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Characterization of Magnetic Tailings from Phosphate-Ore Processing in Alto Paranaíba

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The characterization studies of tailings from mining are crucial for the development of its reuse processes and the reduction of impacts caused by its conditioning on the earth's surface. This study characterizes the magnetic tailings from phosphate-rock processing using X-ray diffraction, X-ray fluorescence spectrometry and quantitative electron microscopy techniques. Samples were obtained from the magnetic tailings deposit of a mining company in the Alto Paranaíba region, Minas Gerais. The tailings are mainly composed of hematite/magnetite (74.92%), ilmenite (8.91%), fluorapatite (8.8%), anatase (3.07%), calcite (1.67%), goethite (1.62%), and quartz (1.02%). The particle size of the tailings is smaller than that specified for the production of sinter feed. The hematite/magnetite phase is strongly associated with ilmenite and fluorapatite. New stages of comminution and separation are needed due to the low degree of liberation of these minerals for a possible reuse of the components.

Keywords: Magnetic tailing, Characterization, QEM.

1. Introduction

Mining companies have been investing in research with tailings obtained from ores processing. They aim to mitigate the environmental impact caused by the dams used for their conditioning and to reuse these materials[1]. Brazil has been researching the development of products based on the characterization of materials that do not yet have specific applications, such as non liberated iron and titanium oxides[1-11]. Brazil has some tailings that contain important amount of iron minerals that can be recycled in the framework of a circular economy context and natural resources conservation. The study of physical, chemical, and mineralogical properties has led to the discovery of new tailings processing technologies, novel alternatives for the sustainable management of ores, resources conservation as well as the definition of the best reuse procedures for commercially exploitable minerals present in the tailings[1].

The phosphate-ore reserves in Alto Paranaíba region, Minas Gerais are extracted to generate raw mater for the production of fertilizers. This ore's mineralogy is complex with various gangue minerals that require the use of different processing techniques. One of the techniques is low-intensity magnetic separation, which generates magnetic waste and represents approximately 15% of the ore mass that feeds the beneficiation plants[12,13]. In magnetic separation, magnetic susceptibility is the mineral's property that determines its response to a magnetic field. Based on this property, materials or minerals are classified into two categories: those that are attracted and those that are repelled by the magnetic field. The former includes ferromagnetic minerals, which are strongly attracted by the field, and paramagnetic minerals, which are weakly attracted by the field. The development of magnetic separation evolved into a technology that separates strongly magnetic materials from weakly magnetic materials, even finely dispersed particles. This resulted in the development of *high intensity magnetic separation* and *high gradient magnetic separation*, which use low-intensity resistant electromagnets[14,15]. The mining companies of Alto Paranaíba use drum-type magnetic separators with resistant low-intensity electromagnets (900 Gauss), which are obtained by the magnetic fraction, magnetic tailings studied here, and diamagnetic fraction that goes to the classification steps and later for the flotation of phosphatic ore. The companies deposit the magnetic tailings separate from the tailings obtained during the flotation stage, hoping to reuse this material as a coproduct later. Currently, the unused magnetic waste is transferred by pumping slurry to specific deposits, in which the water is drained naturally and these are dry conditioned. More than 50 million tons of this material is estimated to have

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been deposited by the mining companies in Alto Paranaíba over the last four decades.

It is worth questioning why this high-iron-content waste continues to be stored thus degrading the environment. Despite the advantages of magnetite in steel processes (sintering and pelletizing) and the fact that it is technically possible to chemically guarantee this waste's use by the steel industry, its processing is rendered unfeasible by the large hematitic iron ore reserves still dominating the steel market[16-18]. Moreover, studies that quantify magnetite formation in ore pellets in hardening furnaces at high temperatures, found that it reduces the produced pellets resistance, thus further undermining its use by the steel industry[19-24].

