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CALCINATION AS ADDITIONAL UNIT OPERATION IN THE PELLETIZING OF IRON ORES PRESENTING HIGH CONTENTS OF LOSS ON IGNITION

C.M.L. Leonel [1], A. E. C. Peres [2]

[1] Gerdau
Rua dos Inconfidentes, 871
30140-120 Belo Horizonte, MG, Brazil
[2] Universidade Federal de Minas Gerais Escola de Engenharia bloco 2 sala 2233 Avenida Antonio Carlos, 6627
31270-901 Belo Horizonte, MG, Brazil
aecperes@demet.ufmg.br

ABSTRACT

Iron ore deposits from the Alegria Complex, in the region of Mariana – Ouro Preto, MG, Brazil, contain a significant fraction of low grade itabirites (iron content below 50% and loss on ignition, LOI, content above 3.5%). This material causes decreased yield in the beneficiation stage and high loss of productivity in the pelletizing process. Studies addressing technological alternatives and/or process routes as additional unit operation to the traditional pelletizing process may help to render feasible the processing of this type of material. Samples presenting different LOI contents were pelletized and calcined at pilot scale. The product was submitted to thermogravimetric, porosity, surface charge, and dispersion degree determinations.

Keywords: calcination, porosity, pelletizing

1. INTRODUCTION

The current plant practice indicates that the utilization of pellet feed presenting high loss contents in travelling grate under standard operation conditions and process leads to: ROM blend with higher goethite content, higher specific surface area of the reground pellet feed, drop in the filtration productivity, and increase in the cake moisture, production of higher specific surface area in the high pressure grinding rolls even for operation at low pressure, loss in the quality of raw pellets (higher moisture and plasticity levels), drop in the travelling grate productivity (reduction of the charge of feed pellets bulk density and difficulty in keeping the physical quality of the indurated pellets).

The LOI content also affects significantly the formation of cracks during the burning process.

Hematite formed by dehydration of oxi-hydroxides at temperatures below 500ºC - 600ºC is porous. According to Prasad et al. (2006), the goethite dehydration at constant rate thermal analysis indicated that, for each specific temperature, the porosity of hematite depends on the dehydration rate and the pressure of the produced water vapor (transformation under vacuum, at atmospheric pressure or in closed system).

Balek and Šubrt (1995), Naomo et al. (1987), and Perez-Maqueda et al. (1999) developed high added value products, via laboratory synthesis, transformation mechanisms studies, products characteristics and analytical methods, from goethite, a stable and low cost mineral.

According to Prasad et al. (2006), the transformation of goethite to hematite may occur by two mechanisms:
(i) formation of an intermittent superstructure (proto-hematite or hydrohematite) prior to the final formation of hematite: $\alpha\text{-FeOOH} \rightarrow$ intermediate superstructure $\rightarrow \alpha\text{-}Fe_2O_3$;
(ii) direct transformation of goethite to hematite: $\alpha\text{-FeOOH} \rightarrow \alpha\text{-}Fe_2O_3 + H_2O$.

The effect of the intrinsic characteristics of concentrate presenting high porosity degrees and high LOI contents on process and operation conditions of filtration, pelletizing, and firing and the impacts on the products quality were investigated by Costa (2005), Costa (2008), and Mangabeira (2009). On the other hand there are indications that the calcination of pellet feed in pilot rotary kiln may bring difficulties to pelletizing and decrease the physical resistance of indurated pellets.

The objective of the present investigation was to characterize the low temperature dehydration of goethite present in reground concentrates from the Alegria Complex, as well as to study indirect techniques for the evaluation of the state of agglomerability/pelletizing of materials presenting high LOI contents, either calcined or not calcined.

2. METHODOLOGY

Aiming to study the use of calcination to reduce the LOI content of pellet feed to approximately 2.5% (reference value for plant practice with adequate performance) two conditions were proposed: i. calcining the raw reground concentrate; ii. splitting the concentrate in coarse and fine fractions, calcining only the fine fraction and, then, blending the calcined fine fraction with the raw coarse fraction yielding a product compatible with the LOI reference value limit. Figure 1 illustrates the route of calcination applied only to the fine fraction.

