

Hydrometallurgical Processes for the Recovery of Rare Earths, Nickel and Cobalt in Chloride Medium

V.I. Lakshmanan, R. Sridhar, D. Tait and M.A. Halim

Abstract Rare earth elements (REEs), nickel and cobalt find their use in developing strategic materials and their demand is consistently increasing in the world while the extractable ores of these metals are gradually depleting. Process Research ORTECH Inc. (PRO) has developed innovative mixed chloride leaching processes for the recovery of REEs from alumino-silicate ores, and nickel and cobalt from laterite ores. The addition of magnesium chloride in hydrochloric acid enhances the activity of the hydrogen ion by orders of magnitude, which permit rapid leaching rates at moderate temperature and atmospheric pressure, along with high metal recovery. Innovative solvent extraction process steps are used for the separation of these metals from pregnant leach solutions. PRO's processes also produce value added by-product of high purity iron oxide and recycle chloride lixiviant to the leaching stage. This paper describes the leaching and separation reaction mechanisms and potential process flowsheets.

Keywords Rare earths · Nickel · Cobalt · Laterite · Mixed chloride · Atmospheric leaching · Solvent extraction

Introduction

Rare earth elements (La to Lu plus Y) are being used in the making of hybrid electric cars, catalytic converters, wind power generators, LEDs, hard disc drives, flat panel displays and portable electronics due to their unique magnetic, electronic, catalytic and optical properties. Rare earth elements (REEs) are commonly divided in two groups: light rare earth elements (LREEs) and heavy rare earth elements (HREEs). Light rare earth elements include elements from lanthanum (La) to neodymium (Nd). Although promethium (Pm) is considered an LREE it is unstable

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and scarcely occurs in nature and is generally excluded. Heavy rare earth elements include elements from samarium (Sm) to lutetium (Lu) plus yttrium. Although rare earth elements are not rare and the rare earth oxides are scattered around the globe, over 95% of REEs+Y are currently produced in China [1]. On one hand the Chinese government is restricting the export of rare earth elements and on the other hand the demand for REEs+Y is increasing in the rest of the world. This has created an imbalance in the supply and demand of rare earth elements and has led to a rush for developing new rare earths process flowsheets.

Demand for nickel and cobalt is consistently increasing in the production of strategic alloys in the world while the supplies of economically and environmentally recoverable resources are gradually depleting. Nickel is produced from laterites which 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 [2, 3]. Laterite ore also contains other metals including cobalt, manganese and chromium.

High temperature and pressure based hydrometallurgical processes are also very capital intensive and require the use of autoclaves, high pressure pumping machines and costly materials of construction [4]. Chloride-based hydrometallurgical processes can be a potential alternative for the production of these value metals by meeting the more stringent environmental requirements, and reducing capital and operating costs compared to current process routes. Recycling of chloride lixiviant and minimizing of unwanted waste production are apparent advantages of chloride-based hydrometallurgical processes. Considering these advantages, innovative mixed-chloride processes have been developed by Process Research ORTECH Inc. [2, 3, 5–16]. In this paper, the recovery of REEs from alumino-silicate ores, and nickel and cobalt from laterite ores is described. Atmospheric pressure leaching of ores in lixiviant containing hydrochloric acid and magnesium chloride followed by separation and purification, and recovery of these metals are presented.

Mixed-Chloride Leaching Process for the Recovery of Rare Earth Elements

Process Research ORTECH Inc. (PRO) has developed an innovative mixed-chloride leaching process for the recovery of REEs from alumino-silicate ores that is cost effective and environmentally friendly [9]. Mixed-chloride containing hydrochloric acid and magnesium chloride is an effective leachant, which permit rapid leaching rates at modest temperatures and atmospheric pressures, with high metal recovery [2, 3, 9–18]. Based on PRO's proprietary mixed chloride leaching technology [9], a rare earths containing ore was subjected to grinding followed by leaching with a lixiviant of hydrochloric acid and magnesium chloride at 95 °C for 4 h. The leach slurry was subjected to solid/liquid separation.

