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Mechanism of sodium sulfate in promoting selective reduction of nickel laterite ore during reduction roasting process☆

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A high nickel grade ferronickel was produced from laterite ore using the selective reduction-wet magnetic separation process, with the addition of sodium sulfate (Na_2SO_4). The ferronickel concentrate assaying 9.87% Ni, with a nickel recovery of 90.90% can be obtained, when laterite ore was reduced at 1200 °C for 50 min with the addition of 10 wt.% Na_2SO_4 and 2 wt.% coal. Based on the results of the X-ray Diffraction, Scanning Electron Microscopy, and Energy Dispersive X-ray Spectroscopy analyses, the thermal decomposition and reduction reaction of Na_2SO_4 were carried out. Sodium oxide from the thermal decomposition of Na_2SO_4 reacted with silicate minerals to form nepheline. The formation of the molten phase accelerated the migration rate of the metallic particles and suppressed the reduction of the ferrous minerals in the weak reduction atmosphere. Sulfur reacted with metallic iron to form troilite, thereby facilitating the aggregation of ferronickel particles to form bigger particles.

1. Introduction

Nickel laterite ore is divided chemically and physically into two distinct types, namely, saprolitic (silicate/hydrosilicate) and limonitic (oxide/hydroxide) ores (Rhamdhani et al., 2009). The nickel in the nickel laterite ore is closely associated with iron oxide and silicate minerals as isomorphous substitution for iron and magnesium in the lattice (Dalvi et al., 2004; Mskalyk and Alfantazi, 2002). Laterites cannot be beneficiated via physical methods because of their complex mineralogy. Thus, the pyrometallurgical method has been applied commercially to extract nickel from the nickel the laterite ore. Pyrometallurgical techniques have been used to treat saprolitic laterite to produce ferronickel concentrate or nickel matte (King, 2005; Kyle, 2010). However, this method is energy intensive during the production of ferronickel concentrate from laterite ores because it involves two high temperature steps: pre-reduction at 850 °C to 1000 °C, followed by smelting at 1500 °C to 1600 °C, in an electric furnace to separate the ferronickel from the silica-magnesia slag (Norgate and Jahanshahi, 2011). Therefore, an alternative route of direct reduction followed by physical separation with less energy consumption has been suggested. The proposed process is an easy and environmentally friendly technique, and exhibits selective extraction of nickel over iron. The ferronickel concentrate obtained from this process can be directly used to make stainless steels.

Recently, several investigations on the reduction roasting of nickel laterite ore followed by magnetic separation to produce ferronickel concentrate have been performed. Kim et al. have investigated the concentration of nickel from low-grade laterite (Ni 1.50%, TFe 22.33%) using calcination at 500 °C for 1 hour and wet magnetic separation. He showed that the nickel grade increased from 1.5% to 2.9%, but the nickel recovery was only 48% (Kim et al., 2010). Li et al. have extracted nickel from low-grade nickel laterite ore (Ni 1.09%, TFe 9.16%) using a solid-state deoxidization method (Li et al., 2012a,b). A ferronickel concentrate with a nickel grade of 4.50% and recovery of 80.00% has been obtained. However, these studies have not obtained ferronickel concentrate with high nickel grade (>8%) via reduction roasting and magnetic separation without additives.

Reduction roasting with additives for obtaining high nickel grade ferronickel concentrate has recently become a hot research topic. Cao et al. studied the reduction roasting-magnetic separation process of low-grade nickel laterite ores, with Ni 1.86% and Fe 13.59%. He found that effective reduction occurred, and the ferronickel concentrate containing 10.83% Ni, with a nickel recovery of 82.15%, was obtained. The reduction was carried out at 1200 °C for 40 min, with the addition of 20% Na_2CO_3 and 15% coal (Cao et al., 2010; Sun et al., 2011). Zhu et al. conducted selective reduction and wet magnetic separation of nickel laterite ores (Ni 1.42%%, Fe 23.16%) at 1100 °C for 60 min, with the addition of 6% calcium sulfate and 5% coal. The experiments showed that the nickel grade of the ferronickel concentrate could reach up to 6.00%, with a nickel recovery of 92.10% (Zhu et al., 2012). Li et al. reported that the nickel grade and recovery of ferronickel were 9.48%

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and 83.01%, respectively, when the nickel laterite (Ni 1.91%, Fe 22.10%) was reduced at 1100 °C for 60 min with the addition of 20% sodium sulfate (Na_2SO_4) (Li et al., 2012a,b).

The reaction mechanism of the selective reduction of nickel laterite ore has also been investigated recently. A number of researchers suggested that the selectivity of reduction depends mainly on the reduction atmosphere and silica level; the presence of sulfur (S) significantly promotes ferronickel particle growth to improve nickel enrichment in the metallic phases (Zhu et al., 2012). However, another researcher reported that the reduction of ferrous minerals in the presence of Na_2SO_4 was not inhibited by the formation of fayalite or forsterite, whereas the decrease of iron metallization was attributed to the formation of troilite (FeS) (Li et al., 2012a,b).

According to the aforementioned studies, relatively few studies have carried out the reduction roasting process of nickel laterite ore with high iron grade of over 30%. In their research, Jiang et al. (2012) obtained a ferronickel concentrate with a nickel grade of 9.52% and a recovery of 84.04% from high iron grade laterite ore (Ni 1.49%, TFe 34.69%) using selective reduction and magnetic separation process, with the addition of 7% Na_2SO_4 at 1200 °C for 50 min. However, the mechanism of Na_2SO_4 that affects the selective reduction of nickel laterite was not investigated.

