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Evaluation of The Reduction of Phosphorus Content In Iron Ore Using The Integrated Baking Acid - Leaching Technique.

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ABSTRACT: *Iron ore is the mineral mineral resource extracted in greater volume from the Earth's crust being the main raw material used in the steel industry. Research carried out in the period from 2010 to 2015 by the Center for Management and Strategic Studies, titled "steel industry in Brazil", emphasizes that there is a great expectation in raising the levels of phosphorus and alumina in ores to be worked. Iron ore when found with phosphorus contents above 0.05% is considered reject due to its interference in the steel making it increase its hardness and causing its fragility. Therefore, an alternative route of higher efficiency for the production of iron ore concentrates with ultra-low phosphorus is required when compared to the current routes used by the mines (minimum 50% of the levels currently practiced). Therefore, the present work intends to evaluate an integrated route using the acid percolation process in iron ore sample located inside a conventional furnace (acid baking), with the optimum values being the mass values of sulfuric acid in analytical concentration in the proportion 05-1 of iron ore for 30 minutes inside the furnace at 1500C followed by the leaching process in water for 20 minutes where near 100% phosphorus extraction values were reached.*
Keywords: Iron ore 1; Sulfuric acid 2; Baking acid 3; Leaching 4

I.   INTRODUCTION

        Acid baking is a process characterized by the percolation of an acid into a solid substance as mineralogical particles, both are located in an furnace where the interaction between the ions released by the acid and the mineral of interest becomes catalyzed by the high temperature inside the furnace .According to Safarzadeh et al 2012 [1] results obtained by the University of Utah have indicated that the baking-acid process is a promising alternative for the treatment of concentrated ores. However a   rare earth double sulfate mixture was prepared and added in the acid baking process using as sulfuric acid followed by leaching in water which not only resulted in 90% rare earth recovery, but also produce hydrofluoric acid as a by-product.

According to Yong-shi's [2] work entitled "Removal of phosphorus from iron ores by chemical leaching", it has been observed that the casting process has great efficacy for the dephosphorization of iron ore, yet it has disadvantages as a very high cost high and high energy consumption (fossil fuel). In the process of physical separation, the comminuted ores must have very fine granulometries with the objective of releasing the mineral

phosphorus located in the mineralogical assembly where they will then be dephosphorized through the flotation or magnetic separation processes. However, such a technique does not apply to most ores because of the complexity of locating the phosphorus atoms in the mineral structure. The distribution of phosphorus along the goethite crystals hinders the efficient use of physical separation techniques, and requires the use of chemical separation techniques [3]. According to Peixoto et al., 1991 [4], when in the iron ore the phosphorus element is in solid solution, in the goethite phase, where through the process of thermal treatment of the ore occurs the structural rearrangement of the goethite phase, which becomes hematite facilitates the release of the phosphorus element for the acidic leaching process. The beneficial effect of heating the ore particles with high phosphorus content followed by the leaching process is already being investigated. However, pretreatment of ore particles by heating is included in the experimental flow chart for the treatment of iron ores found in Kazakhstan [4].

However the acid baking process uses a continuous process of heating the particles in a conventional furnace together with the mass of sulfuric acid of analytical concentration thus promoting the contact of the hydrogen ions with the phosphate structure where catalyzed by the high temperature will occur the break of the phosphate structure where added to a volume of water at ambient temperature will occur the leaching process in tanks with controlled agitation thus causing the release of the phosphorus into the medium in the form of phosphoric acid. The main characteristic of this route is the integration of a beneficiation sequence with heating of the iron ore particles together with the mass of sulfuric acid where the phosphorus release will be possible (see thermodynamic diagram of phase predominance, Figure 6). There are some inherent advantages of this route of reduction of the content of the phosphorus element contained in the iron ore using heating the acid - iron ore mixture in comparison to traditional processes such as:
• Removal of phosphorus in iron ore particles of the order of 100%;
• Leaching in tanks with shaking in water;
• Economical advantages (low cost of reagents and low concentrations);
• Total reuse of the formed by-product;
• Possibility of reformulation of the leaching solution;

Thus, in this work, the route of reduction of the phosphorus content by heating the percolated particles with sulfuric acid in analytical concentration is evaluated followed by the agitated leaching technique using water at room temperature as a leaching agent.

