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SULFURIC ACID LEACHING CHARACTERISTICS OF Ni-DOPED GOETHITE

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Abstract

In the atmospheric acid leaching process of low-grade nickelferous laterite, the leaching mechanisms still remain unclear when sulfuric acid is used as the leaching agent. It is therefore imperative to study the leaching characteristics of Ni-doped goethite. In this work samples of goethite and nickeliferous goethite were synthesized and characterized by chemical composition, surface area and XRD analyses. The results show that part of nickel is incorporated into the lattice of nickeliferous goethite. The synthesized nickeliferous goethite was pre-leached in diluted hydrochloric acid at 25°C to separate the adsorbed nickel. Subsequently, the Ni-doped goethite in which nickel is completely distributed within the lattice was leached in sulfuric acid. The results indicated that the extraction of Ni was incongruent with that of Fe. Sulfuric acid leaching kinetics of Ni and Fe are characteristic of chemical reaction and internal diffusion controlled processes, respectively.

Introduction

Due to the increasing demand for nickel around the world, the utilizization of nickeliferous laterite ores is imperitive as such ores account for approx. 72% of the world reserves of nickel. Classified from the main mineral constituents, limonitic laterite mainly contains goethite which itself contains low nickel concentrations and high iron concentrations, and account for about 28% of the world's Ni resource. Atmospheric acid leaching is a promising method to extract nickel from limonitic laterite. However, some problems still exist in this process such as low selective extraction of nickel relative to iron, large acid consumption, and long leaching time. Since mostnickel exists in goethite of limonitic laterite; it is necessary to study the leaching characteristics of nickeliferous goethite in order to reveal the acid leaching mechanisms of limonitic laterite.

Research studies conducted on the characterization and leaching behavior of pure and

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nickeliferous goethites have been carried out by Rakesh et al. [1]who investigated the leaching behavior of nickeliferous goethites by adsorption and co-precipitation modes. The authors results indicated that high levels of extraction of nickel were achieved for the two types of nickeliferous goethites examined and that extraction of nickel of nickeliferous goethite from co-precipitation mode was superior to that observed from the adsorption mode. Work done by P. Lussiez [2] concerning the acid leaching behaviors of nickeliferous goethites, suggested that part of the Ni^{2+} ions were absorbed on the surface of synthesized goethite, and that the concentration of Ni^{2+} ions lead to an increased rate of dissolution Apparently, the reports mentioned above cannot fully interpret the leaching behaviors of nickeliferous goethite in sulfuric acid, due to the influence of Ni^{2+} ions absorbed on the surface of goethite. So far, it seems that there has been no such report of the leaching behaviors of goethite with Ni^{2+} ions completely incorporated into the crystal lattice when leached in sulfuric acid.

In this paper, the obtained Ni-doped goethite in which nickel was completely distributed within the lattice was leached in sulfuric acid, and the effect of leaching time and temperature on extraction of nickel and iron was studied. The controlling step of leaching process was revealed by evaluating the leaching kinetics of Ni and Fe. The results in this paper may be consulted for use in developing a more effective atmospheric pressure process for extracting nickel from laterite.

Materials and Methods

Reagents

Reagents involving ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), sodium hydroxide (NaOH), nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) and sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$) used in this paper are all of analytical grade.

Synthesis and Characterization of Pure and Nickeliferous Goethite

Pure goethite samples used in the present study were prepared by the co-precipitation method in the laboratory. Following the same procedure as described by Schwertman and Cornell [3, 4], 1 mol/L ferric nitrate and 10 mol/L sodium hydroxide solutions were mixed under the given conditions. preparation of nickeliferous goethite was achieved by simultaneously adding a 8.52 mmol/L $Ni(NO_3)_2$ solution with 10 mol/L sodium hydroxide solution drop wise to a 1 mol/L ferric nitrate solution The suspension was aged for 48 h at 70 °C, and then washed thoroughly with distilled water until a pH of 7-8 was obtained. The samples were subsequently dried and grinded. The total iron grade of both pure and nickeliferous samples was determined by titrimetry method, and the nickel content in the doped sample was determined by atomic absorption spectrophotometry. Samples of goethite and nickeliferous goethite were characterized by chemical composition, surface area and XRD analyses.

Chemical composition and surface area of the both samples of goethite are given in Table I, which shows that surface area has been increased from 47.44 to 57.46 m^2/g by doping Ni^{2+} ions in goethite matrix. The surface area increasing with Ni^{2+} ions doping has been also reported by M. Mohapatra [5].

Table I. Main chemical composition and surface area of pure and Ni-doped goethite

Samples	Surface area (m^2/g)	Fe (mass%)	Ni (mass%)
Pure goethite	47.77	61.81	—
nickeliferous goethite	57.46	62.94	0.84

XRD patterns of both samples of goethite shown in Fig.1, reveal that all of the diffractions of synthetic pure goethite could be indexed to a pure orthorhombic α-FeOOH phase, which was easily detected using data available in the Powder Diffraction File [6]. For nickeliferous goethite, only the intensity of the main diffraction peaks changed comparison to the pure goethite. Internal disorder always exists in synthetic goethite, the degree of which increases with increasing unit cell edge length, c [7]. c-values procured from the pure and nickeliferous goethite were 0.46149, 0.46175nm, respectively, indicating that the internal disorder of nickeliferous goethite was larger, thus demonstrating that nickel was incorporated into the lattice structure of goethite.

