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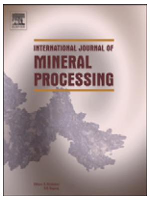

Chlorination roasting of laterite using salt chloride

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ABSTRACT

This paper introduces an application of chlorination roasting process followed by hot-acidulous water leaching that could cause a high extraction selectivity of Ni, Co and Mn over Fe and Mg which can concentrate Ni and Co in laterite ores. Thermodynamic analysis of possible chlorination reactions in roasting process was calculated and the Predominance Area Diagram of Ni–Co–Cl–H–O was shown to indicate the effect of partial pressure of HCl and H_2O on the stability of $NiCl_2$ and $CoCl_2$. The mixture of NaCl and $MgCl_2 \cdot 6H_2O$ was selected as chloride agent and the chlorination mechanism was discussed comprehensively. The results show that the leaching rates of Ni, Co, Mn, Fe and Mg are 87%, 58%, 53%, 3.2% and 5.4% respectively at the optimal conditions, which showed that Ni, Co and Mn could be extracted effectively and the extraction of Fe and Mg was suppressed simultaneously. The Ni/Fe ratio and Ni/Mg ratio can reach 0.97% and 0.25% in leaching solution which can increase 15 times and 8 times respectively in comparison with the Ni/Fe and Ni/Mg ratio in raw ore.

1. Introduction

As a result of escalating mining costs, depleting sulfide reserves, and continuously increasing world demand for nickel, nickeliferrous laterite ores have become the major source of production of nickel as it hosts most of the world's terrestrial nickel resources, comprising about 60% of the total 130 million tons of nickel reserves (Guo et al., 2011). So most of the expansion in nickel production capacity over the next ten years will come from the processing of laterite ores. Nickel laterite occurs in present or past zones of the earth that have experienced prolonged tropical weathering of "ultramafic" rocks containing ferromagnesian minerals. Nickel and cobalt oxides are reported to occur in the lattices of iron and silicate minerals mostly. Goethite is the main nickel-bearing mineral in the laterite (Chang et al., 2010) and cobalt in limonite is found to be associated with a manganese phase rich also in nickel (Georgiou and Papangelakis, 2004). These results indicate that the extraction of nickel and cobalt is highly dependent upon the degree of decomposition of the nickel and cobalt-bearing minerals. Thus the ore cannot be significantly upgraded or concentrated prior to processing, which hinders the development of laterite metallurgy. To improve this situation, numerous pyrometallurgical, hydrometallurgical and hybrid pyro–hydrometallurgical processes for the extraction of metals from laterite ores through breaking up of these lattices have been practiced for several decades (McDonald and Whittington, 2008a,b; Li et al., 2009, 2012; Zhu et al., 2012; Valix and Cheung, 2002).

Chlorination metallurgy is characterized by the high reactivity of chlorine, the high volatility and low melting point of metal chloride, and the big differences in the formation of different metal chlorides (Shen et al., 2009). Therefore, the use and development of chlorination metallurgical processes continue to be of interest to a number of metallurgical applications (Pickles, 2009). Hydrometallurgical applications can be explained by the high solubilities of chloride salts and the option to carry out fast and effective leaching at ambient pressures and relatively low (below the boiling point) temperatures (Flett, 2002). An alternative method for pyrometallurgical treatment of laterite ores is to utilize chlorine as a reagent to chlorinate nickel, cobalt and manganese selectively, and separate them from iron and magnesium which remain in the oxide form. The potential advantages of selective chlorination include that non-ferrous metals can be separated from iron, the chlorine reagent can be recycled, and finally other elements such as nickel and cobalt can be recovered (Fan et al., 2010).

Therefore, chlorination roasting of laterite has continued to remain a subject of interest since it produces soluble chloride of valuable metals with simultaneous rejection of iron and magnesium, and the products of nickel chloride and cobalt chloride can be used as the principal commercial chemicals (Kuck, 2009). Chlorination roasting of metal oxide in the presence of common salt has been reported by a number of workers (Fan et al., 2012; Yu-chun et al., 2010). Contrasted with chlorination roasting process with hydrogen chloride gas, solid chloride agents for chlorination roasting is of preferable merits including simple operation, low cost equipment and more chloride agents except relatively higher roasting temperature. Although some papers have introduced these kinds of work (Fan et al., 2011; Fang-ming et al., 2009), these methods show lower selectivity in the extraction of nickel and cobalt over iron and magnesium, and are relatively complicated to operate. Therefore, the development of a new efficient extraction process for recovery of nickel and cobalt from laterite ores is still needed.

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Table 1
Chemical composition of raw ore.

Constituent	NiO	CoO	MnO	Fe_2O_3	CuO	MgO	Al_2O_3	SiO_2
Content (wt.%)	0.60	0.042	0.171	15.01	0.007	26.4	0.34	57.43

To explore a simple, cost-effective and environmentally-friendly chlorination roasting process for low-grade laterite, more solid chloride agents must be used to extract valuable metals and the chlorination mechanism should be researched comprehensively. In this present research, sodium chloride and magnesium chloride mixed together were used as solid chloride agent due to their popular application, low price and low melting point. This investigation mainly focused on the extraction of valuable metals from laterite ore and the rejection of impurity metals during the selective chlorination process. Various parameters were studied including different solid chloride agents, chloride agent quantity, chlorination temperature, chlorination time and particle size of the sample.

