

AN INNOVATIVE PROCESS FOR THE RECOVERY OF VALUE METALS FROM NICKEL LATERITE ORES IN MIXED-CHLORIDE TECHNOLOGY

V. I. Lakshmanan¹, R. Sridhar¹, J. Chen¹, R. DeLaat¹, D. Tait¹, and M. A. Halim^{1,*}

¹Process Research ORTECH Inc., 2350 Sheridan Park Drive, Mississauga, ON, L5K 2T4, Canada

*Corresponding Author Email: halim@processortech.com

Abstract

Nickel and cobalt are used for strategic alloys and their demand is increasing in the world while the extractable ores of these metals are gradually depleting. Chloride-based processes have several advantages over the conventional pyrometallurgical and hydrometallurgical processes including higher leachability of ores, stability of metal chloro-complexes and regeneration of leaching reagents. Considering these advantages, Process Research ORTECH Inc. (PRO) has developed an innovative mixed-chloride process flowsheet for the recovery of nickel and other value metals from low grade lateritic ores. In this process, the addition of magnesium chloride to hydrochloric acid increases leaching rates of ores at moderate temperatures (<100°C) and atmospheric pressures with resulting high metals recovery. Nickel recovery by solvent extraction with a patented extractant from process solutions is performed at lower pH of 0.5 -2.5, compared to other processes that operate at a pH of 5-6. This process produces value added by-products of high purity cobalt, manganese and iron oxide.

1. Introduction

Nickel is an important strategic base metal which is used in producing alloy steel materials. Demand for nickel is increasing in the world while the economically and environmentally recoverable resources of this metal are gradually depleting. About 70% of the nickel reserves are present in laterite deposits (oxide) however the worldwide production of nickel is mostly obtained from sulphide ores (Agatzini-Leonardou et al., 2009, Wang et al., 2011). Lateritic ores have a number of layers including overburden (about <0.8% nickel) which is usually discarded, limonite ore zone (about 1.2 – 1.7% nickel, about 40% iron and 1 – 4% magnesium oxide), a saprolite ore zone (about 1.6 – 2.3% nickel and about 7 – 25% iron)

and then a layer of rock (Lakshmanan et al., 2014a and 2014b). Laterite ore also contains other value metals including cobalt and manganese.

A large portion of nickel is produced from high grade lateritic ores by the conventional smelting and hydrometallurgical processes; however, treatment of low grade ores by these technologies is not always economically or environmentally succeeded. The conventional pyrometallurgical processes have several detriments including high capital costs, losses of valuable metal by-products in slags and residues, and environmental constraints pertaining to gaseous emissions and solid residues. High temperature and pressure based hydrometallurgical processes are also very capital intensive and require the use of autoclaves and high pressure pumps (Onyedika et al., 2012). In contrast, chloride-based processes have several advantages over the conventional hydrometallurgical and smelting processes including higher leachability of complex ores, stability of chloro-complexes and regeneration of leaching reagents. Considering these advantages, Process Research ORTECH Inc. (PRO) has developed an innovative mixed-chloride process flowsheet for the recovery of nickel and other value metals from low grade lateritic ores. In this process, a mixed-chloride lixiviant containing hydrochloric acid and magnesium chloride has been shown to be an effective leachant, which give rapid leaching rates at modest temperatures and atmospheric pressures, with high metal recovery. Hydrochloric acid is regenerated from the pregnant aqueous strip solution of ferric chloride by pyrohydrolysis, which is a commercially proven process (Adham et al., 2006, Baerhold et al., 2006, Peek et al., 1996). This process also produces value added by-products of high purity cobalt, manganese and iron oxide. Recycling of the chloride lixiviant, production of inert tailings and minimization of unwanted waste production are apparent advantages of this process. In this paper, the PRO process flowsheet for the recovery of nickel and other value metals from laterite ores are described.

2. PRO Mixed-chloride Technology for Nickel Laterite

PRO has developed an innovative atmospheric mixed-chloride process flowsheet for the recovery of nickel and other value metals from lateritic ores. The major process steps are (i) leaching of laterite in mixed-chloride media containing HCl and MgCl₂ to bring Ni, Co, Fe and Mn in solution, (ii) innovative solvent extraction process steps for selective separation of Fe followed by Co, Ni and Mn, (iii) recovery of these metals from their respective pregnant strip solutions, (iv) regeneration of HCl from the pregnant strip solution of ferric chloride and bleed stream of Mn raffinate.

