

# REVISITING PHOSPHATE SEPARATION FROM IRON ORES<sup>1</sup>

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## **Abstract**

Phosphorous is a major contaminant for the vast majority of uses of iron ores, especially all related to iron making. It is found in a variety of forms from separate phosphate minerals to intimate association with iron hydroxide phases, specifically with goethite. It may be also found as strongly adsorbed phosphate anions onto iron and manganese bearing minerals, not necessarily as an individual mineral phase. Different forms of association will lead to processing routes peculiar to each situation. When phosphate minerals can be traced as the major source of phosphorus, physical separation methods are feasible. The phosphorous removal of such ores can be normally carried through magnetic separation and flotation. The Brazilian iron ores with singular phosphorous mineral associations derives predominately from weathered deposits or associated to local intrusive rocks. In the present work a general flowsheet incorporating flotation and magnetic separation to remove phosphorus from iron ores is presented. The selection of proper beneficiation routes based upon mineral characterization is discussed and examples are provided. When flotation is used in reverse flotation circuits where the phosphate mineral represent the froth phase the selection of chemicals has to bear in mind downstream unit processes that may be affected by the reagents. The potential application of hydrometallurgical processes in the cases where mineral liberation is not feasible is also discussed.

**Key words:** Iron ore; Flotation; Phosphorous.

## **REVISITANDO A SEPARAÇÃO DE FOSFATOS EM MINÉRIOS DE FERRO**

### **Resumo**

O fósforo é um dos principais contaminantes para a grande maioria dos usos de minérios de ferro, especialmente durante a produção de gusa ou ferro de redução direta. O fósforo pode ser encontrado em uma grande variedade de formas em minérios de ferro, desde minerais isolados de fosfato e associado intimamente com hidróxidos de ferro especialmente a goethita formando solução sólida através da troca de íons OH<sup>-</sup> por fosfato. Ele pode ser encontrado também na forma de ânions fosfato fortemente adsorvidos nos minerais associados de ferro e manganês. As diferentes formas de associação do fósforo podem levar a rotas de processo peculiares a cada tipo de associação. Quando os minerais de fósforo podem ser definidos como a mais importante fonte de fósforo, métodos físicos de separação podem ser viabilizados. A remoção do fósforo de minérios de ferro pode ser normalmente realizada através de separação magnética e flotação. Os minérios brasileiros de ferro com associações específicas com minerais de fósforo derivam predominantemente de depósitos intemperizados ou associados a rochas intrusivas localmente. No presente trabalho é mostrado um fluxograma genérico incorporando a separação magnética e flotação para remoção dos minerais de fósforo. A seleção de rotas de processo adequadas baseadas em caracterizações mineralógicas é também discutida. Quando a flotação é usada em circuitos reversos onde o mineral de fósforo está presente na espuma, a seleção de reagentes tem de considerar os processos unitários subsequentes que podem ser afetados por esses reagentes. O potencial de aplicação de processos hidrometalúrgicos nos casos onde não é possível a liberação dos minerais é também discutido.