However, the study of this waste's physical, chemical, and mineralogical properties is of paramount importance for unleashing its full potential and enabling the development of its future applications. Several techniques were used during this analysis, including quantitative electron microscopy (QEM). QEM is a powerful imaging ores characterization tool. It identifies and quantifies mineral phases present in a sample, differentiates useful (commercially viable) from nonuseful (ganga) minerals, and determines size; distribution; minerals association; and the degree of phase liberation. Such information is crucial to define next steps in the study of ore tailings reuse. QEM is a technique that uses a software coupled to a modern scanning electron microscope (SEM) for chemical microanalysis[25,26]. Automated image analysis systems integrated to SEM, such as TESCAN Integrated Mineral Analyzer (TIMA), Mineral Liberation Analyzer, and Qualitative Evaluation Minerals by Scanning Microscope, are coupled with QEM[27]. The method extracts a material's mineralogical information from the combination of backscattered electron (BSE) images and characteristic X-ray analysis [28]. In addition to potential mineral-ore recovery[28], quantitative mineralogy studies using automated electron microscopy provide reliable results of liberation degrees and mineral associations, the partition of chemical elements of interest, mineralogical composition, and particle size distribution.

Based on the above, we characterized the chemical composition, the degree of liberation, crystal structure, the mineralogical composition of the phosphate-ore tailings aiming to understand the Alto Paranaíba's tailing and contribute to future studies on tailings reuse.

2. Experimental

This study characterizes magnetic tailings samples from the magnetic separation step of phosphatic ore, from a mining company in the Alto Paranaíba region, Minas Gerais. Samples were randomly obtained from different tailings deposits.

Thereafter, they were dried, homogenized, and quartered in an elongated pile, and aliquots were obtained for chemical and mineralogical analyses. The quantitative chemical analysis was performed using X-ray fluorescence spectrometry (XRF) technique, in three random samples (named AM1, AM2, and AM3) of the Panalytical Zetium model. Fe_2O_3, P_2O_5, and TiO_2 contents were also analyzed. To identify the mineral content in the magnetic tailings and their crystal structure, analyses were conducted via X-ray diffraction and quantitative electron microscopy. The particle size was also obtained through quantitative electron microscopy. A Bruker brand D2 Phaser diffractometer was used in X-ray diffraction with a copper X-ray tube operated at 30.0 kV and 10.0 mA and Ni-filter, set to 0.018° 2θ sweep per step, from 6 to 80° at 1.0 s/step. For the Rietveld refinements, the program Topas version 5.0 from was used. We used TIMA software version 1.5.24 in quantitative electron microscopy (QEM), associated with a scanning electron microscope model MIRA3 LMH with energy dispersion (EDS) via a 25-kV electron beam, with a 70-nm diameter, and 250 times magnification. For the QEM analysis the studied tailing was mounted in a resin. Samples were wet-ground with SiC emery paper to 2000 grit and afterwards polished with 1 μm diamond paste. A carbon coating was used to ensure sample conductivity.

3. Results and Discussion

The sample's X-ray diffractogram (Figure 1) showed peaks the characteristic of magnetite (Fe3O4 - Crystallography Open Database (COD) 1011084), hematite (Fe2O3 - (COD) 9015964), ilmenite (Fe8.4 Ti3.6O18 - (COD) 9006976), and fluorapatite (Ca5P3O12F - (COD) 9001232) presence. In addition, anatase (TiO2 - (COD) 9009086), calcite (CaCO3 - (COD) 9000970), quartz (SiO2 - (COD) 9012600), and goethite (FeHO2 - (COD) 9002159) compounds were identified. The mineral concentration presented in the Figure 1 was accessed by the Rietveld refinement of the XRD pattern. The quality of Rietveld refinement was verified through statistical numerical parameters: Rwp (weighed profile factor) = 12.802 and GOF ($\chi 2$ (Goodness of Fit) = 1.2. It can be observed that the magnetic tailing possesses high amount of iron minerals (85.45%).

