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Behaviour of cobalt during sulphuric acid pressure leaching of a limonitic laterite

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ABSTRACT

Extraction of nickel and cobalt from lateritic ores by sulphuric acid pressure leaching techniques has become increasingly important in recent years. The above hydrometallurgical method has a low operational cost and is environmentally safe compared to the energy-intensive and air-polluting pyrometallurgical processes. High nickel and cobalt recovery of more than 90%, with a high selectivity due to the simultaneous iron and aluminium dissolution and precipitation, can be achieved. Experiments were carried out using batch pressure leaching techniques. A titanium autoclave equipped with acid injection and sample withdrawal units was employed. Conditions close to the industrial practice were tested; pulp density: 10–30%, acid to ore ratio: 0.15–0.35 and temperature ranging from 230 to 270 °C. Raw limonitic laterite and the evolution of the nature of solid products during leaching were thoroughly investigated using Transmission Electron Microscopy (TEM). Whereas nickel is predominately associated with the goethite phase, cobalt was found to exist only in nickel-rich manganese structures. During leaching, goethite dissolves liberating nickel while iron re-precipitates as dense hematite particles in solution by ex situ precipitation. Cobalt dissolves rapidly and remains in the aqueous phase. Manganese follows the cobalt dissolution pattern, however at a much lower rate. In the end of the leaching tests, manganese particles get almost depleted of cobalt. The dissolution rate of cobalt during leaching was insensitive to the increase of temperature in the above tested range. However, increasing the agitation rate of the slurry led to the increase of its dissolution rate. The above findings, along with the TEM photos and the respective mineralogical analysis, indicate that film diffusion is most possibly the rate-controlling step. The shrinking core model could be employed in order to describe cobalt dissolution kinetics.

1. Introduction

Cobalt compounds have been used for centuries to impart a rich blue color to glass, glazes and ceramics. Cobalt has been detected in Egyptian sculpture and Persian jewelry from the third millennium BC, in the ruins of Pompeii (destroyed AD 79), and in China dating from the Tang dynasty (AD 618–907) and the Ming dynasty (AD 1368–1644). However, the free metallic cobalt was not discovered until 1735 by Georg Brandt (Wang, 2006).

Cobalt is not found as a native metal but generally in the form of minerals like cobaltite (CoAsS), erythrite ($Co_3(AsO_4)_2 \cdot 8H_2O$), glaukodot, ((Co,Fe)AsS), sphaero-cobaltite ($CoCO_3$), skutterudite ((Co,Ni,Fe)As_3), etc. Cobalt is usually not mined alone; as a matter of fact, it tends to be produced as a by-product of nickel and copper mining activities (Shedd, 2008; Shedd, 2006).

Most of cobalt is consumed in the production of superalloys. The temperature stability of these alloys makes them suitable for turbine blades within gas turbines and jet aircraft engines. These alloys are also corrosion and wear-resistant (Donachie, 2002). Special cobalt chromium molybdenum alloys are used for prosthetic parts such as hip and knee replacements (Michel et al., 1991), while cobalt alloys are also used for dental prosthetics, where they are useful to avoid allergies to nickel (Disegi, 1999). Some high speed steels also use cobalt to increase heat and wear-resistance. The special alloys of aluminium, nickel, cobalt and iron, known as Alnico, and of samarium and cobalt are used in permanent magnets (Luborsky et al., 1957). Lithium cobalt oxide ($LiCoO_2$) is widely used in lithium ion battery electrodes, while nickel-cadmium (NiCd) and nickel metal hydride (NiMH) batteries also contain significant amounts of cobalt (Hawkins, 2001). Finally, several cobalt compounds are used in chemical reactions as catalysts while other cobalt compounds are used in the pigments and coloring industry (Wang, 2006).

Identified world cobalt resources are about 15 million tons. The vast majority of these resources are in nickel-bearing laterite deposits, while most of the rest occurs in nickel-copper sulphide deposits in Australia, Canada, Russia, and in the sedimentary copper deposits of Congo and Zambia. In addition, millions of tons of hypothetical and speculative cobalt resources exist in manganese nodules and crusts on the ocean floor (Shedd, 2008).

Limonitic laterite deposits contain usually 1–1.5 wt.% nickel, that is mainly associated with goethite (FeOOH), and 0.1–0.2 wt.% cobalt associated, almost exclusively, with a manganese phase (Georgiou

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and Papangelakis, 2004; Monhemius, 1987; Golightly, 1979; Schellmann, 1978). The recovery of nickel and cobalt from the above laterite deposits, using sulphuric acid pressure leaching techniques, has become increasingly important in recent years. The latter technique is most suitable for low-grade laterites and leads to high extraction rates. In addition, this method has low operational cost and is environmentally friendly, especially compared to the current pyrometallurgical extraction methods that utilize the depleting sulphide ores (Georgiou and Papangelakis, 1998; Chou et al., 1977).

