



Calcination and characterisation studies of a Brazilian manganese ore tailing



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ABSTRACT

This paper discusses the systematic analysis of the results of calcination as a function of size fraction performed on a sample of Brazilian silicate–carbonate manganese ore tailing at 800 °C. The raw materials and the corresponding calcination products were analysed using several analytical techniques, including determination of density, specific surface area and porosity, chemical analysis and X-ray diffraction. The morphology and chemical composition of the calcination products were analysed by using scanning electronic microscopy equipped with energy-dispersive X-ray spectrometer (SEM/EDS). Results indicate that the manganese ore tailing consists of silicates, namely, spessartine ($\text{Mn}_3\text{Al}_2(\text{SiO}_4)_3$), tephroite ($\text{Mn}_2(\text{SiO}_4)$) and rhodonite ($(\text{Mn,Fe,Mg,Ca})_5(\text{SiO}_3)_5$) and rhodochrosite (MnCO_3). The loss of CO_2 and OH during the thermal decomposition of the carbonate (rhodochrosite and dolomite) and hydrated minerals (kaolinite, muscovite and antigorite) in air atmosphere at 800 °C resulted in: (1) decrease of the specific surface area and porosity, (2) increase in the density and Mn grade from 27.6% to 32.2% and (3) increase in SiO_2 grade from 26.7% to 30.1%. These results indicate that this material is within the chemical specifications of Fe–Si–Mn alloy.

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1. Introduction

Of the worldwide consumption of manganese, 92% is directly related with the steel industry, given the fact that manganese imparts malleability, tenacity and hardness to steel. Besides, the non-ferrous applications of manganese include the production of dry-cell batteries, important component in plant fertilizer and animal feed, and as colourant for bricks (Hagelstein, 2009; Tangstad et al., 2004).

The world's total resource of manganese is approximately 573.5 million tonnes, of which South Africa, Ukraine, Australia, Brazil and India account for almost 85.3%. Of the 53.5 million tonnes of the Brazilian resources (<http://www.dnpm.gov.br>), the Minas Gerais State has about 87% with a medium Mn content of 24.2%, followed by the Mato Grosso do Sul State (6.5%) and the Pará State (4.3%) (<http://www.ibram.org.br>).

In principle, manganese ores are classified according to the Mn content as high grade (Mn > 44%), medium grade (Mn 40–44%), low grade (Mn 35–40%) and steel mill grade (Mn 28–35%) (Gao et al., 2012). The processing of rich oxidised manganese ores, which are mined selectively, includes crushing and screening operations. The

grosser fraction ($-3/4 + 5/16$) is the final product (lump ore and blast furnace feed), while the smaller size fraction ($-5/16$) is classified again (mechanical or cyclone classifier). Depending on the ore's mineralogy, the underflow from this step is concentrated by gravity, magnetic separation or flotation, or other alternative methods, such as the selective reduction of iron oxide followed by magnetic separation and sulphation–roasting. The concentrates thus obtained are subsequently agglomerated via sintering, pelletizing or briquetting (Aplan, 1985; Singh et al., 2011; Gao et al., 2012; Sahoo and Rao, 1989). The underflow is discharged as tailing.

Lately, the depletion of oxidised high-grade manganese ore and the rising market demand for manganese ore products have resulted in the exploitation of low-grade manganese ore (protores), such as the silicate–carbonate manganese ore of the Morro da Mina Mine located in the Minas Gerais State in Brazil. The main manganese minerals in this ore are silicate (spessartine, rhodonite, tephroite) and carbonate (rhodochrosite). The gangue minerals consist of dolomite, feldspar, muscovite, biotite/phlogopite, quartz, magnetite, zircon, pentlandite, pyrite/pyrrhotite and others (Lima et al., 2010).

Aplan (1985) reported on the manganese recovered from carbonate ores (rhodochrosite) at a dense medium separation plant in Ghana in the early 1960s. Both the products that sink and float (high silica) after agglomeration were used for the production of ferromanganese and silico-manganese, respectively. In the United States, Anaconda operated a flotation plant to recover the rhodochrosite ores mined in Butte,

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Table 1

Chemical composition as a function of size fraction of the silicate–carbonate manganese ore tailing.

Fraction size (μm)	Weight (%)	Grade (%)								
		Mn	Fe	SiO ₂	Al ₂ O ₃	P	Ca	Mg	Ba	Ti
+ 420	2.4	26.23	3.77	30.90	6.56	0.07	1.89	1.30	0.12	0.20
– 420 + 297	1.5	21.64	3.84	39.03	6.52	0.07	1.62	1.32	0.13	0.21
– 297 + 210	3.4	21.74	3.57	38.38	6.83	0.07	1.61	1.38	0.14	0.22
– 210 + 149	6.8	23.44	3.38	35.39	7.36	0.06	1.65	1.46	0.13	0.21
– 149 + 105	14.8	26.11	3.11	30.49	7.38	0.06	1.77	1.51	0.11	0.20
– 105 + 74	17.5	29.66	2.96	25.94	7.25	0.07	1.95	1.53	0.08	0.19
– 74 + 53	17.4	29.15	3.01	23.96	6.92	0.07	2.03	1.61	0.08	0.20
– 53 + 37	19.0	29.52	3.09	23.33	6.30	0.10	2.12	1.77	0.08	0.24
– 37	17.2	26.85	4.06	23.39	6.84	0.13	2.01	1.68	0.09	0.36
Total	100.00	27.63	3.32	26.72	6.56	0.08	1.94	1.59	0.09	0.09

