



## Comparison of effectiveness of citric acid and other acids in leaching of low-grade Indonesian saprolitic ores



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### ABSTRACT

Comparison effect of chemical citric acid and other leaching reagents including inorganic acid and other organic acid on nickel extraction from low-grade Indonesian saprolitic ores was evaluated. Two saprolitic ores from two different mining areas (Sulawesi Island and Halmahera Island) in Indonesia were used to investigate the leaching performance and mineral dissolution behaviors of different ore samples using different leaching reagents. Leaching was performed using citric, sulfuric, nitric, hydrochloric, lactic, and oxalic acids. The saprolitic ore from Sulawesi Island (SS) has higher serpentine and lower goethite contents than the saprolitic ore from Halmahera Island (SH). These differences significantly affect the leaching performances and metal dissolution behaviors. Citric acid and sulfuric acid were more effective than other acid solutions for nickel extraction from both samples. Citric acid was very effective for dissolving nickel from serpentine, but did not recover nickel from goethite. In contrast, inorganic acids, namely sulfuric, nitric, and hydrochloric acids, can extract nickel from lateritic ores by dissolving goethite as well as serpentine, but the nickel recoveries achieved with sulfuric acid were higher than those achieved with other inorganic acids. A comparison of the leaching performances of the two samples shows that nickel recovery from SS was higher than that from SH when citric acid leaching was used, but the samples gave similar nickel recoveries in all inorganic acid and lactic acid leaching processes. Moreover, oxalic acid is the least effective reagent for nickel extraction from both samples, because of nickel oxalate precipitation after nickel dissolution. In addition, the effect of a sulfuric acid–citric acid mixture on the nickel dissolution rate was investigated to confirm the individual influences of citric acid and sulfuric acid on the leaching behavior of each sample. The results show that an increase in the amount of sulfuric acid affected the dissolution rate of nickel in leaching of SH much more than that in leaching of SS. In general, the effect of citric acid in the mixture of sulfuric acid and citric acid is attractive. Moreover, citric acid offers not only high nickel recovery and high selectivity of leaching but also an environmentally safe process and low acid consumption.

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### 1. Introduction

The high-grade saprolitic deposits in regions such as Indonesia, New Caledonia, and Brazil were first commercialized using pyrometallurgical routes in the late 19th and early 20th centuries. However, as these higher-grade deposits became increasingly difficult to find, the mining industry began to develop techniques that could be used to process the vast amounts of lower-grade nickel laterites around the world using hydrometallurgical routes (Oxley and Barcza, 2013). Research on hydrometallurgical metal extraction continues, to develop processes that are less costly, more environmentally friendly, and economically acceptable

(Habbache et al., 2009). The use of various leaching agents, either inorganic or organic solutions, in metal extraction from lateritic ores has been studied, and some of these techniques are already being used in industry (McDonald and Whittington, 2008a, 2008b). To date, sulfuric acid is the only acid that has been used industrially for extracting nickel from saprolitic ores using atmospheric tank leaching at Ravensthorpe Nickel. Sulfuric acid is preferred because of its availability and low price (McDonald and Whittington, 2008a). However, hydrochloric acid and nitric acid have begun to be considered for leaching of nickel laterites as alternatives to sulfuric acid leaching, because sulfuric acid cannot be recycled.

Nitric acid is an acidic lixiviant and a relatively strong oxidant. It can adequately dissolve valuable metals contained in iron minerals and completely oxidize divalent iron for precipitation as hematite (Ma et al., 2013; Van Weert and Boering, 1995;

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Van Weert and Shang, 1993). Furthermore, nitric acid can be readily recycled through external oxidation to nitrous oxides (Ma et al., 2013). Several nitric acid processes for lateritic ores have been developed and patented (Dong et al., 2004; Drinkard, 2010; Drinkard and Woerner, 2010; Ma et al., 2013; Wang et al., 2008). Although they are attractive on the laboratory scale, the details of these techniques have rarely been reported. Furthermore, when hydrochloric acid is used as the leachant, recovery of useful free acid from waste solutions is easier than in the case of sulfuric acid (Olanipekun, 2000). In addition, The separation of metal chlorides through solvent extraction is much easier than that from a sulfate medium because pregnant leaching solution from sulfate medium sometimes produces gypsum from iron precipitation that cause the solvent extraction process of sulfate medium more difficult. Gypsum formation was a severe problem in Australia Bulong's nickel solvent extraction (SX) circuit (Cheng et al., 2015). Moreover, the concentrated chloride liquors containing nickel, iron, and magnesium produced by solvent extraction can be spray roasted to produce pure nickel oxide, hematite, and magnesia, respectively, together with hydrochloric acid (Chander, 1982; McDonald and Whittington, 2008b; Li et al., 2012). Although chloride-based commercial leaching operations are not common, some research has been performed (Amer and Ibrahim, 2001; Chen et al., 2000; Fan et al., 2011; Majima and Awakura, 1985; Neudorf and Arroyo, 2002; Rice and Strong, 1974a, 1974b; Liu et al., 2010). Therefore, it can be suggested that the use of hydrochloric acid and nitric acid will be potential for extracting nickel from lateritic ores.

