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Reductive acid leaching of laterite and metal oxides — A review with new data for Fe(Ni,Co)OOH and a limonitic ore

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ABSTRACT

The reductive leaching of nickel laterite has attracted the interest of many researchers due to the enhanced kinetics of nickel and cobalt dissolution in the presence of acids and reducing agents during atmospheric, pressure, heap or bio leaching processes. Systematic studies on synthetic oxides and natural ores can shed light on the reaction mechanism and lead to investigations of beneficial reagents for further studies. This paper briefly reviews the literature and describes a comparative study of metal leaching from synthetic goethite spiked with nickel or cobalt and a limonitic laterite ore to rationalise the role of reducing agents in acid media. Results are discussed on the basis of the effect of speciation, surface chemical reactivity of oxides and heterogeneous kinetic models.

1. Introduction

Laterite ores are oxides of complex mineralogy and contain nickel and cobalt of low grades (Tables 1–2). Numerous reviews and research activities have focussed on various beneficiation methods to upgrade the nickel content of ores, as well as the advantages and disadvantages. Economic evaluation of different commercial, piloted, or bench scale alternative processing routes, depending upon the location and mineralogy of ore, and availability of technology has also been conducted. These include smelting, reduction roasting to ferronickel and ammonia leaching (Caron process), high pressure acid leaching, strong brine leaching, atmospheric leaching, heap leaching and microbial leaching with fungi or bacteria (Curlook, 2004; Hallberg et al., 2011; Kyle, 1996; McDonald and Whittington, 2008a,b; Muir and Johnson, 2006; Norgate and Jahanshahi, 2011; Simate et al., 2010; Steyl et al., 2008; Whittington and Muir, 2000; Xavier and Ciminelli, 2008). The recovery of a mixed sulphide or hydroxide precipitate (MSP or MHP) of Ni(II) and Co(II) from leach liquors of a widened ore type and grade, which can be sold to existing refineries, is the preferred option when metal production on the minesite is not intended (Curlook, 2004; Kose and Topkaya, 2011; Steyl et al., 2008; White et al., 2006). The purpose of new research is to develop processing routes/plants of lower maintenance which require less energy and reagent inputs, and that are more cost effective to construct and operate under environmentally safe conditions (Curlook, 2004; Harris and Magee, 2003; Le et al., 2006; Lee et al., 2005; Li et al., 2009; Liu et al., 2004, 2009; Luo et al., 2009, 2010; McDonald and Whittington, 2008a,b; Moskalyk and Alfantazi, 2002; Norgate and Jahanshahi, 2011; Simate et al., 2010; Steyl et al., 2008; Tang and Valix, 2006; Whittington and Muir, 2000; Xavier and Ciminelli, 2008).

Non-selective acid leaching at ambient temperature requires long treatment times and consumes large amounts of acid. It produces leach liquors containing iron, magnesium and aluminium which cause difficulties in subsequent unit operations for separation and recovery of metals (Canterford, 1978; Liu et al., 2009). The pressure acid leaching (PAL) process, using conditions described in Table 3, enables high dissolutions of nickel and cobalt at a faster rate, whilst simultaneously precipitating significant proportions of solubilised iron as highly stable Fe_2O_3 residue and recovering acid according to reactions 1–9 in Table 4 (Curlook, 2004; Georgiou and Papangelakis, 1998; Kyle, 1996; Whittington and Muir, 2000; Whittington and Johnson, 2005). The addition of elemental sulphur, $FeSO_4$ or Cu_2O show beneficial effects on nickel and cobalt extraction during pressure acid leaching of a limonitic laterite ore indicating the reductive role of these reagents (Kaya and Topkaya, 2011). Atmospheric leaching with or without reductants or combined pressure/atmospheric acid leaching flow sheets also offer fast leaching kinetics and the option of precipitating iron in different forms such as hematitie, goethite or jarosite (Chang et al., 2010; Harris and Magee, 2003; Harris et al., 2006; Liu et al., 2004; Steyl et al., 2008).

Leaching rates are generally controlled by a surface chemical reaction, mass transfer, or pore diffusion of reactants or products. A proper understanding of the reactions of dissolution and precipitation of metal values during laterite leaching in the absence or presence of reducing agents is essential for developing new leaching and separation strategies for ores which involve economically viable and

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Table 1
Metal or oxide composition of laterite ores.

