilíbrium Fe_3O_4/ Fe_2O_3

$2Fe_3O_4 + H_2O \Leftrightarrow 3Fe_2O_3 + 2H^+ + 2e$

$E_{Fe3O4/Fe2O3} = E^0 + (0{,}059/2)\text{Log}[Fe_2O_3]^3 + (0{,}059/2)\text{Log}[H^+]^2$

$E_{Fe3O4/Fe2O3} = E^0 + (0{,}059/2)\text{Log}[Fe_2O_3]^3 - (0{,}059pH)$ (8)

Equilíbrium O_2

$O_2 + 2H_2O + 4e \Leftrightarrow 4OH^-$

$E = 1{,}23 - 0{,}059pH$ (9)

Equilíbrium H_2

$2H^+ + 2e \Leftrightarrow H_2$

$E = -0{,}059pH$ (10)

3 RESULTS AND DISCUSSION

3.1 Adsorption of H^+ íons on the Iron Ore Particle

According to Zhang et al.[5] the mechanism of acid leaching can be summarized as follows:

$Ca_{10}(PO_4)6X(s) + 20H^+ \rightarrow 6H_3\,PO_4 + 10Ca^{2+} + H_2X$ (11)

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According to equation 11 are required for interaction of 20 H^+ ions to the reaction of dephosphorization of iron ore. However, the intraparticle diffusion model describes the transport of the ion solution through the interface solution / particle[6,7]. This model follows the equation:

$$Q_t = K_{dif}\, t^{1/2} \tag{12}$$

In that:
K_{dif} = rate constant intraparticle diffusion..

It is possible to understand the stages of adsorption of H^+ íons on the particle of iron ore. Typically, the first adsorption step indicates to the external surface of the adsorbent, the second step, is characteristic of the speed of on the adsorption region is the intraparticle diffusion rate determining and indicating the final stage adsorption equilibrium due to the low concentration of H^+ íon in solution, but also a small number of adsorption sites. The rapid passage from the second to the third step indicates that few H^+ ions in solution or the difficulty of contact of the H^+ íons with the active sites, i.e. the surface of the iron ore particles in solution. It should, however, note that some of Fe ions in the solution may be distributed in several different species, including ion pair complex, protolíticss different species or complex. There is also aqueous solution forming salts so there is through dissociation of these salts with the formation of solutions where positive and negative charges which tend to cause electroneutrality of the aqueous solution thus interfering with the concentration of H^+ ions in aqueous solution.

3.2 Modeling the Variation of pH in the Leach Liquor Having Fe Ions in Solution

With the problem of diffusion of H^+ ion as the species formed around the particle of ore was used chemical equilibrium software (Medusa) to evaluate the effect of pH on the formation of ionic species and the precipitation of the species $FePO_4{:}2H_2O$. However, it is shown the variation of pH of the reaction of iron ore and sulfuric acid being displayed range 1-7.

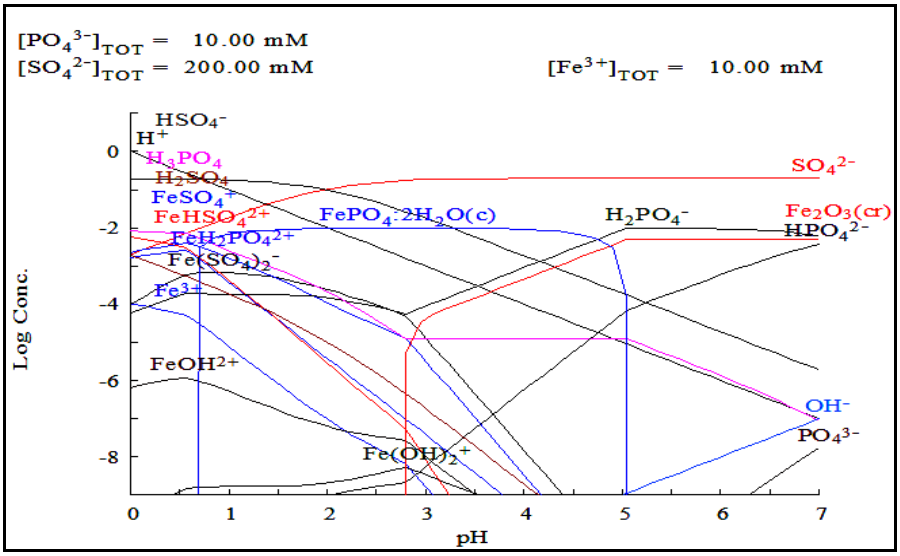

Figure 2. Speciation of reaction of phosphorus with sulfuric acid at different pH values. Calculated using the Medusa software.

