

Evaluation of the Influence of Particle Size in the Acid Baking Process for the Reduction of Phosphorus Content in Iron Ore

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Demand for iron ore worldwide has been steadily increasing, thus implying an increase in the volume of mining resulting in the extraction of ores with higher levels of silicon, phosphorus and sulfur impurities. An extensively used alternative is to perform a pre-treatment of the particles in order to reach the acceptable phosphorus limit in iron ore before its use in steel production. This study aims at the evaluation of the heating process and decrease of the phosphorus content of the particles using microwave energy in iron ore samples percolated by sulfuric acid followed by the leaching technique as a feasible route for the remotion of the phosphorus content in iron ore particles. Using the scanning electron microscopy (SEM) and statistical analysis techniques, it was possible to observe the characteristics of the iron ore particles after treatment with microwave energy. The results indicated that the developed process is feasible. The results of the kinetic simulation contribute to a better understanding of the phenomena of heating using microwave energy and also to the development of new cleaner technologies aiming to improve the efficiency of the acid baking - leaching technique for the reduction of the phosphorus content in iron ore particles.

Keywords: Microwave, Leaching, Reduction of phosphorus, Iron ore.

1. Introduction

Iron ore is the most widely mined mineral resource in the Earth's crust, being the main raw material used in the steel industry. However, according to the Center for Management and Strategic Studies in its publication entitled "Steel Industry in Brazil 2010-2015", it was reported the expectation that plowed ores will have higher levels of phosphorus and alumina. Such ores, when used as raw material in the steel industry, cause serious damage due to mineralogy and the formation of compounds complexed with phosphorus, which causes significant impacts on the costs and waste generated. This justifies a constant search for alternative routes for the removal of the phosphorus element in iron ores. Currently, the process of removal of phosphorus in iron ore occurs after the melting of the ore, where oxygen is injected aiming at the formation of phosphates. The increasing phosphorus concentration in the ore particles also leads to an increase in the oxygen demand used in the process. Therefore, great efforts are made to reduce the concentration of the phosphorus element in the iron ore particles to acceptable levels, aiming at the reuse of the contaminated overburden, which brings environmental benefits such as the reduction of new deposits extraction. According to Omran et al.1 in order to improve oolitic iron with high phosphorus ores, many hydrometallurgical and pyrometallurgical processes were proposed. Although some of these methods have achieved the purpose of removing phosphorus, they suffer from some drawbacks. For example, the low dephosphorization efficiency, environmental pollution, relatively high cost, and low iron recovery content represent drawbacks which render these techniques impractical. The development of a successful and economical process to remove phosphorus from iron ores with high phosphorus content would significantly extend the reserves of these ores and the development of the iron and steel industries. According to the work of Young-shi et al.2 titled "Removal of phosphorus from iron ores by chemical leaching", it was reported that the casting process obtains great efficiency for the dephosphorization of the iron ore, however the process has disadvantages, such as high cost and high energy consumption (fossil fuel). This fact can be attributed to the way in which the element phosphorus can be found in iron ore particles. In some cases, the phosphorus element can be found in the ore particles complexed with

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goethite molecules, FeO(OH), as a solid solution³. A more plausible mechanism involving adsorption surface was proposed by Morris and Barbour^{4,5} and supported by Dukino⁶. It was suggested that before dehydration of hydrated iron in goethite, a surface hydroxyl group is replaced by a phosphate binder, as demonstrated in model shown in Figure 1.

In this sense, Gooden et al.⁷ reports that the distribution of phosphorus along the goethite crystals hinders the efficient use of physical separation techniques, thus requiring the use of chemical separation techniques. However, according to Young-shi et al.² the process of chemical leaching using alkaline solutions was not effective in dephosphorization. This fact occurs due to the reprecipitation of the phosphorus with other metallic ions released during the process. Another fact that makes it impossible for the chemical leaching to be used directly on the iron ore particles in nature can be explained by Figure 2, where the M3P species that indicates the presence of the goethite-phosphate complex demonstrated by Dukino et al.⁶ is presented and shown in Figure 1.

