Particle disintegration of an important brazilian manganese lump ore

Degradação granulométrica de um importante minério de manganês do Brasil

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Abstract

The manganese lump ore from Morro da Mina mine is typically silicate carbonated and presents a great economic potential for the ferroalloy companies installed in Minas Gerais. However, its low manganese content, associated with the lack of knowledge about its metallurgical properties makes it difficult for large scale application. This pioneering study aimed to amply investigate this lump ore's particle disintegration. One ton of ore from the mine was homogenized and quartered. Representative samples were characterized by different techniques, such as ICP-AES, XRD, SEM, BET and OM. Aiming to characterize particle disintegration, three parameters were proposed: Cold Disintegration Index (CDI), Decrepitation Index (DI) and Heating Disintegration Index (HDI). By using these indexes, it was possible to conclude that this manganese lump ore did not present significant disintegration at room temperature. At medium temperature test, slight decrepitation occurred, and at high temperatures, intense disintegration was detected. The carbonate decomposition and porosity growth were the main responsible factors for the ore hot particle disintegration.

Key-words: *Manganese Ore, Technologic Characterization, Decrepitation, Particle Size Disintegration, Fines.*

Resumo

O Produto Granulado de Morro da Mina é um minério de manganês silicatado carbonatado que apresenta grande potencial econômico para as empresas de ferro ligas instaladas em Minas Gerais. Entretanto o baixo teor de manganês e o pouco conhecimento a respeito de suas propriedades metalúrgicas dificultam a sua aplicação. Esse trabalho, pioneiramente, propõe um estudo a respeito da degradação granulométrica das suas partículas a frio e a quente. Uma tonelada do material foi recebida, homogeneizada e quarteada. Amostras representativas foram caracterizadas pelas técnicas de ICP-AES, DRX, MEV-EDS, BET e MO. Foram propostos três parâmetros para a caracterização da degradação: índice de desintegração granulométrica a frio (DGF), o índice de crepitação (IC) e o índice de desintegração granulométrica a quente (DGQ). Por meio deles, foi possível observar que o Granulado de Morro da Mina não apresenta significativa degradação granulométrica por crepitação, entretanto apresenta uma intensa degradação após ser submetido a ciclos térmicos de calcinação e de pré-redução, não existindo significativas diferenças entre os dois. A decomposição térmica dos carbonatos de manganês e o consequente aumento da porosidade são os principais fatores responsáveis pela desintegração do minério.

Palavras-chave: Minério de Manganês, Caracterização Tecnológica, Decomposição Térmica, Crepitação, Degradação Granulométrica, Finos.

1. Introduction

The electric reduction furnace is the one most used in the manganese ferroalloy production around the world. One of the most important parts of the reduction process is the pre-reduction zone, where the solid raw materials are heated by the heat exchange with the hot gases flowing upward. On the furnace top, the moisture and structural water are evaporated and a part of the manganese oxides are decomposed by the ascendant gases. Only if the furnace charge has a high permeability will the water be adequately evaporated and the oxides pre-reduced [Tangstad et al (2004), Olsen et al (2007), Faria (2008), Faria et al (2010), Faria (2011), Faria et al (2011), Faria et al (2012)].

In this context, the ore particle disintegration is an important metallurgical parameter which has not yet been well studied for manganese lump ores. The breakage of ore particles as they are heated in the furnace may produce a big amount of fines and diminishes the charge permeability. The low gas flux will not heat the charge adequately and the oxides will not be completely pre-reduced. This scenario will be responsible for a top gas at high temperatures and with a high CO content. Therefore, the use of manganese ore mixtures with high fine generation susceptibility may decrease the heat exchange efficiency and be a problem for the furnace operation and productivity [Faria (2011), Faria et al (2011), Tangstad et al (2004), Olsen et al (2007)].

In technical literature, only three papers about manganese ore disintegration were found. Yoshikoshi et al (1983) and Tangstad et al (2004) studied manganese ore fine generation by tumbling tests. The authors concluded that the more porous the ore, the lower its mechanical strength. However, they did not correlate their observations to the ore mineralogy. Faria et al (2012) studied the decrepitation behavior of three Brazilian manganese ores. The author showed that the evaporation of structural water and the oxide pre-reduction were the main causes for the decrepitation phenomenon in manganese ores.