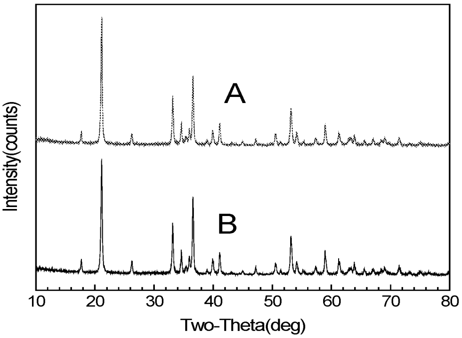

Figure 1. XRD patterns of pure (A) and Ni-doped goethite (B)

Preparation of Ni-doped Goethite

On the basis of evaluating the mechanisms of synthesizing α-FeOOH via the hydrothermal method [8] and characterization of nickeliferous goethite, part of nickel was incorporated into the crystal lattice of nickeliferous goethite, while the other part absorbed on the surface in the form of hydroxo complexes.

The research was focused on the acid leaching mechanism of goethite with nickel incorporated into goethite structure totally. Therefore, it was necessary to examine the synthesized nickeliferous goethite.

R. M. Cornell [9] determined that nickel hydroxo complexes could be removed by diluted hydrochloric acid liquor at room temperature, without effecting the internal structure of goethite. The procedure was as follows: A measured amount of synthesized nickeliferous goethite was leached in 0.4mol/L hydrochloric acid for 2h at 25 °C, and then filtered, washed, dried, and grinded.

Acid Leaching Tests

Leaching tests were conducted in a DY-8 autoclave equipped with eight 70 ml stainless steel vessels rotating end to end in glycerin bath. The bath was electrically heated and its temperature controlled by a thermostat. At the beginning of each trial, 5g of the Ni-doped goethite sample were combined with 50 ml of 8% (w/w) sulfuric acid inside the stainless steel autoclave vessels. The sealed vessels were subsequently soaked in the bath at a certaintemperature and rotated at 30 rpm. Filtration was performed immediately after leaching, followed by atomic absorption analysis of the filtrate to determine the nickel content, while the residue was dried and analyzed for total iron content by titration [10].

Results and Discussion

Sulfuric Acid Leaching

As shown in Fig.2 extraction of nickel increases with increasing temperature and time, however the variability of leaching differed at different temperatures, the higher temperature resulting in faster leaching of nickel with extended time. Rakesh et al. [1] also determined that extraction of nickel from synthesized nickeliferous goethite in sulfuric acid at lower temperatures increased considerably (>50%) within a short time, due to the absorption of Ni on the surface of the nickeliferous goethite as hydroxo complexes. For leaching of Ni-doped goethite in Fig.2, extraction of nickel decreased to approx. 12% within 15 minutes.

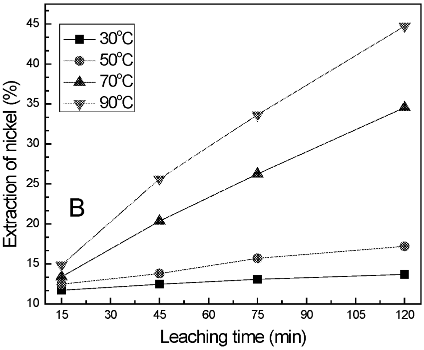

Figure 2. Effects of leaching time on extraction of nickel of Ni-doped goethite at

different temperatures

Fig.3 shows the effect of leaching time and temperature on the leaching of iron in sulfuric acid pre-leached Ni-doped goethite. Evident from the results was the low extraction of iron (< 9%), which increased with increasing temperature and time .

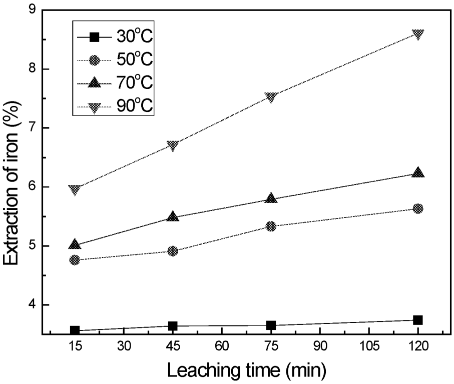

Figure 3. Effects of leaching time on extraction of iron at different temperatures (pre-leached Ni-doped goethite)

Fig.4 shows the relationship between the extraction of nickel and iron (leaching temperature 50 °C) in the acid leaching tests of Ni-doped goethite (in similar 20°C increments from 30 to 90°C). From the results it appears as though the extraction of nickel and iron is incongruent, which suggests that nickel is distributed non-uniformly within the lattice of goethite, possibly towards the core or periphery of the crystals. R. Lim-Nunez and R. J. Gilkes [11] proposed a similar belief that goethite doped with Co, Al, Mn all satisfy homogeneous leaching regularity, while goethite doped with Ni and Cr, did not due to that no statistically significant systematic displacement of unit-cell dimensions from those for unsubstituted goethites was observed for Cr- and Ni-goethites. A similar conclusion was made by R. M. Cornell [9] in that Ni distribution in α-FeOOH is non-uniform; a significant concentration of Ni observed concentrated near the surface of the crystals, furthermore this distribution is in accord with what would be expected from the crystallization kinetics of α-Ni, FeOOH. A. Manceau [12] indicated that the Ni site in synthetic goethite is strongly relaxed with a contraction of the goethite structure in the plane of edge-sharing double chains (bc plane), and an expansion in the direction of corner linkages (approximately the ab plane). This anisotropic relaxation of the Ni site locally reduces the distortion of the goethite structure.

