ATMOSPHERIC LEACHING OF NICKEL FROM LOW-GRADE INDONESIAN SAPROLITE ORES BY BIOGENIC CITRIC ACID

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by

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ABSTRACT

Nickel laterite ores are abundant in Indonesia. Many studies have focused on discovering effective, profitable, inexpensive, and environmentally friendly methods for extracting nickel from these resources. Methods suitable for low grade ores are of particular interest. For laterite processing, leaching by organic acids and fungal bioleaching at atmospheric pressure are emerging technologies. Some studies have investigated the application of these techniques to Indonesian saprolite ores, but the leaching mechanisms are not well understood. In this research, the leaching mechanism with citric acid and biogenic citric acid was investigated with two low-grade Indonesian saprolite ores from different regions of the country. The low-grade Indonesian saprolite ores used in the study were obtained from Sulawesi (ore SS) and Halmahera (ore SH). These ores were used to study the influence of mineralogical composition on the nickel leaching. The comprehensive investigations conducted in this research include a comparison of citric acid with other leaching reagents, optimization of citric acid leaching, and kinetic modeling of the citric acid leaching process. In addition, biogenic of citric acid is produced, and the effectiveness of this acid for nickel recovery is investigated. Several techniques are used to study the mineral dissolution behavior during nickel leaching.

This thesis contains six chapters. Chapter 1 presents the background and objectives of this study, an overview of the leaching and bioleaching of laterite ores, citric acid production, and kinetics of the laterite leaching process. Previous studies of relevance are also discussed in this chapter.

In Chapter 2, nickel extraction is investigated with citric acid and other leaching reagents, including inorganic acids (sulfuric, nitric, and hydrochloric acids) and other organic acids (lactic and oxalic acids). The leaching performance and mineral dissolution behavior for the two ores (SS and SH) with the different leaching reagents are evaluated. X-ray diffraction (XRD), thermogravimetric-differential thermal analysis, and scanning electron microscopy/energy-dispersive X-ray spectroscopy results for the chemical and mineral compositions of the raw ores are presented. These results showed the SS ore had lizardite (serpentine group mineral), goethite, and clinochlore (chlorite group) as major minerals, while the SH ore contained talc and goethite as predominant minerals. These differences affected the leaching results and metal dissolution behavior. Citric acid and sulfuric acid were more effective than the other acids tested for nickel extraction from both ores. Citric acid was very effective for dissolving nickel from serpentine group minerals, but did not recover nickel from goethite. By contrast, the inorganic acids (sulfuric, nitric, and hydrochloric) could extract nickel from goethite and serpentine group minerals. The nickel recoveries achieved with sulfuric acid were higher than those achieved with the other inorganic acids. Using citric acid, the nickel recovery from SS was higher than that from SH. By contrast, with the inorganic acids and lactic acids, the nickel recoveries from SS and SH were similar. Oxalic acid was the least effective reagent for nickel extraction because of nickel oxalate precipitation after nickel dissolution. In addition, the effect of sulfuric acid–citric acid mixtures 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 showed that an increase in the proportion of sulfuric acid in the mixture affected the dissolution rate of nickel leached from SH much more than it affected nickel leaching from SS. The metal and mineral dissolution behaviors of the raw saprolite ores and leaching residues were studied using XRD.

In Chapter 3, the nickel dissolution mechanism and optimum conditions for nickel extraction using citric acid are evaluated. The effects of leaching temperature, citric acid concentration, pulp density, and ore particle size on leaching are investigated for the two saprolite ores. The maximum nickel recovery was achieved under the following leaching conditions: citric acid concentration 1 M, leaching temperature 40 °C, leaching time 15 days, ore particle size 212–355 µm, shaking speed 200 rpm, and pulp density 20 % w/v. The maximum nickel recovery from SS (96 %) was higher than that from SH (73 %) under the same leaching conditions. The dissolution behaviors of the raw saprolite ores and leaching residues were studied using XRD. The mineral contents of the ores greatly affected the leaching performance and mineral dissolution behavior. The results suggested that all dissolved nickel originated from serpentine group mineral (lizardite), which were more easily leached than goethite, talc, and clinochlore (chlorite group mineral). The lizardite content of SH was lower than that of SS, and therefore, nickel recovery from SH was lower than that from SS. In terms of the kinetics of nickel extraction, although the rate of nickel extraction for SS was faster than that for SH, the kinetics for leaching from the two ores was similar. Nickel leaching from SS and SH followed the shrinking-core model (SCM) and was controlled by diffusion through the solid product layer.

In Chapter 4, kinetics modeling of leaching of the ores by citric acid at atmospheric pressure is presented in more detail. The experimental data were well explained by the SCM, with the rate of reaction controlled by diffusion through the solid product layer. The apparent activation energy for the dissolution of nickel was around 12 kJ/mol. Based on the SCM, an empirical kinetic model for leaching of nickel from the Indonesian saprolite ore is proposed. This mathematical model is consistent with the observed experimental results.

In Chapter 5, the production of biogenic citric acid from corn starch and corn cobs using *A. niger* is described. Application of this biogenic citric acid to nickel leaching from Indonesian saprolite ores is also presented. The citric acid concentration was determined using ultraviolet-visible spectrophotometry, and high performance liquid chromatography was used to identify the products in the culture filtrate. The concentration of citric acid (0.05 M) was produced from 50 g/L corn starch after 5 days incubation at 30 °C with 3 % (volume fraction) methanol as an additive. This gave a citric acid yield of 230.4 g per kilogram of dry corn starch. Optimization of nickel leaching with the biogenic citric acid was attempted by varying several leaching parameters. The maximum nickel recovery (38–39 %) from SS and SH was achieved with a leaching temperature of 40 °C, 5 % of pulp density, <75 µm ore particle size, and 200 rpm shaker speed. The maximum nickel recovery from SS was reached quicker (3 days) than that from SH (7 days). The metal and mineral dissolution behaviors of the raw saprolite ores and leaching residues were studied using XRD. The results suggested that most nickel in the leaching solution originated from serpentine group mineral (lizardite). This result was consistent with that obtained using citric acid. Compared with citric acid, biogenic citric acid was more effective for nickel leaching. Nickel extraction using biogenic citric acid from the fermentation of corn starch and corn cobs with *A. niger* will be a profitable method for processing of low-grade Indonesian saprolite ores.

Chapter 6 summarizes the conclusions of this study and recommendations for further study.

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CHAPTER 1

INTRODUCTION

This chapter introduces the conducted study. Background and objectives of the study are presented as well as how this thesis is structured. Generally speaking, along with the industrialization and human civilization’s development, world’s nickel consumption is increasing significantly. Nickel is a strategic metal mainly utilized in the preparation of stainless steel, non-ferrous alloys, and super-alloys with impact strength, corrosion resistance, and other electrical, heat, and magnetic properties. Approximately 70% of land-based nickel reserves are contained in laterite ores. Therefore, the exploitation of nickel laterite ores could not be avoided. Indonesian nickel laterite deposits are recognized as one of the biggest deposits in the world and represent one of the most important sectors of the Indonesian economy. However, only high-grade of Indonesian saprolite ores have been utilized by pyrometallurgical method in industry to produce ferronickel and nickel matte. Unprofitable economically and technically to be applied for low-grade saprolite ores is still found in the existing technique leading to the further studies to investigate the most suitable method for processing those ores.

1.1. Background

1.1.1. Nickel consumption, nickel resources, and the existing lateritic processing

Nickel is one of the most important metals that significantly contribute to the human life development and industrialization. Nickel is a lustrous and silvery-white metal. Moreover, nickel has some of metallurgical advantages including high melting point of 1453 ^{o}C, high resistance to corrosion and oxidation, good thermal and electrical conductivity, ferromagnetic properties, catalytic behavior, easy of electroplating, and excellent strength and toughness at elevated temperatures. The final product of nickel can be available in the form of cathode, briquettes, pellet, powder, ferronickel, and nickel chemical. The most important and main application of nickel is in the production of stainless steels, nonferrous alloys as well as super-alloys, which are used in infrastructure construction as world-wide urbanization grows, military application, cutlery, the auto industry, household appliance industry, aerospace industry, and also jewelry industry. In addition, nickel is also a significant raw material in the rechargeable batteries, fuel cell, metal coin, chemical, petrochemical, and energy industry. Since its discovery in 1751 by the Swedish chemist Axel Fredrik Cronstedt, nickel demand increases continuously along with the rising of human population. The last three decades have shown a steady growth in world nickel production and consumption, mainly driven by the world stainless steel demand and productions in emerging economies. The world production of nickel is increasing continuously from 1.3 Mt in 2008 to about 1.8 Mt in 2014 and it is predicted to rise constantly (Fig. 1-1) (Mudd, 2010; New, 2011).

Nickel metallurgy is challenging because the average abundance of nickel in the earth crust is low at only 0.0084 wt. % (Kerfoot, 2000, p40); the element is more dispersed than other lower abundance elements, such as copper. Nickel sulfides (30% of world reserves) and nickel laterite (70% of world reserves) are the two main ore sources of nickel (Dalvi et al., 2004; Sudol, 2005). Sulfide ores typically have 0.4-2.0 wt. % nickel, while the nickel laterite ore grade varies depending on the deposit profile, location, and the weathering conditions (Kerfoot, 2000, p41). Laterite ores are formed near the surface following extensive weathering of ultramafic rocks, and occur abundantly in tropical climates around the equator (Indonesia, Philippines, Papua New Guinea, New Caledonia, Cuba, India), the arid regions of central Western Australia, as well as humid areas of Eastern Europe (Russia, Greece, and Turkey) (Elias, 2002). The weathering leads to distinct nickel laterite ore types, namely limonite, nontronite, and saprolite or garnierite, with different impurity levels of magnesium, iron, and silica, as well as a transition zone between the ore types (Elias, 2002; Dalvi et al., 2004; Wedderburn, 2009). A typical laterite profile especially in Indonesia can be illustrated in Fig. 1-2 (Fu et al., 2014). In addition, Table 1-2 presents the chemical composition of each layer in laterite profile (Dalvi et al., 2004).

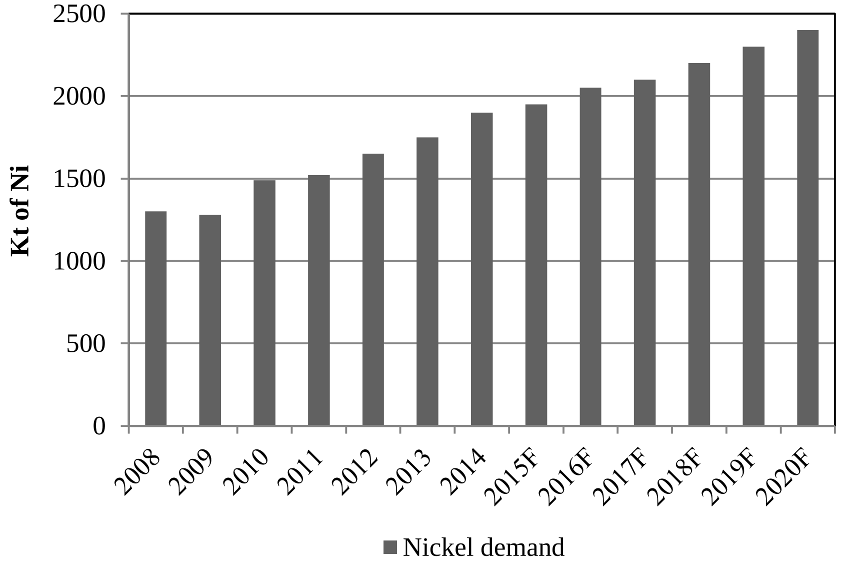
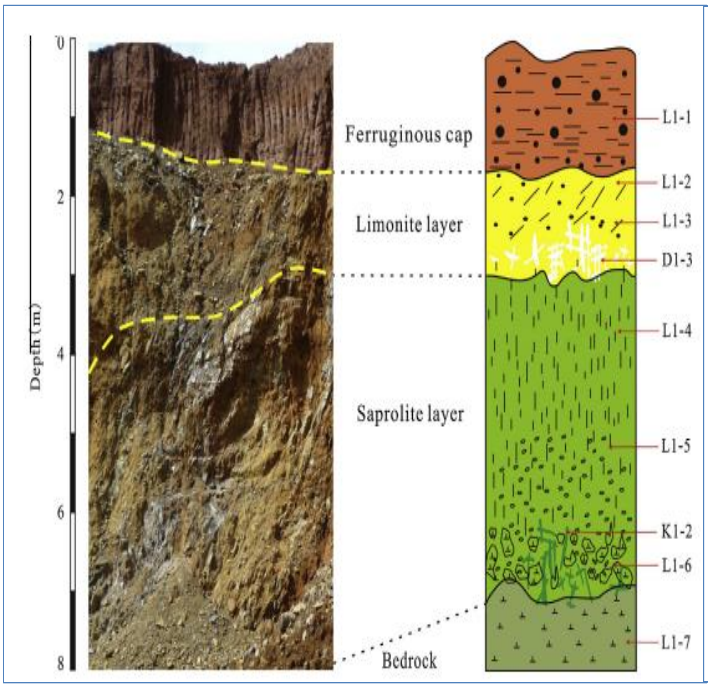


Fig. 1-1. Primary world nickel demand (Source: HDR Salva, 2014)



L1-1, Purple-red, friable, porous, low density and generally with earthy texture, easy forms aggregates after long exposure;
L1-2, Brownish-red, friable, porous, low density and generally earthy or nodular texture, easy forms aggregates;
L1-3, Brownish, friable, low density and mainly earthy texture;
D1-3, Whitish, moderately dense, showing yellow clayey materials cemented by intensive white silica stock works;
L1-4, Yellow, friable, moderately dense, earthy and massive texture with few rocky fragments;
L1-5, Sage green, moderately hard and dense, earthy and massive texture, mixed with some rocky fragments;
K1-2, Green, moderately dense and generally massive texture, some clayey materials are trapped;
L1-6, dark brown, moderately hard and dense, mixed with many clayey and rocky fragments;
L1-7, Black, high density and massive texture

Fig. 1-2. A typical laterite profile in Sulawesi Island, Indonesia (Fu et al., 2014）

Table 1-2. Approximate analysis of each layer in laterite profile (Dalvi et al., 2004)

Layer name	**Content (%)**			
	Ni	**Co**	**Fe**	**MgO**
Red Limonite (ferruginous cap)	<0.8	<0.1	>50	<0.5
Yellow Limonite	0.8 – 1.5	0.1 – 0.2	40 – 50	0.5 – 5
Saprolite	1.8 – 3	0.02 – 0.1	10 – 25	15 – 35
Bedrock	0.3	0.01	5	35 – 45

Historically, most nickel production has been derived from sulfide ores with laterite ores providing only a modest source. The major reason for this is the difficulty of processing nickel laterites compared to sulfides that lateritic ores require extensive and complex treatment to extract nickel, and have historically been more expensive than sulfide ores (Simons, 1988). Due to the large nickel reserves contained in laterite ores and depleting global reserves of nickel sulfide; therefore, nickel laterites are receiving more attention as an important nickel source, and are forming an increasing part of world nickel production (Singh & Gilkes, 1992; Brand et al., 1998; Gleeson et al., 2003; Dalvi et al., 2004; McDonald & Whittington, 2008a).

To date, there are three major process for concentrating nickel from laterite ores in industry namely rotary kiln electric furnaces (pyrometallurgical method) to produce ferronickel or nickel matte, the Caron ammonia leach process (combination of pyro-hydrometallurgical method), and high pressure acid leaching (hydrometallurgical method). In addition, nickel pig iron (NPI) processing is becoming one of the alternative pyrometallurgical routes that are mainly applied to treat limonitic types that contain high iron content. However, hydrometallurgical treatment of nickel is an energy-efficient process with less exhaust gas emission compared to pyrometallurgical concentration. The hydrometallurgical process control and leachate circulation is also simpler than that of the pyrometallurgical process. Therefore nickel particularly in low-grade laterite ores is mainly recovered through the hydrometallurgical process.

The existing hydrometallurgical processing options for laterite currently include ammonia leaching of a reduced roast product (de Graaf, 1980; Chander and Sharma, 1981; Senanayake et al., 2010), direct high pressure acid leaching of high grade laterite ores (Whittington & Muir, 2000; Whittington et al., 2003a; Whittington et al., 2003b; Whittington & Johnson, 2005), and assisted by air pressure leaching or heap leaching of low-grade laterite ores (McDonald & Whittington, 2008a, b; Agatzini-Leonardou et al., 2009). High pressure acid leaching (HPAL) has been commercialized for higher grade (e.g. >1.2 wt.% Ni) of limonitic laterite ores, with Canadian-Cuban HPAL operation at Moa Bay in operation for more than 45 years (Sudol, 2005). However, many recent operations commencing in Western Australia have suffered setbacks and been include the Bulong and Cawse operations (suspended), Murrin Murrin (previously Anaconda now Minara, which operates at below name plate capacity), Ravensthorpe (BHP ceased operations in 2009 but sold the project to First Quantum Minerals who have recommended production (First Quantum Minerals Ltd., 2011).

For low-grade nickel laterite ores, atmospheric leaching with sulfuric acid in agitated tanks is a desirable hydrometallurgical route, based upon its lower capital and operating expenditures in contrast to HPAL. Sulfuric acid is preferred because of its availability and low price (McDonald and Whittington, 2008a). However, hydrochloric acid and nitric acid began to be considered for applying in the leaching of nickel laterites to reduce the domination of sulfuric acid leaching due to the inability of sulfuric acid to be recycled. Unfortunately, these inorganic acids are still having the environmental problems when the treatment of leaching process is not in well procedure. To address those issues and to provide environmentally accepted technologies, some organic leaching reagents have been tried to be utilized for nickel extraction from laterite ores. Although some processing challenges persist during atmospheric leaching of complex ores which can make the whole operation inefficient, the further application of atmospheric leaching is still interesting to be studied more particularly for treating of low-grade laterite ores.

1.1.2. Nickel laterite ore in Indonesia and its processing challenges

Nickel production is increasingly occurring in a range of countries although mostly from laterites projects in Indonesia, Cuba, Colombia, Brazil, Eastern Europe and others. Indonesia is rich in laterite resources which is has been developing over recent decades to become a major global producer (±190 kt Ni/year) (Mudd, 2010). In 2013, Indonesia was the largest producer of nickel followed by Russia, the Philippines and New Caledonia. Indonesia has contributed around 29% of world nickel production (HDR Salva, 2014). These nickel laterite resources are distributed and spread in some islands and some locations in Indonesia as depicted in Fig. 1-3. Moreover, the nickel supplies from Indonesia increase continuously and significantly during five years (Fig. 1-4). The two biggest producers are PT INCO (Canadian) on Sorowako area, Sulawesi Island, which began in 1978 and now produces about 73 kt Ni/year (as Ni matte), and PT Aneka Tambang (Antam) which also operates in Sulawesi Island particularly on Pomaala area (producing ferronickel) as well as mines on Halmahera Island to the east, producing about 26 kt Ni/year. Some ore is exported by PT Antam and other small mining companies to Japan, Yabulu in Queensland or China for nickel pig iron production (Mudd, 2010).

A major issue in Indonesia is the potential conflict between nickel mining and high value biodiversity areas, often conservation and/or popular tourist areas, such as BHP Billiton’s Gag Island project (just south east of Halmahera) or Eramet’s Weda Bay project (also in Halmahera Island) (Mudd, 2010). In addition, the Government of Indonesia has issued Law No. 4/2009 that ban the export of raw lateritic ores without refining. Every mining company has to refine their mining product including lateritic ores domestically prior to export. Nickel laterite ores should be processed to become some final as well as intermediate products such as Ni matte (≥ 70%Ni), FeNi (≥ 10%Ni), Nickel pig iron (NPI, ≥ 4% Ni), Ni metal (≥ 93% Ni), mix hydroxide precipitate (MHP, ≥ 25%Ni), mix sulfide precipitate (MSP, ≥45% Ni), hydroxide nickel carbonate (HNC, ≥ 40%Ni), and NiO (≥ 70%Ni) (Winzenried and Adhitya, 2014).

Consequently, Indonesia's raw material export ban has removed almost 30% of mined nickel production from the global market.

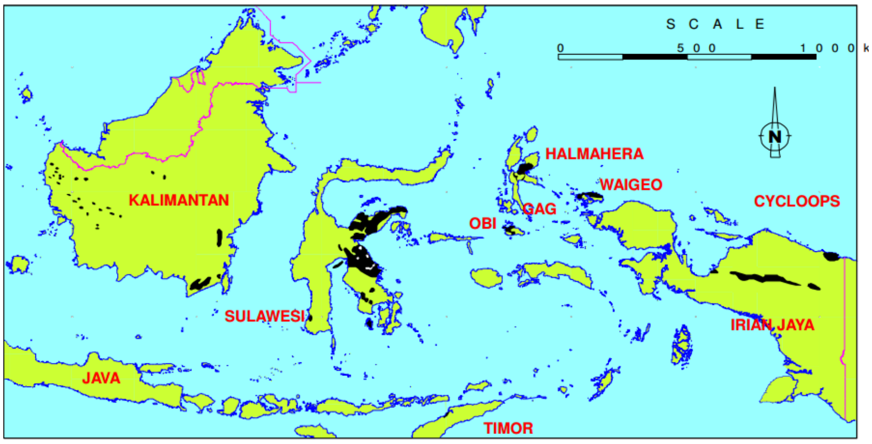


Fig. 1-3. Map of nickel lateritic ores mining in Indonesia (marked with the black spots) (Source: Elias, 2013)

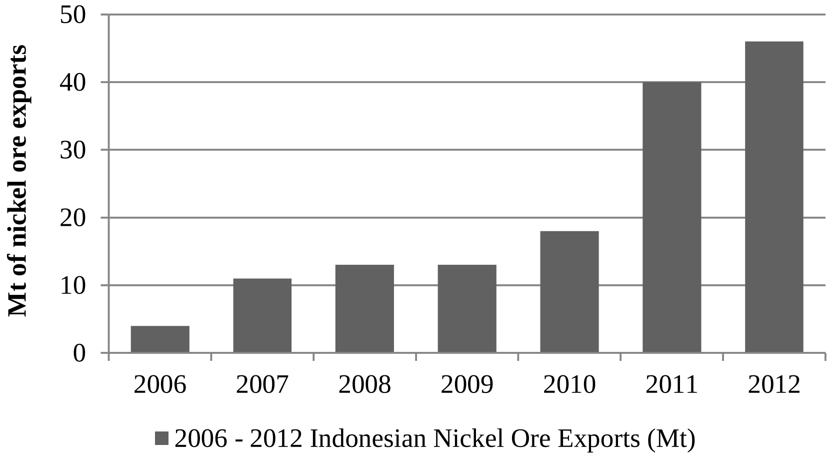


Fig. 1-4. Indonesian nickel laterite ore exports (Mt) (Source: HDR Salva, 2014)

To date, only high-grade saprolite ores have been processed domestically in PT INCO and PT Antam; however, there are great amount of limonitic ores and low-grade saprolite ores that are not processed yet and only as an overburden in the mining site. Before the law has been run, the raw limonitic ores are usually exported mainly to China to be processed in some furnaces to produce NPI. This regulation bring out the interesting challenges to Indonesian government as well as private mining companies to decide the suitable technology for utilizing of nickel lateritic resources that spread in some areas in Indonesia. Currently, some mining companies and also some research institutions in Indonesia are trying to apply NPI production technology that is adopted from China. Indonesia is likely to see a boost in NPI project construction activities. Tsingshan Group's Sulawesi Project is the most advanced and is expected to be commissioned by early 2015. According to official estimates, 40 new NPI plants are planned for Indonesia (HDR Salva, 2014). However, most of them are located quite a long way inland and have limited infrastructure. Investment in these plants and infrastructure is hampered by Indonesian laws which restrict foreign ownership to 49% (HDR Salva, 2014). Additionally, only limonitic ores can be used in that process. That technology is not suitable to utilize low-grade saprolite ores due to the low iron content in the latest ore type. Anyhow, low-grade saprolite ores in Indonesia are still big nickel and other metal resources because of the great amount of this ore even as the greatest of world's saprolite resources (Elias, 2013) (Fig. 1-5).

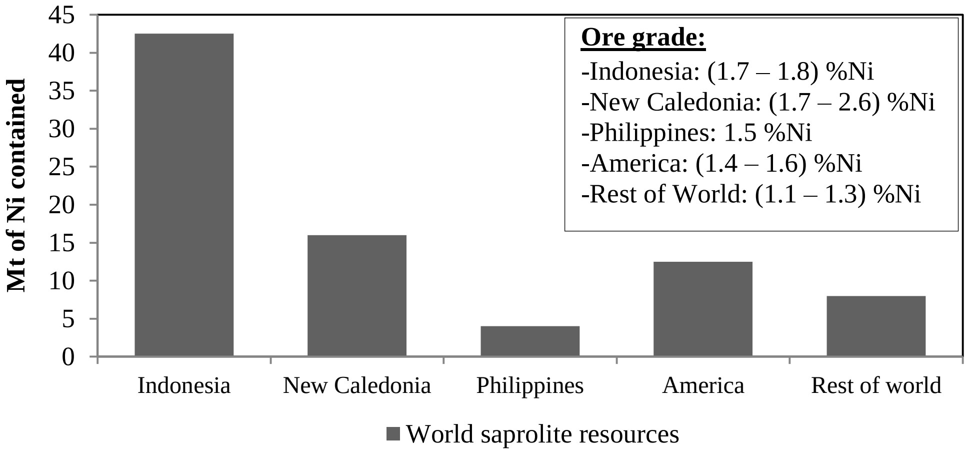


Fig. 1-5. World saprolite ore resources (Mt Ni contained) (Source: Elias, 2013)

Some efforts to investigate the suitable and profitable technology to process low-grade saprolite ores are therefore still necessary. The hydrometallurgical method particularly atmospheric leaching can be applied to leach valuable metals from low-grade saprolite ores. However, it is important to apply the technology that is suitable to be built in Indonesia. Indonesia has abundance of carbon sources that can be fermented to produce some organic acids especially citric acid that is one of the potential leaching reagents for extracting nickel from lateritic ores. On the other hand, Indonesia has some problems in infrastructures such as the lack of electricity and transportation facility. Those strength and weakness can be used to choose the most suitable technology that can be applied to process some low-grade saprolite resources in Indonesia. Citric acid as well as biogenic citric acid leaching at atmospheric pressure and modest temperature may be one of the alternative methods in this challenge.

Moreover, the properties of lateritic ores differ, depending on the sample origins (Liu et al., 2010; Watling et al., 2011); this is also the case for all Indonesian saprolite ores. The chemical and mineral compositions of laterites from different origins or even from different depths in one area can vary significantly; therefore, different extraction methods should be used. Although some nickel lateritic ores have similar mineralogical compositions, they show radically different atmospheric acid leaching performances (Watling et al., 2011). Specific mineralogical research should therefore always be conducted when a new laterite ore sample is found (Wang et al., 2012). Indonesian nickel laterite ores have been the subject of a number of previous mineralogical studies (Fan and Gerson, 2013; Wang et al., 2012). Considerable effort has been devoted to the study of atmospheric and pressure leaching of laterites, but little emphasis has been placed on understanding the detailed nickel mineralogy as a function of leaching (Liu et al., 2009), particularly citric acid leaching at atmospheric pressure. A general lack of knowledge regarding the mineralogy and chemistry of the leached products also hampers understanding of the leaching behavior and kinetics of the other mineral components present in ores (Fan and Gerson, 2013). Therefore, it is necessary to observe the effectiveness of using citric acid as well as biogenic citric acid in the atmospheric leaching of low-grade saprolite ores from Indonesia and to study clearly the mechanism of this leaching process.

1.2. Literature review

1.2.1. Atmospheric leaching of nickel laterite ore: chemical leaching and bioleaching

Atmospheric leaching of lateritic ores at lower temperature and in open vessels avoids the need for expensive high pressure acid leaching (HPAL) autoclaves. AL is principally grouped into in-situ leaching, heap or dump leaching, and agitation leaching or vat leaching while atmospheric pressure leaching of laterites is carried out in one of the two distinct processes which are heap (or column) leaching and agitation leaching at atmospheric pressure and temperature up to 105°C either by inorganic acids, organic acids, as well as bioleaching.

Chemical leaching

Chemical acid leaching of nickel laterite ores at atmospheric pressure has been pioneered and patented by BHP Billiton (BHP Billiton, July 2001). The formation of an iron jarosite or goethite that will remove a significant amount of the iron from solution and in the process regenerate sulfuric acid for further leaching of saprolite ore is the most important part of the patent. Atmospheric leaching of laterite ores involves contacting the laterite ore (usually limonite) with a concentrated solution of a mineral acid (usually sulfuric acid) to partially or completely dissolve the iron and nickel into solution. This process is carried out at just below the boiling point of the slurry at atmospheric pressure (usually about 100 °C) for up to 12 hours. During this process, sulfur dioxide, or another suitable reducing agent, can be added to the leach slurry to assist in cobalt dissolution. The long leach time is to not only leach the nickel into solution but also to encourage the precipitation of iron from solution. BHP Billiton have not as yet commercialized atmospheric leaching technology in its own right although it was used in at Ravensthorpe in conjunction with HPAL in a process they have called enhanced pressure acid leaching (EPAL) (Kyle, 2010) .

Moreover, sulfuric acid has been applied in some studies to leach nickel from lateritic ores either limonitic or saprolite ores. Eramet has developed over the last ten years for their Weda Bay deposit in Indonesia as well as their Prony and Creek Pernod deposits in New Caledonia (Steel Guru, 2009). Oriel Resources pic (October, 2007), the London-based chrome and nickel mining and processing company, has completed an extensive comparative analysis of all appropriate technologies for the development of the Shevchenko Nickel Project, Kazakhstan, including ferronickel production, atmospheric tank leaching and heap leaching. Heron has also been looking at options for its 100% owned Yerilla nickel-cobalt project. In February 2008, heap leach development was put on hold in favor of pursuing atmospheric leaching. Atmospheric leaching eliminates the risk of maintaining the integrity of the ore heaps during leaching, and has the additional benefits of using upgraded ore as feed, faster leaching times compared to heap leaching, and better control of leach chemistry resulting in improved recoveries and more efficient reagent use (Heron, 2010b). Following acquisition of the Greenvale and Lucknow nickel-cobalt projects, Metallica Minerals have suspended a feasibility study for the Nornico heap leach project and have investigated an atmospheric acid leach process to produce 10,000 tonnes per annum of nickel metal and more than 1,000 tonnes cobalt as sulfide. The project will process 1.0 million tonnes per annum of ore and have its own acid and power plants (Metallica Minerals, 2010). Skye Resources (now HudBay Minerals) have successfully completed pilot plant testing of its proprietary Sulfation Atmospheric Leach ("SAL") Process using bulk samples of nickel and cobalt bearing laterites taken from their Fenix Project in Guatemala in 2004-05 (Verbaan et aI., 2007).

In the laboratory scale, many experiments regarding on sulfuric acid leaching at atmospheric pressure have been conducted for some lateritic ores from Indonesia, West Australia, China, South Africa, Turkey, Serbia, Greece, and Cuba (Li et al., 2011; Liu et al., 2009; Liu et al., 2010; Fan and Gerson, 2013; Sufriadin et al. , 2011). The presence of sodium sulfite as well as Cu(II)/SO_2 in the sulfuric acid leaching was also investigated to look for the optimum conditions of nickel leaching by sulfuric acid (Das and de Lange, 2011; Senanayake et al, 2015). However, sulfuric acid leaching shows some disadvantages that low leaching selectivity, high acid consumption as well as the difficulty of sulfuric acid to be recycled.

Usage of other lixiviants offers potential for improving nickel laterite processing technologies. Hydrochloric acid has been proposed to have several advantages over sulfuric acid for the atmospheric leaching of nickel laterites. These include: the production of hematite as a final iron product meaning less acid is required; the hematite may be a saleable product, or is disposed more readily than goethite or jarosite (McDonald and Whittington, 2008b); the use of lime to precipitate the MHP without production of gypsum; the ability to recycle the acid by pyrohydrolysis or other means; the ability to treat both limonitic and saprolite ores; the leach liquor is more amenable to downstream processing by solvent extraction and spray roasting to produce a final nickel oxide product (Gibson and Rice, 1977; Kyle, 2010). Three new processes using hydrochloric acid are developed namely the Jaguar Nickel Atmospheric Chloride Leach Process, the Intec Laterite Process, and the Anglo Research Nickel Process (ARNi process) (Kyle, 2010). However, those processes are still having some problems particularly on the environmental impacts (corrosion problems) and higher capital cost.

Moreover, environmental considerations have forced modern society to look for innovative, sustainable, and green processes in every activity. To address those requirements, some studies focus on the organic acid leaching for extracting nickel from lateritic ores have been carried out. McDonald and Whittington have summarized several important studies on organic acid leaching (McDonald and Whittington, 2008b). The employing various organic acids on the leaching of nickel from some lateritic ores has been observed in a number of studies (Chander 1982; Bosecker 1985, 1988; McKenzie et al., 1987; Birke, 1988; Alibhai et al., 1991; Tzeferis et al., 1991; Alibhai et al., 1993; Sukla and Panchanadikar, 1993; Paul and Henning 1993; Tarasova et al., 1993; Tzeferis 1994a, 1994b; Tzeferis and Agatzini-Leonardou 1994; Coto et al., 2001;Valix et al., 2001a; Tang et al., 2004; Tang and Valix 2006b; Deepatana et al., 2006). Different with inorganic acid like sulfuric acid and hydrochloric acid, organic acids are thought to operate by two mechanisms in the dissolution of minerals involving (1) acid attack and displacement of metal ions by hydrogen ions and (2) chelation of metals to form soluble metal-ligand complexes (McDonald and Whittington, 2008b).

It has been proved by many references that citric acid is the most effective organic acid for recovering of nickel from lateritic ores (Bosecker 1985, 1988; Birke 1988; Paul and Henning 1993; Tarasova et al., 1993; Tzeferis and Agatzini-Leonardou 1994; Tzeferis 1994a, 1994b; Coto et al., 2001). Moreover, McKenzie et al. (1987) noted that citric, tartartic, and pyruvic acids all significantly increased the yield of nickel extracted at pH 2.3 relative to sulfuric acid for low-iron laterite ores. This study also confirmed that citric acid forms chelation complexes with both iron and nickel at low pH. Tang and Valix (2006a) reported that cobalt extraction from a limonite ore using citric acid, as well as malic and lactic acids, is higher than nickel extraction, whereas the reverse is true for a saprolite ore. This and subsequent studies suggested little relative difference between the acids in terms of the overall extractions (Tang and Valix, 2006b; Deepatana et al., 2006). Generally, it was proposed that the rates of nickel and other metals dissolution were dependent on the acid activity, pulp density, mineralogy and the oxidation–reduction potential.

Citric acid leaching has been investigated in some studies; however, there is no clearly report regarding on the effectiveness of citric acid leaching as well as its leaching mechanism and kinetics for extracting nickel from different Indonesian saprolite ores. Moreover, the difference in mineralogy may impact significantly on the leaching performance of each ore sample. Therefore, the more investigation on the citric acid leaching of different Indonesian lateritic ores especially low-grade saprolite ores is very necessary in order to obtain comprehensive information regarding on citric acid leaching behavior, mechanism, as well as kinetics.

Bioleaching

Bioleaching also seems to address a clean and green technology for recovering metals from nickel laterite ores with lower costs and lower energy demand than the existing processes. It has been claimed to provide the potential for a step change in the technology for treating these ores (Valix et al., 2001a) using a more selective leaching agent targeting the nickel and cobalt, rather than the currently used mineral acids that dissolve almost all the ore. Including nonsulfidic ores, nickel lateritic ores is not suitable to be leached biologically by chemolithoautotrophic such as *Acidithiobacillus ferrooxidans* because the ores contain no energy source (i.e. sulfur and sulfur containing materials) for utilizing of microorganisms. Moreover, leaching using heterotrophic fungi is necessary to extract nickel and other metals from lateritic ores. This is because the organic acids metabolically produced by fungi have a dual effect of providing hydrogen ions for acidolysis of minerals and complexing metals due to their chelating capacity (Tzeferis, 1994a; Gadd, 2001). Therefore, the leaching of nickel laterites by fungi, which are heterotrophic microorganisms, has continued to be the main focus of research in the recent past. These microorganisms, in direct contrast to autotrophs, ingest biomass to obtain their energy and nutrition. *Aspergillus* and *Penicillium* are the two widely studied strains of fungi that can be used in the microbial leaching (Bosecker, 1986, 1989, 1997; Franz et al., 1991; Coto et al., 2001, 2003, 2005; Valix et al., 2001a, b, c).

Metal leaching by fungi generally involves an indirect process with microbial production of organic acids, amino acids, and other metabolites. Four mechanisms have been identified: (i) acidolysis, (ii) complexolysis, (iii) redoxolysis (Berthelin, 1983), and (iv) bioaccumulation (Weed et al., 1969). The first three processes occur through metabolites excreted by the fungus, while the fourth process can be observed if the fungus accumulates the metal ion from the solution and – by disturbing the equilibrium between solid and dissolved metal – causes the continuous solubilisation of the metal (Burgstaller and Schinner, 1993). The following are some of the possible reactions that can take place to finally produce nickel ions (Tzeferis, 1992):

Proton attack

$NiO + 2H^+ \rightarrow Ni^{2+} + H_2O$ **(1-1)**

$MCO_3 + 2H^+ \rightarrow M^{2+} + H_2O + CO_2$ **(1-2)**

where M is Fe, Mg, Mn, or Ca, etc.

Reduction

$MnO_2 + 2e^- + 4H^+ \rightarrow Mn^{2+} + 2H_2O$ **(1-3)**

Complexation/chelation

$Ni^{2+} + C_6H_8O_7 \rightarrow Ni(C_6H_5O_7)^- + 3H^+$ **(1-4)**

In Eq. (1-1), the protons produced by organic acids contribute to proton promoted mineral dissolution. Nickel laterite is considered as having a complex mineralogy, i.e., few nickel atoms are spread in a solid solution of atoms of other elements which appear in large quantities, such as Fe, Mg, Al, Mn, Ca, etc. As a result, acid attack (Eq. (1-2)) of any carbonate material in the ore also enhances nickel liberation. However, this reaction requires the generation of excess acid. Furthermore, the reduction of soluble manganese (Eq. (1-3)) can result in the equilibrium between solid phase Mn^{4+} and soluble phase Mn^{2+} being shifted somewhat, accelerating the dissolution of the mineral, thus liberating nickel. In Eq. (1-4), organic acids complex with metal ions in solution lowering metal activity, thus increasing the apparent solubility of the mineral (McKenzie et al., 1987).