Having in mind the strategic and logistic importance of Morro da Mina Mine, associated with the lack of knowledge about its ore disintegration behavior, this pioneering study proposed an experimental method that allowed the characterization of this important metallurgical parameter. The data generated and good industrial planning may be important for the definition of technical criteria that may guide the selection of ore mixtures, aiming to improve the process control and functionality.

2. Materials and methods

2. 1 Chemical and Mineralogical Characterization

A ton of the studied lump ore was homogenized and quartered. Two representative samples were screened and two particle sizes were collected: 1) between 15.9mm and 9.5mm; 2) between 19mm and 6.3mm. These particle sizes were characterized.

The Mn, Fe, CaO, MgO, SiO_2, Al_2O_3, TiO_2 and P contents were determined by ICP-OES and titration. The mineralogical characterization was performed by XRD (1.2º/minute – Cu source), optical microscopy and thermogravimetry.

2.2 Particle Disintegration

The first proposed index allowed for the characterization of the particle disintegration at room temperature. This index measured the ore's mechanical strength under abrasion and impact procedures. This index was defined as Cold Disintegration Index (CDI). Aiming to determine the CDI, the particle size between 15.9mm and 9.5mm were dried and tumbled (3x10minutes) in a rotative tumbler AN4696TR standardized by ISO9246-1 and ISO9246-2. The percentage weight of fines generated below 9.5mm, 6.3mm, 3.35mm, 1.18mm, 0.6mm and 100# sieves were defined as the CDI.

Two parameters were defined aiming to evaluate the mechanical behavior of the heated ores. The first index was proposed aiming to simulate the top of the electric furnace. This index was defined as Decrepitation Index (DI). The particle sizes between 19mm and 6.3mm were introduced into a pre-heated oven (700oC). The residence time was 30 minutes. After, the samples were cooled naturally at room temperature and screened at 6.3mm, 3.35mm, 1.18mm and 0.5mm mesh. Ten tests were performed and the average weight percentage below each sieve was defined as DI. Two extra conditions were analyzed: decrepitation of the wet sample (without drying procedure) and decrepitation of samples heated under reducing gas flux [1.5NL/min of H2 (6%), CO2 (38%) and CO (56%) – similar to the constitution of the furnace top gas].

The second index was proposed to simulate the ore mechanical behavior in the pre-reduction zone, where the samples were heated in constant contact with a strong reducing gas. This index was defined as Heating Disintegration Index (HDI). The particle sizes between 15.9mm and 6.3mm were dried and sampled in amounts of 500g. Each sample was heated (25oC/min) in a crucible standardized by ISO4696-1and ISO4696-2 under continuous flux of 5NL/min N2 (100%) until 1000oC. After, the nitrogen flux was interrupted and a flux of CO (99.5%) and N2 (0.5%) were established (Three conditions were tested: 2NL/min, 5NL/min and 15NL/min) and the residence time was one hour. Aiming to build a reference, one test was done with only N2 (100%).

The samples were cooled under a 5NL/min N2 (100%) flux until room temperature. They were screened at 9.5mm, 6.3mm, 3.35mm, 1.18mm, 0,6mm and 100#. The samples were recomposed and submitted to tumbling procedures in an AN4696TR tumbler with a frequency of 30rpm (10 minutes, 20 minutes and 30 minutes). The HDI was defined as the average weight percentage below each sieve (tests were done twice).

3. Results and discussions

3.1. Chemical and Mineralogical Characterization

Table 2 presents the chemical composition for each particle size from Morro da Mina's lump ore.

Samples	Mn	Fe	SiO_2	P	Al_2O_3	CaO	MgO	TiO_2
	wt%	wt%	wt%	wt%	wt%	wt%	wt%	wt%
-19.0mm +6.3mm	24.48	2.89	23.02	0.076	5.42	2.865	2.226	0.268
-15.9mm +9.5mm	32.10	3.32	21.00	0.093	7.34	4.880	1.680	0.127

Table 2
Chemical analysis of Morro da Mina's lump ore (studied particle sizes).

The studied particle sizes presented low manganese contents. The particle sizes between 15.9mm and 9.5mm were the richest. These manganese contents as well as the high SiO_2 contents, can be justified by the ore's mineralogical constitution presented in Table 3. Both particle sizes are mainly constituted by rhodochrosite [$MnCO_3$] and spessartite [$Mn3Al_2(SiO_4)_3$].