Figure 2 shows the phase diagram of iron ore in different compositions of Fe, O, Si and Al, where it shows the existence of the M3P complex in mass values of the element phosphorus below 0.4% at temperatures between 0 and 300°C. It is also observed that with the increase in temperature, there is an increase in the region where the presence of the M3P structure is not observed, showing that with the increase in temperature the complex goetite phosphorus is dissociated. the complex meeting was demonstrated by Dukino⁶ and presented in Figure 1.

Omran et al.¹ investigated the reduction of phosphorus in iron ore particles and indicated that the FTIR analysis showed that, after microwave radiation, chemical functional



Figure 1. Mechanism of phosphorus occurrence in goethite.



Figure 2. Phase diagram of iron ore with composition: Fe 60%, O 20%, Si 10%, Al 9.99%. Calculated using Thermocalc[®] software.

groups of phosphorus-containing minerals (fluorapatite and others) dissociate from the gangue due to the different interactions with the microwaves of the minerals and the gangue. High-resolution XPS analyses showed values for treated and untreated samples, showing that after the radiation a portion of Fe^{3+} was reduced to Fe^{2+} this means that after microwave radiation, iron oxide (hematite, Fe3+) has been transformed into a more magnetic phase Fe2+.

The experiments were carried out following the factorial planning methodology with central and axial points. This model involves statistically significant independent variables, taking into account (P <0.05). Multiple regressions were applied in the analysis of experimental data to predict the coefficients seen in the second-order polynomial model. Many researchers have investigated the influence of microwave pretreatment on magnetic separation and mineral surface characteristics. They concluded that the microwave treatment of ore particles is a potentially efficient technique in relation to energy consumption. Thus, additional effort to obtain lower phosphorus in the raw materials for the ironmaking process is an active and actual research field. However, it is emphasized that further decrease of the phosphorus content in the iron ore is desirable and an economical issue since the traditional route of reduction processes in the ironmaking does not favors the phosphorous removal. Moreover, for raw materials with such low concentrations of phosphorous, its remotion becomes more difficult with important cost and waste of materials associated (increase of energy and slag requirements). Thus, the reduction in phosphorus content from a state that requires higher energy and offers additional operational difficulties becomes an important issue to be addressed using alternative approaches. In this paper we propose one of these approaches using combined hydrothermal metallurgical process.

Therefore, in this work, the route of reduction of the phosphorus content by heating using microwaves energy in iron ore particles percolated by sulfuric acid, as well as its heating rate followed by the controlled leaching technique, is evaluated. Using the temperature controller, it was possible to observe the heating rate of the particles in the first 3 minutes of contact with the microwave energy. The fundamental feature of this route is the integration of a beneficiation sequence with heating the iron ore particles in the range of 100°C per minute to approximately 300°C, which makes the release of phosphorus possible. The iron ore particles are then added in a volume of water at room temperature, thereby causing a temperature drop at the rate of 100°C per second, where they will pass through the controlled leaching process.

2. Materials and Methods

2.1 Characterization of the iron ore

X-ray diffraction (XRD) and scanning electron microscopy (SEM) were performed for the characterization of samples treated and not treated with microwave energy.

The samples of iron ore originated in the *Quadrilátero Ferrifero* region of Minas Gerais, Brazil. All samples were comminuted in a bar mill at the facilities of the Mineral Technology Center - CETEM, generating particle size fractions smaller than 0.234mm



Figure 3. X-ray diffraction spectrum of the iron ore sample.

Table 1. Levels used in factorial planning.

Variables	-1.41	-1	0	1	+1.41
Time (min)	2	5	8	11	14
Granulometry (mm)	0.355	0.297	0.710	2.830	4.000

Figure 3 shows the X-ray diffraction spectrum of the iron ore used in this investigation and Table 1 shows the mineralogical composition of the iron ore sample.