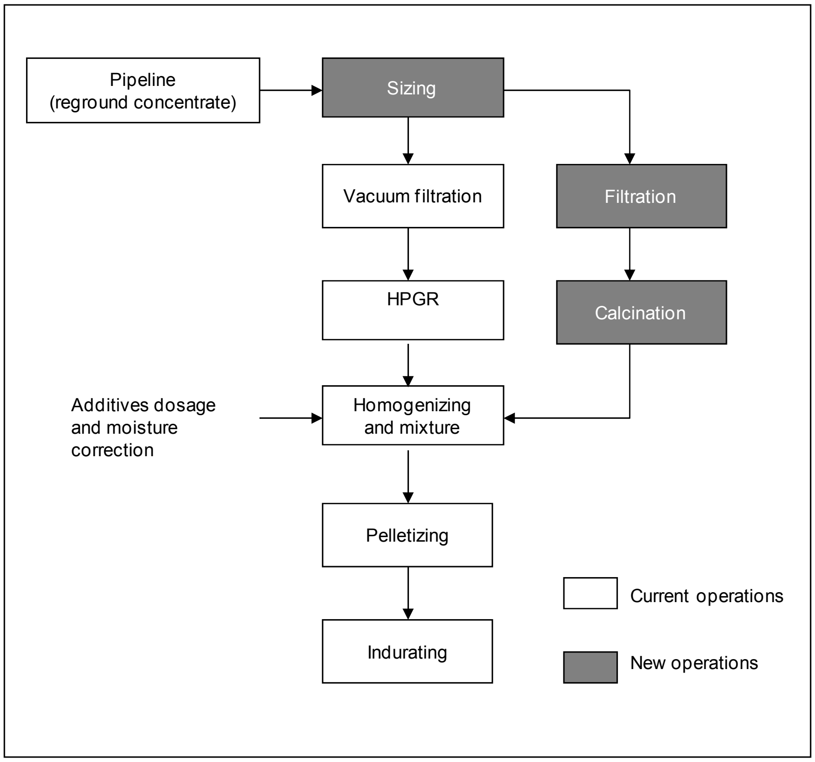

Figure 1. Process route of calcination of the fine fraction.

The main characteristics of reground concentrates, presenting different LOI contents, used in the experiments are illustrated in table 1.

Table 1. Chemical, physical, and mineralogical characteristics of samples 01, 02, and 03 (sample 01 – reference sample for the condition normal LOI content pellet feed).

Sample	Contents (%)								Physical analyses			Mineralogical analyses (%)			
	Fe	FeO	SiO_2	CaO	MgO	Al_2O_3	P	LOI	Density (g/cm^3)	<45 m (%)	BSA (cm^2/g)	S.H.	P.H.	Goethite	Magnetite
Sample 01 LOI 2.89%	66.69	1.09	1.17	0.09	0.03	0.36	0.040	2.89	4.95	87.4	1520	36.5	39.9	20.5	2.7

Sample	Contents (%)								Physical analyses			Mineralogical analyses (%)			
	Fe	FeO	SiO_2	CaO	MgO	Al_2O_3	P	LOI	Density (g/cm^3)	<45 μm (%)	BSA (cm^2/g)	S.H.	P.H.	Goethite	Magnetite
Sample 02 LOI 4.45%	65.54	1.52	1.34	0.03	0.03	0.35	0.056	4.45	4.70	88.4	2080	18.6	35.3	40.4	4.3

Sample	Contents (%)								Physical analyses			Mineralogical analyses (%)			
	Fe	FeO	SiO_2	CaO	MgO	Al_2O_3	P	LOI	Density (g/cm^3)	<45 m (%)	BSA (cm^2/g)	S.H.	P.H.	Goethite	Magnetite
Sample 03 LOI 3.83%	65.99	0.81	1.12	0.11	0.03	0.40	0.048	3.83	4.78	91.6	1874	22.4	38.7	37.8	1.4

BSA = blaine surface area; S. H. = specular hematite; P. H. = porous hematite

The determinations of total Fe and FeO were done via wet chemistry. The determinations of Al_2O_3, CaO, MgO, MnO_2, P, and SiO_2 were done in an ICP spectrometer, model Cirus, manufactured by Spectro Instruments. The LOI content was determined via calcinations under specific standard methodology.

Thermogravimetric determinations were done with the use of two different equipments: Navas Instruments TGA-2000 and Netzsch 409 CD STA, which includes also differential thermal analysis. Besides the characterization of goethite dehydration, these analyses aimed to prepare small amounts of samples presenting different LOI contents to be used in porosity, degree of dispersion, and surface charge determinations.

