ANALYTICAL METHODS TO DETERMINE POROSITY IN SAMARCO IRON ORE SAMPLES [1]

Alessandra Prata de Almeida [2]
Paulo Roberto Gomes Brandão [3]

Abstract

In order to investigate the porosity in the ores that feed the Samarco Concentrator and their process products and to compare the porosimetry methods, four iron ore samples from Alegria Mine (Mariana, MG) were submitted to different porosimetry methods. The methods used were nitrogen adsorption-condensation porosimetry (NACP) and mercury intrusion porosimetry (MIP) with the support of scanning electron microscopy (SEM). The total pore volume and the pore size distribution have been determined by means of NACP, using the BJH model, and by MIP. Porosity qualitative analyses were carried out using SEM. The specific surface area (SSA) was measured by the BET method (nitrogen adsorption), as well. The mineral and microstructure compositions were carried out by reflected light microscopy and SEM with the support of microanalysis by energy-dispersive spectrometry (EDS). In the superposition range between the two porosimetry methods (NACP and MIP) – from 3nm to 100nm – the results were consistent but not identical. Below the detection boundary of gas adsorption (100nm), the NACP was more effective in distinguishing the samples than MIP. This was due to the microporosity shown by one of the samples. For the pore sizes from 50nm or more, SEM yielded qualitative results consistent with MIP for the samples studied.

Key words: Porosity; Iron ore; Porosimetry; Mercury intrusion; NItrogen adsorption-condensation.

MÉTODOS ANALÍTICOS USADOS NA DETERMINAÇÃO DE POROSIDADE DE AMOSTRAS DE MINÉRIO DE FERRO DA SAMARCO

Resumo

Visando investigar a porosidade dos minérios que alimentam o concentrador da Samarco e os produtos de cada etapa do processo, bem como comparar métodos de determinação de porosidade, quatro amostras minério de ferro da Mina de Alegria (Mariana, MG) foram submetidas a diferentes métodos de porosimetria. Os métodos usados foram porosimetria de adsorção-condensação gasosa (PACG) e porosimetria de intrusão de mercúrio (PIM) com apoio da microscopia eletrônica de varredura (MEV). O volume total e a distribuição de tamanho de poro foram determinados pela PACG, usando o modelo BJH, e pela PIM. Análises qualitativas de porosidade foram feitas através da microscopia eletrônica de varredura. A área superficial específica foi medida pelo método BET (PACG). As composições mineralógicas e microestruturais foram obtidas através da microscopia ótica de luz refletida e MEV com apoio de microanálise de raios-X dispersivo em energia. Na faixa de valores onde os dois métodos de porosimetria (PACG e PIM) são aplicáveis – 3nm a 100nm – os resultados foram consistentes mas não idênticos. Abaixo do limite de detecção da adsorção gasosa (100nm), a PACG foi mais efetiva em distinguir as amostras do que a PIM. Isto foi devido à microporosidade apresentada por uma das amostras. Para poros maiores ou igual a 50nm, MEV apresentou resultados qualitativos consistentes com os de MIP para as amostras estudadas.

Palavras-chave: Porosidade; Minério de ferro; Porosimetria; Intrusão de mercúrio; Adsorção-condensação gasosa.

[1] *Contribuição técnica ao 39º Seminário de Redução de Minério de Ferro e Matérias-primas e 10º Seminário Brasileiro de Minério de Ferro, 22 a 26 de novembro de 2009, Ouro Preto, MG.*

[2] *Chemical Engineer*

[3] *Professor Emeritus, Dept. of Mining Engineering, UFMG, Ph.D.*

INTRODUCTION

The current requirement for process productivity and iron ore concentrate quality in combination with the complexity and variety of ore bodies present in the various deposits of the Alegria Complex has led to the search for knowledge on the variables that influence the behavior of these materials in the various phases of the beneficiation processes.

For the purpose of improving reserve estimation, mine planning and quality control, Samarco has conceived a geological-typological model for deposits currently being mined (Alegria 3/4/5, Alegria 1/2/6 and Alegria 9). Until now, this model has been based on a systematic geological mapping of the deposits, information derived from geological descriptions of drill cores and results of chemical, physical and mineralogical analyses of samples generated by the exploration work, apart from the results of the technological testing after Costa, Rocha, Bonfioli and Vieira [(1)].