II. MATERIALS AND METHODS

4.2 Characterization of iron ore

In order to understand the structure of the complex formed between the phosphorus element and the goethite mineral phase, thermodynamic diagrams using the Thermocalc software followed by X-ray diffractometry (XRD) were developed. However, for the understanding of the reduction of the phosphorus element in the iron ore particles, specimens were developed in water solution using Hydra software produced by Royal Institute Technology. To quantify the concentration of the reduced elements of the iron ore sample, before and after the process, the inductively coupled plasma optical emission spectrometry (ICP - OES) technique was used. The obtained fractions were submitted in powder form and the X-ray diffraction analysis used the Ritveld method, this one is based on the simulation of a whole diffraction profile starting from structural parameters of the component phases, allowing in this way that quantitative information of the phases minerals can be extracted from the diffractograms [4]. This method also considers the overlap of the peaks of all the phases present and the contributions of the background noise (backgroud). Figure 1 shows the X-ray diffraction spectrum of the iron ore used in this investigation and Table 3 shows the mineralogical composition of the iron ore sample.
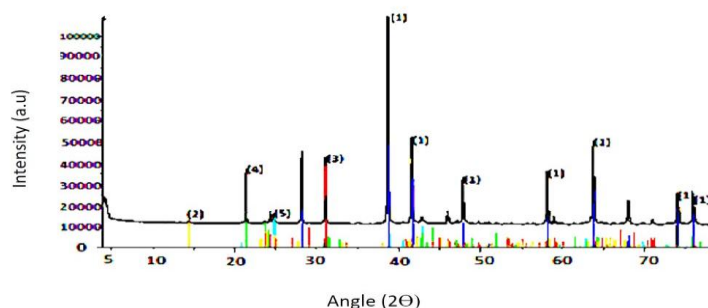

Figure 1.X-ray diffraction spectrum of the iron ore sample used in the work.

Table 1. Mineral composition of the iron ore sample (% weigth).

Mineral	%Weigth
Hematite (Fe_2O_3) (1)	72,89
Kaolinite [$Al_2Si_2O_5(OH)_4$] (2)	4,64
Quartz (SiO_2) (3)	12,05

Gibsita[Al(Oh)$_3$] (4)	3,18
Goethita [Feo(Oh)] (5)	7,25

As main phases identified through the X-ray diffraometry method to hematite, quartzo and goetite due to the absence of apatite and aluminosilicate composts. A chemical analysis was carried out using the method of spectrometry of emissão optic com plasma indutively coupled performed not CETEM. Or phosphorus theory at a minimum of 346 mg / kg or corresponding to 0.0346%.Aeletronic microscopy was performed at the Fluminense Federal University - UFF.

2.4 Analyst statistics

For analysis of the baking acid - leaching process the methodology of multivariate statistical analysis was chosen, having four independent variables where it was possible to analyze statistically the process of reduction of the phosphorus content according to the technique of planning two - level factorial experiments. The analyzes are based on ANOVA and the calculation was developed using the software Statistica developed by the company Statsoft. The Anova statistical method of repeated measures compares 3 or more correlated groups.

To carry out the process a volume of 300 mL of water was added to a glass reactor with a capacity of 500 mL. Samples of different iron ore masses were reacted according to a schedule including levels from -1 to +1 and the variables ore mass in the furnace, mass of sulfuric acid added for percolation of the ore inside the furnace, temperature of the ore mixture - acid inside the furnace, the residence time of the ore - acid mixture inside the furnace, time of leaching, and these variables are presented in Table 1.