The use of fungi in a quest to recover nickel from low-grade nickel laterite ores has been studied by several researchers (Bosecker, 1986; McKenzie et al., 1987; Alibhai et al., 1993; Tzeferis, 1994; Valix et al., 2001a, b; Le et al., 2006; Tang and Valix, 2006). However, commercial application of these microorganisms has been less successful due to process inefficiencies such as poor metal recovery (Tang and Valix, 2006). This problem is particularly prevalent in limonite ore, characterized by high iron content in the form of goethite (FeOOH), and nontronite ore, characterized by clay minerals consisting of illite, kaolinite, and chlorite (Tang and Valix, 2006). The effectiveness of these microorganisms was found to depend on their ability to produce hydroxycarboxylic acids (citric, lactic, gluconic, pyruvic and tartaric), and also other metabolites, which are excreted in culture media (Burgstaller and Schinner, 1993; Tzeferis, 1994; Castro et al., 2000; Le et al., 2006), and their resistant to heavy metals (Burgstaller and Schinner, 1993; Le et al., 2006). The results of these studies showed that microbiological leaching is more effective compared to chemical leaching. The more favourable results obtained in the bioleaching process suggest that microbiological activity, apart from bio-acid production is participating in the leaching process (Valix et al., 2001a).

It is suggested, for example, that fungal hyphae physically attach onto surfaces of minerals with possibility of high acid concentration formed at hyphal tips reacting directly with adjacent mineral surfaces without greatly affecting the pH of the bulk medium (Alibhai et al., 1993). Alibhai et al. (1993) examined different samples of nickel laterites from different locations. The chemical composition of these samples varied. Less definitive information, such as effects observed with different particle size fractions was employed because direct linkage of mineralogical characteristics with leaching efficiency was found difficult. The results of these experiments showed that more leachable nickel-bearing phases were generally more readily available in the larger particles, even though the smaller particles carried a higher initial concentration of nickel (Alibhai et al., 1993).

The studies by Tzeferis and Agatzini-Leonardou (1994), Castro et al. (2000), and Valix et al. (2001a) clearly showed differences in the leachability of different minerals (and/or the metal present in it), i.e., the mineralogy of the ores had significant effects on the metal recovery and selectivity of the leaching process. Extraction of nickel appeared more effective from the silicate ores, the saprolite and weathered saprolite, and least effective from limonite ores (Valix et al., 2001a,b). The nickel in the silicate ores, on the other hand, which are present in the brucite layer of the clay minerals, is weakly bound and, therefore, easily dissolved (Valix et al., 2001b). Valix et al. (2001b) further studied the effects of electrosorption, physical properties and the mineralogy of the ores in an attempt to establish the reasons for the difference in the amenability of saprolite and limonite minerals toward biological leaching. The results showed that leaching below the isoelectric point increased the nickel and cobalt recoveries for both the saprolite and limonite. This is because the positively charged gangue inhibits the re-adsorption of nickel and cobalt complexes on it. However, Beukes et al. (2000) found that the ability of goethite and hematite to adsorb nickel was also dependent on the surface area, i.e., the larger the surface area, the higher the adsorption per surface area of the mineral. It was also found that high recovery of nickel and cobalt appears to be associated with acid dehydration of the mineral phase in which nickel and cobalt are associated. This phase change was clearly seen with the saprolite ores where the magnesium hydro-silicate mineral formed an amorphous magnesium silicate phase, in which nickel became unstable and was susceptible to acid attack. The acid was found to be less effective in dehydrating goethite to hematite, which resulted in poorer nickel and cobalt extraction. These observations indicate that the choice of the suitable type of nickel laterites is paramount in the development and optimization of such a process (McDonald and Whittington, 2008b).

Burgstaller and Schinner (1993) also provide an overview of conditions necessary for the optimum leaching of metals by fungi and concluded that such processes are suited to stirred tank reactors but not dump or heap leaching because of the high oxygen consumption rate. *Aspergillus* species are less suited to the leaching of nickel laterites due to their high sensitivity to nickel (Bosecker, 1988). In comparison one strain of the *Penicillium simplicissimum* species was adapted to grow at 30,000 ppm nickel whereas the highest concentration at which a strain of *Aspergillus niger* was found to be active was 1300 ppm. Other tests to develop the tolerance of fungi to heavy metals were applied to strains of various *Penicillium* and *Aspergillus* species though at levels of just up to 2000 ppm (Valix et al., 2001b; Valix and Loon 2003). However, it seems to be more important that species are adapted to multi-metal mixtures rather than single metals (Le et al., 2006) and are halide-tolerant given the high salinity of water supplies and soils in the vicinity of certain nickel laterite ore bodies (Thangavelu et al., 2006a, 2006b).

Alternatively, it should be possible to use a two steps procedure where the production of citric acid and the leaching of nickel are carried out as separate processes. Leaching conducted in the presence of fungal metabolites (e.g. citric acid) after pH adjustment by sulfuric acid was found to be more effective than chemical leaching with either citric acid or sulfuric acid at the same initial free acid concentration (Tzeferis, 1994b). Although this makes the process more expensive, it was noted that the washed and dried mycelium produced during fermentation could represent a valuable protein-rich foodstuff. Other studies have found that acidification to a predetermined level also enhances the extraction of nickel by organic acids (McKenzie et al., 1987) and this has been attributed to stronger chelation under more acidic conditions (Tzeferis and Agatzini-Leonardou 1994). However, Valix et al., (2001a, 2001c) and Tang and Valix (2006a) have shown that the surface charge of the various gangue minerals strongly influences the electrosorption of nickel and that this in turn can be controlled by adjusting the acidity to below the isoelectric pH for the ore type concerned. Previously nickel losses during bioleaching had been ascribed to uptake by the fungal biomass (Tzeferis 1994b). It has been concluded that biological leaching appears to be more effective than chemical leaching based on the same acid concentration (Valix et al., 2001c); the suggestion was that the bioleaching mechanism was not simply chemical attack but that the fungus participates in the leaching process. A similar observation was made by Bosecker (1985).

Furthermore, the use of biogenic citric acid that is produced from metabolism of fungi (*Aspergillus* or *Penicillium*) in nickel extraction from low-grade Indonesian saprolite ores is less investigated. There is no clear report regarding on the leaching mechanism of Indonesian saprolite ores using biogenic citric acid. Anyhow, the production of biogenic citric acid by employing some agricultural products and wastes in Indonesia is very profitable in order to provide the leaching reagent for nickel recovery. Hence, it is interesting to investigate the nickel leaching mechanism from low-grade Indonesian saprolite ores using biogenic citric acid in order to obtain the more effective and suitable method for utilizing of those ores.

1.2.2. Citric acid production

Production of citric acid is one of important steps in the current study. Citric acid, 2-hydroxypropane-1,2,3-tricarboxylic acid, is a key metabolic intermediate and is the starting point of the tricarboxylic acid (TCA) cycle (Kirimura et al., 2011). From the viewpoints of production volume and utility, citric acid is one of the most important bio-products. The annual worldwide output reached approximately 1.9 million ton in 2012. Various plants, especially citrus fruits such as lemon and orange, contain large quantities of citric acid, and citric acid is ubiquitous in nature because it is an intermediate in aerobic metabolism through the TCA cycle whereby carbohydrates are oxidized to carbon dioxide. The widespread presence of citric acid in the animal and plant kingdoms is an assurance of its nontoxic nature, and nowadays citric acid is accepted as generally recognized as safe (GRAS) by the Joint FAO/WHO Expert Committee on Food Additives (Kirimura et al., 2011).

Citric acid and its salt form (citrate) are commodity chemicals and are used in many industrial fields. It has long been used as an acidulant in the manufacture of soft drinks, as an aid to the setting of jams and in other ways in the confectionery industry because of its general recognition as safe, pleasant acid taste, and high water solubility. Citric acid has been also used as a complexing agent in metal treatment, as a monomer for functional and/or biodegradable polymers, and as a water softener in detergents, because of its organic acid, chelating, and buffering properties (Kirimura et al., 2011).

Today, citric acid is industrially produced by fermentation, and the filamentous fungus *Aspergillus niger* is exclusively used due to its high citric acid productivity at low pH without the secretion of toxic byproducts. Citric acid as a product is sold either in the anhydrous form or as the monohydrate. The transition temperature between the two forms is 36.6°C. The pKa values of citric acid, with its three dissociation steps, are 3.13, 4.78, and 6.43 (25 °C). A 1% solution of citric acid in pure water has a pH of 2.2. With its three carboxyl and one hydroxyl groups, citric acid functions as an excellent complexing agent for di-and trivalent cations. The equilibrium constants are K_1=8.2x10^{-4}, K_2 =1.8x10^{-5}, and K_3=1.0x10^{-7} (18 °C) (Kirimura et al., 2011).

Citrate is able to complex heavy metals such as iron, nickel, and copper. This property has led to its increasing use as a stabilizer of oils and fats where it greatly reduces oxidation catalyzed by these metals. The ability to complex metals combined with its low degree of attack on special steels allows the use of solutions of citrate in the cleaning of power station boilers and similar installations. Because citrate is readily able to complex magnesium and calcium ions, tri-sodium citrate is widely used as a water-softening agent in commercial detergents and cleaners.

A large number of microorganisms containing filamentous fungi, yeasts, and bacteria have been known to accumulate citric acid and have been tested for citric acid production (Roehr, 1998; Röhr et al., 1996). Among them, *Aspergillus niger* has been recognized as the best producer; the main advantages of the use of *Aspergillus niger* are high-yield production and ease of handling (Roehr, 1998; Röhr et al., 1996). Large quantities of citric acid are secreted by *Aspergillus niger* during and after the late logarithmic growth phase, provided there is an excess of carbon source (carbohydrate) and oxygen. The metabolic pathway in relation to citric acid production is shown in Figs. 1-6. The yield of citric acid in the fermentation is expressed as kilograms of citric acid monohydrate per 100 kg of carbohydrate supplied. It should be noted that the theoretical yield of citric acid monohydrate from sucrose, assuming no carbon is diverted to mycelia (biomass), carbon dioxide, or other byproducts, is 123% and that from anhydrous glucose is 117% (Kirimura et al, 2011).

Citric acid production by *Aspergillus niger* is strongly affected by the compositions of media and cultivation conditions. Types and concentrations of carbon, nitrogen, and phosphorus sources are important factors affecting citric acid production, as well as trace elements, pH, temperature, oxygen supply, and additives as promoting substances (Roehr, 1998; Röhr et al., 1996; Ruijter et al., 2002; Usami, 1978). In summary, for high-yield production of citric acid, the following conditions are favorable: excess amounts of readily metabolized carbon sources (carbohydrates) with low concentrations of growth-promoting elements such as nitrogen, phosphorus, and trace elements containing heavy metal ions (Kirimura et al., 2011).

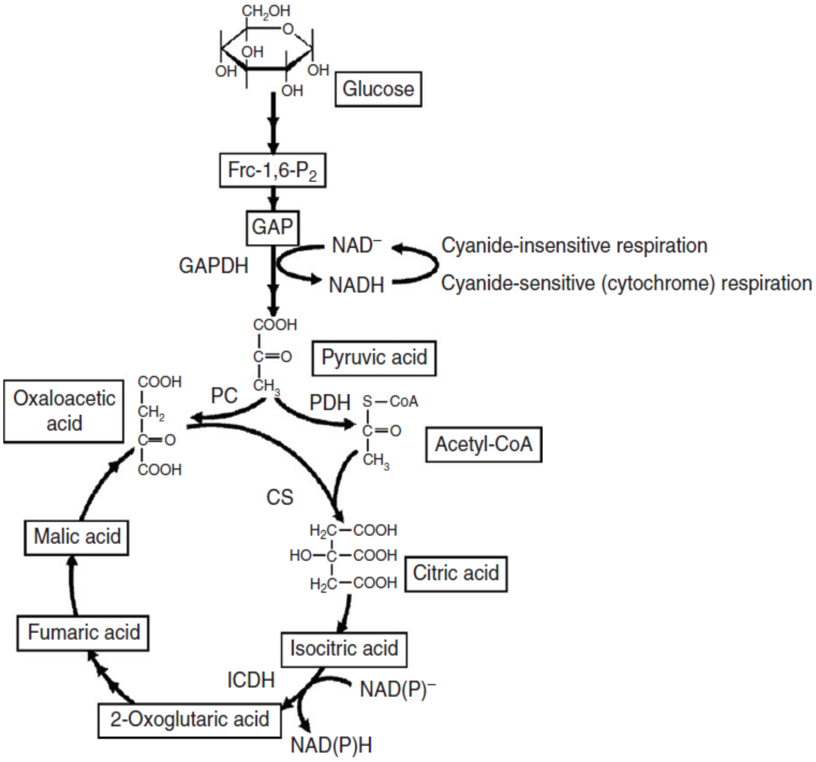


Fig. 1-6. Citric acid production in relation to glycolytic pathway and tricarboxylic acid (TCA) cycle (Kirimura et al., 2011).

Glucose and sucrose are usually the main carbon sources in citric acid production. However, a variety of agricultural products and wastes are suited to the production of citric acid by *Penicillium* as well as *Aspergillus* species including molasses, green syrup and sugar beet chips (obtained by beet sugar production), pear pulp, yeast pulp, whey permeate (from cheese making), pineapple peels, apple pomace, sugarcane molasses, corn starch, corn cob, corn husk, coffee husk, banana peel, beet molasses, date syrup, oil palm empty fruit bunch, tapioca starch etc (Kirimura et al., 2011). As tropical as well as agriculture country, Indonesia has a big potential in agricultural products as well as wastes. Hence, it is suggested that citric acid production from those agricultural products in Indonesia must be an interesting challenge in order to supply an excellence leaching reagent for extracting nickel from Indonesian saprolite ores.

1.2.3. Kinetics of leaching process

Leaching of saprolite ores is a solid-liquid reaction. Solid in this system must be minerals contained in the saprolite ores, while liquid is leaching reagent used. In such a reaction system, soluble reactants diffuse across the interface and/or through a porous solid layer and then the chemical reactions occur. The leaching rate is generally controlled by one of the following steps: (i) diffusion through the fluid film, (ii) diffusion through solid product layer on the particle surface, and/or (iii) the chemical reaction at the surface of the unreacted core/particle. The rate of the process is controlled by the slowest of these sequential steps (Levenspiel, 1999). The reaction model between solid and liquid may be given as follows (Eq. (1-5)):

$$A_{(liquid)} + B_{(solid)} \rightarrow Products \qquad \textbf{(1-5)}$$

Depending on the parameter conditions as well as type and nature of the solid materials and leaching reagent, different reaction mechanisms and kinetics has been suggested (Gharabaghi et al., 2010). To analyze the kinetics of nickel dissolution from saprolite ores, two types of solid-liquid kinetic models proposed by Levenspiel (1999) namely the shrinking-core model (SCM) and the shrinking-particle model (SPM) as described in the Fig. 1-7 can be applied. In the SCM, the three possible rate-determining steps explained above are applied in the kinetic analysis. There are only possible two rate-determining steps, diffusion through the fluid film and the chemical reaction at the surface of the unreacted particles, in the SPM (Levenspiel, 1999).

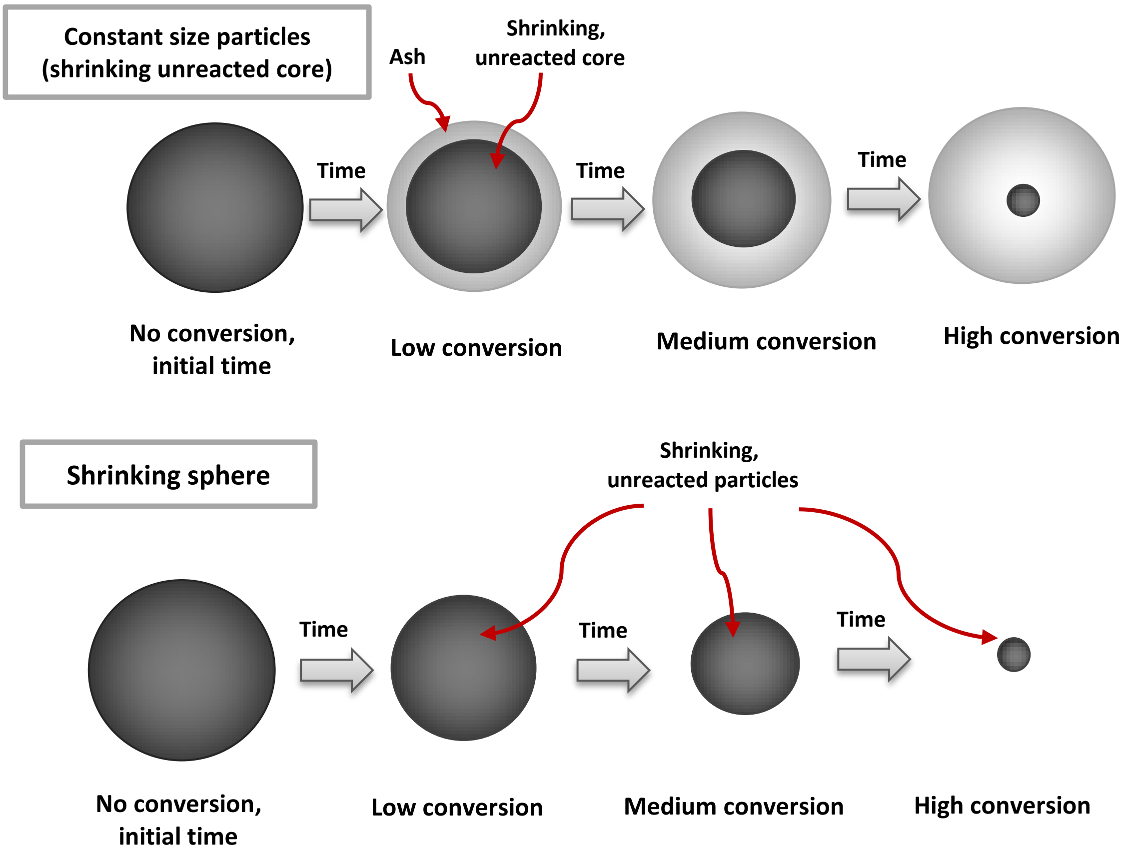


Fig. 1-7. Schematic mechanism of shrinking core model (SCM) and shrinking particle model (SPM) modified from Levenspiel (1999).

The SCM equations for the three rate-determining steps can be written as follows (Eqs. (1-6) to (1-8)) (Levenspiel, 1999):

Fluid film diffusion control:

$$x = k_f t = k \exp\left(-\frac{E_a}{RT}\right) t \qquad \textbf{(1-6)}$$

Diffusion through solid product layer control:

$$1 - 3(1-x)^{\frac{2}{3}} + 2(1-x) = k_d t = k \exp\left(-\frac{E_a}{RT}\right) t \qquad \textbf{(1-7)}$$

Chemical reaction control:

$$1 - (1-x)^{\frac{1}{3}} = k_r t = k \exp\left(-\frac{E_a}{RT}\right) t \qquad \textbf{(1-8)}$$

Equations 1-9 and 1-10 are the mathematical model equations for the SPM:

Fluid film diffusion control:

$$1 - (1-x)^{\frac{2}{3}} = k_f t = k \exp\left(-\frac{E_a}{RT}\right) t \qquad \textbf{(1-9)}$$

Chemical reaction control:

$$1 - (1-x)^{\frac{1}{3}} = k_r t = k \exp\left(-\frac{E_a}{RT}\right) t \qquad \textbf{(1-10)}$$

where x is the fraction reacted, k is the overall reaction rate constant in min^{-1}, A is the frequency factor in min^{-1}, E_a is the apparent activation energy in J mol^{-1}, R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the reaction temperature in K, k_f, k_d, and k_r are the rate constants, and t is the leaching time.

SCM as well as SPM has been applied for evaluating of lateritic leaching kinetics in some studies. The kinetics of saprolite ores leaching using sulfuric acid at atmospheric pressure has been evaluated by Luo et al. (2012) and they reported that the nickel dissolution kinetics was found to fit well to the SCM with chemical reaction as the rate controlling step. The kinetics of citric acid leaching as well as other organic acids leaching, however, has not been evaluated yet.

1.3. Objectives of study

It is proposed that citric acid as well as biogenic citric acid is one of the excellent leaching reagents for extracting nickel from saprolite ores using atmospheric leaching. However, study on citric acid as well as biogenic citric acid leaching for nickel recovery from low-grade Indonesian saprolite ores is less reported. Moreover, the nickel leaching mechanism of those methods from low-grade Indonesian saprolite ores has not been investigated yet. Comparative leaching performance of different saprolite ores using citric acid as well as biogenic citric acid is also another interesting study in order to obtain the comprehensive nickel leaching mechanism.

The major objective of this study is, therefore, to investigate the nickel leaching mechanism and mineral dissolution behavior of Indonesian low-grade saprolite ores in the atmospheric leaching process using either chemical citric acid as well as biogenic citric acid solutions; thus, the most profitable atmospheric leaching process for utilizing of Indonesian low-grade saprolite ores with high selectivity and with the most effective leaching reagent could be applied. In order to achieve that major objective, experiments were carried out in four specified objectives:

1. To study the effectiveness of citric acid compared to other leaching reagents for extracting nickel from two different Indonesian low-grade saprolite ores by atmospheric leaching process at low temperature as well as the behavior of those leaching processes.

2. To investigate the nickel leaching mechanism of Indonesian low-grade saprolite ores using citric acid at atmospheric pressure and to determine the optimum conditions of this leaching process.
3. To analyze the kinetic modeling of nickel extraction from Indonesian low-grade saprolite ores by atmospheric leaching and to create the mathematical model of nickel leaching kinetic.
4. To study the production of biogenic citric acid from fermentation of agriculture products and wastes by *Aspergillus niger* and to evaluate the effectiveness of the biogenic citric acid on the leaching of Indonesian low-grade saprolite ores.

1.4. Structure of the thesis

This thesis consists of six chapters. This chapter introduces the conducted study. Background and objectives of the study are presented as well as how this thesis is structured. Moreover, an overview of atmospheric chemical leaching as well as biological leaching of nickel lateritic ores is presented in order to provide basic understanding on atmospheric nickel leaching and factors affecting the leaching behaviors. Citric acid production is also described to gain basic information regarding on parameters influencing the high-yield production of this acid. In addition, a brief study of leaching kinetics is expressed in this chapter as consideration in the kinetic analysis of saprolite ores leaching process.

In this chapter, the acid leaching of different saprolite ores was investigated in different acid media with the aim of quantifying and obtaining insights into the mineral dissolution mechanism. Two saprolite ores from two different mining site areas in Indonesia were used to investigate the effect of ore mineralogy on the leaching performance and mineral dissolution behavior with different leaching reagents. The metal and mineral dissolution behaviors of the raw saprolite ores and leaching residues were studied using X-ray diffraction (XRD), thermogravimetric-differential thermal analysis (TG-DTA), and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM-EDS). Some different acid solutions either inorganic or organic acid were utilized in the current experiment to study the effectiveness of those acids and to investigate the comparison of effectiveness of citric acid and other acid solutions on the dissolution of nickel from saprolite ores. The XRD was also applied in order to evaluate the mineral dissolution behavior in each leaching reagent.

Chapter 3 examined the comparative leaching performances, mineral dissolution behaviors, and leaching kinetics of nickel extraction from two different Indonesian low-grade saprolite ores, using citric acid as the leaching reagent, at atmospheric pressure to investigate clearly the nickel leaching mechanism from different Indonesian saprolite ores using citric acid. The effects on nickel extraction of leaching temperature, citric acid concentration, pulp density, and ore particle size were carried out to investigate the leaching performances and leaching kinetics of the two saprolite ores as well as to determine the optimum leaching conditions. The XRD analysis of leaching residues was applied in order to observe mineral dissolution behavior of nickel extraction. Finally, the nickel leaching mechanism from saprolite ores using citric acid was proposed.

The detail kinetics modeling of atmospheric leaching of an Indonesian saprolite ore by citric acid was studied in chapter 4 to create the mathematical model of leaching kinetics based on the experimental results. The empirical kinetic model for leaching of nickel from this Indonesian saprolite ore was also proposed in mathematical expression.

In chapter 5, production of biogenic citric acid from the fermentation of corn starch and corn cob by *Aspergillus niger* was investigated. Corn starch and corn cob were used as carbon sources because the big amount of those carbon sources in Indonesia. The effectiveness of biogenic citric acid on the nickel leaching of Indonesian saprolite ores was also evaluated employing various leaching parameters. Mineral dissolution behavior in this leaching process was also observed from the XRD of solid residue. Finally, the mechanism of nickel extraction from low-grade Indonesian saprolite ores by atmospheric leaching using biogenic citric acid was proposed.

The study concludes in chapter 6 which presents overall conclusion and recommendations for further experiments.

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CHAPTER 2

Comparison of Effectiveness of Citric Acid and Other Acids in Leaching of Different Low-Grade Indonesian Saprolite Ores

In this chapter, the acid leaching of different saprolite ores was investigated in different acid media with the aim of quantifying and obtaining insights into the mineral dissolution mechanism. Two saprolite ores from two different mining site areas in Indonesia were used to investigate the effect of ore mineralogy on the leaching performance and mineral dissolution behavior with different leaching reagents. Some different acid solutions either inorganic or organic acid were utilized in the current experiment to study the effectiveness of those acids and to investigate the comparison of effectiveness of citric acid and other acid solutions on the dissolution of nickel from saprolite ores.

2.1. Introduction

The high-grade saprolite 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 leaching of nickel laterite, using high-pressure acid leaching, heap leaching, and in a pilot plant for atmospheric tank leaching. 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; Weert and Boering, 1995; 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., 2009; 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. 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, and 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). Although chloride-based commercial leaching operations are not common, some research has been performed (Amer and Ibrahim 2001; Chen et al., 2000; Chuanlin Fan et al., 2011; Majima and Awakura, 1985; Neudorf and Arroyo, 2002; Rice and Strong, 1974; Wan-rong et al., 2010).

These inorganic acids still cause environmental problems when the leaching treatment is not performed well. To address these issues and to provide environmentally acceptable techniques, organic leaching agents have been used for nickel extraction from lateritic ores. 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, α-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. In the future, citric acid and metabolic citric acid are expected to be used as leaching agents in nickel extraction from lateritic ores. 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 saprolite ores to investigate whether citric acid performs better than other acid solutions.

2.2. Materials and methods

2.2.1. Materials

Saprolite ores from two different mining areas in Indonesia, namely Sulawesi Island and Halmahera Island, were first jaw-crushed and vibration-milled to <75 μm. 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 saprolite ores. The nickel content of the Sulawesi saprolite (SS) sample was 1.76 wt% and that of the Halmahera saprolite (SH) sample was 1.28 wt% (i.e., both less than 2 wt% nickel; Table 2-1). The mineral phases of the raw ore samples were identified by X-ray diffraction (XRD; Ultima IV, Rigaku, Tokyo, Japan), using Cu Kα radiation, at an accelerating voltage and applied current of 40 kV and 40 mA, respectively, in the 2θ range 5° to 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, Mahwah, NJ, USA).

Table 2-1. Chemical compositions of raw ore samples (determined using XRF and ICP-OES).

Ore samples	**Component (wt%)**							
	SiO_2	**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

2.2.2. Leaching experiments

Leaching tests were performed in a shaker at a constant shaking speed of 200 rpm. Mixtures of screened samples (ore particle size <75 µm) 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. The temperature was kept constant at 30 °C. Six types of leaching agent, 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. 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 distilled water and dried for 4 h at 100 °C using a forced air-flow oven (WFO-500, Eyela, Tokyo, Japan). After drying, the residues were finely ground using a mortar and pestle and thoroughly mixed for XRD analysis.

2.3. Results and discussion

2.3.1. Mineralogical study of saprolite laterites

Different ore samples from different locations may have different mineral and elemental compositions. These differences can affect the leaching performances of the samples. In addition, the effectiveness of leaching agents for different minerals may differ. Analysis and mineralogical studies of saprolite samples are therefore important in investigating the leaching mechanism of each sample in various acid solutions. The XRD patterns of the saprolite ores are shown in Figs. 2-1 and 2-2. Although the chemical compositions of the two samples are similar, the mineral compositions differ. In SS, lizardite (serpentine group mineral) [$Mg_3Si_2O_5(OH)_4$], goethite (FeOOH), and clinochlore (chlorite group mineral) [$Mg_6Si_3O_{10}(OH)_8$] are the main minerals. In contrast, the major minerals in SH are talc [$Mg_3Si_4O_{10}(OH)_2$] and goethite. Small amount of quartz (SiO_2) and chromite ($FeCr_2O_4$) was also found in both samples. However, some peaks detected cannot be analyzed yet from both samples because of the complexity of mineral content in the ores. High chromium content in both ores (1.07% and 1.18% in ore SS and SH respectively) may originate from chromite mineral. It has been reported by some studies that serpentine group mineral and goethite are usually the main host nickel mineral in the laterite ores (McDonald and Whittington, 2008a).

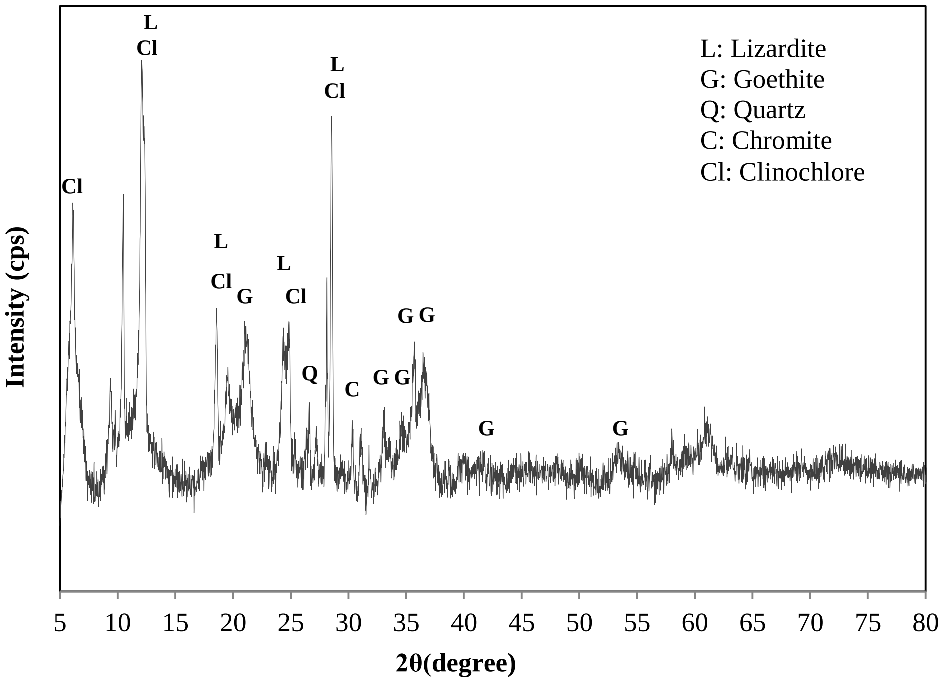

Fig. 2-1. XRD pattern of sample SS.

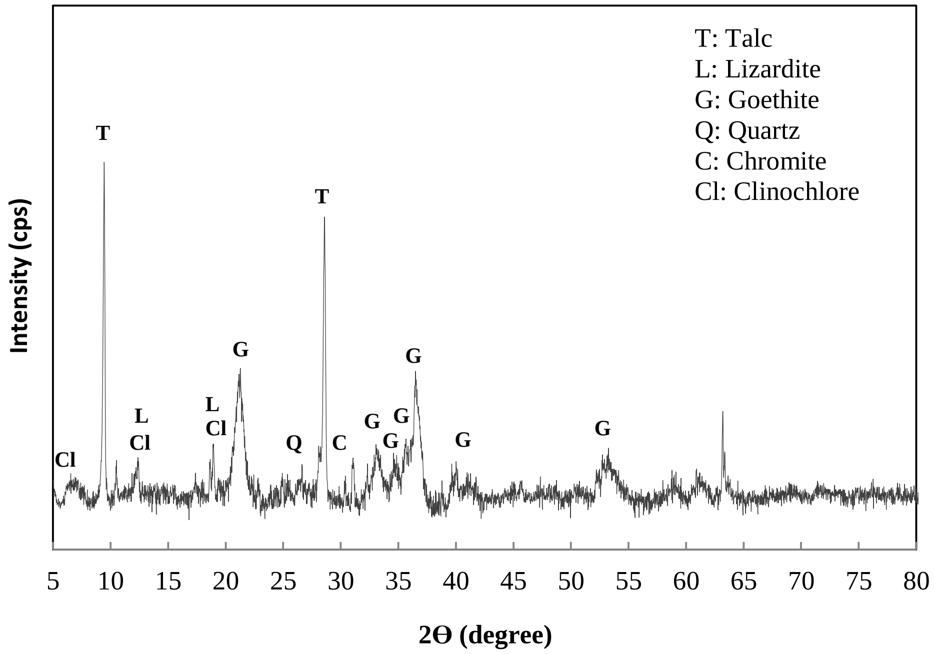

Fig. 2-2. XRD pattern of sample SH.

TG-DTA was used to confirm the XRD data. The TG-DTA patterns of the samples (Fig. 2-3) show that SS and SH has different thermal decomposition and phase-transformation behaviors. The TG-DTA trace from SS (Fig. 2-3(a)) has four endothermic peaks, at 70, 260, 567, and 1165 °C, and an exothermic peak at 805 °C. The endothermic peaks at 70 and 260 °C are associated with moisture evaporation and goethite decomposition, respectively. The endothermic peak at 567 °C arises from dehydroxylation of lizardite, and the exothermic peak at 805 °C is associated with recrystallization of forsterite (Mg_2SiO_4); these observations confirm the presence of lizardite (Brindley and De Souza, 1975; Fan and Gerson, 2011; Tartaj et al., 2000). The endothermic peak at 1165 °C is assigned to dehydroxylation of talc sheets, accompanied by formation of enstatite ($Mg_2Si_2O_6$) and silica. The TG-DTA pattern of SH (Fig. 2-3(b)) shows that its thermal decomposition behavior differs from that of SS. For SH, there are only three endothermic peaks, at 50, 250, and 1150 °C. An exothermic peak is also observed, at 838 °C, but it is much smaller than the exothermic peak for SS; this indicates that the lizardite content of SH is lower than that of SS. The TG-DTA results support those obtained using XRD.

Nickel in lateritic ores is usually associated with, and incorporated in, the mineral constituents of the ore. The XRD patterns (Figs. 2-1 and 2-2) show no independent nickel compound peaks. Information on the nickel-bearing minerals present is important in studying nickel-leaching behavior. SEM/EDS analysis is a simple method for element mapping, and the data can be used to identify the minerals associated with nickel and other metals. Typically, most nickel is incorporated into saprolite ores by substituting for magnesium in lizardite. Although goethite is the major component of limonitic ores, some saprolite ores also contain goethite as a minor component and nickel is sometimes also incorporated into goethite. Figs. 2-4 and 2-5 show the metal mapping for each sample obtained using SEM/EDS analysis. The figures show that most of the nickel in both samples is closely associated with magnesium- and silicate-containing minerals such as lizardite and talc. In the next section, we will discuss the effect of differences among the mineral compositions on the nickel- and metal-leaching performances when different acid solutions are used.

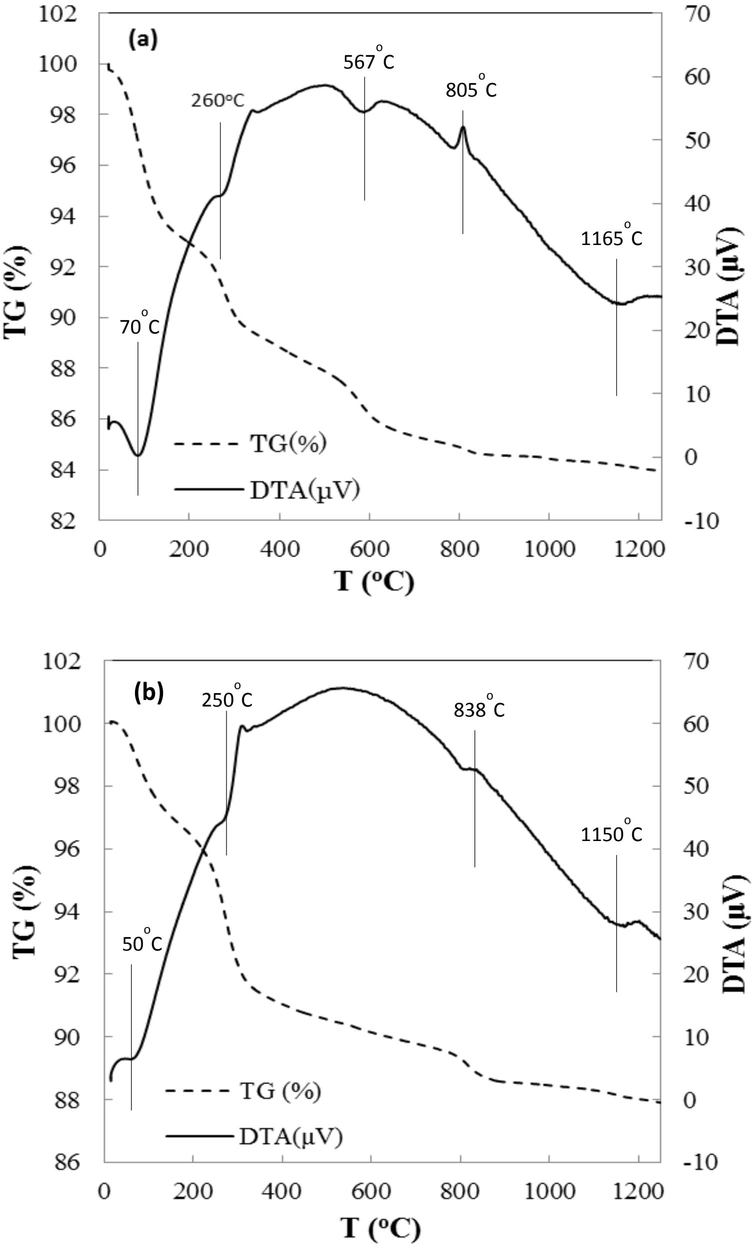

Fig. 2-3. TG-DTA patterns: (a) sample SS and (b) sample SH.

