DECREPITATION OF BRAZILIAN MANGANESE LUMP ORES

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ABSTRACT

A common problem in the production of ferromanganese alloys is the lack of knowledge about the mineralogical and metallurgical properties of the manganese lump ores. An important quality parameter of the lump ores is the decrepitation, which has not been studied adequately yet. This work presents physical, chemical and mineralogical characterizations of manganese lump ores from the three main Brazilian mines, Azul, Morro da Mina and Urucum, as well as their decrepitation behaviors. The samples, after characterization, were separated in three batches, one as received, the second after drying at 105°C, and the third after thermal treatment at 200°C. They were then tested for decrepitation at the temperature of 700°C for 30 min, with the particle size range kept between 19 and 6.3mm. The influence of the thermal history was studied together with the influence of the typological classifications of the ores, i.e., anhydrous-oxide for Urucum, hydrated-oxide for Azul, silicate-carbonate for Morro da Mina. A significant difference amongst the decrepitation behaviors was observed for the lump ores from Azul, Urucum and Morro da Mina. The oxide ores from Urucum (-6.3mm = 10%) and Azul (-6.3mm = 6%) present a high susceptibility to decrepitation, whilst the silicate-carbonate from Morro da Mina shows no decrepitation. The presence of moisture increased the decrepitation intensity of the Azul and Urucum lump ores. The bench-scale thermal treatment reduced in more then 60% the decrepitation indexes of both ores.

1 INTRODUCTION

The manganese lump ores are largely employed as raw material for the production of ferromanganese alloys. The mixture of these ores, originated from various mines or even different pits in the same mine, are usually defined at the ferroalloy plants according solely to their chemical and granulometric characteristics [1].

A common problem at the operation procedure of metallurgical furnaces in the production of ferromanganese alloys is the lack of knowledge about the mineralogical and metallurgical properties of the manganese lump ores. In this context, an important quality parameter of the lump ores is the decrepitation, which has not been studied adequately yet. The decrepitation, which is the breakage of lump ores upon heating, with the production of fine materials, causes efficiency loss of the reduction reactors, due to the reduced permeability of the mineral bed. Furthermore, the use of ore mixtures with high susceptibility to decrepitation causes less efficiency of heat exchanges and changes on the charge´s electric resistivity, leading also to damages to the operation and to the thermal efficiency of the reactor [1, 2].

This is a pioneer work as it studies the decrepitation of various typological categories of Brazilian manganese lump ores, as well as the employment of heat treatments aiming at reducing the intensity of this phenomenon. This information, combined with a better mineralogical characterization of these materials, is of great importance for the definition of technical criteria that can guide the selection of ore mixtures from different mines, in addition to the improvement of the process control and functionality.

Manganese has great economical significance in Brazil. The three main mines are Urucum, Azul and Morro da Mina [1].The mineralogy of manganese ores is varied and complex. Manganese occurs in more than 300 minerals, but only a few of those have a significant amount of the element and they make up the ores of higher values. The manganese ores normally exist as oxides, hydroxides, silicates and carbonates. The manganese can have bivalent, trivalent and tetravalent states [2, 3].

The Urucum manganese mine is located at the state of Mato Grosso do Sul, in the city of Corumba, near the Brazilian border with Bolivia. The manganese occurs as an oxide. This manganese mine is one of the most important in Brazil, since the beginning of its exploration. It is sedimentary, with the deposition of primary manganese oxides. The ore is formed mainly by cryptomelane and pyrolusite[4]. Nowadays, the exploited ore is classified in two kinds according to their phosphorus content, the main contaminant of this ore. One kind is the Standard (ST) containing more than 0.12% of phosphorus. The other is the Low Phosphorus (LP), presenting less than 0.12% of phosphorus. The mine lump ores are generated from these two kinds [5].

The Morro da Mina mine is located in the city of Conselheiro Lafaiete, in the metallurgical region of the state of Minas Gerais. The rocks from this mine belong to the Rio das Velhas group, identified as a vulcanic-sedimentary sequence of greenstone belt, included in the Iron Quadrangle [5]. The main products of Morro da Mina are the *carbon-silicates*, which present as main constituent minerals: rhodochrosite ($MnCO_3$), pyroxmangite ($MnSiO_3$), espessartite ($Mn_3Al_2(SiO_4)_3$) and tephroite (Mn_2SiO_4). The *silicon-carbonate* ore is characterized by its dark grey color; it is compact and fine to medium grained. It is commonly found in *brownish to pinkish* color, in *lens* and plates that create a *thin compositional banding* [5].

