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Clareti Pereira, Antônio; Magriotis Papini, Rísia

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Processes for phosphorus removal from iron ore - a review

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Antônio Clareti Pereira

Researcher

Instituto Tecnológico Vale

Ouro Preto - Minas Gerais - Brazil

casead@oi.com.br

Rísia Magriotis Papini

Professor

Universidade Federal de Minas Gerais

Escola de Engenharia,

Departamento de Engenharia de Minas.

Belo Horizonte - Minas Gerais - Brazil

risia@demin.ufmg.br

Abstract

This paper aims at reviewing literature on the occurrence of phosphorus in iron ores from the mines around the world. The review extends to the phosphorus removal processes of this mineral to meet the specifications of the steel industry. Phosphorus is a contaminant that can be hard to remove, especially when one does not know its mode of occurrence in the ores. Phosphorus can be removed from iron ore by very different routes of treatment. The genesis of the reserve, the mineralogy, the cost and sustainability define the technology to be applied. The articles surveyed cite removal by physical processes (flotation and selective agglomeration), chemical (leaching), thermal and bioleaching processes. Removal results of above 90% and less than 0.05% residual phosphorus are noticed, which is the maximum value required in most of the products generated in the processing of iron ore.

keywords: iron ore, phosphorus removal.

1. Introduction

Sometimes, the usual methods of processing are not able to completely remove the phosphorus present in some types of iron ore when trying to make the content of this contamination acceptable (below 0.05%).

The way in which phosphorus is found in iron ore is not well known. Based on results for synthetic samples of goethite

(α -FeOOH) and hematite (α -Fe₂O₃), it can be inferred that phosphorus occurs, probably, in the form of phosphate adsorbed on the particle surface or occluded in the micropores. Another possibility is that the phosphorus is located within the structure of the oxyhydroxides or as a phosphate mineral. For synthetic samples, literature

reports that goethite has a greater adsorption capacity of phosphate than hematite, certainly due to the higher surface area and porosity of the particles of goethite. Understanding the mode of occurrence of this element in ores will bring new information that can inform the development of methods for their removal (Curi, 1991).

2 Results and discussion

2.1 Phosphate occurrences

Iron ore of high phosphorus content coexists with other minerals in the form of apatite or fluorapatite. Phosphorus is spread on the edge of mineral particles

of iron oxide and embedded in quartz or carbonate minerals and a small amount is present in the iron mineral grid (Xia *et al.*, 2011).

The most frequent and important constituent of the class of phosphates is apatite. Besides apatite, various other phosphates may be found in deposits of iron ore (Table 1).

Mineral	Chemical Formula
Apatite	Ca ₅ (PO ₄)(F,Cl,OH)
Wavellite	Al ₃ (PO ₄) ₂ (OH) ₃ ·5(H ₂ O)
Senegalite	Al ₂ (PO ₄)(OH) ₃ ·H ₂ O
Turquoise	CuAl ₆ (PO ₄) ₄ (OH) ₈ ·5(H ₂ O)
Strengite	Fe ³⁺ (PO ₄)·2(H ₂ O)
Rockbridgeite	Fe ²⁺ 0.75Mn ²⁺ 0.25Fe ³⁺ 4(PO ₄) ₃ (OH) ₅
Frondeite	Mn ²⁺ Fe ³⁺ 4(PO ₄) ₃ (OH) ₅
Gorceixite	BaAl ₃ (PO ₄) ₂ (OH) ₅ ·H ₂ O
Barrandite	(Al,Fe)PO ₄ ·2(H ₂ O)
Variscite	Al(PO ₄)·2(H ₂ O)

Table 1
Main Phosphorus Minerals
Found in Iron Ore (Nunes, 2012)

The most common side phosphates in iron ore are rich in aluminum

phosphate or iron phosphate. The wavellite, senegalite and turquoise are

commonly found in Brazilian iron ore (Nunes, 2012).

2.2 Extraction processes

2.2.1 Chemical Processes

Acid leaching has been considered as an alternative to flotation for removing phosphorus from iron ore. Technologically, the leaching process is a simpler way to treat the fine-particle sinter feed without the restrictions that are necessary in flotation.