However, due to the various geological settings, even samples that are mineralogically similar can present variation of porosity parameters, after Pena [(2)]. Variations of characteristics relative to total volume, dimension, shape and degree of pore connectivity can generate significant behavior alterations in the phases of the concentration processes.

In order to investigate the porosity in the ores that feed the Samarco Concentrator and their process products and to compare the porosimetry methods, four iron ore samples from the Alegria Mine (Mariana, MG) were submitted to different porosimetry methods. The methods used were nitrogen adsorption-condensation porosimetry (NACP) and mercury intrusion porosimetry (MIP) with the support of scanning electron microscopy (SEM).

Materials and Methods

Two iron ore samples collected at the Alegria Mine 3/4/5 working faces were used jointly with one Alegria Mine 9 sample. The samples have a similar percentage (about 50%) of porous phases (porous hematite and goethite), which allows detecting any difference in porosity parameters, despite the similar mineralogical composition. A sample collected at an Alegria Mine 3/4/5 working face with far lower porous phase percentage (5.6%) was used to check the sensitivity of the porosity determination methods. The samples were named 5/4, 9/4, 5/14 and 5/35, where the first number indicates the source mine and the second the working face.

After being duly prepared, these samples were subjected to technological testing and characterization analyses. The technological testing and characterization route is shown in Figure 1.

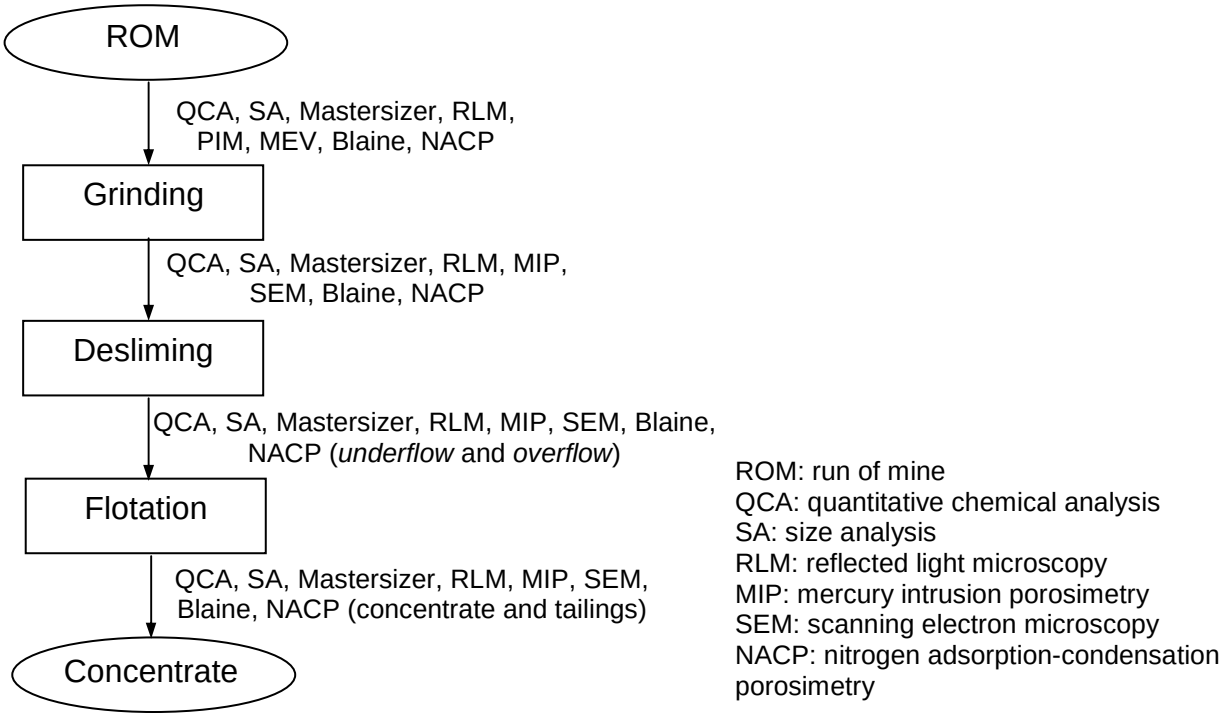

Figure 1 – Characterization route and technological testing.

The technological testing (desliming and flotation) were conducted following the Samarco standard.

The grinding stage was carried out in a ball mill for generating samples to be used in the desliming and flotation tests. Grinding took place in a 25.4cm x 20.3cm mill with 10 kg of grinding media consisting of balls with diameter varying between 20 and 30mm. The sample mass used was 1700g.