Table 1 shows the semi-quantitative results of the P_2O_5, Fe_2O_3, and TiO_2 contents obtained via XRF for samples AM1, AM2, and AM3, respectively. These three samples had a

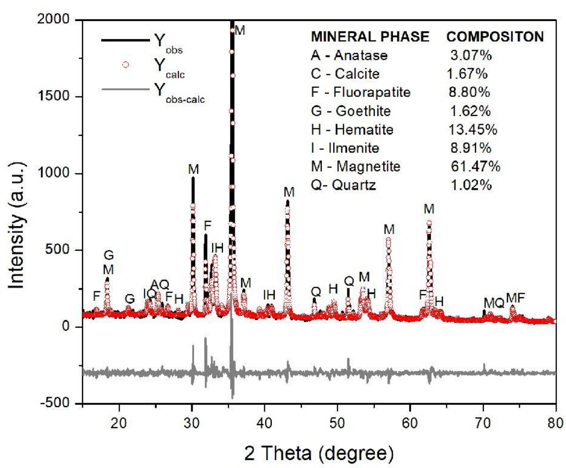

Figure 1. X-ray diffractogram of the magnetic tailings obtained from phosphate-rock processing in Alto Paranaíba.

Table 1. XRF semi-quantitative results of the magnetic tailings.

Sample	P_2O_5 (%)	Fe_2O_3 (%)	TiO_2 (%)
AM1	1.26	80.79	11.82
AM2	1.29	93.07	11.56
AM3	1.75	83.49	9.07

high Fe_2O_3 content, in which sample AM2 was the highest. P_2O_5 content was low in all three samples, which reveal the useful element losses in the magnetic separation step of the phosphatic ore. TiO_2 content was also detected in these three samples, as the phosphatic ore is superimposed on a layer of rock composed mainly of titanium minerals. This fact is explained by the phosphatic ore mine's geological profile (Figure 2), in which the mineralized titanium zone, immediately below the overburden zone with a 30-m thickness, has more than 10% TiO_2 and less than 5% soluble P_2O_5[12,29]. The main distinction between this zone and the previous one is a decreased frequency of clay components and a considerable TiO_2 increase.

The QEM technique produced mineral characterization results such as the identification and quantification of mineral phases, particle size distribution, mineral associations and the liberation spectrum of the relevant mineral phase (which, in this study, is the hematite phase /magnetite). Figure 3 illustrates the phase map of the global sample used in this analysis. It shows a disaggregated and dispersed sample, which is a premise for a good results representation.

Hematite/magnetite phase predominance is clear, and although the magnetic tailings are mainly composed of iron minerals, they are differently sized and their grain shape and phase distribution varied as shown in detail by the illustrated Energy Dispersion Spectroscopy (EDS) image (Figure 4a).

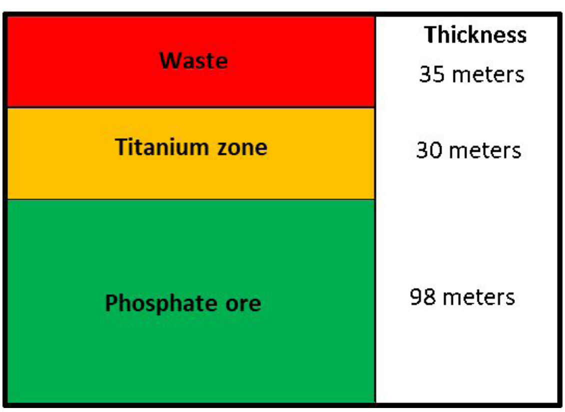

Figure 2. Geological profile of the phosphate-ore mine in Alto Paranaíba[29].

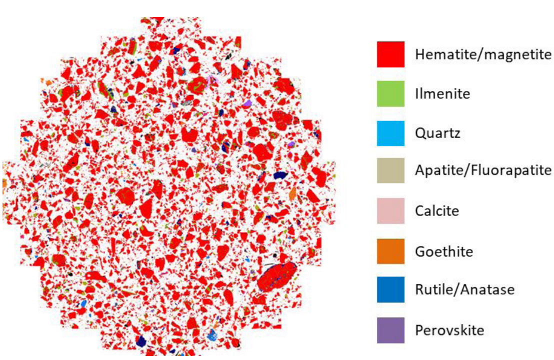

Figure 3. Phase map of the ferromagnetic tailings sample using the Quantitative Electronic Microscope (QEM).

Figure 4b show EDS spectrum of the elements identified in a microregion of the sample. Beside iron, other elements (titanium, calcium, and phosphorus already identified by other techniques) are also present in smaller quantities indicating the presence of other minerals than hematite and magnetite.

