Separation and Purification of Value Metals from Aqueous Chloride Solutions by Solvent Extraction

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Abstract The demand for elements such as nickel, cobalt, titanium and gold in various applications has increased significantly. Innovation to recover these elements now plays a major role in metallurgical processes as established technologies have challenges in treating the types of ores that are available while meeting the increasingly stricter environmental regulations. Alternative chloride based processes have been developed that can be used to recover the value elements from the available feed stocks with potentially lower environmental impact. Chloride-based hydrometallurgical processes have several advantages, including higher leachability of complex ores/tailings and relative stability of chloro-complexes of the metals. Process Research ORTECH Inc. (PRO) has developed mixed-chloride process flowsheets, where innovative solvent extraction process steps are used for the separation of nickel, cobalt titanium and gold from their respective chloride solutions. This paper will discuss the potential aqueous chloro-chemistry of these metals and separation reaction mechanisms involved in the solvent extraction process.
Keywords: Titanium, Nickel, Cobalt, Gold, Mixed-chloride, Atmospheric leaching, solvent extraction

1. Introduction

The demand for elements such as nickel, cobalt, titanium and gold in various applications has increased significantly. Nickel, cobalt and titanium are being used in several fields including strategic alloys and advanced energy materials. Similarly for gold, long considered one of the important strategic metals for economic security is also a critical component for electronic devices.

With the continued global growth in population, demand of these metals is consistently increasing while easily accessible resources are being depleted. Innovation now plays a major role in metallurgical processes as established technologies have challenges in treating the types of ores that are available (ie. refractory, low grade) or cannot meet the increasingly stricter environmental regulations. Alternative chloride based processes have been developed that can be used to recover the value elements from the available feed stocks with potentially lower environmental impact. Chloride-based hydrometallurgical processes have several advantages, including higher leachability of complex ores/tailings and relative stability of chloro-complexes of the metals. By understanding the chloride chemistry and separation technologies, Process Research ORTECH Inc. (PRO) has developed mixed-chloride process flowsheets, where innovative solvent extraction process steps are used for the separation of nickel, cobalt, titanium and gold from their respective chloride solutions.

Nickel is primarily produced from lateritic ores 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 [1, 2]. Laterite ore also contains other value metals including cobalt, manganese and chromium. Titanium is produced from mineral sources of rutile and increasingly from ilmenite ores. Gold is found in a range of rock types and most of the high grade ores have already been exploited and focus on low grade, refractory ores and tailings is increasing.

With fewer high grade deposits and easily processed ores being discovered, current processing technologies are not economically or technically viable on the material that will be available. Pyrometallurgical/smelting processes have challenges due to high capital costs, production of dusts, 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 also have challenges and can be very capital intensive requiring the use of autoclaves, high pressure pumping machines and costly materials of construction [3]. Gold is typically processed through cyanidation, which has several limitations such as extremely hazardous hydrogen cyanide formation and large volumes of toxic solid and liquid waste generation which require costly treatment before disposal.

Chloride-based hydrometallurgical processes can be a potential alternative for the production of these value metals by appropriately meeting environmental requirements (ie. water balance, tailings and waste residues), and reducing

capital and operating costs compared to current process routes. Recycling of chloride lixiviant and minimization of unwanted waste production are apparent advantages of chloride-based hydrometallurgical processes. Hydrochloric acid is regenerated from pregnant aqueous solutions of ferric chloride by pyrohydrolysis, which has been largely practiced in the pickling steel industry [4 − 6] and by QIT in its UGS Process [7]. This process also produces a value added by-product of high purity iron oxide. Considering these advantages, innovative mixed chloride processes have been developed by PRO, a world leader in the development of chloride metallurgy [1, 2, 8 − 21].

2. Aqueous Chemistry

Magnesium chloride ($MgCl_2$) is a stable salt and readily soluble in aqueous solutions. The kinetics of dissolution for most ores, concentrates and tailings in mixed-chloride containing HCl and $MgCl_2$ media is faster than in other systems such as sulphate due to the chloride ion forming complexes with most metals and complex formation reduces the growth of passivating films. Addition of $MgCl_2$ to HCl solution increases the activity of the hydrogen ion (H^+) by orders of magnitude which help to increase value metals extraction efficiency of the lixiviant with a lower concentration of HCl [1, 2, 12, 13, 22 − 25]. Understanding the chemistry of metal species in acidic aqueous solutions is one of the most important tasks for their separation by solvent extraction to produce a high grade product.

