

CHARACTERIZATION OF ULTRAFINES TAILINGS OF IRON ORES¹

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Abstract

This paper presents a characterization study of ultra fine solid particles contained in the mud of some iron-ore mines from Vale. Particle-size separations were done by wet sieving and elutriation, whereas the particle-size distributions were checked by laser diffraction (Cilas). The chemical analyses were performed by Inductively Coupled Plasma and wet methods. The materials were also characterized by X-ray diffraction, scanning electron microscopy with energy dispersive spectroscopy and Mössbauer spectroscopy. The tailings showed a significant level of iron (from 44% to 64%), mainly in the forms of hematite (α -Fe₂O₃) and goethite (α -FeOOH). Mössbauer results showed that as the particle-size decreases the amount of goethite increases. Furthermore, the hematite content is always greater in the coarser fractions (+10 μ m). The MEV analysis showed that the vast majority of the particles are not spherical, and that the cyclosizer is not efficient to properly separate the material in the intended fractions. In this respect, the particles obtained by wet sieving showed to be much more uniform in terms of shape and size.

Key words: Iron ore; Mud; Ultrafine tailing; Iron oxides.

CARACTERIZAÇÃO DE REJEITOS ULTRAFINOS DE MINÉRIOS DE FERRO

Resumo

O presente trabalho apresenta um estudo de caracterização dos sólidos ultrafinos contidos nos rejeitos do beneficiamento mineral de algumas minas de minério de ferro da Vale. As separações granulométricas foram feitas por peneiramento a úmido e elutriação (cyclosizer). A determinação da distribuição granulométrica foi feita pela técnica de difração de laser (Cilas). As análises químicas foram realizadas por espectrometria de plasma de acoplamento indutivo e por via úmida. As demais técnicas de caracterização foram: difração de raios-X, microscopia eletrônica de varredura com microanálise química e a espectroscopia Mössbauer. Os rejeitos ultrafinos apresentaram um teor significativo de ferro (de 44% a 64%), principalmente nas formas de hematita (α -Fe₂O₃) e goethita (α -FeOOH). A espectroscopia Mössbauer mostra que à medida que a granulometria das partículas diminui o teor de goethita aumenta e o teor de hematita é maior nas frações mais grosseiras (+10 μ m). A análise no MEV revelou que as partículas dos rejeitos não são esféricas e que o cyclosizer não é tão eficiente na separação, ao contrário do peneiramento, cuja separação se mostrou mais uniforme e condiz mais com o tamanho real das partículas.

Palavras-chave: Minério de ferro; Rejeitos ultrafinos; Óxidos de ferro.

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1 INTRODUCTION

The mining industry has a very important role in generating wealth of a country through the exploitation of natural resources and is often responsible for a major percentage of the gross national product. However, this type of activity can cause severe impacts to the environment, and for this reason has been the subject of concern to the public and government agencies. This leads this sector to face a challenge in this new millennium: the achieving of sustainability.

As an attempt to solve this challenge, mining companies have been engaged in improving their mineral processing techniques to reprocess the tailings generated throughout the industrial processes.

The beneficiation of iron ores from Vale results in three products, which have small variations between different mines and minerals: coarse ore lumps having sizes in the range of 8-80 mm, which are directly charged to a blast furnace; fines of sizes from 8 mm to 0.15 mm for the sinter plants; pellet feed with particle size smaller than 0.15 mm which is used to produce pellets. The ultra fine tailings with particle sizes below 10 μm are discarded in dams.

Hernandez et al.⁽¹⁾ reports that the sludges of iron ores typically contain 30% to 50% of solid (by weight), including coarse and fine particles.⁽²⁾ Iron can be present in significant amounts of up to 60%, and hematite is the predominantly mineral.^(3,4)

However, the sludge can not be used in the manufacture of pig iron in blast furnaces or in the agglomeration processes due to restrictions of particle size and quality.⁽⁴⁾

The physical-chemical properties of the sludges depend on the type of ore, the operations used in the milling and processing of water in the effluent.⁽²⁾

