

Evaluation of iron loss during the simultaneous acid leaching process for phosphorus and aluminum decrease in iron ore

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Abstract The high levels of phosphorus demand operations of dephosphorization for steel manufacturing steps resulting in high costs. One way to minimize these costs is the removal of phosphorus in the iron ore particles using the acid leaching process; however, depending on how the phosphorus is complexed in the mineral phase requires the application of additional energy. However, when the phosphorus removal process using acid leaching also occur in the ore particles loss of iron and leaching aluminum. The loss of iron is undesirable for the beneficiation process while aluminum is benefic for the efficiency of the concentration and has positive effect on the subsequent step of reduction. Currently, there is no viable technology for simultaneously removal of phosphorus and aluminum in iron ore. Understanding the mode of occurrence of these elements in minerals will surely bring new information that eventually may subsidize the development of methods for their removal. In this work, we propose, the addition of energy in the iron ore particles using microwave energy due to its efficiency in heat generation. Therefore, in this study, we evaluated the acid leaching process in the iron ore particles targeting of reducing the phosphorus and aluminum contents and was also evaluated the removal of iron in the particles. Through factorial statistical design technique with central and axial points, we determine the optimum conditions employed in the acid leaching process. The following values for experimental optimum conditions were: 19,25g mass of ore, leaching time 20 min, temperature 650C leaching, agitation speed of 620rpm, average particle size of 595 microns, having a 3-minute contact time with the power of microwave. Under these conditions, the reduction of phosphorus content in iron ore sample reached a value of 52.47%.

Keywords - Microwave; leaching; Phosphorous reduction; Iron ore

Introduction

The Currently, for acceptable phosphorus content in iron ore used at the steelmaking industry is in the order of 0.075% [1]. In Brazil and in several places in the world are found large quantities of iron ore with deposits levels above of 0.1 which may generate high costs for its removal in the steelmaking processes or the regarded as unviable deposits by high generation of sterile [2].

The chemical approach, in which the ore is leached with an appropriate solution, is a relatively simple process and can directly treat the granules without fines and strict requirements for the particle size [3]. Usually in phosphate ores, the main mineral is apatite and its secondary phosphates such as wavelita, senegalita and turquoise, which can easily be leached by acid solution [3]. Another important source of these impurities is the molecule of goethite, FeO(OH), in the form of solid solution [1]. Conversely, when the phosphorus is in complexed form, the acid leaching treatment under the usual conditions, do not present satisfactory performance due to the need for high concentrations of leaching acid solution and low removal efficiency [3].

An alternative and technically feasible way for phosphorus removal is to heat the ore above 300 °C which allows the phosphorus element to release the crystal structure and incorporate into the leaching solution. However, to increase phosphorus removal percentage of particles of iron ore acid solution should be in relatively low concentrations (0.1 to 0.3M). However according to Silva et al. [4], this technique can promote the simultaneous removal of other elements such as iron and aluminum. In this paper, it is proposed the improvement of these techniques by two mechanisms that can substantially increase the percentage of phosphorous removal. The first is the volumetric heating at high rates allowing the concentrate to interact with microwave energy and subsequent cooling. The second is the same combination but with fast cooling in water and then, the particles are exposed to the leaching solution. With these two procedures, we simultaneously promote the release of phosphorus from the crystal lattice and the generation of additional surface contact

through the cracks generation mechanism and micro-cracks, which can improve removal efficiency. However, other elements may also be removed; of particular interest are iron, which would be undesirable because it would reduce its content in the final concentrate and aluminum, which can be highly desirable.

According Couto et al. [5] in their paper was observed that for most samples a correlation exists between the aluminum and phosphorus extraction, suggesting that both elements are associated with iron oxides, probably the goethite. However, Peixoto et al. [6] reported in his work that when the iron ore phosphorus element is in solid solution in the goethite phase, one can use the heat treatment process to the iron ore particles. Such treatment enables the structural rearrangement of the goethite phase into hematite that facilitates the release of the phosphorous element to the leaching process in an acid medium. Thus, for heating the iron ore and release the phosphorus is used the microwave energy applied directly to the particles releasing the molecule to the leaching solution as shown in Figure 1.

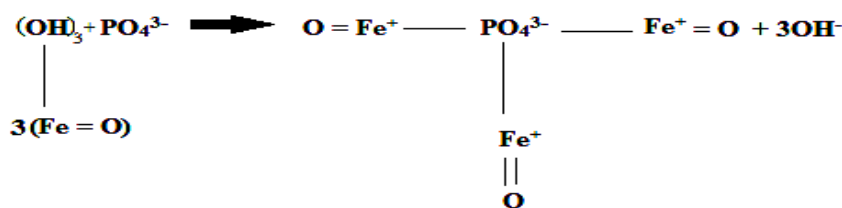


Fig 1. phosphorus occurrence mechanism in goethite.