Cobalt and nickel exist as divalent hexahydrated ions in aqueous solutions. The formation of an ion complex often proceeds much more readily with divalent cobalt than with nickel due to the rate of water exchange on the cobalt ion which is much higher than for nickel [27]. The trivalent cobalt ion is much less labile and forms in preference to nickel even though the redox potentials for the $Co^{2+} - Co^{3+}$ and $Ni^{2+} - Ni^{3+}$ couples are nearly identical. 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 Co^{2+} from Ni^{2+} with an anion exchange extractant in mixed chloride medium [2].
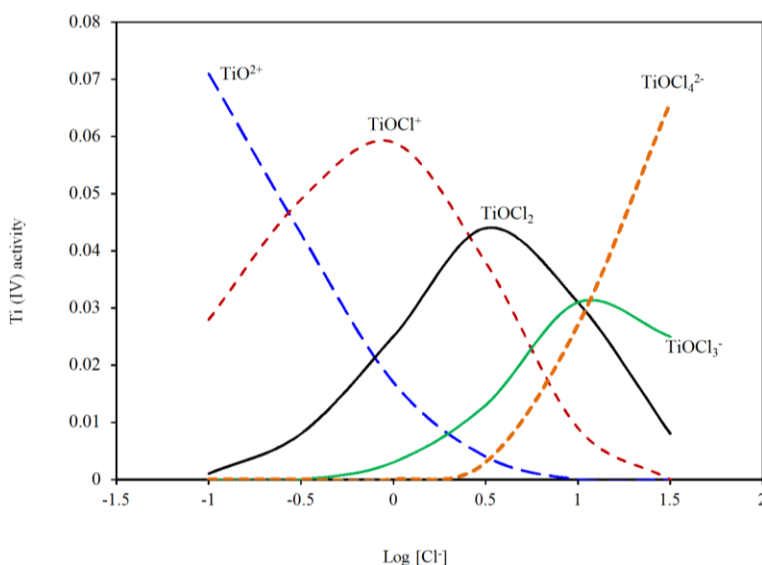

Figure 1 Distribution diagram of 0.1 M Ti(IV) chloride species in 1.0 M HCl solution at different chloride ion concentrations at 25 °C [22, 28]

Titanium could be dominant as TiO^{2+} in the aqueous solution with the acid activity of greater than 1.0 M and Ti^{4+} forms $TiO_2 \cdot H_2O$ precipitate in the pH range greater than 5. Activity of 0.1 M Ti^{4+} in 1.0 M HCl solution at 25 ^{0}C is shown in Figure 1 [22, 28]. In chloride solutions, TiO^{2+} tends to combine with the Cl^- ion to form different chloro-complexes. The maximum $TiOCl^+$ and $TiOCl_2$ form in Cl^- ion concentration of about 1.0 M and 4.5 M, respectively. These positive and neutral charge ions may extract with a cation ion exchange extractant and solvating reagents respectively in high Cl^- ion containing acidic solutions [22].

Gold mainly exists in one of the two oxidation states, Au^+ or Au^{3+} in aqueous solution depending on redox potential and complexing ion present in solution [12, 33]. In an oxidizing environment, gold dissolves readily in

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aqueous chloride solutions to form an anionic chloro-complex ($AuCl_4^-$) or neutral chloro-complex ($HAuCl_4$). These chloro-complexes of gold can be selectively separated from the process solution by solvent extraction with ion exchange and neutral extractants.

3. Recovery of Value Metals in Mixed-chloride Medium

3.1 Recovery of Nickel and Cobalt from Laterites

Nickel is one of the most important and strategic base metals which occurs in different types of ore bodies. About 70% of the nickel reserves are present in laterite deposits (oxide), while the worldwide production of nickel is mostly obtained from sulphide ores [34, 35]. Nickel is mainly produced via the pyrometallurgical route from high grade ores. This route is energy intensive and is economically marginal when ore with 0.95–1% nickel is treated and is uneconomic for lower grade laterite ores. Considering the advantages of chloro-chemistry over the conventional hydrometallurgical and smelting processes as explained in the previous section, an innovative mixed-chloride (HCl + $MgCl_2$) atmospheric leaching process has been developed for the recovery of nickel, cobalt and iron from low-grade laterite ores [1, 2].