**Palavras-chave:** Minério de ferro; Flotação; Fósforo.

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## 1 INTRODUCTION

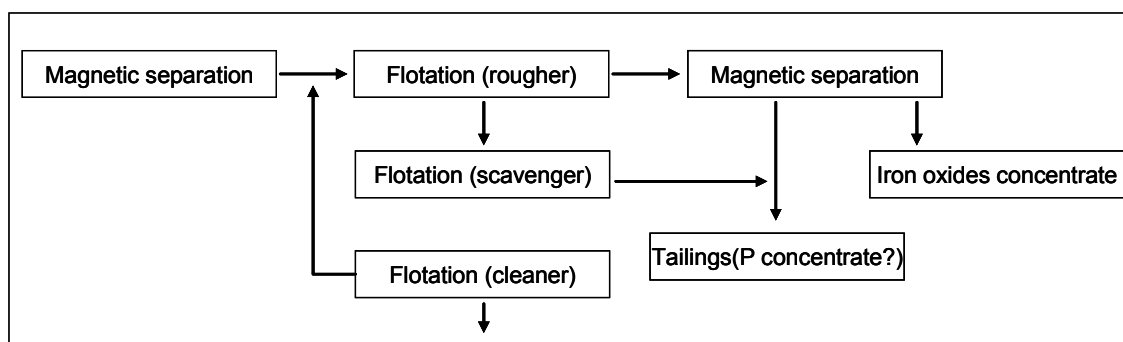
The association of the phosphorous in Brazilian iron ores has been characterized several times by various researchers as intrinsic to the crystalline structure of the iron minerals and particularly in the goethite and for this reason it is impossible the phosphorous separation through flotation which is the most common method of fines beneficiation. Although acid leaching techniques have not been currently viable, the application of acid leaching techniques of materials thermally treated can be efficient in these cases for the phosphorous removal contained in the structures of iron minerals. On the other hand, in certain types of not weathered iron ore deposits the phosphorous removal is normally carried through magnetic separation and flotation. The most prominent references in the world are the mines of Kiruna-Sweden, Hercules-Mexico and Chador Malu-Iran where the apatite is selectively floated with anionic and amphoteric reagents after magnetic separation of most iron minerals. The Iron Ore Quadrangle of Minas Gerais presents mineralization originated by supergenic enrichment processes that generated rich itabirites with iron contents normally higher than 60%. However, the fluids generated in the weathered events carried in their solution some deleterious elements being the phosphorous among these elements (COELHO et al., 1999). The presence of phosphorous minerals of the type found in phosphorites like apatite can be detected however (KOKAL, 1990). Morris (1985) considers that the main iron ore deposits of the world had been formed entirely or initially by supergenic enrichment process. The supergenic models include the residual concentration and the enrichment through the leaching of gangue with oxidation and hydration of primary iron minerals, being possible the occurrence of a posterior metamorphism. The primary source of the phosphorous in the iron ore deposits would be the mafic intrusive rocks and, in some cases, the intrusive granite bodies. In the case of the iron quadrangle and other deposits in the north of Brazil the origin of the phosphorous is the result of the weathering of intrusive rocks that contain apatite. The weathering makes the phosphorous available in such a way that in the rainy season it percolates in the iron formation. In the iron formations the phosphorous has few possibilities to form a phosphate due to absence of free cations, remaining as an adsorbed anionic phase in the microporous of the goethite. In some cases the association of the phosphorous with aluminum is possible, forming the wavellite mineral  $[Al_3(PO_4)_2(OH,F)_3 \cdot 5H_2O]$  (COELHO et al., 1999). A hypothesis for the preferential occurrence of the phosphorous intimately associated to the goethite in comparison with the hematite is related to the goethite capacity of accepting the phosphorous in solid solution where the crystal charges can be balanced through the exchange of some hydroxyls by phosphate ions whereas the phosphorous associated with the hematite depends probably on vacancies in the crystalline structure of the hematite (GRAHAM, 1973). In the case of the goethite the adsorption of the phosphorous is initially fast, occurring together with the crystallization of the goethite, followed by a deceleration due to the diffusion in the goethite microporous where the adsorption is slower. The precipitation of the goethite instantaneously absorbs great amounts of phosphate in solution (TORRENT, 1991). The laterization related to the weathering can be considered as responsible by the appearing of various phosphates like the crandalite, gorceixite, variscite and aluminum phosphates in the iron ore deposits. As an example of the different ways phosphorous can occur in the iron ore it could be observed in a iron deposit located

in the Bahia state the presence of the following secondary phosphates: frondelite  $[\text{Mn}^{2+}\text{Fe}^{3+}_4(\text{PO}_4)_3(5\text{OH})]$ , strengite  $[\text{Fe}^{3+}(\text{PO}_4)\cdot 2(\text{H}_2\text{O})]$ , rockbridgeite  $[\text{Fe}^{2+}0.75\text{Mn}^{2+}0.25\text{Fe}^{3+}_4(\text{PO}_4)_3(5\text{OH})]$ , barrandite  $[(\text{Al},\text{Fe})\text{PO}_4\cdot 2\text{H}_2\text{O}]$  wavellite and variscite  $[\text{Al}(\text{PO}_4)\cdot 2(\text{H}_2\text{O})]$ . In the Carajas body N4E the phosphorous has as primary source the apatite and presents itself mainly in the adsorbed anionic form in goethite and in a small portion, as a secondary phosphate - senegalite  $[\text{Al}_3(\text{PO}_4)(\text{OH})\cdot \text{H}_2\text{O}]$ . The senegalite is a hydrated aluminum phosphate that generally occurs in the oxidation zones of magnetite iron ore deposits and frequently is associated to other phosphates like the turquoise, augelite, wavellite and crandalite. The senegalite crystals are tabular and elongated with well defined prismatic termination. The turquoise mineral  $[\text{Cu}(\text{Al}, \text{Fe}^{3+})_6[(\text{OH})_4(\text{PO}_4)_2]_2\cdot 4\text{H}_2\text{O}]$  is a secondary phosphate that rarely form crystals and when this occurs the crystals are short prismatic ones. The wavellite also is a secondary phosphate, and rarely form crystals. When wavellite crystals occur they present in the form of esferolitic globular aggregates in the colors white, yellow, green and brown. Another common mineral associate to iron ores is the gorceixite  $[\text{BaAl}_3[\text{PO}_4]_2(\text{OH})_5\cdot \text{H}_2\text{O}]$  that occurs both in the iron quadrangle and in some iron ores in the north of Brazil. Eventually the gorceixite occurs in great amount and already liberated in the millimeter size range.