Due to the reduction of ores with high grades and the increasing loss of minerals of interest during processing, it has become imperative the development of successful processing routes with low effective costs to recover such minerals from the sludge. However, it is not easy to process this mud mainly because the valuable mineral is normally present as very fine particles. Other difficulties in processing the sludge derive mainly from its intrinsic composition, for example, the presence of clay minerals.⁽³⁾ The iron ores with high contents of clays usually generates more fine particles smaller than 10 μm during the processing. These fines cannot directly be used in a blast furnace, and therefore, are discarded in the tailings dams. For this reason, and to avoid loss of fines in the form of mud, it has become increasingly attractive to investigate concentration techniques to process these fines.⁽³⁾

The presence of high contents of alumina and silica results in loss of quality of the sinter and in the necessity of handling larger quantities of slag, respectively. High alumina in the iron ore and sinter leads to a viscous slag, which in turn, requires a high rate of coke.^(3,4)

The processing of iron-ore sludges is not easy, and the techniques to be used must match the quality of the ore and the requirements of the final product ⁽³⁾. Conventional techniques for the concentration of iron ores are not efficient, but selective flocculation, magnetic separation and micro-flotation are promising techniques that deserves further investigations to be used in the recovering of the iron minerals from the sludge.⁽⁴⁾

The investigation of the use of iron-ore tailings as value-added products has received considerable attention in recent years. Its use as a source of SiO_2 , Al_2O_3 , Fe_2O_3 and CaO was reported by Das et al.⁽⁵⁾ and Kumar et al.⁽⁶⁾ for the production of floor tiles and ceramics. The pieces had high strength and hardness, and showed to meet the specifications required by other parameters. One important advantage of the use of

sludge is the fact that this material does not require intensive grinding, thus saving a huge amount of energy.

Thus, it can be seen that the tailings dams are a large reserve of iron oxides, and in the future, when the technology permits the extraction in a viable way, these dams can become an important source iron.⁽²⁾ This possibility has already been envisioned by some companies: instead of planning a dam to be closed in the future, it is now planned to be reused.

Bearing in mind the future reuse of tailings and the sustainability of activities/operations of a mine, this work is focused on the characterization of the tailings of some iron ore mines from Vale. It is hoped that this characterization will provide information to subsidize the development and choice of mineral-processing techniques suited to the characteristics of each mine tailings.

2 METHODOLOGY

Nine samples were collected in seven mines from Vale, most of them originating in the underflow of the thickener mud. The solid materials were separated by centrifugation, the supernatants were discharged and the solids were dried during 24 hours at 80°C. After drying, the solids were gently crushed in a mortar and sieved to 60 meshes.

Particle-size separation was done in an ultrasonic sieve, resulting in three fractions: -10 µm, -15+10 µm and +15 µm. In addition, separation was also performed in a cyclosizer with the generation of three other fractions: -9 µm, -16+9 µm and +16 µm. All fractions were dried at 80 °C.

Particle-size analysis was done by the diffraction technique using the laser granulometer CILAS model 1064. All global samples in the form of mud and dry solids, as well as all fractions from the wet-sieving and the cyclosizer were analyzed. The analysis of the mud and their dried solids were done with the aim to investigate any possible effect of agglomeration caused by the drying of the mud.

Total iron was analyzed by wet chemical methods and minor elements were determined by ICP after dissolving the samples in hot HCl.

X-ray diffractograms were obtained in a Shimadzu XRD 6000 diffractometer equipped with iron tube and a graphite monochromator. The scans were done between 5-75° (2θ) with a scanning speed of 1°/min. The integrated intensities and widths of the peaks were obtained by fitting the profiles with a Pearson function after subtracting the background and the K_{α2} contribution. Mössbauer spectra were obtained in a conventional spectrometer operating at room temperature. The spectra were computer-fitted with symmetric sextets and/or doublets or with distributions of magnetic hyperfine fields.

The morphologies and particle-size distribution were investigated in a Jeol JSM 5510 scanning electron microscopy (SEM) associated with energy dispersive spectroscopy (EDS). The coarser and finer fractions of both wet-sieving and cyclosizer separations were investigated.