Along with the second dissociation of sulfuric acid and phosphoric acid formation is formed of various complexes in solution such as salts $FeHSO_4^{2-}$, $FeH_2PO_4^{2+}$ and which will consume H^+ íons to their formation. The salts suffer precipitation specific pHs, but there is precipitation of the species in $FePO_4.2H_2O$ pH above 5, which also occur species $H_2PO_4^-$,HPO_4^-,SO_4^2 and the species $H_2PO_4^-$ to species of greatest fraction as shown in Picture 2. The pH of the solution may influence the activities of ions of iron salts and $FePO_4.2H_2O$ as ferric phosphate. Thus, the pH of the solution becomes a factor for effective precipitation of the species $FePO_4.2H_2O$. A number of studies relevant to talk about the effect of pH on the removal of phosphate. Fytianos, Voudrias e Raikos.[8] Obtained the best value for the removal of phosphate pH 4.5 and a molar ratio Fe / P, 1:1. Szabo et al.[9] conducted experiments using iron salts to remove phosphate and had a better removal efficiency of orthophosphate in a pH range of 5.0 to 7.0.

3.3 Modeling the Activities of Species in Phosphate Leaching Liquor Having Fe Ions in Solution

In the ionic compounds dissolved in water is a separation of the ions of the same dispersion with same solvent, changing the equivalent conductance of the solutions. The conductance of the solution of a strong electrolyte is dependent on the number and mobility of these ions. In dilute solutions ionic conductance increased due to increased mobility of the ions. In a very dilute solution find the ions apart from each other, thereby exerting a weak mutual influence, as the concentration increases, the interactions become considerable. In the Figure 3a and 3b are shown the activities of the species formed by ion Fe^{3+}.

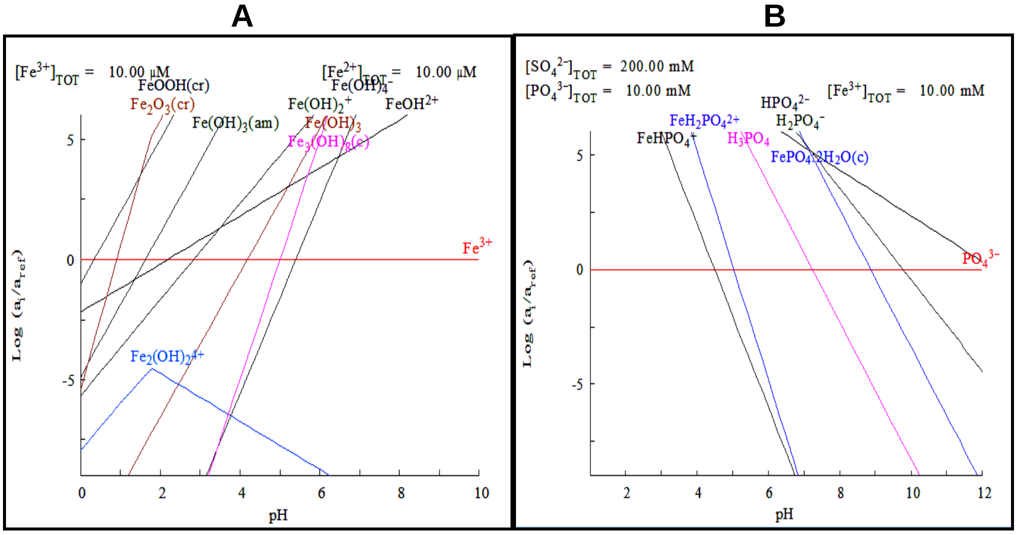

Figure 3. Activities of the species formed by the ions Fe3 + and PO43- on different PHS. Calculated using the Medusa software.