## 2 MAGNETIC SEPARATION , FLOTATION AND LEACHING

### 2.1 Main Industrial Plants

Figure 1 shows a generic flowsheet, which considering some minor modifications, is used in the mines of Kiruna-Sweden, Hercules-Mexico and Chador Malu-Iran for the selective separation of apatite from iron oxides. The general approach is firstly the magnetic separation of the iron minerals followed by a flotation stage of the phosphorous minerals.



**Figure 1.** Generic flowsheet for the magnetic separation and flotation of apatite.

The Chador Malu mine on Iran has its ROM made up of iron minerals and apatite. After grinding for liberation the ore is submitted to several stages of low- and high-intensity magnetic separation and a direct flotation stage for apatite leading to a two different concentrates. The iron ore concentrate has 68% of iron content and 0.045% phosphorus. The apatite concentrate achieves a minimum of 33%  $\text{P}_2\text{O}_5$ . The plant has a nominal capacity of 7.1 million t/year (). The LKAB Kiruna concentrator has also a first step of magnetic separation followed by the direct flotation of apatite. The rougher flotation tailings go to another magnetic separation step before being discarded as final tailings. In the Hercules mine the magnetic separation is made with a Ferrous Wheel separator. The main collector reagents industrially used for the

phosphorous minerals flotation during iron ore treatment are anionic surfactants derived from fatty acids, sarcosinates, hydroximates, phosphoric ester and eventually a mixing of some of these collectors. Sodium silicate and starch are frequently utilized as the iron minerals depressants. A complete list of phosphate collectors and depressants can be found in the work of Sis and Chander (2003).

## 2.2 Flotation

Rabelo (1994) made several bench scale flotation tests utilizing anionic and amphoteric collectors with an iron ore sample from the Alegria mine, Samarco. The anionic collectors used were the oleic acid and the commercial reagent Flotigam HF3594 (a modified carboxylic acid) developed for the phosphate flotation. All results obtained with the use of oleic acid showed that the phosphorous flotability increased in conjunction with the iron oxides flotability. The addition of starch as a depressant decreased the iron oxides flotability but the phosphorous is intimately connected with the iron minerals and the selectivity could not be attained. The results reached with the commercial collector HF 3594 were similar to those obtained with the acid oleic flotation. The phosphate of Western Austrália Mt. Weld was investigated by Gong (GONG *et al*, 1992) for the production of a high grade phosphate concentrate. The ore is comprised mainly by hematite, goethite, apatite and ilmenite with a P<sub>2</sub>O<sub>5</sub> feed grade of 22% and an iron content of 27%. Flotation tests carried out with the ore attained the best results with the use of sodium silicate as depressant for the iron oxides and a fatty acid as the collector for the apatite. The final phosphate concentrate showed a P<sub>2</sub>O<sub>5</sub> content of 38.6% and 1.9% of Fe. Close to 90% of the hematite present in the feed was rejected to the tailings showing the high selectivity obtained with the use of the sodium silicate for the depression of the iron oxides. The maximum selectivity was reached between pH 9.5 and 10. Fenwei Su *et al.*(1998) also confirmed the sodium silicate positive action which decreased the phosphorous content in the magnetite concentrate from Kiruna mine, LKAB. The FENWEI SU work evaluated the influence of temperature during apatite flotation with a fatty acid and sodium silicate. The beneficial effects of a higher temperature in the flotation pulp were attributed to an enhancement in the reagents chemical properties as well as to the removal of slimes from the minerals surface. Subramanian *et al.* (2002) studied the apatite and magnetite dispersion from some samples of LKAB. The work was made with the help of zeta potential measurements when several reagents were added to the pulp (sodium silicate, sodium tripolifosfate, sodium hexametafosfate and lignin sulfonate). Phosphorous contents less than 0.02% were achieved in the magnetite concentrate and the phosphorous recovery to the apatite concentrate was higher with the sodium silicate. It was also observed that the magnetite concentrate fraction of minus 10µm was responsible for the most part of the phosphorous contamination. Most probably the very fine particles aggregate due to attractive hydrophobic forces. A high intensity conditioning would allow for the disaggregation of the particles making feasible the flotation. High dispersant dosages were prejudicial to the phosphorous removal. This fact may be due to the increased depression of the minerals or the activation of the iron oxides flotation as demonstrated in the work of Sun (KEJIN SUN *et al*, 2002) with the ore from Meishan Iron Ore, China .