The Azul manganese mine is the largest producer of manganese ore (oxide) in Latin America, with an annual production of 2.5 Mt. The ore produced is directed mainly to the production of ferroalloys and, in a smaller scale, to the chemical and batteries industry [5].

2 MATERIALS AND METHODS

Representative samples of lump ore product of the three main Brazilian mines (Morro da Mina (MG), Urucum (MS) and Azul (PA)) were selected. Sampling was performed in each one of those mines, selecting a ton of each of the main lump products. Approximately 1,000kg of each sample of lump ore was then homogeneized and quartered. A portion of about 400kg was sampled and classified using Tyler mesh sizes of 37.5; 19; 6.3 and 3mm.

The particle size range chosen for the decrepitation tests was 19 to 6.3mm, with an average particle size of 12.7mm, therefore ideal for the good performance of submerged arc furnaces. The mass of material between 19 and 6.3mm, for each of the ore groups, was again quartered until about 50kg.

The 50kg samples of each of the lump products were divided in order to reserve 10kg for the chemical, physical and mineralogical characterization procedures and 40kg for the decrepitation tests. The samples were not submitted at any time to operations that could induce internal tensions or changes in moisture.

The decrepitation indexes for the lump ores from Morro da Mina, Urucum and Azul mines were measured according to the ISO 8731 standard for iron ores as described below, except for the particle size range used, comprehended between 19 to 6.3mm.

To determine the decrepitation index, 5kg of each ore, between 19 to 6.3mm, dried at 105^oC, was quartered in 10 samples of 0.5kg. Each sample was placed in an oven at 700^oC with residence time of 30 minutes. After this period, each sample was screened at 6.3mm, 3.35mm, 1.18mm and 0.5mm. The decrepitation indexes were obtained by the average of percentage mass below each grid.

The influences of moisture and thermal treatment on the ores decrepitation behaviors were investigated. Each ore with natural moisture was submitted to the same procedures described above without drying. The procedure was also repeated for the three ores, but with a thermal treatment at 200^oC for 48 hours prior to the essay at 700°C.

Figure 1 consists of a flowchart that summarizes the sequence of procedures adopted for the characterization study of the decrepitation behavior of manganese lump ores from Urucum, Morro da Mina and Azul mines.

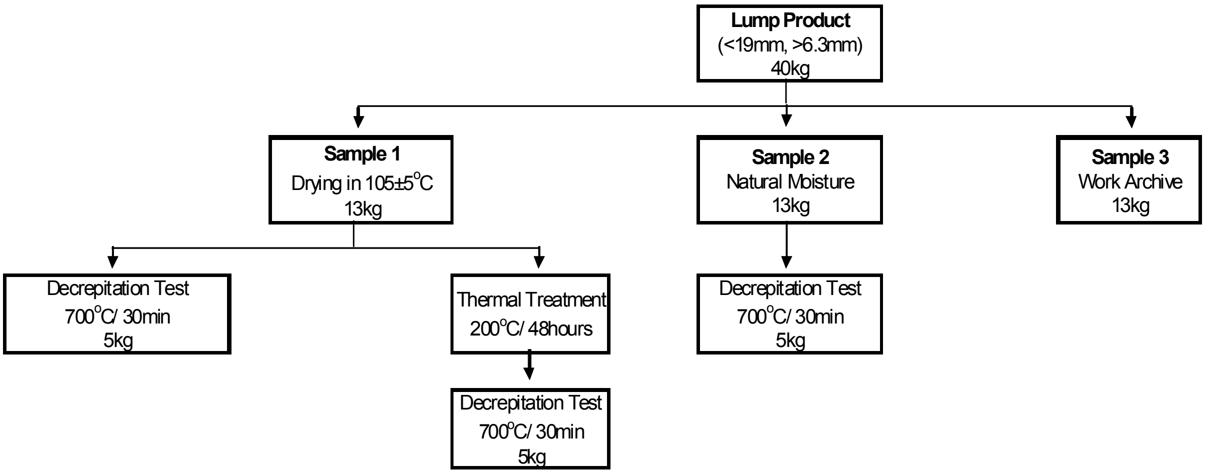

Figure 1: Procedure applied to the decrepitation tests of the lump ore samples.