In the current study, extracting ferronickel concentrate from nickel laterite ore was carried out using the reduction roasting and magnetic separation processes, with the addition of Na_2SO_4. The phase and microstructure transformation of nickel laterite ore in the reduction process were investigated using X-ray Diffraction Analysis (XRD) and Scanning Electron Microscopy with X-ray Energy Dispersive Spectrum (SEM-EDS). Moreover, the effects of different additives were also observed.

2. Materials and methods

2.1. Raw material

The chemical analysis of the nickel laterite ore from Philippines was determined by X-ray Fluorescence, as shown in Table 1. The distribution of nickel in the laterite ore was obtained using the chemical phase analysis methodology, as shown in Table 2, in which 95.94% of nickel is associated with silicates. Thus, the laterite used belongs to the saprolitic laterite ore.

The sodium sulfide (Na_2S), sodium oxide (Na_2O), S, and Na_2SO_4 used in the study were of chemical grade. Bituminous coal was used as reductant. The proximate analysis of the coal shows that fixed carbon, ash, volatile matter, and S content are of 30.65%, 46.36%, 23.00%, and 2.32%, respectively.

2.2. Experimental methods

The nickel laterite ore was crushed to 95 wt.% passing 4 mm. The crushed laterite sample was thoroughly mixed with different additives (the amount of additive varied from 0 wt.% to 10 wt.%) and 2% soft coal. The laterite mixture, additive, and coal were placed in a graphite crucible, in which the reducing atmosphere could be maintained. The crucible was then placed into a muffle furnace chamber at 1200 °C, and then withdrawn after 50 min.

Table 1
Chemical analysis of laterite ores.

	Fe_{total}	Ni	MgO	SiO_2	Al_2O_3	Cr_2O_3	MnO	SO_3
Content wt.%	34.69	1.49	12.28	20.05	3.03	2.27	1.34	0.37
	Co_2O_3	RuO_2	CaO	ZnO	TiO_2	V_2O_5	LOI	
Content wt.%	0.28	0.2	0.15	0.05	0.05	0.03	23.72	

Table 2
Nickel distribution ratio at different phases in the raw ore.

Existential phases	Sulfides	Oxides	Silicates	Total
Nickel grade (%)	0.012	0.048	1.43	1.49
Fraction (%)	3.25	0.81	95.94	100.00

The roasted ore was cooled to room temperature and ground to about 90.00 wt.% passing 0.043 mm in a rod mill. The slurry was separated in a CXG-99 Davies Magnetic Tube at a magnetic field intensity of 0.18 T. The magnetic product obtained was referred to as ferronickel concentrate. Nickel grade, nickel recovery, and iron recovery in the ferronickel concentrate were used to determine the effect of selective reduction on the final ferronickel concentrate.

2.3. XRD and SEM-EDS analysis

XRD patterns were recorded using a diffractometer (Rigaku D/Max 2500, Japan) under the following conditions: radiation Cu Kα of 150 mA, tube current and voltage of 40 kV, scanning range of 10° to 90°, step size of 0.02°, and scanning speed of 5°/min. Polished sections were prepared to observe the morphological changes and analyze the element content of the reduced products using Scanning Electron Microscopy (Carl Zeiss EVO18, Germany) equipped with an Energy Dispersive X-ray Spectroscopy (EDS) detector (Bruke XFlash Detector 5010, Germany). ESEM images were recorded in backscatter electron modes operating in low vacuum mode at 20 kV.

3. Results and discussion

Our results show that the nickel grade of the ferronickel concentrate increased from 3.69% to 9.52% and the nickel recovery increased to 84.04% with the addition of 7% Na_2SO_4, in contrast to those ferronickel concentrate without additive (Jiang et al., 2012). Thus, the enrichment of nickel in ferronickel concentrate is more effective in the presence of Na_2SO_4.

The products of thermal decomposition and reducing reaction of Na_2SO_4, including Na_2S, Na_2O, and S, were used as additives to be mixed with laterite ores to investigate the mechanism of Na_2SO_4 that affects the selective reduction of the nickel laterite ore. The mixtures were roasted at 1200 °C for 50 min with the addition of 2% coal as reductant. The results can determine whether Na_2SO_4 produces the thermal decomposition and reduces the reaction in the reduction roasting process.

3.1. Effect of different additives on nickel grade and recovery

The magnetic separation results of the roasted ore with the addition dosage ranging from 0% to 10% are shown in Fig. 1. The additives are Na_2S, Na_2O, S, and Na_2SO_4, respectively.

With the increase of Na_2S dosages to 10% as shown in Fig. 1, the nickel grade exhibited a significant improvement, from 3.69% to 10.86%; nickel recovery also increased to 92.09%. However, the additive dosage further increased the results in a corresponding decrease of nickel recovery, from 92.09% to 88.56%. A sharp decrease in iron recovery from 62.39% to 24.62% was also observed. These results prove that the effect of Na_2S on the enrichment and recovery of nickel is efficient.

The experimental results of different S dosages show that the nickel grade of ferronickel concentrate increased to 7.21% although the nickel and iron recovery decreased sharply from 82.47% to 73.07% and 62.39% to 29.43%. The decrease in iron recovery indicates that S significantly affects the selective reduction of the nickel laterite ore.

The nickel grade increased marginally from 3.69% to 4.62% when the dosage of Na_2O was up to 10%, as shown in Fig. 1(c). The nickel recovery increased significantly from 82.47% to 96.35%, whereas