***International Journal of Minerals, Metallurgy and Materials***
***Volume 19, Number 2, Feb 2012, Page 100***
**DOI: 10.1007/s12613-012-0522-5**

# Activation pretreatment of limonitic laterite ores by alkali-roasting using NaOH

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(Received: 9 December 2010; revised: 17 January 2011; accepted: 25 January 2011)

**Abstract:** Activation pretreatment of Cr-containing limonitic laterite ores by NaOH roasting to remove Cr, Al, and Si, as well as its effect on Ni and Co extraction in the subsequent pressure acid leaching process was investigated. Characterization results of X-ray diffraction (XRD) and scanning electron microscopy/X-ray energy dispersive spectroscopy (SEM/XEDS) show that goethite is the major Ni-bearing mineral, and chromite is the minor one. Experimental results show that the leaching rates of Cr, Al, and Si are 95.6wt%, 83.8wt%, and 40.1wt%, respectively, under the optimal alkali-roasting conditions. Compared with the direct pressure acid leaching of laterite ores, the leaching rates of Ni and Co increase from 80.1wt% to 96.9wt% and 70.2wt% to 95.1wt% after pretreatment, respectively. Meanwhile, the grade of acid leaching iron residues increases from 54.4wt% to 62.5wt%, and these residues with low Cr content are more suitable raw materials for iron making.

**Keywords:** laterite ores; sodium hydroxide; roasting; activation; pretreatment; pressure acid leaching

[*This work was financially supported by the National Key Technology R&D Program (No.2011BAC06B07).*]

## 1. Introduction

The increased demand for nickel has depleted the easily extractable Ni sulphide deposits, and makes the mining industry look towards to the lateritic extraction technologies [1]. About 60wt% of land-based nickel reserves are contained in laterite ores [2]. Laterite ores are iron-rich soil types formed in the tropical climates through prolonging the mechanical and chemical weathering of ultramafic (ultra-basic) rocks [3]. In laterite deposits, commonly known as limonite [4], divalent iron is oxidized and precipitated as ferric (oxy) hydroxides (goethite predominantly and hematite, to a lesser extent), which is together comprised of the most common Ni-containing minerals [1]. Complex mineralogy, heterogeneous nature, and low Ni content of limonitic laterite ores make the physical beneficiation almost impossible, as well as its costly extraction by the traditional metallurgical technologies [5-6], which include the pyrometallurgical refining technology [7], the reduction roasting-ammoniacal ammonium carbonate leaching technology [8], the high-pressure acid leaching (HPAL) technology [9], the atmospheric pressure acid leaching technology [10], and so on. Recently, the HPAL technology has become an industrial application hotspot in hydrometallurgy. However, the technology was used to treat the Cr-containing limonitic laterite ores from Indonesia, but the leaching rates of Ni and Co were only 80.1wt% and 70.2wt%, respectively, because some of Ni and Co were embedded in chromite or other minerals in the laterite ores. In the last 30 years, utilization of the acid leaching iron residues was not possible due to the presence of impurities, particularly Cr [11]. Furthermore, large quantities of the acid leaching residues with impurities became the unexploited resources that are a serious burden to the environment [12].

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Keeping in mind the above situation, a new extraction technology called alkali roasting-acid leaching (ARAL) was developed by our research group to process the Cr-containing limonitic laterite ores [13-15]. The general process flow sheet of ARAL technology is shown in Fig. 1. The technology extracts all the valuable components of laterite ores comprehensively. It also reduces the costs by operating in the milder acid leaching conditions and recycling the alkali and acid media. The advantages of ARAL technology are as follows: first, the alkali-roasting activation pretreatment breaks the lateritic mineral lattices and exposes Ni and Co, leading to a higher extraction of these two metals under the milder operating conditions in the subsequent pressure acid leaching process; second, the grade of acid leaching iron residues is increased due to the removal of some impurities during the pretreatment, making the iron-making easier; lastly, Cr and Al extracted in the alkali solution can be concentrated and recovered as various types of by-products, such as chromic oxide and alumina.