Table 2

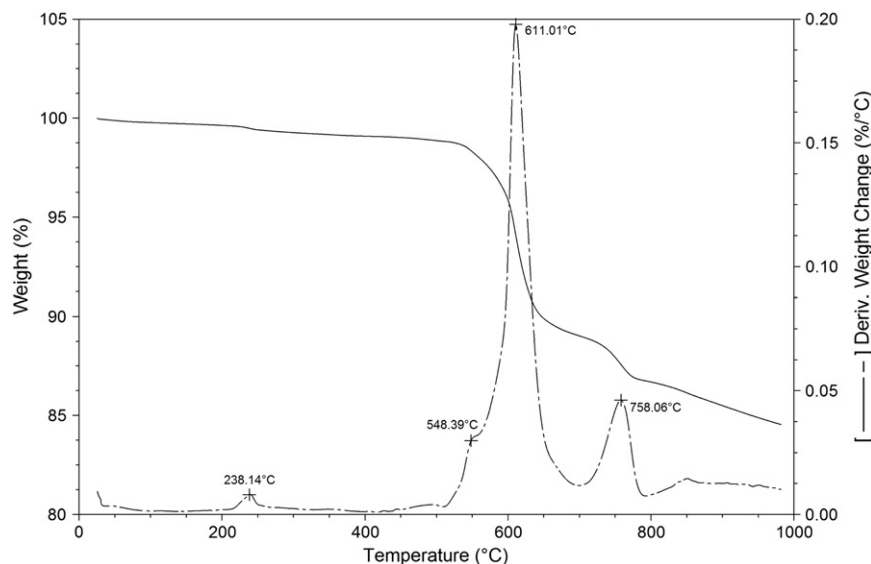
Minerals identified from the XRD patterns of the silicate–carbonate manganese ore tailing as a function of size fraction.

Minerals identified	Chemical formula	Fraction size (μm)									
		+ 420	– 420 + 297	– 297 + 210	– 210 + 149	– 149 + 105	– 105 + 074	– 74 + 53	– 53 + 37	– 37	
Spessartine	(Mn ₃ Al ₂ (SiO ₄) ₃)	X	X	X	X	X	X	X	X	X	
Rhodochrosite	(MnCO ₃)	X		X	X	X	X	X	X	X	
Tephroite	(Mn ₂ SiO ₄)				X	X	X	X	X	X	
Quartz	(SiO ₂)				X	X	X	X	X	X	
Rhodonite	(MnSiO ₃)			X							
Kaolinite	(Al ₂ Si ₂ O ₅ (OH) ₄)	X	X							X	
Cordierite	(Mg ₂ Al ₄ Si ₅ O ₁₈)	X	X			X	X			X	
Muscovite	(KAl ₂ (Si ₃ Al)O ₁₀ (OH,F) ₂)	X	X	X							
Antigorite	(Mg,Fe) ₃ (Si ₂ O ₅)(OH) ₄)				X						
Dolomite	((Ca,Mg)CO ₃)				X	X					

Montana. The feed was a tailing of 21% Mn from the flotation plant for copper ore. The concentrate thus produced had Mn content between 38 and 40%. This was subsequently increased to ~60% Mn by CO₂ loss in kiln, resulting in the yield of 86%.

The industrial beneficiation plant for silicate–carbonate manganese ore (queluzite) in the Minas Gerais State in Brazil is producing lump ore for Fe–Si–Mn alloys. During this, about 23,800 tonnes of tailing (overflow from the classifier step) is being discharged every year. Given the fact that the Mn grade of tailings is very high of the order of ~27% (Reis and Lima, 2005), processing the tailing discharged from the classifier step could maximise the overall metal recovery. The Mn enrichment of this material is only about 4% for both gravity separation

(Humphrey's spiral and shaking table) and flotation. The maximum Mn recovery is 59% (gravity separation) and 72.5% (flotation). The medium Mn content in the wastes of the flotation tests is about 23%, which is very high when compared to the Mn content in the feed (Reis and Lima, 2005; Lima et al., 2008). One of the possible approaches for upgrading this material would be thermal processing, given the fact that its mineralogy consists of silicates and carbonate minerals, such as the low-grade calcareous phosphate ores of sedimentary origin. In such cases, P₂O₅ upgrade is performed by calcination at temperatures ranging from 800° to 1000 °C (Zafar et al., 1995; Issahary and Pelly, 1985; Kaljuvee et al., 1995; Guo and Li, 2010; Abouzeid, 2008).

**Fig. 1.** Typical thermogram of the silicate–carbonate manganese ore tailing.

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