Table 2 shows the mineralogical composition obtained from the QEM and database correlation, which detected hematite/magnetite (85.6%), ilmenite (4.6%), rutile/anatase (2.3%), goethite (2.1%), apatite/fluorapatite (1.5%), perovskite (0.4%), quartz (0.3%), and calcite (0.2%) mineral phases among other unidentified minerals (3.0%). It is worth explaining that analyses with less than 5% of unidentified minerals are considered representative for QEM technique[1]. It was technically difficult to distinguish the hematite from magnetite minerals given their similar BSE images brightness. They were therefore classified as a single hematite/magnetite phase[1]. It worth to mention that QEM results are in good agreement with XRD results considering that QEM analyses a well-limited sample amount quantity.

The Alto Paranaíba Brazil tailing has a particular composition and it is completely different from the waste from phosphate extraction produced worldwide. For instance, at Ben Guerir deposit, in the central part of the Gantour basin-Morocco, the waste produced is mainly composed of CaO, SiO_2, and Al_2O_3 and can be destinated to other applications than the Brazilian tailing[30].

Figure 5 depicts the particle size analysis obtained by QEM, according to the accumulated distribution of particle sizes. It shows that the hematite/magnetite phase has a particle size distribution very close to that of the global sample, comprising 85.6% of the same, and particle size below other phases. Approximately, 18% of hematite/magnetite particles are below 125 µm; whereas, the ilmenite, rutile/anatase, and apatite/fluorapatite phases are 14.6%, 12.8%, and 13% below 125 µm, respectively.

The cumulative particle size distribution shows that the mineral phases D_{50} (50%) ranges from 300 µm to 400 µm. The iron ore commonly used for sintering and subsequently used in steelmaking must have an adequate particle size distribution: 45% to 60% of the fraction between 1000 and 6350 µm[31]. Approximately 99% (D_{99}) of the studied magnetic waste has a particle size smaller than 1000 µm, and a high agglomeration power which renders it unusable for *sinter feed* manufacture.

Figure 6 graph shows that more than 60% of the total hematite/magnetite particles volume (in the liberation forms and associated with other minerals) are sized 249 to 704 µm.

Table 2. Mineralogical composition of magnetic tailings by QEM.

Mineral Fase	Composition (%)
Hematite/magnetite	85.6
Ilmenite	4.6
Rutile/Anatase	2.3
Goethite	2.1
Apatite/Fluorapatite	1.5
Perovskite	0.4
Quartz	0.3
Calcite	0.2
Other minerals	3.0

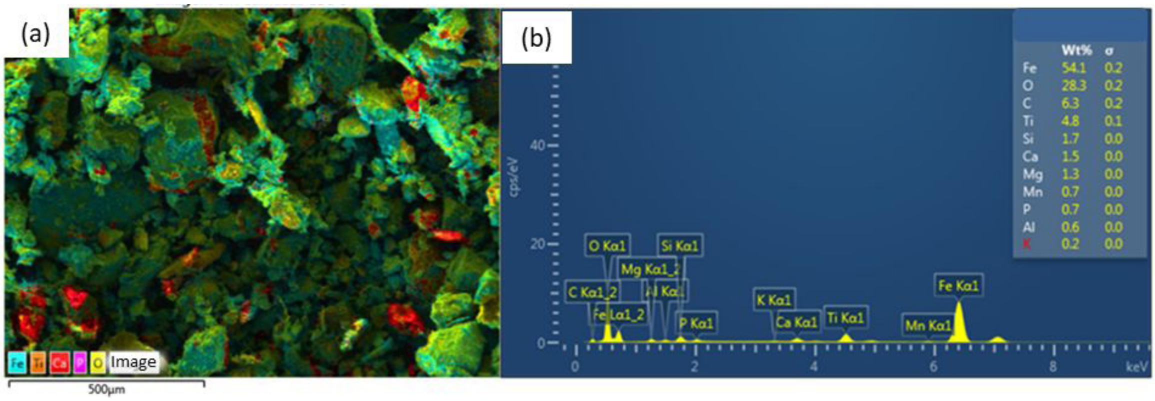

Figure 4. (a) Image and (b) dispersive energy spectrum of a magnetic-waste sample obtained from phosphate-rock processing.