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The Table 1 showed mineralogical composition of the iron ore sample (% by mass fraction). The obtained fractions were submitted in the powder form to X-ray diffraction analyses using the Rietveld method in parallel to scanning electron microscopy. The X-ray diffraction technique using the Rietveld method is based on the simulation of an entire diffractive profile starting from structural parameters of the component phases, allowing more information to be extracted from the diffractograms. The Rietveld method takes into account the overlap of the peaks of all the phases present and the contributions of the background noise. Hematite, Quartz and Goethite were the main phases identified by the X-ray diffraction method, where the absence of apatite and aluminosilicate compounds was observed. The chemical analysis was carried out using the inductively coupled plasma optical emission spectrometry method performed at CETEM. The phosphorus content in the ore sample was 346 mg/kg, corresponding to 0.0346%. Scanning electron microscopy analyses were carried out at Universidade Federal Fluminense - UFF.

For analysis of the acid baking-leaching process, a volume of 300 mL of water was used, which was added to a 500 mL beaker that served as a reactor. The particles were agitated with the aid of an IKA mechanical stirrer model RW20. After the reaction time was over, the mixture was vacuum filtered on Büchner's funnel and taken to the oven for drying at 40°C for 1 hour. All the samples were then sent for quantitative analysis of the phosphorus content, where the ultraviolet radiation emission in the visible spectrum (UV-VIS) measurement technique was used.

The calculation of the removal percentage is as follows:

$$\% = \frac{C_f - C_i}{C_i} .100$$
 (1)

Where c_f is the final concentration of the phosphorus element after the leaching process and c_o is the initial concentration of the phosphorus element prior to the leaching process.

2.2 Mechanism of emission and control of microwaves

A conventional microwave reactor (Model: PMS-24) with 1200W of power and emitting microwave radiation with a frequency of 2450MHz was used to treat the ore fines. In the conventional microwave reactor, the microwaves are generated through a device called magnetron, located in the superior part to the right of the reactor. Thus, the iron ore sample was placed in the lower left part of the equipment, where it was observed to be the place of greatest incidence of microwave radiation. The inside of the reactor had dimensions of 260mm (height), 460mm (width) and 320.3mm (length). Figure 4 is presented the schematic drawing of the microwave apparatus and temperature controller.

Figure 4 shows the schematic drawing of the microwave device and temperature controller where the temperature controller was used to monitor the heating rate of 50g of iron ore particles in different granulometries percolated with 25g of sulfuric acid in the first 3 minutes of contact with the microwave energy. The mixture was then added to a beaker containing 300 ml of water, with the mixture being stirred for 30 minutes at 620 rpm. Figure 5 shows the schematic drawing of the leach tank in water.

It has been suggested that the microwave heating process can accumulate internal energy in the materials. In this study, it was found that the samples accumulate enough energy to promote cracking during quenching, and also that the increase of the sample mass allowed the required heating time to decrease. According to Haque et al.⁸ the microwave energy provides a possible mechanism to induce rupture between the minerals of value in the ore and the gangue or the host rock. This fact can be explained by the differential in the absorption of the energy of the microwaves and the thermal differences given by the coefficients of expansion between the various mineral phases in the iron ore particles.

According to Walkiewicz et al.⁹ the rapid heating of the ore occurs due to the presence of the high energy of the microwaves, which can be absorbed in minerals that contain high iron content. On the other hand, the matrix with a greater amount of gangue of difficult absorption of microwave energy can generate large thermal gradients that allow tension to occur in the particle.

This thermal stress causes microfractures along the borders of the mineral grains, and as a result, the sample of iron ore becomes more favorable for grinding. Kingman et al.¹⁰ demonstrated that the fracture in samples of iron ore caused by microwave treatment is a function of the electric field strength. Numerical simulations of the heating of pyrite-containing samples showed that the rapid heating occurs with microwave contact in a transparent matrix and that the sample was fractured due to temperature gradients across the grain boundaries. The process of reducing the phosphorus content using microwave energy in acid baking followed by leaching is shown in Figure 6.