Table 1 Results on extraction of REEs+Y by PRO's proprietary mixed chloride leaching technology [9]

100 mesh (%)	HCl (N)	MgCl ₂ (g/L)	Solids (% w/w)	Temp (°C)	Time (h)	REEs (%)	REEs+Y (%)
85	5.8	225	10.4	95	4	86.1	83.3

The ore sample and the solid residue were digested and analyzed by Inductively Coupled Plasma (ICP). The elemental concentrations in the pregnant leach solution (PLS) were also determined by ICP. Leaching conditions and recovery of rare earth elements are shown in Table 1. Extractions of REEs and REEs plus yttrium (REEs+Y) were 86.1 and 83.3%, respectively.

The PLS undergoes multiple stage solvent extraction to selectively remove Fe and other impurities (including U, Th, Cu, and Zn) followed by the recovery of Zr. A ketone and a tertiary amine (Alamine 336) in kerosene were used for the removal of Fe and impurities, respectively, while 2-ethylhexyl phosphonic acid mono-2-ethylhexylester (PC-88A) in kerosene was used for separation of Zr. Free hydrochloric acid was extracted from Zr raffinate with EXXAL™ 13, which can be recycled to the leaching stage. REEs+Y were precipitated from acid and Zr extracted raffinate with 10% oxalic acid at pH 2.0. Around 99% of the REEs+Y were precipitated at room temperature. Results are shown in Table 2. The rare earth oxalate obtained was washed with water, dried, calcined, and dissolved in

Table 2 Results on REEs+Y precipitation from Zr raffinate with 10% oxalic acid

	Fe	Zr	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb
Zirconium raffinate, mg/L	0.5	5	768	1550	174	612	146	8	152	30
REEs+Y ppt.* filtrate, mg/L	0.5	<0.5	46.2	32.0	2.4	6.6	1.2	0.1	1.5	0.3
REEs+Y precipitation, %			94	98	99	99	99	99	99	99
	Dy	Ho	Er	Tm	Yb	Lu	Y	Cu	Zn	U
Zirconium raffinate, mg/L	208	41	115	15	71	8	772	1	2	<0.05
REEs+Y ppt.* filtrate	1.2	0.3	0.7	0.1	0.1	0.5	10	1	4	<0.05
REEs+Y precipitation (%)	99	99	99	99	100	94	99			
	Hf	Al	Ca	K	Mg	Mn	Na	S	Si	Sr
Zirconium raffinate, mg/L	1	1170	8750	915	58700	172	1590	123	9	125
REEs+Y ppt.* filtrate	<0.02	1710	7860	1320	66700	160	2140	121	17	155

*Precipitate

hydrochloric acid to give a REEs+Y concentrate for individual separation by solvent extraction.

Alternatively, PRO has tested the use of D2EHPA with EXXAL™ 13 in kerosene for direct extraction of REEs+Y from Zr raffinate after acid extraction (Table 3). Pregnant strip solution of REEs+Y could potentially be used as a feed for the individual separation of REEs+Y via solvent extraction process steps. The raffinate from the final solvent extraction stage is recycled to the leaching stage as shown in Fig. 1.

Table 3 Results on REEs+Y extraction from acid-extracted Zr raffinate (mg/L)

	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm
Zr Raffinate after acid extraction	50	70	6	54	13	<5	19	7	28	7	19	<5
REEs+Y Raffinate	<5	5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5
	Yb	Lu	Y	Zr	Fe	Ti	Al	Ca	Cu	K	Na	Zn
Zr Raffinate after acid extraction	16	5	184	<5	<5	<5	7180	5710	<5	1610	4400	<5
REEs+Y Raffinate	<5	<5	<5	<5	<5	<5	6680	5630	<5	1470	4410	<5