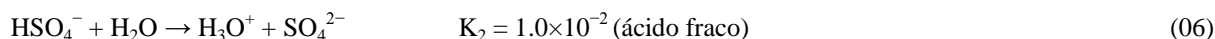
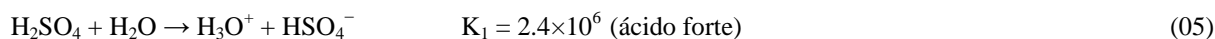
After the release of phosphorus into the liquid medium to dephosphorization reaction will occur using an acidic environment as leaching agent being introduced in Eq (1)



According to Equation 1 is required for the interaction 21 H⁺ ions for dephosphorization reaction of iron ore [4]. However, Arrouvela et al. [7] assumed that decoupling the first acidity of H₂SO₄ molecule involves only the formation of species H₃O⁺ and HOSO₃⁻ and the second cleavage is required to liberate H⁺ ions existing in the anion HOSO₃⁻. Also according to Arrouvela et al. [7], the hydration of the dimer (H₂SO₄)₂ always leads the form ionic but the dissociation becomes easier for larger systems where there is an increase of the number of water molecules or even increase in the number of sulfuric acid molecules. Thus, it becomes very important the knowledge of acid reaction and a thorough understanding of acid-base systems to the construction and interpretation of speciation diagrams (log [species] x pH). It is well known that in aqueous solution the polyprotic acids in the form HNY donating protons react, one at a time, in n steps:



The addition of water to the acid ensures that the limiting reagent is the acid.



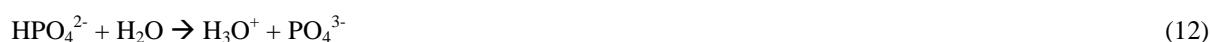
However according to the K₁ and K₂ values can be in the leaching solution in low pH values the H⁺ species; H₂SO₄; SO₄²⁻ and HSO₄⁻. With the release of Al species; Fe; and P by heating promoted by the microwave in iron ore particles can be release in solution the Fe³⁺ species; Al³⁺; PO₄³⁻ that can be formed with anions the following salts:



With the release of P we have the following equation:



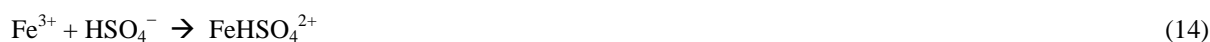
In the Equation (9) is observed the formation of weak acid H_3PO_4 . However, when an acid or weak base is dissolved in water, a partial dissociation is carried out. In the case of phosphoric acid (H_3PO_4) dissociations there will be three, and thus, the acid presents three constants with different values. This statement is because of polyprotic acids, such as in the case of the phosphoric acids, dissociate in subsequent steps as shown in Equations (10) – (12):



The successive ionization stages are primary, secondary and tertiary ionization respectively, not occurring to the same degree. The intensity undergoes considerable decreases from first to third ionization. So we have the values of $\text{pk}_1 = 2.12$; $\text{pk}_2 = 7.21$ and $\text{pk}_3 = 12.30$ at 25°C . As the pH value observed refers to pK_1 value has together with the Fe^{3+} ions released into solution as shown by equation (13):



The iron ions occurs in solution with HSO_4^- species that can behave as an acid or as a base depending on the species present in solution and with the metal ions released into the leaching solution the formation of several hydrogen salts can be formed, as presented in Equations (14) and (15):



Using the the formation of salts through leaching acid, the present study aims at evaluating the removal conditions of phosphorus and aluminum elements simultaneously during the acid leaching process of iron ore particles and minimizing the iron losses.