Desliming consisted of three phases at pH = 10.5 set with caustic soda (3% solution by volume). A 1700g sample was used.

Reverse cationic flotation was carried out, performed in a Wemco cell. Corn starch was used as an iron depressor (supplied by GEM), which was jellified with caustic soda (5:1 proportion), in a 1% solution by volume. Amine was used as silica collector – mixture of etheramine (Clariant's Flotigam EDA-3) and etherdiamine (Clariant's Flotigam LDD-O) at 3:1 proportion in a 1% solution by volume. The processed mass was 1500g, pH = 10.0, until reaching a silica content lower than 3.5% (specification for the conventional flotation phase in low silica campaign).

The analyses performed according to the BET (Brunauer, Emmett and Teller) method and the characterization of porosity parameters via NACP were conducted in the Particulate Solids Characterization Laboratory – DEMET (Metallurgical and Materials Engineering Department), EE-UFMG (Engineering School – Federal University of Minas Gerais), through a Quantachrome equipment, NOVA-1200 model. Sample degasification under vacuum conditions was carried out for two hours at a constant temperature of 180℃ for contaminant elimination. The sample was subjected to a flow of gaseous nitrogen. During specific surface area (SSA) determination, the cell containing the sample was immersed into liquid nitrogen (-196ºC).

The analysis of the porosity parameters following the MIP procedure was carried out at the Science and Materials Technology Center – CCTM, Energy and Nuclear Research Institute, São Paulo, using Micromeritics' AutoPore III 9410 equipment. For such, the sample was dried for 24 hours at 70ºC and subjected to vacuum for about one hour. Mercury was introduced upon reaching 6.7 Pa pressure. In this type of equipment, low-pressure analysis is not automated and nitrogen is used to exert pressure. High-pressure analysis is automated and oil is used to deliver pressure. A $5cm^3$ powder penetrometer was used.
Scanning electron microscopy was carried out on a Jeol microscope, JSM-5410 model, fitted with a Noran dispersive X-ray microanalysis device, TN-M3055 model (SEM-EDS).
The samples were analyzed in two ways: whole particles and polished sections. This analysis was carried out at the Electron Microscopy and Microanalysis Laboratory – DEMIN (Mining Engineering Department), EE-UFMG. The images obtained were of the type: SEI (secondary electron images) and BEI (backscattered electron images).
This technique was used aiming at a more detailed investigation of the existing mineralogical phases, a morphological evaluation of these phases and a qualitative evaluation of sample porosity – Brandão [3]. Microanalysis was carried out just to support the investigation work.

RESULTS AND DISCUSSION

The results of the chemical analyses and mineralogical analysis, by means of reflected light microscopy (RLM), of the four ROM samples are presented in tables 1 and 2, respectively.

Table 1 – Chemical analysis of the four ROM samples

Sample	Fe%	SiO_2%	Al_2O_3%	P%	LOI
5/35	38.06	44.58	0.36	0.029	0.56
5/14	52.73	23.38	0.72	0.039	0.47
9/4	46.45	33.21	0.26	0.034	1.00
5/4	55.95	19.37	0.56	0.027	1.12

Table 2 – Mineralogical analysis of the four ROM samples

Sample	LH%	MH%	G%	MH%+ G%	M%	Q%
5/35	52.81	0.93	1.58	2.51	0.00	44.69
5/14	30.21	34.76	13.22	47.98	1.49	20.33
9/4	23.44	45.63	4.42	50.05	0.35	26.16
5/4	30.40	47.25	4.61	51.86	0.05	17.69

Where: LH - lamellar hematite, MH - martitic hematite, G - goethite, M - magnetite, Q - quartz

The ROM samples were subjected to grinding tests to generate samples to be used in the desliming and flotation tests. Thus, the results of the chemical, physical, mineralogical and porosity characterization conducted for the four samples to be used in the following process phases could be presented: grinding product, desliming underflow and overflow, flotation concentrate and tailings.
The MIP methodology allowed characterizing the pores of the four samples for the aforementioned process stages. Pore size is expressed in terms of pore diameter (or radius) or slit opening after Webb and Orr[4]. Figures 2 and 3 show pore size distribution obtained through the intrusion process. From these distributions it is

possible to state that average pore diameter is about 10μm, i.e., mainly macropores are present.
For all samples, except for the desliming overflow, the average diameter is approximately the same and the curves are quite similar, even for sample 5/35. Therefore, figures 2 and 3 are considered representative of all samples (except for the desliming overflow, which has a broader pore size range, with average diameter around 1μm).

