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A geometallurgical comparison between lump ore and pellets of manganese ore

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ABSTRACT

Manganese lump ores are still the main raw material used in the manufacture of manganese ferroalloys, but the processing of the ore to the beneficiation point generates fines. So an alternative to be studied is making pellets. This work compares the main geometallurgical characteristics of the lump ore from the Azul Mine and the pellets made from fines generated during beneficiation of this lump ore on a small scale. The characteristics assessed were: the chemical composition, mineralogical constitution, hot and cold particle disintegration, thermal decomposition and solid state reduction. It can be observed that the pellets contain a greater proportion of manganese oxides than the lump ore and they are also richer in Mn. In the pellets the hot and cold particle disintegration phenomena are minimal when compared with those found in lump ore. Lump ore can be efficiently reduced in the solid state, while most of the manganese minerals in the pellets have already been reduced to MnO. The conclusion is that manufacturing pellets in order to take advantage of the manganese ore fines is a path that must be studied further, since the pellets can be used as a viable source of manganese and act as agents that contribute to the increase in permeability of the charge. But possible reductions in the temperature of the granular zone during solid state reduction need to be considered.

1. Introduction

Manganese ferroalloys are mainly produced in electric reduction furnaces and are widely used as elements in steel alloys (Faria, 2011; Olsen et al., 2007; Tangstad et al., 2004).

Manganese lump ores are widely used as raw material for producing manganese ferroalloys. The mixtures of these ores, which come from various mines or even from different mining fronts in the same mine, are usually defined in ferroalloy plants exclusively according to their chemical and granulometric characteristics (Faria, 2011; Olsen et al., 2007; Tangstad et al., 2004; Faria et al., 2013a).

A frequently encountered problem in the mineral processing of limp ore from mines is the significant generation of fines that are rich in manganese, but whose granulometry is unsuitable for the reduction process in an electric furnace. In this context, this work presents a comparative study of the quality parameters (that are still little studied aspects) of the lump ore from the Azul Mine, which are solid state reduction, cold particle disintegration, granular crepitation and hot particle disintegration, and of manganese ore pellets made on a small scale from fines resulting from the processing of lump ore from Azul (Faria, 2011; Yoshikoshi et al., 1983).

The Azul manganese mine is the largest producer of manganese ore in Latin America, with annual production of 2.5 million tons. The ore produced is used mainly for producing ferroalloys and, to a lesser extent, in the chemical and battery industries. This mine is located in the mineral province of Carajás, in the Carajás National Forest, in the State of Pará. The ore extracted from this mine mainly comprises oxides like cryptomelane, in the biggest proportion, and others like magnetite and pyrolusite. Hydroxides, like n-sutite and gibbsite also occur (Faria, 2011; Faria et al., 2013a).

The focus of this research is on the metallurgical properties of the lump ore from Azul and the pellets produced from its fines in the solid state reduction zone of the electric reduction furnace. This is an important region in the alloy-making process. By comparing the chemical, mineral and metallurgical characteristics it is intended to evaluate the possibility of making manganese ore pellets as a possible way of taking advantage of the fines generated in the beneficiation process of lump ore.

In the solid state reduction zone of the electric furnace the solid raw materials undergo an increase in temperature as they flow down. The temperature of the charge in this zone varies between 500 °C and 1100 °C, on average. In this region the water, present in the form of humidity, evaporates and the manganese oxides are reduced by the rising

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Table 1
A comparison of the chemical composition of lump ore from Azul and pellets.

Sample	Mn	Fe	SiO_2	P	Al_2O_3	CaO	MgO	TiO_2
	%	%	%	%	%	%	%	%
MG60 (overall)	47.68	3.59	3.16	0.097	5.22	0.120	0.180	0.240
MG60 (−15.9 mm + 9.5 mm)	49.10	3.37	2.46	0.100	4.86	0.154	0.100	0.259
Pellets (−13 mm + 11 mm)	50.94	7.53	8.00	0.092	7.80	0.27	0.32	0.43

flow of CO. In order for the process involved in this zone to be effective it is important that the permeability of the gas flow is high and homogenous throughout the charge (Faria, 2011; Berg and Olsen, 2000; Faria et al., 2012, 2013b).

According to Berg and Olsen (2000) and Wang and Sundman (1992) in addition to the physical integrity of the charge it is important that the reduction of the higher oxides is effective. According to the authors, the main reduction reactions in manganese oxides can be described in the following sequence: in the temperature band between 600 °C and 700 °C there is a significant reduction from MnO_2 to Mn_2O_3, with a loss of mass of the order of 9.2%. Between 900 °C and 1000 °C there is a significant reduction from Mn_2O_3 to Mn_3O_4, with a loss of mass of the order of 3.3%. When it reaches temperatures in excess of 1200 °C, which vary depending on the raw material and the type of alloy to be produced, the charge, with the exception of carbon, softens and melts (Faria, 2011; Faria et al., 2010, 2013b; Wang and Sundman, 1992; Zaki et al., 1997).