Materials and methods

X-ray diffraction (XRD), scanning electron microscopy (SEM) and optical emission spectrometry with inductively coupled plasma (ICP-OES) were performed to characterize the samples treated and not treated with microwave energy. The ore samples used in this study were purchased from the Iron Quadrangle region of Minas Gerais, Brazil. All samples were comminuted in rod mill in Mineral Technology Center facilities - CETEM - RJ generating size fractions of 75, 297, 500, 595 and 2380 micrometers. The passing fraction was homogenized, generating representative samples for particle size characterization, chemical and mineralogical analysis. The samples were heat pretreated and leaching experiments were performed at laboratory scale. For the process of pre-treating of iron ore particles conventional microwave reactor was used (Model: PMS - 24), with power of 1200W, radiation emitting frequency of 2450MHz. In each experiment 0.5 to 25.5 g of ore particles were used. The sample was treated with the highest level of power in the air. It was observed that on reaching the stipulated statistically residence time, the treatment was stopped immediately, thereby the sample was added to a reactor containing 500 ml of water at room temperature. The obtained fractions were submitted as powder analysis of X-ray diffraction analysis of the crystalline phases using successive refinement of Ritveld method. Cracks structures and micro cracks were visualized by scanning electron microscopy (SEM). The Ritveld method takes into account the overlapping of peaks of all phases present with the background noise contributions with a standard spectrum for the analysis of the ore in question. It used the optical emission spectroscopy inductively coupled plasma (ICP-OES) for quantifying the elements found in the medium before and after the leaching process.

For analysis of the leaching process a statistical method was used. The method is based on the central composite design with central and axial points. The central composite design is a symmetrical design and second order, consisting of two parts: the factorial 2^k , with one or more central points, and the axial part. Among the design patterns, the Design Central Composite (DCC) is considered a satisfactory method for problems treated in this study. According to Atkinson and Donev (1992), this method of analysis belongs to a family of efficient designs, which require few trials for achieving good performance. As regards the efficiency

measures, Lucas (1976) and Atkinson and Donev (1988) showed that DCC is suitable according to the optimization criteria. In addition, it has interesting characteristics for searching the point that gives the optimal response, which are a smaller number of treatments in relation to full factorial and can be performed sequentially to move in the direction of the system optimization, i.e. through the implementation of a part of the experiment (applying factorial experiments 2k or fraction-experiment of the first order). To guarantee the desired goal within the appropriate ranges, Equations (16) and (17) are used.

$$2^6 = 64 + 4 \text{ midpoints} + 12 \text{ axial points} = 80 \text{ test}; \tag{16}$$

$$2^{6-1} + 4 \text{ midpoints} + 12 \text{ axial points} = 48 \text{ test}; \tag{17}$$

The Equation (17) indicates the central composite design and fractionated fraction for 1/2 where the 6th column is the multiplication of previous columns 5th or the main effects occur only for mixture to the 4th order and the 1st-order interactions with the interactions of 3rd order. In this planning fractionated there is only a generating relationship, and the main effects only mingle with the effects of complementary 4th order. Thus, the information of the main effects of the variables in relation to the answer of this 1/2 fraction is practically equivalent to a complete design. Even the interactions of 1st order mingle only with effect of 3rd order, which normally tends to zero. Thus the samples of different mass of iron ore were reacted according to the methodology of factorial design with central and axial points including levels of -1.68 to +1.68. Therefore, the following variables were analyzed: ore concentration in solution, leaching time, leaching temperature, average particle size size, stirring speed and contact time with the energy of microwave shown in Table 1.

Table 1. Variables and levels used in experimental design

Variables	-1,68	-1	0	1	+1,68
Concentration (g / L)	2	27	52	77	102
Lixviação Time (min)	2	20	38	56	74
Leaching Temperature (0C)	5	25	45	65	85
Particle size (micrometer)	75	297	500	595	2380
Agtação speed (RPM)	155	310	465	620	775
Contact time with the power microwave (min).	0	1	2	3	4

In this study, sulfuric acid was used for the preparation of leaching solutions due to numerous advantages over other acids. To calculate the best match of the removal conditions of leaching tests were performed using mechanical stirrer with digital display RW20 model, where the agitation can be varied. Becher in a volume of 500 ml was added to 250 ml sulfuric acid solution at a concentration of 0.2M different values of iron ore masses with different granulometry values. For the evaluation of the best leaching conditions was used factorial design method with axial points and focal points where it was possible to obtain useful information about the behavior of answers acquired from the levels and the factors initially taxes can also highlight the quality of repeatability the process [8]. The leached sample of iron ore was filtered on a vacuum filter and the leach liquor was separated thereby generating the ore sample leached iron. The iron ore sample was dried in an oven at 400 °C and then homogenized and used for analysis. The phosphorus element quantification was conducted by the Chemical Analysis Laboratory located in Mineral Technology Center maintained by the Ministry of Science Technology and Innovation (CETEM / MCTI), where we used the optical emission spectroscopy with inductively coupled plasma (ICP-OES).