Table 2. Variables used in the baking acid-leaching process.

Variables	-1	+1
Mass in acid bank (g)	15	50
Mixing time in the furnace (min)	30	60
Furnace time (^{0}C)	150	300
Leaching time (min)	10	20

The reaction mixture was shaken with the aid of an IKA mechanical stirrer model RW20. After completion of the reaction time the mixture was vacuum filtered on Büchner funnel and brought to the oven for drying at 40 ° C for 1 hour. All samples were then sent for quantitative analysis of the phosphorus contained by the ICP-OES "

Figure 2 shows the schematic flowchart of the sample preparation and the phosphorus reduction processing in the iron ore samples.
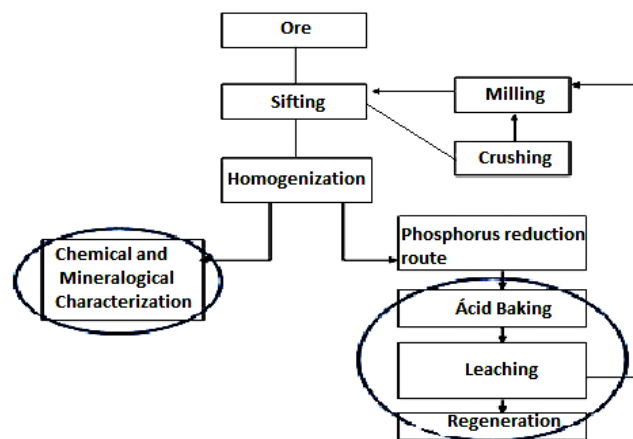

Figure 2.General flowchart of evaluation of the Baking acid-leaching route to reduce the phosphorus content in iron ore.

Figure 2 shows the general flowchart of the evaluation of the acid - leaching Baking route to reduce the phosphorus content in the iron ore where it was observed that the beginning of the process occurred by obtaining the sample of iron ore followed by classification by sieving, the average particle size of the particles remains. However, a possible difficulty occurred in the classification stage of the iron ore particles, so the same one went to the secondary grinding stage. After the conclusion of the classification stage of the iron ore sample, it was divided

in two fractions where a fraction followed for the step of chemical and mineralogical analysis and another fraction followed for the route of reduction of the phosphorus content in the iron ore composed of process of percolation of the sulfuric acid in the mass of the sample into the conventional kiln at elevated temperature for a time (acid baking) followed by the leaching process controlled by stirring using water at ambient temperature as the leaching agent. After the residue from the leaching stage composed of phosphoric acid should be concentrated and recovered for possible reuse in another process. In the next step, the results of the analysis of the occurrence of the phosphorus element in the iron ore particles as well as the analysis of the removal of the phosphorus element of the iron ore sample will be demonstrated

III.   RESULTS
3.1 Analysis of the occurrence of the phosphorus element in iron ore particles
        Phosphorus can occur as a primary material of the type found in phosphorites (apatite or francolite) in coexistence with iron ores. It may also be secondary mineral redeposited, or forming solid solutions with oxidized iron minerals. In weathered deposits, phosphorus can be found in the form of a solid solution in goethites or associated (contained) with secondary minerals bearing iron and aluminum. According to Graham, 1973[5], phosphorus can be found in iron ore in complexed form with goethite molecules, FeO (OH), as a solid solution. However, in the investigations of MORRIS et al., 1973, [6] it was verified by theories that, probably, the phosphorus is adsorbed on the surface of the goethite forming the Fe-O-P-O-Fe binuclear bonds. Studies conducted by Ler and Stanforth [7]   suggest that the interaction between phosphate and goethite includes ternary adsorption / surface precipitation as well as formation of a surface complex. The ternary adsorption and surface precipitation processes involve the dissolution of goethite crystal and the subsequent adsorption of iron at the phosphate binding surface. The precipitating surface of the anions involved in the model encompasses the dissolution of the goethite crystal that provides the iron ions in the crystalline structure. The proposed process is outlined in Figure 8. The steps involved are as follows:
Step 1 - The arrival of phosphate forms a mono or bidentate complex with hydroxyls on the surface of goethite (studies reveal the possibility of both forms).
Step 2 - The adsorbed phosphate acts as a sorption site for dissolved iron, forming a ternary complex and reducing the iron concentration in solution.
Step 3 - The goethite is dissolved to then supply the iron ion in solution, which can thus adsorb phosphate on its surface. It has been shown that adsorbed anions can form ternary complexes with metals in solution.
Step 4 - The adsorbed iron acts as a sorption site for the phosphate, and the process continues.