Jin *et al.* (2006) studied the extraction using either an acid media or basic media. Samples of Changde (China) were submitted to assays. Samples were ground to a particle size smaller than 0.075mm and the chemical analyzes indicated a phosphorus concentration of 1.12%. The minerals were hematite, quartz and kaolinite. The phosphorus was distributed as follows: 22.3% occurring as apatite, 67.9% was disseminated in the iron matrix and only 9.8% was present in silicates. The following leaching media were used: sodium, hydrochloric acid, sulfuric acid and nitric acid hydroxide. The following considerations were taken

for chemical treatment:

- Alkaline leaching is ineffective in removing phosphorus from the wide-spread iron matrix, even increasing the concentration of sodium hydroxide. The increased residence time decreases the removal of phosphorus due to the re-precipitation phenomena;

- Alkaline leaching is effective for removal of the phosphorus present in apatite and silicates;

- Acid leaching is the most efficient method for removal of phosphorus from iron ore. Among the tested acids, sulfuric acid is the most effective for this purpose. The leaching time is low (~20 minutes) and the iron loss is negligible (less than 0.25%).

Zhang and Muhammad (1989) used nitric acid to remove phosphorus from the iron ore of the Kiruna region, Sweden. A concentrate of sinter, moist, and without treatment was used. Chemi-

cal analysis showed the composition of 0.98% phosphorus (as P_2O_5 22.25%) and 60.85% iron. Nitric acid was chosen due to the low reactivity of the acid with the magnetite which was the major constituent of the ore tested. The disadvantage of using nitric acid was the formation of NO_2 or NH_4^+ . The main conclusions of the researchers were:

- The content of the final match of sinter met the specification required for the production of steel;

- The removal of phosphorus reached 95%;

- Controlling the acidity of the solution, maintained at high concentration, resulted in a low extraction of iron, causing a loss of less than 0.5% because the dissolution of magnetite is very sensitive;

- Small increase in humidity from 2% to 2.7%;

- The control of the reaction of dissolution of apatite is by diffusion.

2.2.2 Bioleaching

The main methods used in the operation of bioleaching processes are: heap leaching, dump leaching and leaching in stirred tanks (Watling, 2006).

Biometallurgy is an option for the

removal of phosphorus of iron ore, as there are many microorganisms, especially in environments with limited nutrients which are able to extract the phosphorus contained in minerals (Nautiyal, 1999).

Some studies have been published on the removal of phosphate from iron ore using acid-producing microorganisms, including filamentous fungi and iron-oxidizing bacteria (Buis, 1995).

2.2.3 Physical processes

2.2.3.1 Selective agglomeration

Selective agglomeration is a technology of agglomeration where an immiscible product is added to a suspension of fine particles. This causes the formation of a second phase consisting of particles with the immiscible product. The main cohesive forces are the capillary forces. The result is the formation of flakes or spherical clusters with diameters up to 5mm. The process of removing phosphorus from iron ore linked to the concept of selective agglomeration is well grounded in the work of Sirianni *et al.* (1969).

Sparks and Sirianni (1974) applied the technique to remove the iron ore's phosphorus from Snake River, northern Canada. The content of phosphorus was in the range of 0.34% unacceptable for steel production. The iron content was from 44% to 53%, making it very at-

tractive for exploration considering this item. The mineral body mainly consists of the mineral hematite and microcrystalline chalcedonic quartz aggregate in various proportions. Calcite ($CaCO_3$), dolomite ($Ca,Mg (CO_3)_2$), apatite $Ca_5(PO_4)_3(Cl,F,OH)$ goethite ($FeOOH$) and very fine quartz crystals were the smallest constituents which were locally abundant. The gravity separation by jigging achieved an acceptable enrichment of iron concentrate, but the phosphorus was beyond the acceptable level for commercialization (less than 0.07% at that time). Acid leaching, using H_2SO_4 , applied directly on the jig, did not get good results because of the precipitation of sulfur compounds. The pH dependence on the collection of fatty acids had already been studied by the authors in

a previous work (Sirianni, *et al.*, 1968). The results showed the possibility of using selective agglomeration to separate iron ore and apatite. The assays were applied to a concentrate obtained by jigging. The sample was ground to a particle size smaller than 400 meshes, to ensure release of the apatite. Oleic acid was used as collector and the pH was controlled with NaOH or H_2SO_4 . Raw or refined petroleum was used for clustering. Anhydrous calcium chloride was used as the source of calcium ion for activation and sodium silicate as a depressant of iron oxides. The agglomeration process was performed in a ball mill, in which conditioners were added, collector and binder. The dilution of the pulp allowed the formation of agglomerates of phosphorus-bearing mineral

with large lumps. The pulp (5 to 10% solids) was placed in a mixer with light oil, like kerosene, after which it was separated by differential sedimentation.