The fraction removal were determined as follows:

$$Fraction = \frac{C_f - C_i}{C_i} \tag{18}$$

There C_f is the final phosphorus concentration after the leaching process, and C_i is the initial phosphorus concentration before leaching.

results and discussions

Figure 2 shows the diffraction X-ray spectrum of the iron ore used in this study and its mineralogical composition of the sample of iron ore shown in Table 2.

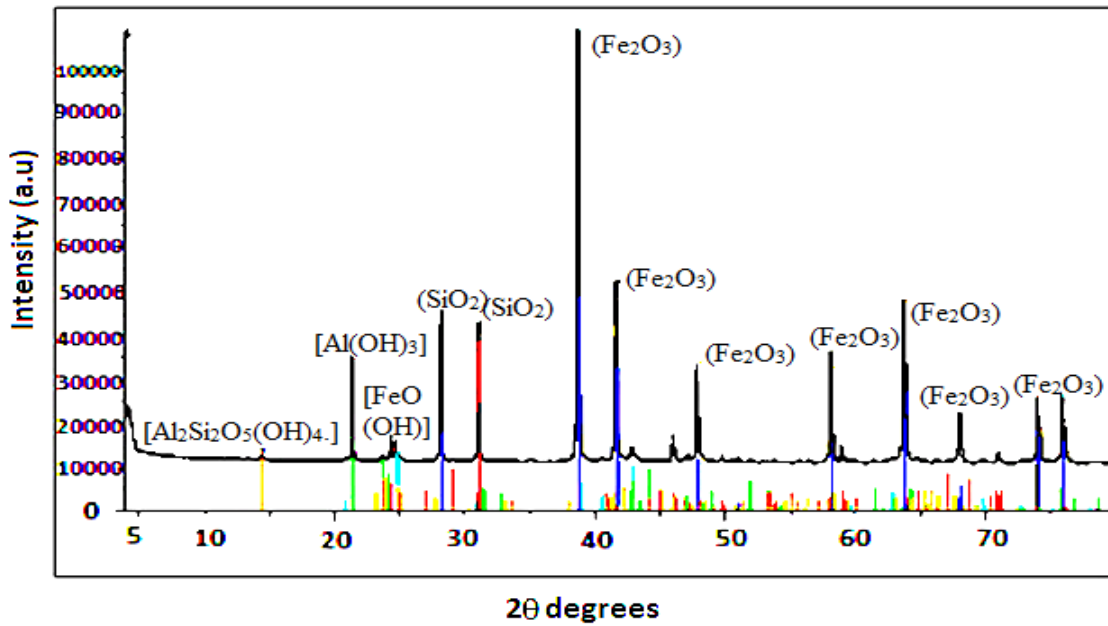


Fig 2. X Ray- diffraction spectrum of the sample of iron ore used in this work.

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

MINERAL	CHEMICAL FORMULA	MASS FRACTION,%
hematite	(Fe ₂ O ₃)	72,89
kaolinite	[Al ₂ Si ₂ O ₅ (OH) ₄]	4,64
quartz	(SiO ₂)	12,05
gibbsite	[Al(OH) ₃]	3,18
goethite	[FeO(OH)]	7,25

From the XRD analysis it was found that the ore is mainly composed of five phases: hematite, kaolinite, quartz, gibbsite and goethite. It was observed the presence of phosphates or aluminum phosphates that can be found in 3 goethite complexed molecules, as shown in Figure 1.

In order to assess the relevant species for the phosphorus elements remotion; iron and aluminum in iron ore particle simulations were performed using the software medusa® where it was possible to obtain the speciation of element phosphorus; solution containing iron and aluminum in sulfuric acid as the leaching medium. In Figure 3 is shown fractions of different species found in the leaching process for reducing the phosphorus element content in iron ore particles as a function of the concentration of Fe²⁺ in solution.