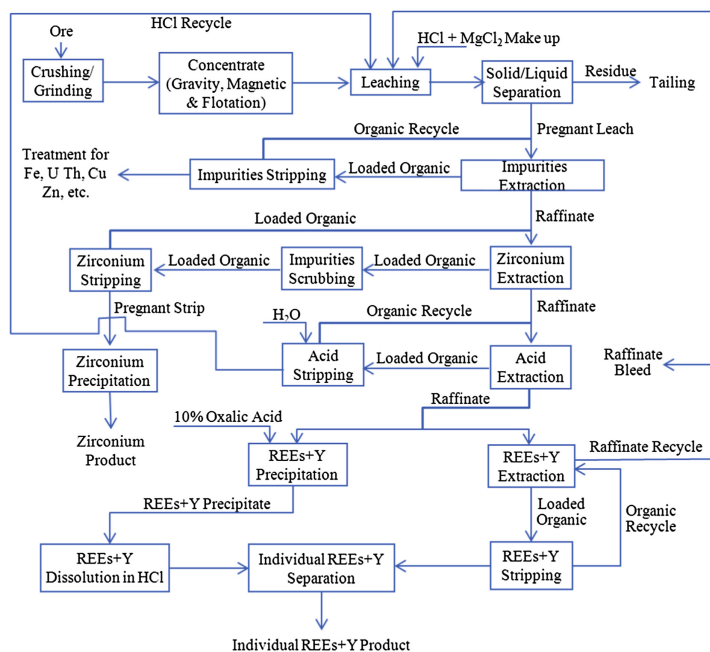


Fig. 1 Flowsheet for REEs+Y recovery by PRO's mixed chloride leaching process [9]

Mixed-Chloride Leaching Process for the Recovery of Nickel and Cobalt from Laterite

Process Research ORTECH Inc. (PRO) has developed an innovative atmospheric mixed-chloride leaching process for the recovery of nickel (Ni) and cobalt (Co) from laterite ores [2, 3]. As discussed in the previous section, addition of MgCl_2 to HCl solution increases the activity of the hydrogen ion (H^+) by orders of magnitude which help to increase Ni and Co extraction efficiency of the lixiviant with a lower concentration of HCl. Atmospheric leaching tests were conducted at 90–95 °C using a lixiviant containing HCl and MgCl_2 with a laterite ore having a composition of 0.74% Ni, 0.10% Co and 37.6% Fe; and with a concentrate which contains 4.02% Ni, 0.10% Co and 43.44% Fe. Under the optimal conditions, leach recoveries of Ni, Co and Fe were 98–99%, 86–93% and 98–99%, respectively (Table 4). After solid–liquid separation, pregnant leach liquor (PLS) went through a series of solvent extraction (SX) process steps to subsequently separate Fe, Co and Ni.

Under the oxidizing condition, the predominant oxidation state of iron is ferric ion (Fe^{3+}), which has strong affinity to form complexes with the chloride ion, such as FeCl^{2+} , FeCl_2^+ , FeCl_3° and FeCl_4^- . Lee et al. [19] suggest that the mole fraction of FeCl_4^- increases with increasing HCl concentration, while those of FeCl^{2+} and Fe^{3+} decrease with the HCl concentration. Cobalt and Ni exist as divalent hexahydrated ions in aqueous solutions. The formation of ion complex often proceeds much more readily with divalent Co than with Ni due to the rate of water exchange on the cobalt ion is much higher than for nickel [20]. The trivalent Co ion is much less labile and forms in preference to Ni even though the redox potentials for the Co^{2+} – Co^{3+} and Ni^{2+} – Ni^{3+} couples are nearly identical. The divalent Co has a strong tendency to form tetrahedral anionic chloro-complex such as CoCl_3^- and CoCl_4^{2-} in a strong chloride ion solution, whereas divalent Ni does not form such complexes and Ni^{2+} retains a hexa-coordinated complex. This difference in chemical behavior allows for selective separation of Co^{2+} from Ni^{2+} with an anion exchange extractant in mixed chloride medium [2]. Understanding this chloro-chemistry of Fe, Co and Ni species has greatly helped to separate them by SX process steps (Table 5).