2. Experimental

2.1. Mineralogy analysis

A limonite laterite ore from Yunnan province in China were ground to 100% passing 100 mesh, dried at 105 °C for 12 h and analyzed by flame atomic absorption spectrometry (AAS) and X-ray fluorescence (XRF) which gave the results shown in Table 1. A mineralogical study was also performed comprehensively to determine the distribution of nickel and cobalt in main minerals using a Rint-2000 X-ray diffractometer (XRD) with Cu Kα radiation from 5° to 85° (2θ) and a TSU-70C optical microscope. The main minerals, which are evident in Fig. 1, are lizardite ($Mg_3Si_2(OH)_4O_5$), goethite ($FeO(OH)$), hematite (Fe_2O_3), magnetite (Fe_3O_4) and quartz (SiO_2). The result of optical microscope analysis shows that goethite in about 0.002 mm particle is cocooned and distributes within magnetite mineral (Fig. 2), and maghemite (white) and limonite (gray) locate in other minerals (Fig. 3), where maghemite size is below 0.01 mm and limonite size is between 0.05 and 0.3 mm.

The main valuable metals of nickel and cobalt distributing in different minerals, such as goethite, limonite, sulfite, lizardite and etc., are shown in Tables 2 and 3. It could be found that nickel (about 86%) and cobalt (about 65%) mainly exist in iron minerals, suggesting that they have a number of mineral hosts within this ore, which show that the extraction of nickel and cobalt would lead iron extracted correspondingly with ordinary process. To avoid more extraction of iron, some chlorination roasting conditions should be researched comprehensively. Combined with Figs. 2 and 3, it could be speculated that the ore must be ground to small particle so as to increase the reaction chances between iron minerals and hydrogen chloride generated by solid chloride agents, which could improve reaction rate.

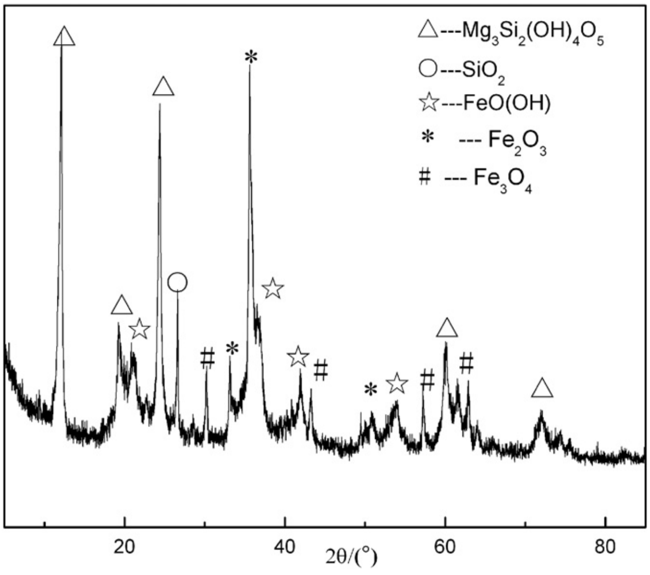

Fig. 1. Powder XRD pattern of raw laterite.

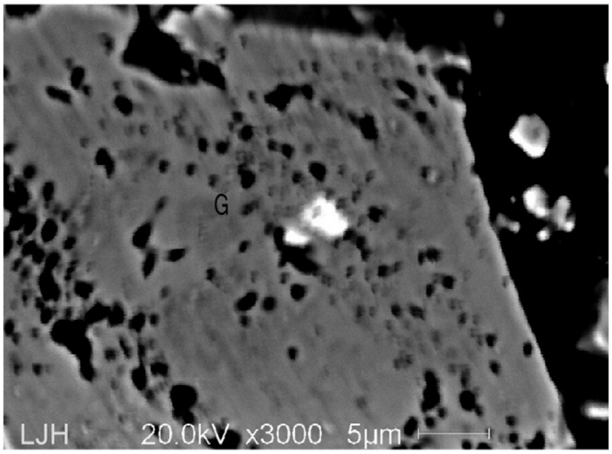

Fig. 2. Fine goethite (white) in magnetite mineral.

2.2. Apparatus and procedures

The ore weighed 8 g and mixed with solid chloride agent in the desired stoichiometry in each experiment was pelletized with the diameter range of 2–3 cm. Roasting experiments were conducted in a fixed horizontal electric tube furnace shown in Fig. 4, where the temperature of the sample was monitored using a Chromel–Alumel thermocouple inserted into the bed. All of the roasting experiments in the tube furnace were carried out under a flowing Ar atmosphere at a flow rate of 100 ml/min until the ores were cooled down to room temperature. After each roasting experiment, the roasted ore was

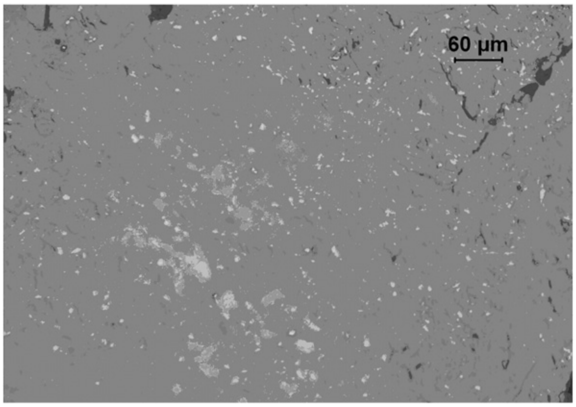

Fig. 3. Fine maghemite (white) and limonite (gray) located in gangue.

Table 2
The distribution of nickel in main minerals of the ore.

Ni phase	Goethite	Limonite	Sulfide	Lizardite	Total
Content (wt.%)	0.46	0.25	0.02	0.14	0.87
Distribution rate (%)	69.18	16.97	1.64	12.21	100.00