### 2.3 Leaching - When There Is No Liberation at All

Many researchers proposed and tested alkali-leaching and acid-leaching for the dephosphorization of iron ores. The tested reagents normally considered are sodium hydroxide, sulfuric acid, hydrochloric and nitric acids. SHI (JIN YONG-SHI et al, 2006) showed that phosphorus occurring as apatite could be removed by alkali-leaching, but those occurring in the iron oxides could not be removed. Sulfuric acid was alleged to be the most effective acid. A total 91.61% phosphorus removal was attained with 1% sulfuric acid after leaching for 20 min at room temperature. Iron loss during acid-leaching was negligible, which was less than 0.25%. The pH value of solution after leaching with 1% sulfuric acid was about 0.86, which means acid would not be exhausted during the process and it could be recycled, and the recycle of sulfuric acid solution would make the dephosphorization process more economical. Cheng (C.Y. CHENG et al, 1999) based on the previous research made by many researchers observed that for the western Australian iron ore: roasting is necessary, leaching with mineral acid is effective after roasting and the use of minimum acid concentration and cheap mineral acid makes the process economically viable. CHENG tested a sample from Pilbara region of Western Australia. The process used sulfuric acid and was very effective in terms of phosphorus extraction. Over 60-70% of the phosphorus was extracted. Figure 2 shows the phosphorus reduction during leaching. The lump ore sample and the two pellet samples were batch roasted separately in an electric furnace for one hour. The furnace was heated from room temperature to 1250°C in 6 hours. After holding at that temperature for one hour, the furnace was cooled from to room temperature in 17 hours. The leach solution and ore were heated separately to 60°C and the leaching started. The phosphorus feed content of 0.126% in the three samples was successfully reduced, after 5 hours leaching, from 0.13% to 0.044%, 0.055% and 0.042%, respectively.

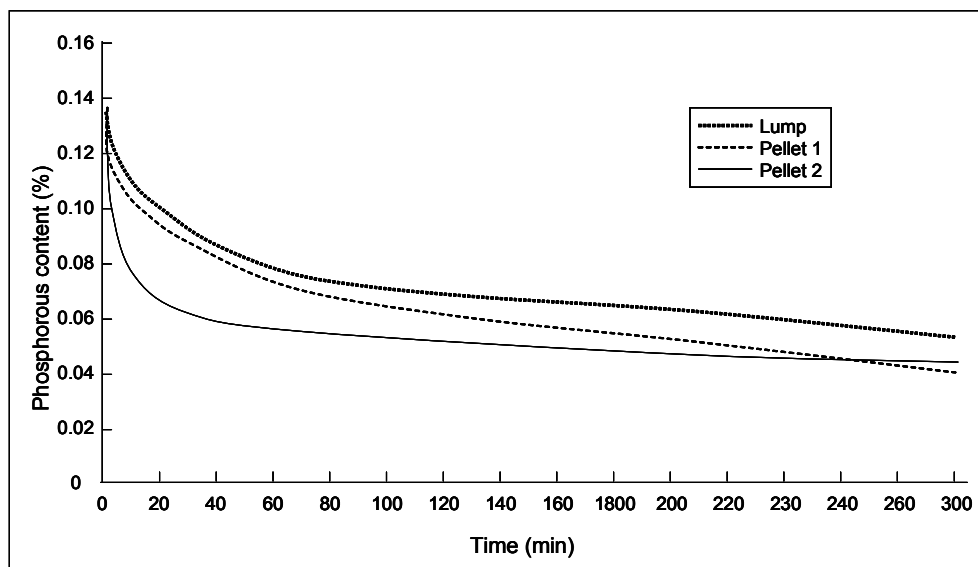


Figure 2. Phosphorous reduction during leaching with sulphuric acid.

The iron loss in the lump ore was the highest: about 0.06% iron loss in the first 10 minutes and 0.16% after 5 hours of leaching. The iron loss in the two pellet samples was negligible.

## SOME MINERALOGICAL ILLUSTRATIONS – SAMPLES FROM THE IRON QUADRANGLE (MINAS GERAIS) AND FROM A NORTHERN STATE (BRASIL)

Two samples representing the iron quadrangle and a Northern Brazilian state were investigated in the current work. SEM/EDS and x-ray diffraction were used to study the samples.

