Mineralogical Aspects of Nickeliferous Limonite Ores: 
An Implication for Hydrometallurgical Processing

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Abstract

Due to the high energy requirement in recovery of Ni from laterite ores by means of pyrometallurgy, there is an increase the research interest in extraction of Ni from laterite ores by hydrometallurgical processing. However, both of these methods are sensitive to ore properties. It is generally accepted that mineralogy of nickel laterite ores is one of the key factors in determining the choice of process flow system. Two nickel limonite ores used in this study were collected from Soroako mining district. Mineralogical characterization was performed by means of X ray diffractometry (XRD) and optical microscopy. Results show that west limonite ore contains goethite, talc, and silica; whereas the east limonite ore (Petea block) is mainly composed of goethite with subordinate chlorite, serpentine and lithiophorite. From hydrometallurgical perspective, it is estimated that the higher dissolution of goethite in west block result in the formation of hematite. Conversely the lower dissolution rates of talc-like phases may lead to decrease Ni extraction due to refractory nature of those minerals. In the case of east limonite ore, it is predicted that the higher dissolution rates of chlorite and residual serpentine would have led to high Ni extraction, however, it may also result extensive formation of silica gel due to depolymerization of tetrahedral sheets in chlorite and serpentine structures. Results of initial mineralogical studies should be a key in understanding the future potential hydrometallurgical process and in building up the future planning test work.

Key words: limonite, goethite, dissolution, hydrometallurgy

Introduction

Continuous depletion of global nickel sulfide ore reserves has led to an increase research interest in the extraction of nickel from laterite ores which account for about 70 % of world land-based resources (Dalvi et al., 2004). Nickel in laterite ores can be recovered either by smelting (pyrometallurgy) or leaching (hydrometallurgy). Due to high energy requirement of smelting process, many investigations have recently been focused on the extraction of nickel from laterite ores by leaching process (e.g. Whittington and Muir, 2000; Rubisov et al., 2000; McDonald and Whittington, 2008; Kaya and Topkaya, 2011).

The suitability of the process that can be economically employed is largely dependent on the mineralogical and chemical composition of the ores. It is generally accepted that the high pressure acid leaching (HPAL) is amenable to treat limonite ore; while atmospheric pressure leaching (AL) is suitable for the treatment both limonite and saprolite ores (Girgin at al., 2011).

The aim of this paper is to present the mineralogical aspects of nickeliferous limonite ore samples and their relation to dissolution behavior with an implication for hydrometallurgical processing.

Samples and Methods

Nickel laterite ore samples used in this study were collected from Soroako mining district of Sulawesi, Indonesia. The west limonite (WL) ore sample is a composite material taken from three different limonite horizons which have been formed by a chemical weathering process of unserpentinized peridotite. The
east limonite ore (EL) sample is a composite material of three different limonite zones from Petea block that typically formed over serpentinized ultramafic rocks.

The mineralogy of the ore samples was characterized through XRD, optical microscopy, and SEM-EDX. The XRD analysis of powder samples was performed using a Rigaku X-ray diffractometer. Microscopic examination was executed using Nikon Eclipse polarizing microscope, and SEM/EDX analysis was conducted through JEOL-JSM6030.

Leaching experiment of these samples was carried out using autoclave with the following conditions: H$_2$SO$_4$ concentration: 25 %, oxygen pressure: 2 MPa, stirring speed: 500 rpm, temperature: 90°C and pulp density 10 %. Leaching time was set at 15 and 60 minutes respectively. After leaching, residues were filtered, dried at 100°C and analyzed by XRD to determine their mineralogical content.

**Results and Discussion**

**Mineralogical characterization**

The XRD patterns of limonite sample from west block (Fig.1-a) show that the minerals are composed of goethite [FeO(OH)] with subordinate quartz (SiO$_2$) and talc [Mg$_3$Si$_2$O$_5$(OH)$_4$]. It is inferred that goethite is the principal Ni-bearing materials contained in the west limonite sample, although talc could also be host for nickel in small amounts. Nickel concentrations in goethite of dried-ore sample from Soroako range between 0.4 and 2.5 wt % with an average of 1.4 wt% (Chen et al., 2004).