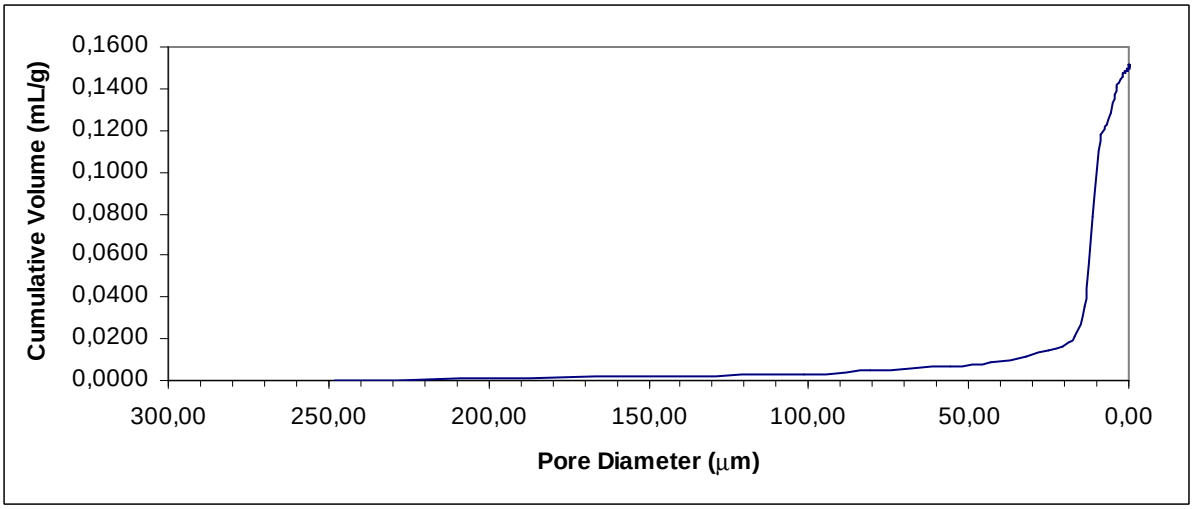

Figure 2 – Intrusion curve for sample 5/35 – flotation concentrate.

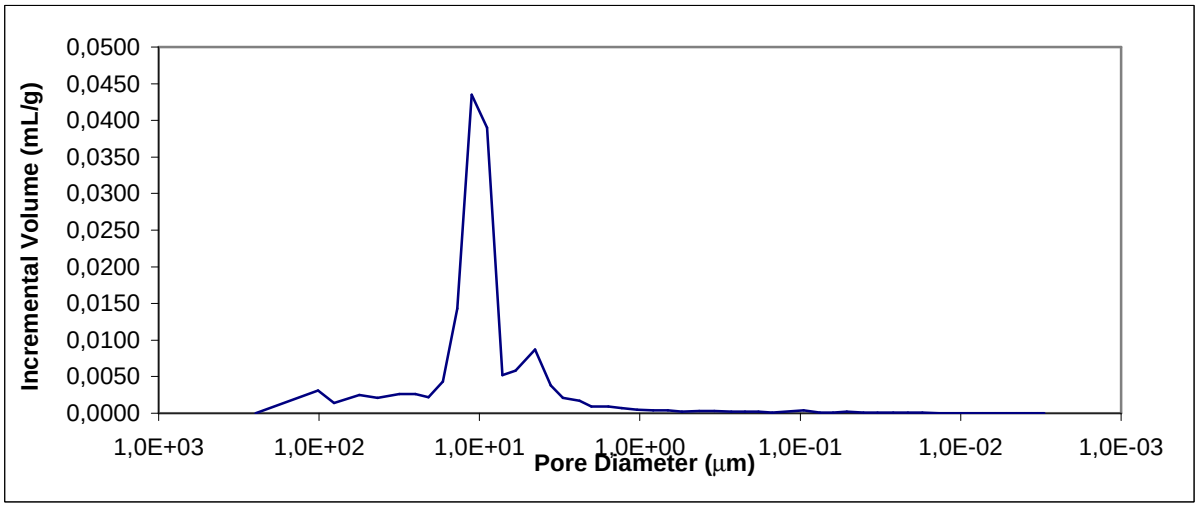

Figure 3 – Pore size distribution for sample 5/35 – flotation concentrate.