### 3.1 Sample from the Iron Quadrangle

The sample CCQ, depicted in Figure 3, was obtained removing the surface material from a block after crushing the initial sample. The EDS analysis shows that the material is an aluminum phosphate (dark particles in the SEM image). The copper content indicates the presence of another phosphate mineral: the turquoise. The “white” particles are iron minerals that contaminated the sample during the collecting. The size of phosphate mineral particles gives an indirect suggestion of easy liberation of the minerals in the size range of 0.15 to 0.1 mm

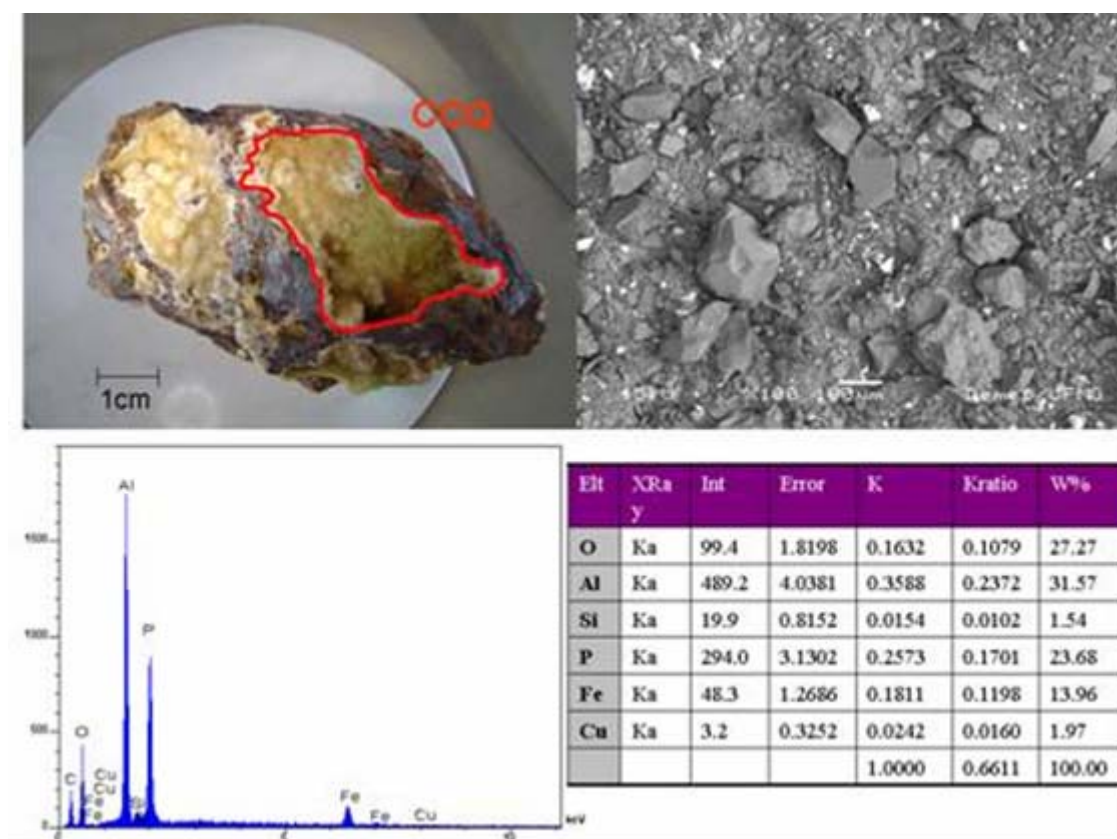


Figure 3. SEM/EDS from the CCQ sample.

The sample LL1, presented in the Figure 4, is a small portion of the sample CCQ that was entirely (one piece) submitted to SEM/EDS study. The reason was to verify the specific crystals shapes. The tabular and elongated crystals and the EDS analysis indicate that the mineral is the senegalite.