Figure 4. Schematic drawing of the microwave apparatus and temperature controller. Where: 1 Microwave transmitter; 2 percolation of sulfuric acid in the iron ore particles; 3 temperature controller.



Figure 5. Schematic drawing of the leaching tank in water; Where: 4 leaching tank having water as a leaching agent and 5 mechanical stirrer at the speed of 620 rpm.

Figure 6 shows the process of reduction of phosphorus content using microwave energy in acid baking followed by leaching, where it is possible to observe that chemical and mineralogical analyses of the samples are carried out before and after the process.

For the evaluation of the acid baking process using microwave energy, the central composite rotational design (DCCR) was used to evaluate the influence of the independent variables, time and power of the microwave oven, during the interaction of the 50 g iron ore sample with an average particle size of 0.234 mm percolated by 25 g of concentrated sulfuric acid.

2.3 Evaluation statistic of the process

Using experimental planning based on statistical principles researchers can extract from the system under study as much useful information as possible by doing a minimum number of experiments. In its applications, Haaland et al.11 indicated, for choice of factors, the factorials 2^k or 2^{k-p} and for a better analysis of response surfaces, the centered face cube design is used (the DCC of $\alpha = 1$). The DCC is a design that was developed with the objective of making it possible to find the point of maximum or minimum response, in tests with k factors, each with five levels, and with a number of points lower than other types of designs used, for example, the 3k factorial. However when it comes to the total of stationary points, using the parametric test for difference of proportion, the proportions of maximum in each interval of experimental coefficient were found to be significantly different, mainly in relation to the rotational DCC, that is, the rotational DCC always obtained a greater number of experiments in which the maximum points were between levels -1 and 1.

Table 2 presents the values used in the factorial planning within each experimental coefficient range and also within the levels (-1, 1), and outside these levels.

The values presented in Table 2 were stipulated considering the mean between the upper and lower axial values. Table 3 presents the results of interactions between the independent variables followed by the surface response.

Among the standard designs, the Central Composite Design (DCC) is considered an optimal design. According to Atkinson and Donev¹² the composite designs belong to a family of efficient designs, which require few tests for their performance. As for efficiency measures, Donev and Atkinson and Lucas^{12,13} show that the DCC behaves well



Figure 6. Process route for the remotion of phosphorus content using microwave energy using acid baking followed by leaching.

according to the optimization criteria D and G. In addition, it has interesting characteristics for the search for the point that gives the optimal answer, which are: a smaller number of treatments in relation to the complete factorials and can be performed sequentially, in order to move towards the optimization of the system, that is, through the execution of a part of the experiment (applying 2^k factorial experiments or first order fraction-experiment) through the "steepest ascent technique".

3. Results and Discussion

According to Graham¹⁴ calcination of iron ore causes dehydration of goethite into hematite, releasing phosphorus in solution as an acid soluble compound. The equilibrium composition of sulfuric acid as a function of temperature using the HSC Chemistry TM 7.1 equilibration modulus can be seen in Figure 7, where it shows that the sulfuric acid solution is decomposed at temperatures above 200°C.

As can be seen in Figure 7, the decomposition of sulfuric acid is insignificant at temperatures below 250 °C. In this work, the samples were treated with different levels of time and power presented by the microwave oven and under air atmosphere. When the residence time was reached, delimited by the factorial design for the sample in the reactor, treatment interruption occurred, and the sample was then added in a reactor containing 500 mL of water at room temperature. After insertion, the formations presented in Figures 8A and 8B and 8C were observed, where, through x-ray dispersion analysis, it was also possible to present the different elements found on the surface of the iron ore particle, as well as the distribution of the element phosphorus throughout the particle. Figures 8A, B and C show the images of the ore fines with a mean particle size of 4mm treated by microwave energy as well as their composition and phosphorus distribution graphs.