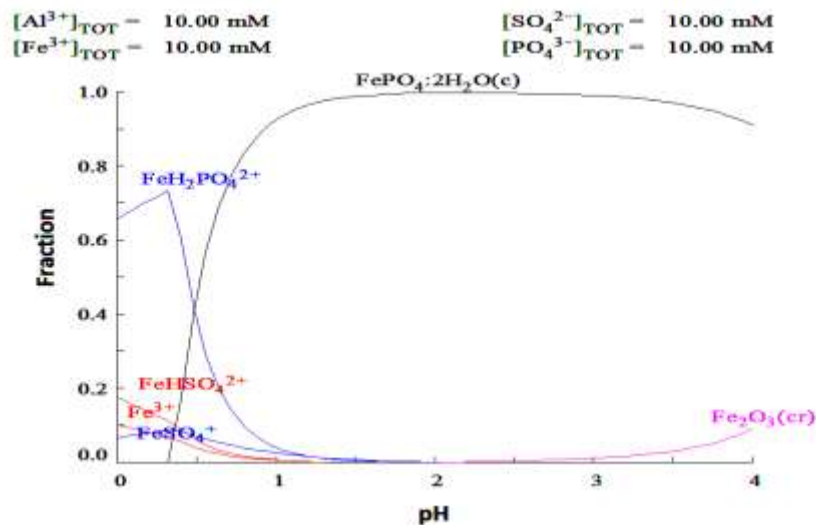


Fig 3. Speciation of fractions of species formed as a function of concentration of Fe²⁺ in solution

It can be observed in Figure 3 the occurrence of species of ferric phosphates at optimal pH values for the leaching process of iron ore particles aiming at phosphorus removal. This can be explained by observing the dissociation values of phosphoric acid which occur in values of $pK_1 = 2, 12$; $pK_2 = 7.21$ and $pK_3 = 12, 30$ at 25°C . Figure 4 shows the fractions of the different species found in the leaching process to reduce the phosphorus content in iron ore particles as a function of the concentration of Al^{3+} in solution.

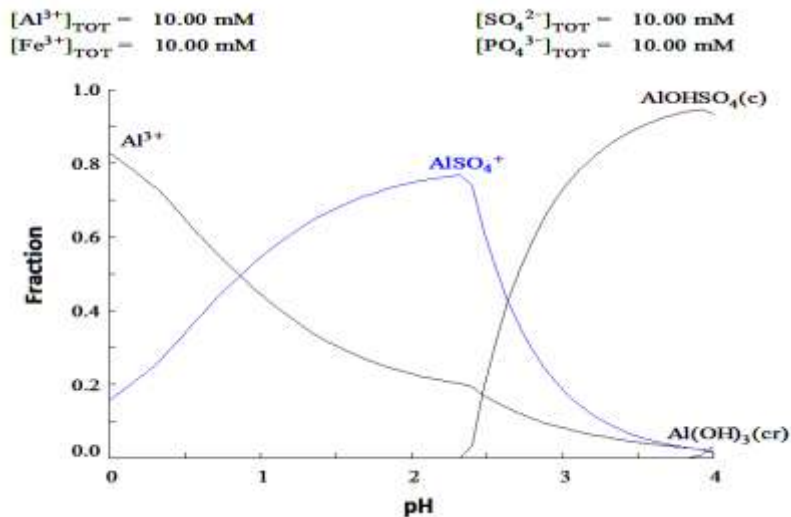


Fig 4. Speciation of fractions species formed depending on the concentration of Al^{3+} in solution.

In Figure 4 can be observed the occurrence of aluminum sulphate species at pH values optimal for the leaching process of the iron ore aimed phosphor particle removal. This can be explained by looking at the value of the second dissociation of sulfuric acid occurring in value $pK_2 = -2$ at 25°C . In Figure 5 is presented fractions of different species found in the leaching process of the iron ore particles due to the PO_4^{3-} concentration in solution.

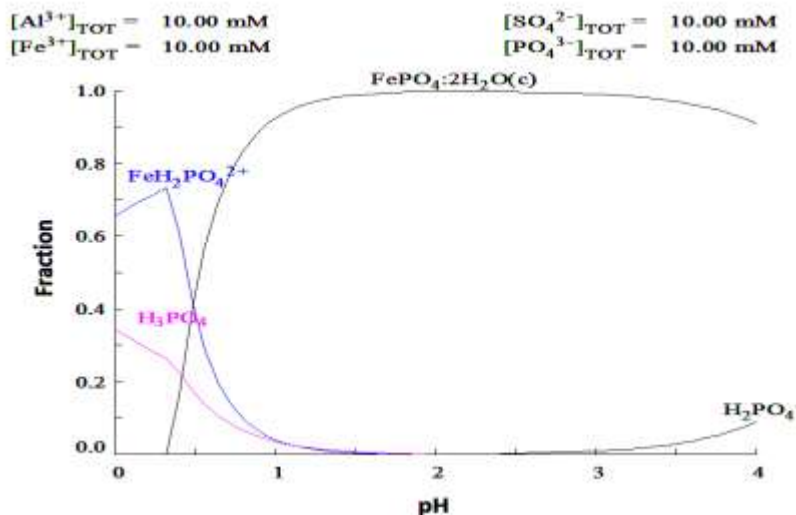


Fig. 5 Speciation of fractions species formed depending on the concentration of PO_4^{3-} in solution.

