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Mineralogical characterization and design of a treatment process for Yunnan nickel laterite ore, China



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ABSTRACT

The use of laterite ore as a major nickel source is gradually increasing because of the depletion of sulphide ores. However, in contrast to high-grade nickel sulphide ore, low-grade nickel laterite ore cannot be as easily upgraded by current technologies due to its complicated mineral structure and nickel distribution. This study investigated the mineralogical characteristics, occurrence state and dissemination characteristics of nickel within Yunnan nickel laterite ore in China. Nickel laterite ore had a complex internal structure and mainly consisted of limonite (10 wt.%) and serpentine (87 wt.%). Sulphides were not a significant part of this laterite ore and were rarely observed. Furthermore, the nickel was mainly hosted in serpentine by substitution for Mg or by adsorption. Serpentine had a mean grade of approximately 0.77 wt.% Ni and represented approximately 81.49 wt.% of the total laterite resource. A portion of the laterite ore had a pore structure that was formed by destruction of the original protolith during and after its formation, with a specific surface area of 70.042 m²/g. The actual temperature for the reduction of metal oxides within the ore was analysed by H₂-TPR (temperature-programmed reduction), which indicated that it was higher than the reduction temperature of the pure metal oxides. Finally, based on the above analyses, a non-melting reduction treatment process was proposed for efficient and reasonable utilization of Yunnan laterite ore.

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1. Introduction

As a major nickel resource, laterite ores were exploited to produce nickel products until the discovery of sulphide deposits in the early part of the 20th century (Dalvi et al., 2004). However, along with a growing demand for nickel production and declining supply of sulphide ores, the focus gradually shifted to low-grade nickel laterite ore. Approximately 73% of the land-based nickel resources in the world are contained in laterites (Dalvi et al., 2004; Fan and Gerson, 2011), while approximately 85% of Ni laterite resources are located in the accretionary terranes of the Circum-Pacific belt, the Caribbean and the Balkans on mainly serpentinized ophiolitic dunite and harzburgite peridotite (Butt and Cluzel, 2013). Indonesia, which is the world's largest supplier of nickel ore, issued an injunction against ore exports at the beginning of 2014. This injunction may have a negative impact on the market for nickel products in other countries, in which there is a shortage of nickel resources. Thus, it is imperative to further investigate the characteristics of the low-grade nickel laterite ore characteristics for the comprehensive utilization of this nickel resource.

Laterite ore deposits are formed by nickeliferous olivines via prolonged weathering and leaching processes and are mainly distributed in tropical and subtropical regions near the equator (Dalvi et al., 2004). Moreover, the formation of a nickel laterite may be influenced by the composition, topography, structure, climate, and duration of the formation of the protolith (Thorne et al., 2012a). All of these geological variables led to complex structural characteristics of nickel laterite ore. Generally, laterite deposits mainly contain iron oxide deposits and silicate deposits. Iron oxide deposits, which contain residual concentrations of Ni, are produced by the transformation of Ni-bearing minerals, such as serpentine and olivine, in an oxidizing environment during the weathering process (Freyssinent et al., 2005).

Many scholars have performed intensive studies of laterite ore deposits from various regions around the world, such as Greece, Brazil, Turkey, Albania, Australia and so on (Oliveira et al., 1992; Thorne et al., 2009, 2012b; Butt and Cluzel, 2013). Research on the internal microstructure of nickel laterite ore is important for optimizing the process of metallurgy, especially for lower grades of nickel laterite ore (<1 wt.%

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Table 1 Chemical analysis of the laterite ore sample

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	Component	Fe (total)	Ni	Со	MgO	SiO ₂	Al_2O_3	CaO	S	Mn
	Content wt.%	9.67	0.82	0.033	31.49	37.37	1.89	0.033	0.01	0.083

Ni). Chen et al. (2004) studied the mineralogy and characterization of nickel laterites from New Caledonia and Indonesia. The microstructure and phase characterization during reduction roasting were investigated by Rhamdhani et al. (2009). Recently, the mineralogy and crystal chemistry of a low-grade nickel laterite ore (0.97 wt.% Ni; 40.09 wt.% Fe) from Indonesia were studied by Zhu et al. (2012); Ma et al. (2013) used Philippine laterite ore to design a technical route based on its mineral-ogical analysis; Cristina et al. (2014) investigated the textures, mineralogy and geochemistry of the Falcondo nickel laterite deposit.

The Yunnan nickel laterite deposit, located in the southwest of China, contains an estimated ore resource of 0.43 Mt of nickel ore. It belongs to high magnesium (>30.0 wt.% MgO), low iron (<10.0 wt.% total Fe) and low nickel (<1.0 wt.% Ni) laterite ore. Hydrometallurgy was an unwise route to process the high magnesium laterite ore due to the disadvantages of large amounts of both slag and acid consumption (McDonald and Whittington, 2008). Rotary kiln-electric furnace (RKEF) smelting, which was widely used to treat high nickel laterite ore (>2 wt.% Ni), has become the dominant technology for ferronickel production. However, it is not suitable for processing low nickel laterite ore from an economic perspective (Nayak, 1985). Moreover, according to the Oheyama process, nickel laterite ore was smelted at a high temperature (~1400 °C) in a semi-fused state within a rotary kiln. This was deemed to be the most economic method to treat high-magnesium laterite ore. However, the problem of kiln ring formation was not completely solved and was harmful to the operation of the kiln (Rao et al., 2013). Thus, the current study has investigated the mineralogical characteristics, occurrence state and dissemination characteristics of nickel in Yunnan nickel laterite ore. Furthermore, the thermal properties and reduction behaviour of nickel laterite ore were also investigated. Finally, a non-melting reduction treatment process was proposed for the reasonable utilization of the Yunnan nickel laterite ore.

