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Selective leaching of valuable metals from laterite nickel ore with ammonium chloride-hydrochloric acid solution

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ABSTRACT

During the recent years, selective leaching from laterite ore has gained considerable interest from the scientific community because of the growing demand of valuable metals including nickel and cobalt. However, high energy consumption and serious environmental pollution have been the major drawbacks of the current leaching methods, leading to a strong desire for the development of alternative approaches. Herein, we have successfully developed a clean method to selectively leach nickel from laterite ore using chlorination hydrometallurgical technology, which has a greatly reduced environmental impact and mild reaction requirements. In this work, ammonium chloride solution was used as the chlorination agent and the process was achieved under 2 M of hydrochloric acid, 3 M of ammonium chloride and a liquid/solid ratio of 6:1 (mL/g) at 90 °C for 90 min. Notably, the process resulted in a good yield, with nickel (87.7%), cobalt (75.1%), manganese (95.6%), and iron (only 21.1%). The leaching mechanism was demonstrated by the analysis of XRD pattern of leaching residue and raw ore, suggesting that chloride ions are beneficial to the dissolution of goethite mineral in nickel laterite. When comparing with other chloride solutions which exhibit high leaching in weak acid, ammonium chloride has demonstrated a promising ability to activate hydrogen ion, as evidenced in the simulation result of OLI system. The reusability of ammonia chloride in leaching raffinate showed that this method has great potential for eco-friendly and practical industrial application toward sustainable refining of valuable metals from laterite nickel ores.

1. Introduction

Nickel is a valuable metal which widely used in alloy, batteries, fuel cells, electroplating and etc. (Park and Nam, 2008; MacCarthy et al., 2016) and is commonly found in laterite, sulphide ores and deep-sea nodules (Moskalyk and Alfantazi, 2002). During the past decades, native nickel is mainly extracted from sulfide ores due to its low extraction cost. Recently, the increasing global demand and fluctuating price of this valuable metal in the commercial market, as well as the expected depletion of sulfide ores have sparked considerable interest for the development of alternative strategies for selective leaching from laterite ores. Meanwhile, laterite nickel ore has emerged as an increasingly important source of nickel (Tong et al., 2013; Marrero et al., 2015), which account for the majority (70%) of world's nickel reserves. In contrast to the sulfide ores, the extraction of nickel from laterites generally require difficult processing procedures and high energy consumption, leading to a relatively low nickel production from laterite which is only 42% of the total Ni production from ores (Quast et al., 2013; Xu et al., 2013).

Based on the above considerations, an increasing number of studies have endeavored to develop new methods to exploit laterite resources, including sulphuric acid technologies, chloride and bio-technologies (McDonald and Whittington, 2008). Over the past years, conventional sulfuric acid pressure leaching (PAL) process had been a preferred route to extract nickel and cobalt from laterites (mostly limonite), in which iron is precipitated as hematite during the leaching process. A kinetic equation was derived using the concentration of hydrogen ion "at temperature" calculated from a solution speciation approach in PAL, and the assumption that nickel associated with magnesium dissolves instantaneously (Rubisov et al., 2000). To precipitate iron as hematite, the use of oxygen in PAL was investigated and a few tests with oxygen were

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performed (B.K. Loveday, 2008). However, the major drawbacks of PAL process include the high operational cost, more energy consumption, as well as the more difficult construction of PAL at commercial level when comparing with atmospheric pressure leaching (AL) (Büyükakinci and Topkaya, 2009). The development of atmospheric hydrometallurgical hydrochloric acid based leaching process for the treatment of nickeliferous laterites of various types was described (Rice, 2016). To enhance the atmosphere sulfuric acid leaching, sodium sulfite was used and the leaching mechanism was investigated (Luo et al., 2015). Thubakgale et al. (2013) leached a low-grade South African saprolitic laterite using sulphuric acid and the kinetic model was established. Citric acid was used to selectively extract cobalt from limonite-type laterite ores in the presence of ammonium bifluoride (Li et al., 2010). Oxley et al. (2016) proved that heap leaching could be used to deal with laterite ores both technically and commercially. While leaching process at atmospheric pressure has successfully been used to extract Ni and Co in an efficient manner, the high acid consumption and low selectivity of this process have greatly impeded its further development (Wang et al., 2012). Therefore, the development of a more economical and eco-friendly process is of extreme interest and importance among the scientific research in laterite metallurgy.

Chloride-based processes have several advantages over the conventional hydrometallurgical and smelting processes including higher leachability of complex ores, higher stability of chloro-complexes and regeneration of leaching reagents (Lakshmanan et al., 2016). Ferric chloride leaching was ever successfully performed in saprolitic ore for the selective leaching of Ni and Co with a more eco-friendly process, and the leaching mechanism was analyzed comprehensively (Zhang et al., 2016).