A very important value, according to Micromeritics (equipment manual)[5], is the maximum intrusion percentage practiced (stem volume used). This figure relates estimated sample pore volume to maximum measurable intrusion volume of penetrometer. It can be used as a guideline for penetrometer selection and must lie between 25 and 90% to obtain good resolution results.

As this specification was not met by some analyses, those were redone. In addition, some results seemed to be anomalous and new analyses were conducted in a different laboratory. In some situations, four repeats were required. These repeats were conducted during the investigation to determine which data could be used

rather than obtaining a certain sample size that allowed presenting the data in conjunction with an evaluation of their statistical significance.
MIP method was less replicable and the equipment had a low availability rate, in addition to the difficulty of importing parts or penetrometers. Four laboratories were contacted, but the equipment of the first two labs was inoperative and they could not inform when it would start operating again; the third lab was not able to reach maximum pressure and the penetrometer available broke down during the analyses and had to be replaced; then, the analyses were conducted at the fourth laboratory – CCTM – Energy and Nuclear Research Institute, São Paulo, SP.
Through the NACP methodology, it was possible to obtain adsorption isotherms for all samples being studied. They are basically type II, according to Lowell and Shields,[6] as shown in figure 4.
Desorption isotherm curves were also prepared and showed the occurrence of hysteresis (also shown in figure 4). This explains the existence of pores that, according to the typical hysteresis curves, are mesopores shaped as fissures, cones or pyramids, since hysteresis is classified as type H3, after Santilli and Pulcinelli [7]. However, the use of this methodology for pore shape determination is valid just when pores of ideal geometric shapes are present, which is not the case for the samples in question, as shown in photomicrographs taken during the SEM analyses (figures 5 and 6).

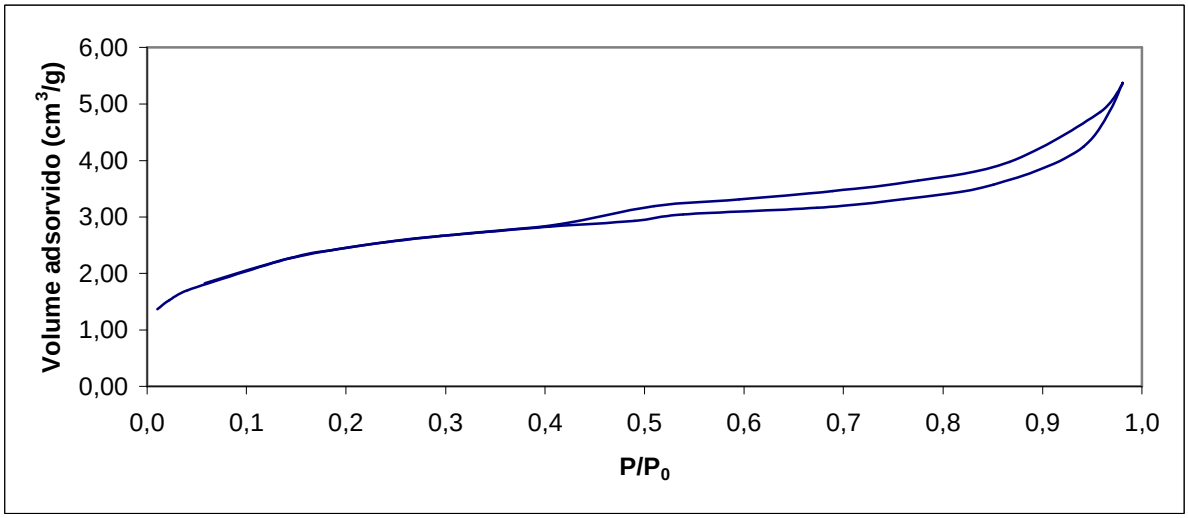

Figure 4 – Adsorption and desorption isotherms for sample 5/4 - desliming underflow.

Other output data of the equipment are micropore volume (de Boer method) and mesopores volume (BJH – Barret, Joyner and Halenda method). Only sample 5/4 and sample 9/4 desliming underflow showed micropores. By comparing those two volumes, as shown in table 3, it is possible to observe that the micropore volume is significant in case of samples 5/4, representing about 30%.
In addition, when analyzing data relative to total micropore SSA (specific surface area) mentioned in table 4, one can see that in samples 5/4 the micropore SSA practically corresponds to 65% of total SSA.