![XRD patterns of two limonite ore samples from Soroako: (a) west ore sample (b) Petea ore sample.](image)

In the east limonite ore sample (Petea block), XRD patterns show that goethite [FeO(OH)] is predominant mineral with lesser amounts of chlorite, lizardite (Mg,Fe)$_3$Si$_2$O$_5$(OH)$_4$, lithiophorite, and quartz (SiO$_2$) (Fig. 1b). According to Chen et al. (2004), chlorite in Soroako laterite contains an average of 0.9 wt% Ni, whereas lizardite (serpentine group) varies in Ni ranging between 0.8 – 5.0 with the average of 2.2 wt% Ni. Lithiophorite can contain high Ni over other phases but it shows only trace components within the ore. It is suggested that goethite is the most significant because it is the dominant phase occurring in the ore.

Microscopic analysis under reflected light mode shows the acicular texture indicating the characteristic of goethite (Fig.2). The acicular and platy morphology of goethite crystals are shown in SEM image (Fig.3)

![Figure 2. Photomicrograph of limonite sample showing the acicular texture of goethite observed under reflection light mode.](image)

![Figure 3. SEM image of limonite sample from west block showing acicular and platy morphology of goethite.](image)
Dissolution of minerals in the ores

Results of XRD analysis of solid residues (Fig.4) show that nearly all peaks of goethite collapse after leaching at 15 and 60 minutes. This indicates that goethite in both ore samples was readily dissolved in sulfuric acid. Reflections of chlorite and serpentine in east ore sample (Fig. 4b) were lost after leaching implying easy or fast dissolution. In contrast, the peaks of talc in west samples remain preserved after leaching exhibiting that talc was not dissolved during leaching. The strong intensity of quartz peaks which is shown in the two solid residues also indicate that this phase was not dissolved at all.

![Figure 4. XRD patterns of solid residues of west limonite sample (a) and east limonite/Petea sample (b) for 15 and 60 minutes leaching.](image)

The presence of hematite in solid residues of west sample is likely the result of iron precipitation derived from goethite dissolution. Considering the goethite reaction with sulfuric acid, it is likely that the complete dissolution of goethite is required in order to maximize Ni extraction (Buyukakinci and Topkaya, 2009). In contrast Girgin et al. (2011) concluded that it was not necessary to dissolved all goethite for leaching all nickel contained in the sample. Poorly ordered crystallinity of studied goethite is characteristic of laterite material. This feature might also be one factor for the higher dissolution rate in sulfuric acid (Cornell and Swhwertmann, 2003).

With respect to silicate phases (serpentine, chlorite, talc, and quartz), Terry (1983a) suggests that acid dissolution of these minerals may result to one or more of the following: (1) complete dissolution of silicate structure with leaching of metal cations and silica, (2) partial decomposition of silicate structure causing dissolution of cations and leaving silica residues, and (3) eventually no dissolution at all.

Differences in dissolution rates of silicate minerals in acid solution can be related to their crystal structure, e.g. relative number of Si-O bonds present and degree to which these bonds are bridged together to form polymerized Si-O network (Wolff-Boenisch et al., 2006). It is likely that, during acid leaching, the proton attack is easily accessed to cation sites without any barrier of Si-O networks. Brantley (2008) suggested that dissolution rates of silicate minerals decrease with an increase in the number of bridging oxygens.

On the basis of leaching studies in connection with silicate structure of minerals as above mentioned, it is inferred that dissolution rates of silicate mineral would be in the reducing order: serpentine > chlorite > talc > quartz/silica.

Nickel (Ni) is commonly held in sheet silicate minerals such as serpentine and talc. It is important to compare the structure of layer silicates as a basis to deduce their dissolution rate in acid solution. In layer silicates, the octahedral Mg-O bonds break more quickly than tetrahedral Si-O bonds (Saldi et al., 2007). This evidence reveals faster release of Mg from octahedral than Si from tetrahedral coordination.