The calcination of samples to be used in pelletizing pilot scale experiments was done in rotary kiln. In order to calibrate the kiln, the corderite trays were filled with approximately 2.5 kg of iron ore concentrate and then taken to the kiln. The residence time was set at two hours and the temperature was varied at the sequence: 385, 400, 410, and 420ºC, the reground concentrate sample 02 being used in the first test. The calcinations target was a final product with 2.5% LOI content. The temperature selected for the calcinations was 405ºC, and 450 kg of calcined material were produced.

The same procedure was employed in the calibration for the second test. The sample used was the overflow of hydrocyclone classification of sample 02. The starting temperature was set at 500ºC, considered ideal for the target of residual LOI content 1.2%. Approximately 350 kg of calcined fine material were produced.

Porosity and gaseous N_2 adsorption/desorption determinations were done in the equipment Quantachrome NOVA 1200.

The dispersion degree of the reground concentrate suspensions was determined in a sedimentation apparatus consisting of a glass tube of 4.0 cm of internal diameter, 18.5 cm of height, with an outlet of 0.8 cm of diameter at the height of 2.0 cm for the removal of the supernatant.

Zeta potential determinations were done in a Zeta-Meter 3.0 equipment.
Quantitative and qualitative mineralogical analyses were performed under reflected and transmitted light microscope. The estimated volumetric percentages of the mineral species present in the observed particles were converted into weight with the use of the theoretical density of each phase.

3. RESULTS

3.1. Pilot scale pelletizing without calcination

Table 2 presents the results of wet compression strength (wet-CS), dry compression strength (dry-CS) and drop test of iron ore pellets obtained in pilot scale pelletizing of samples 01, 02, and 03. The drop test consists of letting the pellet fall from a height of 45 cm and determination of the number of drops until the pellet cracks.

Table 2. Results of parameters determination of pellets produced without calcinations.

Parameters	Sample 01 (2.89% LOI)			Sample 03 (3.83% LOI)			Sample 02 (4.45% LOI)		
Test	1	2	3	4	5	6	7	8	9
Drop test (number of drops)	4.0	4.3	3.1	5.0	5.2	4.5	7.4	6.1	6.7
Wet-CS (gf/pellet)	1,936	2,032	1,970	2,275	2,325	2,134	2,689	2,256	2,544
Dry-CS (gf/pellet)	7,530	8,902	9,647	9,977	9,987	9,978	12,492	11,838	12,004
Moisture (%)	8.83	8.91	8.77	9.61	9.45	9.21	9.84	9.94	9.84

The same results are graphically illustrated in figures 2, 3, and 4.

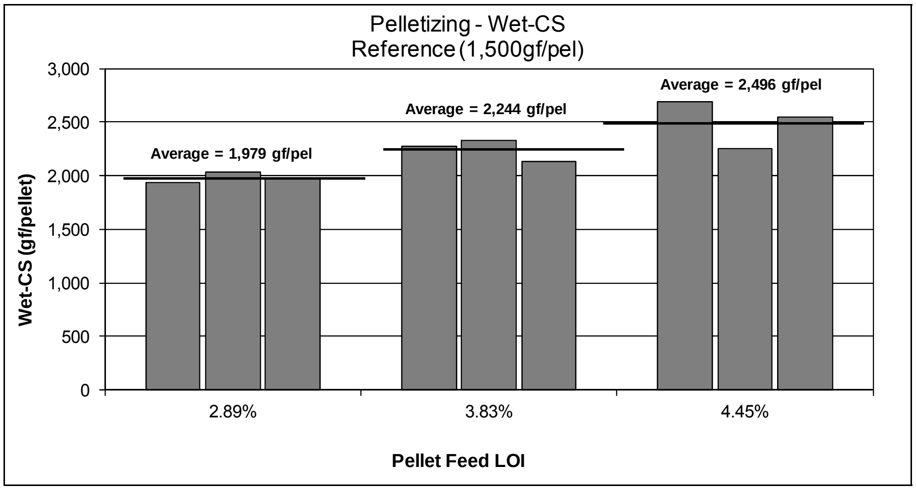

Figure 2. Results of wet compression strength (wet-CS) determinations.