Understanding the solution chemistry and separation technology are the key parameters to develop this mixed-chloride process for the recovery of nickel and other value metals from lateritic ores. Dissolution kinetics of laterite ores in mixed-chloride containing HCl and MgCl₂ media is faster than in other systems

such as sulphate due to the chloride ion forming complexes with most metals. Addition of MgCl_2 to HCl solutions increases the activity of the hydrogen ion (H^+) by orders of magnitude which help to increase the nickel and cobalt leaching efficiency of the lixiviant with a lower concentration of HCl (Lakshmanan et al., 2013, 2010, 2014a, 2014b, 2014c, 2014d, Königsberger et al., 2008, Jansz, 1983).

In an oxidative mixed-chloride media, iron is easily leached as Fe^{3+} to form iron chloro-complexes such as FeCl^{2+} , FeCl_2^+ , FeCl_3^0 and FeCl_4^- . The formation of FeCl_4^- increases with increasing HCl concentration, while those of FeCl^{2+} , FeCl_2^+ and FeCl_3^0 decrease with the HCl concentration (Lee et al., 2004). Cobalt and nickel exist as divalent hexahydrated ions in aqueous solutions. The formation of ionic chloro-complex often proceed more readily with divalent cobalt (Co^{2+}) than with divalent nickel (Ni^{2+}) due to the rate of water exchange on the cobalt ion which is much higher than that of nickel (Cox, 2004). The divalent cobalt has a strong tendency to form tetrahedral anionic chloro-complexes such as CoCl_3^- and CoCl_4^{2-} in a strong chloride ion solution, whereas divalent nickel does not form such complexes and Ni^{2+} retains a hexa-coordinated complex. This difference in chemical behaviour allows for selective separation of Fe followed by Co, Ni and Mn with solvent extraction process steps in mixed chloride medium (Lakshmanan et al., 2014b).

Atmospheric mixed-chloride leaching tests were conducted using a lixiviant containing HCl and MgCl_2 on a laterite ore with a composition of 0.74% Ni, 0.10% Co and 37.6% Fe. Under optimal conditions, leach recoveries of Ni, Co and Fe were 98%, 93% and 98%, respectively (Table 1). After solid-liquid separation, the pregnant leach liquor went through a series of solvent extraction process steps to subsequently separate Fe, Co and Ni (Table 2). Iron was selectively extracted over cobalt and nickel by contacting the leach solution with an organic phase (*S*) containing a solvating extractant, a modifier (e.g. Exxal™ 13 tridecyl alcohol) and a diluent (e.g. Exxsol™ D80) (Lakshmanan et al., 2014a and 2014b). Stripping of Fe^{3+} from the loaded organic phase was carried out with a dilute HCl solution.

Table 1: Recoveries of nickel, cobalt and iron with atmospheric mixed chloride leaching process.

	Ni	Co	Mn	Fe
	%			
Ore (grade)	0.74	0.1	0.72	37.6
Recovery	98	93	96	98

Table 2: Separations of Fe, Co and Ni from mixed-chloride leach solution by subsequent solvent extraction process steps. A three stage Fe extraction was conducted.

	Fe	Co	Ni	Mn
	mg/L			
Pregnant leach liquor	44600	64.4	1050	691
Fe raffinate at the O/A ratio of 1:2	< 5	57	958	650
Co raffinate at the O/A ratio of 1	<5	<5	957	561
Ni raffinate at the O/A ratio of 1	<5	<5	28	562
Mn raffinate at the O/A ratio of 1	<5	<5	27	38

The iron raffinate was subsequently subjected to selective solvent extraction of Co, Ni and Mn with organic phases containing a tertiary amine, oxime and quaternary amine, respectively (Lakshmanan et al., 2014a and 2014b, Shen et al., 2008). In these organic phases, Exxal™ 13 tridecyl alcohol and Exxsol™ D80 were used as a modifier and a diluent, respectively. Stripping of Co, Ni and Mn from loaded organic phases was conducted with dilute HCl solution.