In the Figure 3b is observed that the salts of Fe has optimum activity at PHS below 5 such as salts $FeHSO_4^2$ and $FeH_2PO_4^{2+}$ However in Figure 3b is observed that at pH values below 5 is lower amounts of oxide and hydroxide species given the presence of ferric salts of Fe. According to Zhang et al.[5] the effect of ionic strength in the precipitation of species was investigated $FePO_4.2H_2O$ concluded that with increasing ionic strength increases the saturation index $FePO_4.2H_2O$ species decreased following a logarithmic function of ionic strength, however, the increase in ionic strength causes a decrease in the precipitation of the species $FePO_4.2H_2O$.

3.4 Modeling the Relation Fe / P in Leach Liquor

In the Figure 5 is shown in detail the curve precipitation of ferric phosphate on pH value close to 5 the pH value of higher concentration is formed $H_2PO_4^-$ originating from dissociation of H_3PO_4 With increasing pH the fraction there is a drop $H_2PO_4^-$ and a shift in reaction to a lower formation of the product.

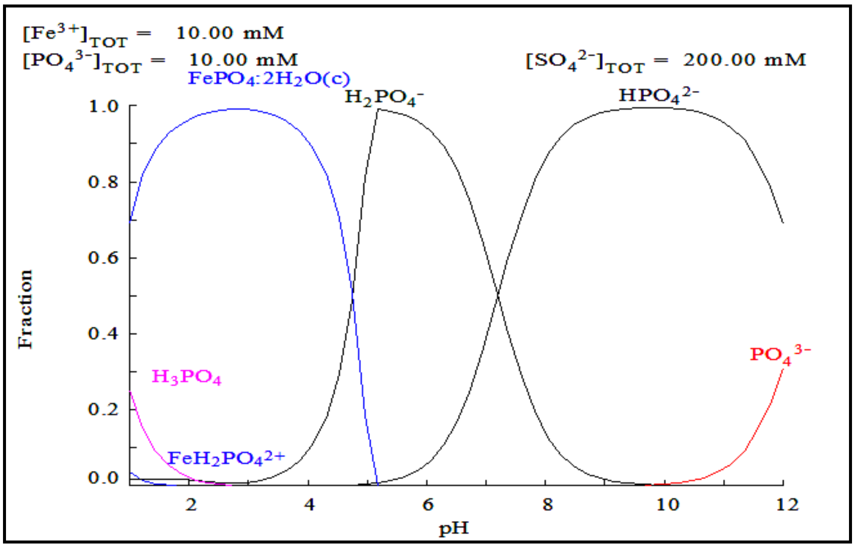

Figure 4. Fraction phosphate species on the leaching solution on different pHs. Calculated using the Medusa software.

In the Figure 4 is shown in detail the curve precipitation of ferric phosphate on pH value close to 5, where the pH value of higher concentration is formed H_2PO_4 originating from the dissociation of H_3PO_4 With increasing pH the fraction there is a drop $H_2PO_4^-$. According to Zhang et al.,[5] the saturation index $FePO_4.2H_2O$ is correlated with the concentration of Fe^{3+},PO_4^{3-} and their activity coefficient which is a function where the concentrations of the two ionic Fe^{3+}, PO_4^{3-} and ionic strength. According to Zhang et al.,[5] the saturation index of the species $FePO_4.2H_2O$ below a logarithmic function of the concentration of the two ions Fe^{3+},PO_4^{3-}. Considering the high value of the fraction of $H_2PO_4^-$ species in solution, pH 5 is found to this optimum pH value for the precipitation of phosphorus process as ferric phosphate.

3.5 Modeling of the EH-pH Diagram for Fe-H_2O System

One way to avoid the formation of phosphorylated species is in solution to obtain a pH in solution is avoiding the formation of Fe^{3+} ions in solution. For this the use of pH-EH diagram becomes indispensable. In the Figure 5 is shown the diagram EH-pH for the Fe-H_2O at a concentration of 0.01M are shown where the balance between the ions and species of Fe gives the variation of electrochemical potential and pH.