After all these stages of processing and treatment, the initial ore which came with 54.6% iron, 0.39% phosphorus, resulted in a concentrate with 65.9%

iron, less than 0.02% phosphorus and 5.3% silica. Figure 1 summarizes the operations for this phosphorus removal process:

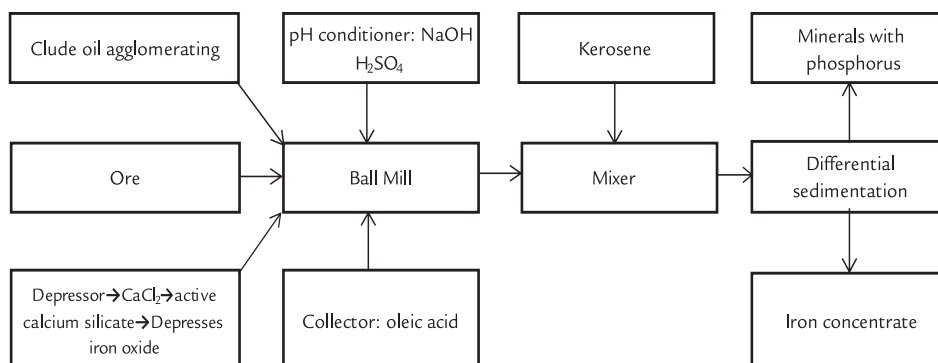


Figure 1

Flowsheet for Selective Agglomeration.

2.2.3.2 Flotation

There are many citations in literature on the reduction of phosphorus in iron ore through anionic flotation, using a fatty acid as collector and sodium silicate as a depressant of iron oxides, when the main phosphorus-bearing mineral is apatite (Ranjbar, 2002; Siirak and Hancock, 1990; Pyatt, 1990).

Nunes *et al.* (2012) conducted research on floatability of the mineral phosphorus-bearing wavellite. They evaluated the reduction of the phosphorus content of a Brazilian iron ore with an initial phosphorus content of 0.82%. The best result was obtained with dodecyl amine (approximately 100% of floatability) in pH 8. A concentrate

containing 0.201% phosphorus, 62.31% mass recovery was obtained at a dosage of 150g/t of Flotigam EDA (etheramine collector). The authors evaluated Flotigam 2835-2L (collector) in an ore concentrate containing 0.654% phosphorus. The phosphorus content dropped to 0.312% and the mass recovery was 90.24%.

2.2.3.3 Thermal Process - sintering

Sintering is a thermally activated phenomenon that transforms a shaped body composed of crystalline and / or amorphous particles into a rigid body due to diffusion phenomena. A common feature is the decrease in surface area of particles (or grains) with a simultaneous increase of resistance of the shaped body. It can be divided, when considering ceramic reactions, at sintering in states: liquid, solid and viscous (Molisani, 2009).

Feld *et al.* (1966) patented a process consisting of the mixture of chlorides of alkali metals (sodium, lithium, calcium, magnesium, strontium and barium) with ammonium chlorides, manganese, zirconium and copper in ore in a proportion of 10% by weight. The mixture of ore and additives is calcined at a temperature of 900°C for 120 minutes. The mixture is cooled and leached at room temperature for 30 minutes with hydrochloric, sulfuric or nitric acid

for dissolving the phosphorus compound formed in the furnace. The phosphorus extraction was above 80%, reaching final values of 0.018% from an initial value of 0.421% power.

Xu *et al.* (2012) investigated the phosphorus removal of oolitic hematite ore of high content of iron by applying a reductive calcination with dephosphorizing agent (Na_2SO_4 and Na_2CO_3). The calcined mass was subjected to two stages of magnetic separation and grinding. The phosphorus content dropped from 0.82% to 0.06% and iron from 43.65% to 60.23% with 87% mass recovery. Analysis showed that 20% of apatite reacted with SiO_2 , Al_2O_3 and carbon, generating elemental phosphorus in the form of gas. About 80% of the phosphorus was incorporated into the slag and it was separated from the grinding and magnetic separation. A small residual remains in the apatite concentrate.