It can be observed in Figure 5 the occurrence of species of ferric phosphates similar to those observed in Figure 3. This fact leads to the conclusion that the removal of the iron component of the iron ore particles occurs due to the formation and dissociation of phosphoric acid in the leaching solution. After the formation of phosphoric acid in the leaching solution and the dissociation of corresponding anion, which binds to the iron ions, forming the FePO_4 salts and $\text{FeH}_2\text{PO}_4^{2+} \cdot 2\text{H}_2\text{O}$ in solution. In Figure 6 is shown fractions of different

species found in the leaching process to reduce the phosphorus content in iron ore particles as a function of the concentration of H_2SO_4 in the solution. Figure 6 presents the leaching solution having a sulfuric acid concentration of 0.2M in the pH range 1.0 to 7.0. It was observed that sulfuric acid has its second dissociation pH 2 wherein the weak acid is considered as due to its slow dissociation which generates and where the sulphate anion having a highly exothermic hydration reaction. It was also observed that at pH values below 1 formation of different phosphate species occur which include the elements iron, phosphorus and aluminum. In water, sulfuric acid behaves as a strong acid in its first dissociation, and as a weak acid in the second dissociation, furnishing the sulfate anion with a strong exothermic hydration.

According to Manmdouh et al. [9] There are several benefits in the treatment of iron ore using microwave energy to reduce the ore comminution energy and improve the effectiveness of the leaching process. However, one of the most important benefit in the treatment of iron ore to microwave energy consists in the possibility of treating larger granulometric sizes. In Figure 7 is shown micrographs of iron ore of 48 μm before and after heating in microwave oven. It can be observed in Fig. 7, the fractures formed by the rapid cooling of the sample. According to Kumar et al, [10] the basic principle to obtain fractures is the ability of microwaves to heat the individual phases generating faster heating values within the iron ore structure. The heating is generated by molecular friction inside the phase structure of the material gives a response to the electromagnetic field and thus to heat transfer occurs by thermal conduction to neighboring phases.

Tang Wen et al. [11] reported that acid leaching is an effective method for dephosphorization. The phosphate contained in ore particles do not need to be completely dissociated provided that contact can occur between the exposed portion and mineral leaching solution in order to remove the combined phosphorus.

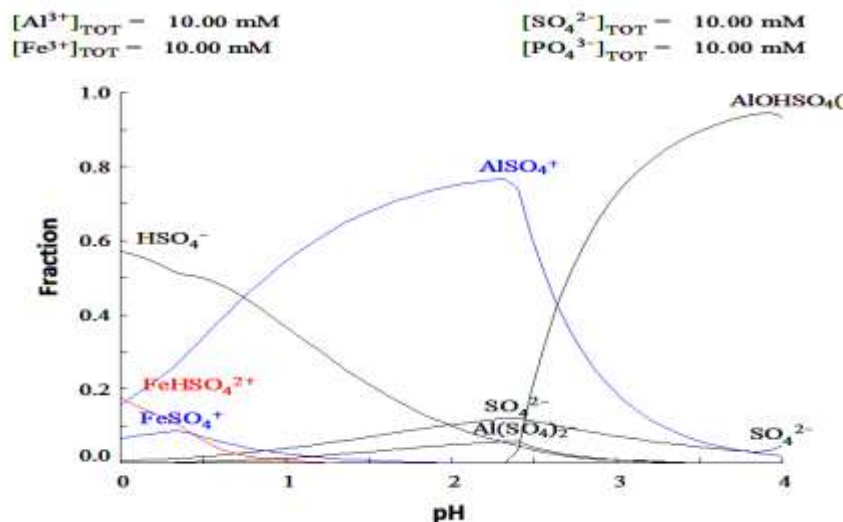


Fig. 6. Speciation of fractions of species formed as a function of concentration H_2SO_4 solution