Iron was selectively extracted over Co and Ni by contacting the pregnant leach solution (PLS) with an organic phase (S) containing a solvating extractant, more specifically a high molecular weight of ketone, a modifier (e.g. Exxal™ 13 tridecyl alcohol) and a diluent (e.g. Exxsol™ D80) by the Reaction 1. Stripping of Fe^{3+}

Table 4 Leach recoveries of Ni, Co and Fe with atmospheric mixed chloride leaching process

	Ni	Co	Fe
	%		
Ore (grade)	0.74	0.1	37.6
Recovery	98	93	98
Concentrate (grade)	4.02	0.10	43.44
Recovery	99	86	99

Table 5 Separations of Fe, Co and Ni from PLS by subsequent SX process steps

	Fe	Co	Ni
	mg/L		
Pregnant leach liquor	33,150	58	3331
Fe raffinate at the O/A ratio of 1:2	<5	63	3376
Co raffinate at the O/A ratio of 1	<5	<5	3356
Ni raffinate at the O/A ratio of 1	<5	<5	28

A three stage Fe extraction was conducted

from the loaded organic phase was carried out with a dilute HCl solution. Iron raffinate was subjected to subsequent selective SX of Co^{2+} and Ni^{2+} with organic phases containing a tertiary amine (e.g. AlamineTM 336 (R_3N)) and oxime (e.g. LIX 63 (RH)), respectively, following the reactions of 2–4 [2, 3, 21]. In both organic phases, ExxalTM 13 tridecyl alcohol and ExxsolTM D80 were used as a modifier and a diluent, respectively. Stripping of both Co^{2+} and Ni^{2+} from loaded organic phases was conducted with a dilute HCl solution. The McCabe–Thiele extraction and stripping isotherms for Co^{2+} and Ni^{2+} are shown in Figs. 2 and 3, respectively.

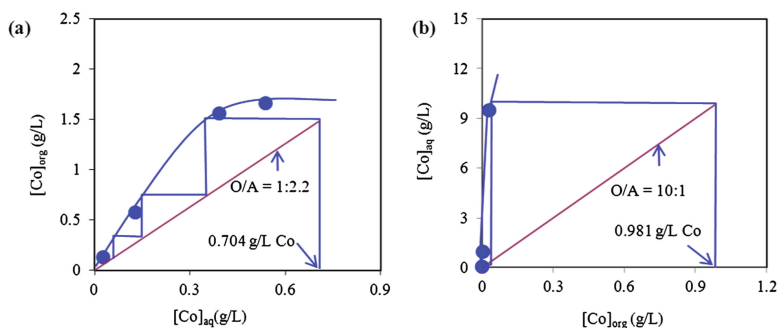


Fig. 2 The McCabe–Thiele isotherms for Co^{2+} **a** extraction isotherm and **b** stripping isotherm [2, 3]

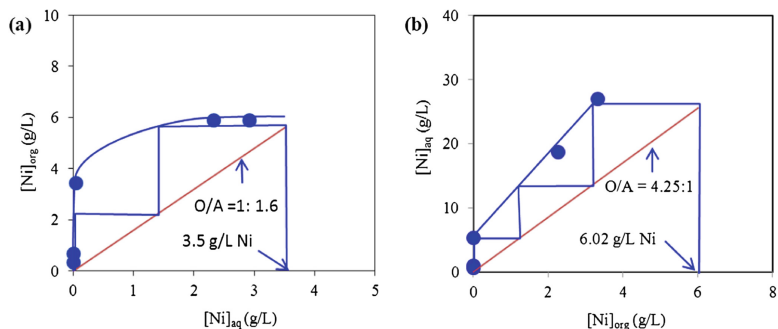
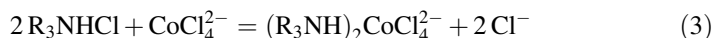
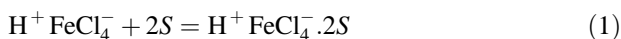