To reduce the energy consumption and reagent cost, an alternative cleaner approach for the selective leaching of Ni and Co from laterite ore was developed with ammonium chloride, which contained a lower content of hydrochloric acid solution. The impacts of dissolution of nickel, cobalt, manganese and iron, including reaction time, temperature, L/S (liquid/solid) ratio (vol/wt.), hydrochloric acid concentration and ammonia chloride concentration were investigated. In particular, the selective leaching mechanism was investigated extensively in parallel with the analysis of X-ray diffraction (XRD), Energy Dispersive Spectrometer (EDS) and OLI software. OLI-Systems is a commercial software which can simulate multicomponent aqueous electrolyte systems over a wide range of conditions: temperature −50 to −300 °C, pressure 0–1500 bar, species concentration 0–30 mol/L, solid-aqueous and vapour-aqueous equilibria, as well as the support of advanced thermodynamic framework and convenient data regression (Rafal et al., 1994). In this work, OLI software was mainly used to estimate and predict the hydrogen activity and vapor pressure for the elucidation of leaching mechanism.

2. Experimental method

2.1. Mineralogical investigation

The mineral sample from the mixed ore with different surface depth was collected from Yuanjiang Laterite deposit. The sample was dried, crushed and sieved, and a particle size fraction of 0.074–0.15 mm was selected as material for the subsequent experiment. The results of trace elements and major elements contents using Atomic Absorption Spectrophotometry and titrimetry are shown in Table 1.

Table 1
Typical chemical analysis of the laterite sample.

Elements	Ni	Co	Mn	Fe	Cu	Ca	Mg	Al	Si	Na
Content%	1.15	0.08	0.35	14.06	0.07	0.12	29.35	0.34	23.13	0.26

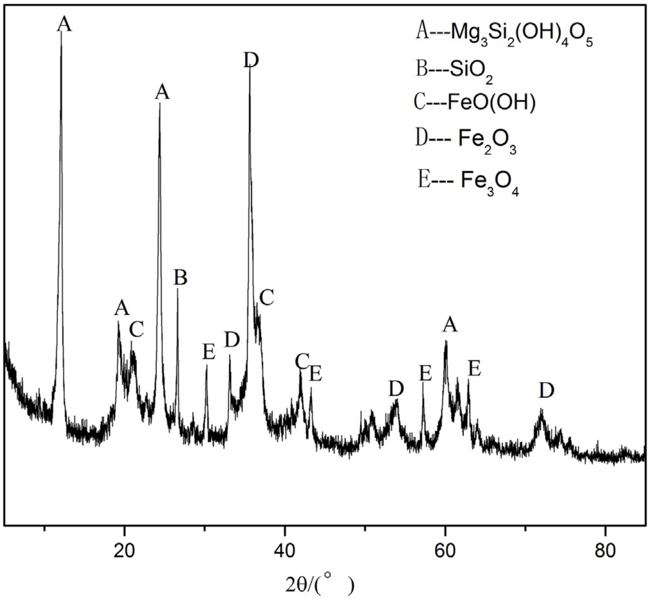

Fig. 1. XRD pattern of the laterite sample.

Mineralogical composition was obtained by phase analysis, which illustrated in the X-ray diffraction pattern (Fig. 1). The main mineral phases were serpentine ($Mg_3[Si_2O_5(OH)_4]$), goethite (FeO(OH)), silica (SiO_2) and some iron oxides such as magnetite (Fe_3O_4) and hematite (Fe_2O_3). Therefore, the sample could be categorized as garnierite ore.

2.2. Experimental setup

Leaching experiments were conducted at atmospheric pressure. Lixiviant was prepared using ammonium chloride and hydrochloric acid at a certain concentration, followed by mixing with mineral sample and leaching at a certain temperature for some time. Subsequently, the residue was removed from the lixiviant by filtration. The extraction of nickel, cobalt, manganese, and iron was determined as a function of ammonium chloride concentration, hydrochloric acid concentration, liquid-solid ratio (mL/g), leaching temperature and leaching time. All of the leaching experiments were carried out in a beaker set in water bath with a fixed stirring speed of 300 rpm.

2.3. Chemical analysis and simulation calculation

The content of nickel, cobalt and manganese in lixivium was determined by WFX-1380 Atomic Absorption Spectrophotometry instrument produced by China company called Beijing Beifen-Ruili, while the concentration of iron was titrated in potassium permanganate methods. The phase of feed ores and residues were analyzed by D8 Advance X-ray diffraction analyzer produced by a German company called Bruker. D8 Advance X-ray diffraction analyzer was implemented with energy dispersive X-ray spectrometric microanalysis of residue to determine the structure and main elements on residue surface. The SEM-EDS analysis was implemented by SU8000 instrument produced by Japan company called Hitachi. OLI-system was used to simulate and calculate the properties of a series of chloride-containing solutions.