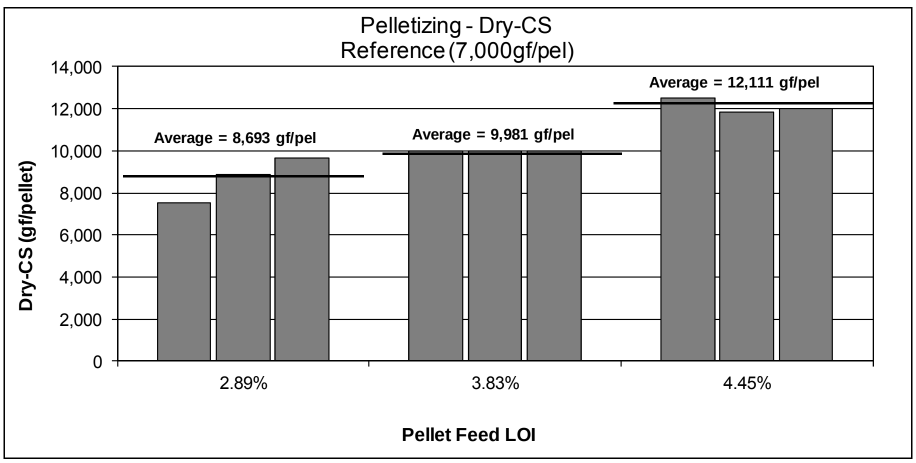

Figure 3. Results of dry compression strength (dry-CS) determinations.

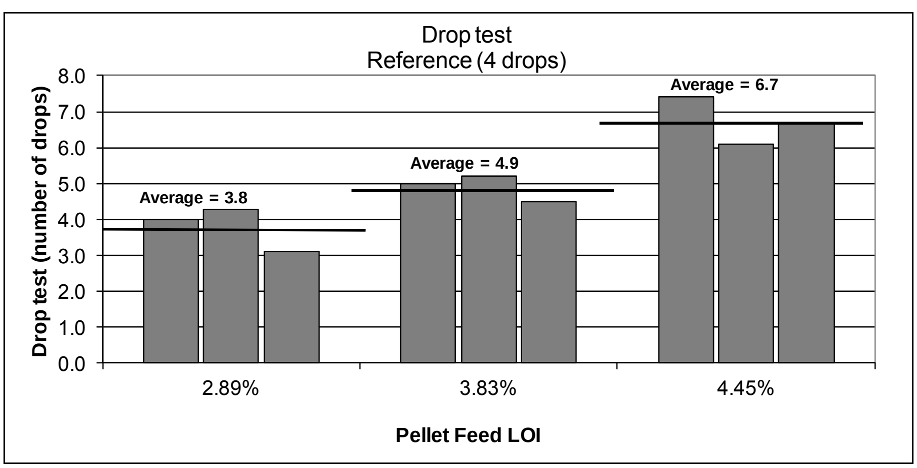

Figure 4. Results of drop test.

It was observed that the values of strength (wet-CS) and dry compression strength (dry-CS), and also the number of drops until the pellet cracks were higher for higher LOI contents in the pellet feed samples.

The compression resistance in kgf/pellet drops sharply with increase in the LOI content from 2.89% to 3.83% and remains constant with further increase to 4.45%, as shown in figure 5.

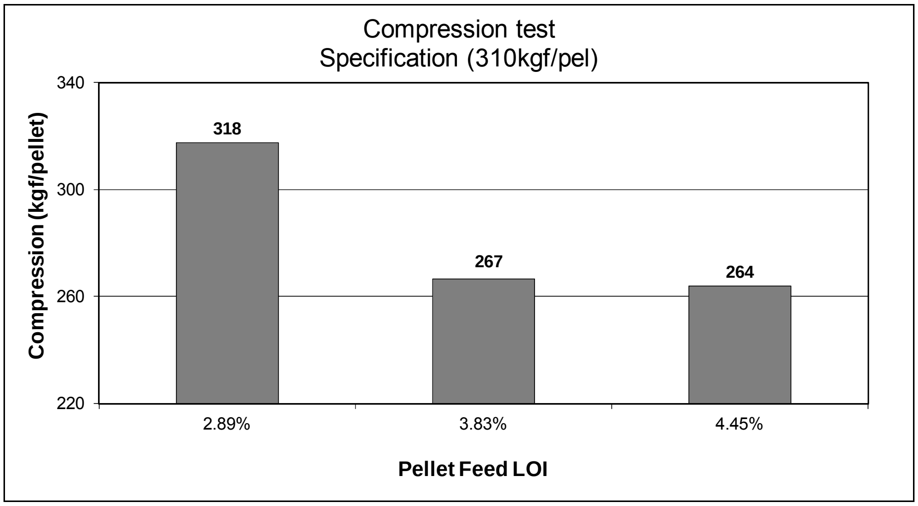

Figure 5. Compression test results as a function of LOI content in the pellet feed.