        According to Barbour AndCoutinho[8], Studies carried out with iron ore from the Itabira region (MG) have confirmed the existence of hydrated aluminate phosphates filling, in millimetric thicknesses, fractures of schist - hematite iron ore in highly occluded fractured crystals. The minerals identified by optical microscopy were: wavellita (greater quantity), features of wardita (smaller quantity), ceruleolacita (doubtful identification) and lehiite (associated with wavellite, filling certain cavities). However, in the studies carried out by Coelho et al. 1999 [9] for the removal of phosphorus contained in iron ore from the Samitri Mine of Alegria, it was not possible to identify the minerals bearing phosphorus. The main conclusions obtained are in agreement with the hypotheses previously raised by the several researchers mentioned, that is, the greatest association of phosphorus was found with the goethites / limonites and not with the hematítica minerals. However, the contents of P, Si, Al and Fe varied considerably in the samples studied. The authors of these studies suggest that there should be clayey minerals, containing phosphorus in the structure, or adsorbed on the surface, as submicron sized grains, which would be filling fractures or even even pores.
        A more plausible mechanism was proposed by Morris and Barbour, 1973 [6] and supported by Dukino, 1997 [10] involving surface adsorption. It has been suggested that prior to dehydration of hydrated iron in goethite, a hydroxyl group on the surface is replaced by a phosphate binder, as shown in the model shown in Figure 3

$$(OH)_3 + PO_4^{3-} \longrightarrow O=Fe^+ \!\!-\!\!-\!\!-\!\! PO_4^{3-} \!\!-\!\!-\!\!-\!\! Fe^+=O + 3OH^-$$

$$3(Fe=O) \qquad\qquad\qquad Fe^+$$
$$\qquad\qquad\qquad\qquad\qquad \| $$
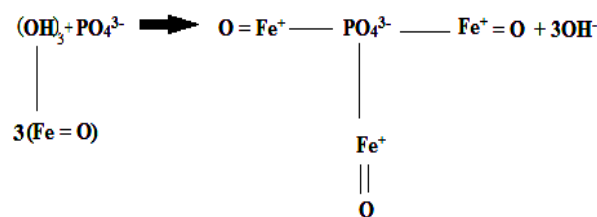$$\qquad\qquad\qquad\qquad\qquad O$$

Figure 3. Model of the mechanism of occurrence of phosphorus in goethite

According to Young shi et al 2006 [2] the process of chemical leaching using alkaline solutions is not effective in dephosphorization due to reprecipitation of phosphorus with other metal ions released during the process. According to Peixoto et al., 1991 [4], when in the iron ore the phosphorus element is in solid solution, in the goethite phase, where through the process of thermal treatment of the ore occurs the structural rearrangement of the goethite phase, which becomes hematite facilitates the release of the phosphorus element for the acidic leaching process.

Figure 4 shows the phase diagram of the iron ore in different compositions of the elements Fe, O, Si and Al and as a function of the percentage variation of the element phosphorus in the iron ore particles.
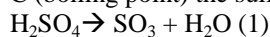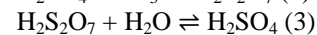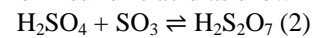

Figure 4. Phase diagram of iron ore composition: Fe 60%, O 20%, Si 10%, Al 9.99%. Calculated using Thermocalc® software.