3 RESULTS AND DISCUSSION

3.1 Chemical Characterization

Table 1 shows the chemical analysis on dry basis of the particle size range between 19 to 6.3mm of the manganese lump ores from Azul, Morro da Mina and Urucum mines.

Table 1: Chemical analysis of the manganese lump ore products in the range between 19 and 6.3mm.

Samples (<19mm > 6.3 mm)	Al_2O_3 (wt%)	CaO (wt%)	Fe (wt%)	MgO (wt%)	Mn (wt%)	P (wt%)	TiO_2 (wt%)	SiO_2 (wt%)
Azul	6.11	0.093	4.124	0.119	46.96	0.0972	0.2590	3.99
Morro da Mina	5.42	2.865	2.893	2.226	24.48	0.0761	0.2681	23.02
Urucum	0.78	0.069	6.920	0.054	32.58	0.1086	0.0817	2.11

The manganese ores studied in this work presented very distinct chemical characteristics. In the range between 19 and 6.3mm, the manganese content in the ore from Azul (46.96wt%) is much higher than in the others. The sample from Morro da Mina has the lowest manganese content, of 24.48wt%. The ore from Urucum has an intermediate manganese content of 32.85wt%. The content of SiO_2 is higher in the ore from Morro da Mina (23.02wt%) than in the others. The SiO_2 content in the samples from Urucum (2.11wt%) and Azul (3.99wt%) are respectively 20.91 and 19.02 percentual points lower than the content in the Morro da Mina ore.

3.2 Mineralogical Characterization

Table 2 shows theminerals identified and *semi-quantified* by the X-ray difraction, in the range between 19 and 6.3mm of the Azul, Morro da Mina and Urucum manganese ores.

It is noticed that the lump ores of Urucum and Azul mines are mainly composed by oxides, with the prevalence of cryptomelane. The ore from Urucum also presents other mineral constituents, such as braunite, pyrolusite, hematite, goethite and quartz. Other constituents of Azul ore are todorokite, pyrolusite, gibbsite, espessartite, magnetite and N-sutite. It is remarkable that this ore has the largest fraction of hydrated minerals.

The lump ore from Morro da Mina is composed mainly by carbonates and silicates, more specifically by rhodochrosite and espessartite. The other minerals found are fayalite, ferrosilite, manganosite and magnetite, in addition to the amphiboles and pyroxenes.

The prevailing mineral phases in the three lump ore samples studied were identified by optical microscopy and by electron microscopy combined with electron microprobe (EDS). Figure 2 shows a combined image of secondary and backscattered electrons from Azul sample, with a matrix of cryptomelane (dark grey) identified with the aid of the electron microprobe. The dark spots are pores or cracks at the matrix surface.

Figure 3 is a combined image of secondary and backscattered electrons of the Morro da Mina sample, where grains of espessartite (ES) as well as amphiboles (AN) with acicular aspect can be noted.

Table 2: Summary of the identified minerals in the lump ores from Azul, Morro da Mina and Urucum, for the range between 19 and 6.3mm.

Sample	Identified Mineral			
	Prevailing (>40%)	**Higher (<20%)**	**Lower (<10%)**	**Minor (<3%)**
Azul (-19mm +6.3mm)	**Cryptomelane** [KMn_8O_{16}]	**Todorokite** [$(Na,Ca,K)_2Mn_6O_{12}$ ·3a4.5(H_2O)]	**Gibbsite** [$Al(OH)_3$] **Pyrolusite** [MnO_2]	**Spessartine** [$Mn_3Al_2(SiO_4)_3$] **Magnetite** [Fe_3O_4] **Nsutite** [$Mn(O,OH)_2$]
Morro da Mina (-19mm, +6.3mm)	**Spessartine** [$Mn_3Al_2(SiO_4)_3$] **Rhodochrosite** [$MnCO_3$]	**Fayalite** (*) [$(Fe,Mn)SiO_4$]	**Anphibole** **Ferrosilite** [$(Fe,Mg)SiO_3$] **Manganosite** [MnO]	**Magnetite** [Fe_3O_4] **Pyroxmangite** [$MnSiO_3$]
Urucum (-19mm, +6.3mm)	**Cryptomelane** [KMn_8O_{16}]	**Pyrolusite** [MnO_2]	**Braunite** [$(Mn_2O_3)MnSiO_3$] **Hematite** [Fe_2O_3]	**Goethite** [FeO.OH] **Quartz** [SiO_2]

(*) Mineral phase with similar diffraction spectrum to the tephroite (Mn_2SiO_4).