3 RESULTS AND DISCUSSION

The results of chemical analysis for the global samples and for the fractions of the cyclosizer are shown in Tables 1 and 2, respectively. It can be seen that the percentage of iron is considerable, ranging from 44 to 64%, and that the amounts of phosphorus (0.1 - 0.4%) and aluminum (1.0 - 3.0%) are also high. For all samples

the amounts of impurities, in especial phosphorus and aluminum, increases as the particle-sizes decreases

Table 1. Chemical analysis of the global samples.

Sample	Fe (%)	Al (%)	Mn (%)	P (%)
A	56.3	1.3	4.6	0.3
B	44.8	3.1	0.2	0.2
C	46.5	2.0	1.1	0.1
D	44.3	1.0	1.9	0.1
E	45.6	1.1	2.1	0.1
F	53.4	1.1	0.3	0.2
G	51.8	2.4	0.2	0.2
H	48.6	1.2	0.4	0.2
I	64.0	0.8	0.9	0.1

Table 2. Chemical analysis (% w/w) of the cyclosizer fractions.

Sample	Fraction (µm)	Fe (%)	Al (%)	Mn (%)	P (%)
A	+16	70.0	0.1	0.4	0.019
	-16+9	65.4	0.2	1.1	0.082
	-9	49.1	1.9	7.4	0.37
B	+18	48.9	1.4	0.1	0.074
	-18+9	52.7	2.0	0.1	0.095
	-9	42.1	2.6	0.2	0.14
C	+17	50.6	0.7	0.3	0.038
	-17+9	52.1	1.3	0.6	0.079
	-9	47.5	2.3	1.8	0.16
D	+17	46.9	0.1	0.4	0.016
	-17+9	56.5	0.3	1.0	0.046
	-9	33.3	1.6	4.9	0.24
E	+16	58.8	0.1	0.2	0.020
	-16+9	58.7	0.3	0.7	0.057
	-9	27.9	1.5	4.6	0.21
F	+16	59.4	0.3	0.2	0.074
	-16+9	58.4	0.5	0.2	0.13
	-9	47.3	1.3	0.4	0.19
G	+16	61.4	0.3	0.1	0.058
	-16+9	60.6	1.1	0.2	0.14
	-9	47.6	3.4	0.3	0.27
H	+16	55.8	0.1	0.1	0.029
	-16+9	56.2	0.5	0.2	0.084
	-9	43.1	1.9	0.7	0.22
I	+16	64.5	0.8	0.6	0.034
	-16+9	67.3	0.6	0.6	0.047
	-9	61.1	1.3	1.3	0.12

A typical result for the separation in the cyclosizer is shown in Table 3 for sample A. These results refer to the dried solid sample, but another test done with the original mud showed that the differences between the two results are within 4%, which can be considered small and acceptable.

Table 3. Results of the cyclosizer separation for sample A.

Size (µm)	Retained Simple %	Cum. Retained %	Cum. Passing %
30	6.6	6.6	93.4
22	1.0	7.6	92.4
16	2.1	9.7	90.3
11	7.8	17.5	82.5
9	8.8	26.3	73.7
-9	73.7	100.00	0.0
Total	100.0	-	-

The results of the Cilas for the global samples in the form of mud and solid showed significant differences in the derived parameter. The typical curves are shown in Figure 1 for sample A. The results for the dried solid show that 61% of the particles are below 9 µm, whereas for the mud the value is 76%. The cyclosizer results (Table 3) show that 74% of the particles are below 9 microns, in good agreement with the Cilas for the mud. For some samples the relative error between the average diameter D90 for the mud and the solid was about 40%. This difference is probably caused by agglomeration in the solid sample, and the ultrasound treatment prior the Cilas analysis was not enough to completely separate the particles. No correlation between the dimension of the error and the pH of the mud was found.