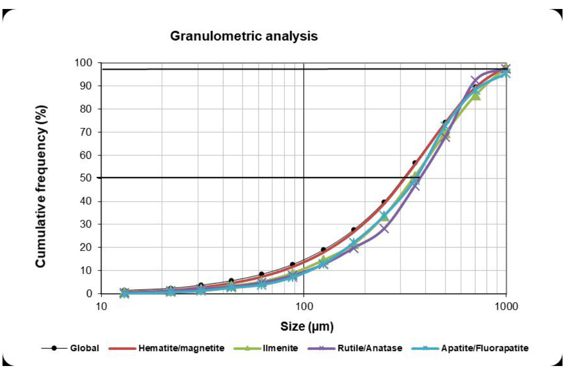

Figure 5. Cumulative particle size distribution.

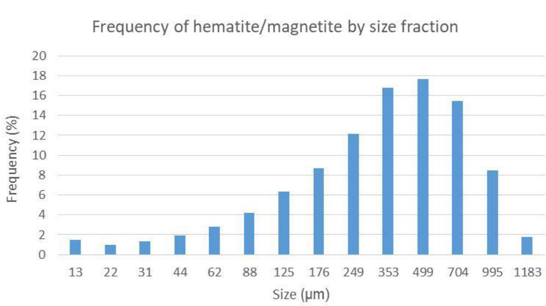

Figure 6. Particle size distribution of only hematite/magnetite by size.

Figure 7 shows the liberation spectrum of hematite/magnetite, ilmenite, rutile, and apatite phases. Two criteria can be used to calculate particle liberation: volume or exposed surface. In volume analysis, particle liberation is the fraction of the area of the primary phases in relation to the particle's total area, in percentile. Whereas in exposed surface analysis, particle liberation is the fraction of the length of the particle's outer perimeter covered by primary phases in relation to the entire particle's outer perimeter, in percentile[1]. This study analyzes the liberation of phases by volume.

Approximately 81% of the total hematite/magnetite phase volume present in the magnetic-waste sample (belonging to classes ≥ 80< 90% and ≥ 90%, with 24% and 57%, respectively) has a liberation degree above 80%. More than 70% of Ilmenite and rutile/anatase particles volumes have a low liberation degree (between <10% and ≥ 40< 50%). This shows that mineral particles containing titanium oxide are mainly mixed. Approximately 28% of the hematite/magnetite phase volume is associated with the ilmenite phase (Figure 8).

Meanwhile, the apatite/fluorapatite phase presents approximately 50% of its volume with a degree of liberation between < 10% and ≥40< 50%, revealing a high concentration of mixed particles, which is strongly associated with hematite/magnetite. Apatite, the commercially interesting phase for the mining industry (for apatite recovered from magnetic tailings), would certainly have to liberate these particles possibly in new comminution and magnetic separation stages, which would make processing too costly for the fertilizing companies.

In the steel industry, the maximum phosphorus content is strictly controlled in steels, ranging between 0.005% and 0.1%, depending on the desired quality and the application for which the steel is intended[16]. It is important to mention that phosphorus, in the appropriate percentages, increases the steel's wear and corrosion resistance, improves fast-cutting steel's machinability, and increases its mechanical strength. If excessive, however, it is considered an impurity[16]. Therefore, the use of magnetic waste for Blast Furnaces, without new comminution processes to liberate the mixed particles, could harm steel production. At certain levels, the presence of phosphorus weakens the steel therefore becoming a restrictive element for the use of important mineral resources[31]. Moreover, considering that 100% of the phosphorus goes into pig iron, it is estimated that for every 0.1% of phosphorus in pig iron, 1.0 kg of carbon/t pig iron is needed[31].