3.2. Dehydration of goethite

Figure 6 illustrates thermogravimetric analysis (TGA) curves obtained with the three samples under investigation, showing the temperature range in which the goethite dehydration occurs (from 200ºC to 400ºC).

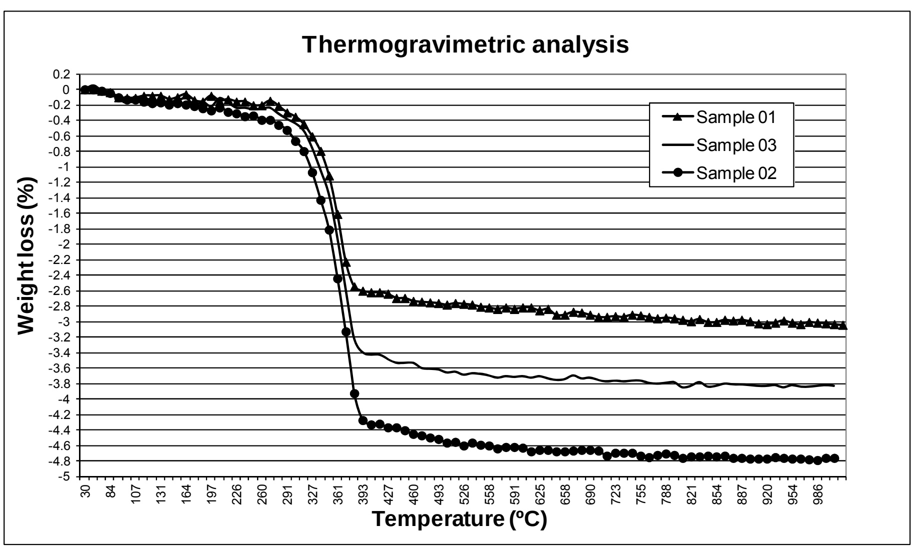

Figure 6. Thermogravimetric analyses of samples 01, 02, and 03.

3.3. Characterization of the calcination effect on parameters related to wet agglomerability of final reground concentrates.

3.3.1. Porosity of calcined materials

Table 3 and 4 present a summary of results achieved in the experiments of porosity determination of the overall final reground concentrate and of its fine fraction (<22 µm) from sample 02, respectively.

Table 3. Results of porosity determination: overall final reground concentrate from sample 02

Calcination degree (% LOI)	Density (g/cm^3)	Porosity				Surface area BET (m^2/g)
		Total pores volume (cm^3/g)	Average diameter (Å)	Pores volume t-method (cm^3/g)	Pores volume BJH (cm^3/g)	
NC	4.92	0.0110	99.1	-	0.011	4.5
4.0	4.86	0.0138	77.9	-	0.012	7.1
3.5	4.99	0.0164	49.3	0.0031	0.013	13.2
3.0	4.85	0.0202	40.3	0.0064	0.013	19.8
2.5	4.87	0.0228	35.4	0.0093	0.013	25.5
2.0	4.80	0.0263	35.5	0.0107	0.015	29.4
1.5	4.89	0.0307	32.4	0.0148	0.015	37.6
1.0	4.90	0.0319	32.2	0.0155	0.016	39.3
0.5	4.89	0.0265	46.2	0.0066	0.021	22.6

Table 4. Results of porosity determination: fine fraction (<22 µm) of the reground concentrate from sample 02

Calcination degree (% LOI)	Density (g/cm^3)	Porosity				Surface area BET (m^2/g)
		Total pores volume (cm^3/g)	Average diameter (Å)	Pores volume t-method (cm^3/g)	Pores volume BJH (cm^3/g)	
NC	4.90	0.0150	106.4	-	0.014	5.6
4.0	4.88	0.0180	76.2	-	0.016	9.4
3.5	4.96	0.0196	50.5	0.0035	0.015	15.4
3.0	4.95	0.0248	46.4	0.0056	0.018	21.1
2.5	5.01	0.0281	38.3	0.0100	0.016	29.1
2.0	4.91	0.0314	35.9	0.0126	0.017	34.7
1.5	5.02	0.0344	34.6	0.0147	0.018	39.4
1.0	5.00	0.0409	48.7	0.0082	0.036	33.1
0.5	4.93	0.0287	71.1	0.0012	0.029	15.9

Figure and 8 illustrate the pores volume as a function of the calcination degree of the overall final reground concentrate and of its fine fraction (<22 µm) from sample 02, respectively.