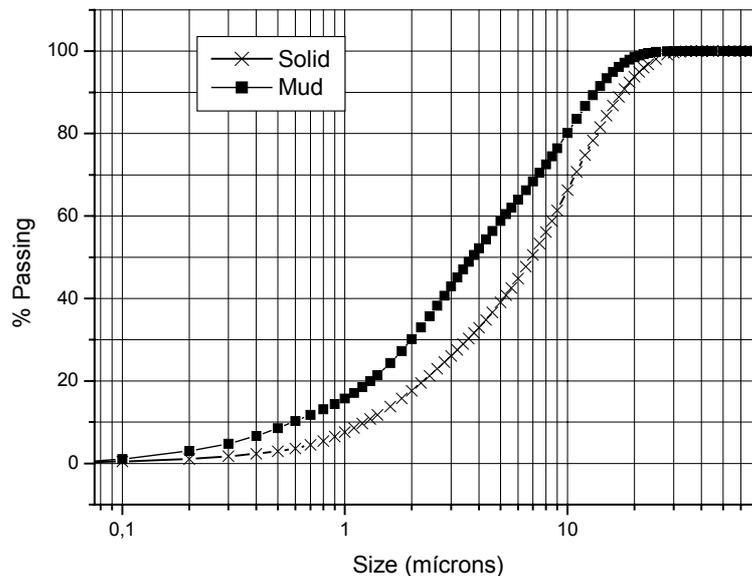


Figure 1. Particle size distribution for the dried solid and mud of sample A.

Similar differences are also noticed when examining in the Cilas the fractions obtained by wet sieving and in the cyclosizer. For the finer fraction of the wet sieving (-10 µm) the Cilas showed that 67% of the particles are below 10 µm. On the other hand, the Cilas results for the - 9 µm fraction of the cyclosizer showed that only 51% of the particles are below this size. In principle both fractions should have all particles below the above mentioned sizes, but some relevant aspects must be considered. First of all, it is very likely that particles are agglomerated, and hence the Cilas will

detect one agglomerate as a single particle. In addition, as the particles are not spherical, the Cilas can detect different sizes depending on the particle's position. Therefore, it is seen that the results of the Cilas and the cyclosizer can be quite different. This is not surprising because we are comparing data obtained by different methodologies and therefore it is now possible to compare the two results since they reflect different physical quantities. The wet sieving gives the sizes in absolute terms, i.e., the aperture of the sieve is a direct measurement of the particle size. On the other hand, the Cilas calculates a particle-size distribution in terms of equivalent spheres, which is the diameter of a sphere that produces an angular scattering of light identical to the that measured for the sample.⁽⁷⁾ The size obtained in the cyclosizer is the equivalent size of Stokes,⁽⁷⁾ which is the diameter of a free-falling particle in laminar flow ($Re < 0.2$). The results of the microscopy indeed show that the vast majority of the particles are not spherical (see below), thus corroborating the above discussion.

The X-ray diffraction (Figure 2) indicated the presence of kaolinite, quartz, gibbsite, talc and muscovite, in addition to the iron oxides (hematite, goethite and magnetite). The particle-sizes for hematite are generally above 1000 Å for all fractions, but for the goethite all fractions showed nanometric particles with mean sizes around 460 nm.