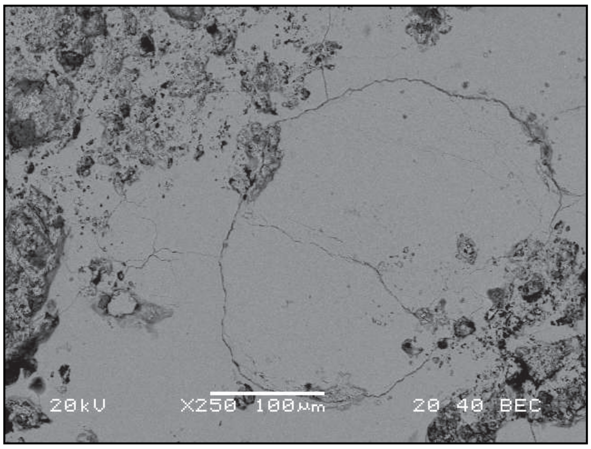

Figure 2: Electron micrograph of Mn lump ore from from Azul (*cryptomelane* matrix).

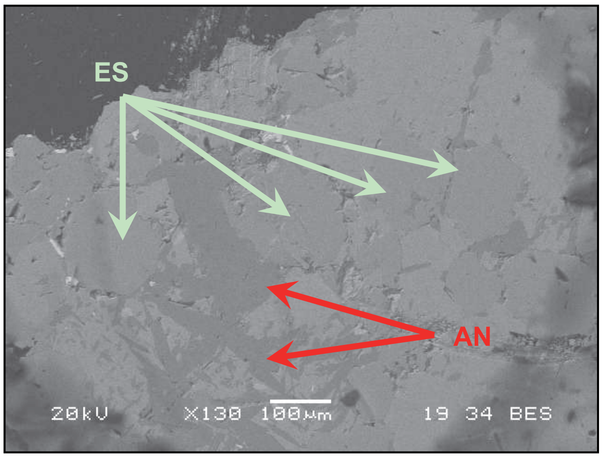

Figure 3: Electron micrograph of Mn lump ore from Morro da Mina (ES – Spessartine, AN – Amphibole).

Figure 4 is a combined image of secondary and backscattered electrons from Urucum sample, where the prevalence of the *cryptomelane* is identified by its dark grey color, as well as the presence of hematite, characterized by lighter regions. The black regions correspond to the fissures and pores of the ore.

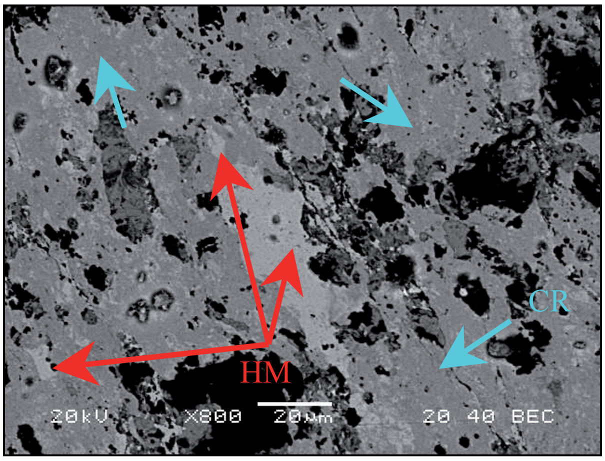

Figure 4: Electron micrograph of Mn lump ore from Urucum (CR – Cryptomelane, HM – Hematite).

3.3 Porosimetry

Table 3 shows the main results of surface area and porosity measured by nitrogen adsorption, for manganese lump ore samples between 19 to 6.3mm.

Table 3: Main parameters defined by the BET method for manganese lump ore samples between 19 to 6.3mm from Azul, Morro da Mina and Urucum.