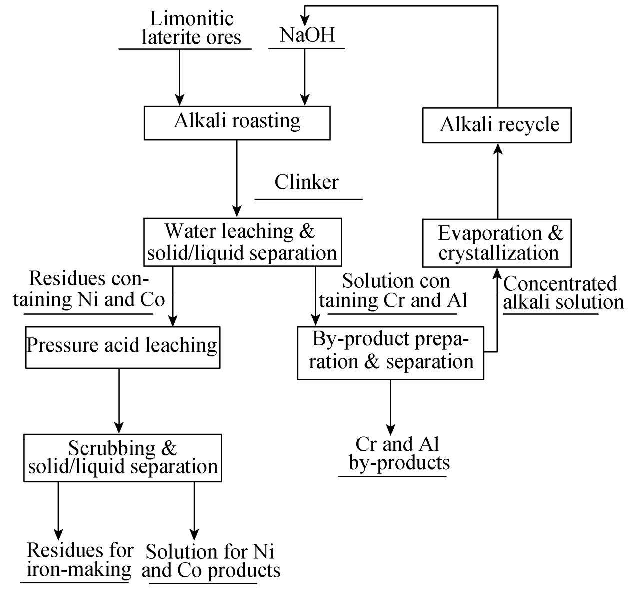

**Fig. 1. Brief flow sheet of ARAL technology for Cr-containing limonitic laterite ores.**

The first part of ARAL technology was present in this paper, *i.e.*, the activation pretreatment of Cr-containing limonitic laterite ores by NaOH roasting to remove Cr, Al, and Si in the laterite ores, and the effects on the leaching of Ni and Co in the subsequent pressure acid leaching process were investigated.

## 2. Experimental procedures

### 2.1. Materials

Limonitic laterite ores used in the present work were collected from Indonesia, and they were about 150 million tons of this type of laterite ore reserves in Indonesia. The composition analysis by inductively coupled plasma-optical emission spectrometry (ICP-OES) is presented in Table 1. The laterite samples were crushed, and the size analysis was carried out by the wet sieving, which indicated that the fine particle fraction by mass (<–74 μm) constituted 80%-85% of the samples. The solid NaOH was of reagent grade. Water for experiment and analysis was super purified by a water super-purification machine.

**Table 1 Composition of Cr-containing limonitic laterite ores wt%**

| Fe | Ni | Co | $Cr_2O_3$ | $Al_2O_3$ | MgO | $SiO_2$ | Mn |
|---|---|---|---|---|---|---|---|
| 47.58 | 0.58 | 0.04 | 3.31 | 7.86 | 0.54 | 4.74 | 0.31 |

### 2.2. Experimental apparatus and procedure

Alkali-roasting tests were performed in a muffle furnace using the corundum crucibles. The temperature of the muffle furnace was controlled by a programmable temperature controller with a precision of ±1°C. The laterite samples and NaOH with a certain NaOH/ore ratio by mass were mixed in the corundum crucibles homogeneously, placed into the muffle furnace, and heated to a preset temperature for a required time with the free access of air.

To analyze the extraction of Cr and Al, the molten product was taken out rapidly at high temperature and then cooled in the air. The cooled alkali-roasting clinker was ground and put into the glass beakers with water to form a slurry. After washing with water, the slurry was separated by a Buchner funnel into a filtrate rich in Cr, Al, and Si and a filter cake rich in Ni, Co, and Fe. The filter cake was melted and then dissolved in diluted HCl solution. After dissolving completely, the HCl solution was analyzed for the contents of Cr, Al, and Si by ICP-OES. Leaching rate was calculated as

$$X = 1 - \frac{G_l V M}{G_i m_p C} \tag{1}$$

where $X$ is the conversion fraction of Cr, Al, or Si by mass; $M$ the concentration of Cr, Al, or Si in the HCl solution, g/L; $G_l$ and $G_i$ the total mass of filter cake and laterite ores, respectively, g; $m_p$ the mass of the used filter sample, g; $C$ the mass fraction of Cr, Al, or Si in the laterite ores; and $V$ the volume of HCl solution used, L.

## 3. Results and discussion

### 3.1. Characterization of laterite ores and water leaching residues after alkali roasting

3.1.1. X-ray diffraction (XRD) analysis

The XRD analysis results of laterite ores and water leaching residues after alkali roasting are shown in Fig. 2. Goethite is the major mineral in the laterite ores, and hematite and magnetite are the minor ones. The diffraction peaks also demonstrate the presence of chromite, gibbsite, manganite, and silicate minerals. After alkali roasting and leaching with water, the diffraction peaks associated with the crystalline minerals disappear and are replaced by the little amorphous curve bread peaks. These little peaks are attributed to the amorphous phase of ferric oxide. This indicates that the alkali-roasting pretreatment breaks the lattices of Ni- and Co-bearing minerals mainly, making Ni and Co more available for leaching under the milder operating conditions in the subsequent acid leaching process.