Table 3 – Micropores and mesopores volumes in samples 5/4 and 9/4 – desliming underflow

	Sample	Micropore volume - de Boer (cm^3/g)	Mesopore volume - BJH (cm^3/g)
5/4	Grinding product	0.002741	0.01001
	Desliming OF	0.010453	0.03847
	Desliming UF	0.002596	0.00828
	Concentrate	0.003397	0.00928
	Tailings	0.000475	0.00140
9/4	Desliming UF	0.000263	0.00203

Table 4 – Total specific and micropore surface area of samples 5/4 and 9/4 – desliming underflow

	Sample	Micropore SSA - de Boer (m^2/g)	Total SSA - BET (m^2/g)	$SSA_{Micropore}/SSA_{Total}$
5/4	Grinding product	5.9733	9.6055	0.62
	Desliming OF	22.3602	36.8799	0.61
	Desliming UF	5.6190	8.4626	0.66
	Concentrate	7.2024	10.2514	0.70
	Tailings	1.0526	1.4977	0.70
9/4	Desliming UF	0.6775	1.6457	0.41

SSA, pore volume and diameter data of the four flotation concentrate samples were organized in table 5 in conjunction with other physical and mineralogical data to allow making a comparison between porosity determination methods.

Table 5 – Comparison between MIP and NACP data – flotation concentrate

	Flotation concentrate			
Parameters	**5/14**	**9/4**	**5/4**	**5/35**
Ds picnometer He g/cm^3	4.73	4.98	5.05	5.06
Porous phases %	72.8	69.4	56.1	5.0
SSA-BET m^2/g	2.3	2.4	10.3	0.8
SSA-Blaine m^2/g	0.0599	0.0475	0.059	0.0562
SSA-MIP m^2/g	1.684	0.554	1.095	0.204
Pore volume - BJH cm^3/g	0.0063	0.0046	0.0093	0.0020
Pore volume (-100nm) - MIP cm^3/g	0.0082	0.0034	0.0052	0.0009
Total porosity % - MIP	4.2	1.8	2.9	0.6
Pore volume (-1.0µm) - MIP cm^3/g	0.0164	0.0079	0.0105	0.0035
Total porosity % - MIP	8.5	4.1	5.8	2.3
Pore volume (-10.0µm) - MIP cm^3/g	0.0688	0.0420	0.0509	0.0520
Total porosity % - MIP	35.3	21.8	28.4	34.3
Total pore volume - MIP cm^3/g	0.1951	0.1931	0.1795	0.1515
dmax µm (MIP)	103.5	100.4	102.5	101.4
dmid µm(MIP)	11.6	13.2	11.9	11.3
dmin µm (MIP)	0.004	0.011	0.003	0.017
dmid nm (NACP)	11.05	7.47	3.62	10.51

As shown in the table above, the porosity parameters of sample 5/35, which had porous phases composition much lower than the other samples, were perceived as different through NACP (lower SSA and pore volume and higher average diameter – except for the flotation concentrate, whose values were similar to those of sample 5/14).
When using the MIP methodology, different and lower SSA values were found; however, the figures relative to pore volume and average diameter were the same. When the pore volume per size fraction was obtained (via linear interpolation) and just for fractions below 1µm and 100nm, it was possible to perceive a differentiation consistent with the NACP data, as expected due to the composition of potentially porous phases (porous hematite and goethite). This consistency between pore volumes by NACP and pore volume (below 1mm and 100nm) by MIP occurred for all samples and not only for sample 5/35.
Another issue to be highlighted in this table is the differentiation of sample 5/4 in relation to other samples. This sample has higher SSA (BET) and lower pore diameter (BJH), which is coherent with the existence of micropores, mentioned above. The specific surface areas obtained through the Blaine method were all similar. It is important to emphasize that these observations are also valid for samples of the grinding product, desliming underflow and flotation tailings.
Among the samples investigated by means of SEM analyses it was not possible to notice any difference in porosity. It is worth emphasizing that this is a predominantly qualitative approach. On the other hand, among the typical microstructural features of iron ores (lamellar-specular hematite, martitic hematite, compact goethite, botryoidal goethite, earthen goethite and quartz), clear differences could be noticed.
Thus, lamellar hematite always presented very low porosity levels, whereas martitic hematite and goethite showed significant porosity distribution, from not very porous to extremely porous. In those porous features, the distribution range of pore diameter and shape was very large, with pores varying from dimensions of several µm to below 50 nm.