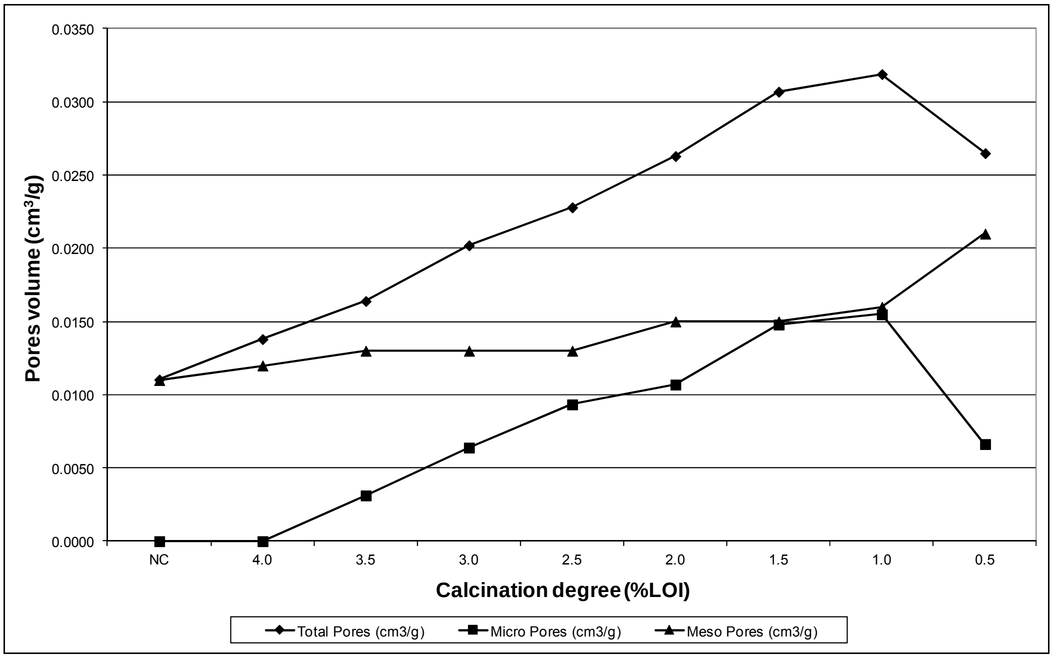

Figure 7. Pores volume as a function of calcination degree of the overall final reground concentrate from sample 02.

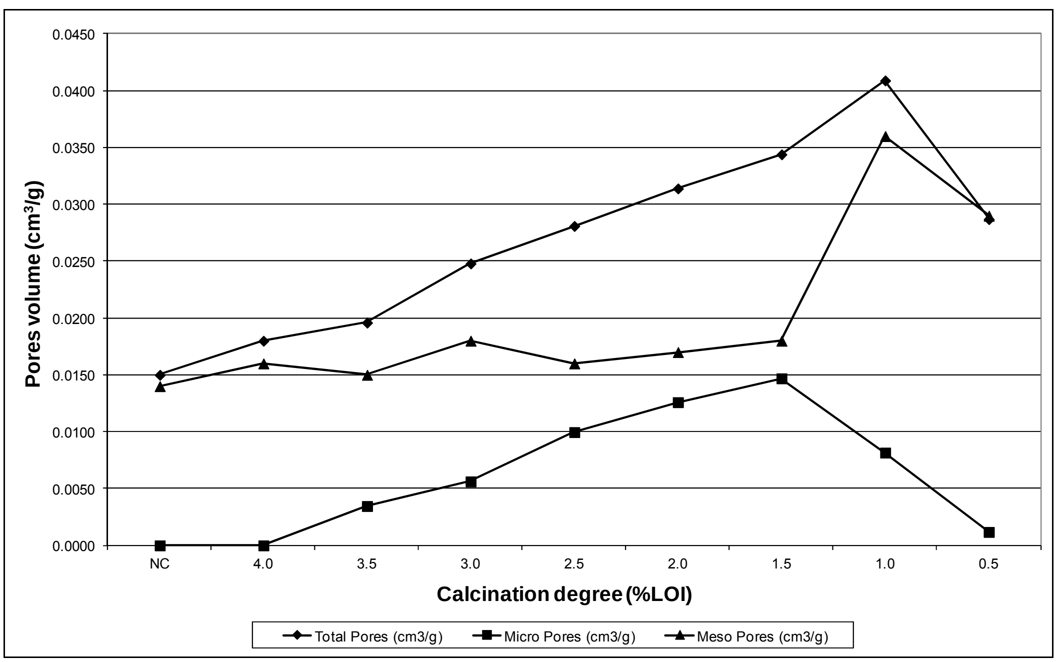

Figure 8. Pores volume as a function of calcination degree of the fine fraction (<22 μm) from sample 02.