The relatively higher dissolution rates of serpentine (Mg/Si=3/2) in acid solution compared to those of talc (Mg/Si=3/4) could be explained by considering their crystal structures. In serpentine structure, one octahedral layer is bound to one tetrahedral layer. The octahedral sheet is mainly formed by Mg-O bonds and tetrahedral sheet is occupied by Si-O bonds. Other cations such as Ni^{2+}, Co^{2+}, and Fe^{2+} may replace Mg^{2+} in octahedral sheets. Accordingly in order to leach the
valuable metals from serpentine structures, it is only required for breaking the octahedral sheet without disruption of tetrahedral sheet. The proton attack to cations in octahedral sheets of serpentine structure may take place through the edges of crystal and sideways access (Lin and Clemency 1981; Kaviratna and Pinnavaia 1994; Saldi et al., 2007), (see Fig. 5A).

In contrast, talc belong to 2:1 layer silicates in which one octahedral sheet sandwiched between two tetrahedral layers. In the structure of talc, octahedral sheets are also composed predominantly of Mg-O bonds whereas tetrahedral layers mainly consist of Si-O bonds. Acid attack on octahedral sheets in talc structure only take place via edge of grains (Fig. 5B). This fact indicates that talc is more resistant to acid attack and dissolution rates is very slow compared with many other sheet silicate minerals including serpentine (Jurinski and Rimstidt, 2001; Okada et al., 2003).

Another factor that may affect dissolution behavior of minerals is bond strength. According Lide (1984), the strength of Si-O bond is 799.6 kJ/mol. This is the highest value over the other molecular functional groups in silicate structures. The Al-O bond with strength 511 kJ/mol is much higher than Cr-O (461 kJ/mol), Mn-O (402.9 kJ/mol), Fe-O (390.4 kJ/mol), Co-O (384.5 kJ/mol), Ni-O (382.0 kJ/mol), and Mg-O (363.2 kJ/mol).

The extent of hydroxyl bonded to metal cations in silicate and oxide minerals would be expected to increase the dissolution rate because their bond strength are weaker (Terry, 1983). It is shown that, the higher dissolution rates of goethite could be influenced by the higher hydroxyl group contained in its structure. Comparison between serpentine and talc, it is clear that the former phase has higher content of crystal water (ideal value ~12.9 wt% H2O) than the latter (~4.8 wt% H2O). The rapid dissolution occurs preferentially for residual serpentine in EO sample with higher iron content and low crystal order.

Implication for hydrometallurgical processing

Result of leaching study indicated that goethite is completely dissolved from both ores implying that Ni is expected to be extracted effectively. However, much iron would also enter the pregnant solution. Dissolution of iron requires significant amounts of acid, although this can be minimized if iron is precipitated in the form of hematite rather than jarosite (Whittington and Muir, 2000). The degree of iron hydrolysis may influence the filterability and settling properties of the post digestion slurry.

In the case of silicate dissolution, the problem may arise with the higher leachability of Mg from serpentine and chlorite due to the higher acid consumption. Unleached silica residues may also hinder further separation of valuable metals (e.g Ni and Co) from leached solution (Terry, 1983b). The presence of free silica in both ores may not influence to the extent of Ni extraction, but it can result large amounts of solid waste that will increase production cost.

Conclusions

The mineralogical characterization and leaching study under high pressure condition of the two limonitic nickel ores from Soroko has been carried out. The conclusion can be drawn as follows:

1. West limonite ore is composed mainly of
goethite with subordinate talc and silica/quartz; whereas in east limonite sample the principal phase is goethite with lesser chlorite, serpentine, litiophorite, and silica. 

2. Goethite, serpentine, and chlorite are completely dissolved with sulfuric acid under high pressure condition implying that much of Ni could be extracted from these ores. Conversely, talc, litiophorite and silica are unleached.

3. The higher dissolution of goethite may result in the excess of iron in solution leading to higher acid consumption; whereas dissolution of sheet silicates not only resulted in higher Mg but they also led to formation of silica residues which may inhibit further separation of Ni and Co from leached solution.

4. The presence of unleached free silica could cause negative impact in hydrometallurgical processing due to added solid waste handling problem.

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