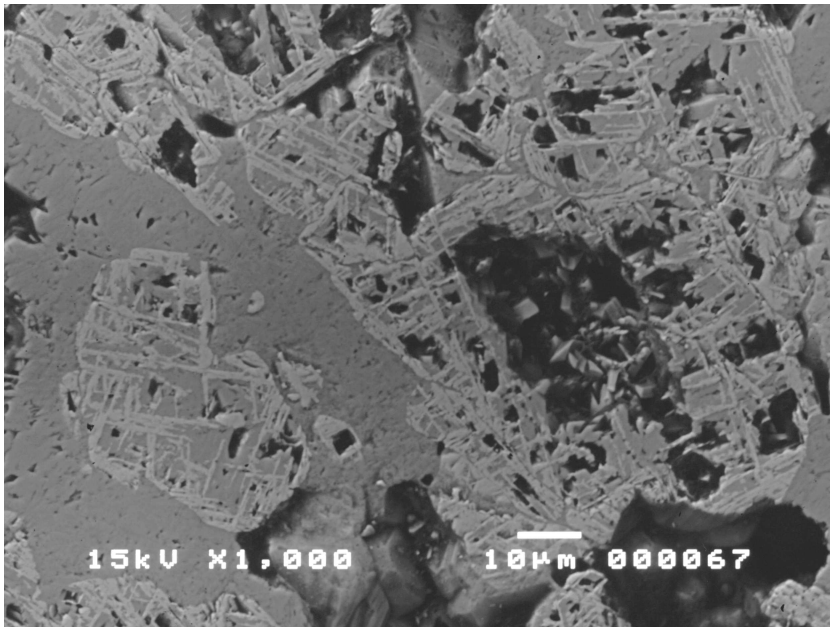

Figure 5 – Sample 5/14 – concentrate. Polished section. SEM, BEI. Mixed particle with martitic hematite, compact goethite and few earthen goethite. Pores vary from 40µm, 20µm to 10µm, 5µm to 3µm, 1.0µm.

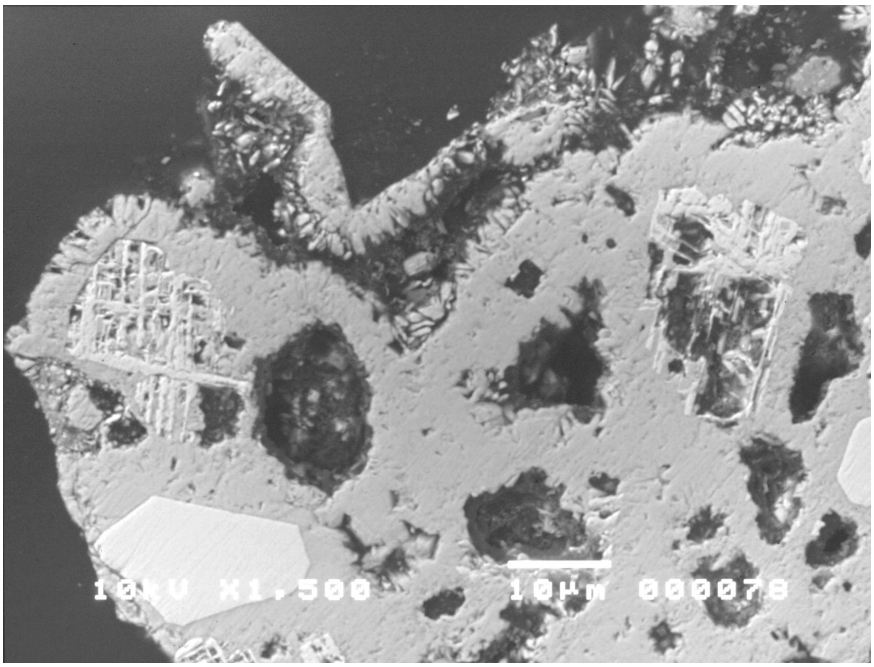

Figure 6 - Sample 5/14 – concentrate. Polished section. SEM, BEI. Particle with various features bearing porous martitic hematite, porous botryoidal goethite, earthen goethite and few lamellar hematite. Pores vary from 15.0µm to 1.0µm.