Figure 2 shows the phase diagram of the iron miner in different compositions of the elements Fe, O, Si and Al, where maintaining the percentage of the element phosphorus in values close to 0,05, it is observed that the disappearance of the phosphorus - goethite in temperatures close to 300^0C. According to Graham, 1973 [5] the calcination of iron ore causes dehydration of goethite to hematite, releasing phosphorus in solution as an acid soluble compound.

However, it is important to observe the occurrence of the phenomenon of the high dissociation of sulfuric acid when subjected to high temperatures where from 30ºC starts to emit vapors. Above the temperature value of 290 ° C (boiling point) the sulfuric acid decomposes to sulfur trioxide and water as shown in eq 1
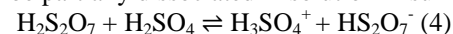
$H_2SO_4 \rightarrow SO_3 + H_2O$ (1)

The undissociated sulfuric acid reacts with SO3 easily to produce disulphuric acid and it reacts with water to again form sulfuric acid as shown in eq 2 and eq 3.

$H_2SO_4 + SO_3 \rightleftharpoons H_2S_2O_7$ (2)

$H_2S_2O_7 + H_2O \rightleftharpoons H_2SO_4$ (3)

Non-dissociated species of disulfuric acid occur in water, which theoretically corresponds to oleum with 44.9% by weight of SO3. It can be partially dissociated in solution in sulfuric acid as shown in Eq. 4.

If disulfurized acid species in water, which theoretically corresponds to oleum with 44.9% by weight of SO_3, it can be partially dissociated in solution in sulfuric acid as shown in Eq.

$H_2S_2O_7 + H_2SO_4 \rightleftharpoons H_3SO_4^+ + HS_2O_7^-$ (4)

3.1 Analyzes of the leaching step for the reduction of the phosphorus content of the iron ore particles

Immediately after the release of the phosphorus element into the liquid medium the dephosphorication reaction will occur using water as a leaching medium as follows:
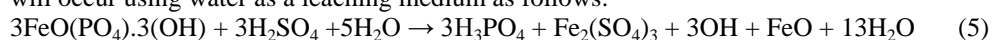
$3FeO(PO_4).3(OH) + 3H_2SO_4 + 5H_2O \rightarrow 3H_3PO_4 + Fe_2(SO_4)_3 + 3OH + FeO + 13H_2O$ (5)

Figure 5 shows the speciation of the reduction reaction of the phosphorus element content in iron ore using sulfuric acid as the leaching agent.

$[PO_4^{3-}]_{TOT} = 10.00\ mM$
$[Si(OH)_4]_{TOT} = 10.00\ mM$ $[Fe^{3+}]_{TOT} = 10.00\ \mu M$
$[Al^{3+}]_{TOT} = 10.00\ \mu M$ $[SO_4^{2-}]_{TOT} = 200.00\ mM$
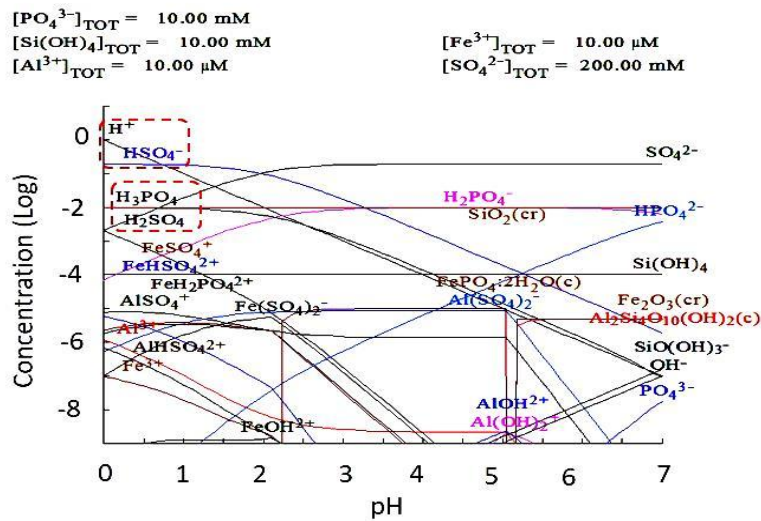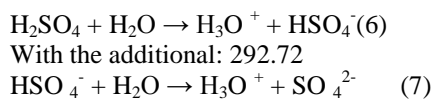

Figure 5. Speciation of iron ore leaching solution using sulfuric acid.