Figure 8 (A) shows the formation of fractures in the iron ore particle with a mean particle size of 4 mm, using scanning electron microscopy where it is also possible to observe the place where the scanning originated from the electron beam occurred, where through their penetration into the particle surface it generates a dispersive energy variation of the electronic sub-layers of atoms being captured by detectors makes it possible to identify and quantify the elements present on that surface. So Figure 8 (B) shows the composition of the iron ore particle where the signal representative of the iron element with high intensity was observed, as well as the signal representative of some pollutants such as sulfur, silicon, aluminum, and phosphorus. Going against the previous statements Figure 8 (C) shows the graph representing the phosphorus distribution on the surface of the iron ore particle, where it was possible to observe the homogeneous profile of the phosphorus concentration reaching values of up to 9%, however, there was a large number of values in percentages below 3%. The analysis of EDS obtained in the scanning electron microscope is an extremely punctual analysis, the concentration of phosphorus can vary at different points on the surface of the particle, thus being able to detect lower or higher concentrations of the phosphorus element in different punctual surface locations, indicating the formation of constituents rich in phosphorous. As argued by Clever et al.5

 Table 2. Mineralogical composition of the iron ore sample (% by mass fraction).

MINERAL	MASS FRACTION, %		
HEMATITE (Fe_2O_3) (1)	72.89		
KAOLINITE $[Al_2Si_2O_5(OH)_4]$ (2)	4.64		
QUARTZ (SiO_2) (3)	12.05		
GIBBSITE [Al(OH) ₃] (4)	3.18		
GOETHITA [FeO(OH)] (5)	7.25		

Table 3. Levels used in factorial planning

Test	Granulometry (mm)	P removal (%)	Time (min)
1	0.355	21.60	5
2	0.355	2.30	11
3	2.830	13.10	5
4	2.830	7.36	11
5	0.710	6.79	2
6	0.710	11.72	14
7	0.297	93.48	8
8	4.000	18.41	8
9	0.710	15.22	8



Figure 7. Composition of sulfuric acid at the equilibrium as a function of temperature using the HSC Chemistry[®] 7.1 equilibration modulus (sulfuric acid at 1 kmol, total pressure: 1 bar).

the great advantage of the EDS technique lies on the fact that the analysis is carried out from a small volume of material which allows punctual identification of the elements. Considering the interaction of the electron beam with the material, signals can be captured from volumes with linear dimensions around 1 µm. Ler and Stanforth¹⁶ suggest that phosphorus interacts with the surface of goethite through ternary adsorption and surface precipitation, in addition to the formation of a superficial complex. In this process, goethite dissolves providing iron ions for the solution, whose sites will be formed by hydroxy complexes with phosphates on the surface of goethite. These measurements proved that the phosphorous complexes are volumetrically distributed within the iron ore alternating high and low concentrations when scanning techniques are used to analyze. The bulk concentrations in the iron ore particle, however, are relatively low as indicated by the raw material's chemical analysis.

Figures 9A, B and C show the images of the ore fines with a mean particle size of 0.35 mm treated by microwave



Figure 8. Micrographs of the ore fines with mean particle size of 4 mm treated by microwave energy (A) graphs of particle surface composition (B) and distribution of phosphorus along the particle (C).

energy as well as their composition and phosphorus distribution graphs.