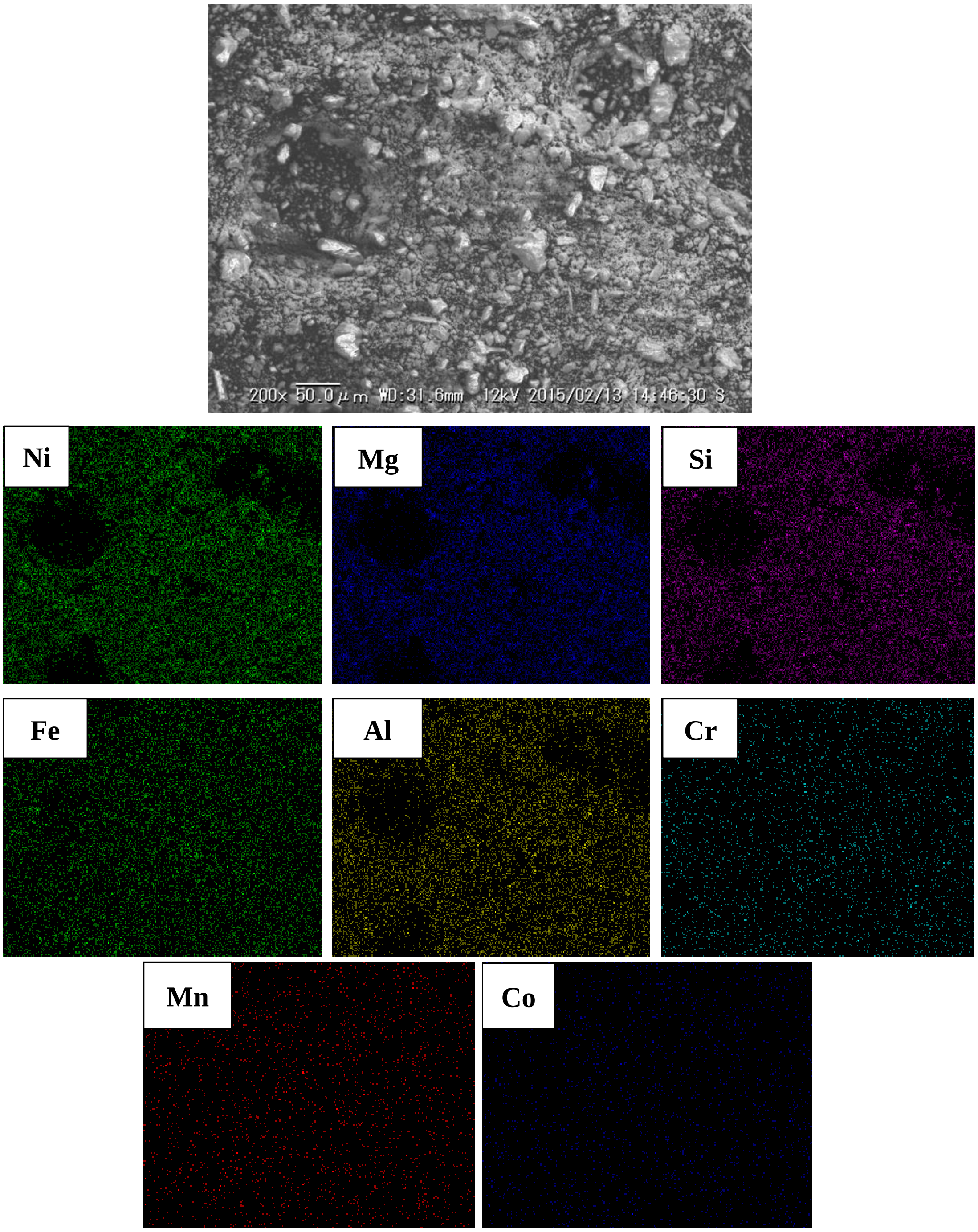

Fig. 2-4. SEM/EDS metal mapping of sample SS.

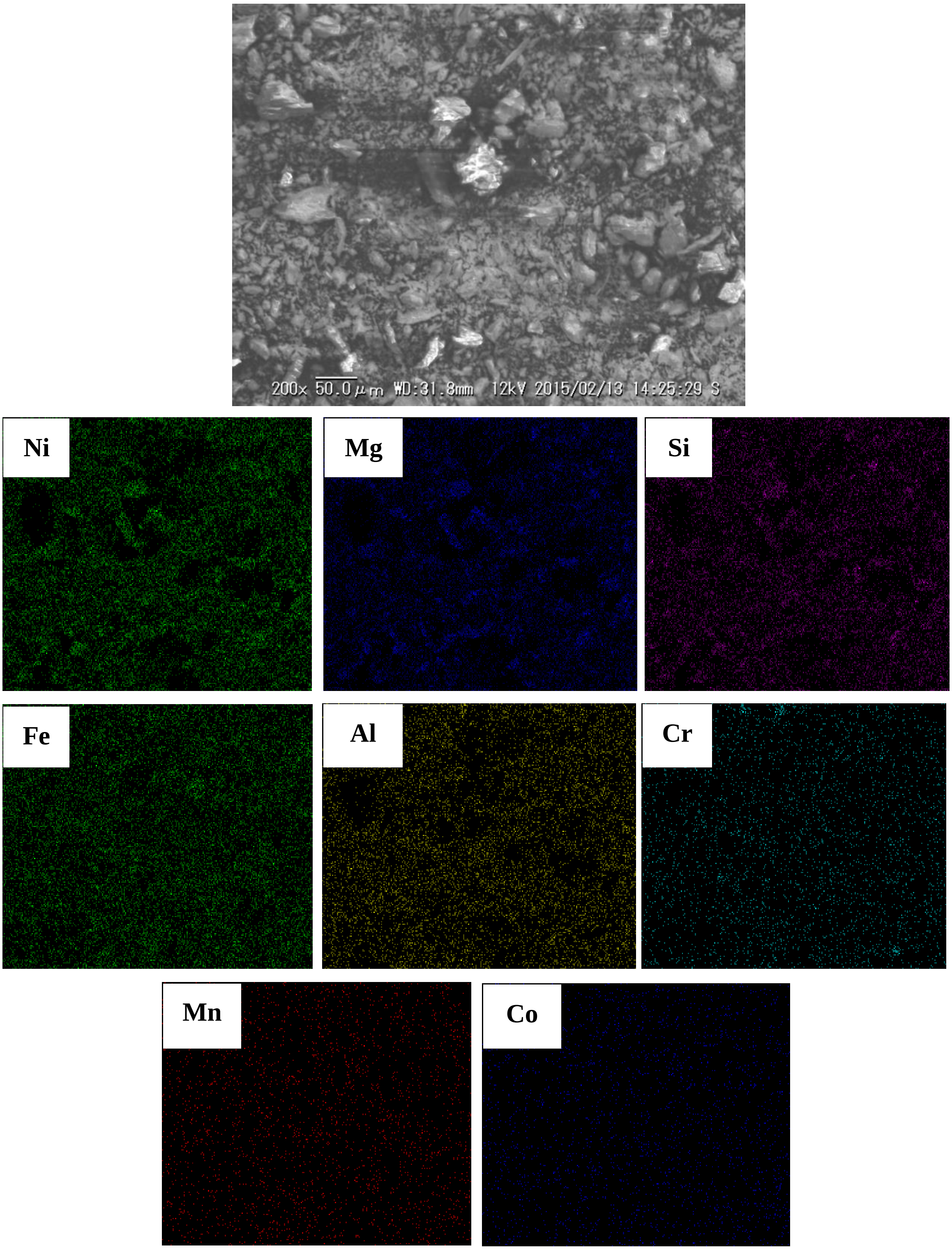

Fig. 2-5. SEM/EDS metal mapping of sample SH.

2.3.2. Effectiveness of citric acid versus inorganic acids (sulfuric, nitric, and hydrochloric acids)

The results of a comparison of the effects of citric acid with those of inorganic acid solutions (i.e., sulfuric, nitric, and hydrochloric acids) on nickel, iron, and magnesium dissolutions for each saprolite ore sample are reported in this section. Leaching processes were conducted at atmospheric pressure using acids of concentration 1 M, a shaker speed of 200 rpm, a leaching temperature of 30 °C, ore particles of size <75 μm, and a 20% w/v pulp density. Nickel, iron, and magnesium recoveries were used to investigate the mineral dissolution mechanism in the leaching process with each acid solution, because, as described previously in section *2.3.1. Mineralogical study of saprolite laterites*, nickel is mainly incorporated into lizardite and goethite. Lizardite is a magnesium-bearing mineral, whereas goethite is an iron-containing mineral. Data on iron and magnesium dissolution behaviors are therefore important in understanding the nickel-leaching mechanism.

The effects of different leaching agents on the nickel, iron, and magnesium dissolution rates for SS and SH are shown in Figs. 2-6 and 2-7. Figure 2-6 shows that for SS, the leaching processes using sulfuric acid and citric acid produce higher nickel recoveries than those using nitric acid and hydrochloric acid. This figure also shows that the optimum nickel recovery with each leaching agent was achieved at 7 days of leaching. Citric acid and sulfuric acid leaching gave similar maximum nickel recoveries, i.e., approximately 71% at 7 days of leaching. The maximum nickel recoveries achieved in nitric acid and hydrochloric acid leaching were similar to each other, i.e., around 43–45%. The order of the effectiveness of acid attack on nickel in SS is therefore sulfuric acid ≈ citric acid > nitric acid ≈ hydrochloric acid. However, the iron and magnesium dissolution behaviors differ from those of nickel dissolution. The iron and magnesium dissolution rates in sulfuric acid leaching were higher than those using other acids. The order of the effectiveness of acid attack on iron and magnesium in SS is therefore sulfuric acid > citric acid > nitric acid ≈ hydrochloric acid. Figure 2-7 shows that for SH, sulfuric acid leaching produced the highest nickel dissolution rate. Nitric acid, hydrochloric acid, and citric acid leaching gave similar nickel dissolution rates. Similar trends were observed for the dissolution of iron. The order of the effectiveness of acid attack on nickel and iron in SH is sulfuric acid > citric acid ≈ hydrochloric acid ≈ nitric acid. In the case of magnesium dissolution (Fig. 2-7(c)), all the acid solutions produced similar results. The order of the effectiveness of acid attack on magnesium in SH is sulfuric acid ≈ citric acid ≈ hydrochloric acid ≈ nitric acid.

The results show that there are differences between the leaching performances of the two samples. When sulfuric acid leaching was used, the nickel recoveries for SS and SH for the same leaching period were similar. However, a different trend was observed for leaching with other acids. When nitric acid and hydrochloric acid leaching were performed, the nickel recovery from SS was slightly greater than that from SH. Citric acid leaching extracted a much larger amount of nickel from SS than from SH. The mineralogical composition of each raw material should be an important parameter in the leaching mechanism. The explanation regarding on this issue will be discussed in the last section of this chapter.

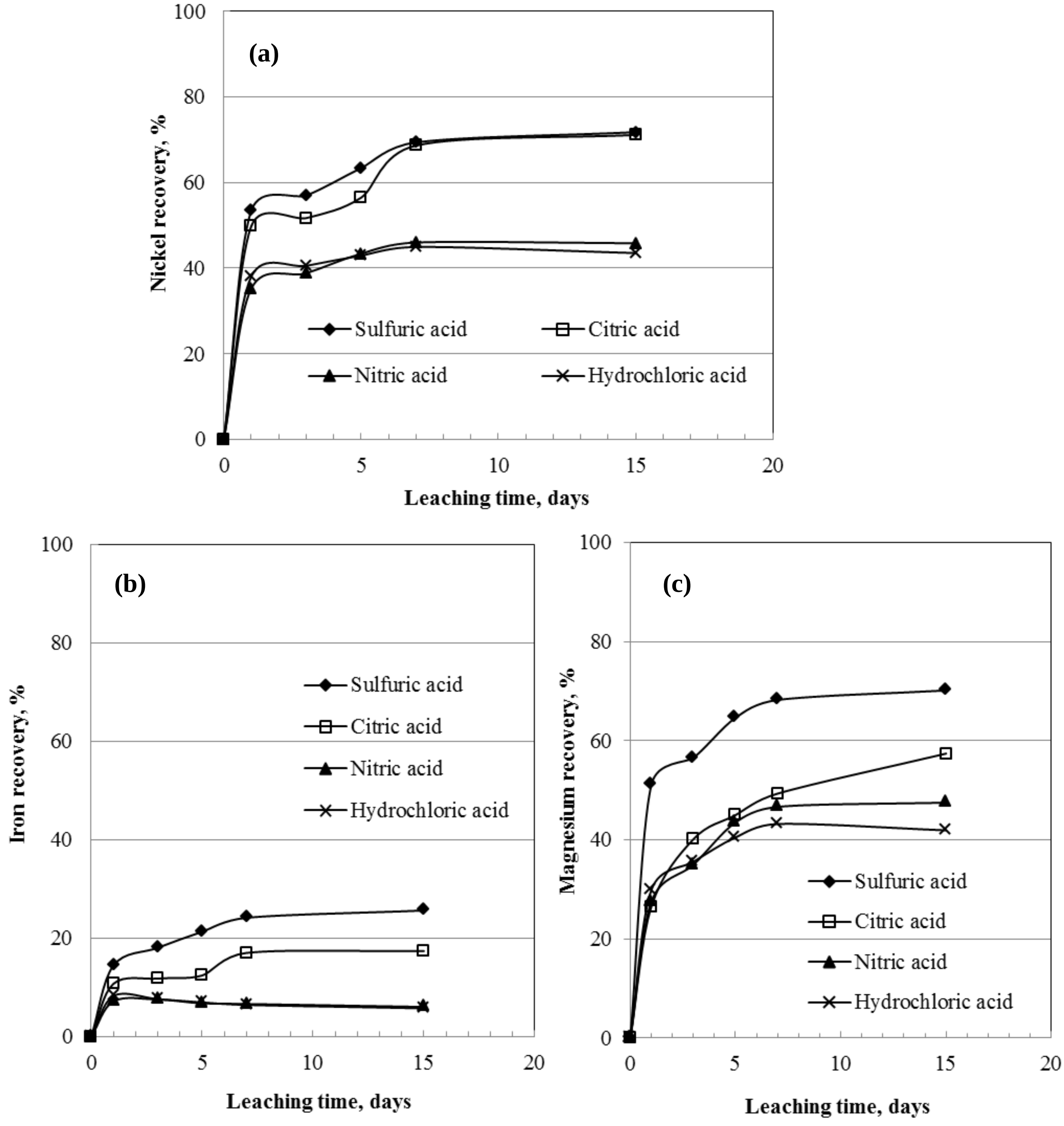

Fig. 2-6. Effectiveness of leaching reagents (citric, sulfuric, nitric, and hydrochloric acids) on the metal dissolution (a) Nickel; (b) Iron; (c) Magnesium of sample SS.

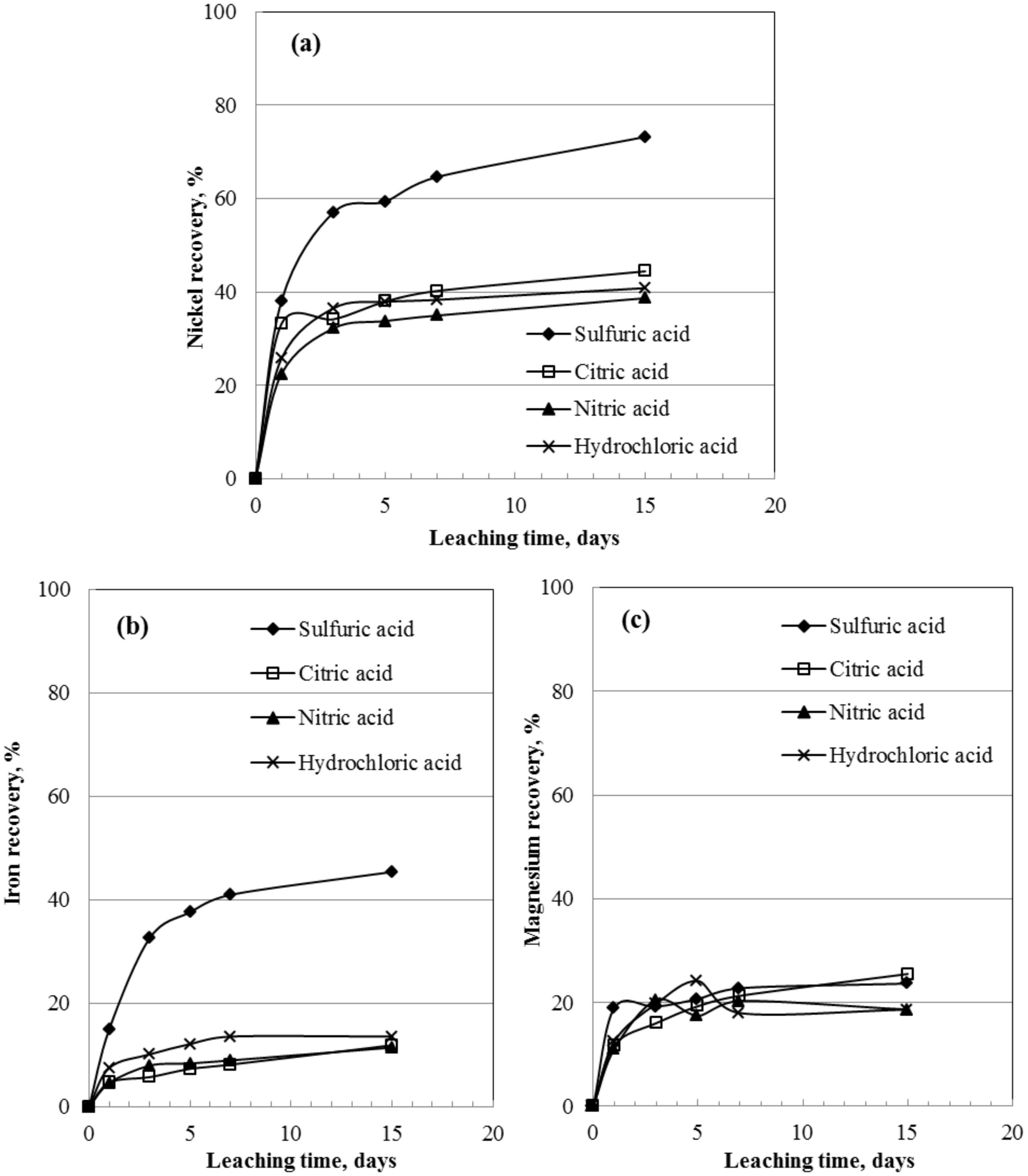

Fig. 2-7. Effectiveness of leaching reagents (citric, sulfuric, nitric, and hydrochloric acids) on the metal dissolution (a) Nickel; (b) Iron; (c) Magnesium of sample SH.

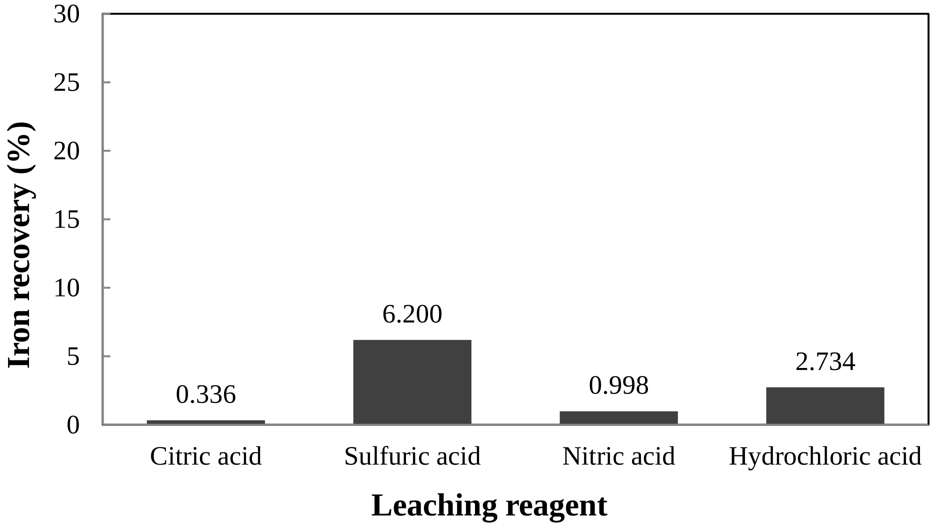

Fig. 2-8. Iron recovery from pure goethite by various acid solutions after 15 days of leaching process

Moreover, the goethite dissolution behavior was observed by iron leaching of pure goethite using all leaching reagents used in this study. It is proposed in Fig. 2-8, which show the iron recoveries from pure goethite in all acid solutions at atmospheric pressure and 30 °C, that iron recovery using citric acid is the least, while sulfuric acid is the most effective leaching reagent for dissolving goethite. In addition, nitric acid and hydrochloric acid can dissolve goethite in little amount. These results are also consistent with those for the dissolution of natural goethite using hydrochloric acid and nitric acid under atmospheric conditions reported by Abdus-Salam and Adekola (2006). They showed that iron can be dissolved from goethite by these acid solutions, despite the low amount of iron. Furthermore, citric acid has been proved that is very effective for serpentine dissolution (Valix et al., 2006). In terms of the effectiveness of inorganic acid solutions in the dissolution of serpentine, Teir et al. (2007) found that sulfuric acid is also effective for dissolving serpentine and more effective than nitric acid and hydrochloric acid.

The mechanism of metal dissolution from minerals by citric acid, which is an organic acid, is different from those when inorganic acid solutions are used. Although citric acid is a weak acid, it is an excellent chelating agent and metal binder. Ligands or chelating agents aid mineral dissolution by specifically adsorbing on mineral surfaces and forming highly soluble complexes with metal ions (e.g., magnesium and nickel in serpentine). The formation of ligand–metal complexes at the mineral surface shifts the electron density toward the metal ion, which destabilizes the Me–O lattice bonds and facilitates detachment of metal ions into solution (Stumm, 1992). Ligands also enhance the dissolution of minerals by forming complexes with leached ions in solution, thereby lowering the apparent solubilization of the mineral (Prigiobbe and Mazzotti, 2011). In summary, citric acid can dissolve heavy metals via two possible mechanisms, i.e., direct displacement of metal ions from the ore matrix or mineral matrix by hydrogen ions (acidolysis), and the formation of soluble metal complexes and chelates (complexolysis) (McDonald and Whittington, 2008b). These beneficial mechanisms may lead to the effectiveness of citric acid in attacking metals, particularly nickel, being as good as that of sulfuric acid.

In contrast, sulfuric acid, nitric acid, and hydrochloric acid, which are strong inorganic acids, only use one mechanism for attacking the reactive metals contained in minerals; they displace metal ions by hydrogen ions formed by complete dissociation of the acids. At the same concentration, however, sulfuric acid releases twice as many hydrogen ions as nitric acid and hydrochloric acid. Sulfuric acid is therefore more effective in metal dissolution than other inorganic acids, as found in this study.

2.3.3. Effectiveness of citric acid versus other organic acids (lactic and oxalic acids)

If metabolic citric acid produced by *A. niger* is to be used in nickel leaching, it is necessary to investigate the effects of other organic acids that are produced along with citric acid, to ascertain the effect of each organic acid on the extraction of nickel and other metals. In this study, the effects of citric acid on the nickel-leaching performance and behavior were compared with those of other organic acids, namely lactic acid and oxalic acid. Lactic acid and oxalic acid were used because these organic acids can also be major metabolic products in the production of citric acid by *A. niger*. Leaching processes were conducted under the same conditions as the previous leaching experiments, i.e., pulp density 20% w/v, leaching temperature 30 °C, shaker speed 200 rpm, and ore particle size <75 μm. Figs. 2-9 and 2-10 show the effects of citric acid, lactic acid, and oxalic acid on the nickel-, iron-, and magnesium-leaching rates of SS and SH. The figures show that the trends in the metal-leaching behaviors of the two samples were different. Fig. 2-9 shows that for SS, citric acid is the most effective nickel-leaching agent, whereas oxalic acid is the least effective. No nickel was recovered from SS using oxalic acid solution. In contrast, as shown in Fig. 2-10, oxalic acid can recover nickel from SH, although the nickel-leaching rate is very low. The maximum nickel recovery achieved from SH by oxalic acid leaching was around 2%. The effectiveness of citric acid and lactic acid in terms of SH leaching were similar to each other, but citric acid was much more effective than lactic acid for nickel leaching from SS.

The order of the activities of the organic acids in nickel extraction for both samples was citric acid > lactic acid > oxalic acid. Citric acid gives the best nickel extraction because of its high dissociation constant and its ability to form nickel–citrate complexes during metal dissolution. In contrast, although oxalic acid has a higher dissociation constant and is one of the best metal-chelating agents, it gives the lowest nickel recovery for both samples. Figs. 2-9 and 2-10 show that the effectiveness of oxalic acid attack on iron is the highest, and is much higher than those of citric and lactic acid for both SS and SH. Magnesium leaching by oxalic acid is also higher than that by lactic acid, but lower than that by citric acid. Oxalic acid is therefore expected to dissolve iron- and magnesium-containing minerals such as goethite, lizardite, and talc. Nickel should be leached during dissolution of these minerals, but the nickel concentration in the pregnant leaching solution with oxalic acid is very low, because of nickel oxalate precipitation. This is attributed to the ability of oxalic acid to form stable nickel oxalate precipitates with dissolved nickel (Alibhai et al, 1993; McDonald and Whittington, 2008b).

A comparison of Figs. 2-9 and 2-10 also shows that the maximum nickel-leaching rate for SS is higher than that for SH when citric acid and lactic acid were used in the leaching process. Approximately 72% of nickel was recovered from SS after 15 days of leaching with citric acid, whereas only 44% of nickel was extracted from SH after 15 days of leaching with the same acid solution. Similar results were obtained for lactic acid leaching, i.e., around 38% of nickel was leached from SS, but only 30% of nickel was recovered from SH. Nickel recovery using oxalic acid was very low, even zero, but nickel recovery from SH was higher than that from SS. Differences between the mineral compositions of the two samples may lead to differences in their leaching performances. Figs. 2-9 and 2-10 suggest that the ability of oxalic acid to dissolve goethite is high, and much higher than those of citric and lactic acid. Fig. 2-11 shows that oxalic acid can dissolve larger amounts of iron from pure goethite than can citric acid and lactic acid. Oxalic acid can dissolve iron oxides effectively by both complexation and reduction (Sellars and Williams, 1984), therefore because the goethite content of SH is higher than that of SS, iron recovery from SH is higher, as shown in Figs. 2-9 and 2-10. This may lead to a higher nickel concentration in the pregnant leaching solution from SH than in that from SS.

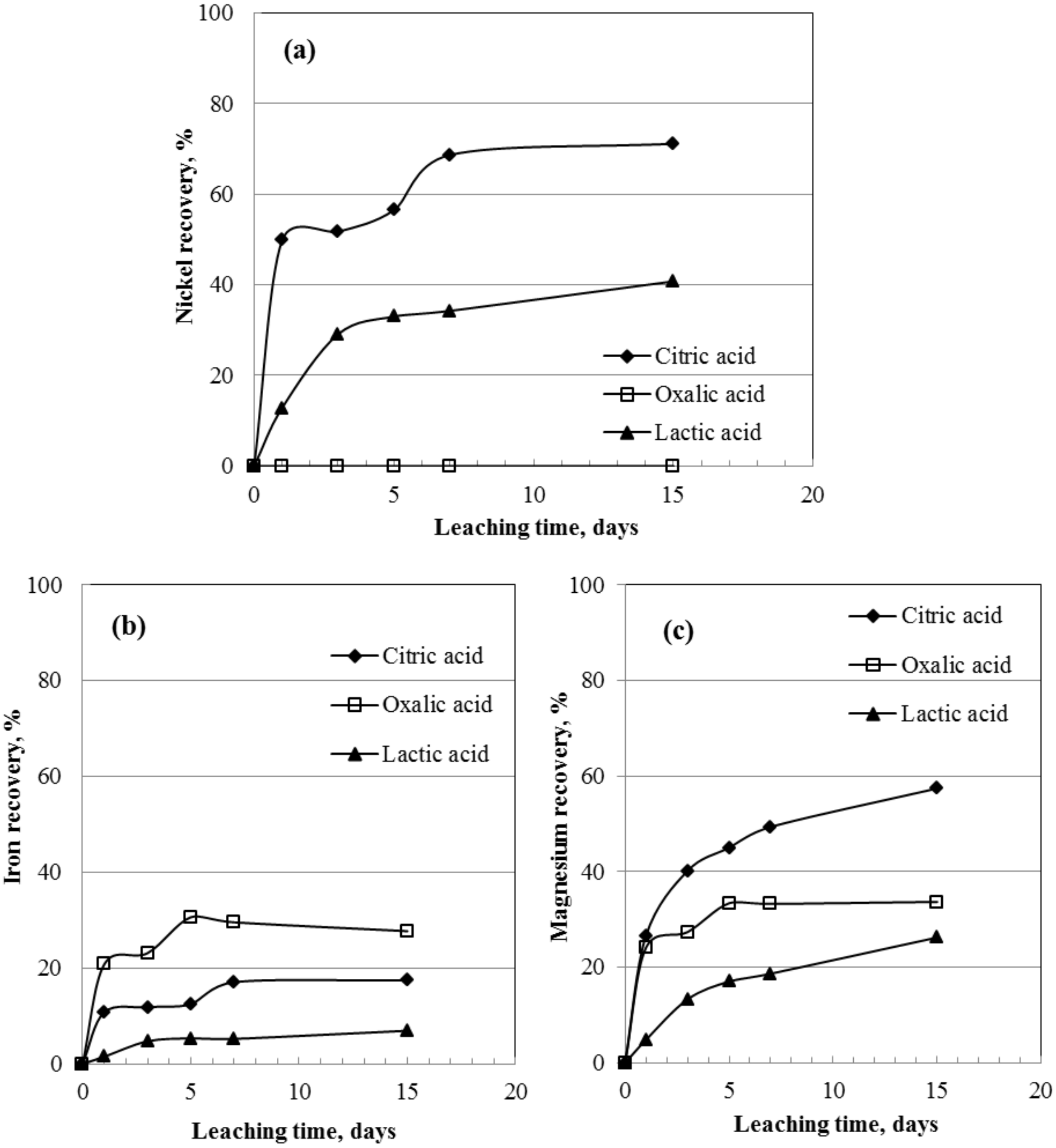

Fig. 2-9. Effectiveness of leaching reagents (citric, lactic, and oxalic acids) on the metal dissolution (a) Nickel; (b) Iron; (c) Magnesium of sample SS.

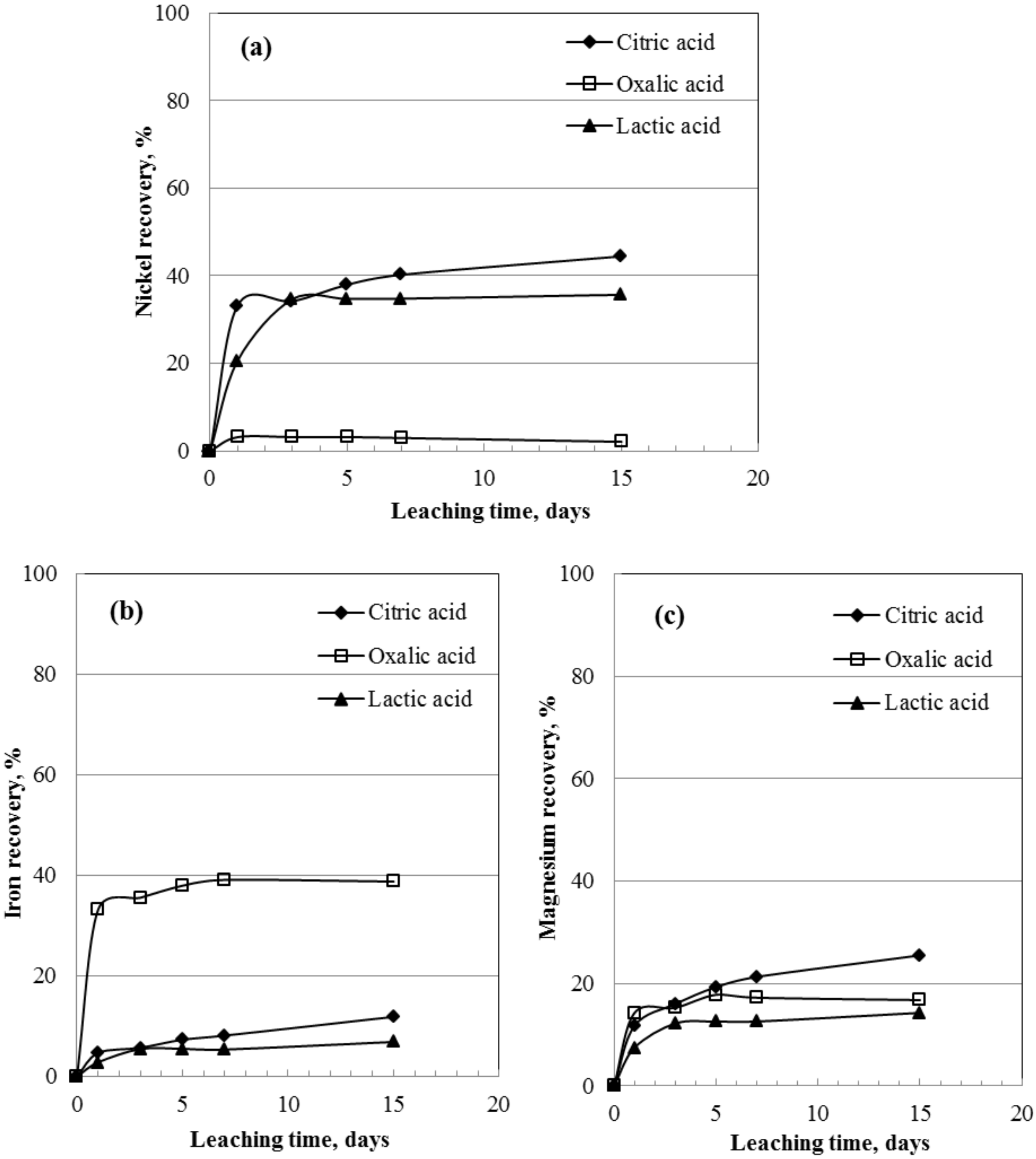

Fig. 2-10. Effectiveness of leaching reagents (citric, lactic, and oxalic acids) on the metal dissolution (a) Nickel; (b) Iron; (c) Magnesium of sample SH.

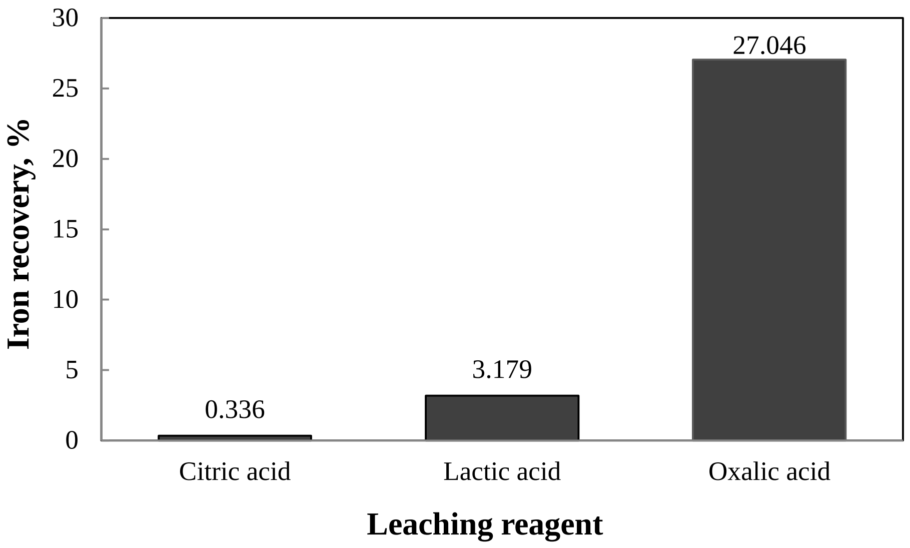

Fig. 2-11. Iron recovery from pure goethite by various acid solutions after 15 days of leaching process

2.3.4. Effectiveness of mixtures of citric acid and sulfuric acid

The leaching abilities of sulfuric acid and citric acid show interesting trends. The nickel recoveries achieved using sulfuric acid leaching was higher than those achieved with other inorganic acids. Although citric acid is a weak organic acid, the nickel dissolution rates with this acid were similar to those for sulfuric acid leaching, especially in the case of SS. The influence of sulfuric acid and citric acid on the nickel-leaching rates and mineral dissolution behaviors of different saprolite samples were further investigated using mixtures of sulfuric acid and citric acid at various concentrations. Three mixtures of sulfuric acid and citric acid were used: (a) 0.25 M sulfuric acid + 0.75 M citric acid; (b) 0.5 M sulfuric acid + 0.5 M citric acid; and (c) 0.75 M sulfuric acid + 0.25 M citric acid. Leaching was performed under the same conditions as for the previous leaching experiments, i.e., pulp density 20% w/v, leaching temperature 30 °C, shaker speed 200 rpm, and ore particle size <75 µm.