Sulphuric acid pressure leaching of limonitic laterites is performed at elevated temperatures (250–280 °C) in acid resistant titanium autoclaves. During leaching, goethite dissolves liberating nickel in the aqueous phase while iron precipitates simultaneously forming hematite (Fe_2O_3) according to the reactions 1–3. Cobalt, associated with the manganese phase, dissolves in the same manner and remains in the aqueous phase (reaction 4).

$$FeOOH_{(s)} + 3H^+ \rightarrow Fe^{3+} + 2H_2O \tag{1}$$

$$2Fe^{3+} + 3H_2O \rightarrow Fe_2O_{3(s)} + 6H^+ \tag{2}$$

$$NiO_{(s)} + 2H^+ \rightarrow Ni^{2+} + H_2O \tag{3}$$

$$CoO_{(s)} + 2H^+ \rightarrow Co^{2+} + H_2O \tag{4}$$

Extensive studies on sulphuric acid pressure leaching of limonitic laterite have been contacted at the University of Toronto in recent years in cooperation with Inco Ltd, which led to the derivation of nickel dissolution kinetic models (Georgiou and Papangelakis, 1998; Rubisov and Papangelakis, 2000). Also, in depth mineralogical analysis of laterite and the solids formed during leaching was performed using Transmission Electron Microscopy. The latter technique proved crucial to the understanding of the physicochemical nature of leaching (Georgiou and Papangelakis, 2004; Georgiou, 1995).

Although, numerous data for cobalt dissolution kinetics were also collected during the above studies (Georgiou, 1995), no article has been published so far. Thus, this work aims at revealing the behaviour of cobalt during sulphuric acid pressure leaching of limonitic laterite and investigating the possible leaching mechanism, comparing at the same time, the respective well-studied nickel dissolution process.

2. Experimental

2.1. The ore

The limonitic laterite utilized in this study originated from Soroako, Indonesia and its elemental analysis is shown in Table 1. It was a reddish-brown, clay-like solid, containing 42 to 44% water. Laterite is a highly porous material with very fine size pores and a high specific surface area (Table 2).

2.2. Experimental set-up and procedure

Leaching tests were performed in a 2-L titanium autoclave, manufactured by Parr Instrument. Temperature was controlled within ±2 °C by a temperature control system, manipulating both an electrical heating mantle and a water-cooling stream. Agitation was provided by a titanium-made twin impeller that was magnetically driven. The autoclave was equipped with an acid injection device designed by INCO Ltd.

Table 1
Elemental composition of the laterite in wt.% of dried solids (INCO Ltd).

Fe	Si	Al	Cr	Ni	Mg	Mn	S	Co
47.7	3.87	1.9	1.56	1.22	1.03	0.97	0.26	0.14

Table 2
Solid characteristics of limonitic laterite.

Bulk density	1.09 $g\,cm^{-3}$
Absolute density	3.73 $g\,cm^{-3}$
Porosity	0.708
Specific surface area	64.82 $m^2\,g^{-1}$
Average pore diameter	0.04 μm
Median particle size	0.97 μm
Mean particle size	1.70 μm

A certain amount of “as mined” laterite was mixed with a pre-calculated amount of deionised water and placed in the reactor. The slurry was then heated up to a predetermined temperature in the range of 230 to 270 °C under continuous agitation. Upon temperature stabilisation, a certain amount of concentrated sulphuric acid (96 wt.%), corresponding to different acid to ore ratios, was injected into the autoclave under nitrogen pressure.

Samples were withdrawn through a dip tube and cooled by a co-current heat exchanger. A 30 mm pore graphite filter, manufactured by Union Carbide, was utilized in order to prevent solids from passing through the sampling tube. Solution aliquots were periodically withdrawn and analysed. After the end of the experiment, the solids were analysed for Ni and Co. A mass balance check on these metals was always within 1 to 5% of the initial metal content.

In the case of experiments performed to monitor the evolution of solids composition with time, the filter was removed. The slurry samples obtained were filtered and the solids washed with deionized water and dried in an oven at about 60 °C for 24 h. The dry solids were then prepared for transmission electron microscopy analysis.

2.3. Chemical analysis of solution

Flame atomic absorption spectroscopy (FAAS) was utilized to analyse the liquid samples, after the proper dilution, for nickel, cobalt, iron, aluminium and manganese. A fully automated instrument (VARIAN SpectrAA 250 Plus) was employed for this purpose. In calculating Ni and Co extractions, a volume correction formula was used (Georgiou and Papangelakis, 1998).

2.4. Mineralogical analysis

In depth mineralogical analysis of the ore and the solids took place at Mt. Sinai Hospital (Toronto, Canada) utilizing Transmission Electron Microscopy. Details of the above technique can be found in previous publications (Georgiou and Papangelakis, 2004; Georgiou, 1995). High magnification and resolution photos of the ore and the solids were obtained. The elemental composition of the samples was revealed using X-ray analysis while the mineralogical composition was determined using electron diffraction analysis.

3. Results and discussion

3.1. Effect of acid to ore ratio

Several acid to ore ratio values at different leaching conditions were tested, as depicted in Figs. 1–4. As expected, the higher the acid to ore ratio, the higher the extraction efficiency. Cobalt extractions of as high as 98–99% can be achieved if the proper amount of sulphuric acid is utilized. For slurry densities of 10–30%, an acid to ore ratio of 0.20 to 0.25 is usually adequate for an efficient extraction of cobalt.

The above acid to ore ratio range was also applicable for the extraction of nickel from the same ore (Georgiou and Papangelakis, 1998).