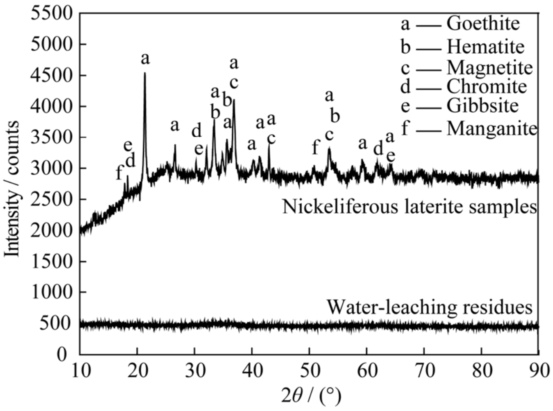

**Fig. 2. XRD patterns of limonitic laterite ores and water leaching residues after alkali roasting using NaOH.**

3.1.2. Scanning electron microscopy (SEM) observation

The laterite ores and water leaching residues after alkali roasting are both collected for SEM observation as shown in Fig. 3. Goethite with a columnar shape is the major mineral in Fig. 3(a). Spheroidal particles are mainly the grains of Ni oxide, which are rich in the goethite lattice. $Cr_2O_3$, $Al_2O_3$, and MnO may also exist in the goethite lattice, because in some extent, $Cr^{3+}$, $Al^{3+}$, and $Mn^{2+}$ can substitute for $Fe^{3+}$ in the goethite lattice [5]. As shown in Fig. 3(b), the goethite lattice is broken after alkali-roasting pretreatment, and the amorphous ferric oxide is the main mineral in the water leaching residues after the soluble compounds being dissolved into the liquid phase.

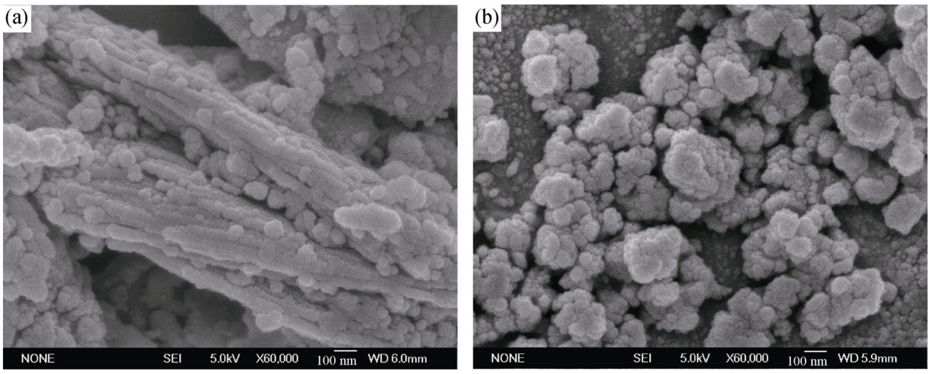

**Fig. 3. SEM observation of limonitic laterite ores and water leaching residues after alkali roasting using NaOH: (a) limonitic laterite ores; (b) water leaching residues after alkali roasting.**

3.1.3. X-ray energy dispersive spectroscopy (XEDS) microanalysis

To determine the chemical composition, XEDS microanalysis was carried out on the lateritic minerals and water leaching residues after alkali roasting. The minerals analyzed were goethite, hematite, magnetite, chromite, gibbsite, and manganite. The results of chemical analysis were as follows.

(a) Goethite was the major Ni-bearing mineral in the laterite ores, and the content of Ni by mass was around 0.54wt%. Trace amounts of Co, Cr, and Al were also observed in the goethite lattice, and they were 0.03wt%, 1.07wt%, and 1.03wt%, respectively.

(b) Hematite and magnetite were the minor minerals in the laterite ores with the content of ~10.08wt%, and some of them contained small amounts of Ni (0.21wt%).

(c) Chromite was present in the laterite ores with the content of $Cr_2O_3$ 67.55wt%, $Al_2O_3$ 12.12wt%, and Ni 0.36wt%.

(d) Gibbsite mainly containing $Al_2O_3$ and manganite rich in Co (3.27wt%) were also present in the laterite ores.

(e) Amorphous ferric oxide was the major mineral in the water leaching residues with the content around 95.01wt%. Furthermore, the residues were rich in Ni and Co with the contents of 1.41wt% and 0.11wt%, respectively. This indicated that Ni and Co mainly entered into the amorphous ferric oxide after the alkali-roasting activation pretreatment.