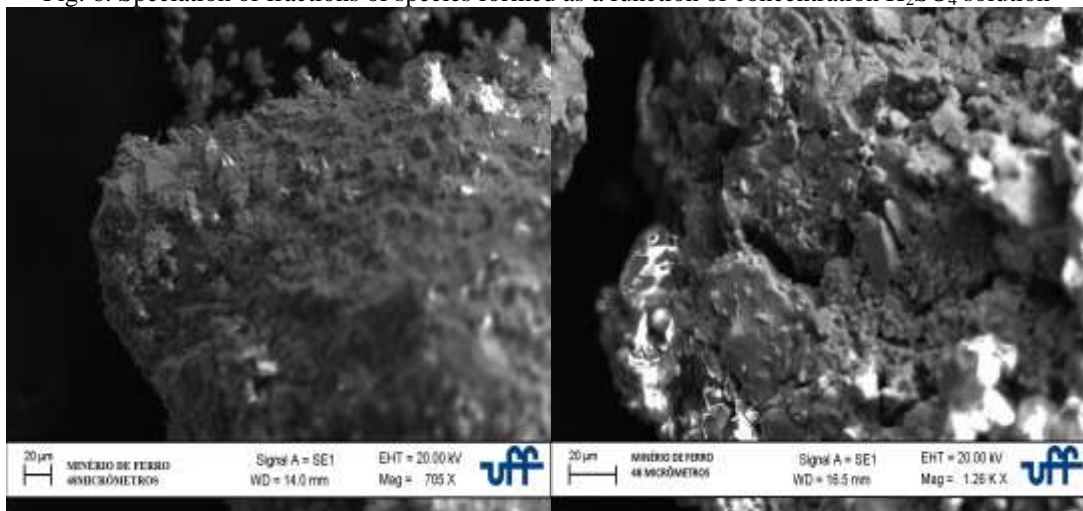


Fig 7. SEM analysis of iron ore at 48 micrometer before and after heating in microwave oven

Figure 8 shows the removal percentages of phosphorus and aluminum and loss of iron element during the leaching process the iron ore particles. As can be observed, the simultaneous removal of phosphorus and aluminum implies in loss of iron and the optimum values can be selected using Fig. 8.

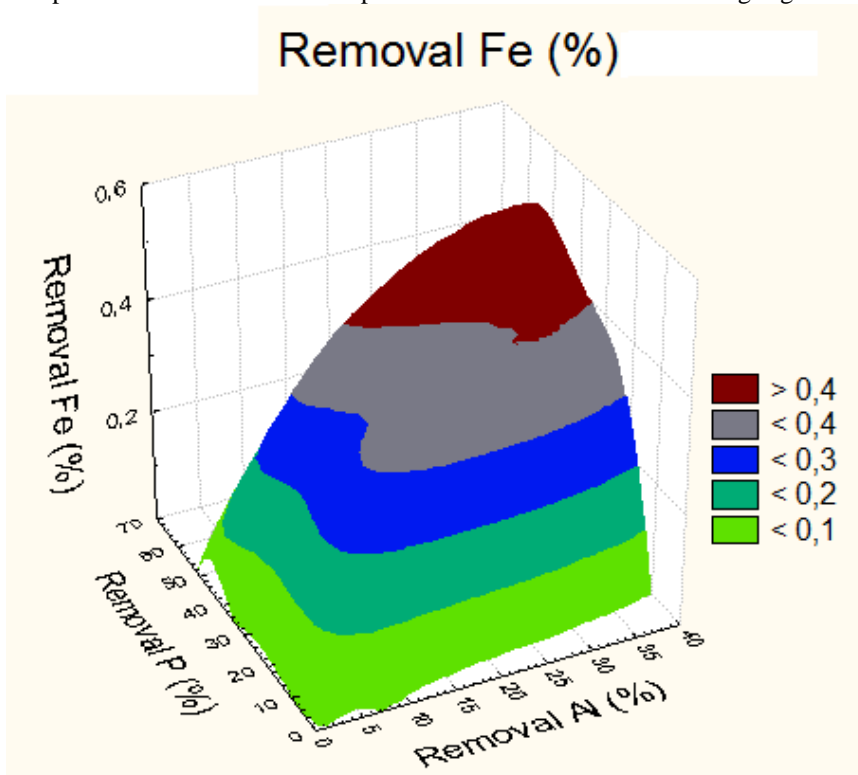


Fig 8. Removal percentages of phosphorus and aluminum and loss of iron during the leaching process the iron ore particles.