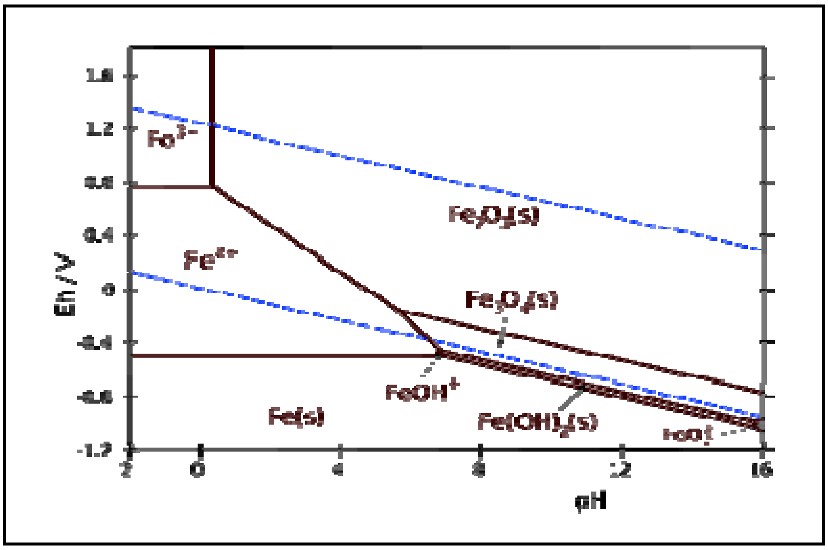

Figure 5 . Diagram EH-pH of the system Fe- O ionic concentration in solution 0.01 M calculated using the software FactSage version 5.3

The diagram EH-pH for the solution of Fe concentration of 0.01 M displays species of soluble Fe between immunities regions and passivity. The existence of corrosion region between immunities areas and passivity indicate the presence of iron ions in solution where the interfering species which form the diffusion of H^+ ions into the interior of the particles of iron ore. Is noted that at pH values below 2, and values of potential stability of the water is released ion Fe^{3+} and Fe^{2+} to the aqueous solution will be formed where the species listed above. In the diagram is also observed the formation of the species Fe_2O_3 species that also causes passivation of Fe preventing them from being released into solution. Based on the pH and potential value in the formation area of the species Fe_2O_3 obtained the following reactions:

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 6H^+ + 3e \tag{13}$$

$$O_2 + 2H_2O + 4e \rightarrow 4OH^- \tag{14}$$

As shown in Figure 5 and in equations 13 and 14 element caused by oxidized Fe is pHs higher potentials and the species forming Fe_2O_3. The increase of the potential oxidizes the Fe atoms to form the species which is formed at pH values above 2 occurring also the formation of OH^- ions through the reaction with O_2 at high values of potentials.
Table 3 demonstrated pHs according to the theoretical concentration of sulfuric acid.

Table 3. Theoretical concentrations of the species H_3O^+ and their pH values.

$[H_2SO_4]$	$[H_3O^+]$	pH
0,1	0,027242	1,56
0,2	0,040353	1,39
0,3	0,050452	1,29
0,4	0,058978	1,22
0,5	0,066496	1,77
0,6	0,073296	1,13
0,7	0,079552	1,09

In Table 3 is demonstrated that with increasing sulfuric acid a concentration there is an increased H_3O^+ ions concentration in solution and a resulting decrease in pH value. However it is shown in Figure 6 the decrease of content of Fe in iron ore with a particle size between 150 and 200 microns in 20 minutes of leaching at 605rpm with sulfuric acid at different concentrations.