Figs. 2-12 and 2-13 show the nickel, iron, and magnesium dissolution behaviors. The figures show that the trends in the leaching behaviors of SS and SH were different when sulfuric acid–citric acid mixtures were used. An increase in the proportion of sulfuric acid in SS leaching did not significantly affect the nickel-leaching rate. Because the most nickel in SS is associated with lizardite and both citric acid and sulfuric acid have similar ability in dissolving lizardite, it is proposed that the use of citric acid alone, sulfuric acid alone, as well as mixture of sulfuric and citric acid will produce similar nickel leaching rate. On the other hand, in terms of SH, sulfuric acid addition significantly increased the nickel dissolution rate due to the higher goethite and lower lizardite content in SH. Sulfuric acid is more effective to dissolve goethite than citric acid as described in section *2.3.3. Effectiveness of citric acid versus inorganic acids (sulfuric, nitric, and hydrochloric acid).* However, the use of citric acid in leaching solutions is still important; as shown in Fig. 2-13, the nickel recovery using 0.75 M sulfuric acid + 0.25 M citric acid was higher than that using 1 M sulfuric acid alone.

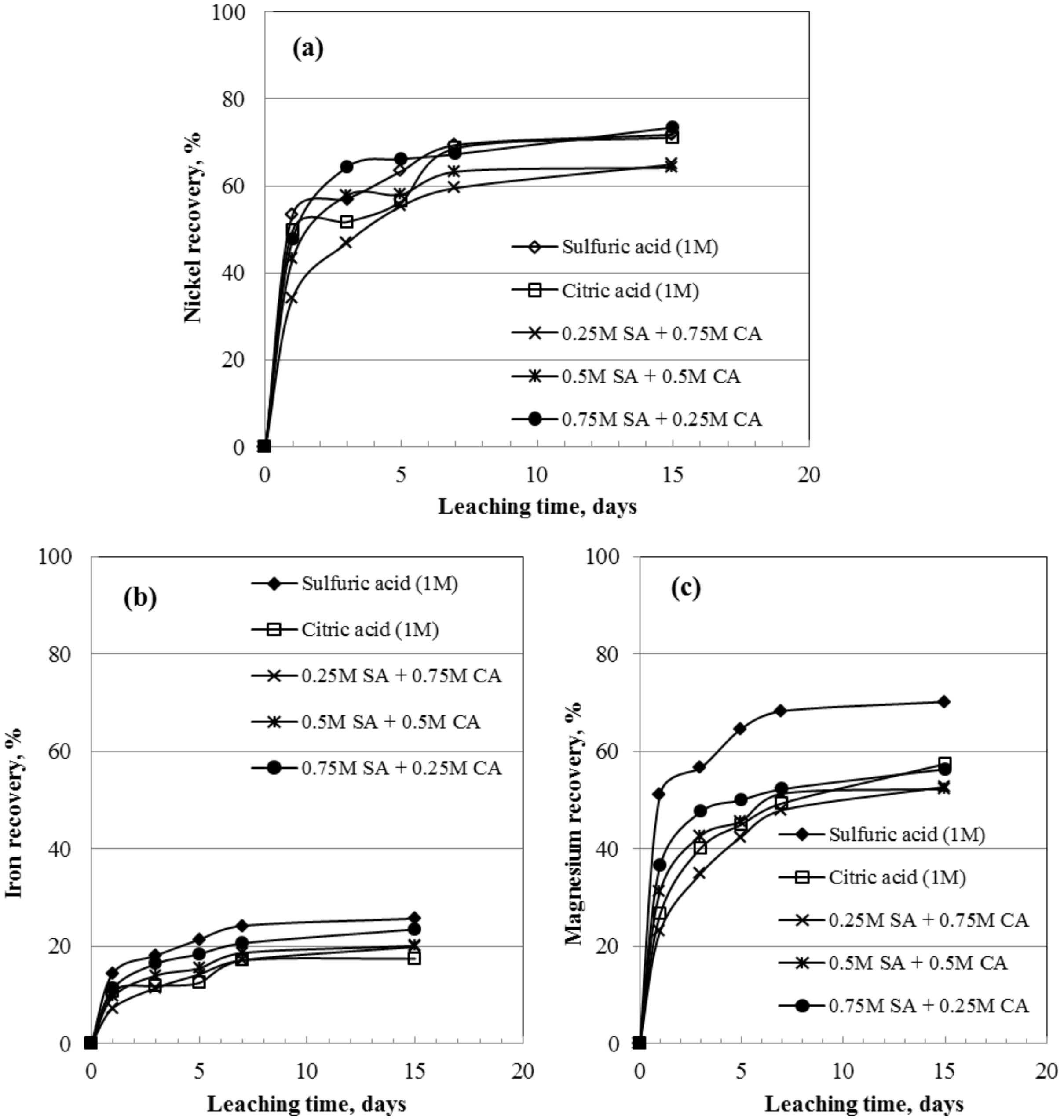

Fig. 2-12. Effectiveness of acids and their combination on the metal dissolution (a) Nickel; (b) Iron; (c) Magnesium of sample SS.

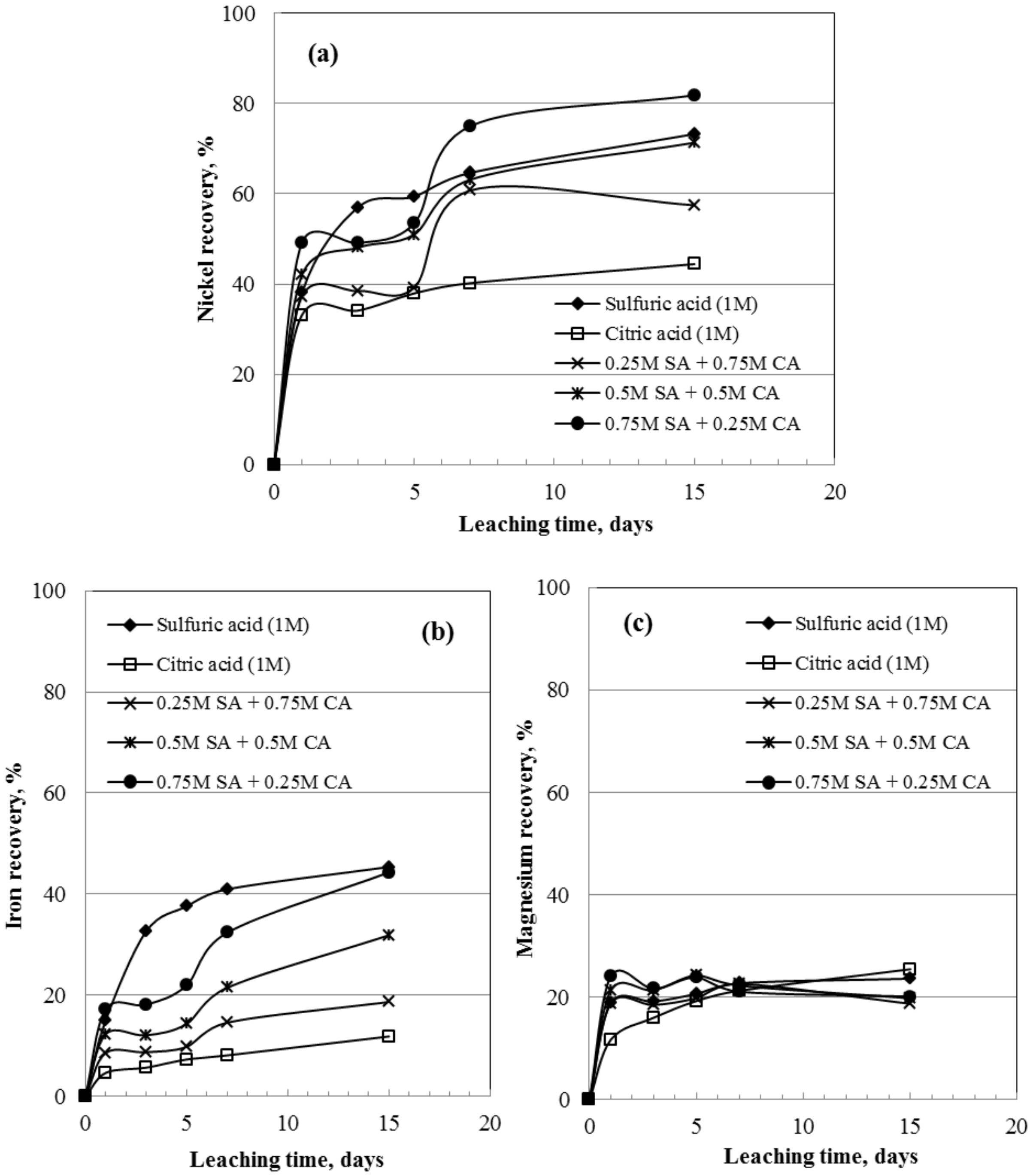

Fig. 2-13. Effectiveness of acids and their combination on the metal dissolution (a) Nickel; (b) Iron; (c) Magnesium of sample SH.

Furthermore, XRD patterns of solid residue were also observed to investigate the mineral dissolution behavior in these experiments. Figs. 2-14 and 2-15 show that after leaching process, the peaks of lizardite, goethite, and talc from both samples decrease significantly. Anyhow, solid residue from leaching process using mixture of 0.75 M sulfuric acid + 0.25 M citric acid show the highest decrease in the peaks of lizardite, goethite, as well as talc. It is suggested that the presence of citric acid in the dissolution of nickel from saprolite ores is significant. This leaching behavior indicates the beneficial interaction between free hydrogen and citrate ions.

Additionally, selectivity of leaching is also one of the important parameters that must be considered in the applying of leaching process. The current experiment shows that even though sulfuric acid leaching produces nickel recovery as maximum as citric acid leaching, the nickel leaching selectivity of sulfuric acid is lower than that of citric acid. Sulfuric acid alone produced the greatest iron leaching rate from both saprolite samples. Moreover, 1 M sulfuric acid alone also dissolved magnesium from SS in the highest amount and much higher than other acid solutions as can be seen in Fig. 2-12(c). Hence, it can be considered that the use of citric acid provides more advantages than other acid leaching applied in this study. Citric acid offers not only high nickel recovery and high selectivity of leaching but also an environmentally safe process and low acid consumption. Moreover, citric acid can be produced from fungal metabolism using several types of carbon sources as fungal nutrients. The use of citric acid for nickel extraction from Indonesian laterite ores can therefore be considered a potentially suitable alternative technology that requires low capital and operational costs owing to the abundance of biodiversity and carbon sources in this country.

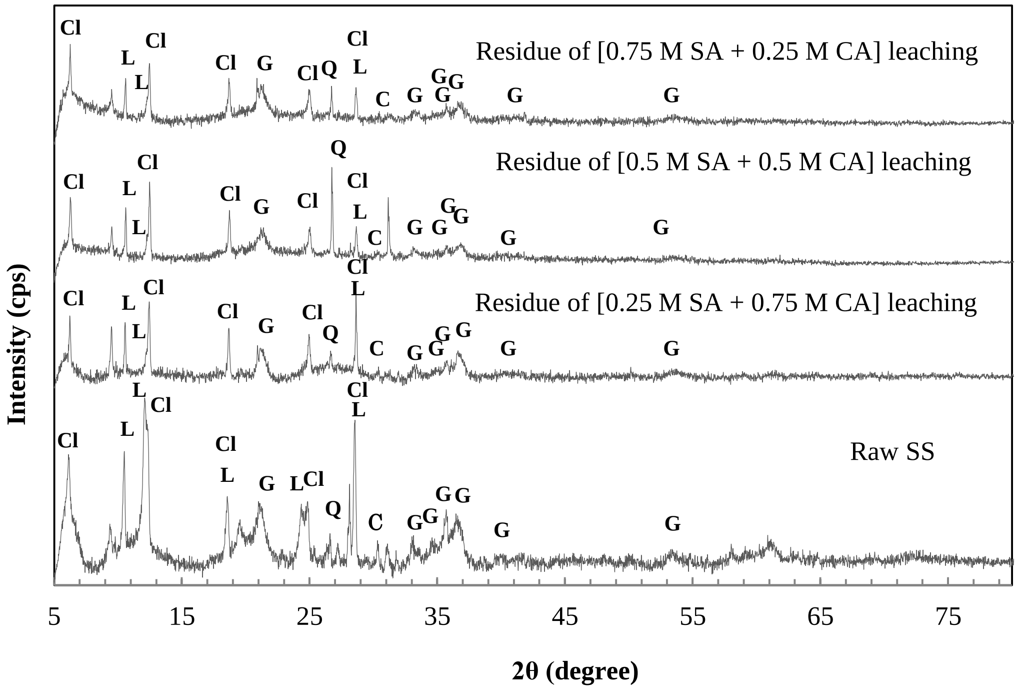

Fig. 2-14. XRD patterns of raw SS and solid residues of SS after leaching by some mixtures of sulfuric-citric acid leaching (L: lizardite, G: goethite, Cl: clinochlore, C: chromite, Q: quartz).

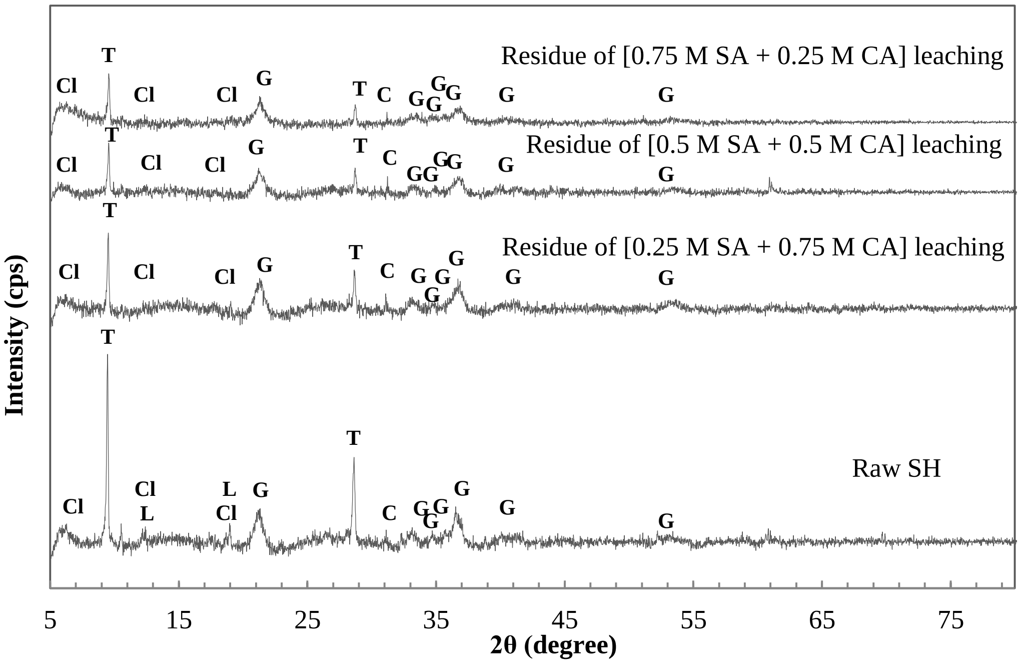

Fig. 2-15. XRD patterns of raw SH and solid residues of SH after leaching by some mixtures of sulfuric-citric acid leaching (L: lizardite,, Cl: clinochlore, G: goethite, T: talc, C: chromite, Q: quartz).

In addition, the effects of a mixture of sulfuric acid and citric acid on leaching were further investigated using an acid solution mixture of higher concentrations, namely 1 M sulfuric acid + 1 M citric acid. The leaching trends for the two samples differed. Figure 2-16 shows that for both samples, this acid mixture produced the highest nickel dissolution rate. However, the increase of nickel leaching rate in SS is insignificant. Nickel recoveries from SS of around 71–73% were achieved using a single acid, i.e., 1 M citric acid or 1 M sulfuric acid. Only around 80% of nickel was extracted from SS when a mixture of 1 M sulfuric acid + 1 M citric acid was used. In terms of SH, on the other hand, increasing the acid concentration in the acid mixture significantly increased the nickel dissolution rate. Only around 71% of nickel was recovered from SH when 1 M sulfuric acid alone was used, and only 44% nickel recovery was achieved using 1 M citric acid alone. However, a mixture of 1 M sulfuric acid + 1 M citric acid completely dissolved the nickel from SH for the same leaching time and conditions. Approximately 100% nickel recovery from SH was achieved when a solution of 1 M sulfuric acid + 1 M citric acid was used.

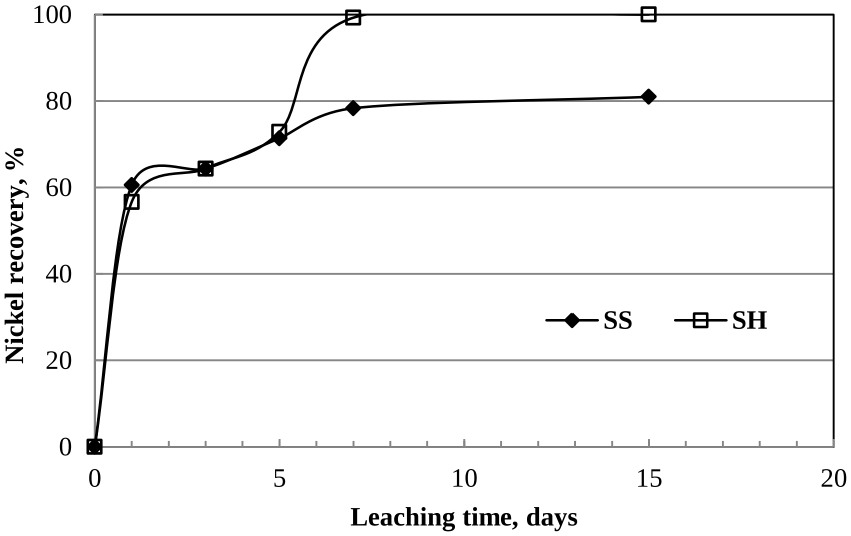

Fig. 2.16. Comparison of nickel leaching rate on SS and SH by mixture of 1M sulfuric acid + 1M citric acid

This last result suggests that for SH, all the lizardite nickel can be extracted using citric acid, and sulfuric acid can be used to recover all the nickel from goethite. The amount of lizardite in SH is small, therefore 1 M citric acid is adequate for dissolving all the nickel from lizardite in SH. Complete nickel dissolution from SH was achieved using a mixture of 1 M sulfuric acid + 1 M citric acid. For SS, only approximately 80% of nickel can be recovered using a mixture of 1 M sulfuric acid + 1 M citric acid. Although 1 M sulfuric acid can leach all the nickel from goethite in SS, 1 M citric acid does not extract all the nickel from lizardite, because of the high lizardite content in SS. Nickel therefore cannot be completely extracted from SS using 1 M sulfuric acid + 1 M citric acid.

It was also proposed that citric acid is more suitable than sulfuric acid for leaching lizardite-bearing lateritic ores, although sulfuric acid can dissolve nickel from both goethite and lizardite. The use of sulfuric acid for goethite-containing lateritic ores is preferable. These findings can be applied to leaching at atmospheric pressure and low temperatures of other lateritic ores containing goethite and lizardite.

2.4. Conclusion

The mineral compositions of raw material ores are crucial in the leaching performances and metal dissolution rates of lateritic ores using various acid solutions. Citric acid and sulfuric acid are more effective than other acid solutions for nickel extraction from SS and SH samples. Citric acid is effective for dissolving nickel from lizardite, but cannot recover nickel from goethite. Inorganic acids, namely sulfuric, nitric, and hydrochloric acids, can extract nickel from lateritic ores by dissolving goethite and lizardite. However, sulfuric acid gives higher nickel recoveries than the other inorganic acids, because a larger number of hydrogen ions are released by sulfuric acid dissociation than by dissociation of the other inorganic acids used. Oxalic acid is the least effective reagent for nickel extraction from both samples, because of nickel oxalate precipitation after nickel dissolution.

Sulfuric acid–citric acid mixtures of various concentrations were used in the leaching of both samples to confirm the influence of either sulfuric acid or citric acid on the leaching performance and mineral dissolution behavior of each sample. The effect of a sulfuric acid–citric acid mixture on the nickel dissolution rate in SS leaching is less than that on SH leaching. An increase in the proportion of sulfuric acid in SS leaching did not significantly affect the nickel-leaching rate. Generally, the effect of citric acid in the mixture of sulfuric acid and citric acid is attractive. Moreover, selectivity of nickel dissolution against magnesium and iron dissolution in citric acid leaching is higher than that in sulfuric acid leaching. Hence, nickel recovery from low-grade Indonesian saprolite ores using citric acid is beneficial in the future because this leaching technique propose some advantages such as high nickel recovery, high nickel leaching selectivity, environmentally safe process, as well as low capital and operational cost.

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CHAPTER 3

Citric Acid Leaching Behaviors and Mechanism of Low-Grade Indonesian Saprolite Ores

The current study examines the comparative leaching performances, mineral dissolution behaviors, and leaching kinetics of nickel extraction from two different Indonesian low-grade saprolite ores, using citric acid as the leaching reagent, at atmospheric pressure to investigate the nickel leaching mechanism from saprolite ores. The effects on nickel extraction of leaching temperature, citric acid concentration, pulp density, and ore particle size were carried out to investigate the leaching performances and leaching kinetics of the two saprolite ores as well as to determine the optimum leaching conditions. The X-ray diffraction (XRD) of the solid residues was analyzed in order to observe mineral dissolution behavior of leaching process.

3.1. Introduction

The use of organic acids in dissolution of the metals in nickel laterite ores is an alternative technique that has advantages in terms of environmental issues. Citric acid was indicated to be the most effective leaching reagent because of its greater ability to dissociate although like all acids. As investigated in the previous chapter, the effectiveness of citric acid on the nickel extraction from Indonesian low-grade saprolite ores is great even greatest than other acid solutions tested. Moreover, since citric acid can be produced from fungal metabolism particularly from *Aspergillus niger*, citric acid leaching become a suitable alternative technique for nickel extraction from Indonesian lateritic ores that requires low capital and operating costs because of the great biodiversity and abundant carbon sources in Indonesia. To apply the citric acid leaching method for recovering nickel from Indonesian low-grade saprolite ores, it is necessary to investigate the optimum leaching conditions that produce the highest nickel recovery. The use of different saprolite ores from different mining locations is also important to ascertain the leaching behavior and mechanism based on the mineralogy of each sample.

The aim of this study; therefore, is to obtain a better understanding of the comparative leaching performances, mineral dissolution behaviors, and leaching kinetics of different Indonesian saprolite ores from two different mining areas, in atmospheric leaching using citric acid in order to investigate the nickel leaching mechanism in this leaching process. The optimum leaching conditions was also determined by investigating of effect various leaching parameters on the nickel recovery and nickel leaching rate. This information is important in the design of alternative techniques for treating such ores. The findings of the study can be adopted for leaching of other lateritic ores from other locations.

3.2. Material and methods

3.2.1. Materials

The ore samples employed in the current experiment are saprolite ores from two different mining areas in Indonesia namely Sulawesi Island (ore SS) and Halmahera Island (ore SH) that are the same samples used in Chapter 2. Those ores were prepared and analyzed in the same way as it was mentioned in Chapter 2 *subtopic 2.2.1. Materials.* Chemical composition of both samples was previously presented in Chapter 2, Table 2-1. Moreover, the mineralogical properties of the ores were also described in Chapter 2 *subtopic 2.3.1. Mineralogical study of saprolite ores.*

3.2.2. Leaching experiments

Chemical leaching experiments were performed using 300 mL flasks in a shaker at 200 rpm and atmospheric pressure. Analytical-grade citric acid (Wako Pure Chemicals Industries, Ltd., Tokyo, Japan) was used to prepare solutions of concentration 0.1, 0.5, and 1 M, to study the effect of citric acid concentration on nickel extraction. The effect of temperature was investigated using leaching temperatures of 30 °C, 40 °C, and 60 °C. The pulp density was varied at 5%, 10%, 20%, and 30% w/v. The effect of particle sizes was investigated using saprolite ore particle sizes of <75 μm, 75–150 μm, 212–355 μm, and 355–850 μm. Leaching was monitored by sampling the slurry periodically; the pH was measured using a pH meter (pH meter/ORP/EC, MM60R Type, DKK-TOA, Tokyo, Japan) and the dissolved metals were analyzed by inductively coupled plasma-optical emission spectroscopy (ICP-OES; Perkin Elmer 8500, Waltham, MA, USA) using standard procedures. The X-ray diffraction (XRD; Ultima IV, Rigaku, Tokyo, Japan), using Cu Kα radiation, at an accelerating voltage and applied current of 40 kV and 40 mA, respectively, in the 2θ range 5° to 80°, with a scanning speed of 2°/min and a scanning step of 0.02°analysis was performed on the leaching residues to determine the mineral phases after leaching and to study the mineral dissolution behaviors. Mineralogical analyses of the raw laterite and leaching residues using the XRD, which were an essential step in investigating the leaching mechanism, were used to study metal dissolution. Kinetic analyses were also performed briefly based on the experimental data for the dissolution of nickel from each saprolite ore sample in order to ascertain the findings of result.

3.3. Results and discussion

3.3.1. Nickel-leaching behaviors of different low-grade saprolite ores

The effects of leaching temperature, citric acid concentration, pulp density, and ore particle size on nickel recovery were investigated to study the nickel-leaching behavior of each saprolite sample.

Effect of leaching temperature

Temperature is usually a significant parameter in determining the optimum leaching conditions. To determine the effect of leaching temperature on nickel extraction for both samples, experiments were conducted at leaching temperatures of 30 °C, 40 °C, and 60 °C, with a constant citric acid concentration of 1 M, particle size of <75 μm, shaking speed of 200 rpm, and pulp density of 20% w/v. The results (Fig.

3-1) show that for both samples, nickel recovery increased with increasing leaching temperature up to the optimum temperature. For SS, as shown in Fig. 3-1(a), nickel recovery increased from 65% to 79% after leaching for 15 days when the leaching temperature was increased from 30 °C to 40 °C. However, increasing the temperature from 40 °C to 60 °C did not significantly increase nickel recovery. Only 80% nickel recovery was achieved at a leaching temperature of 60 °C. Nickel recovery from SH rose from 48% to 68% when the temperature was increased from 30 °C to 40 °C. A similar trend to that for SS leaching was observed, i.e., increasing the leaching temperature above 40 °C did not significantly increase nickel recovery. Fig. 3-1(b) shows that nickel recovery rose slightly, from 68% to 69%, when temperature was increased from 40 °C to 60 °C. A lower leaching temperature is preferable, technically and economically, therefore a leaching temperature of 40 °C was used for subsequent leaching experiments. The current results also show that the rate of nickel leaching from SS was faster than that from SH, and the maximum nickel recovery achieved from SS was higher than that from SH at all leaching temperatures, under the same leaching conditions.

These experiments also showed that longer leaching time leads to higher nickel recovery, up to an optimum value. Nickel dissolution increased rapidly during the first seven days, but slowed down between the 7th and 15th days. The leaching process was essentially complete after 15 days, when no further nickel dissolution occurred.

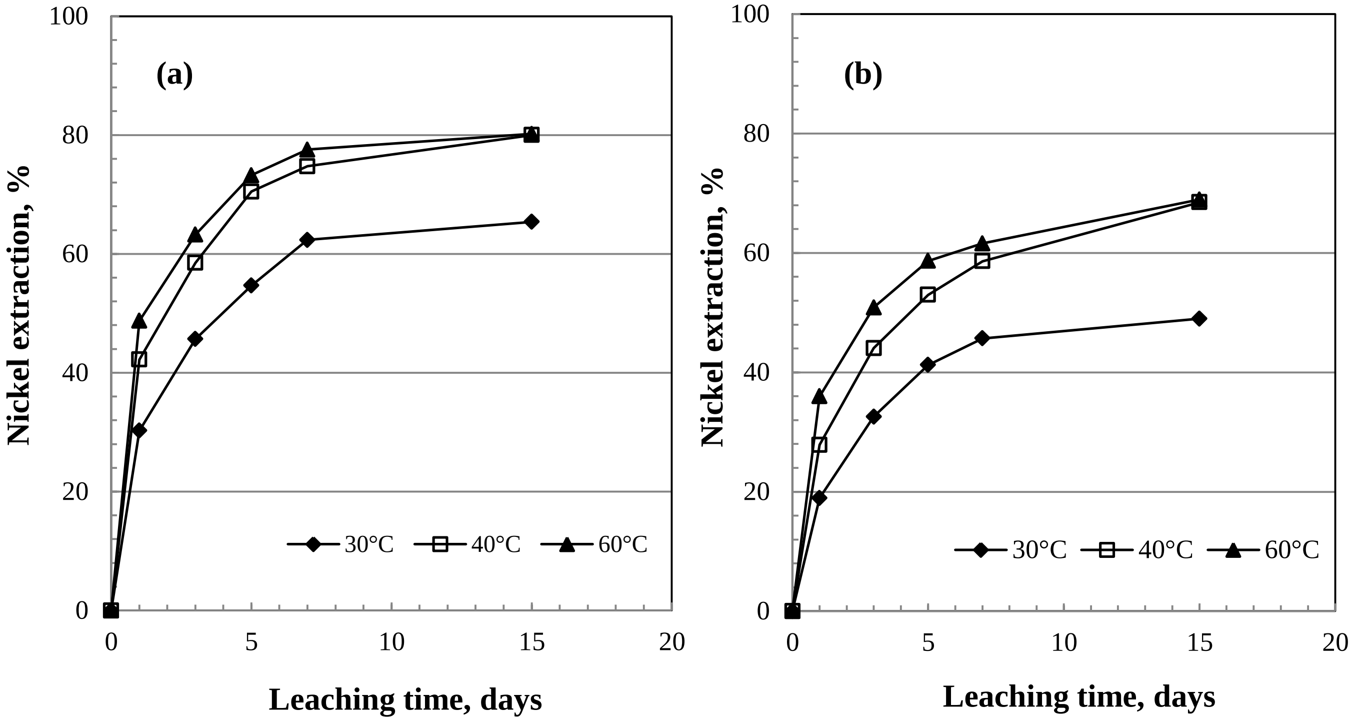

Fig. 3-1. Effect of leaching temperature for sample (a) SS and (b) SH ([citric acid]: 1 M, ore particle size: <75 µm, pulp density: 20% w/v, shaker speed: 200 rpm).

Effect of citric acid concentration

Similar trends were also observed in experiments using different citric acid concentrations. In addition to the temperature, the concentration of the leaching reagent is a significant parameter in the leaching process. The effect of citric acid concentration on nickel recovery was studied by performing leaching experiments under the conditions leaching temperature 40 °C, shaking speed 200 rpm, pulp density 20% (w/v), and particle size <75 µm, using citric acid of different concentrations, i.e., 0.1 M, 0.5 M, and 1 M. The results, as shown in Fig. 3-2, show that the citric acid concentration had a significant effect on nickel recovery, and the trends were similar for both samples. Fig. 3-2 also depicts that nickel recovery increased gradually with increasing citric acid concentration. The maximum nickel extraction was achieved when the citric acid concentration was 1 M. For SS, only 26% nickel was leached in 15 days when the citric acid concentration was 0.1 M; the maximum nickel recovery rose to 67% and 79% when the citric acid concentration was increased to 0.5 M and 1 M, respectively. For SH, the maximum nickel recovery achieved using 0.1 M citric acid was only 20%. The nickel recovery increased to 56% and 68% when the citric acid concentrations used were 0.5 M and 1 M respectively.

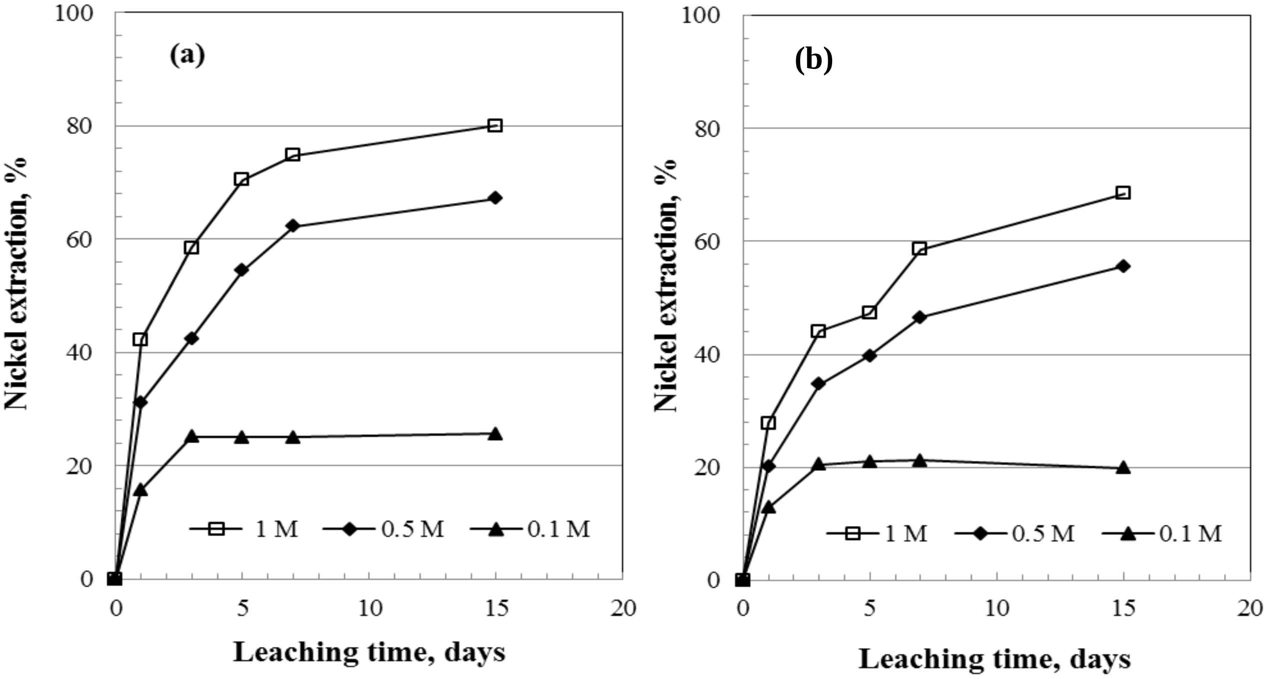

Fig. 3-2. Effect of acid concentration for sample (a) SS and (b) SH (temperature: 40 °C, ore particle size: <75 μm, pulp density: 20% w/v, shaker speed: 200 rpm).

Nickel extraction increases with increasing citric acid concentration because of the increase in the hydronium ion (H^+) activity, which leads to dissolution of nickel-containing materials. The current results show that nickel recovery rates from SS and SH showed similar trends, but the maximum nickel recovery achieved from SS was higher than that from SH at all citric acid concentrations. After leaching for 15 days, around 79% nickel was extracted from SS when 1 M citric acid was used, but only 68% nickel was leached from SH under the same leaching conditions.

Effect of pulp density

The influences of pulp densities at 5%, 10%, 20%, and 30% (w/v) on nickel recovery were also examined. Citric acid concentration (1 M), ore particle size (<75 μm), temperature (40°C), and shaker speed (200 rpm) were kept constant. Figure 3-3 shows the effect of pulp density on the nickel leaching rate of both samples. From these results, it is recognized that there is differences trend in both samples. In terms of sample SS, it can be seen in Fig. 3-3(a) that pulp density impact slightly on the nickel leaching rate. On the other hand, the nickel leaching rate of sample SH was influenced significantly by pulp density. Moreover, it can also be seen that the nickel leaching rate in sample SS was higher than that in sample SH. This result may occur because of the differences of mineral composition of both samples. The observation of this assumption will be discussed in the following section. Nevertheless, it was seen the similar phenomena that the pulp density of 20% w/v show the highest nickel leaching rate. Thus, it can be considered that the optimum pulp density that can be applied for nickel leaching from Indonesian low-grade saprolite ores in the current study is 20% w/v.

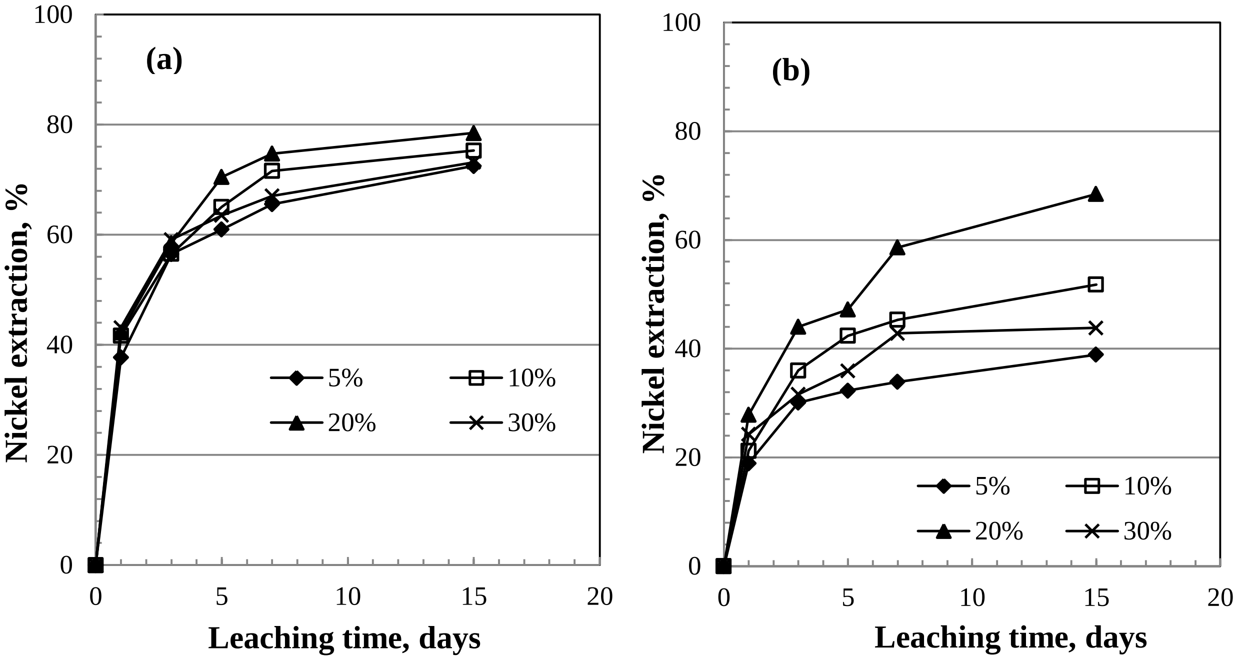

Fig. 3-3. Effect of pulp density for sample (a) SS and (b) SH ([citric acid]: 1 M, temperature: 40°C, particle size: <75 μm, shaker speed: 200 rpm).