The extractants used in this study are highly selective for Ni, Co, Mn and Fe (Table 2), which results in high purity pregnant strip solutions and consequentially high purity Ni, Co and Fe products. Depending on the market value of the product, Ni, Co and Mn can be recovered from their respective pregnant strip solutions in different forms such as carbonate and oxide. The developed flowsheet for the recovery of Ni, Co, Mn and Fe from laterite is shown in Figure 1 (Lakshmanan et al., 2014a and 2014b). The use of MgCl₂ in lixiviant and an oxime (5, 8-diethyl-7-hydroxy-6-dodecanone) permits the recovery of Ni at a lower pH of 0.5 -2.5, compared to other processes that operate at a pH of 5-6. Hydrochloric acid and Fe₂O₃ can be produced from the Fe pregnant strip solution by pyrohydrolysis, which is a commercially proven process.

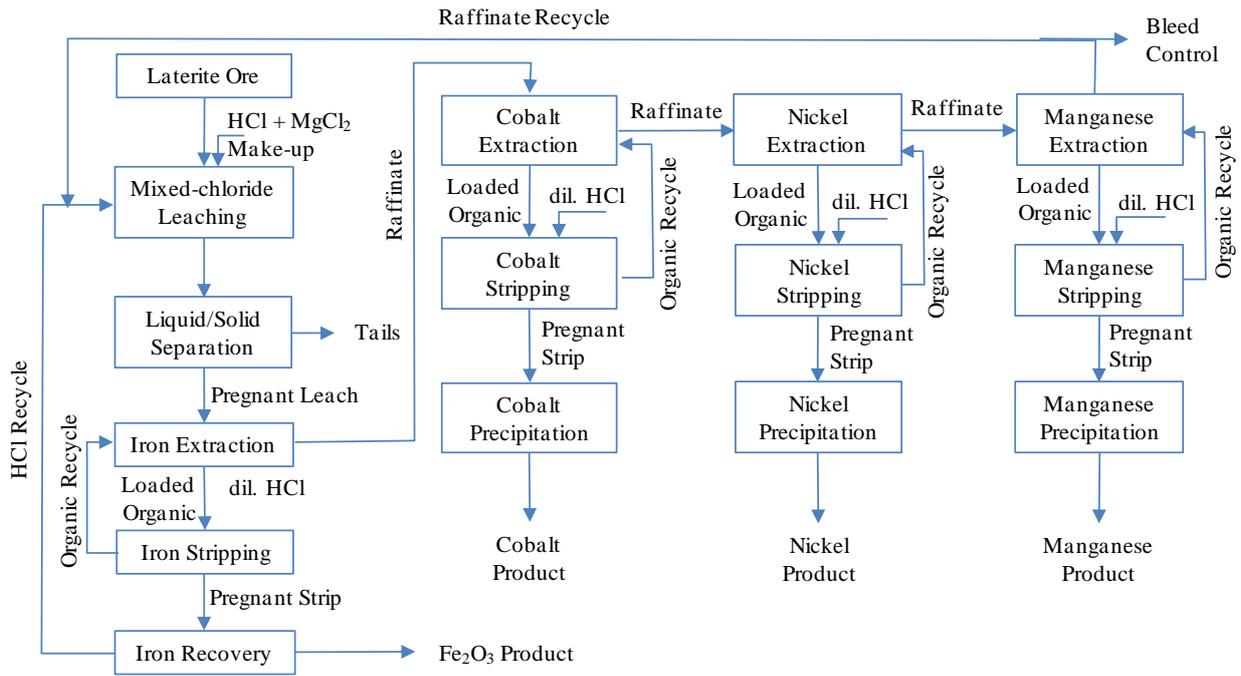


Figure 1: Mixed-chloride process flowsheet for the recovery of Ni, Co, Mn and Fe from laterite (Lakshmanan et al., 2014a and 2014b).

3. Conclusion

Process Research ORTECH Inc. has developed an innovative process utilizing a mixed-chloride atmospheric leach followed by selective solvent extraction process steps for the recovery of nickel, cobalt and other value metals from lateritic ores/concentrates. PRO's process offers many advantages including:

- (i) direct solvent extraction of nickel from process solutions at a lower pH (0.5 – 2.5) without the addition of neutralization reagents,
- (ii) production of concentrated HCl from ferric chloride, which is recycled to the leach step, and
- (iii) recycling of $MgCl_2$ in the manganese raffinate to the leaching stage.

This process produces value added by-products of high purity cobalt, manganese and iron oxide. It also produces inert tailings. Recycling of chloride lixiviant in the manganese raffinate to the leaching stage minimizes waste production. This process has a simplified flowsheet which is closed loop and thus environmentally more friendly.

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