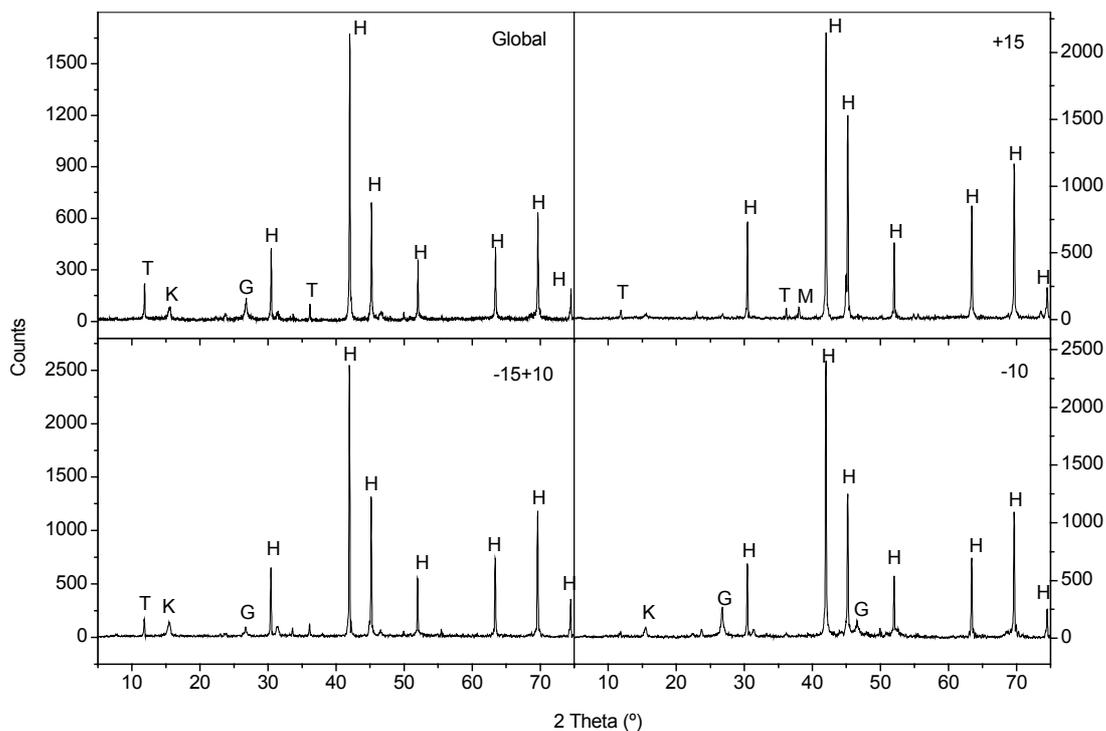


Figure 2. X-ray diffraction patterns of different fractions of sample A. (M: magnetite, H: hematite, G: goethite, K: kaolinite, T: talc).

Figure 3 shows the SEM micrographs of the -9 µm and +18 µm fractions obtained in the cyclosizer for sample B.

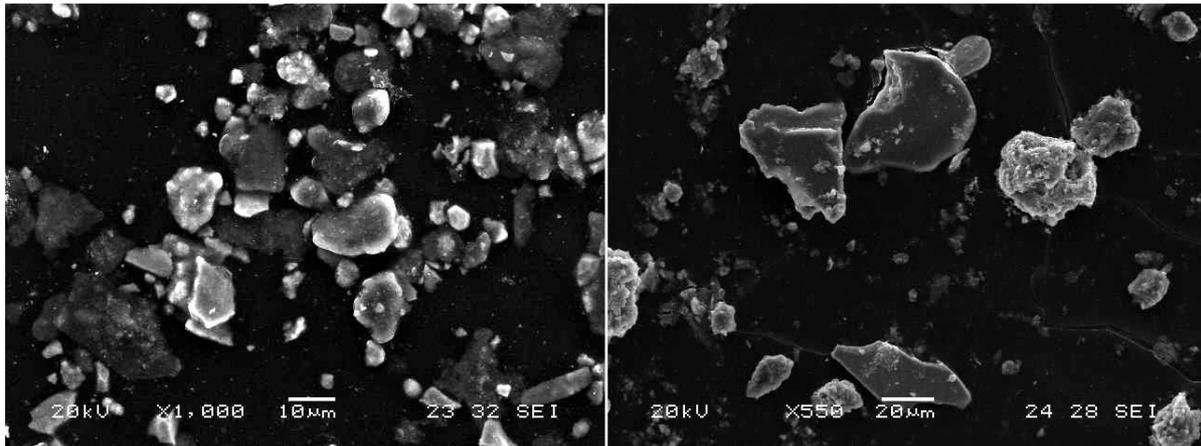


Figure 3. SEM micrographs of fractions -9 µm (left) and +18 µm (right) obtained in the cyclosizer for sample B.

The finest fraction of the cyclosizer was expected to have a narrow particle-size distribution, but this was not observed (Figure 3). It is clear the presence of particles as large as 20 µm. In this micrograph 72 particles were counted, 16 of which are greater than 9 µm (22%), with an average size of 15 µm.

The micrograph of the coarser fraction clearly shows the presence of clusters and a considerable number of particles smaller than 5 µm adhered to the surface of the largest ones. From a total of 16 particles only four are compact, with a length of about 58 µm. These compact particles have an average length of 44 µm and 28 µm wide, in an ratio of 1,6:1.

SEM images of the -10 µm and +15 µm fractions obtained by wet sieving of sample B are shown in Figure 4.