2. Materials and methods

A nickel laterite ore sample from Yunnan Province, China, was used in the experiments. Representative sub-samples were selected from the bulk sample to prepare thin sections and polished blocks for micromorphological investigations. Chemical analysis methods were used to determine the chemical compositions of nickel laterite ore, and the results are listed in Table 1. The mineral compositions and particle sizes within the ore were analysed and are shown in Table 2. The analytical methods and steps are as follows: first, a certain amount of ore was

Ta	ble	2

Mineral compositions and its particles size.

crushed and elutriated to obtain the artificial heavy fraction. Polished thin section authentication and XRD methods were used to determine the composition and phase of the artificial heavy fraction. Subsequently, quantitative detection of these phases was performed by weighing and/ or the chemical analysis method to assure the data accuracy; finally, these data were collected and organized into Table 2.

The X-ray diffraction (XRD) experiment was performed on a Japan Science D/max-R diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å), an operating voltage of 40 kV, and a current of 40 mA. The diffraction angle (2 θ) was scanned from 10° to 90°. Optical microscope (OM) analyses were performed on a LEICA DM4500P, and the microstructures and modes of occurrence were analysed by scanning electron microscopy (SEM; CARL ZEISS-EVO18) coupled with energy dispersive X-ray spectroscopy (EDS; BRUKER-QUANTAX). Electron probe microanalysis (EPMA) was carried out on a JEOL JXA 8230.

The ore pore structure and specific surface area were determined by the adsorption-desorption isotherms. The particle size distribution of the sample was controlled in the range of 20-40 mesh, and determinations were performed with a Quantachrome CHEM BET-3000 Instrument. The TPR Win v 1.50 apparatus, which is produced by Quantachrome, was used for H₂-TPR (temperature-programmed reduction) analysis. This measurement was performed by accurately weighing 40 mg of the sample (with particle size 40–60 mesh) into a U-shaped guartz tube equipped with a temperature sensor. The temperature inside the reactor was elevated from 50 to 650 °C with a N₂ flow rate of 40 mL/min, and the temperature was maintained at 650 °C for 1 h. Afterwards, when the temperature inside the reactor decreased to 100 °C, the injection of the mixed gas (H₂: 10 vol.%; Ar: 90 vol.%) with a flow rate of 75 mL/min was begun in the U-shaped quartz tube. The temperature inside the reactor was then elevated again from 100 to 900 °C with a heating rate of 10 °C/min. The signal from the TC-detector was plotted against the reactor temperature.

3. Results and discussion

3.1. Texture and structure of ore

The ores had no obvious directional structure and mainly consisted of serpentines. The serpentine had a compact structural characteristic, which led to the formation of a blocky structure. The ore was subjected to a strong stress and fractures occurred, leaving behind cracks during and after its formation. Partial cracks were subsequently filled with epigenetic serpentine to form veined structures within the laterite ore. The intergrowth between magnetite and limonite formed maghemite (Mag), which was distributed in serpentines with disseminated and nervate structures (Fig. 1a). Moreover, brecciated and earthy structures also existed in the ore. Olivine exhibited a characteristic idiomorphic granular texture within the protolith and was completely transformed into serpentine after prolonged alteration. Thus, the original olivine

Туре	Name	Molecular formula	Content (wt.%)	Particle size (mm)		
				Max	Common	Min
Oxide	Quartz	SiO ₂	<1	0.2	0.01-0.15	0.002
	Limonite	$Fe_2O_3 \cdot nH_2O$	10	0.3	0.01-0.1	0.002
	Magnetite	Fe ₃ O ₄	0.2	0.6	0.01-0.03	0.002
	Chromite	FeCr ₂ O ₄	<0.002	1	0.06-0.25	0.005
Silicate	Plagioclase	Ca[Al ₂ Si ₂ O ₈]	<0.001	0.8	0.03-0.3	0.01
	Serpentine	$(Mg, Al_2)_3[Si_2O_5](OH)_4$	87	9	0.05-2	0.01
	Tremolite	$Ca_2Mg_5[Si_4O_{11}]_2(OH)_2$	0.006	0.3	0.02-0.1	0.002
	Kaolinite	Al ₄ [Si ₄ O ₁₀](OH) ₈	1–2	-	< 0.005	-
	Montmorillonite	$(Al, Mg)_2[Si_4O_{10}](OH)_2 \cdot nH_2O$	<0.001	-	< 0.005	-
	Nontronite	$Na_{0.33}Fe^{3+}_{2}(Al, Si)_{4}O_{10}(OH)_{2} \cdot nH_{2}O$	<0.001	0.5	0.06-0.3	0.005
Sulphide	Pyrite	FeS ₂	<0.0001	0.7	0.05-0.2	0.002
	Bravoite	(Ni, Fe)S ₂	<0.0001	-	0.005-0.03	-

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