Effect of ore particle size

The differences between the maximum nickel recoveries obtained from the two samples may result from the differences between the mineral contents of the samples, as described in the previous discussion. Lateritic ores are very complex and contain many different minerals. As described previously, most of the nickel in these ores is not present as the independent element or compounds. In any given ore, nickel can be present in various minerals in a solid solution of lateritic ore. As discussed in Chapter 2 Section *2.3.1. Mineralogical study of saprolite ores*, the nickel in these saprolite ores may be incorporated into lizardite and goethite. Nickel extraction is controlled by the dissolution behaviors of these host minerals. Information on the effect of ore particle size on nickel extraction can be used to better understand the leaching behavior of each sample, because every mineral has different particle size distribution. In the current experiments, the effect of ore particle sizes of <75 μm, 75–150 μm, 212–355 μm, and 355–850 μm were investigated at a leaching temperature of 40 °C, shaking speed of 200 rpm, citric acid concentration of 1 M, and pulp density of 20% (w/v). The results (Fig. 3-4) show that the maximum nickel recovery rates for both samples were achieved after leaching for 15 days, with a particle size of 212–355 μm. The results also show that nickel recovery from SS was higher than that from SH under all leaching conditions. Approximately 96% nickel recovery was achieved from SS, whereas only 73% nickel was leached from SH under the optimum leaching conditions.

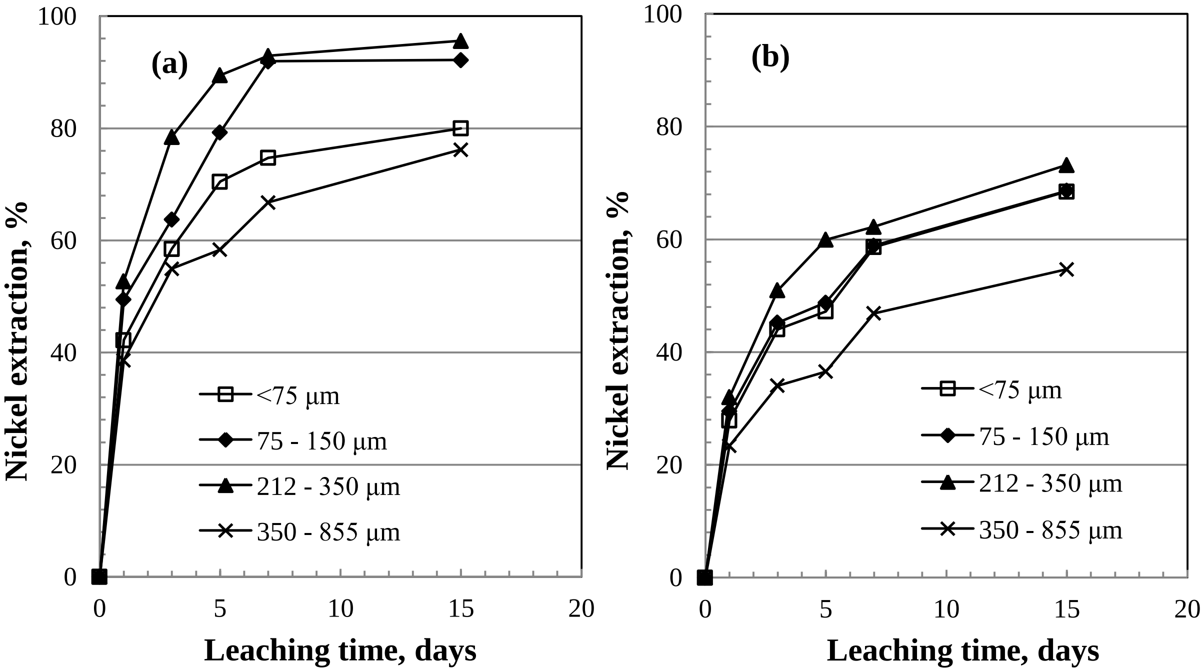

Fig. 3-4. Effect of particle size for sample (a) SS and (b) SH (temperature: 40 °C, [citric acid]: 1 M, pulp density: 20% w/v, shaker speed: 200 rpm).

3.3.2. Mineral dissolution behaviors of different low-grade saprolite ores

The differences between the leaching performances of SS and SH are now discussed further. The saprolite ore samples used in this study contained both lizardite and goethite that are proven as the main nickel host mineral in lateritic ores. Goethite particles are smaller than lizardite particles (Cerpa et al., 1999; Fan and Gerson, 2011). The data in Table 3-1 show that the smaller ore particles had higher iron contents, and it can be predicted that this iron originated from goethite. This means that the smaller ore particles contain more goethite. However, goethite is very difficult to dissolve in atmospheric leaching, even with high-concentration acid solutions, especially citric acid solution. The dissolution of pure goethite using 1 M citric acid was performed in the current study to investigate the leachability of goethite in citric acid solution. Fig. 3-5 shows that iron recovery from pure goethite by 1 M citric acid solution was very low compared with those from SS and SH under the same leaching conditions. These results are consistent with those for the dissolution of natural goethite using HCl and HNO_3 under atmospheric conditions reported by Abdus-Salam and Adekola (2006). The presence of H^+ should contribute in breaking the OH^- groups of goethite and leads its dissolution easier (Valix et al., 2001a); however, goethite is stable at low temperature and dehydrates to hematite only at 130 °C (Ponsjak, 1922). It can therefore be concluded that the higher goethite content decreases the effectiveness of the leaching process. This may be one of the reasons why the highest nickel recovery was achieved with a particle size of 212–355 μm for each sample. It can also be assumed that the more leachable nickel-bearing mineral content of particles of size 212–355 μm is higher than that of the smaller particles. The slowest nickel leaching was observed for particles of size 350–855 μm, i.e., the largest ore particles, because these particles have the smallest surface areas. This result is consistent with Alibhai et al. (1993) that reported more leachable nickel-bearing phases were generally more readily available in the coarser particles, although the smaller particles carried a higher initial concentration of nickel.

Table 3-1. Chemical analyses of different sieve fractions of raw ore samples.

Ore samples	Size (µm)	Element (wt%)							
		SiO_2	Fe	Ni	Co	Mg	Mn	Cr	Al
SS	<75	41.98	17.96	1.71	0.03	9.12	0.28	0.81	2.04
	75-150	46.65	11.73	1.59	0.02	11.78	0.23	0.77	2.07
	212-355	46.50	11.02	1.53	0.02	12.54	0.20	0.71	2.10
	355-850	47.00	8.53	1.47	0.02	13.47	0.15	0.64	2.18
SH	<75	37.12	23.56	1.31	0.02	10.34	0.26	1.15	1.29
	75-150	38.23	21.98	1.27	0.02	11.67	0.21	1.10	1.31
	212-355	39.43	19.54	1.23	0.01	13.76	0.19	0.96	1.34
	355-850	40.12	18.76	1.20	0.01	14.56	0.14	0.92	1.37

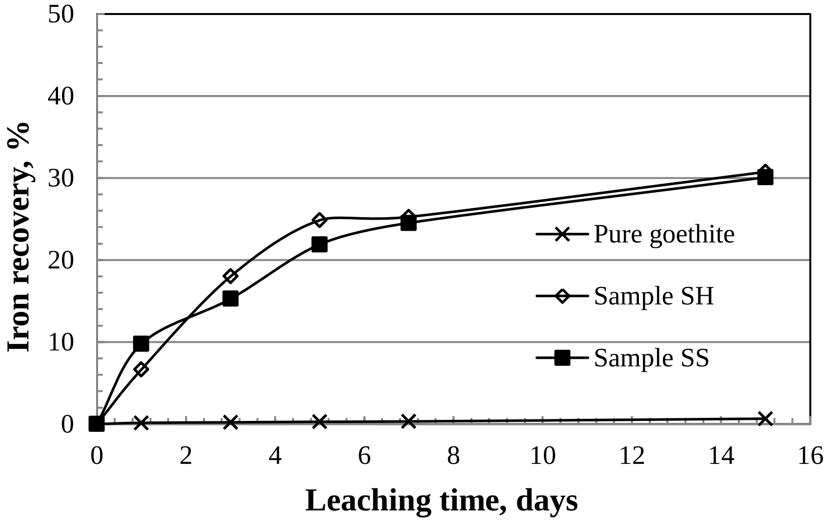

Fig. 3-5. Comparison of iron recovery rates from pure goethite, and samples SS and SH under same leaching conditions ([citric acid]: 1 M, temperature: 40 °C, pulp density: 20% w/v, ore particle size: <75 µm).

Moreover, nickel may be assumed to be incorporated not only in lizardite and goethite, but also in talc and clinochlore; therefore, nickel dissolution must always coincide with the dissolution of the other metals contained in these minerals, particularly magnesium, iron, and aluminum. Fig. 3-6 shows the dissolution of nickel and other metals in SS and SH under the optimum leaching conditions. It can be seen that the nickel recovery rates from SS and SH are both much higher than those of other metals. The figure also shows that the nickel dissolution rate is much higher than those of magnesium and iron. Accordingly, it can be predicted that the nickel originates not only from magnesium-bearing minerals such as lizardite, talc, and clinochlore, but also from other minerals in the ore, e.g., goethite. However, Fig. 3-5 shows that the leachability of goethite in 1 M citric acid solution is very low; therefore, iron and aluminum dissolved in the pregnant leaching solution may not originate from goethite. Some studies have shown that iron and aluminum can be associated with silicate mineral such as serpentine group mineral, talc, as well as clinochlore (Apstolidis, 1978; Suarez et al., 2008; Yoo et al., 2009). The nickel in the silicate ores, which are present in the brucite layer of the clay minerals, are weakly bound and therefore easily dissolved (Valix et al., 2001a). In addition, iron and aluminum can also be originated from chromite mineral. In this study, it was found that chromite can be dissolved by citric acid. In spite of low leaching rate, chromium ions were also detected in the pregnant leaching solution that is presented in Fig. 3-7.

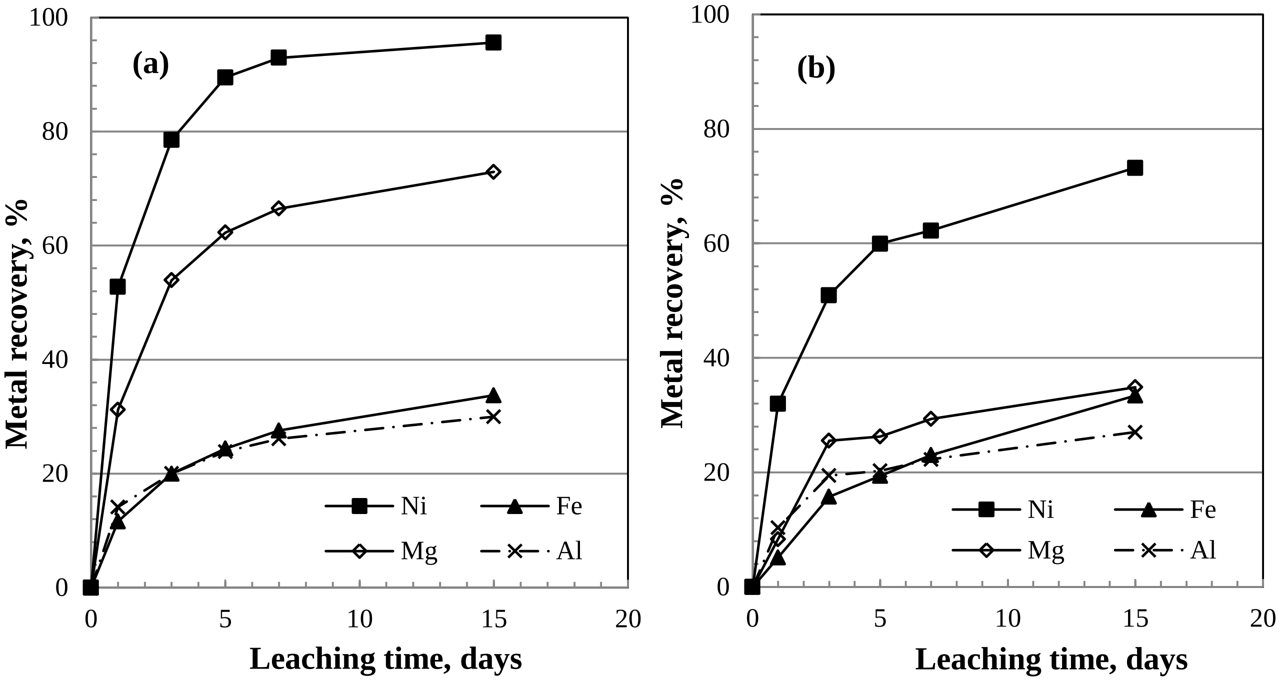

Fig. 3-6. Metal dissolutions under optimum leaching conditions: (a) sample SS and (b) sample SH (temperature: 40 °C, [citric acid]: 1 M, ore particle size: 212–355 μm, pulp density: 20% w/v, shaker speed: 200 rpm).

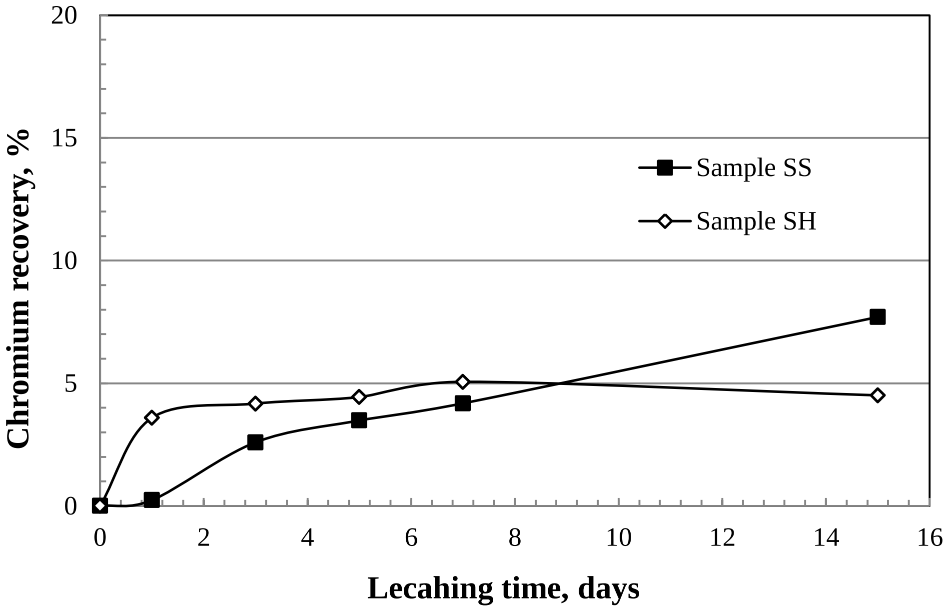

Fig. 3-7. Chromium recovery from sample SS and sample SH.

Furthermore, in order to ascertain the leachability of mineral, the XRD analyses of solid residue after leaching were observed. Figs. 3-8 and 3-9 show the XRD patterns of the solid residues from SS and SH, respectively, after leaching under the optimum conditions. Figure 3-8 shows that lizardite peaks in the solid residue from SS were significantly smaller even almost disappear than those for the original sample, whereas the goethite and clinochlore peaks still remain. Similar results were obtained for SH, as can be seen from Fig. 3-9. The lizardite peaks for the solid residue from this sample decline significantly, but those for goethite and talc remain the same.

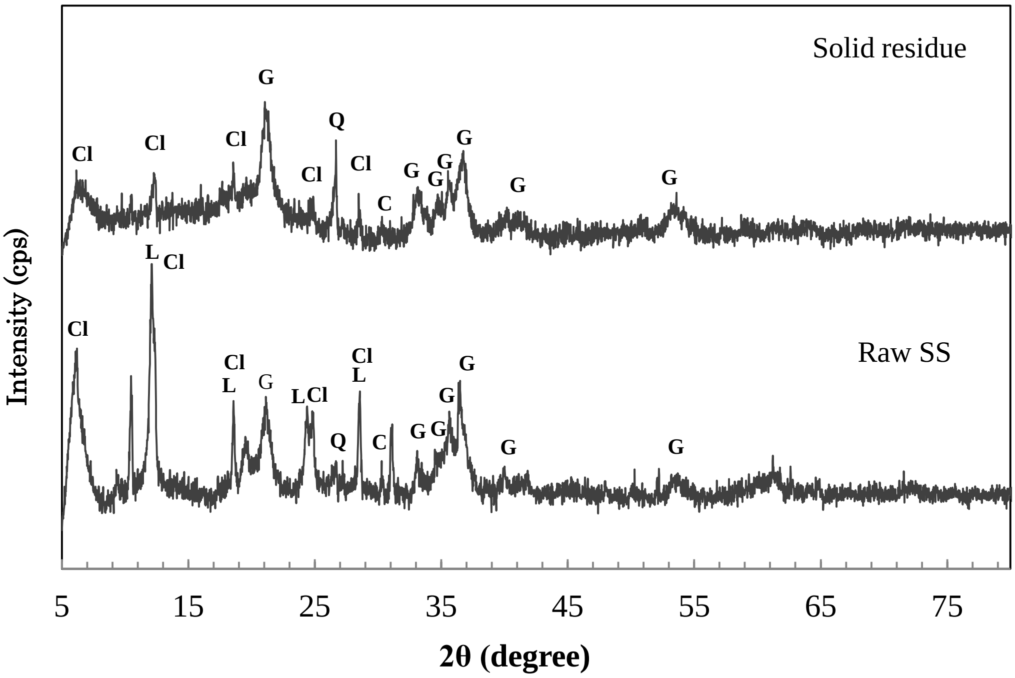

Fig. 3-8. XRD patterns of raw SS and solid residue after leaching under optimum conditions (temperature: 40 °C, [citric acid]: 1 M, ore particle size: 212–355 μm, pulp density: 20% w/v, shaker speed: 200 rpm) (L: lizardite, Cl: clinochlore, G: goethite, T: talc, C: chromite, Q: quartz).

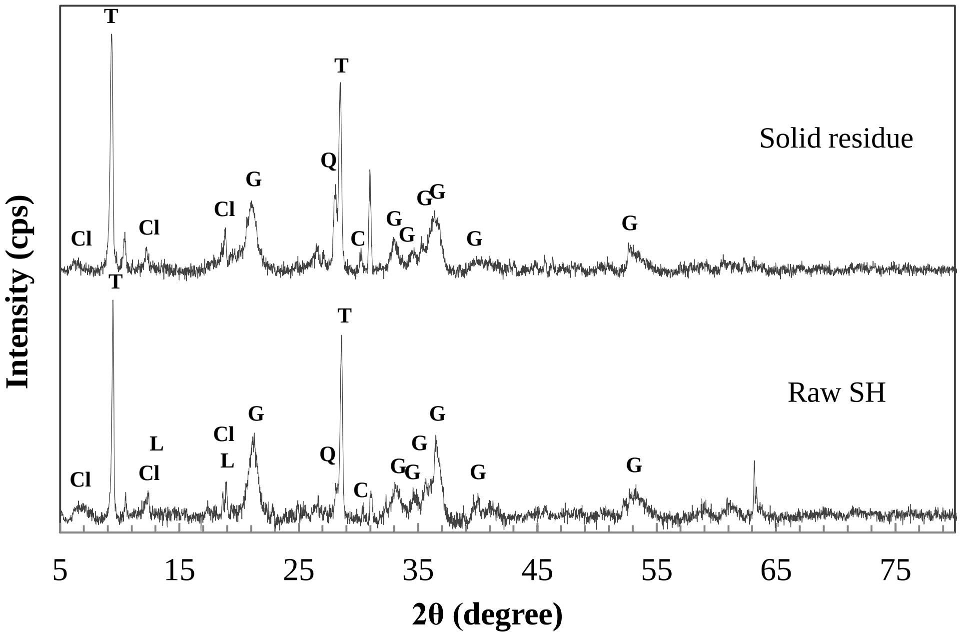

Fig. 3-9. XRD patterns of raw SH and solid residue after leaching under optimum conditions (temperature: 40 °C, [citric acid]: 1 M, ore particle size: 212–355 μm, pulp density: 20% w/v, shaker speed: 200 rpm) (L: lizardite, Cl: clinochlore, G: goethite, T: talc, C: chromite, Q: quartz).

Although lizardite, talc, and clinochlore are silicate minerals, they have different structures and physicochemical properties. In the lizardite structure, one octahedral layer is bound to one tetrahedral layer (Sufriadin et al., 2011). The octahedral sheet is mainly formed by Mg–O bonds and the tetrahedral sheet consists of Si–O bonds. Other cations such as Ni^{2+}, Co^{2+}, Al^{3+}, and Fe^{3+} may replace Mg^{2+} in the octahedral sheets. Accordingly, to leach valuable metals (Ni, Co, Al, Fe, and Mg) from these structures, it is necessary to break the octahedral sheet without disruption of the tetrahedral sheet. Acid attack on octahedral sheets may take place through both edge and gallery access mechanisms.

In contrast, talc is a 2:1 layered silicate in which one octahedral sheet is sandwiched between two tetrahedral layers. Similar to lizardite, the octahedral sheet in talc consists of Mg–O bonds and the tetrahedral layer mainly contains Si–O bonds. The dissolution rate of talc is slower than that of lizardite because the leaching layer forms only at the grain edges (Sufriadin et al., 2011). In addition, the basal faces of the layers in talc, which account for 90% of the total surface, do not contain hydroxyl groups or active ions, and the edge faces contain only a few –SiOH and –MgOH groups (Chabrol et al., 2010). Consequently, talc is hydrophobic and chemically inert (Chabrol et al., 2010); this is the reason for the low leachability of talc in the current experiments.

Moreover, clinochlore as a member of chlorite group mineral can have a rather complicated formula i.e. $(Mg,Fe,Al)_6(Si,Al)_3O_{10}(OH)_8$. The chlorite group has a structure that consists of phlogopite T-O-T (tetrahedral-octahedral-tetrahedral) layers sandwiching brucite-like octahedral layer. There is substantial substitution of Mg for Fe, and Al can substitute for (Mg, Fe) in both the octahedral sites, as well as for Si in the tetrahedral sites. This is similar to the talc structure, as discussed above, with layers of water molecules occurring between each T-O-T layer. Thus, it is predicted that the dissolution behavior of chlorite group is also similar with that of talc.

The XRD patterns of solid residues from both samples have shown that lizardite contained in the ores is the most leachable mineral using citric acid solution. It has been reported that 96% of nickel can be leached from ore SS with particle size of 212-355 μm. Hence, it is suggested that that amount of leached nickel originated from lizardite. It is also proposed that in the ore particle size of 212-355 μm, almost all nickel is contained in lizardite. It is in accordance with the most references that nickel in saprolite ores is mainly incorporated in lizardite.

In conclusion, the differences of lizardite contents of SS and SH, shown by the TG-DTA and XRD results for the raw ore samples, may be the reason for the differences between the leaching performances of the samples. It can also be concluded that all the nickel dissolved in the leaching solution should originate from lizardite, for both SS and SH. Therefore, due to the lower lizardite content in SH, the maximum nickel recovery reached from SH is less than that from SS.

In addition to strengthening these conclusions, the differences between the changes in the solution pH during the leaching process for each sample (Fig. 3-10) show that the decrease in the amount of H^+ in the leaching solution of SH is slower than that in the case of SS. This means that there are smaller amounts of easily dissolved minerals such as lizardite in SH than in SS. These results reinforce the finding that nickel can be extracted only from lizardite when citric acid solution is used in atmospheric leaching of saprolite. This finding is also consistent with some previous experiments that citric acid has proved in many studies to be the most effective organic acid for nickel extraction from serpentinitic ores in which the major nickel-containing minerals phases are not iron oxides (Bosecker 1985, 1988; Birke 1988; Paul and Henning 1993; Tarasova et al., 1993; Tzeferis and Agatzini-Leonardou 1994; Tzeferis 1994a, 1994b; Coto et al., 2001). Likewise, Bosecker (1985, 1988) noted no significant leaching of limonitic ores with organic acids while Valix et al. (2001a) concluded that although citric acid is able to effect dehydroxylation in serpentine minerals, it is less effective in dissolving goethite.

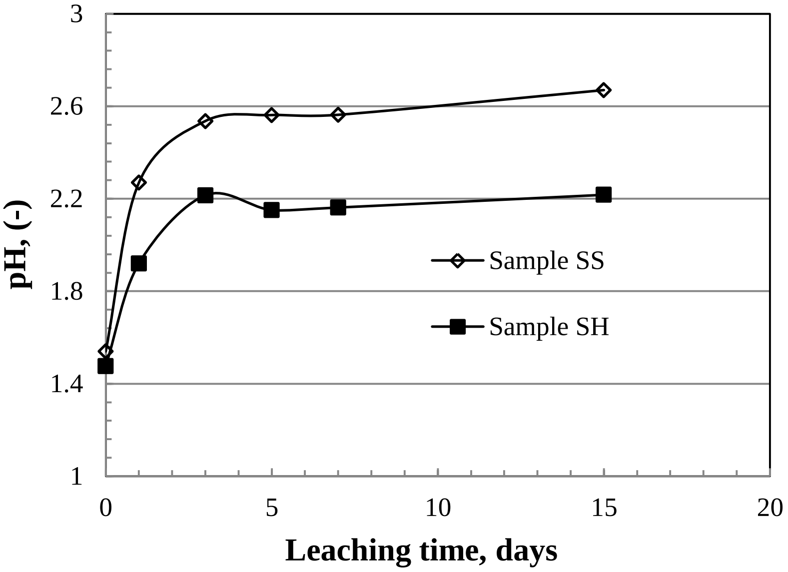

Fig. 3-10. Comparison of pH changes during leaching process for samples SS and SH under optimum conditions (temperature: 40 °C, [citric acid]: 1 M, ore particle size: 212–355 µm, pulp density: 20% w/v, shaker speed: 200 rpm).

3.3.3. Proposed nickel leaching mechanism based on the kinetic analysis and mineral dissolution behavior

A brief of kinetic analysis was performed using the experimental data for nickel dissolution from saprolite samples to ascertain the findings in the previous discussion and to create the proposed nickel leaching mechanism from the saprolite ore samples. As discussed in the previous sections, in citric acid leaching experiments, it was predicted all the nickel dissolved in the pregnant leaching solution originated from lizardite. Nickel extraction from lizardite by citric acid can be described as follows.

$$(Mg,Ni,Fe,Al)_3Si_2O_5(OH)_{4(s)} + 6\ H^+_{(aq)} \rightarrow 3Mg^{2+}_{(aq)} + 3Ni^{2+}_{(aq)} + 3Fe^{3+}_{(aq)} + 3Al^{3+}_{(aq)} + 2\ SiO_{2(s)} + 5\ H_2O_{(l)} \qquad \textbf{(3-1)}$$

H^+ is provided by dissociation of citric acid. Citric acid contains three carboxyl groups. When this acid is fully dissociated, complexation of a nickel cation with a citrate anion can be expressed as (Behera et al., 2011)

$C_6H_8O_7 \leftrightarrow (C_6H_5O_7)^{-3} + 3H^+$ (pKa$_3$ = 6.39) **(3-2)**

$Ni^{2+} + (C_6H_5O_7)^{-3} \leftrightarrow (Ni\ C_6H_5O_7)^-$ **(3-3)**

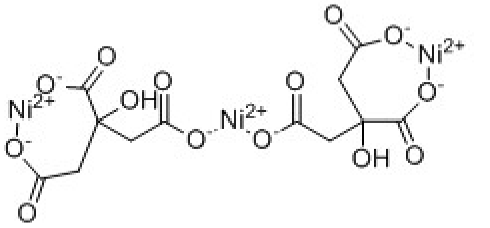

Fig. 3-11. Structure formula of nickel-citrate complex

There are two possible mechanisms for metal dissolution by citric acid: (1) attack of acid and metal ions displacement by hydronium ions, and (2) forming soluble metal–ligand complexes by metals chelation (McDonald and Whittington, 2008).

Nickel extraction from lizardite is a solid–liquid reaction. The kinetics of nickel dissolution can be represented by two solid–liquid kinetic models, proposed by Levenspiel (1999); these are the models generally used in the kinetic analysis of solid–liquid systems, and are known as the shrinking-core model (SCM) and the shrinking-particle model (SPM). In the current study, these models were used for the kinetic analysis of nickel leaching from both saprolite samples. According to the calculated regression correlation coefficients (Tables 3-2 and 3-3), the experimental data best fitted the integral rate equation for diffusion through solid product layers (Figs. 3-12 and 3-13), where X_{Ni} in those figures represents the nickel fraction reacted.

Table 3-2. Multiples regression coefficients for experimental kinetic data fitted to unreacted core models of constant size spherical particles (SCM) for all leaching parameters studied.

Sample	Model	Equation	$R^2_{min} – R^2_{max}$
SS	Product layer diffusion	$kt = 1 – 3(1 – X_{Ni})^{2/3} + 2(1 – X_{Ni})$	0.8567 – 0.9945
	Chemical reaction controls	$kt = 1 – (1 – X_{Ni})^{1/3}$	0.6561 – 0.9513
	Film diffusion	$kt = X_{Ni}$	0.6442 – 0.8528
SH	Product layer diffusion	$kt = 1 – 3(1 – X_{Ni})^{2/3} + 2(1 – X_{Ni})$	0.8848 – 0.9942
	Chemical reaction controls	$kt = 1 – (1 – X_{Ni})^{1/3}$	0.6850 – 0.8987
	Film diffusion	$kt = X_{Ni}$	0.6736 – 0.8621

Table 3-3. Multiples regression coefficients for experimental kinetic data fitted to shrinking spherical particles model (SPM) for all leaching parameters studied.

Sample	Model	Equation	$R^2_{min} – R^2_{max}$
SS	Chemical reaction controls	$kt = 1 – (1 – X_{Ni})^{1/3}$	0.6561 – 0.9513
	Film diffusion	$kt = 1 – (1 – X_{Ni})^{2/3}$	0.6502 – 0.8993
SH	Chemical reaction controls	$kt = 1 – (1 – X_{Ni})^{1/3}$	0.6850 – 0.8987
	Film diffusion	$kt = 1 – (1 – X_{Ni})^{2/3}$	0.6793 – 0.8809

The apparent rate constants were determined from the slopes of the lines in Figs. 3-12(b) and 3-13(b). The apparent rate constant can be used to determine the temperature dependence, based on the Arrhenius equation:

$$k_d = \mathrm{A}\exp(-\frac{E_a}{RT}) \qquad \textbf{(3-4a)}$$

$$\ln k_d = \ln A - \frac{E_a}{RT} \qquad \textbf{(3-4b)}$$

The activation energies (*E*) were determined from Arrhenius plots of the apparent rate constants for each experiment (Figs. 3-12(b) and 3-13(b)). The results show that the activation energies of the leaching process for both samples are similar amount, around 14 to 17 kJ/mol. This low-activation energy corresponds to a process controlled by diffusion through a solid product layer. These results are in agreement with those reported by Luce et al. (1972) and Teir et al. (2007), who found that either diffusion of ions in the mineral lattice itself or through a product layer is the rate-controlling mechanism for serpentine dissolution. The undetected silicon in the pregnant leaching solution, based on ICP-OES analysis in the current study, supports the proposal that a product layer of silica builds up on the particles.

The current analysis also shows that the kinetic behaviors of nickel leaching from both SS and SH are similar, although the nickel-leaching performances of the samples are different. These results support the finding that for both samples all the dissolved nickel originated from the same mineral, i.e., lizardite. The differences between the nickel-leaching performances are influenced purely by the differences between the lizardite contents of the samples. It can therefore be concluded that the performances in atmospheric leaching of nickel from saprolite ores by citric acid depend on the lizardite contents.

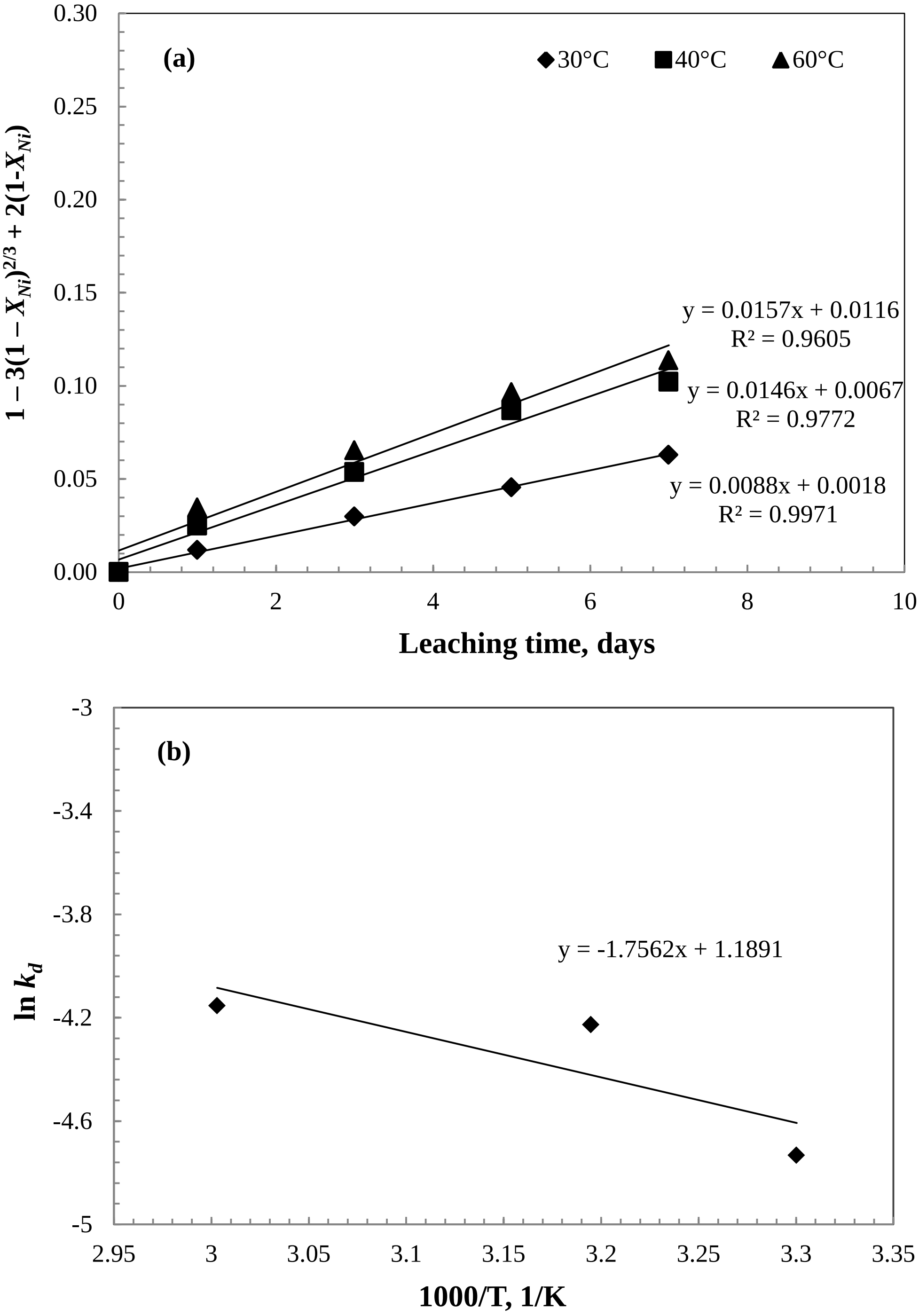

Fig. 3-12. (a) Plot of $1 - 3(1 - X_{\mathrm{Ni}})^{2/3} + 2(1 - X_{\mathrm{Ni}})$ vs leaching time at different temperatures for extraction of nickel from sample SS and (b) Arrhenius plot for nickel leaching (1 M citric acid, 20% (w/v) pulp density, <75 μm particle size, 200 rpm shaker speed).

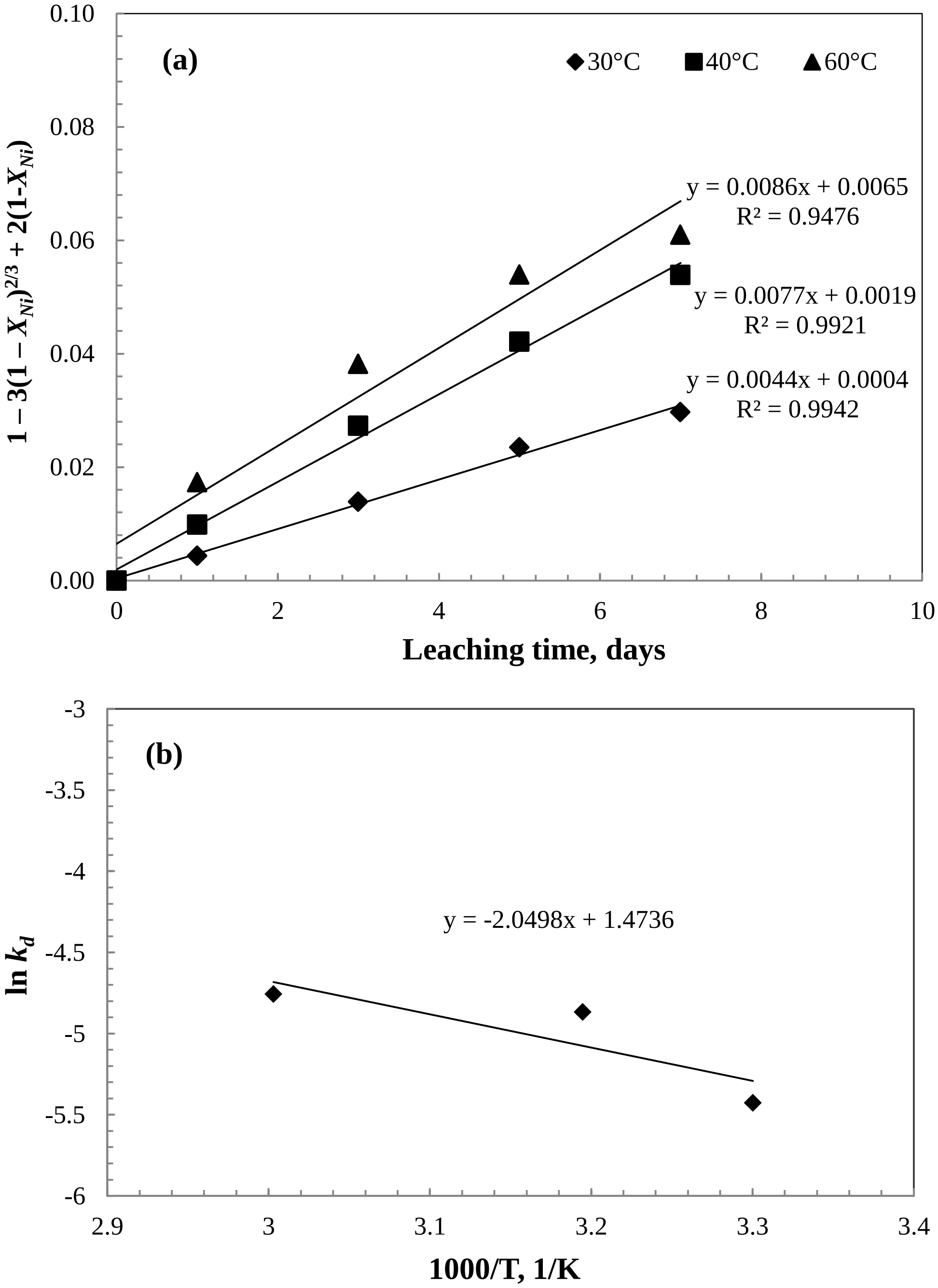

Fig. 3-13. (a) Plot of $1 - 3(1 - X_{\mathrm{Ni}})^{2/3} + 2(1 - X_{\mathrm{Ni}})$ vs leaching time at different temperatures for extraction of nickel from sample SH and (b) Arrhenius plot for nickel leaching (1 M citric acid, 20% (w/v) pulp density, <75 μm particle size, 200 rpm shaker speed).