Type	% composition										
	Ni	Co	Fe	S	As	SiO_2	MgO	Al_2O_3	MnO	CuO	Cr_2O_3
Limonite[a]	1.0–1.5	0.1–0.2	>40	–	–	6	3	6	–	–	–
Saprolite[a]	2.4	0.05	<15	–	–	38	25	–	–	–	–
Limonite[b]	1.3	0.083	29	0.43	0.68	28.8	2.26	5.83	0.59	0.039	1.99
Nontronite[b]	1.2	0.044	16	<0.01	0.02	44.9	6.91	4.17	0.34	0.009	0.99
Smectite[c]	1.1	0.03	17.1	–	–	(19.4)	(7.8)	(2.1)	(0.23)	–	(0.52)

[a] Reid (1996).
[b] Buyukakinci and Topkaya (2009).
[c] Das and de Lange (2011), values in brackets show metal assays, not oxides.

environmentally safe reagents/residues. Studies on individual metal oxides play a vital role in rationalising the leaching behaviour of laterite ores containing mixed oxides–silicates–aluminates. The aims of this paper are to:

(i) briefly review the current status and previous studies on acidic and/or reductive leaching of base metal oxides relevant to laterite ores,
(ii) present a comparative study of leaching metals from synthetic FeOOH, NiFeOOH, CoFeOOH and a limonitic laterite ore,
(iii) rationalise the role of acids, anions and reducing agents on the basis of the effect of speciation, chemical reactivity of oxide systems, and heterogeneous kinetic models.

2. Current status

2.1. Pre-treatment and iron removal

The removal of coarse silica and spinels by screening is an economical option for beneficiating laterite ores. This allows up to 60–70% mass rejection, provided the coarse fraction contains little nickel (Muir and Johnson, 2006; White et al., 2006). Pre-treatment leads to the separation of nickel from gangue or the retardation of iron leaching (Das et al., 2011; Guo et al., 2011; Harris et al., 2011; Li et al., 2009). For example, selective sulphidation of iron-rich limonitic ore by roasting with sulphur extracts up to 80% Ni from ore and produces a nickel–iron sulphide, thus allowing physical separation from the gangue minerals (Harris et al., 2011). Limonitic laterite ores undergo complete dehydroxilation (removal of crystalline water) during pre-roasting at temperatures around 900 °C, producing NiO, $NiFe_2O_4$ and Fe_2O_3; and retard iron leaching, while the increased surface area and porosity facilitate acid leaching of nickel (Harris et al., 2011; Li et al., 2009). The destruction of limonitic laterite mineral lattice by alkali-roasting with Na_2CO_3 at 1000 °C allows water leaching of 99% Cr and 80% Al from the roasted calcine. Subsequent pressure acid leaching under mild conditions extracts 97.5% Ni and 95.3% Co (Guo et al., 2011).

Table 2
Oxides and minerals of interest in laterite processing.