Samples	Constituents (wt%)					
	$MnCO_3$	$Mn_3Al_2(SiO_4)_3$	Mn_2SiO_4	$(Fe, Mg)_2Si_2O_6$	SiO_2	Others
	(Rhodochrosite)	(Spessartite)	(Tephroite)	(Ferrosilite)	(Quartz)	
-19.0mm +6.3mm	31 – 26	31 – 24	13 – 6	13 – 10	3 – 1	15 – 13
-15.9mm +9.5mm	35 – 30	30 – 23	17 – 10	10 – 7	4 – 2	17 – 15

Table 3
Mineralogical constitution of Morro da Mina's ore (studied particle sizes).

3.2. Particle Disintegration

The CDI indexes and their standard deviations are presented in Figure 1. For the studied tumbling conditions, the Morro da Mina's lump ore presented low susceptibility to the cold fines generation. This ore presented only 0.7% of material below 6.3mm mesh after 30 minutes of the tumbling process.

Figure 2 presents the decrepitation indexes for the three studied conditions. The studied ore also presented low susceptibility to the decrepitation phenomenon for all conditions. The fines generation was more significant in the reducing atmosphere.

According to Faria's researches (between 2008 and 2011)(1,5), oxidized ores, different from the lump ore studied herein, have high decrepitation indexes. According to him, the structural water evaporation and the oxide heat decompositions are the main causes for this phenomenon.

The Morro da Mina's lump ore consists mainly of carbonates and silicates which are thermodynamically stable at 700oC (decrepitation test temperature). This characteristic coupled with the low content of hydrated minerals is responsible for the structural integrity maintenance during the fast heating of the ore until the decrepitation test temperature, justifying the small amount of fines generated.

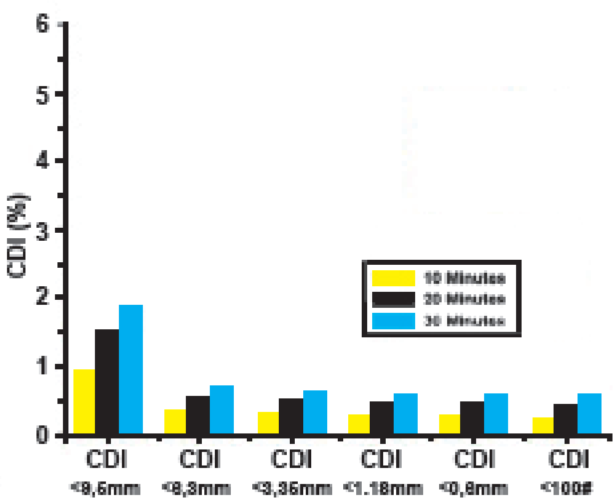

Figure 1
Cold Disintegration Indexes (CDI).

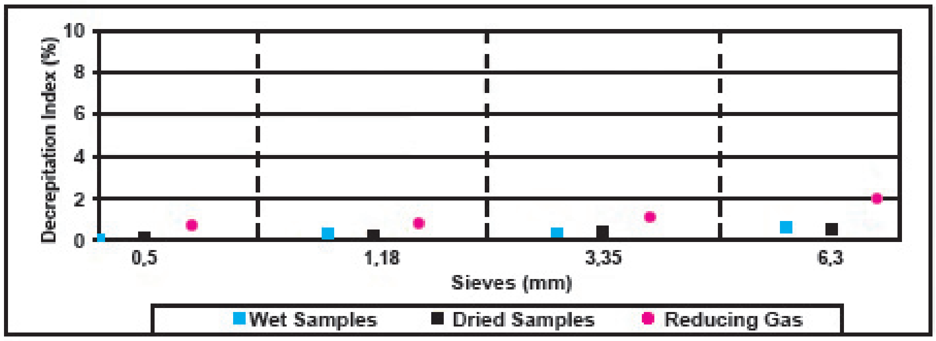

Figure 2
Measured Decrepitation Indexes (DI).