The kinetic analysis results also verify that nickel would not be extracted from goethite because nickel dissolution from goethite should follow the SPM kinetically, according to the goethite dissolution reaction:

$$\alpha\text{-(Fe,Al,Ni)OOH}_{(s)} + 3H^{+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + Al^{3+}_{(aq)} + Ni^{2+}_{(aq)} + 2H_2O_{(l)} \quad \textbf{(3-5)}$$

It can be seen that goethite dissolution by an acid does not produce a solid product. Canterford (1978) also suggested that to extract all the nickel from goethite phase, it is necessary to dissolve the whole nickel-bearing goethite grain. This means that there is no solid product to create a porous solid product layer, as required by the SCM. This reaction differs from lizardite dissolution (Eq. 3-1), in which the silica in lizardite is the solid product during and after leaching. This silica forms a product layer, which causes the particle size of lizardite during and after leaching to be constant. It was consistent with the microstructure of lizardite that was evaluated before and after leaching using SEM-EDS as shown in Fig. 3-14. It can be seen that lizardite mineral after leaching process become porous and silica content increase. It is proven that the solid product layer (SiO_2) in the solid residue occurs during leaching that is in accordance with equation (3) in the manuscript. This result was consistent with the shrinking core model requirement.

Widi Astuti et al. (2015, in press) proposed a scheme for the mechanism of nickel leaching from lizardite by citric acid. Based on some of the results of the present study, a scheme for the leaching mechanism of some metals (Ni, Fe, Mg, and Al) from lizardite minerals in saprolite ores using citric acid solution at atmospheric pressure is proposed; the mechanism is shown in Fig. 3-15. In this mechanism, lizardite is represented as a nonporous solid. The chemical reaction between the leaching agent, i.e., citric acid, and a metal (Ni, Fe, Mg, or Al) occurs at the lizardite surface, and nickel and other metals are dissolved. Silica remains in the reacted layer, as shown in Eq. (3-1), and the reacted layer becomes porous. The next step is penetration and diffusion of citric acid through the reacted layer to the surface of the unreacted core, and a chemical reaction at the surface of the unreacted core. Finally, the dissolved product diffuses through the solid reacted layer back to the exterior surface of the solid and into the main bulk of the fluid.

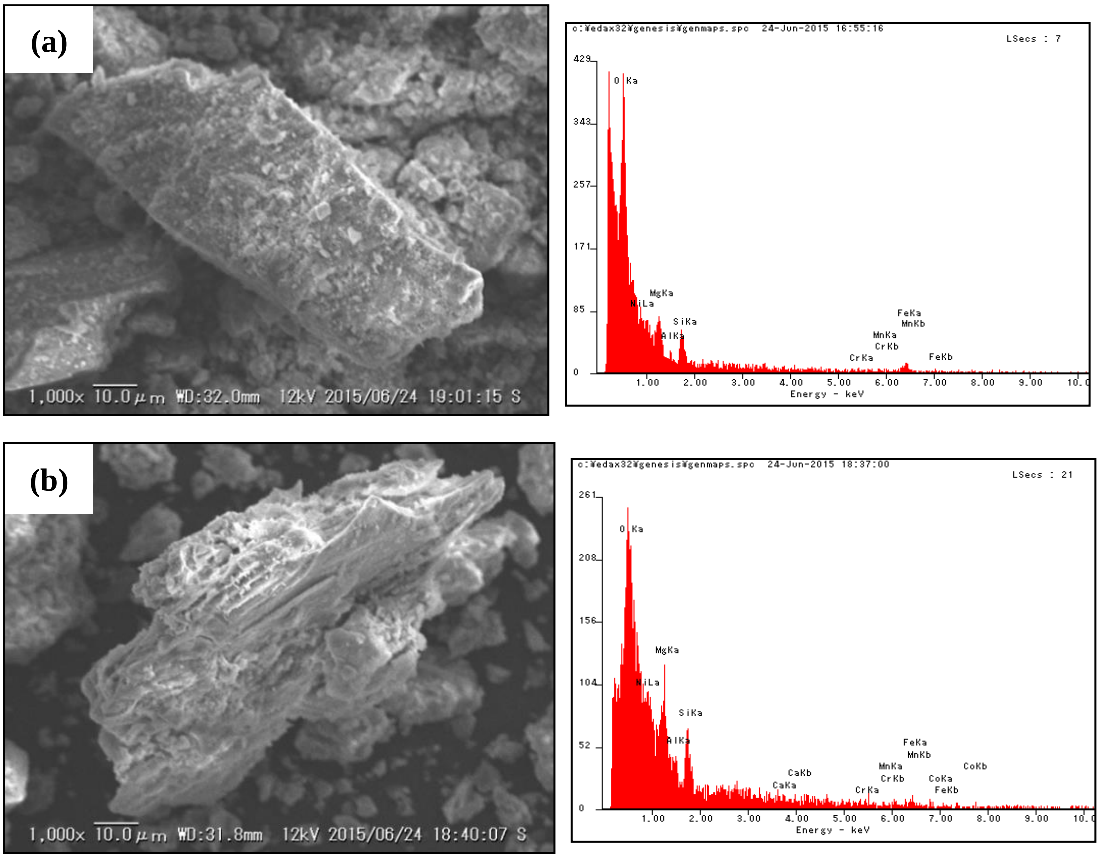

Fig. 3-14. Microstructure and EDS analyses of lizardite in **(a)** raw ore and **(b)** solid residue.

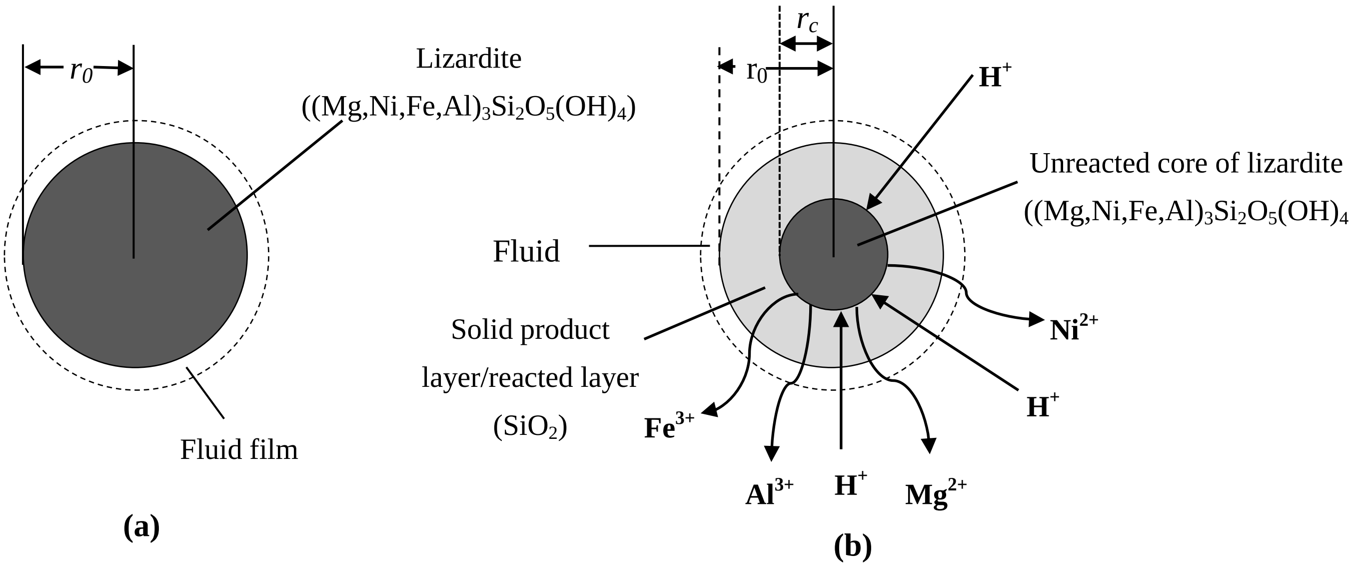

Fig. 3-15. Schematic diagram of nickel-leaching process from lizardite based on shrinking-core model: (a) initial state and (b) state at time *t*.

3.4. Conclusions

From the findings specified in this paper, it can be concluded that the effects of the experimental parameters on nickel extraction are significant. The optimum recovery of nickel was achieved from saprolite ore under suitable leaching conditions, i.e., citric acid concentration 1 M, leaching temperature 40 °C, leaching time 15 days, ore particle size 212–355 μm, shaking speed 200 rpm, and pulp density 20% w/v. Nickel recovery from SS was higher than that from SH under the same leaching conditions. Around 96% nickel recovery was achieved from SS, but only 73% nickel was leached from SH under the optimum leaching conditions.

The nickel recovery results and analysis of the solid residues using XRD indicated that all dissolved nickel originated from lizardite, which is more easily leached than goethite, clinochlore, and talc. Because of the lower lizardite content of SH, nickel recovery from this sample was lower than that from SS. In terms of the kinetics of nickel extraction, the results for both ore samples were similar, and showed that nickel leaching from SS and SH follow the SCM and are controlled by diffusion through a solid product layer. This kinetic analysis ascertain the finding that all nickel in the pregnant leaching solution absolutely originated from lizardite, while nickel from goethite mineral cannot be dissolved by citric acid solution even in high citric acid concentration. From this experimental result, it can be concluded that the nickel recovery value from citric acid leaching process can be predicted from lizardite composition contained in ore samples. These finding are also significant for the design of nickel-leaching processes for different lateritic ores using citric acid at atmospheric conditions and low temperature.

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CHAPTER 4

Kinetic Modeling of Nickel Extraction from Low-Grade Indonesian Saprolite Ore by Citric Acid Leaching

In this chapter, the detail kinetics modeling of leaching of a low-grade saprolite ore from Sulawesi Island (Indonesia) by citric acid solution under atmospheric pressure was investigated. The experimental data were well interpreted by the shrinking core model with the rate of reaction controlled by diffusion through the solid product layer. Finally, on the basis of the shrinking core model, the empirical kinetic model for leaching of nickel from this Indonesian saprolite ore was proposed in the mathematical expression.

4.1. Introduction

The rate of leaching is the most important parameter when batch leaching systems have to be designed. Moreover, kinetic analysis and modeling is used to determine the rate of leaching process. Therefore, kinetic study of any chemical reaction is an indispensable part in designing the chemical process at leaching stage. Most of the leaching processes are reactions occur between liquid and solid phases. The models that have been used to express kinetics of non-catalytic liquid–solid reactions are the homogeneous, grain, uniform pore and random pore models, shrinking models (including shrinking particle and shrinking core model), (Gbor and Jia, 2004; Georgiou and Papangelakis, 1998).

In the previous chapter, numerous citric acid leaching processes have been studied in an attempt to find a suitable explanation for the citric acid leaching mechanism and a brief of the leaching kinetics. However, all the parameters affecting the Indonesian low-grade saprolite leaching kinetics modeling have not been investigated in detail. The present study therefore investigates the effects of various leaching parameters (i.e. leaching temperatures, citric acid concentration, pulp density, and ore particle size) on the leaching kinetics of a low-grade saprolite from Sulawesi Island (Indonesia) by citric acid solution at atmospheric pressure. Kinetic measurements were modeled and used to identify the rate-determining step of the leaching process and to calculate the kinetic parameters. Empirical mathematical model of nickel leaching kinetic was created to express the nickel leaching rate based on the experimental results. Moreover, the kinetic aspects of nickel-leaching by citric acid solution which provided a theoretical basis for the industrial application in the future had been studied.

4.2. Material and methods

4.2.1. Material

Saprolite ore was collected from one of the mining site areas in Sulawesi Island, Indonesia. The sample was mineralogically and chemically characterized. The mineral phases of the sample were determined using X-ray diffractometry (XRD; Ultima IV, Rigaku, Tokyo, Japan) with Cu Kα radiation between 5° and 80° 2θ. The XRD pattern of this raw ore has been depicted in Chapter 2, Fig. 2-1. Lizardite [$Mg_3Si_2O_5(OH)_4$], goethite (FeOOH), and chlorite group (clinochlore) [$Mg_6Si_4O_{10}(OH)_8$] were the predominant minerals, while chromite ($FeCr_2O_4$) and quartz (SiO_2) were minor phases. X-ray fluorescence (XRF; ZSX Primus II, Rigaku, Tokyo, Japan) and inductively coupled plasma-optical emission spectroscopy (ICP-OES; Perkin Elmer 8500, Waltham, MA, USA) were used to determine the chemical composition. Chemical content of the ore from ICP-OES and XRF analyses showed that this ore contains 1.76% Ni, 0.06% Co, 8.44% Mg, 21.64% Fe, 36.30% SiO_2, 2.04% Al, and 0.43% Mn. This ore also contains high chromium (1.07 %) that is mainly incorporated in chromite mineral.

4.2.2. Chemical leaching procedures

Chemical leaching experiments were performed using a 300-mL flask placed in a mechanical shaker using a 200-rpm shaker speed at atmospheric pressure. Analytically pure citric acid was used as the leaching agent. Solution samples were periodically withdrawn for pH measurement and chemical analyses for nickel and other elements by ICP-OES using standard procedures.

The kinetic analysis was performed based on experimental data for the dissolution of nickel. Kinetic experiments were carried out under the following reaction conditions: leaching temperatures of 30°C, 40°C, and 60°C; citric acid concentrations of 0.1 M, 0.5 M, and 1 M; shaking speed of 200 rpm, pulp densities of 5%, 10%, 20%, and 30% (w/v); and ore particle sizes of <75 μm, 75–150 μm, 212–355 μm, and 355–850 μm.

4.3. Results and discussion

4.3.1. Effect of various leaching parameters on nickel extraction

As discussed previously in Chapter 3, the shrinking core model (SCM) was the best kinetic model that fit with the nickel leaching process from saprolite ores. In this chapter, the more detail of leaching kinetics study including the calculation of mathematical model of this leaching system was investigated. Various leaching parameter effects namely leaching temperature, citric acid concentration, pulp density, and ore particle size were applied to construct the mathematical model of leaching kinetics.

Effect of leaching temperature on nickel extraction

Leaching temperature is a significant parameter influencing nickel extraction. The leaching tests were carried out using 1 M citric acid, 5% (w/v) pulp density, ore particle size of <75 μm, and 200 rpm shaker speed at three different leaching temperatures (30°C, 40°C, and 60°C). The results, shown in Fig. 4-1, indicate that temperature has appreciable effect on nickel extraction. The maximum nickel leaching recovery increased from 63% at 30°C to 73% at 40°C after 15 days of leaching. However, nickel recovery was not strongly influenced on further increasing the temperature: the nickel recovery rose slightly from 73% at 40°C to 77% at 60°C.

Moreover, the leaching selectivity of nickel over other metals at 60°C is lower than that at 40°C, as can be seen in Fig. 4-2. A lower leaching temperature is preferable, technically and economically, therefore a leaching temperature of 40 °C was used for subsequent leaching experiments. These experiments also showed that longer leaching time leads to higher nickel recovery, up to an optimum value.

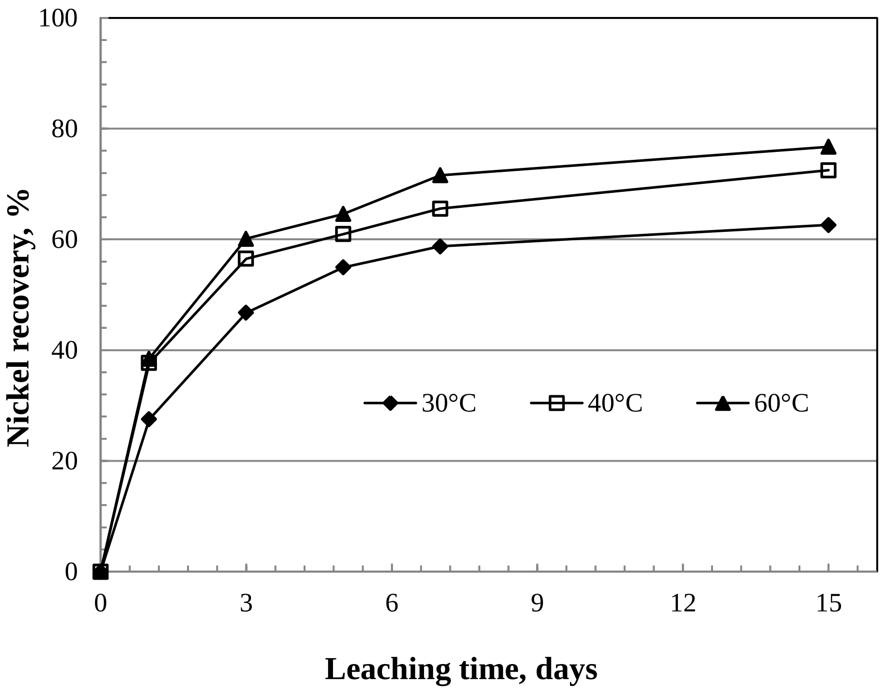

Fig. 4-1. Effect of leaching temperature on the nickel recovery (1 M citric acid, 5% (w/v) pulp density, <75 µm particle size, 200 rpm shaker speed).

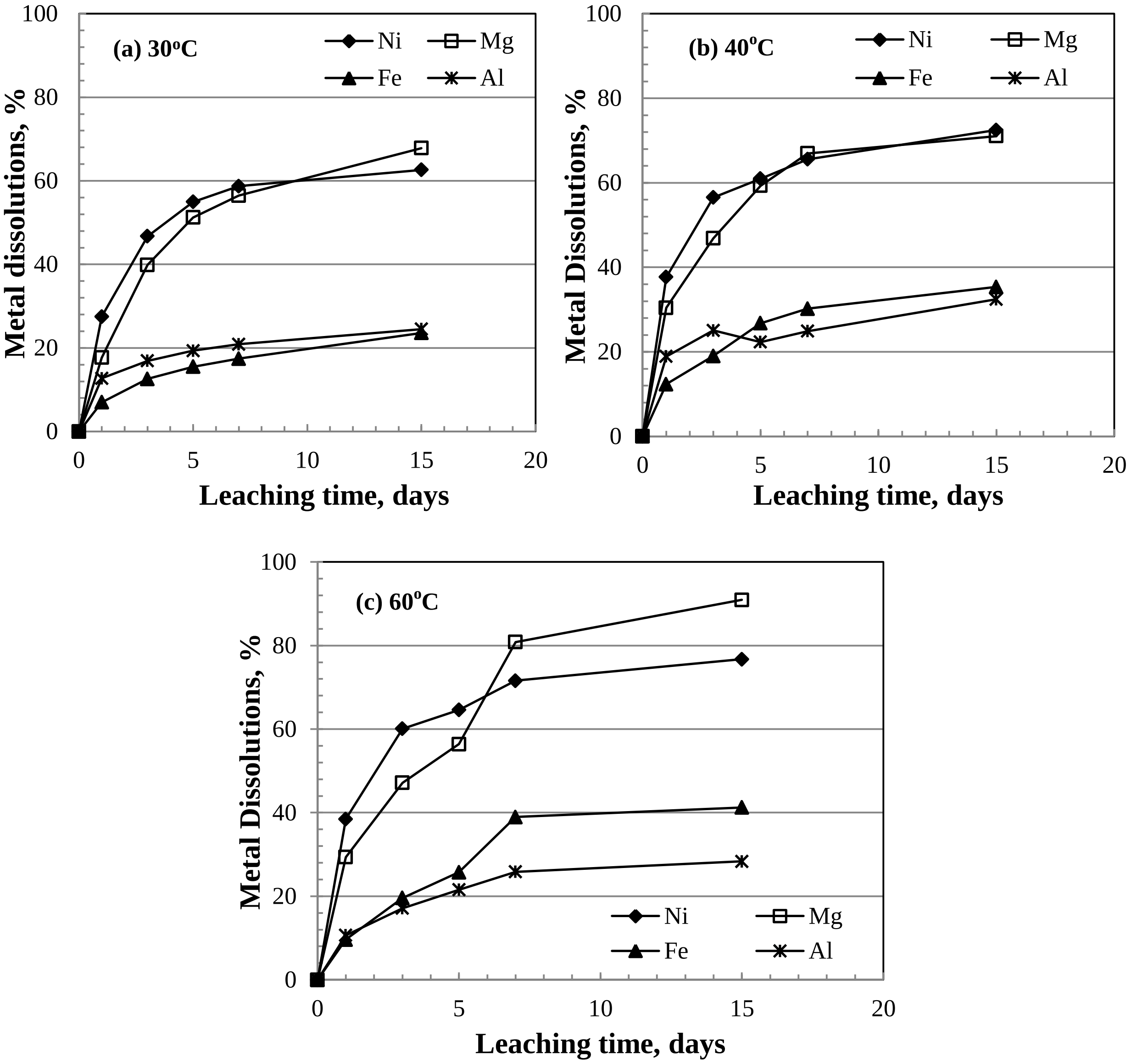

Fig. 4-2. Effect of leaching temperature on metal dissolutions **(a)** 30°C; **(b)** 40°C; **(c)** 60°C (1 M citric acid, 5% (w/v) pulp density, <75 μm particle size, 200 rpm shaker speed).

Effect of citric acid concentration on nickel extraction

Citric acid concentration is also a significant parameter influencing nickel extraction. The effects of citric acid on the nickel recovery were studied for concentrations of 0.1 M, 0.5 M, and 1 M at 40°C, 200 rpm shaker speed, and atmospheric pressure using <75 μm ore particle size and 5% (w/v) pulp density. The results presented in Fig. 4-3 show that the nickel dissolution and leaching rate are strongly dependent on the citric acid concentration. The citric acid concentration could be increased to a certain limit. Using the low acid concentration, namely 0.1 M, there was an acid deficiency and only 49% of the nickel was extracted after 15 days. Nickel extraction increased to 70% and 73% when the citric acid concentrations increased to 0.5 M and 1 M, respectively. This effect is attributed to an increase in the hydronium ion (H^+) activity with increasing acid concentration, which leads to further dissolution of nickel-containing material.

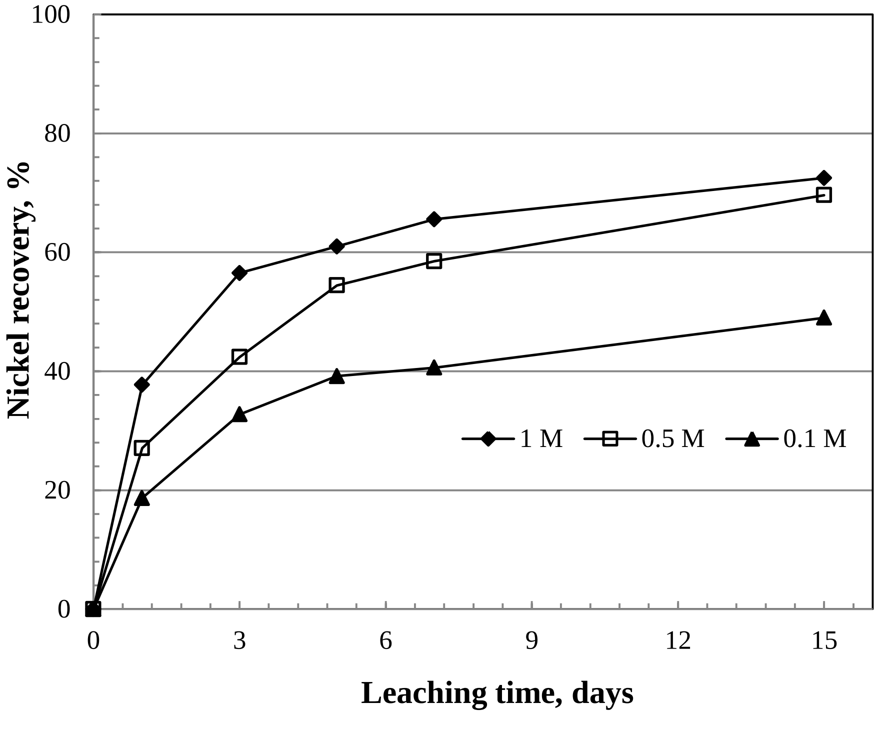

Fig. 4-3. Effect of citric acid concentration on nickel recovery (40°C, 5% (w/v) pulp density, <75 μm particle size, 200 rpm shaker speed).

Effect of pulp density on nickel extraction

The influences of pulp densities at 5%, 10%, 20%, and 30% (w/v) on nickel recovery were also examined. Citric acid concentration (1 M), ore particle size (<75 μm), temperature (40°C), and shaker speed (200 rpm) were kept constant. The experimental results in Fig. 4-4 show that nickel concentration in the filtrate increased sharply with an increase in pulp density. However, when nickel recoveries are calculated, Fig. 4-5 shows that nickel recovery after 15 days rose slightly from 73% at a pulp density of 5% (w/v) to 75% and 79% at pulp densities of 10% (w/v) and 20% (w/v), respectively, and then decreased to 73% at a pulp density of 30% (w/v). From these results, it is recognized that a moderate pulp density of 20% (w/v) was adequate in the current study. This value was used in all subsequent leaching tests.

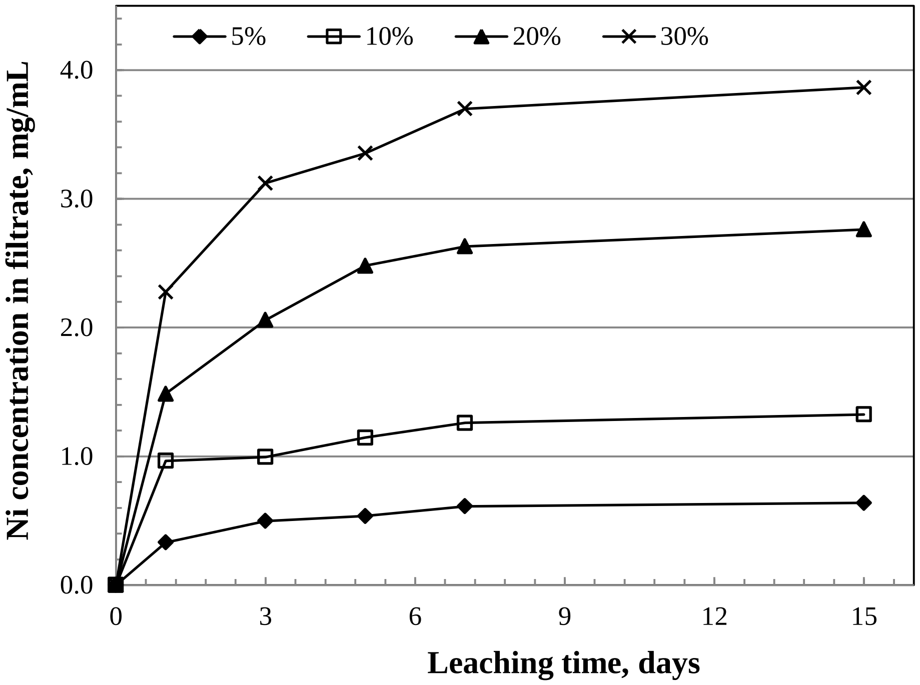

Fig. 4-4. Nickel concentration in the filtrate for various pulp densities (1 M citric acid, 40°C, <75 μm particle size, 200 rpm shaker speed).

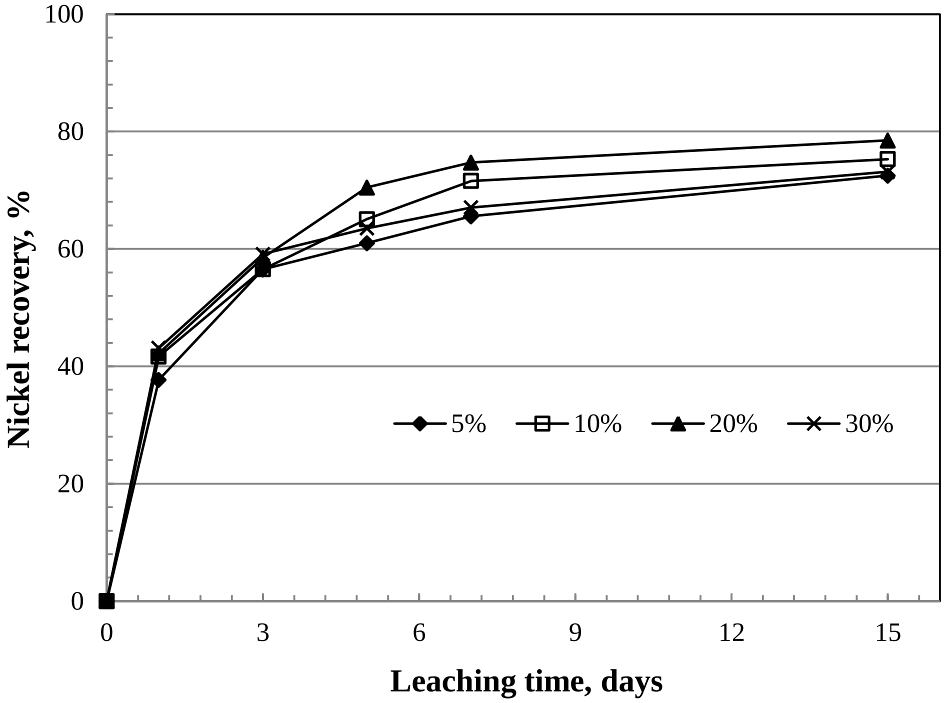

Fig. 4-5. Effect of pulp density on nickel recovery (1 M citric acid, 40°C, <75 μm particle size, 200 rpm shaker speed).

Effect of ore particle size on nickel extraction

The effect of ore particle size on nickel recovery was studied for four different size ranges: <75 μm, 75−150 μm, 212−355 μm, and 355−850 μm. All experiments were conducted at 40°C, 200 rpm shaker speed, and atmospheric pressure using 1 M citric acid concentration and 20% pulp density. As demonstrated in Fig. 4-6, an increasing particle size offered improved nickel recovery up to 212–355 μm. This particle size yielded the maximum nickel recovery (96%), followed by the 75–150 μm, <75 μm, and 355–850 μm particle sizes that produced 92%, 79%, and 76% nickel recovery, respectively, after 15 days of leaching. The optimum particle size was selected as the 212–355 μm range.

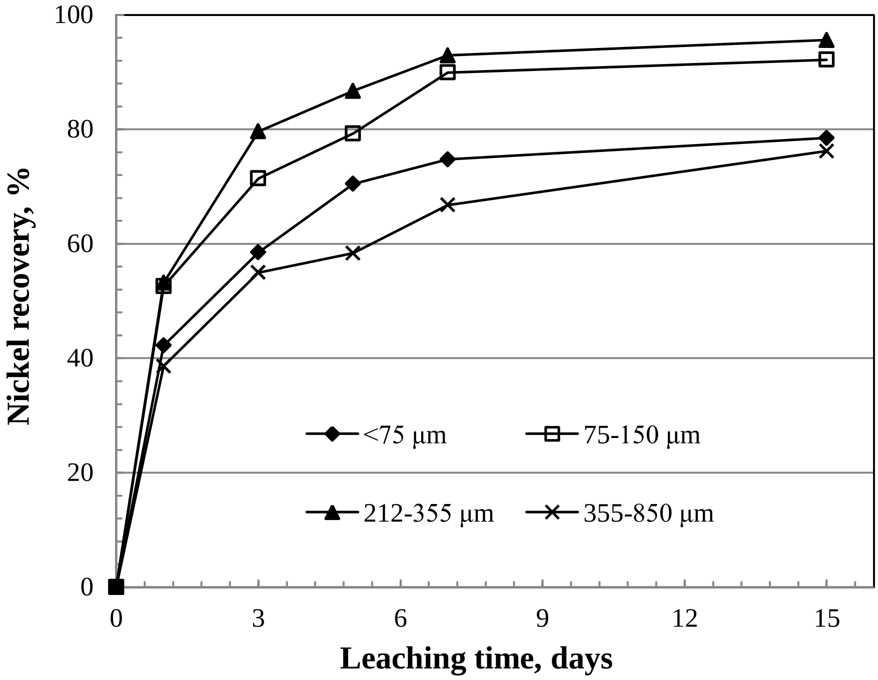

Fig. 4-6. Effect of ore particle size on nickel recovery (1 M citric acid, 40°C, 20% w/v pulp density, 200 rpm shaker speed).

4.3.2. Kinetic analysis and modeling of nickel extraction

As discussed in Chapter 3 that kinetics of nickel leaching in this study followed the shrinking core model (SCM). In this chapter, the mathematical model of nickel leaching kinetics is calculated based on the experimental data obtained as shown in section *4.3.1. Effect of various leaching parameters on nickel extraction*. The SCM equations for the three rate-determining steps can be written as follows (Equations 4-1 to 4-3) (Levenspiel, 1999):

Fluid film diffusion control:

$$x = k_f t = k \exp\left(-\frac{E_a}{RT}\right) t \qquad \textbf{(4-1)}$$

Diffusion through solid product layer control:

$$1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) = k_d t = k \exp\left(-\frac{E_a}{RT}\right) t \qquad \textbf{(4-2)}$$

Chemical reaction control:

$$1 - (1 - x)^{\frac{1}{3}} = k_r t = k \exp\left(-\frac{E_a}{RT}\right) t \qquad \textbf{(4-3)}$$

where x is the fraction reacted, k is the overall reaction rate constant in min^{-1}, A is the frequency factor in min^{-1}, E_a is the apparent activation energy in J mol^{-1}, R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the reaction temperature in K, k_f, k_d, and k_r are the rate constants, and t is the leaching time in day.

The left-hand sides of Equations 4-1 to 4-3 were plotted with respect to leaching time and the dependencies of these models on the kinetic data were evaluated using the correlation coefficient (R^2) values. The slopes of these plots give the apparent rate constants (k_f , k_d, and k_r).

The apparent activation energy was calculated based on the Arrhenius equation (Equations 4-4a and 4-4b):

$$k_d = \mathrm{A} \exp(-\frac{E_a}{RT}) \qquad \textbf{(4-4a)}$$

$$\ln k_d = \ln A - \frac{E_a}{RT} \qquad \textbf{(4-4b)}$$

Arrhenius plots of ln k_d (the apparent rate constant for control by diffusion through the solid product layer for the SCM) against 1000/T for the experimental data are shown in Fig. 4-7 and Table 4-1. The apparent activation energy determined for nickel extraction from this Indonesian saprolite using citric acid at atmospheric pressure was approximately 12.38 kJ/mol.

Table 4-3. Reaction rate constant at various temperatures

T, (^{o}C)	T, (K)	1000/T, (1/K)	k_d	ln k_d
30	303	3.3003	0.0080	-4.828
40	313	3.1949	0.0100	-4.605
60	333	3.0030	0.0126	-4.374
Activation energy	12.38 kJ/mol			

This low activation energy is appropriate for a process that is controlled by the diffusion through a solid product layer and provides further confirmation of the importance of diffusion through product layer as the kinetic-limiting step (Veglio et al., 2001). Previously reported low values (<24 kJ/mol) for the activation energy of diffusion-controlled reactions are: 4–12 kJ/mol (Hou et al., 2010; Habashi, 1969), 8–20 kJ/mol (Liu et al., 2012), and 12–24 kJ/mol (Romankiw et al., 1964). In contrast, a leaching process controlled by a surface chemical reaction has higher activation energies: 40–80 kJ/mol (Habashi, 1969; Sohn and Wadsworth, 1979; Luo et al., 2010).

The current work also found that the kinetic behavior of citric acid leaching differs from that of sulfuric acid leaching under atmospheric conditions. Luo et al. (2010) analyzed the kinetics of saprolite leaching by sulfuric acid and reported that the chemical reaction is the rate-determining step. However, in the current work using citric acid, it is found that diffusion through the solid product layer is rate limiting. A diffusion-controlled process is usually slightly dependent on temperature while a chemically controlled process is very sensitive to temperature (Habashi, 1969; Sohn and Wadsworth, 1979). These experiments show that citric acid leaching can produce high nickel recoveries at lower temperature and atmospheric conditions. The optimum nickel recovery achieved in this study was 96% at 40°C. Previous work on the sulfuric acid leaching of saprolite ore under atmospheric pressure only produced maximum nickel recoveries of 84.8% (Luo et al., 2010) and 58% (Sufriadin et al., 2011), respectively, at 90°C leaching temperature.