In Figure 9 (A), fracture formation in the iron ore particle with a mean particle size of 0.35 mm are presented through images generated by scanning electron microscopy where it is possible to observe the increase of porosity caused by the interaction of the largest surface of the particles with the generated microwaves and the place where the sweep originated from the electron beam occurred. So the Figure 9 (B) shows the composition of the iron ore particle, where the increase of the signal intensity representative of the iron element was observed, as well as the presence of representative signals of some contaminants such as sulfur, silicon, aluminum, and phosphorus. Thus the Figure 9 (C) shows the graph of the distribution of the phosphorus element on the surface of the iron ore particle, where it was possible to observe lower concentration values of the phosphorus element on the surface of the iron ore particle, thus indicating a higher reduction of phosphorus concentration on the surface of the iron ore particle. Still according to Figure 9 (C), heterogeneity of the presented profile of the phosphorus element concentration of the iron ore surface was observed, thus indicating a

possible formation of fractures and porosities in the iron ore particle in average grain size values of 0.35mm, under a power of 1200W of emission of microwaves. Thus, the evidence presented through the macrostructural analysis leads to the conclusion that microwave radiation induces rapid heating, which generates cracks in the ore, resulting in a possible weakening of the particles. Going back to what was previously reported in the work by Roy and Agrawal¹⁷, it was indicated that the interaction of the magnetic field with some materials contributes greatly in the heating rate when compared to the materials exposed to the electric field. According to Haque⁸, the maximum temperature reached occurs due to the increase of the magnetic saturation and the remaining magnetization of the samples of iron ore.

When the 2450 MHz frequency is used, the alignment of the molecules and their return to the disordered state occurs 4.9×10^9 times per second, which results in rapid and efficient heating. However, heating due to this process depends on the relaxation time of the sample, is defined as the time required to totally order and clutter 63% of the sample¹⁷. Still according to Haque⁸, the microwave energy provides a possible mechanism to induce rupture between



Figure 9. Micrographs of ore fines with a mean particle size of 0.35 mm treated by microwave energy (A) graphs of particle surface composition (B) and distribution of phosphorus along the particle (C).

the minerals of value in the ore and the gangue, or host rock. This fact can be explained by the differential in the absorption of the energy of the microwaves and the thermal differences given by the coefficients of expansion between the various mineral phases in the iron ore particles. Huang et al.¹⁸ used microwave heating prior to the processing of oolitic iron ore from Yichang, China. The ore was ground to <74 µm, aiming to achieve the release of the hematite from the gangue. Reducers used included residual iron, coke and coal dust, and the reduced product was tested using magnetic separation or reverse flotation. The ideal temperature for ore reduction prior to magnetic separation was 500°C. Jin-hong et al.¹⁹ showed how microwave treatment in a lot of Chinese oolitic iron ore produced many intergranular fractures under appropriate frequencies and potencies. After the treatment with microwaves, the oolitic iron ore was ground, presenting a 20-30% increase in the release of hematite and gangue minerals due to the fact that hematite responds to microwave heating, but this fact did not happen with quartz of the gangue.

Omran et al.¹ in their study found that microwave treatment in a batch of oolitic iron ore from eastern Aswan,

Egypt, increased the properties of weakly magnetic minerals, altering them to stronger magnetic phases. Recovery using a magnetic separator in iron ore tailings increased from 39.54% in untreated iron ore to 97.95% in samples of microwaved iron ore using 1T force magnetic field separators. Treatment by microwave 900 W and 2.45 GHz by 90s raised the temperature of the iron ore particles from 22 to 684 °C. Subsequent work by Omran et al.1 used MEE to estimate and compare the percentages of intergranular fractures using microwave radiation at 900 W and 2.45 GHz with conventional heating at similar temperatures using a furnace. At temperatures of approximately 600°C, microwaved ore contained > 80% intergranular fractures for energy consumption of 0.02 kWh, compared with ~30% intergranular fractures for conventional heating using 5.33 kWh. The milling tests indicated that iron ore treated with microwave ground more easily compared to the treated iron ore in a conventional kiln. This was attributed to the greater amount of intergranular fractures that formed in the oolitic iron ore after treatment with microwave radiation.