Figures 3 and 4 present respectively the weight lost during the heating procedure and isothermal (1000°C) treatment. The figures 5 and 6 present respectively the comparison between the CDI and HDI indexes, measured by 6.3mm and 0.6mm sieves.

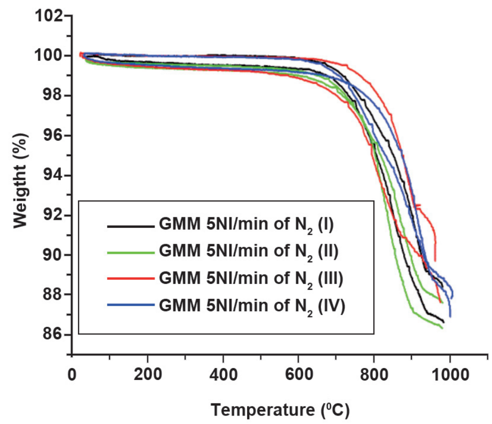

Figure 3
Weight decrease during heating procedure.

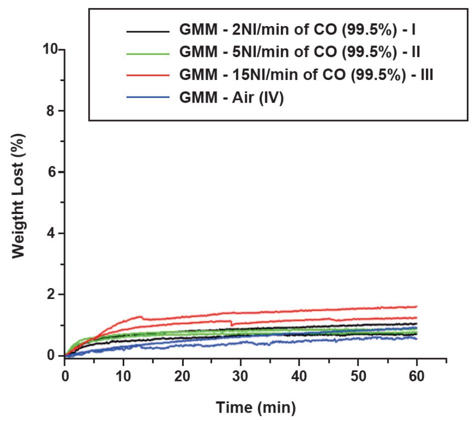

Figure 4
Weight lost during isothermal treatment (1000°C).

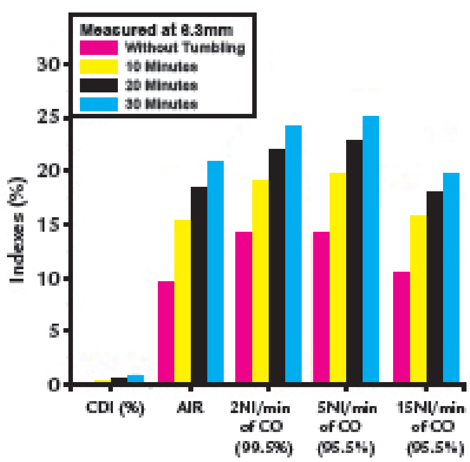

Figure 5
Comparison between the CDI and HDI indexes measured by a 6.3mm sieve.

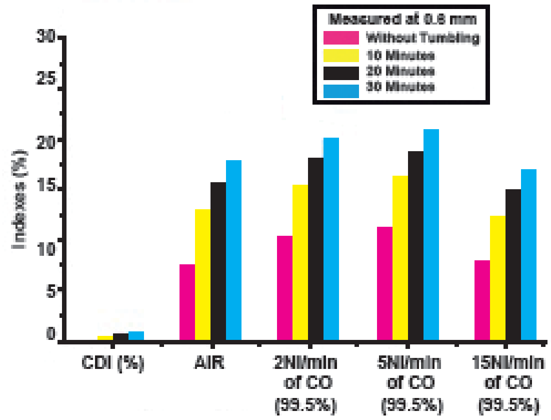

Figure 6
Comparison between the CDI and HDI indexes measured by a 0.6mm sieve.

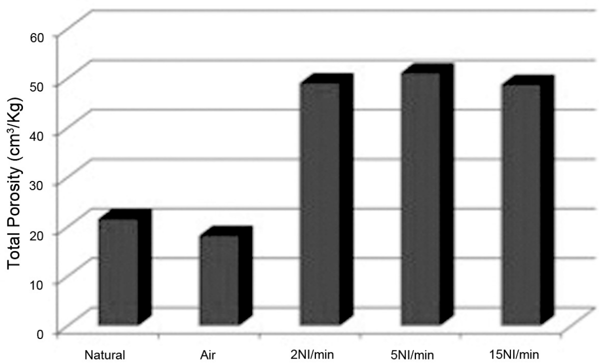

Figure 7
Comparison between total porosities of the natural and heat treated samples.