Fig. 3 The McCabe–Thiele isotherms for Ni^{2+} **a** extraction isotherm and **b** stripping isotherm [2]



The extractants used in this study are highly selective for Ni^{2+} , Co^{2+} and Fe^{3+} (Table 5), which results in high purity pregnant strip solutions. Depending on the market value of the product, Ni and Co can be recovered from their respective pregnant strip solutions in different forms such as carbonate and oxide. Hydrochloric acid can be regenerated from the pregnant strip solution of Fe by pyrohydrolysis, which has been commercially practiced in the pickling steel industry [22–24]. This process also produces a value added by-product of high purity iron oxide (Fe_2O_3). The developed flowsheet for the recovery of Ni, Co and Fe from laterite is shown in Fig. 4 [2, 3]. The use of MgCl_2 in lixiviant and LIX 63 permits the recovery of Ni^{2+} at a lower pH of 0.5–2.5, compared to other processes that operate at a pH of 5–6.

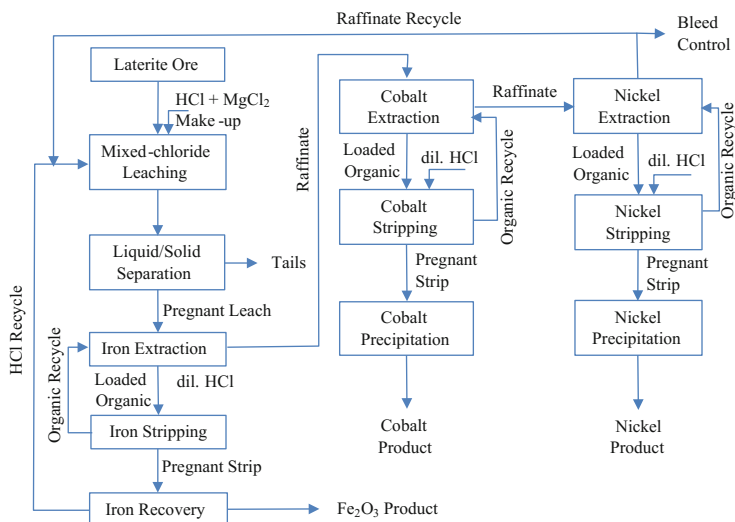


Fig. 4 PRO's mixed-chloride process flowsheet for the recovery of Ni and Co from laterite [2, 3]

Conclusions

Process Research ORTECH Inc. has developed hydrometallurgical processes for the recovery of rare earths from alumino-silicate ores; and nickel and cobalt from low grade laterite. Leaching of these ores was conducted with mixed chloride lixiviant containing HCl and $MgCl_2$ at atmospheric pressure and varying temperature between 90 and 95 °C. After leaching, the leach slurries were subjected to liquid/solid separation. By understanding the chloro-chemistry and separation technology, these metals were selectively separated from pregnant leach liquors by solvent extraction process steps. Around 99% of REEs+Y was precipitated from acid-extracted Zr raffinate with 10% oxalic acid. Alternatively, REEs+Y were directly extracted from acid-extracted Zr raffinate. PRO's mixed-chloride processes have several advantages over the conventional processes such as (i) addition of $MgCl_2$ to HCl in the leaching stage increased H^+ activity in the lixiviant by order of magnitude which helps to increase metal recovery with a lower concentration of HCl, (ii) regeneration and recycling of HCl and raffinate to the leaching stage reduces reagent costs, (iii) the use of $MgCl_2$ in lixiviant and LIX 63 permits the separation of Ni^{2+} at a lower pH of 0.5–2.5 and (iv) PRO process can be a potential alternative to the conventional hydrometallurgical and smelting processes by meeting the more stringent environmental requirements, and reducing capital and operating costs.

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