According to Ownran et al.¹ the main disadvantage of thermally assisted release is the fact that the balance of energy input required to reduce the force contained in the ore is greater than the reduction in milling energy. With microwave assisted release, however, the input of energy required to induce significant damage to the ore is greatly reduced when compared to the energy input required for the thermally assisted conventional release. There is a substantial difference between the amount of energy consumed during the treatments using microwave and conventional oven. For example, according to Omran et al.¹ during conventional heating at 600°C for 1 h, approximately 5.33 kWh of energy were required to increase the grinding capacity of iron ore from 46.60% to 50.80%, and the use of microwave treatment required approximately 0.0237 kWh of energy to increase grinding from 46.60% to 59.76% (microwave energy uses 224 times less energy than a conventional oven). This large difference in the amount of energy consumption between the use of microwaves and the conventional oven occurred due to microwave heating of the "responsive" or "active" phases; therefore, no energy is wasted during heating the entire sample.

Another important factor is the time of the contact particles under the experimental conditions. The time spent with microwave treatment is only a few seconds. Chen et al.3 investigated the influence of microwave pretreatment on magnetic separation and surface characteristics of ilmenite ores. Chen et al.3 concluded that microwave treatment of ilmenite ore is a potentially efficient pre-treatment technique for magnetic separation with low energy consumption. The influence of microwave irradiation on the grinding of gold ores was investigated. It was concluded that the microwave-assisted grinding produced good results, particularly for grinding characteristics. Therefore, a more detailed analysis of the heating rate of the iron ore particles in different sizes is important. Figure 10 shows the heating rate of the iron ore particles in the range of 0-3min in different sizes and the amount of energy absorbed by the iron ore particles.

A relevant factor for the reduction of the phosphorus content in iron ore particles is indicated in Figure 2, where the temperature value 300 °C is presented to reduce the

phosphorus content. However, in Figure 10 the heating rate of the iron ore particles in the range of 0 to 3 minutes in different sizes is shown, where it was observed that in the size-values of 0.355 mm the highest temperature value was presented. It was also observed in Figure 10 that the energy absorption accompanies the temperature variation, and it is possible to affirm that the temperature rate of the particles has values similar to those presented by the hematite and magnetite minerals. Thus, it becomes possible to observe that the high interaction of the magnetite molecules generates an alignment effect in relation to the magnetic field generated by the microwaves. However, the effect of non-interaction generated by kaolinite makes it possible to explain the friction heating in the iron ore particle. The results of the present work are in agreement with the results presented by Haque et al.8 in which magnetite, hematite, aluminosilicate and silica samples were tested, being magnetite considered to be hyperactive, hematite being active, and silica being considered inactive. The extent of microwave heating is also dependent on the size of the material, in addition, materials with low loss or insulation materials can be heated with microwave heat facilitators, such as magnetite, silicon, carbide or carbon. The microwave energy first heats the facilitator, which subsequently heats the insulation material or material with low loss. Using the properties mentioned above, Tang et al.²⁰ developed their research aiming the pretreatment of ore fines with microwave energy to reduce the phosphorus content after the process of reduction and melting of the iron ore particles. In this study, a microwave power of 450 W was used for 4 minutes, and a pronounced effect was obtained on gaseous reduction in high phosphorus ore fines. With the temperature of 1273 K being used in a period of 1.5 hours to 2 hours and with CO or H₂ as the reducing agent, the treated ore fines were reduced to metallization values in the range of 85-92%. Research by Roy and Agrawal¹⁷ showed that the interaction of the magnetic field with some materials contributes greatly to the heating values when compared to the materials exposed to the electric field. Figure 11 shows



Figure 10. Heating rate and amount of energy absorbed by iron ore particles in the range of 0 to 3 minutes for different mean particle sizes.

the percentage reduction profile of the phosphorus as a function of the contact time with the microwave energy.

Figure 11 shows the profile of the percentage reduction in phosphorus content as a function of the time of contact with microwave energy, where it was possible to observe that the highest percentage value of reduction of phosphorus and content occurred at the contact time of 8 minutes. It was also possible to observe that in time values greater than 8 minutes the reduction of the phosphorus content did not reach the value of 50%. Figure 12 shows the percentage reduction profile of the phosphorus content as a function of the mean particle size of the iron ore particles.