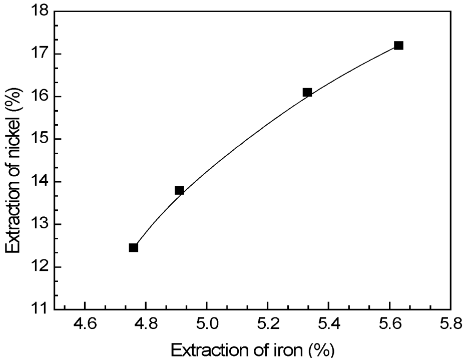

Figure 4. Variation of extraction of nickel with iron (50 ^{o}C)

Leaching Kinetics of Ni and Fe

To determine the kinetic parameters and rate-controlling step for the leaching of metals, the experimental data were analyzed according to the shrinking core model.

It was found that leaching of nickel fits for the equation $1\text{-}(1\text{-}R)^{1/3} = k*t$, while the equation $1\text{-}2R/3\text{-}(1\text{-}R)^{2/3} = (2D_2C_0/r_0^2\alpha\rho)t$ for iron, and both of them present straight lines for a good approximation (Fig.5). This suggests that leaching kinetics of Ni and Fe are characteristic for chemical reaction and internal diffusion controlled processes, respectively.

According to Arrhenius equation:

$$\ln k = -E/(RT) + \ln$$

The *lnk* vs *1/T* is plotted, and slope of the line is the activation energy of leaching reaction.

Arrhenius fitting curves of leaching of nickel and iron are shown in Fig.6, and the activation energies of nickel and iron are 46.1kJ/mol and 38.7kJ/mol, respectively.

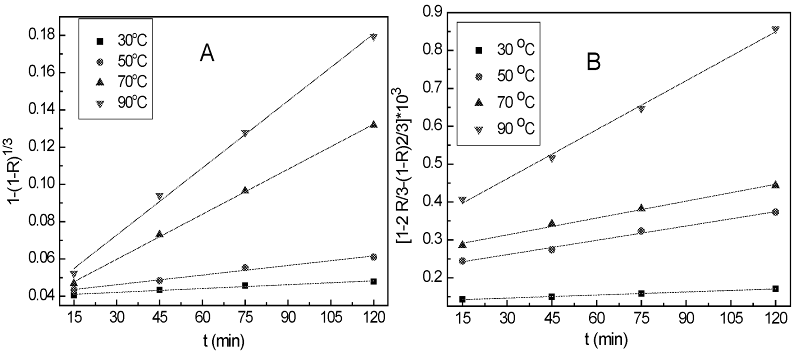

Figure 5. Curve of leaching kinetics of Ni (A), Fe (B)

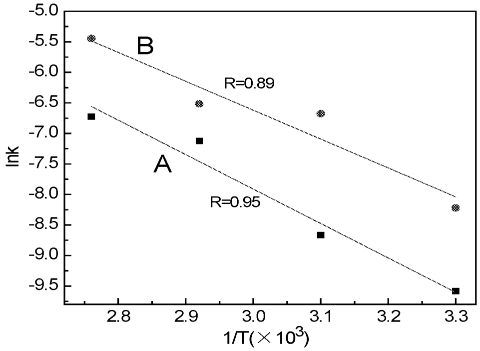

Figure 6. Arrhenius fitting curves of leaching of Ni (A) and Fe (B)

Conclusions

(1) Samples of goethite and nickeliferous goethite were synthesized and characterized by chemical composition, surface area and XRD analyses. The results show that the bulk of nickel was incorporated into the crystal lattice of nickeliferous goethite, and the rest of nickel was absorbed on the surface in the form of hydroxo complexes.

(2) The results obtained from the Ni-doped goethite in which nickel was completely distributed throughout the lattice was leached in sulfuric acid, indicated that extraction of nickel and iron increased with increasing temperature and time. As the leaching ratio of nickel was as low as 44.74% even at 90 °C for 120min, for that the internal structure of goethite is hardly destroyed. Meanwhile, the extraction of Ni was incongruent with that of Fe, which demonstrates that incorporated Ni is nonuniformly distributed in the lattice.

(3) Sulfuric acid leaching kinetics of Ni and Fe were characteristic of chemical reaction and internal diffusion controlled processes, respectively. The calculated activation energies for Ni and Fe were 46.1 and 38.7 kJ/mol, respectively.

Acknowledgments

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