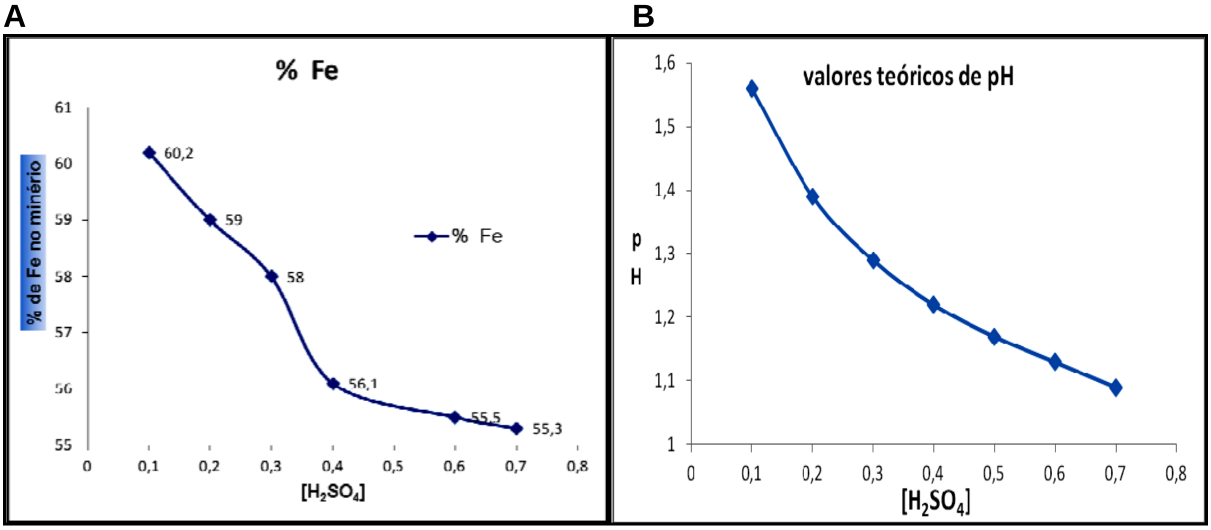

Figure 6 .% of Fe in solution after leaching with aqueous sulfuric acid for 20 minutes at 605rpm in pH and theoretical values at different concentrations of sulfuric acid.

It is observed in Figure 6a with increasing sulfuric acid concentrations there is an increased loss of Fe in the iron ore in the aqueous solution. With increase in concentration of sulfuric acid there is a decrease in pH value, however according to the diagram EH-pH (Figure 5) at pH below 2 for corrosion of atoms of Fe as ions Fe^{3+} in an acid solution and the decrease in pH and the concentration of H^+ ions is increased loss in the Fe content of the ore because of its insertion within the area where the corrosion even give rise to lower levels of iron in the ore thus having a devaluation of the same. It also occurs because of corrosion of Fe in solution to form various salts which interfere with the H^+ ion diffusion into the ore particle.

5 CONCLUSION

In order to study the removal of phosphorus in iron ore in the region of the iron quadrangle, Brazil, and also taking the objective to avoid the loss of iron in iron ore caused by the leaching process to remove phosphorus assessment modeling physico - chemical dissociation of sulfuric acid was investigated and investigating also the equilibrium diagram of electrochemical potential depending on the pH of the solution with the following conclusions:

- In the leach liquor at pH below 2 there is dissociation of sulfuric acid and phosphoric acid followed by corrosion of hematite, magnetite and goethite no release of Fe^{3+} to the solution causing formation of various salts and hydrxides ferrous interfering ion diffusion H^+ into the iron.
- The precipitation of the species $FePO_4.2H_2O$ is obtained at pH 5 where it is caused by the PO_4^{3-} ion concentration in solution.
- The pH of the lixiviant solution to remove phosphorus in the iron ore must be adjusted to pH3 where the value of which according to EH-pH diagram in corrosion of Fe element to the aqueous solution thus maintaining the concentration of the element in ore avoiding its devaluation.

- The absence of the element Fe^{3+} in aqueous solution inhibits the formation of salts of iron $FeHSO_4^{2-}$ $FeH_2PO_4^{2+}$ e $FePO_4.2H_2O$ and thus having lower consumption of H^+ ions in aqueous solution while maintaining its concentration in solution.
- The absence of the element Fe^{3+} in aqueous solution inhibits the formation of salts of iron $FeHSO_4^{2-}$ $FeH_2PO_4^{2+}$ and $FePO_4.2H_2O$ thus having lower consumption of H^+ ions in aqueous solution while maintaining its concentration in solution.

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