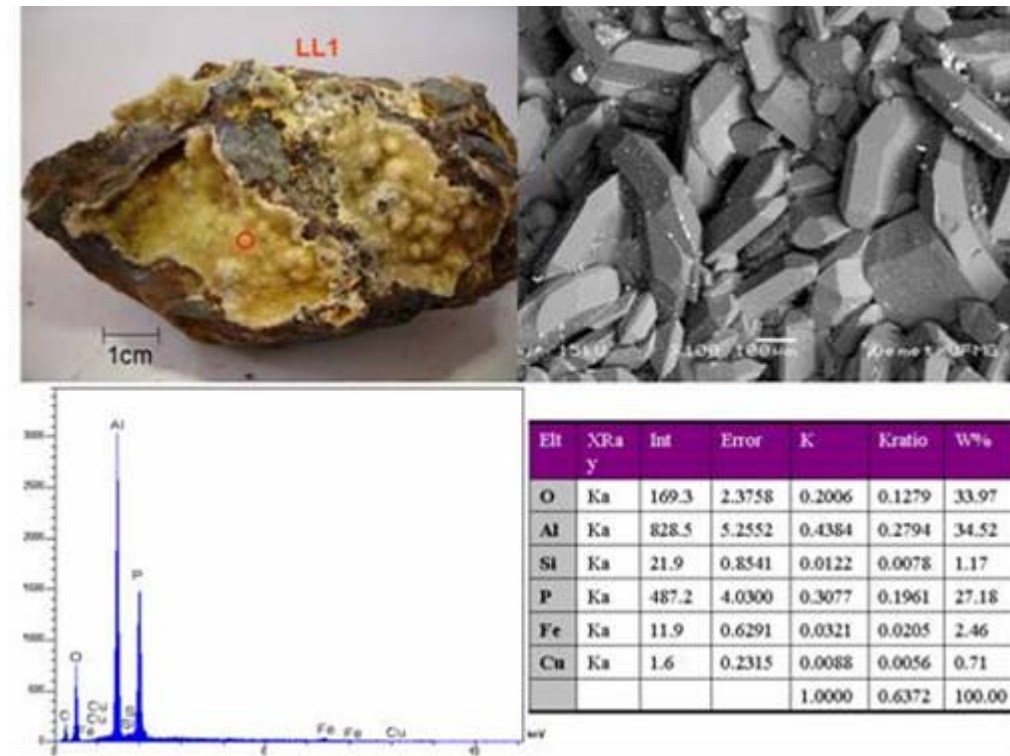


Figure 4. SEM/EDS from sample LL1.

The x-ray diffraction analysis from samples CCQ and LL1, depicted in Figure 5, showed the senegalite as the predominant phase. Other phosphates present in the samples are the wavellite and turquoise. Goethite was the prevailing phase among the iron oxides.

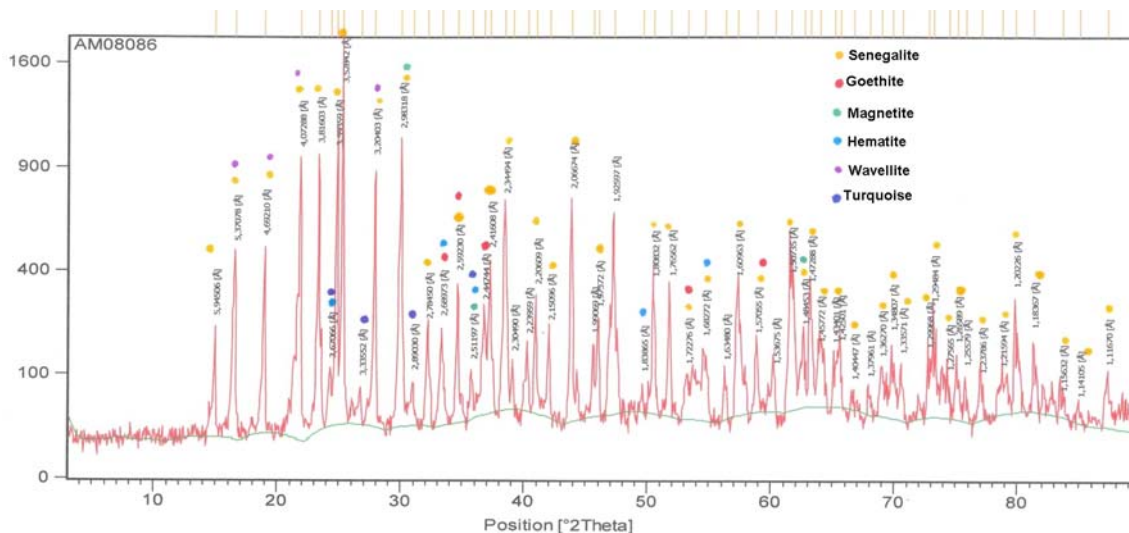


Figure 5. Diffractogram from samples CCQ and LL1.