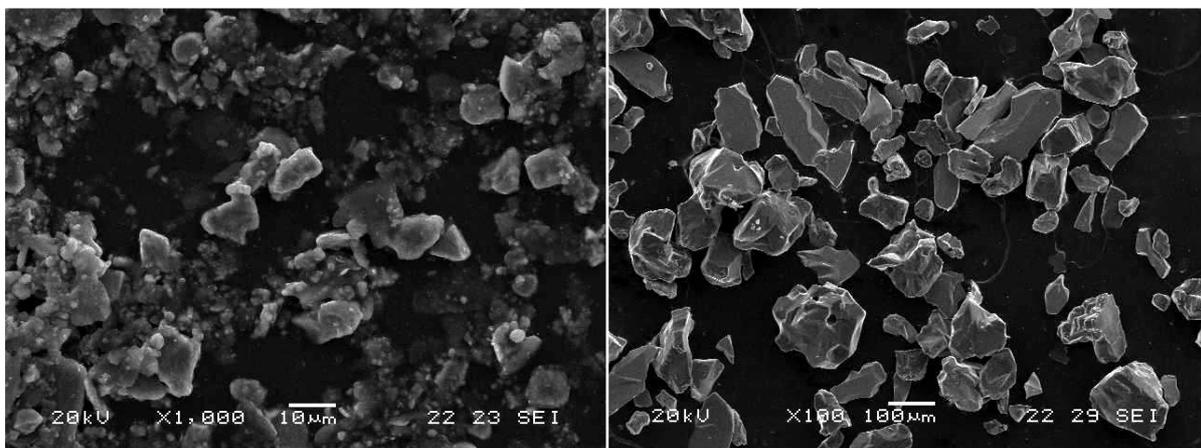


Figure 4. SEM micrographs of the -10 µm and +15 µm fractions obtained by wet sieving of sample B.

The image of the fraction smaller than 10 µm shows the uniformity of sizes, which are in fact below this diameter. There are few particles with sizes above this limit, and the mean size is around 14 µm. The micrograph for the +15 µm fraction clearly shows the absence of small particles or clusters, which is totally different from the images obtained for the samples from the cyclosizer (Figure 3). It can be seen in Figure 4 that the coarser fraction contains particles ranging from about 15 µm up to 215 µm. For a total of 43 particles, the mean length was found to be 100 µm and the mean width was found as 56 µm, giving a ratio of 1.8:1. This ratio is an additional proof that indeed the particles are not spherical.

The Mössbauer spectra of all fractions obtained by wet sieving of sample A are shown in Figure 5, and the numerical results derived from computational adjustments are listed in Table 4. The mineralogy was calculated taking into account the iron contents obtained by ICP (Table 2).

Table 4. Mineralogy of some selected samples.

Sample	Fraction (µm)	Fe (%)	The mineral content (%)			
			H	G	M	Others *
A	+15	70.0	89	-	11	-
	-15+10	65.4	88	6	-	6
	-10	49.1	54	18	-	28
B	+15	48.9	64	7	-	29
	-15+10	52.7	46	33	-	21
	-10	42.1	26	38	-	36
C	+15	50.6	56	18	-	26
	-15+10	52.1	52	25	-	23
	-10	47.5	28	44	-	28
D	+15	46.9	65	2	-	33
	-15+10	56.5	78	3	-	19
	-10	33.3	40	11	-	49

* Others: Muscovite, Gibbsite, Kaolinite, Talc, Quartz.