The results of porosity determinations are summarized in table 5.

Table 5. Summary of porosity determinations results

Sample	Condition	Total pores volume (Cm^3/g)	proportion of pores	Proportion goethite/hematite
01	overall final reground concentrate - not calcined (LOI - 2.89%) reference	0.0074	1.0	23/75
02	overall final reground concentrate - not calcined (LOI - 4.45%)	0.0114	1.5	53/46
02	co arse fraction (>600#) - not calcined (LOI - 4.06%)	0.0069	0.9	49/48
02	fine fraction (<600#) - not calcined (LOI - 5.59%)	0.0150	2	50/49
02	overall final reground concentrate - calcined (LOI - 2.50%)	0.0228	3.1	28/70
02	fine fraction (<600#) - calcined (LOI - 1.20%)	0.0409	5.5	12/86
02	coarse + fine fractions - calcined (LOI - 2.50%)	0.0232	3.1	31/66

3.3.2. Surface charge of calcined materials

Table 6 and figure 9 present the results of zeta potential determinations as a function of pH, modulated with NaOH, for different levels of calcination of sample 02.

Table 6. Results of zeta potential determinations: cyclone overflow, sample 2.

Sample	Average pH	Number of particles	ZP (mV)	Standard deviation
cyclone overflow not calcined	3.93	20	36.41	2.16
	5.00	10	12.52	2.42
	5.64	20	14.24	2.73
	9.20	30	-25.10	4.16
	9.91	20	-22.20	2.20
	11.17	20	-27.00	3.23
cyclone overflow calcined LOI 4.0%	3.90	20	33.64	2.02
	5.04	20	31.29	2.61
	5.66	20	20.55	3.27
	9.20	20	-25.10	3.61
	9.83	20	-23.20	3.81
	11.24	20	-30.80	3.62
cyclone overflow calcined LOI 3.0%	3.92	30	44.79	2.67
	5.04	10	18.81	2.67
	5.72	22	8.67	3.08
	9.05	20	-27.00	4.53
	9.93	20	-25.20	3.36
	11.26	31	-30.00	3.80
cyclone overflow calcined LOI 2.5%	4.01	19	40.96	2.67
	5.05	30	19.04	4.91
	5.70	20	22.43	4.44
	9.20	31	-33.10	6.28
	9.83	20	-26.70	3.91
	11.14	20	-31.00	3.37
cyclone overflow calcined LOI 2.0%	3.97	30	42.92	2.53
	5.05	10	12.39	3.03
	5.72	20	17.53	4.47
	9.20	20	-24.80	3.70
	9.90	20	-25.40	4.28
	11.16	20	-28.50	4.09
cyclone overflow calcined LOI 1.0%	3.97	20	42.47	2.28
	4.92	20	21.75	5.00
	5.72	20	18.84	3.20
	9.20	22	-29.20	4.28
	9.90	21	-27.30	3.49
	11.14	20	-33.40	2.92