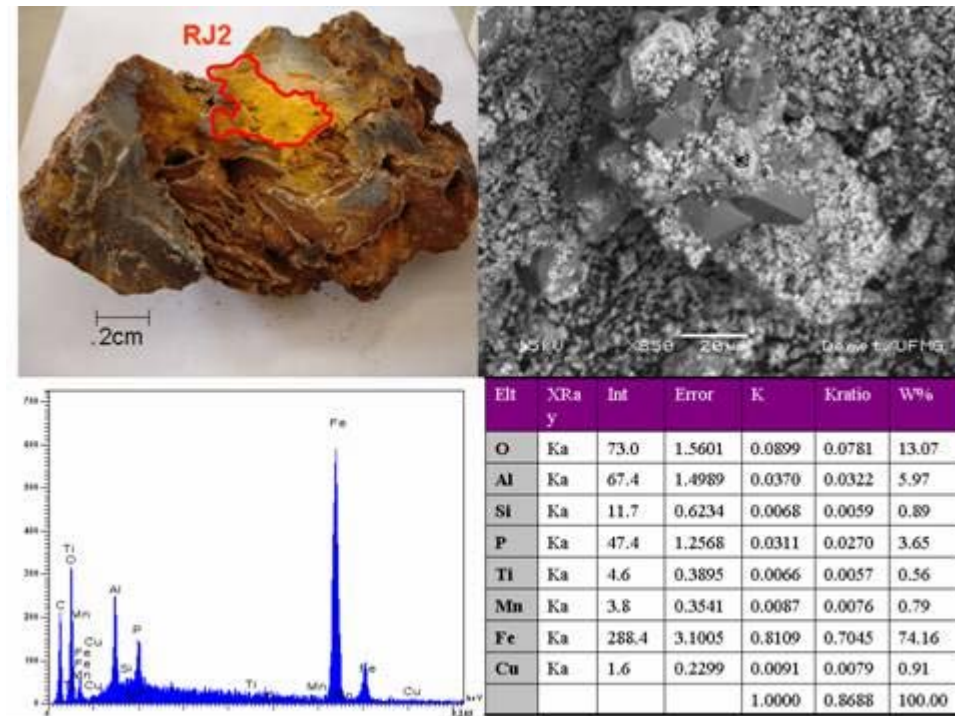


Figure 6. SEM/EDS -sample RJ2.

The sample denominated as sample RJ2, depicted in Figure 6, in opposition to the sample CCQ that had perfect crystals in the size range of 0.15 to 0.1 mm, showed to be extremely friable. The analysis refers to the area external to the area delimited by the line in the picture and represents very fine iron oxides. Other important detected elements are titanium, manganese and copper.

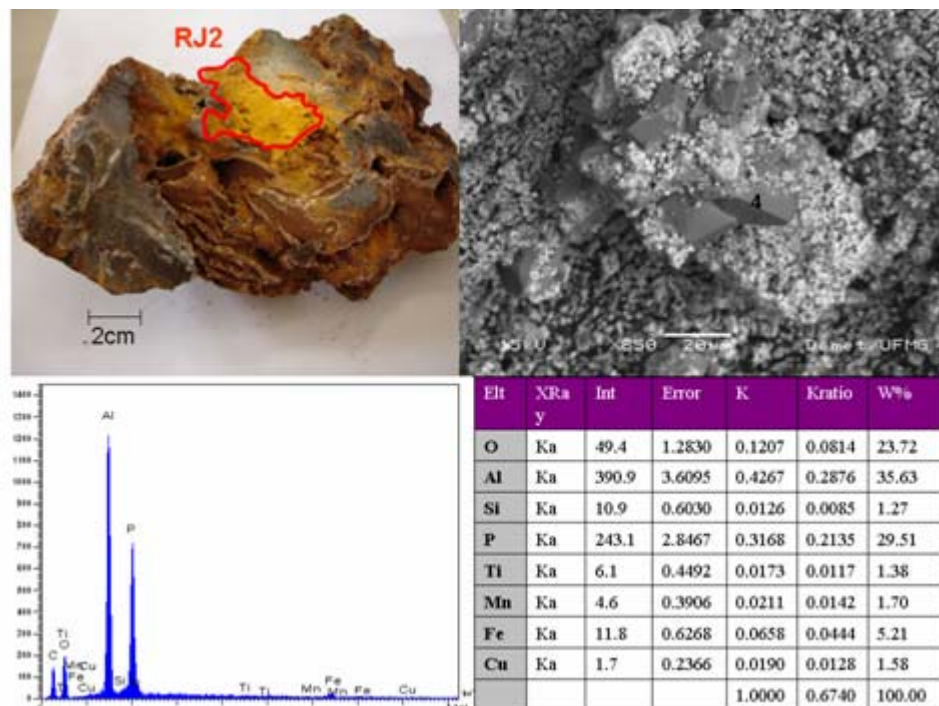


Figure 7. SEM/EDS from sample RJ2



The analysis presented in Figure 7 refers to the area inside the area delimited by the line in the picture. The crystal is an aluminum phosphate and the shape is similar to the crystals shape detailed in the Figure 4.