### 3.2. Alkali roasting of laterite ores using NaOH

#### 3.2.1. Alkali roasting reactions

NaOH and chromite existing in the laterite ores takes place the following main chemical reactions during the roasting process.

$$2NaOH+1/2Cr_2O_3+3/4O_2=Na_2CrO_4+H_2O \quad (2)$$

$$2NaOH+1/2FeO{\cdot}Cr_2O_3+7/8O_2=Na_2CrO_4+1/4Fe_2O_3+H_2O \quad (3)$$

NaOH, gibbsite, and silicate existing in the laterite ores undergo the following main chemical reactions during the roasting process.

$$Al_2O_3{\cdot}3H_2O=Al_2O_3+3H_2O \quad (4)$$

$$2NaOH+Al_2O_3=2NaAlO_2+H_2O \quad (5)$$

$$2NaOH+SiO_2=Na_2SiO_3+H_2O \quad (6)$$

$$2NaAlO_2+nNa_2SiO_3=Na_2O{\cdot}Al_2O_3{\cdot}nSiO_2+nNa_2O \quad (7)$$

The steps of roasting reactions are as follows: first, NaOH reacts with chromite, gibbsite, and silicate to form $Na_2CrO_4$, $NaAlO_2$, and $Na_2SiO_3$ at high temperature; then, the reaction between $NaAlO_2$ and $Na_2SiO_3$ occurs with the continued increase of roasting temperature and roasting time as Eq. (7).

#### 3.2.2. Effect of roasting temperature

The influence of roasting temperature on the leaching of Cr, Al, and Si is investigated, as shown in Fig. 4. The leaching rate of Cr increases obviously from 300 to 700°C and maintains steady beyond. The leaching rates of Al and Si both increase slightly with the increase in temperature from 300 to 700°C and then decrease. This may be due to the fact that high temperature is suited to the production of insoluble alumino silicate precipitate, which leads to a loss in soluble Al and Si. Furthermore, the preferential generation of albite ($Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2$) at high temperature may result in a lower leaching rate of Si than that of Al [16]. To sum up, the optimal roasting temperature is 700°C.

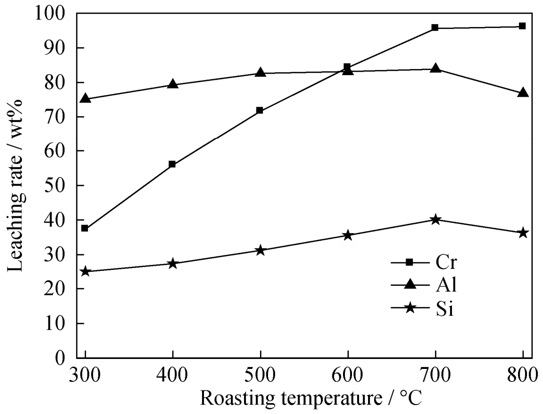

**Fig. 4. Effect of roasting temperature on the leaching of Cr, Al, and Si at NaOH-ore ratio by mass of 1.2 for roasting 150 min.**

#### 3.2.3. Effect of NaOH-ore ratio by mass

The influence of NaOH-ore ratio on the leaching of Cr, Al, and Si is investigated, as shown in Fig. 5. The NaOH-ore ratio increases steadily with the leaching rates of Cr, Al, and Si increasing until the NaOH-ore ratio reaches 1.2. This indicates that the NaOH-ore ratio affects the leaching of Cr, Al, and Si, and the optimal NaOH-ore ratio is 1.2.

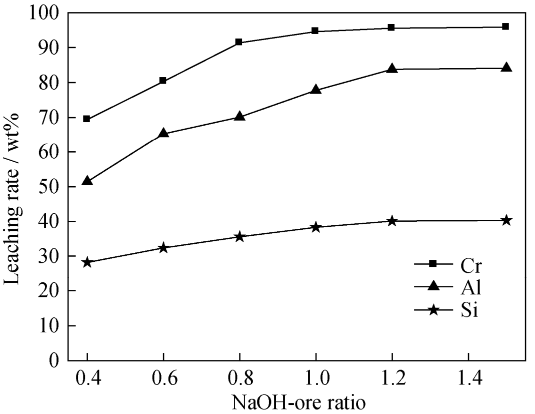

**Fig. 5. Effect of NaOH-ore ratio on the leaching of Cr, Al, and Si at roasting temperature of 700°C for roasting 150 min.**

#### 3.2.4. Effect of roasting time

The influence of roasting time on the leaching of Cr, Al, and Si is investigated, as shown in Fig. 6. The leaching rate of Cr increases considerably at the initial stage of roasting and maintains steadily after 150 min. This demonstrates that the reaction between NaOH and Cr occurs easily at 700°C.