Sample (-19mm +6.3mm)	Specific Surface (m^2/g)	Total Volume of Pores (cm^3/kg) (0.3-300nm)	Maximum Size of Pores (Å)	Average Diameter of *Micropores* (Å)	*Micropores* Volume (cm^3/kg) (0.3 – 2nm)	*Micropores* Area (m^2/g)
Azul	12,30	35,75	1382,8	116,3	5,228	14,80
Morro da Mina	1,21	3,59	1340,6	118,9	0,513	1,452
Urucum	4,41	15,56	1540,6	110,8	2,426	6,870

The data obtained by the BET method on specific surface and porosity are important parameters for the understanding of decrepitation, once the vapor pressure, which is originated from the elimination of structural water, can be relieved depending on the ore´s pore structure.

According to the data obtained with the BET method, the porosities of the ores studied show large differences. The most porous ore is the one from Azul (35.75cm^3/kg) followed by Urucum (15.56cm^3/kg) and then Morro da Mina (3.59cm^3/kg).

3.4 Thermogravimetry

Figure 5 shows the thermogravimetry curve of the manganese lump ore samples from Azul, Morro da Mina and Urucum. Table 4 highlights the losses of mass in relation to the temperature for each of the samples.

The mass loss during heating, from room temperature to 280°C, for the samples from Azul, Morro da Mina and Urucum is related to moisture loss. The deep mass loss initiated close to 400°C, seen on samples from Azul and from Urucum, is related to the beginning of the thermal decomposition of the hydrated mineral phases. In the samples from Azul, these phases are the todokorite and n-sutite. In the ones from Urucum, the hydrated phase is the goethite present in small amount.

It is thought that the mass loss verified close to 500 °C in the manganese lump ore from Morro da Mina is related mainly to the elimination of structural water, which occurs in amphiboles, *superimposed to the decomposition of some carbonates originated from ion substitution in rhodochrosite.*

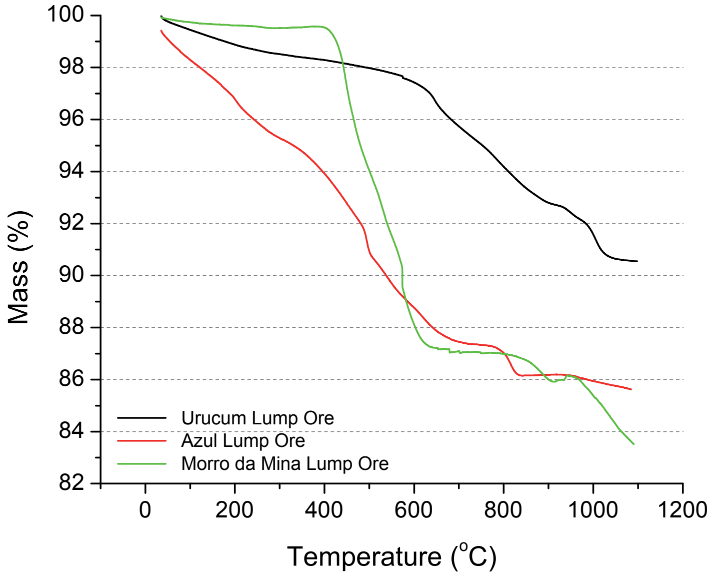

Figure 5: Thermogravimetric curves for the ores from Urucum, Azul and Morro da Mina

Table 4: Mass loss for the ore samples from Urucum, Azul and Morro da Mina

Sample	200°C	300°C	500°C	700°C	900°C	1000°C
Azul	3%	4.1%	6.6%	11%	12.7%	14%
Morro da Mina	0.4%	0.4%	0.6%	10%	12.9%	13.1%
Urucum	1.1%	1.5%	2.0%	4.3%	7.3%	8.4%

The decomposition of some oxides (cryptomelane and pyrolusite), more specifically the transformation from MnO_2 into Mn_2O_3, begins close to 700°C in the samples from Azul and Urucum. The mass variation observed in these samples close to 1000°C is related to the transformation of Mn_2O_3 into Mn_3O_4. The cryptomelane and pyrolusite probably turn into bixbyite (Mn_2O_3) between 700 and 900°C, which together with the braunite begin their decomposition at 950°C, turning into hausmannite (Mn_3O_4).