In this context, this work proposes a physical simulation methodology of the solid state reduction process under similar conditions to those found in an electric reduction furnace, in order to assess the physical integrity of the lump ore and pellets, as well as their reduction characteristics.

2. Materials and methods

A ton of lump ore from Azul was homogenized, quartered and representative samples weighing 100 kg were taken from both the overall sample and from the granulometric band containing particle sizes between 9.5 mm and 15.9 mm. Both the overall sample and the sample from the granulometric band chosen were submitted to chemical, physical and mineralogical characterization procedures. A part of the sample, whose average particle size was between 9.5 mm and 15.9 mm, was set aside for metallurgical tests.

A 100 kg batch of manganese ore pellets (74% in weight, with an average diameter of between 11 mm and 13 mm) made on a small scale from fines generated in processing the lump ore from Azul was also homogenized and quartered. Representative samples were sent for chemical, physical, mineralogical and metallurgical testing.

The Mn, Fe, CaO, MgO, SiO_2, Al_2O_3, TiO_2 and P concentrations were determined. The concentrations of Mn and SiO_2 were determined by titration and the other components by ICP-OES (inductively coupled plasma optical emission spectrometry).

The main mineral constituents in the sample studied were quantitatively determined. The results were obtained by a combination of techniques involving optical microscopy, X-ray diffractometry, the total powder method, an electronic microprobe coupled to a scanning electron microscope, thermogravimetry and mass scales. The physical properties assessed were density (apparent and structural) and the porosity parameters.

Table 3
Microstructural constitution of pellets made from lump ore fines from Azul.

Sample	Constituents (% in weight)			
	MnO (Manganosite)	Mn_3O_4 (Hausmannite)	Fe_3O_4 (Magnetite)	Others
Pellets	64–60	5–3	12–9	25–20

Once the samples had been characterized, methodologies were proposed for the metallurgical characterization of the materials that are the focus of this work. Over and above the chemical, physical and mineralogical characteristics, the experimental methods allowed for a comparison of the thermal decomposition behaviors to air, solid state reduction and particle disintegration.

The first experimental methodology allowed for a comparison of the thermal decomposition and solid state reduction of the materials. The studies of thermal decomposition and the solid state reduction efficiency were undertaken by submitting samples to heating, from room temperature to as much as 1000 °C, at a constant rate of 25 °C/min. The time it stayed at this temperature was 1 h. The assays were carried out in a vertical resistance furnace, with a thermobalance. For the thermal decomposition tests the atmosphere used was fresh air. For the solid state reduction efficiency tests, however, an atmosphere comprising 5 NL/min of 100% N_2 was used during heating, while different outputs of 99.5% CO and 0.5% N_2 (2 Nl/min, 5 Nl/min and 15 Nl/min) were used during the isotherm test.

By the chemical analysis and X-ray diffractometry of the assay products, as well as the mass losses observed during heating, the temperatures at the beginning of decomposition of the less stable phases were determined, as were the fractions in the final sample structure of each product resulting from the decomposition and reduction. Each assay was carried out twice.

A quantitative index was proposed for assessing the mechanical behavior of the materials when cold; their resistance to impact and abrasion. This index was defined as the Cold Disintegration Index (CDI) (Faria, 2011). The ore sample from the granulometric band between 9.5 mm and 15.9 mm was dried and then tumbled (for 30 min, in three 10-minute spells) in an ISO9246-1 and ISO9246-2 certified rotating tumbler. The percentages in mass of material produced below the 9.5 mm, 6.3 mm, 3.3 mm, 5 mm, 1.18 mm, 0.6 mm and 0.150 mm meshes provided the CDIs. The pellets were submitted to the same methodology, but the average size band of the pellets used was between 11 mm and 13 mm.

The aim was to try and assess the mechanical behavior of the material as it flows down the metallurgical reactor, against a rising jet of gas that is rich in CO, while undergoing heating. A parameter was proposed and defined as the Heating Disintegration Index (HDI) (Faria, 2011). The granulometric band chosen for measuring this index was also located between 9.5 mm and 15.9 mm for the lump ore from Azul and between 11 mm and 13 mm for the pellets. The granulometric bands used for the lump ore and pellets were selected because they were considered optimal bands for the operation of the electric furnace.

To determine the HDIs, two amounts of 500 g of material were individually placed in a retort that was 75 mm in diameter and heated in a

Table 2
Mineralogical constitution of the lump ore from Azul (MG60).

Sample	Constituents (% in weight)						
	KMn_8O_{16} (Cryptomelane)	(Na, Ca, K)$_2Mn_6O_{12}$.3a4,5(H_2O) (Todorokite)	$Mn(O,OH)_2$ (N-Sutite)	$Al(OH)_3$ (Gibbsite)	MnO_2 (Pyrolusite)	Fe_3O_4 (Magnetite)	Others
MG60 (overall)	33–23	33–23	16–10	13–10	4–2	7–5	8–7
MG60 (−15.9 mm +9.5 mm)	35–25	31–21	16–10	10–7	5–3	6–4	8–7