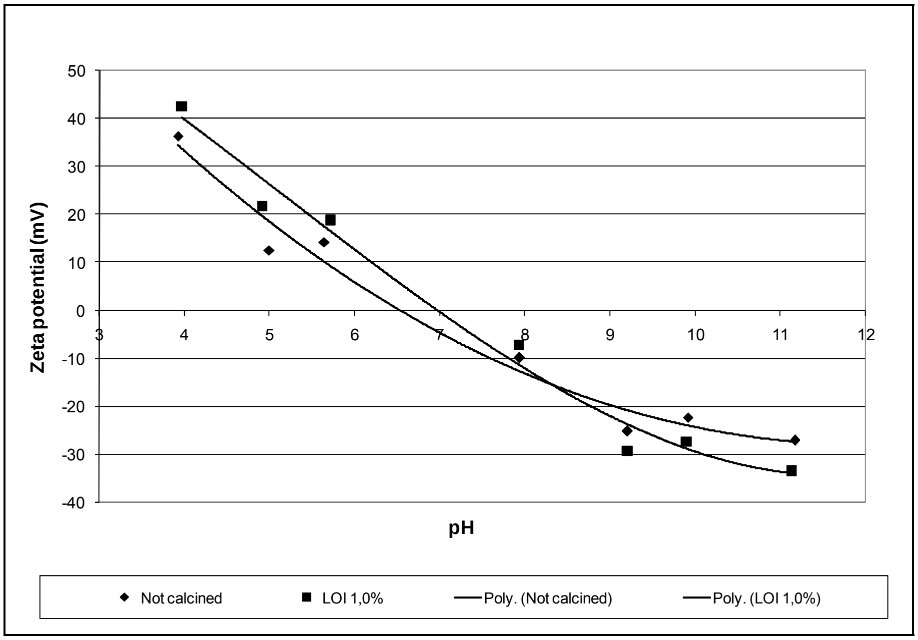

Figure 9. Zeta potential as a function of pH for sample cyclone overflow in the conditions not calcined and calcined to residual LOI content of 1.0%.

3.3.3. Dispersion degree of calcined materials

Figure 10 illustrates the effect of pH on the dispersion degree of calcined samples of the overall final reground concentrate and of its hydrocyclone overflow.

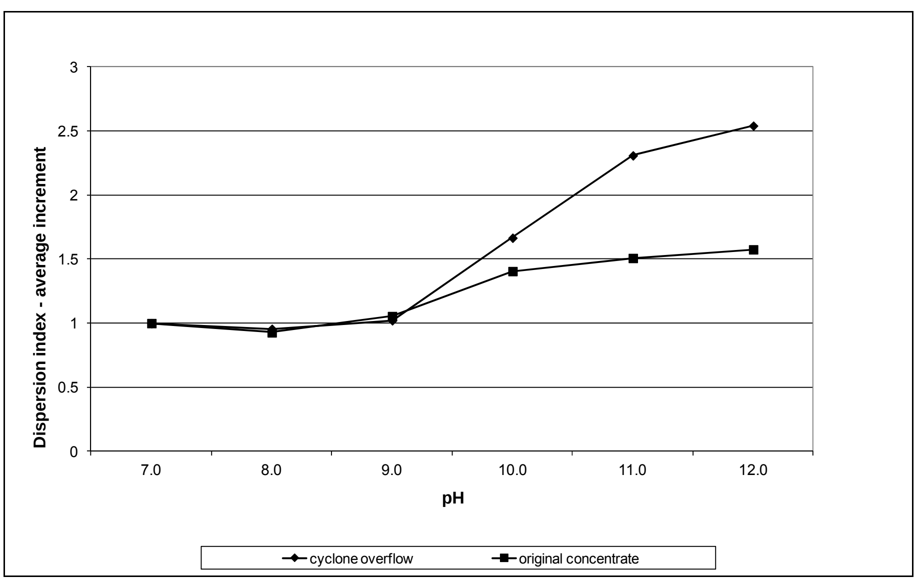

Figure 10. Effect of pH on the dispersion degree of calcined samples of the overall final reground concentrate and of its hydrocyclone overflow.

4. CONCLUSIONS

Iron ore concentrates presenting high LOI contents (3.83% to 4.45%) impair significantly the pelletizing and indurating stages.

Pilot scale pelletizing experiments done with materials presenting high LOI content indicated:

- ✓ wet pellet compression strength and dry pellet compression strength below the minimum recommended limits;
- ✓ drop resistance significantly higher (37%) than that for the reference sample (green pellets);
- ✓ 17% drop in the compression index after the indurating stage.

The dehydration of goethite presented an endothermic peak at 350ºC. Pilot flash kiln is a viable technique for the calcination of concentrates at low temperature (350ºC to 500ºC).

Porosity studies by adsorption/desorption of N_2 demonstrated:

- ✓ porosity of the high LOI content sample 50% higher than that of the reference sample;
- ✓ porosity of the high LOI content sample calcined at low temperature to residual LOI content 2.5% three times higher than that of the reference sample;
- ✓ porosity of the fine fraction of the high LOI content sample calcined at low temperature to residual LOI content 1.1% five times higher than that of the reference sample.

The calcination degree has little effect on the zeta potential. The isoelectric point was observed in the pH range between 6.5 and 7.0. Alkaline pH values, above 9.0, modulated with caustic soda, increase significantly the negative values of the zeta potential, resulting in enhanced dispersion degree of the particles in the pulp.

5. REFERENCES

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