The leaching rates of Al and Si both increase considerably during the first 150 min of roasting and then decrease gradually. This can be explained by the fact that the extending roasting time induces the generation of insoluble sodium alumino silicate precipitates, as shown in Eq. (7), which results in the decline of Al and Si extraction. Consequently, 150 min is favorable roasting time for the leaching of Cr, Al, and Si.

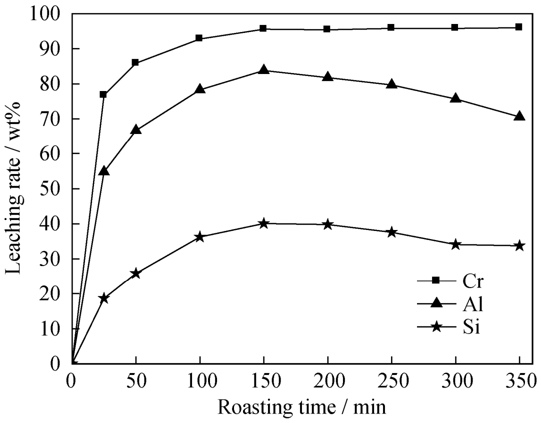

**Fig. 6. Effect of roasting time on the leaching of Cr, Al and Si at a NaOH-ore ratio of 1.2 and a roasting temperature of 700°C.**

### 3.3. Contrast test on leaching of Ni and Co by pressure acid leaching

The subsequent contrast tests of pressure acid leaching of laterite ores with and without pretreatment by alkali roasting were performed to evaluate the effect of pretreatment and the grade of acid leaching iron residues. The water leaching residues were obtained from the NaOH-roasting pretreatment of the laterite ores under the optimal conditions proposed above. The composition analysis by ICP-OES is listed in Table 2. After pretreatment by alkali roasting, Cr and Al evidently decrease in the water leaching residues, whereas Fe, Ni, and Co increase.

**Table 2. Composition of water leaching residues of the alkali-roasting clinker wt%**

| Fe | Ni | Co | Cr | $Al_2O_3$ | $SiO_2$ |
|---|---|---|---|---|---|
| 54.40 | 0.64 | 0.043 | 0.11 | 1.55 | 3.59 |

The contrast test condition was as follows: liquid-solid mass ratio 4:1, free acid concentration 35 g/L, leaching temperature 200°C, leaching time 2 h, and leaching pressure 1.6 MPa. The results shown in Table 3 indicate that the leaching rates of Ni and Co from the water leaching residues are clearly higher than that of direct pressure acid leaching of laterite ores without alkali roasting. After alkali-roasting pretreatment, the leaching rate of Ni increases from 80.1wt% to 96.9wt%, and Co increases from 70.2wt% to 95.1wt% in the subsequent pressure acid leaching process. Furthermore, the acid leaching operation conditions of ARAL process were milder, compared with those of the traditional HPAL technology. Meanwhile, the grade of acid leaching iron residues increases from 54.4wt% to 62.5wt%, mainly due to the removal of impurities in the laterite ores.

**Table 3. Contrast test results on the pressure acid leaching of Ni and Co**

| Test method | Leaching rate of Ni / wt% | Leaching rate of Co / wt% | Pressure acid leaching iron residue grade / wt% |
|---|---|---|---|
| Direct pressure acid leaching of raw laterite ores without alkali roasting | 80.1 | 70.2 | 54.4 |
| Pressure acid leaching of water leaching residues after alkali roasting | 96.9 | 95.1 | 62.5 |

## 4. Conclusions

(1) Goethite is the major mineral in the Cr-containing limonitic laterite ores, but magnetite, hematite, and chromite are the minor ones. Goethite is also the major Ni-bearing mineral, whereas chromite is the minor one. Experimental results show that the leaching rates of Ni and Co from the laterite ores by the HPAL technology are only 80.1wt% and 70.2wt%, respectively. Furthermore, the higher-Cr acid leaching iron residues are difficult to use in iron making.

(2) The optimal alkali-roasting conditions are as follows: and roasting temperature 700°C, NaOH-ore ratio by mass 1.2, roasting time 150 min. Experimental results show that 95.6wt% of Cr, 83.8wt% of Al, and 40.1wt% of Si in the laterite ores can be leached out under the optimal conditions.

(3) The leaching rate of Ni increases from 80.1wt% to 96.9wt%, and that of Co increases from 70.2wt% to 95.1wt% after pretreatment compared with the direct pressure acid leaching. Meanwhile, the grade of acid leaching iron residues increases from 54.4wt% to 62.5wt%. These residues with low Cr content are more suitable raw materials for iron making.

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