Between 300°C and 600°C, the structural water present in some amphiboles was evaporated and a low weight loss was observed. The rhodochrosite (manganese carbonate) started its decomposition around 700oC. The weight loss of 12% indicates that during the ore heating, all rhodochrosite was decomposed in MnO. Due to the happening of the decomposition reaction under natural air, no differences were found between the tests done under air or reducing gas flux.

This ore presented high susceptibility to the fines generation during heating decomposition. During the sample heating until 1000oC under continuous air flux, 10% of the material falls below 6.3mm mesh and 7% falls below 0.6mm mesh. After 30 minutes of tumbling, 24% of the material falls below 6.3mm mesh and 16% falls below 0.6mm mesh. These results indicate the low mechanical resistance of the heat decomposed ore.

The disintegration of this ore during heat decomposition under an oxidizing atmosphere (air) may be associated with rhodochrosite's heat decomposition, which increases particle porosity and changes the particle surface shape. Some small crystals of espessartite, initially coupled to the rhodochrosite, lose their fixation, being freed in very small particles. The progressive HDI index growth in function of the tumbling time was associated with the espessartite small crystal's presence, which is a hard silicate that works as an abrasive.

Figure 7 compares total porosities between the natural and heat treated samples. As in the previously mentioned hypotheses, the heat decomposed samples present the highest total porosities, justifying the ore's decreasing mechanical resistance.

Figure 8 presents the comparison between natural and heat treated particles. It was possible to observe that granades, characterized for their spherical crystal shape, continue stable in the ore structure after heat decomposition and pre-reducing. However the amount of rhodochrosite crystals that occupied spaces between granades decreased, leaving empty places and increasing particle porosity, while decreasing the ore's mechanical resistance.

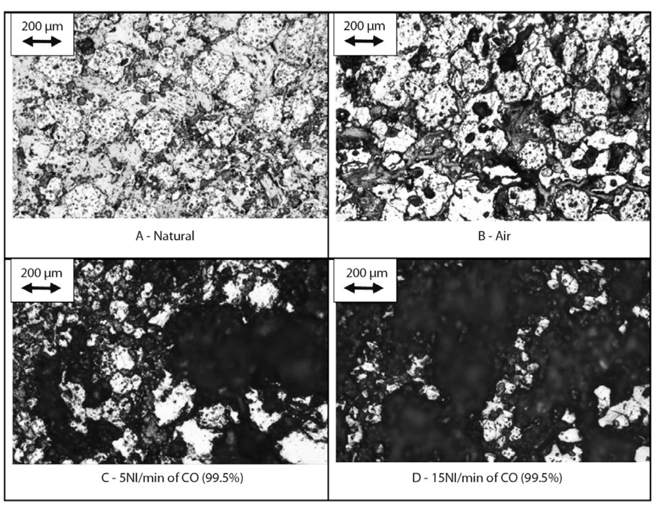

Figure 8
Comparison between the microstructure porosities of natural and heat treated samples.

4. Conclusions

1. The lump ore from Morro da Mina mine had low manganese content in comparison to the oxidized ores and an intermediary Mn/Fe ratio. These characteristics, associated with the high SiO2, Al2O3 and CaO contents, may be responsible for a low metal/slag ratio, which may produce a highly reactive basic slag.

2. The studied ore mainly consisted of silicates (spessartite and tephroite) and of one manganese carbonate (rhodochrosite). According to the ore constitution, it is possible to classify it as silicate carbonated ore.

3. The proposed indexes (CDI – Cold Disintegration Index, DI – Decrepitation Index, and HDI – Heating Disintegration Index) are efficient for the quantitative characterization of the studied ore particle disintegration.

4. This ore has low susceptibility to cold particle disintegration and to the decrepitation phenomena. The moisture and the reducing atmosphere were not influents on decrepitation phenomenon.

5. The ore produced a big amount of fines during heat decomposition and pre-reduction at 1000oC. No significant differences were observed between the tests with different gas flow rates [2Nl/min, 5Nl/min and 15Nl/min of CO (99.5%) and N2 (0.5%)].

6. The rhodochrosite heat decomposition is the main factor responsible for the ore particle disintegration. From all the fines below 6.3mm, 75% of them passed through a 0.6mm mesh sieve. This result shows that Morro da Mina's lump ore when heat decomposed has a low abrasion resistance.

5. Acknowledgement

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