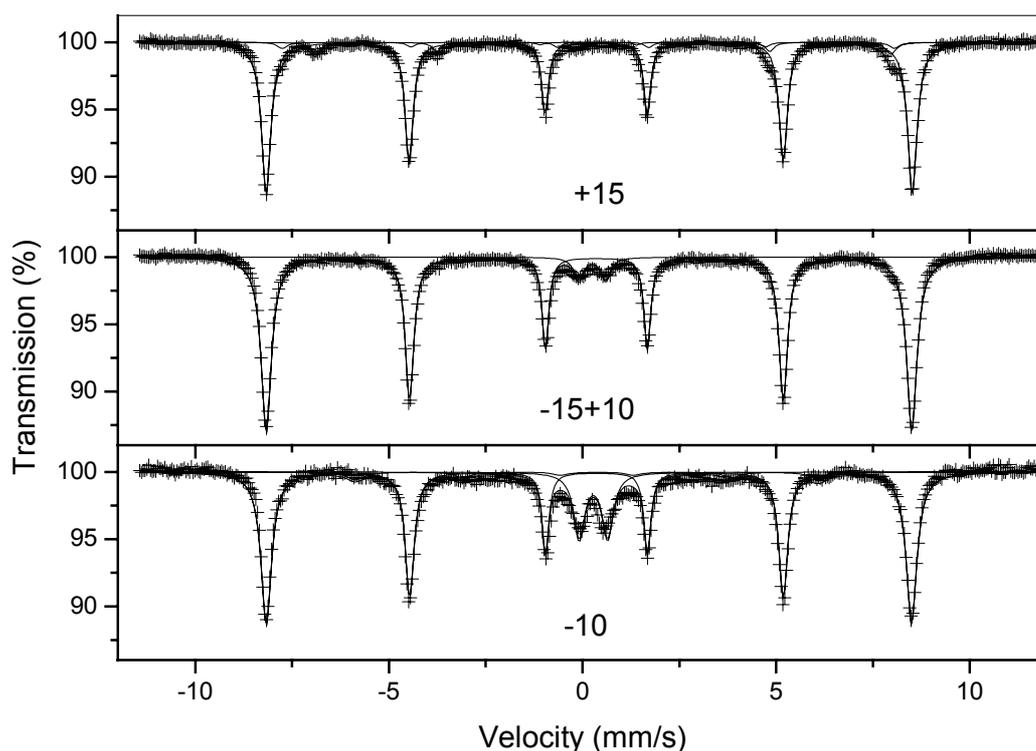


Figure 5. Mössbauer spectrum at 295 K of fractions of sample A.

4 CONCLUSIONS

The ultra fine tailings showed significant amounts of iron (from 44% to 64%), mostly as hematite and goethite. In addition to the iron oxy-hydroxides, kaolinite, quartz, gibbsite, talc and muscovite were also detected.

The results from the wet sieving, cyclosizer and Cilas show significant differences, and care must be taken when using such a data.

SEM images proved that the particles are not spherical, and that the wet sieving produced the most uniform particle-size distribution.

The Mössbauer spectra showed that the hematite is well crystallized and without significant isomorphic substitution. The amounts of goethite increases as the particle size decreases. Phosphorus and aluminum, present in high amounts, showed the same trend, indicating a possible association between these elements and the mineral goethite.

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REFERENCES

- 1 HERNANDEZ, C.A.O, DE ARAUJO, A.C., VALADÃO, G.E.S and AMARANTE, S.C. Pasting characteristics of hematite/quartz systems. *Minerals Engineering*. v.18, p.935-939, 2005.
- 2 GHOSE, M.K. and SEN, P.K. Characteristics of iron ore tailing slime in India and its test for required pond size. *Environmental Monitoring and Assessment*. v.68, p.51-61, 2001.
- 3 SRIVASTAVA, M.P., PAN, S.K., PRASAD, N. and MISHRA, B.K. Characterization and processing of iron ore fines of Kiriburu deposit of Índia. *International Journal of Mineral Processing*. v.61, p. 93-107, 2001.
- 4 PRAKASH, B., DAS, J.K. and VENUGOPAL. The recovery of fine iron minerals from quartz and corundum mixtures using selective magnetic coating. *International Journal of Mineral Processing*. V.57, p. 87-103, 1999.
- 5 DAS, S.K., KUMAR, S. and RAMACHANDRARAO, P. Explotation of iron ore tailing for the development of ceramic tiles. *Waste Management*. v.20, p.725-729, 2000.
- 6 KUMAR, S., KUMAR, R. and BANDOPADHYAY, A. Innovative methodologies for the utilization of wastes from metallurgical and allied industries. *Resources Conservation and Recycling*. v.48, p. 301-314, 2006.
- 7 SCHNEIDER, C.L. NEUMANN, R. and SOUZA, A.S. Determination of the distribution of size of irregularly shaped particles from laser diffractometer measurements. *International Journal of Mineral Processing*. v. 82, p. 30-40, 2007.