Figure 5 shows the concentration of sulfuric acid in the range of 1.0 - 7.0, being the ph range found during the leaching process of the iron ore in water after baking, acid being demonstrated that the sulfuric acid has its second dissociation in pH 2 where it is considered as weak acid due to its slow dissociation and where it generates the sulfate anion having a highly exothermic hydration reaction. It was also observed that at pH values below 1 the formation of several phosphate species occurs. In water, sulfuric acid behaves as a strong acid in its first dissociation, and as a weak acid in the second, giving the sulfate anion where it presents an extremely exothermic reaction of hydration as can be observed by equations 6 and 7:

$H_2SO_4 + H_2O \rightarrow H_3O^+ + HSO_4^-$ (6)
With the additional: 292.72
$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$ (7)

The concentration of sulfuric acid in aqueous solution plays an extremely important role in its dissociation. It is observed that being a polyprotic acid sulfuric acid releases higher concentrations of the H_3O^+ ion in solution, but given the great stability of its anion sulfuric acid has a great advantage against monoprotic acids such as hydrochloric acid and nitric acid. Being a weak acid does not occur its complete dissociation in solution, which means that the acid would not be exhausted during the process being able to be recycled. Recycling the sulfuric acid solution lowers the cost of acid consumption. In some researches, phosphorus recovery was obtained by being removed as a by-product making the entire process more economical.

3.1 Statistical analyzes of the reduction of phosphorus content of iron ore particles
Thus, as analyzed previously the water volume value in the leach was maintained at 300 mL (maximum value). Table 3 presents the experimental planning results with linear regression models valid for the ranges of variables investigated.

Table 3. Variables used and results of experiment planning.

Test	T1	t1	R1	V1	t1b	% of removal P	% of removal Fe
1	300.0	1.0	1.0	300.0	10	61,17	9,2
2	150.0	1.0	1.0	300.0	20	38,12	8,6
3	300.0	0.5	1.0	300.0	10	42,93	7,1
4	150.0	0.5	1.0	300.0	20	85,28	6,5
5	300.0	1.0	0.5	300.0	20	100,00	7,4
6	150.0	1.0	0.5	300.0	10	33,09	16,0
7	300.0	0.5	0.5	300.0	20	49,87	8,4
8	150.0	0.5	0.5	300.0	10	57,23	4,5

Statistical Planning was used to identify optimal processing conditions with the response variables. The effects of the independent variables, which consist of variables related to the leaching process [furnace temperature (T); Remaining time of the sample - acid mixture (t1); Sample - acid ratio (R1); volume of the leaching agent (V1); leaching time (t1b)] were evaluated where they were observed in trials 1; 4 and 5 the rates of reduction of the content of phosphorus contained in the iron ore of the order of 61.17%, 85.28% and 100.00% .