It is remarkable that the ore from Azul presented the biggest mass loss. This is partly due to its high natural moisture and to the number of hydrated phases. The ore from Morro da Mina presented the second highest mass loss and lower natural moisture. The most significant variations happened between 500 to 800°C and are related to the decomposition of amphiboles and rhodochrosite. The Urucum ore presented the lowest mass loss. The main mass variations are related to the decomposition of its constituent oxides.

3.5 Decrepitation

Figure 6 is a comparative graph of the decrepitation indexes (<6.3mm, <3.35mm, <1.18mm, <0.5mm) measured from the wet, dry and heat treated manganese lump ore samples from Azul, Morro da Mina and Urucum.

It can be noticed that the manganese lump ores from Azul, Morro da Mina and Urucum show distinct decrepitation behaviors. Urucum ore has the highest decrepitation index ($I_{-6,3mm}$ = 10%) followed by Azul ($I_{-6,3mm}$ = 6%). The decrepitation for Morro da Mina dry ore ($I_{-6,3mm}$ = 0,5%) is negligible. It is also noticed that the Urucum ore has the highest standard deviation, indicating a non homogeneous decrepitation behavior, with some particles very susceptible to decrepitation but not all.

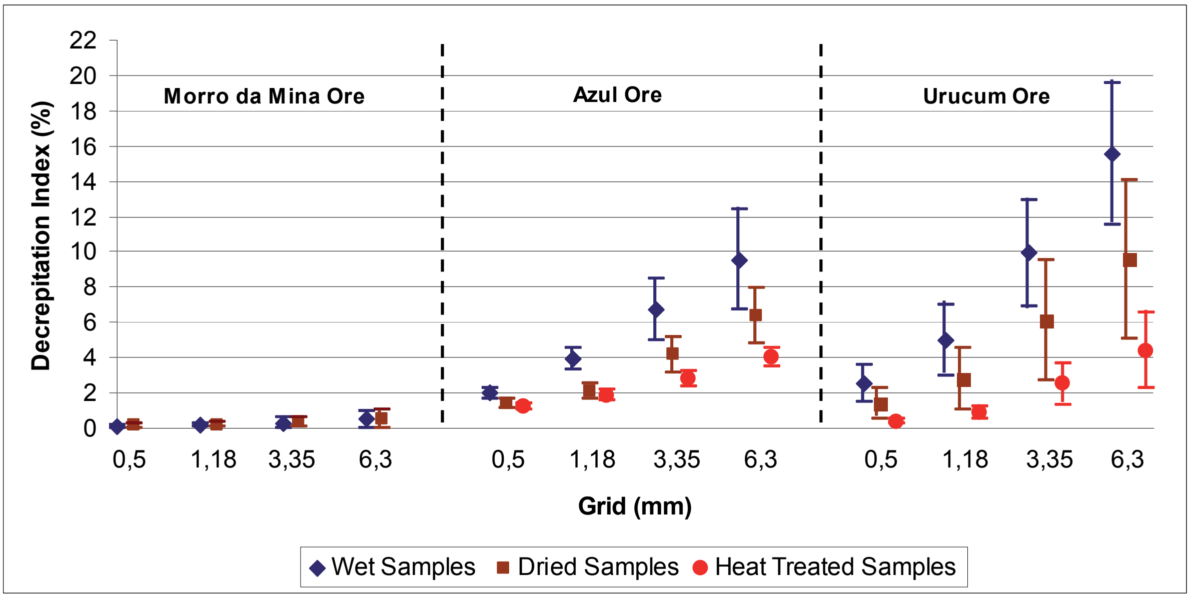

Figure 6: Comparative graph of the decrepitation indexes of the wet, dry and heat treated manganese lump ores from Azul, Morro da Mina and Urucum in the range of 19 to 6.3mm.

It is important to observe that the ores with the highest decrepitation indexes are the ones that showed some mineralogical phase transformation at test temperature. Azul lump ore has a considerable fraction of hydrated minerals and manganese oxides that break down during decrepitation tests. The mass loss for the manganese *oxide* ore from Urucum is the lowest at 700^{o}C and it is related mainly to the decomposition of the cryptomelane and pyrolusite. The *silicate carbonate amphibole ore from Morro da Mina* was the only one that did not decrepitate.