Similar plots of $1 - 3(1-x)^{\frac{2}{3}} + 2(1-x)$ as a function of leaching time were obtained for different citric acid concentrations [$C_6H_8O_7$], solid-liquid ratios (or pulp densities) (S/L), and ore particle sizes (r_0) (Figs. 4-8(a), 4-9(a), and 4-10(a)). These control factors were used to formulate the kinetic model. The relationship between the apparent rate constant of diffusion through the solid product (k_d) and these factors is given by the following equation:

$$k_d = k_0[C_6H_8O_7]^a(S/L)^b(r_0)^c e^{\frac{-E_a}{RT}} \quad \textbf{(4-5)}$$

Hence, the total kinetic model from Equations 4 and 10 is obtained as:

$$1 - 3(1-x)^{\frac{2}{3}} + 2(1-x) = k_d t = k_0[C_6H_8O_7]^a(S/L)^b(r_0)^c e^{\frac{-E_a}{RT}} t$$

where k_0 is the Arrhenius constant, which can be calculated from the intercept of the straight line in Fig. 4-7.

The apparent rate constant (k_d) values were determined from the slopes of the straight lines. Plots of ln (k_d) against ln [$C_6H_8O_7$], ln (S/L), and ln (r_0) (Figs. 4-8(b), 4-9(b), and 4-10(b), respectively) were established to calculate the empirical orders of dependency with respect to citric acid concentration, pulp density, and ore particle size as 0.48, 0.27, and 0.32, respectively. The Arrhenius equation obtained from Fig. 4-7 is $\ln k_d = 0.1100 - \frac{1488}{\mathrm{T}}$.

Thus, $k_0\,[\mathrm{C_6H_8O_7}]^{0.48}(\mathrm{S/L})^{0.27}(\mathrm{r_0})^{0.32} = \exp(0.1100) = 1.1163.$

Substituting $[\mathrm{C_6H_8O_7}] = 1\ \mathrm{M}$, $(\mathrm{S/L}) = 0.05\ (w/v)$, and $r_0 = 15\ \mu\mathrm{m}$, gives $k_0 = 7.32\ x\ 10^{-4}\ \mathrm{min}^{-1}$. Therefore, the empirical kinetic model for nickel extraction from this Indonesian saprolite by citric acid leaching under atmospheric pressure is:

$$k_d t = 1 - 3(1-x)^{\frac{2}{3}} + 2(1-x)$$

$$= 7.32\ x\ 10^{-4}[C_6H_8O_7]^{0.48}(S/L)^{0.27}(r_0)^{0.32}e^{\frac{-12{,}380}{RT}}t$$

To validate this empirical kinetic model, the values of $1 - 3(1-x)^{\frac{2}{3}} + 2(1-x)$ at selected leaching conditions of temperature, citric acid concentration, pulp density, and particle size were calculated from the empirical mathematical model. The plots of $[1 - 3(1-x)^{\frac{2}{3}} + 2(1-x)]_{equation}$ against $[1 - 3(1-x)^{\frac{2}{3}} + 2(1-x)]_{experimental}$ for some experimental data in Fig. 4-11 show good correlation between the empirical kinetic equation and the experimental data. It is concluded that the proposed empirical kinetic model from the present study can be used to calculate the nickel dissolution rate of this saprolite ore using citric acid under atmospheric pressure and the current leaching conditions.

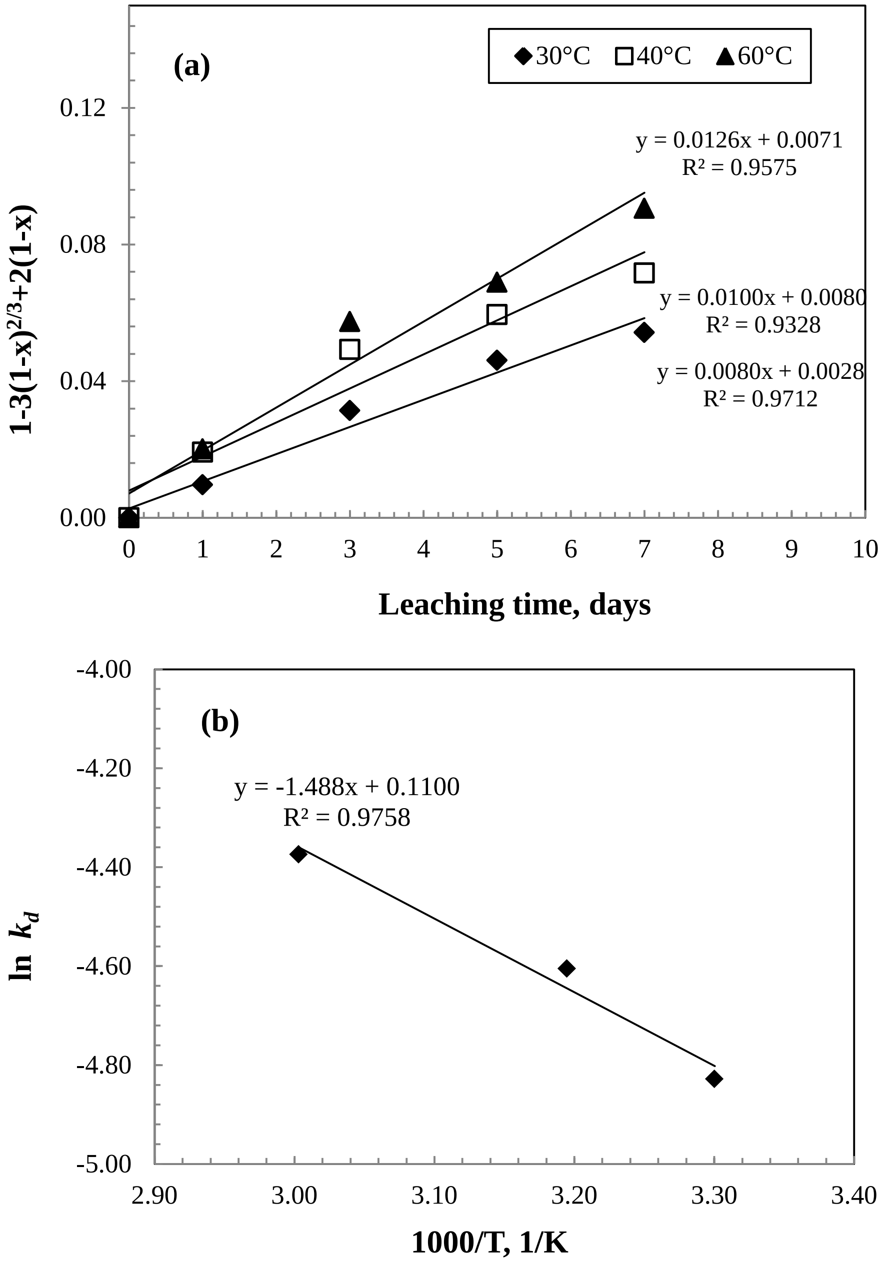

Fig. 4-7. (a) Plot of diffusion through the solid product layer for the SCM with leaching time at various temperatures; **(b)** Arrhenius plot for nickel leaching (1 M citric acid, 5% (w/v) pulp density, <75 μm particle size, 200 rpm shaker speed).

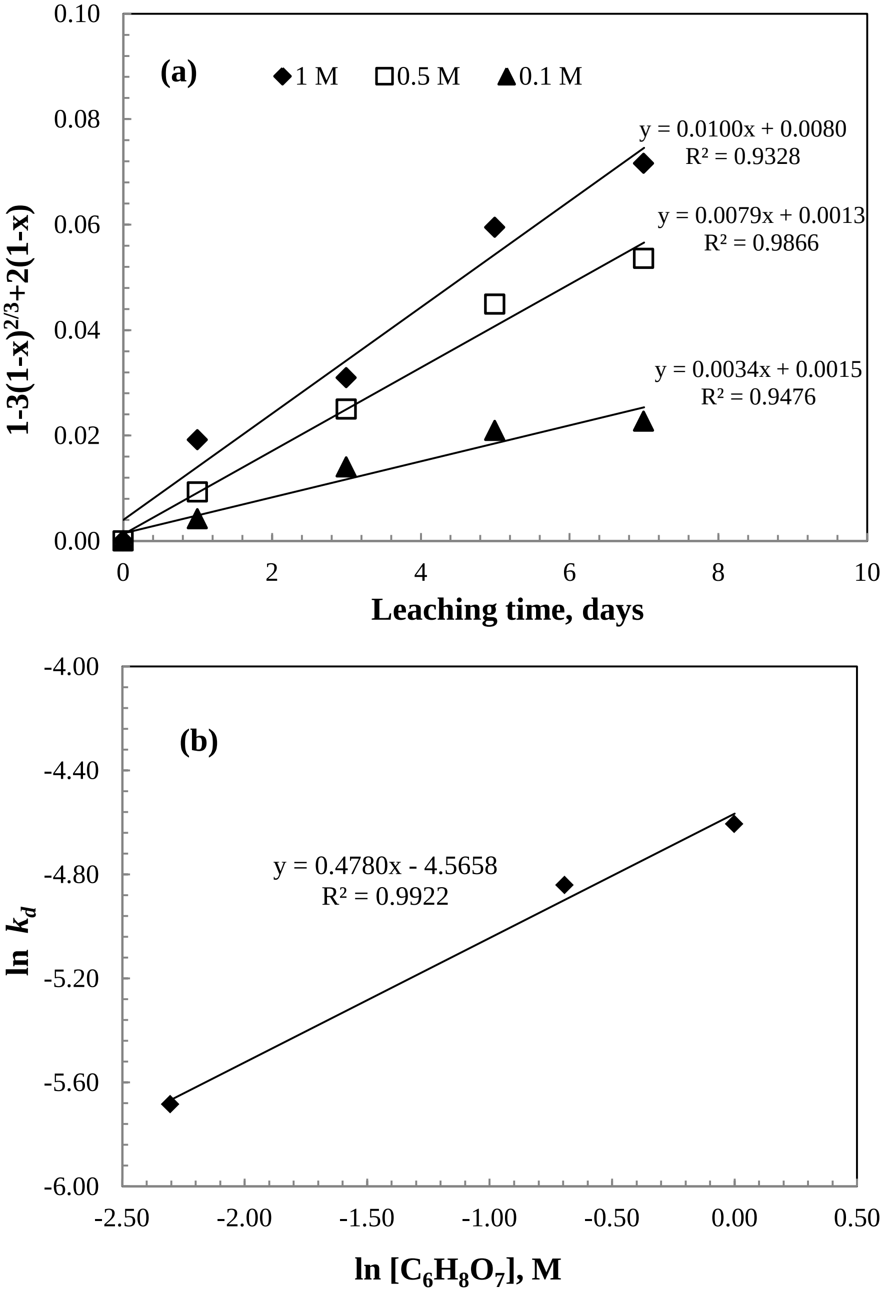

Fig. 4-8. (a) Plot of diffusion through the solid product layer for the SCM with leaching time at various citric acid concentrations; **(b)** Plot of ln k_d vs ln [$C_6H_8O_7$] (40°C, 5% (w/v) pulp density, <75 μm particle size, 200 rpm shaker speed).

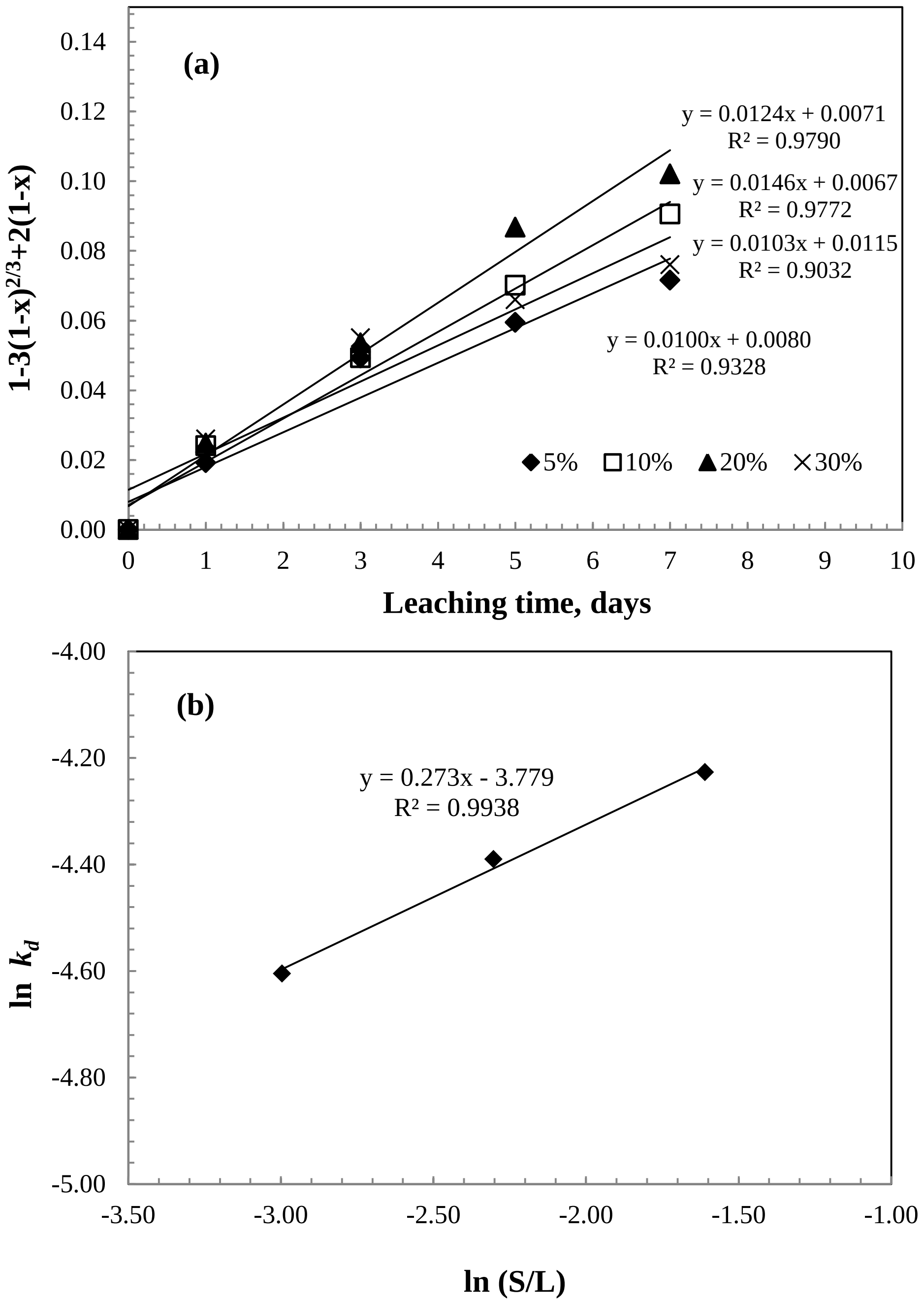

Fig. 4-9. (a) Plot of diffusion through the solid product layer for the SCM with leaching time at various pulp densities; **(b)** Plot of ln k_d vs ln (S/L) (40°C, 1 M citric acid, <75 μm particle size, 200 rpm shaker speed).

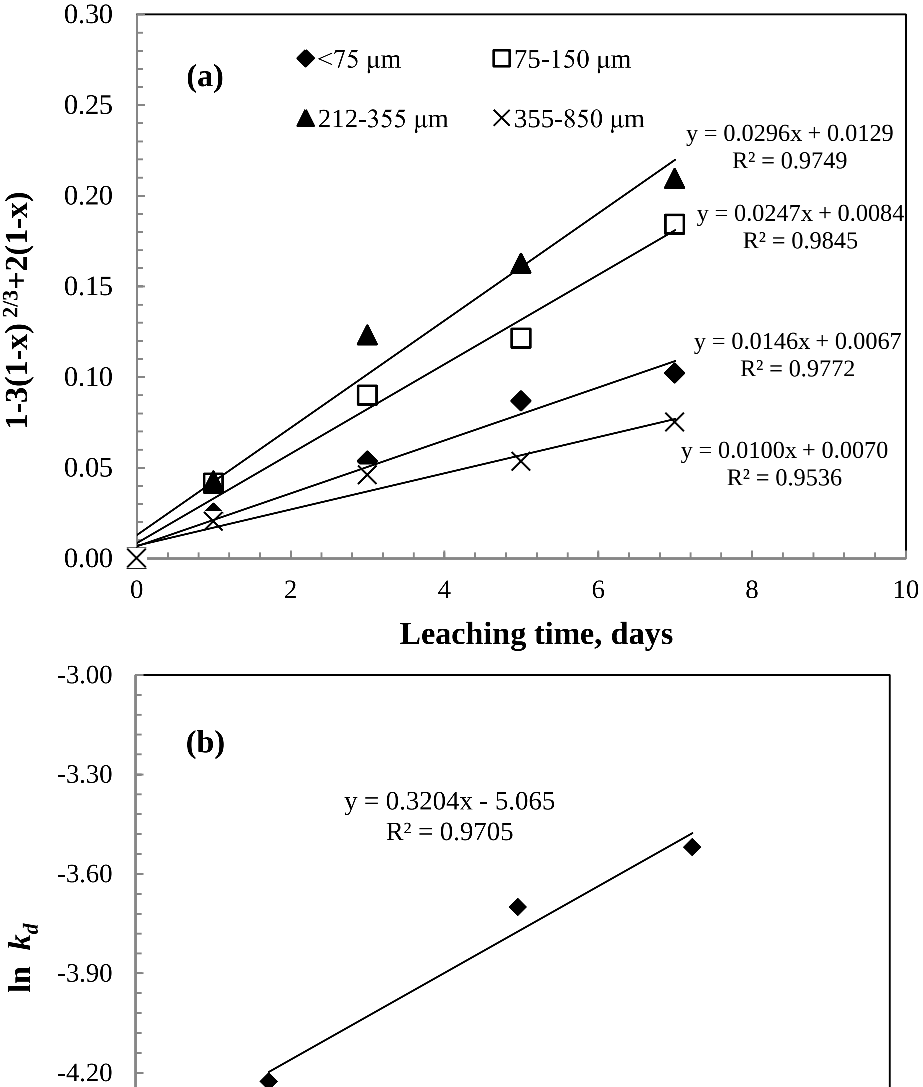

Fig. 4-10. (a) Plot of diffusion through the solid product layer for the SCM with leaching time at various ore particle sizes; **(b)** Plot of ln k_d vs ln (r_o) (40°C, 20% (w/v) pulp density, 1 M citric acid, 200 rpm shaker speed).

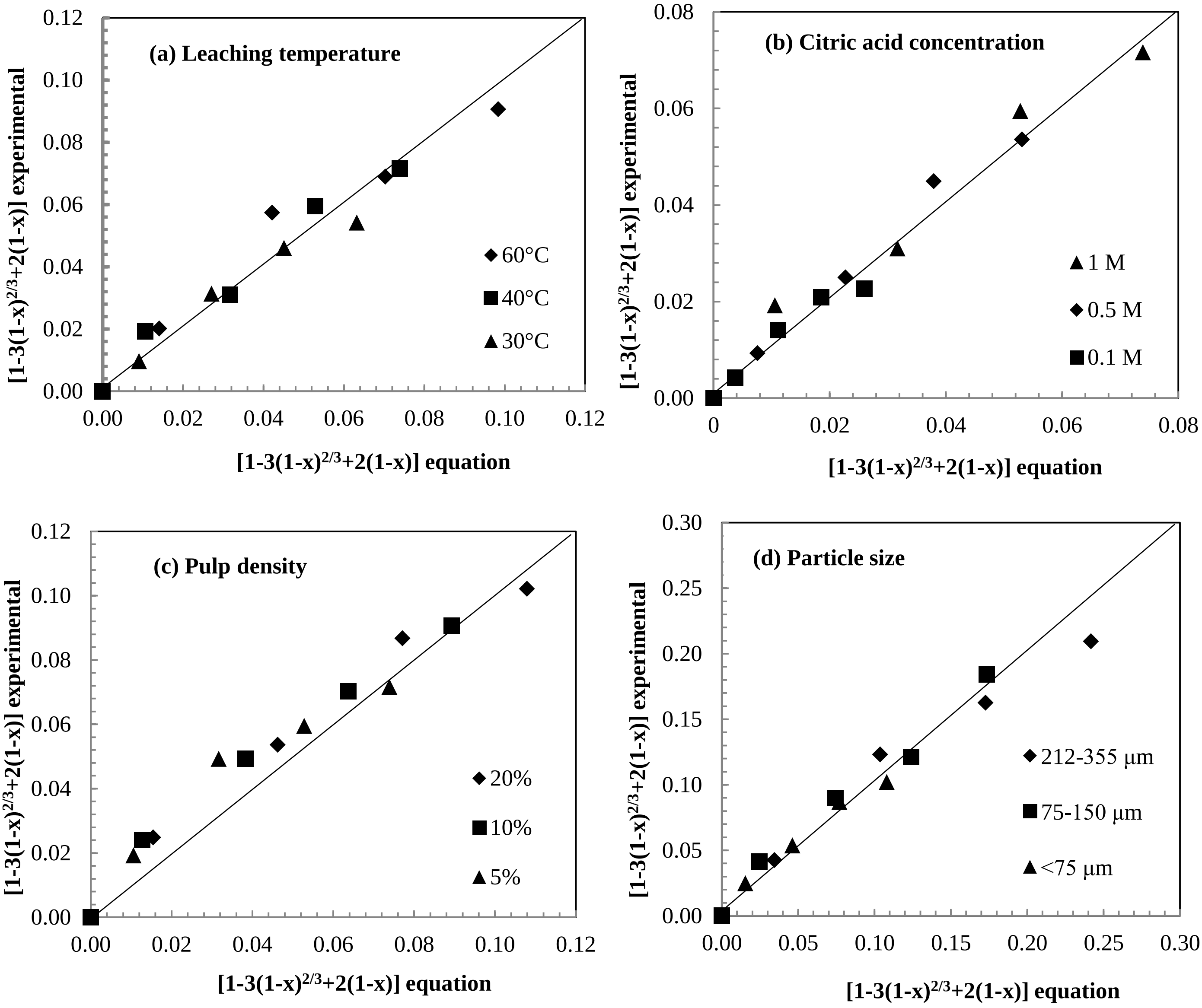

Fig. 4-11. Validation of the empirical kinetic model for various leaching parameters (a) Leaching temperature; (b) Citric acid concentration; (c) Pulp density; (d) Particle size.

A schematic of nickel dissolution from lizardite according to the SCM is illustrated in Figure 4-12, where lizardite is represented as the nonporous solids. The chemical reaction between leaching agent, *i.e.*, citric acid, and nickel occurs at the lizardite surface, dissolving nickel and magnesium. Silica remains in the reacted layer, as presented in Chapter 3, Eq. 3-1, and the reacted layer becomes porous. The next step is penetration and diffusion of citric acid through the reacted layer to the surface of the unreacted core and chemical reaction will occur at the surface of the unreacted core. Finally, the dissolved product diffuses through the solid reacted layer back to the exterior surface of the solid and into the main bulk of the fluid.

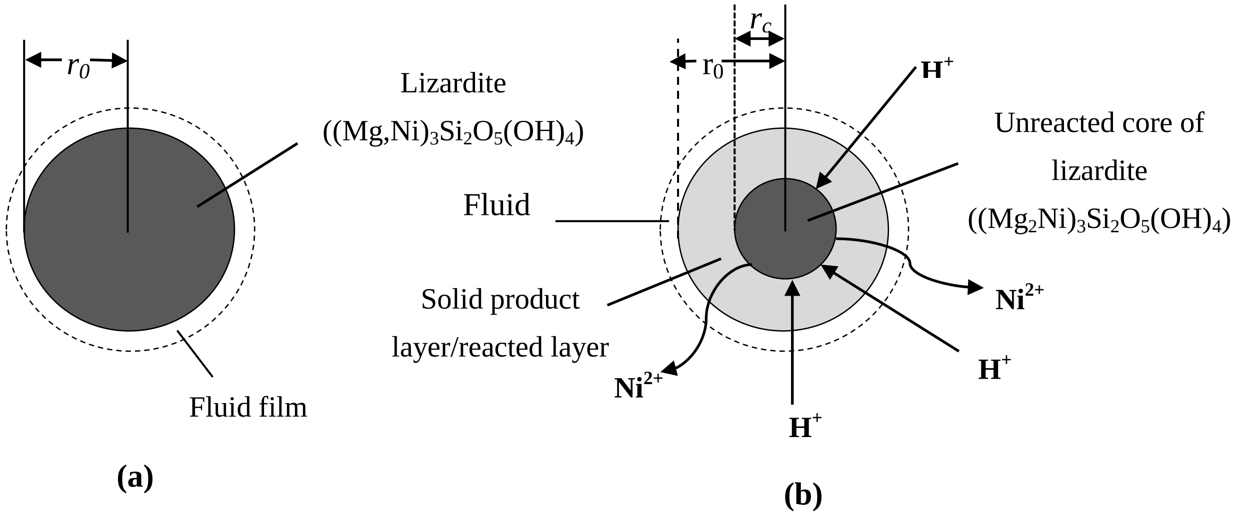

Fig. 4-12 Schematic of the nickel leaching process from lizardite based on the SCM: (a) initial state; (b) state at time *t*.

4.4. Conclusions

The optimum recovery of nickel (around 96%) from an Indonesian saprolite from Sulawesi Island was achieved under leaching conditions of a particle size of 212–355 μm, 1 M citric acid, 15 days leaching time, 20% (w/v) pulp density, a temperature of 40°C, and 200 rpm shaker speed. The experimental data were well interpreted by a shrinking-core model under diffusion control through the product layer. Using the

Arrhenius expression, the apparent activation energy for the dissolution of nickel was 12.38 kJ mol^{-1}. The low activation energy is consistent with that for a process controlled by diffusion through a solid product layer. The reaction orders with respect to citric acid concentration, pulp density, and ore particle size were determined to be 0.48, 0.27, and 0.32, respectively. The proposed empirical model of the leaching kinetics of this saprolite ore using citric acid under atmospheric pressure can be expressed as follows:

$$k_d t = 1 - 3(1-x)^{\frac{2}{3}} + 2(1-x) = 7.32\, x\, 10^{-4}[C_6H_8O_7]^{0.48}(S/L)^{0.27}(r_0)^{0.32}e^{\frac{-12{,}380}{RT}}t$$

This mathematical model was consistent with the observed experimental results.

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CHAPTER 5

Leaching of Nickel from Low-Grade Indonesian Saprolite Ores by Citric Acid Produced from Fermentation of Corn Products

In this chapter, biogenic citric acid produced from the fermentation of corn starch and corn cobs by *Aspergillus niger* was used for leaching nickel from laterite ores. Corn starch and corn cobs were used as carbon sources because they are abundant in Indonesia. The effectiveness of biogenic citric acid in nickel extraction from low-grade Indonesian saprolite ores by atmospheric leaching was investigated.

5.1. Introduction

Environmental considerations have forced modern society to develop innovative, sustainable, and green processes. Bioleaching is an emerging green technology for recovery of metals from various sources (Biswas et al., 2013). In addition to its environmental friendliness, the low capital cost and energy requirements are other major advantages of bioleaching over conventional leaching processes. Fungal bioleaching uses fungi, which are heterotrophic microbes, to produce organic acids such as citric acid, oxalic acid, and lactic acid, which are then used as leaching agents in bioleaching to extract metals from ores (Biswas et al., 2013).

Aspergillus niger is a common fungus in soils and plays an important role in the global carbon cycle and mineral mobilization by producing organic acids, including citric acid and oxalic acid, other metabolites, and extracellular enzymes (Biswas et al., 2013). *A. niger* has been used commercially to produce citric acid. It is capable of producing very high yields of citric acid at about 90 % of the theoretical yield from a carbohydrate source (Peksel et al., 2001). Citric acid is an excellent chelating agent and binds well to metals. Moreover, many studies have shown that citric acid performs well in the leaching of nickel laterite ores compared with other organic acids (Tzeferis and Agatzini-Leonardou, 1994; Tang and Valix, 2006; McDonald and Whittington, 2008). Bioleaching of nickel and other metals using *A. niger* has been reported in several studies using both in situ leaching (*i.e.* direct contact of the ore with a fungal culture) and indirect leaching with a culture filtrate (*i.e.* microbe-free medium).

Indonesia is a large tropical country that produces a variety of agricultural products and their associated wastes. Indonesia is also one of the largest producers of nickel laterite ores, and approximately 16 % of world’s nickel reserves are located in

Indonesia. The agricultural and mining industries in Indonesia could be to develop a green, alternative technology for nickel and metal extraction from nickel laterite ores. This could be achieved by producing citric acid from agricultural products for use as a leaching agent to recover nickel from Indonesian laterite ores.

Sucrose or glucose is the main carbon source in citric acid production. Carbon sources that have investigated include sugarcane molasses, sugarcane bagasse, corn cobs, corn starch, pineapple waste, coffee husks, corn husks, banana peel, apple pomace, and carrot pod. In Indonesia, corn is an important crop with production reaching 20 million tons in 2014 (Wright and Meylinah, 2014). Corn cobs are a common by-product of the corn processing industry, where they represent about 15 % of total corn production (Ashour et al., 2014). Corn cobs are rich in cellulose and hemicellulose, which have been used as inexpensive raw materials for production of soluble sugars and other value-added products by enzymatic and microbial fermentation processes. Both corn and its waste products are potential carbon sources for production of citric acid. The production of citric acid from corn starch and corn cobs has been evaluated in some studies (Ashour et al., 2014; Mourya and Jauhri, 2000; Hang and Woodams, 2001; Farias et al., 2010, Kirimura et al., 2011, Roehr, 1998; Röhr et al., 1996). In Indonesia, there are many corn fields located near the nickel laterite mines on Sulawesi and in Maluku Province, which makes corn an attractive carbon source for production of citric acid for nickel leaching in Indonesia.

While citric acid production from corn starch and corn cobs have been investigated, the use of the product for leaching of nickel laterite ores has not been studied. In this research, corn starch and corn cobs were used as carbon sources for production of citric acid by *A. niger*. The biogenic citric acid was then applied to nickel extraction from Indonesian saprolite ores, and the nickel recovery was optimized by varying the leaching parameters.

5.2. Materials and methods

5.2.1. Preparation of culture filtrate containing citric acid

Microorganism

A strain of the fungus *A. niger* was obtained from School of Life Sciences and Technology, Bandung Institute of Technology (Bandung, Indonesia). The strain was grown in potato dextrose agar (PDA (3.9 % m/v) as described by Bousshard et al. (1996), maintained in nutrient agar at 4 °C, and subcultured at intervals of 1–2 months.

Biogenic citric acid production and analysis

Citric acid was produced from fermentation of corn starch and corn cobs by *A. niger*. Experiments were conducted in 250 mL flasks, each containing 5 g corn starch or corn cob with 100 mL inorganic medium adjusted to pH 3.5. The inorganic medium used in this experiment contained (per 1000 mL of solution in deionized water): 10 g of KH_2PO_4; 2.0 g of NH_4NO_3; 250 mg of $MgSO_4.7H_2O$; 14 mg of $MnSO_4.5H_2O$; and 21 mg of $FeCl_3.6H_2O$. All chemicals used were of analytical grade and purchased from Wako Pure Chemicals Industries, Ltd. (Osaka, Japan). Milli-Q water (Millipore, Billerica, MA) was used in all experiments. All flasks containing these medium were sterilized at 121˚C for 15 min, cooled and inoculated with *A. niger* used. Concentration of spores was adjusted to around 10^7/ml. All experiments were done in duplicates. 3% v/v of methanol was added in each flask as an additive to improve the citric acid concentration produced. All flasks were incubated at 30˚C and shaker speed of 120 rpm with 5 days incubation.

The citric acid concentration was determined using the colorimetric method of Marrier and Boulet (1958). One milliliter of each clear culture filtrate and 1.30 mL of pyridine (Wako Pure Chemicals Industries, Ltd.) were added to individual test tubes and mixed. Then, 5.70 mL of acetic anhydride (Wako Pure Chemicals Industries, Ltd.) was added to each tube. The tubes were placed in a water bath at 32 °C for 30 min. A blank was run in parallel, and was prepared by replacing the 1 mL of sample with distilled water. The intensity of yellow color obtained was measured at 405 nm using a ultraviolet-visible spectrophotometry (UV-Vis spectrometer; UV-1800, Shimadzu, Kyoto, Japan). A calibration curve was constructed with the citric acid concentration on the *x*-axis and the optical density on the *y*-axis. The citric acid concentrations for each sample were calculated using the calibration curve. High performance liquid chromatography (HPLC; CO-2065 Plus, JASCO, Tokyo, Japan) was used to identify the products in the culture filtrate.

5.2.2. Leaching process using clear culture filtrate

Low-grade saprolite ores

Saprolite ores were collected from two different mining areas in Indonesia (Sulawesi and Halmahera) that are the same samples used in Chapter 2. The ores were ground in a jaw-crusher and vibration mill to two different particle sizes namely <75 µm and 212-355 µm. Those ores were analyzed in the same way as it was mentioned in Chapter 2 *subtopic 2.2.1. Materials.* Chemical composition of both samples was previously presented in Chapter 2, Table 2-1. Moreover, the mineralogical properties of the ores were also described in Chapter 2 *subtopic 2.3.1. Mineralogical study of saprolite ores.*

Leaching experiments

A clear culture filtrate that contained citric acid was collected by separation of the fungal biomass using filtration. A culture filtrate with a high citric acid concentration would be useful for leaching of laterite ores. Leaching tests were performed in a shaker equipment with a constant shaker speed of 200 rpm. Mixtures of the ground ore samples and culture filtrate (50 mL) were placed in 300 mL flasks. The effects of leaching time, leaching temperature (30 °C, 40 °C, and 60 °C), pulp density (percentage of solids in the leaching solution, 5 and 20 % w/v), and ore particle size (<75 µm and 212–355 µm) on nickel extraction were examined. The leaching process was monitored by sampling the slurry periodically (1, 3, 5, 7, and 15 days) and measuring the levels of dissolved metals by inductively coupled plasma optical emission spectrometry (ICP-OES) using standard procedures. The mineral dissolution behavior using citric acid was also investigated in X-ray diffraction (XRD) experiments in the same way as it was mentioned in Chapter 2 *subtopic 2.2.1. Materials.*

5.3. Results and discussion

5.3.1. Biogenic citric acid production

The yield of citric acid and citric acid concentration was depicted in Fig. 5-1. The citric acid concentration obtained from corn starch was around 0.05 M, and the yield of citric acid was approximately 230.4 g of citric acid per kilogram of dry corn starch. This concentration was obtained in repeat experiments. The culture filtrate from this fermentation was selected for use in leaching experiments. Compared with corn starch, corn cob produce a lower concentration of citric acid (around 0.015 M), and the yield of citric acid was only approximately 54 g of citric acid per kilogram of dry corn cobs. In the current study, the HPLC results (Fig. 5-2) also showed that lactic acid was also produced in the fermentation of corn starch as well as corn cobs by *A. niger*. Moreover, HPLC analysis also indicated that unfermented glucose still remained in the culture filtrate of both corn starch and corn cob. It is suggested that the citric acid yield should be able to increase. To obtain a higher citric acid concentration using corn cob as well as corn starch as the carbon source, it was necessary to optimize the fermentation process. Hang and Woodams (2001) could increase the yield of citric acid produced from corn cob by *A. niger* using enzymatic treatment, and obtained 603.5 g of citric acid per kilogram of dry corn cob. Furthermore, the clear culture filtrate from corn starch fermentation that was separated from fungal biomass was utilized directly in the leaching experiments.

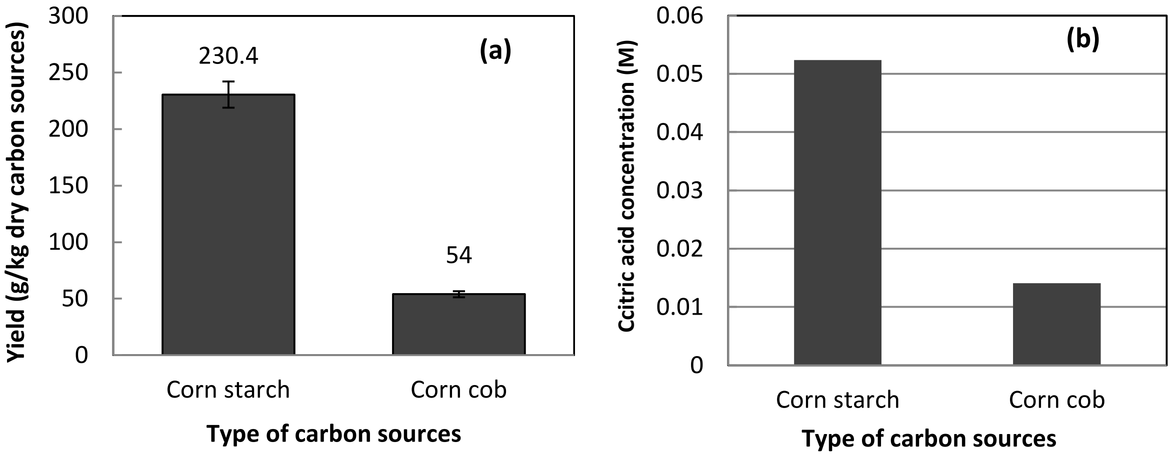

Fig. 5-1. Citric acid production (a) Yield of citric acid; (b) Concentration of citric acid.