Type of oxides	Examples
Single metal oxides of multiple valency	NiO, NiOOH
	CoO, CoOOH, $Co(OH)_3$, Co_3O_4, CoO_2
	FeO, FeOOH, Fe_2O_3, Fe_3O_4
	MnO, MnOOH, Mn_3O_4, MnO_2
Mixed oxides or oxyhydroxides	MFeOOH (oxyhydroxides) (M = Ni, Co)
	$MO.Fe_2O_3$ (ferrites) (M = Mg, Mn, Zn, Fe, Ni, Co, Cu)
	$MO.Mn_2O_3$ (M = Mg, Mn, Zn, Fe, Ni,Co, Cu)
	$MO.Al_2O_3$ (aluminates) (M = Mg, Mn, Zn, Fe, Ni, Co, Cu)
	$(MO)_2.SiO_2$ (silicates) (M = Mg, Mn, Zn, Fe, Ni, Co)
Typical minerals[a]	Goethite: α-FeOOH
	Hematite: α-Fe_2O_3
	Maghemite: γ-Fe_2O_3
	Magnetite: Fe_3O_4
	Chromite: $FeCr_2O_4$
	Limonite: $(Fe,Ni)O(OH).nH_2O$
	Garnierite: $(Ni,Mg)SiO_3.nH_2O$
	Saprolite: $(Mg,Ni)_2Si_2O_5(OH)_4$
	Serpentine: $(Mg,Al,Fe,Mn,Ni)_{2–3}(Si,Al,Fe)_2O_5(OH)_4$
	Smectite: $Mg_{0.2}(Fe_{1.2}Mg_{0.5}Ni_{0.1}Al_{0.3})(Si_{3.8}Al_{0.2})O_{10}(OH)_{2.2}H_2O$
	Asbolane: $(Co,Ni)_{1-y}(MnO_2)_{2-x}(OH)_{2-2y+2x}n(H_2O)$
	Lithiophorite: $(Al,Li)MnO_2(OH)_2$
	Ringwoodite: $(Mg,Fe)_2SiO_4$
	Nontronite: $Na_{0.3}Fe_2Si_4O_{10}(OH)_2.4H_2O$
	Lizardite: $(Mg,Al)_3((Si,Fe)_2O_5)(OH)_4$
	Phlogopite: $KMg_3(Si_3Al)O_{10}(OH)_2$
	Kaolinite/illite: $Al_4Si_4O_{10}(OH)_8$
	Chlorite: $(Mg,Fe,Al)_{5–6}(Si,Al)_4O_{10}(OH)_8$
	Clinchlore: $(Mg_{10.6}Al)Fe_{0.4}(Si_{6.7}Al_{1.3})O_{20}(OH)_{16}$

[a] Reported by Rubisov and Papangelakis (2000), Whittington and Muir (2000), Whittington et al., (2003a,b), Liu et al. (2004), Tang and Valix (2006), Lu et al. (2009), Luo et al. (2010), Simate et al. (2010), Das and de Lange (2011).

The leaching methods can be adjusted to choose the nature of the discarded iron residue. The use of saline process liquors and mixing of discharge streams from pressure acid leaching of limonitic ore (with H_2SO_4 at 250 °C) and atmospheric pre-leaching of saprolytic ore (with H_2SO_4 at 95 °C) is a novelty in the Ravensthorpe plant. This leads to continued nickel and cobalt leaching under atmospheric conditions at 95 °C and iron precipitation as sodium/potassium jarosite according to reactions 10–12 (White et al., 2006). Likewise, the first stage atmospheric leaching of limonitic ore (with H_2SO_4 at 95–105 °C) according to reaction 6, followed by the addition of pre-heated saprolyte slurry and goethite seed for second stage leaching, combined with neutralisation with limestone, leads to the precipitation of goethite according to reactions 13–14. The disposal of stable goethite/gypsum by this route is safer and more advantageous compared to acid releasing jarosite tailings (Liu et al., 2004). Strong chloride (brine) leaching under atmospheric pressure at temperatures close to the boiling point of the solution (>95 °C) produces hematite that is more readily filtered and environmentally stable (reactions 15–16) with high iron content, high density and low amounts of other base metals (Harris and Magee, 2003; Harris et al., 2006; Steyl et al., 2008).

2.2. Requirement for different acid strengths

Rates and products of leaching depend upon mineralogy and leach conditions. The sulphuric acid leachability of metal values associated with different iron minerals listed in Table 2 follows the order: lizardite > goethite > maghemite > magnetite ≈ hematite > chromite ≈ ringwoodite. Thus, the required H_2SO_4 concentration and temperature varies from 0.5 mol dm^{-3} at 60 °C (lizardite) to 2.5 mol dm^{-3} at 80 °C (goethite) and >6.2 mol dm^{-3} at 105 °C (hematite), whilst ringwoodite and chromite cannot be dissolved (Liu et al., 2009). The association of nickel and cobalt with high-valent oxides also plays a key role during leaching. The presence of minerals such as nickeliferrous limonite, garnierite, serpentine, nontronite or smectite, listed in Table 2 (Das and de Lange, 2011; Simate et al., 2010; Whittington et al., 2003a,b), indicate the possibility of co-dissolution of Fe–Ni and Ni–Mg in acid media. Thus, strong acid leaching