One may question where this particular magnetic tailing may be used in the context of a circular economy and resources conservation. Considering the hardness of the main minerals composing the tailing (hematite, magnetite, ilmenite, anatase, and goethite) being 5 to 6.5 mohs there is the possibility to use it as a secondary phase of a composite of a polymer coating, e. g. polyurethane. Another possibility is the incorporation of magnetic tailing in the construction sector to serve as aggregates for embankments, concrete, and pavements[32,33]. Drif et al.[32] have shown the recycling of

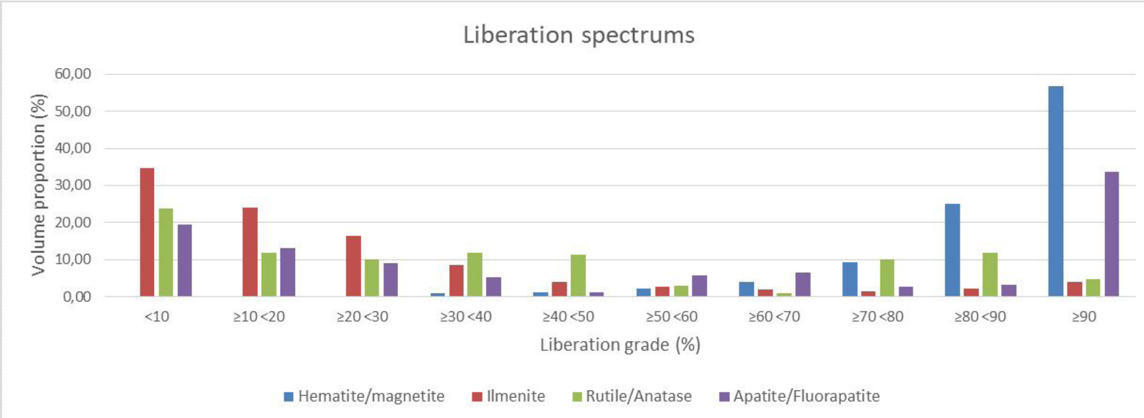

Figure 7. Volume liberation spectrum of the mineral phases of magnetic tailings obtained from phosphate-rock processing.

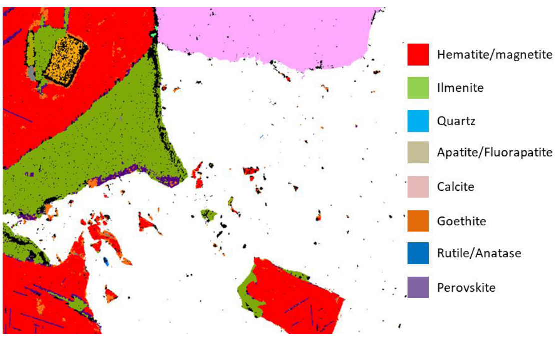

Figure 8. Mineral phase map of phosphate-ore tailings obtained from QEM.

silver mine tailings, composed mainly of silica, alumina, and iron oxides, in the manufacture of sintered ceramics as an effective and sustainable way to reduce the natural sources consumption and environmental impacts.

4. Conclusions

The evaluated magnetic tailings are mainly composed of hematite/magnetite, with more than 80% of its mass sufficiently liberated. The D_{50} of the studied mineral phases ranges between 300 and 400 µm, and 70% of the hematite/magnetite mass is between 176 and 704 µm. Among the studied mineral phases, hematite/magnetite is the one with the smallest particle median size (D_{50}) and the highest percentage of particles liberation, which is a promising scenario for this material reuse as a coproduct of the phosphate-ore mining company. Ilmenite stood out as the mineral phase that is most strongly associated with hematite/magnetite, with 75% of its mass. The apatite phase, presenting a higher mixed particles concentration (mainly associated with hematite/magnetite), would result in higher reuse reprocessing costs for mining companies. Given how onerous the reprocessing of tailings phosphate is, its recovery becomes unviable for the fertilizer industry. As for the tailings usage by the national steel industry, processing is not yet a viable scenario given that the ore is mainly composed of magnetite, has low granulometry, and has high levels of ilmenite and fluorapatite for steel production. It is in this sense that our group has been developing products aimed at reducing the environmental impact of the waste characterized in this study and recycle the waste in the framework of a circular economy.

5. Acknowledgments

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