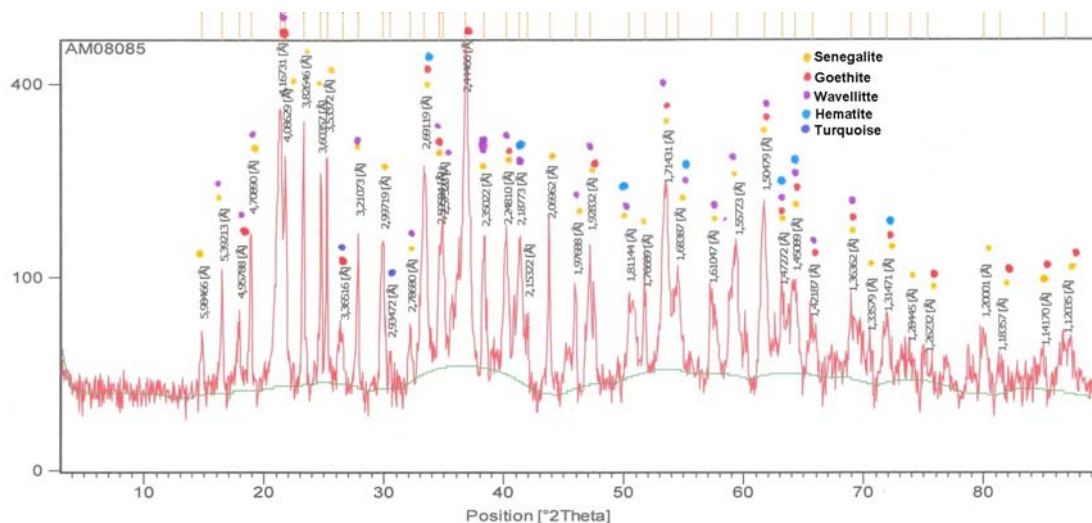


Figure 8. Diffractogram - sample RJ2.

The diffractogram from sample RJ2 is depicted in the Figure 8. The friable aspect of the sample already indicated a major presence of wavellite once it rarely develop crystals. The hematite phase appears more intense compared to the samples CCQ e LL1.

### 3.2 Sample from the Northern State- Brasil

Most particles with high phosphorous content in the investigated sample averaged 11% to 12 % phosphorous, 17% to 18% aluminum, 25% to 27% barium and 36% to 37% oxygen characterizing the gorceixite mineral as depicted in the Figure 9.

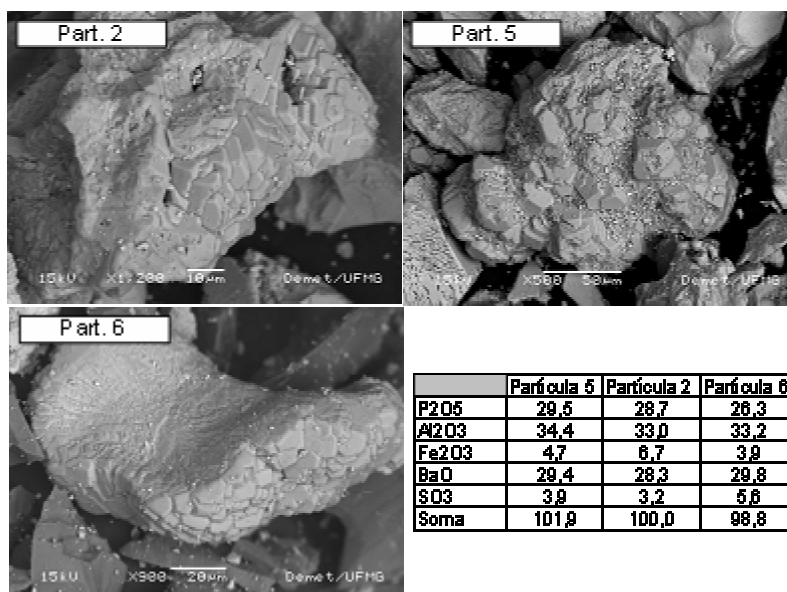


Figure 9. Gorceixite particles images and chemical analysis.

Despite the existence of locked gorceixite particles in the studied sample, the vast majority of the detected phosphate particles were liberated in the size range of 0.2 to 0.1 mm. A few locked particles were found in the size range of 0.03 to 0.044 mm. These data indicated the possibility of concentration of the phosphate particles through magnetic separation, flotation or a combination of the two methods. A single bench scale flotation test, after grinding the sample to minus 0.15 mm, made possible a phosphorous reduction of 35% in the iron oxides concentrate.

### 3 CONCLUSION

The most Brazilian iron ores present the phosphorous intimately associated to the iron minerals and particularly associated to the goethite. Despite this fact, there exist in the iron quadrangle and in the northern as well as in the northeast regions, iron ores that present well defined phosphorous minerals like apatite, gorceixite, senegalite, vawelite and others. These minerals, frequently occurs in such a way that there exists the possibility of being liberated in a size range where the magnetic separation and flotation can be utilized for a selective separation. Acid leaching after thermal treatment can be considered as an option for those ores where the phosphorous makes a solid solution with goethite. The conventional route of magnetic separation followed by flotation and the acid leaching may become a reality in Brazil due to the growing need for high quality iron concentrates allied to the shortage of concentrate in the transoceanic market.

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