One of the reasons for the decrepitation, is the elimination of structural water from the hydrated phases during thermal shock. The vapor pressure from the water gathered in ore pores as well as the elimination of the alkali originated in the phase transformations could be enough to cause catastrophic rupture of particles. The phase transformation experienced by the oxides at 700^{o}C causes volumetric contractions, whichyield anisotropy that induces stress in specific regions of the ore particle, leading to the formation and propagation of cracks.

It is important to observe that the Azul sample has the largest average diameter and volume of *micropores*, although it shows a higher concentration of hydrated mineral phases if compared to Urucum. This could enable a relief of vapor pressure inside ore particles to some extent, decreasing its decrepitation. The Urucum ore has a higher concentration of the pyrolusite mineral phase, which experiences a considerable reduction in volume when it transforms in bixbyite, and this could cause this ore to experience intense decrepitation. Considering this, it is possible that the thermal decompositions of manganese oxides are the factor that contributes most to the decrepitation of manganese lump ores.

Despite the fact that moisture increased considerably the decrepitation intensity in the manganese lump ores from Azul and Urucum, it showed no influence in the ore from Morro da Mina.

It was observed that the wet ores from Azul and Urucum decrepitated more than when dry, therefore confirming the moisture as an important parameter in the control of the decrepitation phenomenon of manganese ores. In the 6.3mm mesh, wet ores from Azul and Urucum showed an increase of 40 and 37.5% respectively in their decrepitation indexes. The increase of the standard deviation is also remarkable, which risks the reliability and operational control of the process.

A decrease of 33.3 and 60% in the average decrepitation indexes in relation to the dry samples and of 60 and 75% in relation to wet samples was observed in heat treated ores from Azul and Urucum respectively. The decrease in the standard deviation is remarkable, which indicates that the heat treated samples show a more homogeneous behavior in respect to the decrepitation phenomenon. This result presents a possible solution for increasing the control over the production of manganese fines in electric reduction furnaces.

In this case, the decrease in decrepitation indexes can be related to the relief of induced tensions from the ore particles, originated during mineral processing. The Urucum manganese lump ore sample shows higher standard deviations due to presenting the pyrolusite phase in higher content than the Azul sample.

4 CONCLUSIONS

1. The manganese lump ores from Azul, Urucum and Morro da Mina tested for decrepitation showed very distinct chemical characteristics. Some of the physical characteristics of the three manganese lump ore samples are very distinct too. These manganese lump ores can be classified in three different typological categories according to their mineralogical compositions and based on the thermogravimetric tests. *Urucum ore is type anhydrous-oxide, Azul is hydrated-oxide and Morro da Mina is hydrated-silicate-carbonate.*

2. At the thermogravimetric tests, the mass loss of the manganese lump ores from Urucum, Morro da Mina and Azul is related to the thermal decomposition of oxides (cryptomelane, pyrolusite e braunite) carbonates (rhodochrosite) and of hydrated mineralogical constituents (being the todorokite and amphiboles the main ones). The three studied lump ores showed different thermal behavior during these tests.

3. There is a significant difference of intensity of the decrepitation phenomenon for the manganese lump ores from Azul, Urucum and Morro da Mina:

- The oxide ores from Urucum ($I_{-6,3mm}$ = 10%) and from Azul ($I_{-6,3mm}$ = 6%) have high susceptibility to decrepitation. The carbonate-silicate ore from Morro da Mina does not decrepitate. At the studied conditions, the volumetric degradation caused by the thermal shock at 700^{o}C is somehow related to the phase transformation occurred during the thermal decomposition of the oxides cryptomelane [KMn_8O_{16}] and pyrolusite [MnO_2].
- There are distinct decrepitation behaviors of the three manganese lump ores with natural moisture (tests without drying). The moisture increased considerably the decrepitation intensity ($I_{-6,3mm}$) of Azul and Urucum lump ores (from 6% to 10% and from 10% to 16% respectively). There was no influence of the moisture on the degradation of Morro da Mina lump ore.
- The heat treatment of 48 hours at 200^{o}C at bench-scale reduced considerably the decrepitation indexes to only 4% for both lump ores from Urucum and Azul, a very promising result. The standard deviations also decreased, causing a more homogeneous decrepitation behavior.
- No direct relation was observed between decrepitation and BET porosity, however studies on total porosity and pore shapes must be done, to investigate the total porosity influence.

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