These inorganic acids still cause environmental problems when the leaching treatment is not performed well. Nowadays, organic acids have been being studied as alternative leaching reagents for nickel extraction from lateritic ores to address those issues and to provide environmentally acceptable techniques. Many researchers have confirmed that citric acid is the most effective organic acid in the leaching of nickel laterites (McDonald and Whittington, 2008b; Tang and Valix, 2006; Tzeferis and Agatzini-Leonardou, 1994). Citric acid is a well-established product of fungal metabolism, particularly from *Aspergillus niger*. Carbon sources such as agriculture wastes have been used in citric acid production, therefore the use of citric acid in the leaching of nickel lateritic ores not only provides a more environmentally friendly process, but is also cheaper than other acid leaching processes. However, not only citric acid but also other organic acids, including lactic, oxalic, malic,  $\alpha$ -ketoglutaric, fumaric, succinic, and pyruvic acids, are metabolized by fungi through the Krebs cycle. It is therefore important to compare the effects of these metabolic acids on the nickel-leaching rate when fungal bioleaching is used.

The effectiveness of citric acid and other acid solutions, either inorganic acids such as sulfuric, hydrochloric, and nitric acids, or organic acids such as lactic and oxalic acids, in the leaching of nickel laterites has been investigated. However, no studies that compare their effects on the dissolution of nickel and other metals from lateritic ores originating from different mining locations have been reported. The current study therefore focuses on comparing the effects of citric acid with those of other acid solutions (i.e., sulfuric, hydrochloric, nitric, lactic, and oxalic acids) on nickel leaching from low-grade saprolitic ores to investigate whether citric acid performs better than other acid solutions.

## 2. Materials and methods

### 2.1. Materials

Saprolitic ores from two different mining areas in Indonesia, namely Sulawesi Island and Halmahera Island, were first jaw-crushed and vibration-milled to <75  $\mu\text{m}$ . The chemical

components of the samples were identified using X-ray fluorescence (ZSX Primus II, Rigaku, Tokyo, Japan) and inductively coupled plasma-optical emission spectroscopy (ICP-OES; Perkin Elmer 8500, Waltham, MA, USA). Chemical content analysis indicated that both ore samples were typical low-grade saprolitic ores. The nickel content of the Sulawesi saprolitic (SS) sample was 1.76 wt % and that of the Halmahera saprolitic (SH) sample was 1.28 wt% (i.e., both less than 2 wt% nickel; Table 1). The mineral phases of the raw ore samples were identified by X-ray diffraction (XRD; Ultima IV, Rigaku, Tokyo, Japan), using Cu K $\alpha$  radiation, at an accelerating voltage and applied current of 40 kV and 40 mA, respectively, in the  $2\theta$  range 5–80°, with a scanning speed of 2°/min and a scanning step of 0.02°. Thermogravimetric–differential thermal analysis (TG–DTA; 2000SA, Bruker, Billerica, MA, USA) was performed on the ore samples from room temperature to 1250 °C, at a heating rate of 10 °C/min, to clarify the mineral content of each sample. The metal content of each mineral was mapped using a combination of scanning electron microscopy and energy-dispersive X-ray spectroscopy (SEM/EDS; VE-9800 SEM, Keyence, Osaka, Japan, and EDAX Genesis, Ametek, NJ, USA).

### 2.2. Leaching experiments

Leaching tests were performed in the shaker equipment at a constant shaking speed of 200 rpm. In this experiment, mixtures of screened samples (ore particle size of <75  $\mu\text{m}$  (100%)) and leaching agent (50 mL by volume of specific acid concentration), with a pulp density of 20% (w/v), were placed in 300-mL flasks and shaken in the incubator shaker (Type Bio-Shaker GBR-200, TAITEC, Saitama, Japan). “Shaking” way was used for leaching experiment in order to prevent the reducing of ore particle size that usually occurs in the leaching experiment using “stirring” way. In addition, with this shaker equipment, all leaching experiments using many flasks can be carried out simultaneously hence it can be ensured that the leaching conditions of all leaching experiments are same and the results from different leaching reagents are comparable. Moreover, regarding the shaker rate, at the shaker rate of 200 rpm, the slurry of ores and leaching reagent has a good suspension. It was ascertained that the slurry has been mixed well.

The leaching temperature was kept constant at 30 °C. Six types of leaching agent in 1 M acid concentration, namely sulfuric acid, nitric acid, hydrochloric acid, citric acid, oxalic acid, and lactic acid (analytical grade, Wako Pure Chemicals Industries, Ltd., Tokyo, Japan), were used to investigate the effect of the leaching agent on the nickel recovery and mineral dissolution behavior. 1 M of acids was used to investigate the comparison of effectiveness of acids on the nickel leaching due to the simpler and easier of stoichiometric calculations. Although the starting point of the proton concentration is different, it will be seen the effect of this difference on the nickel leaching efficiency of each leaching reagent. Moreover, the effectiveness of citric acid was compared with those of other acid solutions.

The water used for the experiments was purified using a water super-purification apparatus (Milli-Q, Millipore). The leaching process was monitored by sampling the slurry periodically and determining the amounts of dissolved metals by ICP-OES, using standard procedures. The collected residues were washed with

**Table 1**  
Chemical compositions of raw ore samples (determined using XRF and ICP-OES).

Ore samples	Element (wt%)							
	SiO <sub>2</sub>	Fe	Ni	Co	Mg	Mn	Cr	Al
SS	36.30	21.64	1.76	0.06	8.44	0.43	1.07	2.04
SH	34.00	22.77	1.28	0.05	11.18	0.34	1.18	1.31

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