Zhu *et al.* (2013) investigated direct reduction technology by adding sodium carbonate (Na_2CO_3) and afterwards magnetic separation, to treat iron ore from Western Australia with high phosphorus content. They found that phosphorus was inside of the limonite in the form of solid solution that cannot be removed by traditional methods. During the reductive calcination, Na_2CO_3 reacts with gangue minerals (SiO_2 and Al_2O_3) forming phosphorus-containing aluminum silicate and modifying the structure of the mineral, promoting the separation of iron and phosphorus during magnetic separation. The composition of iron concentrate obtained: 64.12% Fe and 0.07% phosphorus with an iron recovery of 96.83%, and a rate of dephosphorization of 74.08%. Figure 2 shows a flowsheet for concentration by reductive sintering and removal of phosphorus.

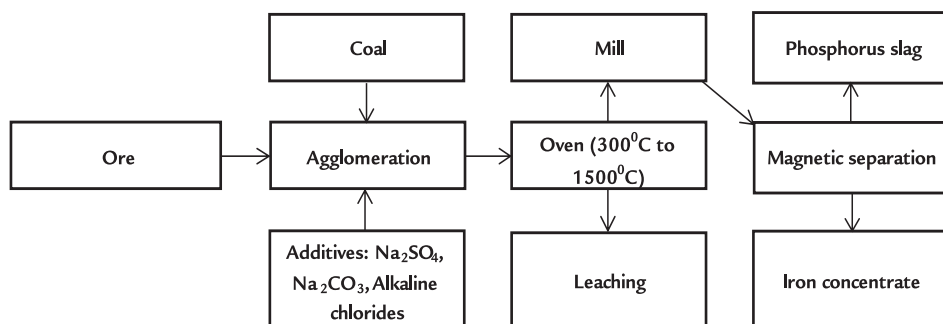


Figure 2

Reductive sintering for phosphorus removing.

2.2.3.4 Mixed processes

Fisher-White *et al.* (2012) investigated ore from the Pilbara region, Western Australia, in two steps: thermal preconditioning and alkaline leaching using caustic soda. Goethite from Pilbara's ores were formed by supergene metasomatic alteration of fine grains of flint and other ganga minerals in the ore initially precipitated as ferrihydrite, initial product of the rapid hydrolysis of Fe (III), with subsequent dehydration and recrystallization to

form goethite. The thermal processing to disrupt the structure of goethite has been shown to be effective in releasing phosphorus associated with this mineral and becoming available to be extracted by a leaching solution. Researchers performed heat treatment in the range of 300-350°C with 10% NaOH and subsequent leaching in water, succeeded in reducing the phosphorus from 0.15% to 0.075%. The same effect was achieved by heating the

ore and leaching the same temperature in a solution of 1.5M sodium hydroxide, close to boiling for three hours.

Yi *et al.* (2008) investigated the reverse flotation of oolitic iron ore from Hubei, China region, previously subjected to a reductive calcination and were able to obtain a concentrate with 60.14% Fe and 0.22% P. They concluded that the result is more effective than when using flotation, in ore, without treatment.

3. Conclusions

Phosphorus can be removed from iron ore by very different routes of treatment. The genesis of the reserve, mineralogy, cost and sustainability define the technology to be applied.

It is important to stimulate fundamental studies of the mineralogy of phosphorus in iron ores, since the more complex ores require more knowledge about the distribution of this element in the iron matrix, which ensures a more effective route to their mobilization.

The development of technologies for phosphorus removal by physical

and biological processes is most likely to achieve economic viability and sustainability to ensure the processing operations of iron ore; that is, those that require minimal amount of reagents, low power requirement, simplicity of facilities, availability of commercial equipment, unskilled labor and do not pollute the environment significantly.

Chinese studies show that for ores with widespread phosphorus in the iron matrix and low release, thermal or mixed processes are closer to reality technical solutions. Due to their higher operating

costs, it will be necessary to rethink the processes of sintering and pelletizing, such that these operations also become phosphorus removal steps.

With the exhaustive processing of the known reserves of hematite from Iron Ore Quadrangle (Minas Gerais-Brasil), there will be no shortage of granules in the not too distant future. Therefore, there is an expectation that the ore mined will have higher levels of phosphorus. This expectation is not reflected in publications of national authors, thus translating into a risk for the activity.

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