Figure 6 shows the response surfaces of the phosphorus removal of the iron ore particles as a function of the independent variables.
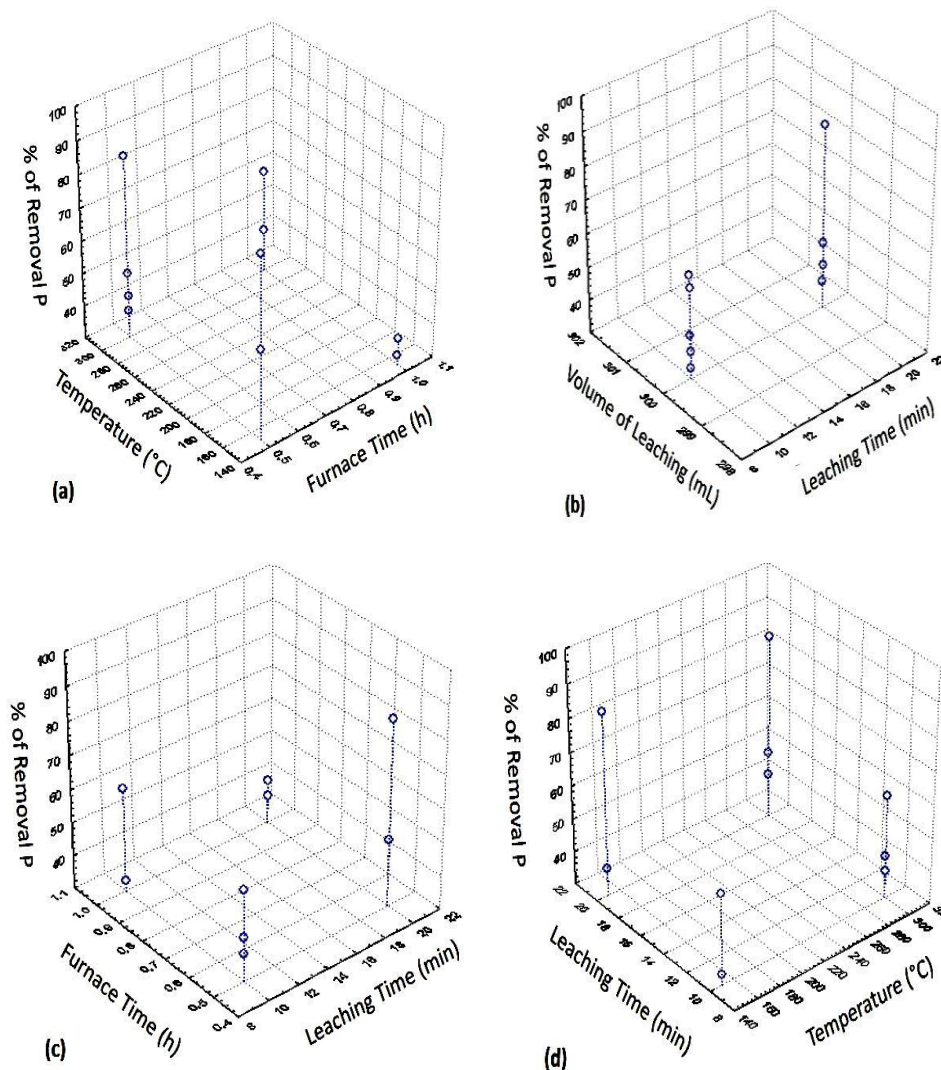

Figure 6. Response surface of the removal of phosphorus from the iron ore particles as a function of the independent variables.