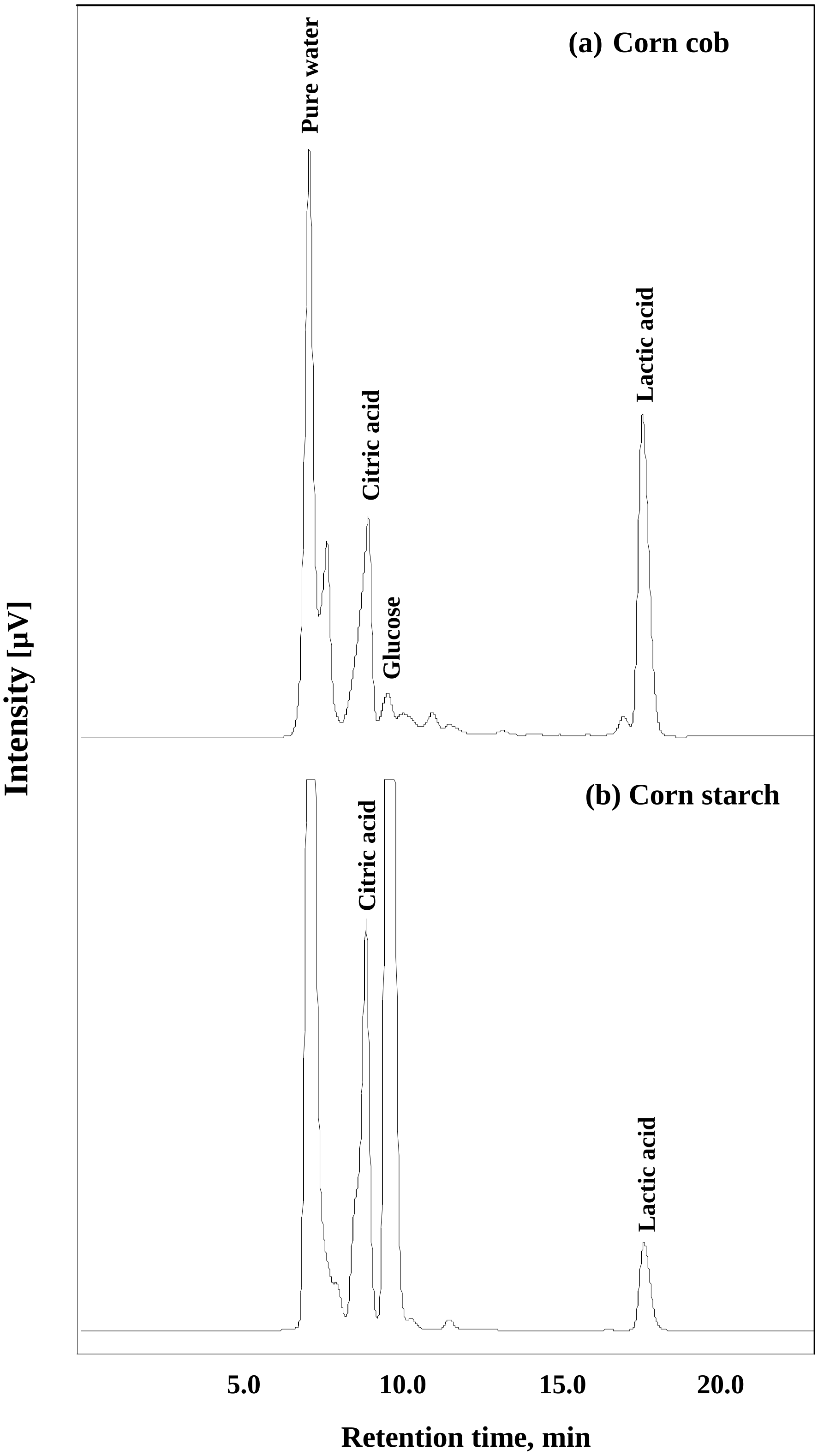

Fig. 5-2. HPLC analyses of clear culture filtrate from corn starch and corn cob fermentation by *A. niger*.

5.3.2. Biogenic citric acid leaching experiments

The nickel-leaching behavior of citric acid contained in the culture filtrate from corn starch fermentation was studied using the two saprolite ores. The effects of leaching temperature, pulp density, and ore particle size on nickel recovery were evaluated. Mineral dissolution behavior was also observed using XRD patterns of the solid residues.

Impact of leaching temperature on nickel dissolution

The influence of the leaching temperature (30 °C, 40 °C, and 60 °C) on leaching of nickel from the saprolite ore samples was evaluated using the following conditions: <75 µm particle size, 5 % pulp density, 200 rpm shaking speed. The leaching rate curves are presented in Fig. 5-3. As the leaching temperature increased from 30 °C to 40 °C the rate of dissolution of nickel from both saprolite ores (SS and SH) also increased. However, when the leaching temperature was increased from 40 °C to 60 °C, the rate of dissolution of nickel remained constant. After 15 d leaching at 40 °C or 60 °C, 37–39 % of the nickel the ore was recovered. This result was similar to that obtained for dissolution with citric acid in Chapter 3. Therefore, 40 °C is the optimum leaching temperature for nickel dissolution from Indonesian saprolite ores using both types of citric acid at atmospheric pressure.

There were some differences in the leaching behavior between the two ores (SS and SH). Even though the maximum nickel recovery from the two samples was similar, the maximum nickel recovery for SS was achieved faster than that for SH. Around 39 % of the nickel was recovered from SS within 3 days at 40 °C, and the nickel recovery remained constant when the leaching period was increased beyond 3 days. By contrast, it took 7 days at 40 °C to reach a nickel recovery of 38 % with SH. As discussed in Chapter 4, citric acid is known to leach nickel only from lizardite. Therefore, the higher lizardite composition in SS allows for faster nickel extraction from this ore than from SH.

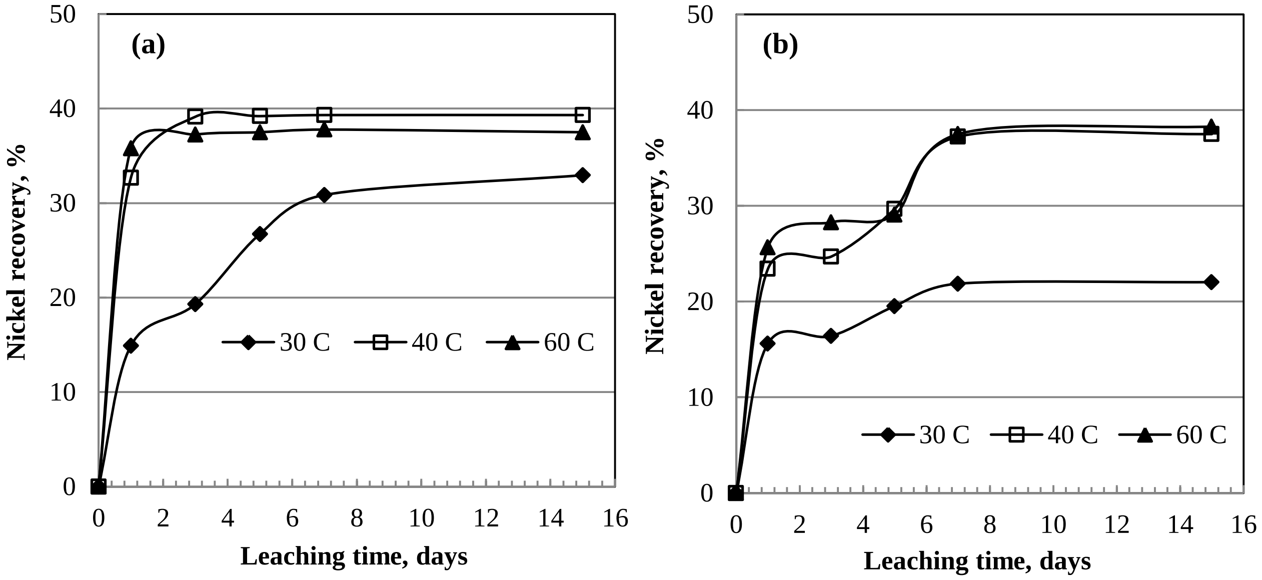

Fig. 5-3. Effect of leaching temperature on nickel leaching rate from (a) SS and (b) SH.

Influence of pulp density on nickel dissolution

The influence the pulp density (5 % or 20 % (w/v)) on nickel recovery was also examined. The ore particle size (<75 μm), leaching temperature (40 °C), and shaker speed (200 rpm) were held constant. Both ores showed that a pulp density of 5 % resulted in better nickel leaching than a pulp density of 20 % (Fig. 5-4). This result was different to that for dissolution of nickel from the ores using citric acid. In Chapter 3, it was observed that a pulp density of 20 % resulted in greater nickel recovery than a pulp density of 5 % using 1 M citric acid as the leaching reagent. This could be caused by differences between the acid concentrations used in the current experiment and in the previous study. In the current study, a 0.05 M citric acid solution was not concentrated enough to dissolve all the nickel in the solution with a 20 % pulp density. Moreover, although a similar maximum nickel recovery was obtained from both ores, Fig. 5-4 showed that the maximum nickel recovery from SS was achieved faster than that from SH.

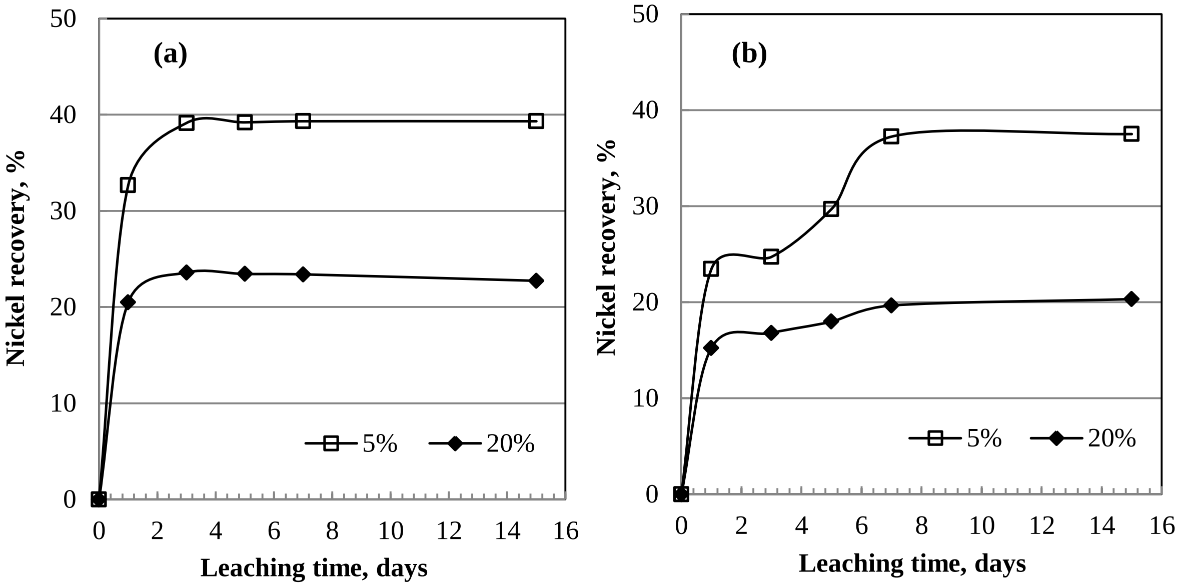

Fig. 5-4. Effect of pulp density on nickel leaching rate from (a) SS and (b) SH.

Effect of ore particle size on nickel dissolution

The impact of ore particle size on dissolution of nickel from the saprolite ores was investigated using two particle sizes (<75 μm and 212−355 μm). These leaching experiments were conducted at 40 °C, with a 5 % pulp density and 200 rpm shaker speed. The results are shown in Fig. 5-5. Changing the particle size from <75 μm to 212−355 μm did not greatly affect the nickel leaching rate. This result differs with that for dissolution of nickel from these ores using 1 M citric acid. In Chapter 3, it was observed that an ore particle size of 212−355 μm resulted in higher nickel recovery than an ore particle size of <75 mm using 1 M citric acid as the leaching reagent. With a lower acid concentration, nickel from the lizardite dissolved at the same rate for both ore particle sizes. The biogenic citric acid produced in this study could dissolve only around 37–39 % of the nickel from the ores.

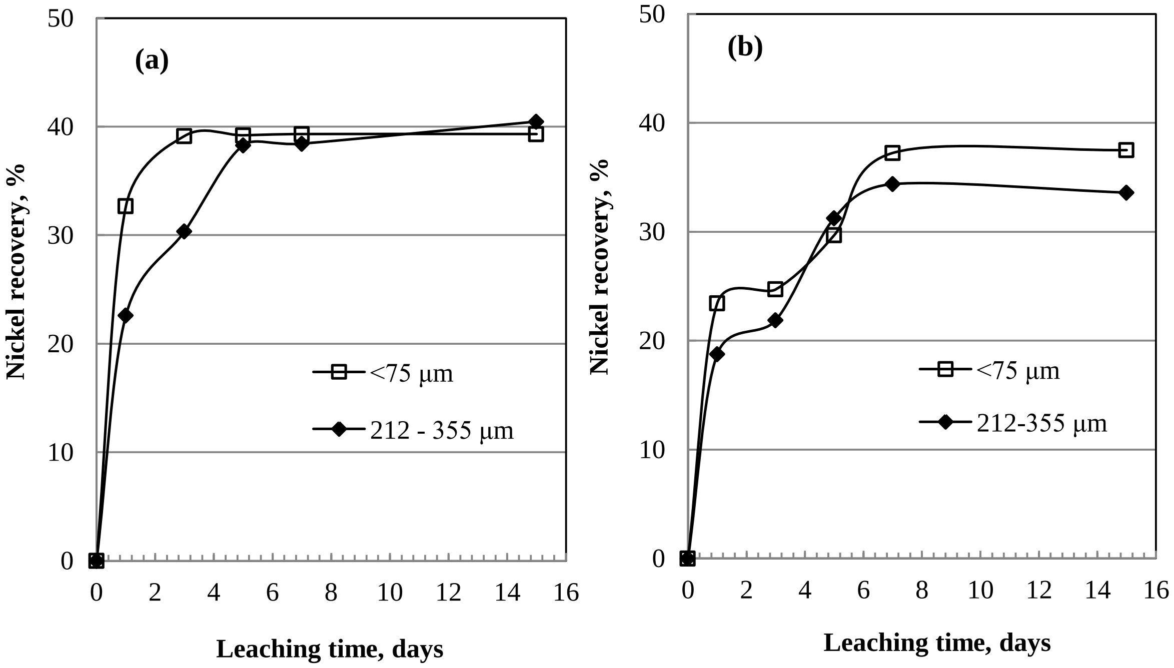

Fig. 5-5. Effect of ore particle size on nickel leaching rate from (a) SS and (b) SH.

Mineral dissolution behavior

Nickel in saprolite ores can be incorporated in lizardite, goethite, clinochlore, and/or talc. Thus, it is important to study the dissolution behavior of these minerals. In the present research, XRD patterns of the solid residues remaining after leaching were obtained to analyze changes of mineral contents after 15 days leaching (Fig. 5-6 and 5-7). These patterns showed that both ores displayed similar trends. Lizardite content decreased after leaching, while the contents of goethite, clinochlore, and talc remained. This is because both citric acid and biogenic citric acid could dissolve lizardite but not goethite, talc, and clinochlore.

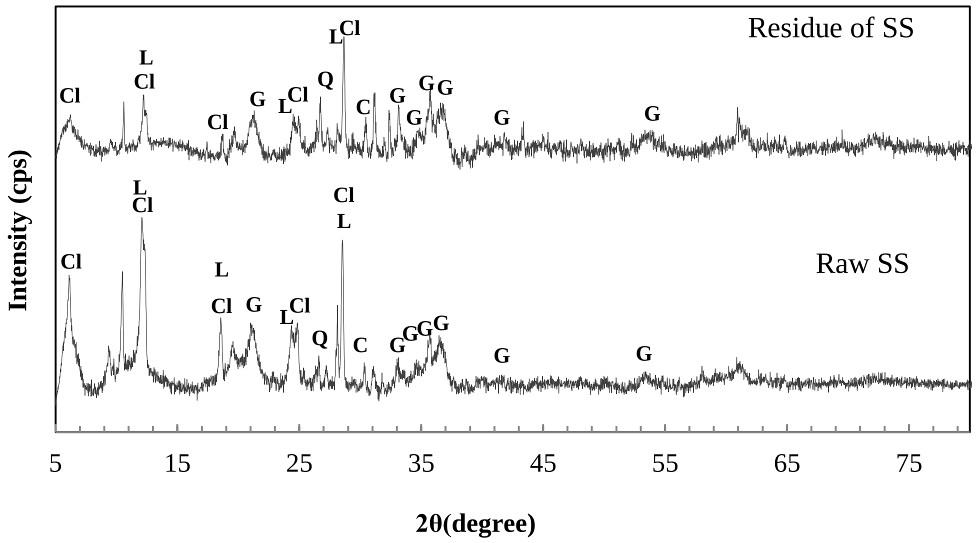

Fig. 5-6. XRD patterns of raw SS and solid residue after leaching (Cl: Clinochlore, L: Lizardite, G: goethite, C: chromite, Q: quartz).

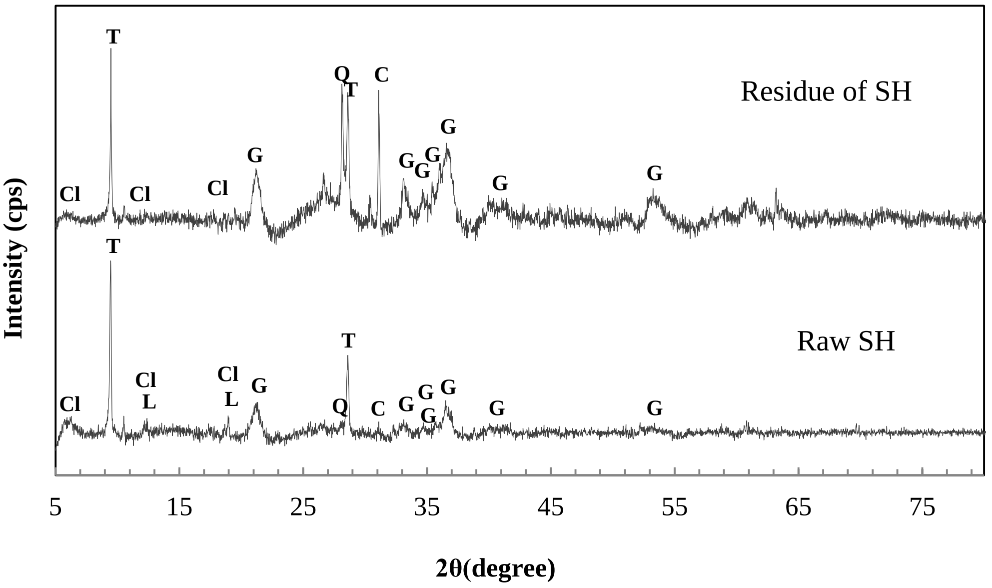

Fig. 5-7. XRD patterns of raw SH and solid residue after leaching (L: lizardite, G: goethite, T: talc, C: chromite, Q: quartz, Cl: clinochlore).

5.3.3. Comparison of nickel recovery with citric and biogenic citric acid

The effectiveness of nickel leaching with biogenic citric acid also compared to that of citric acid with both acids at 0.05 M. Trends were observed in similar for both samples, and biogenic citric acid was as effective for nickel leaching as citric acid (Fig. 5-8). Nickel leaching with biogenic citric acid was even slightly higher than that with citric acid. The leaching rate with biogenic citric acid was also faster than that with citric acid under the same conditions. This suggests that biogenic products in addition to the citric acid could participate in the leaching of nickel and other metals from saprolite ores. This is supported by the as HPLC analysis, which showed the presence of other biogenic products in the culture filtrate namely lactic acid. As discussed in Chapter 2, lactic acid was also effective for leaching of nickel and other metals from saprolite ores. In conclusion, biogenic citric acid produced from corn starch and corn cobs by *A. niger* is an excellent leaching reagent for extracting nickel from Indonesian saprolite ores.

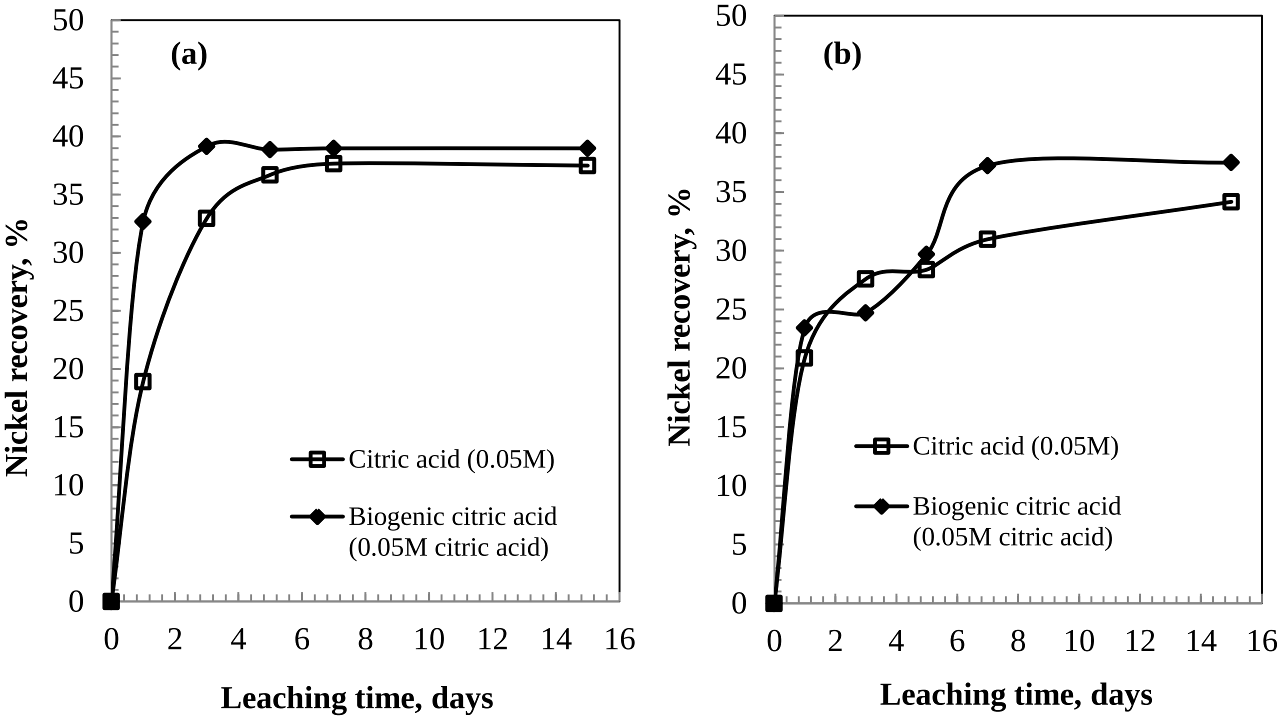

Fig. 5-8. Comparison of effectiveness of biogenic citric acid (0.05M citric acid) and 0.05M citric acid on the nickel recovery of (a) SS ore and (b) SH ore.

5.3.4. Proposed nickel recovery process from Indonesian laterite ores with a combination of biogenic citric acid and sulfuric acid

The results in this study showed that biogenic citric acid could leach nickel from lizardite at atmospheric pressure. To increase the efficiency of the leaching process, it would be necessary to separate lizardite from other minerals contained in the saprolite ores. However, the separation of goethite and lizardite is sometimes difficult. As discussed in Chapter 2, a mixture of sulfuric acid and citric acid increased nickel recovery from saprolite ores, particularly for the SH ore, which contained more goethite than the SS ore. This suggests that addition of sulfuric acid to citric acid assists dissolution of nickel from goethite. Biogenic sulfuric acid can be produced using chemolithotrophs such as *Acidithiobacillus ferrooxidans* (Simate et al., 2010). Primary oxidation of elemental sulfur or sulfur containing materials during the growth of chemolithotrophic bacteria produces a sulfuric acid solution, which can solubilize metals (M) as shown below (Simate et al., 2010).

$$MS_x + (2X-0.5)\,O_2 + H_2O \xrightarrow{bacteria} M^{x+} + XSO_4^{2-} + 2H^+ \quad \textbf{(5-1)}$$

$$NiO + 2H^+ \rightarrow Ni^{2+} + H_2O \quad \textbf{(5-2)}$$

Nickel laterite ores do not contain sulfur, so sulfur needs to be added for chemolithotrophs in the leaching of laterite ores (Simate et al., 2010).

The use of a mixed culture of chemolithotrophs would promote the dissolution of nickel laterites. This is because competition for oxygen by iron oxidizing bacteria (Simate, 2009; Simate et al., 2009b) could lead to reductive dissolution of ferric iron in the nickel laterites, which would destabilizing them (Bridge and Johnson, 1998). As indicated in the following equation (Bridge and Johnson, 1998), the reduction of soluble ferric iron by bacteria can shift the equilibrium between solid-phase iron (III) and soluble-phase iron (III), which will accelerate the dissolution of the mineral (Simate et al., 2010):

$$2Fe^{3+}_{solidphase} + H_2O \leftrightarrow 2Fe^{3+}_{solublephase} + H_2O \rightarrow 2Fe^{2+} + \tfrac{1}{2}\,O_2 + 2H^+ \text{ (by bacterial reduction)} \quad \textbf{(5-3)}$$

Therefore, biogenic citric acid for dissolution of lizardite and biogenic sulfuric acid for goethite dissolution could be combined to optimize nickel extraction from low-grade Indonesian saprolite ores (Fig. 5-9).

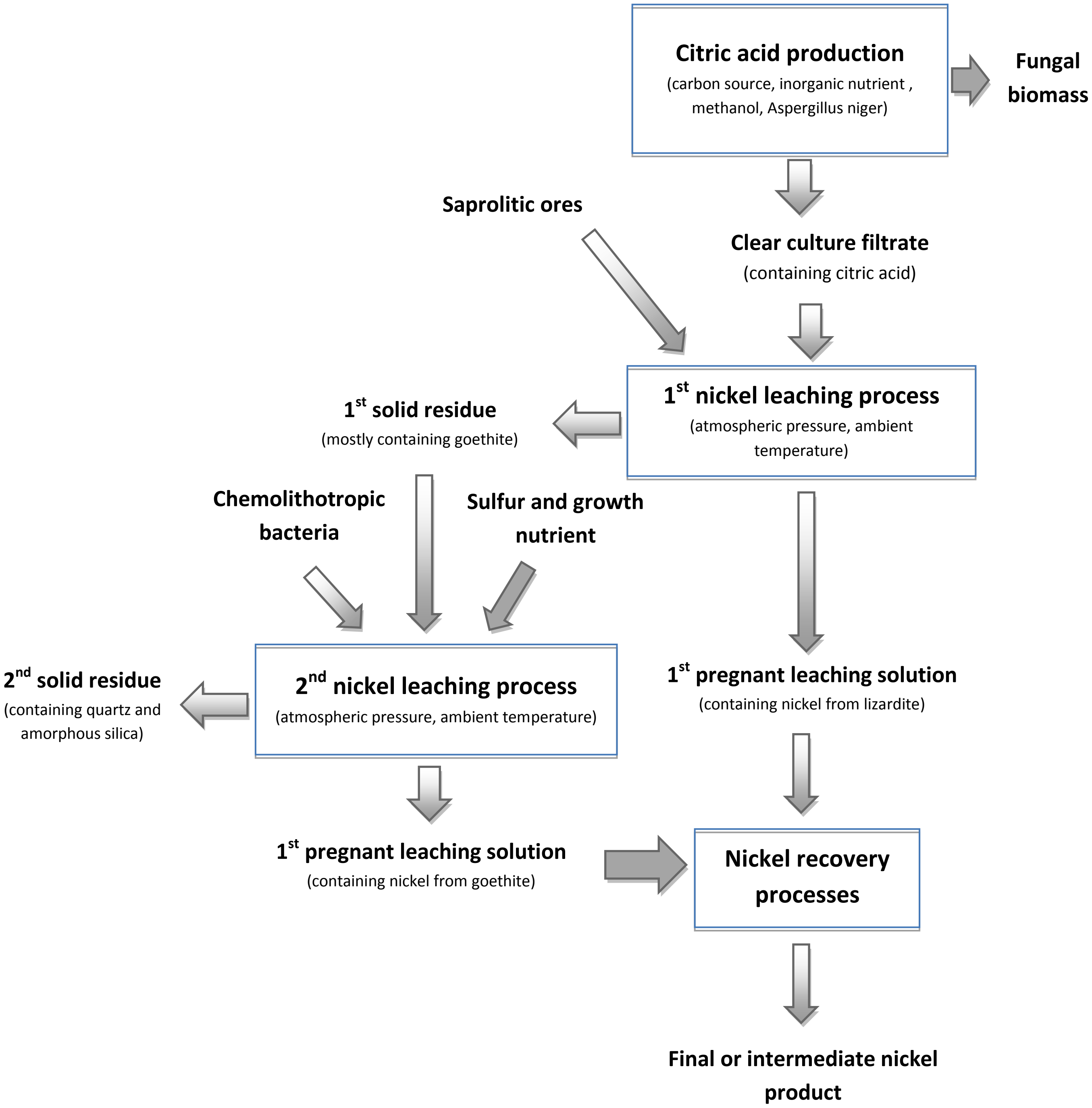

Fig. 5-9. Proposed processing step of nickel leaching from Indonesian saprolitic ores.

5.4. Conclusions

Biogenic citric acid was produced from corn starch and corn cobs using *A. niger*. The concentration of the acid was maximized at 0.05 M under the following conditions: 5 % mass fraction of corn starch, 5 days incubation with *A. niger* at 30 °C, shaker speed of 120 rpm, and addition of 3 % (volume fraction) methanol as an additive. The acid in the culture filtrate was applied to leaching of two Indonesian saprolite ores (SS and SH), and nickel recover was optimized by varying the leaching parameters. Maximum nickel recovery from both ores was achieved with a leaching temperature of 40 °C, pulp density of 5 %, ore particle size of 212–355 μm, and shaker speed of 200 rpm. The maximum nickel recovery from SS was reached faster (3 days leaching period) than that from SH (7 days leaching period). The culture filtrate containing 0.05 M citric acid and other unidentified organic acids provided better leaching of nickel than 0.05 M citric acid. Biogenic citric acid produce from corn starch and corn cobs by *A. niger* is potential leaching reagent for nickel recovery from Indonesian saprolite ores.

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CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

A comprehensive investigation of nickel leaching with various leaching reagents was conducted in this research. The effectiveness of citric acid was compared with other leaching reagents, citric acid leaching was optimized, and kinetic modeling of the process was conducted. Production of biogenic citric acid from corn by-products was investigated, and this acid was also applied to nickel recovery. Several analytical techniques were used to study the mineral dissolution behavior during the nickel leaching process. In this chapter, conclusions from this research are presented along with suggestions for further study that could improve the understanding of nickel leaching using biogenic citric acid. Enhancement of biogenic citric acid production from corn cobs is a future challenge for providing a more effective and cheaper nickel leaching reagent.

6.1. Conclusions

Sustainable industrial processes are of importance for environmental and social reasons. Many studies have investigated increasing the effectiveness and profitability of extraction of nickel from the abundant laterite ores in Indonesia. Low grade ores are of particular interest. For processing of these ores, leaching with organic acids and fungal bioleaching at atmospheric pressure are emerging technologies. A few studies have been conducted on application of these methods to Indonesian saprolite ores. However, the leaching mechanism has not yet been determined. Moreover, these studies have used only saprolite ore from only one region. Laterite ores in Indonesia are widely distributed, and are found on the islands of Kalimantan, Sulawesi, Halmahera, Gag, and Papua. The chemical and mineral compositions of laterites from different regions, or even from different depths in one area, can vary greatly. Therefore, different extraction methods may be required for recovery of nickel from ores from different regions in Indonesia. In addition, although some nickel laterite ores have similar mineralogical compositions, they show radically different leaching results at atmospheric pressure. Therefore, specific mineralogical research should be conducted whenever a new laterite ore is found. Considerable effort has been devoted to studying leaching of laterites at atmospheric pressure, but little emphasis has been placed on understanding the effect of nickel mineralogy on leaching, especially for citric and biogenic citric acid leaching at atmospheric pressure. A general lack of knowledge regarding the mineralogy and chemistry of the leached products hampers understanding of the leaching behavior, leaching mechanism, and kinetics of the other mineral components present in ores. Hence, further study on the leaching mechanism with citric acid is required. The present research explored nickel leaching with citric and biogenic citric acid using two low-grade Indonesian saprolite ores from different regions.

In Chapter 2, citric acid was compared with other leaching reagents, including inorganic acids and organic acids, for nickel extraction from the low-grade Indonesian saprolite ores. Two saprolite ores, SS and SH, were used to investigate the leaching performance and mineral dissolution behaviors using the different leaching reagents. The chemical and mineral compositions of the raw saprolite ores were studied using XRD, TG/DTA, and SEM/EDS. Leaching was performed in flasks on shakers (shaking speed 200 rpm) at 30 °C in a 1 M aqueous solution of citric, sulfuric, nitric, hydrochloric, lactic, or oxalic acid. The pulp density (20 % w/v) and ore particle size (<75 μm) were kept constant. The two ores had different mineral compositions, with the SS having lizardite, goethite, as well as clinochlore contents as major minerals, while the SH ore contains talc and goethite as predominant phases. These differences affected the leaching performance and metal dissolution behavior. Citric acid and sulfuric acid were more effective than the other acid solutions for nickel extraction from both ores. Citric acid was also a more effective reagent for nickel leaching than the other organic acids. Citric acid was very effective for dissolving nickel from lizardite, but not from goethite. By contrast, the inorganic acids (sulfuric, nitric, and hydrochloric acids) could extract nickel from both goethite and lizardite. The nickel recoveries achieved with sulfuric acid were higher than those achieved with the other inorganic acids. A comparison of the leaching performances of citric acid for the two ores showed that the nickel recovery from SS was higher than that from SH. By contrast, with all the inorganic acids, similar nickel recoveries were obtained for both the SS and SH ores. In addition, the effect of sulfuric acid–citric acid mixtures 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 showed that an increase in the proportion of sulfuric acid in the mixture affected the dissolution rate of nickel in leaching of SH much more than that in leaching of SS.

Because the results in Chapter 2 showed that citric acid was effective for nickel recovery from Indonesian saprolite ores, the citric acid leaching mechanism and optimization the leaching process were investigated in Chapter 3. The leaching performance, mineral dissolution behavior, and leaching kinetics of nickel extraction using citric acid were investigated at atmospheric pressure. SS contains goethite and lizardite as major mineral, while SH has talc and goethite as predominant mineral. Most of the nickel was incorporated in a magnesium–silicate-containing mineral. The effects on nickel extraction of leaching temperature, citric acid concentration, and ore particle size were studied. These parameters affected nickel extraction, and the optimum nickel recovery was achieved under the following leaching conditions: citric acid concentration 1 M, leaching temperature 40 °C, leaching time 15 days, ore particle size 212–355 μm, shaking speed 200 rpm, and pulp density 20 % w/v. Nickel recovery from the SS ore (96 %) was higher than that from the SH ore (73 %) under the optimum leaching conditions. This suggests the mineral contents of an ore will affect the leaching performance and mineral dissolution behavior. The nickel recovery results and analysis of the solid residues using XRD suggested that all dissolved nickel originated from lizardite, which were more easily leached than goethite and talc. Lizardite content of SH was lower than that of SS, and therefore, nickel recovery from SH was lower than that from SS. For the kinetics of nickel extraction, although the rate of nickel extraction for SS was faster than that for SH, the leaching kinetic behaviors of the two ores were similar. Nickel leaching from SS and SH followed the SCM and was controlled by diffusion through the solid product layer.

The kinetics modeling of leaching with citric acid under atmospheric pressure was evaluated further in Chapter 4. The effects of leaching temperature, citric acid concentration, pulp density, and ore particle size on the dissolution rate of nickel were examined for calculating the mathematical model of kinetics using the SCM. The dissolution rate of nickel is influenced by all of these variables. The experimental data were well interpreted by the SCM, with the rate of reaction controlled by diffusion through the solid product layer. Using the Arrhenius equation, the apparent activation energy for the dissolution of nickel was calculated at 12.38 kJ/mol. Finally, based on the SCM, the following empirical kinetic model for leaching of nickel from this Indonesian saprolite ore is proposed:

$$k_d t = 1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) = 7.32\, x\, 10^{-4}[C_6H_8O_7]^{0.48}(S/L)^{0.27}(r_0)^{0.32}e^{\frac{-12,380}{RT}}t.$$

This mathematical model was consistent with the observed experimental results.

The findings on the mechanism of citric acid leaching were adopted to investigate nickel leaching using biogenic citric acid in Chapter 5. Biogenic citric acid was produced from corn starch and corn cobs using *A. niger*. This biogenic citric acid was applied to leaching of nickel from the Indonesian saprolite ores under atmospheric pressure. The maximum citric acid concentration (0.05 M) was produced with corn starch, mass fraction of 5 %, 5 days incubation with *A. niger* at 30 °C, a shaker speed of 120 rpm, and addition of 3 % (volume fraction) methanol. Optimization of nickel leaching with the biogenic citric acid was investigated by varying the following leaching parameters: pulp density (5 % and 20 % w/v), ore particle size (<75 μm and 212–355 μm), and leaching temperature (30 °C, 40 °C, and 60 °C). The shaker speed was kept constant at 200 rpm. Similar maximum nickel recoveries (38–39 %) were obtained from both ores with the following leaching conditions: 40 °C leaching temperature, 5 % pulp density, and <75 μm ore particle size.

The maximum nickel recovery from SS was reached faster (3 days leaching period) than it was from SH (7 days leaching period). XRD patterns of the solid residue remaining after leaching suggested that most nickel in the leaching solution originated from lizardite. This was consistent with nickel leaching mechanism with citric acid. Biogenic citric acid was more effective for nickel leaching than citric acid, and provided slightly higher recoveries.

These results suggest that nickel extraction using biogenic citric acid from the fermentation of corn starch and corn cobs with *A. niger* will be a profitable method for utilizing low-grade Indonesian saprolite ores. The proposed leaching mechanism will be useful for designing of nickel-leaching processes for different lateritic ores using citric and biogenic citric acid at atmospheric pressure and low temperature.

6.2. Recommendations

The results obtained in this research suggest that the following studies will be beneficial:

1. Because both citric and biogenic citric acid only dissolves nickel from lizardite, future research could look at separating lizardite from other minerals in the saprolite ores. This would improve the efficiency of the leaching process.
2. While corn cobs are a potential carbon source for the production of biogenic citric acid by *A. niger*, the yield obtained in this study was low. Future work could investigate increasing the yield of citric acid from corn cobs. A higher citric acid yield would increase the recovery of nickel from low-grade Indonesian saprolite ores. Citric acid production from other agricultural wastes in Indonesia could also be investigated.
3. Biogenic sulfuric acid from chemolitotrophs could be used to dissolve goethite from the solid residue remaining after biogenic citric acid leaching. This could be investigated to optimum nickel extraction from Indonesian saprolite ores.

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