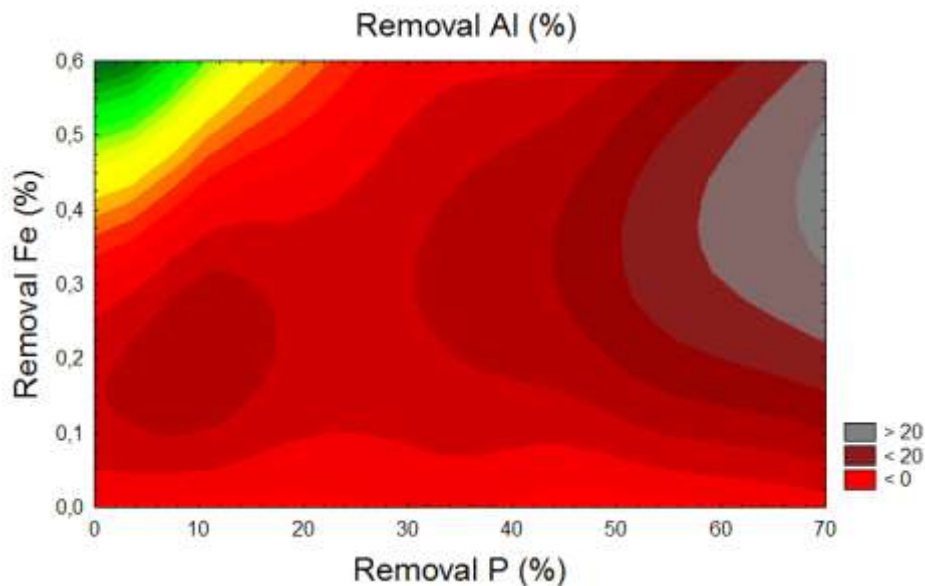


Fig 9. Removal of aluminum in function of removal of phosphorus and loss of iron during the leaching process the iron ore particles.

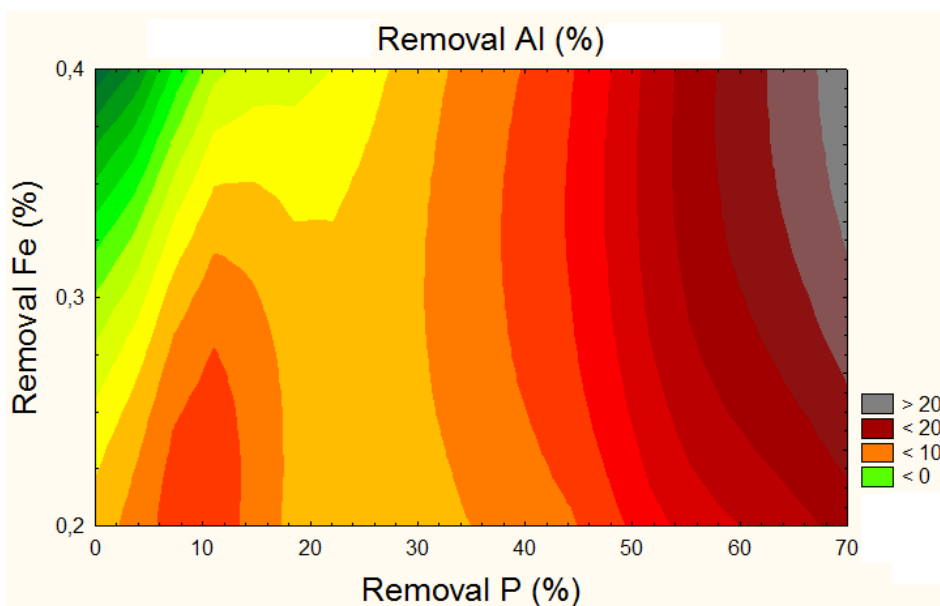


Fig 10. Removal of aluminum in function of removal of phosphorus and loss of iron to values between 0,2 and 0,4% during the leaching process the iron ore particles.

In Figures 8, 9 and 10 is observed that increasing phosphorus removal, iron loss is increased and aluminum removal is enhanced. It was observed that for the removal up to 60% of the phosphorus, the loss of iron was kept below 0.8% and the percentage value of the removed aluminum did not exceed 35%. In Figure 10 it is observed the possibility of aluminum removal at values above 20% and simultaneously phosphorus removal with values greater than 60% for iron loss values between 0.2 and 0.6%.

conclusions

Based on the analysis and results of this study, it is considered that the phosphorus removal viability using heat on microwave followed by acid leaching is confirmed. The removal of aluminum however, depends on the iron loss aimed. Each of the steps of the method of heating the iron ore particles followed by acid leaching process were demonstrated and their impact on final removal of the elements phosphorus, iron and aluminum. The percentage of removal of the aluminum element was close to a value of 30%, which has significant impact on the final concentrate quality. It was confirmed that the percentage loss of iron was less than 1%, which is considered negligible, indicating that the use of acid leaching process for the reduction of phosphorus content in iron ore particles is viable.

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