Thus, the overall differences of average porosity among the samples studies through porosimetry methods would primarily result from the differences of relative quantities of the various microstructural features that characterize these samples within the resolution range of the equipment. This complies with the NACP and MIP (below 10µm) analyses conducted for samples 5/35, which demonstrated lower incidence of porosity due to lower composition of porous features.
The differentiation perceived for samples 5/4, which presented composition of porous phases similar to that of samples 5/14 and 9/4 results from microporosity and also due to the presence of smaller mesopores (average diameter around 3.62nm, as shown in table 5). The equipment used to apply the MIP and SEM-SEI techniques was not able to detect pore with these extremely small dimensions.

CONCLUSIONS

Both porosimetry methods used – mercury intrusion porosimetry (MIP) and nitrogen adsorption-condensation porosimetry (NACP) – and also the BET method used in the determination of the specific surface area (SSA) showed different abilities to characterize and distinguish different types and degrees of porosity found in the samples.
For all samples investigated, the SSA and BJH porosity (mesopores via NACP) analyses showed that sample 5/35 has the lowest porosity and lowest SSA, which is consistent with a lower number of potentially porous mineralogical features. MIP data relative to total volumes of pores smaller than 1.0µm and 100nm also were consistent for this sample. Other MIP data (including total porosity) were not sensitive enough to detect differences in this sample.
On the other hand, sample 5/4 showed SSA much greater than all other samples, which is consistent with a higher BJH porosity (mesopores); in addition, this sample also showed the smallest average mesopore diameter (3.62nm for the concentrate).

In this case, mesopores are present in the lower diameter fraction. Another relevant data is that this was the only sample that showed significant micropore volumes (de Boer model). MIP data did not indicate an exceptional porosity for this sample, but rather, placed it on the same level of samples 5/14 and 9/4.
Apparently, differences in porosity and SSA of sample 5/4 are even more unexpected for concentrate samples, where the number of potentially porous phases of this sample is lower (56.1%) than that of samples 5/14 (72.8%) and 9/4 (69.6%).
Porosity data determined by both methods (MIP and NACP) and SSA data of the two other samples – 5/14 and 9/4 – indicate close but non-identical properties.
A relevant aspect of this investigation is that it allowed comparing the two main porosimetry methods – MIP and NACP – within the value range where both are applicable, i.e., between 100.0nm and 3.0nm. In general, consistent but non-identical values were found for most samples investigated.
MIP was of difficult use due to low availability rates of equipment and maintenance problems.
We recommend the use of the BET and NACP methods, in case fine porosity is present, for SSA and pore distribution determination, respectively, and consequent correlation of the performance of iron ore beneficiation processes, instead of the Blaine method, which was not able to distinguish any sample. However, it is worth emphasizing that it takes a long time to obtain the results through NACP due to the time required to prepare and carry out the analysis, which makes its use difficult in the quality control from mine to final product.

REFERENCES

1 COSTA, A. G. D., ROCHA, J. M., BONFIOLI, L., VIEIRA, C. B. *A Importância do Modelamento Geológico-Tipológico no Controle de Qualidade dos Concentrados e Pelotas de Minério de Ferro da Samarco Mineração S.A*. In: *SEMINÁRIO DE REDUÇÃO E MATÉRIAS PRIMAS DA ABM, 24, 1998, Belo Horizonte*.

2 PENA, E. Q. *Caracterização dos Parâmetros Intrínsecos de Porosidade e de Superfície Específica de Pellet Feed de Mínério de Ferro do Quadrilátero Ferrífero Empregando o Método de Adsorção de Nitrogênio*. Ouro Preto: REDEMAT, 2002. 78p. (Materials Engineering MSc. Dissertation).

3 BRANDÃO, P. R. G. Class Notes, Discipline: “Instrumentation and Analysis Methods”, Metallurgical and Mining Engineering Post-Graduation Course, Universidade Federal de Minas Gerais, 2008.

4 WEBB, P. A., ORR, C. Analytical Methods in Fine Particle Technology. 1.ed. Norcross: Micromeritics Instrument Corporation, 1997. 301p.

5 Micromeritics. PoreSizer 9320. Quick Reference Guide.

6 LOWELL, S., SHIELDS, J. E. Powder Surface Area and Porosity. 2.ed. London: Chapman and Hall Ltd, 1984. 21v.

7 SANTILLI, C. V., PULCINELLI, S. H. *Análise da Textura de Materiais Cerâmicos a partir de Isotermas de Adsorção de Gases*. Cerâmica, 39 (259), 1993, p 11-16.