It was possible to verify in the tests were carried out that the% of extraction of P and Fe varied in the eight tests respectively between 35.5 - 100% and 4.5 - 16.0%. It is observed here an excellent reduction in the extracted Fe contents and a maximization of the extraction of phosphorus reaching values of 100% of extraction. Due to the high extraction values, the statistical results showed little significance, with phosphorus as the dependent variable, showing the leaching time as the most important, but not yet reaching 90% of significance. For the evaluation of the selectivity, the statistical analysis was performed for the% of iron extraction and the results analyzed showed that the furnace time still has significance and consequently there is space for improvements in the route, since this is the last one in significance for phosphorus. Figure 7 shows the pareto diagrams indicating the significance of the removal variables of the element phosphorus and iron of iron ore particles.
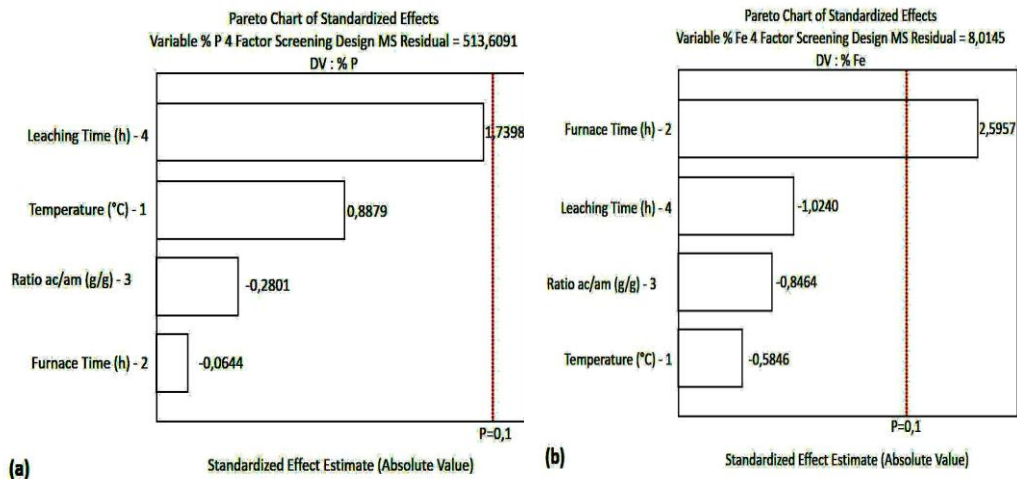
Figure 7 a. Pareto diagrams for the significance of the removal variables of the phosphorus element of the iron ore particles. Figure 7 b. Pareto diagrams for the significance of the iron element removal variables of the iron ore particles.

It was observed in Figure 7a that the main effects for the step of reducing the phosphorus content in the iron ore particles are in the leaching time and furnace temperature stages both having positive effects with increasing them. It was also observed that the sample acid ratio can be reduced as well as the time of the ore sample inside the furnace.

However, it is desirable that during the process of phosphorus reduction the process of reducing the iron content of the iron ore particles should not occur in order not to deplete iron ore for the steel industry.

Thus, in Figure 7 b, the main effects were observed for the step of reducing the iron content in the iron ore particles where it was possible to observe that the furnace time step is the main step for the occurrence of the reduction of the iron element of the particles of iron ore. Such a step has a positive effect with increasing thereof whereby increasing its value becomes undesirable for the process. It was also observed from the pareto diagram that the leaching time step as well as the acid sample rate and furnace temperature may be for a further reduction of the iron content of the iron ore particles because no reduction of the element iron it becomes feasible to increase them for the non-reduction of the iron element of the iron ore particles.

IV.   CONCLUSIONS

In order to evaluate the independent variables of the acid - leaching banking process to reduce the phosphorus content in samples of iron ore extracted from the iron quadrilateral region, Brazil, acid baking tests were carried out followed by aqueous leaching for the extraction of phosphorus contained in a sample of iron ore. Two stages of study were performed. In the first stage 5 process variables were analyzed and the water volume during the aqueous leaching was the most important variable of the process. In a second step, the objective was to optimize the other variables studied and it was verified that for results of high extractions of phosphorus for low iron extraction varoles furnace time seems to be the most important variable still showing optimization possibilities. by the results presented and by the statistical analysis performed, the chosen process parameters are:
1. Furnace temperature: 300OC;
2. Furnace time: 0.5 hour;
3. Sample acid ratio: 0.5;
4. Leaching time: 20 min
5. Leach volume 300 mL.

The assays were performed and the% extraction of P and Fe varied in the eight tests respectively of 61.17%, 85.28% and 100.00%. It is observed for the acid baking tests that of the five parameters evaluated only the volume of leaching agent during the leaching step is significant at a 90% confidence level, and its effect is, in fact, much greater when compared to the effects of variables studied.

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