Figure 12 shows the profile of the reduction percentage of the phosphorus content as a function of the average particle size of the iron ore particles, where it was possible to observe that the highest percentage value of reduction of the content and phosphorus occurred in the particles with granulometric values below 0.4mm. It was also possible to observe that, in higher particle sizes, the reduction of the phosphorus content was found to be less than 50%. In Figure 13 different percentages of removal of the phosphorus element in particles with different granulometric variations are presented.

Figure 13 shows the contours of iso-values of the percent reduction of phosphorus content as a function of the sample's mean particle size and the contact time of the mixture of acid and ore with the microwave energy. It is observed that high values of removal can be obtained both by combinations of higher granulometric values and longer contact times, as well as by lower sizing values and shorter contact times. It can be inferred that chemical equilibrium could occur between the phosphorus removed from the iron ore and the formation of phosphoric acid in the solution, mainly for longer times. High percentages of phosphorus removal were found for 6-10 min times, in granulometric values less than 0.5 micrometers, indicating a possible increase in the phosphorus saturation rate in solution for lower particle sizes. This indicates that with the increase of the contact surface between the acid and iron ore mixture, an increase in the rate of reduction of the phosphorus content of the particles occurs, which indicates that the chemical control kinetics favors the reduction of the phosphorus content by the acid baking process with microwaves.

The results presented and discussed in this paper are in accordance with those reported by Silva et al.²¹⁻²³ and Silva²³, where it was observed that after the pretreatment with



Figure 11. Profile of the percentage of decrease of phosphorus content as a function of contact time with microwave energy.



Figure 12. Profile of percentage reduction of phosphorus content as a function of the mean particle size of iron ore particles.



Figure 13. Different percentages of removal of the phosphorus element as a function of the granulometric variation and the contact time of the iron ore particles.

the microwave energy, the same decrease in the tendency of the diffusional control in the iron ore particles to the particles of the same granulometry without the occurrence of pretreatment²³. This fact demonstrates that with the decrease of the mean value of granulometry, also occurs the decrease of the diffusional control. It was also demonstrated that the pre-treatment process with microwaves can generate fractures in the iron ore particles, thus reducing the tendency to diffusional control in particles with lower particle sizes. Yong-shi et al.² reported that sulfuric acid removed phosphorus from iron ore particles more efficiently in 20 min of leaching, with lower mean particle size.

4. Conclusion

In order to evaluate the profile of the removal of the phosphorus element in the iron ore, as well as the inherent advantages to the process of heating the iron ore in different sizes, a statistical modeling and thermodynamic analysis were elaborated, evaluating the best conditions for the remotion of the phosphorus content in the iron ore particles as well as the evaluation of the energy absorbed by the iron ore samples during the leaching stage. For that, samples percolated with sulfuric acid in different values of time and granulometry were tested. The following conclusions were drawn:

- The increase in temperature and the absorption of microwave energy was observed in grain sizes of 0.355mm, thus demonstrating an interaction between contact surface increase and density of active and inactive minerals for interaction with microwave energy.
- The optimum granulometry for the phosphorus removal process was 0.297 mm, where the iron ore sample deposition process was observed in lower and upper granulometry at the bottom of the reactor.
- The time observed for the best rate of removal of phosphorus in iron ore particles through the leaching process was 8 minutes, where after the

elapsed time, a low phosphorus reduction rate in the ore sample was observed.

- The process of phosphorus removal using acid baking occurs in the first 8 minutes, being disadvantaged by the increase of the contact time of the iron ore with the microwave energy.
- Loss of iron during acid leaching can be considered insignificant, being less than 0.4%.
- The low acid consumption was considered an important factor for the viability of the process, followed by the possibility of recycling of the sulfuric acid solution. It can even be incorporated in the leaching of iron ore, making the process of dephosphorization even more economical.

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