Atmospheric mixed-chloride leaching tests were conducted 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. Extraction mechanisms of Fe, Co and Ni can be written by the following reactions (1 − 6):
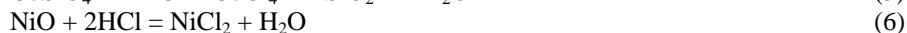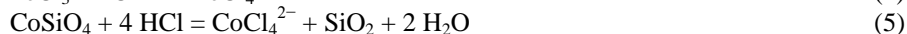
$$Fe_2O_3 + 6\ HCl = 2\ FeCl_3 + 3\ H_2O \tag{1}$$
$$2\ FeO + 4\ HCl = 2\ FeCl_2 + 2\ H_2O \tag{2}$$
$$6\ FeCl_2 + NaClO_3 + 6\ HCl = 6\ FeCl_3 + NaCl + 3\ H_2O \tag{3}$$
$$FeCl_3 + HCl = H^+FeCl_4^- \tag{4}$$
$$CoSiO_4 + 4\ HCl = CoCl_4^{2-} + SiO_2 + 2\ H_2O \tag{5}$$
$$NiO + 2HCl = NiCl_2 + H_2O \tag{6}$$

Table 1 Recoveries of nickel, cobalt and iron 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

Under the optimal conditions, leach recoveries of Ni, Co and Fe were 98 − 99%, 86 − 93% and 98 − 99%, 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, more specifically tributyl phosphate (TBP) an organophosphorous compouond, a modifier (e.g. *Exxal™ 13* tridecyl alcohol) and a diluent (e.g. Exxsol™ D80) by Reaction 7 [1, 2]. Stripping of Fe^{3+} from the loaded organic phase was carried out with a dilute HCl solution. The McCabe–Thiele extraction isotherm for Fe^{3+} is shown in Figure 2. Iron raffinate was subjected to subsequent selective solvent extraction of Co^{2+} and Ni^{2+} with organic phases containing a tertiary amine (e.g. Alamine™ 336 (R_3N)) and oxime (e.g. LIX 63 (RH)) respectively, following the reactions of 8 − 10 [1, 2, 36]. In both organic phases, *Exxal™ 13* tridecyl alcohol and Exxsol™ 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 Figure 3 and Figure 4, respectively.

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
	mg/L		
Pregnant leach liquor	33150	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

$$H^+FeCl_4^- + 2\ S = H^+FeCl_4^- .2\ S \qquad (7)$$
$$R_3N + HCl = R_3NHCl \qquad (8)$$
$$2\ R_3NHCl + CoCl_4^{2-} = (R_3NH)_2CoCl_4^{2-} + 2\ Cl^- \qquad (9)$$
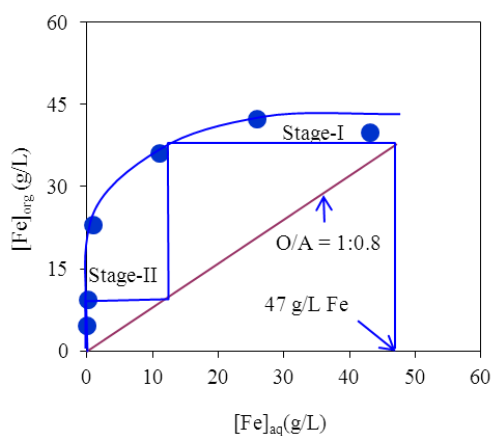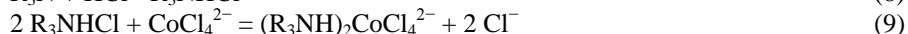$$2\ RH + NiCl_2 = R_2Ni + 2HCl \qquad (10)$$

Figure 2 The McCabe–Thiele extraction isotherm for Fe3+ with a solvating extractant and Exxal™ 13 tridecyl alcohol in Exxsol D80
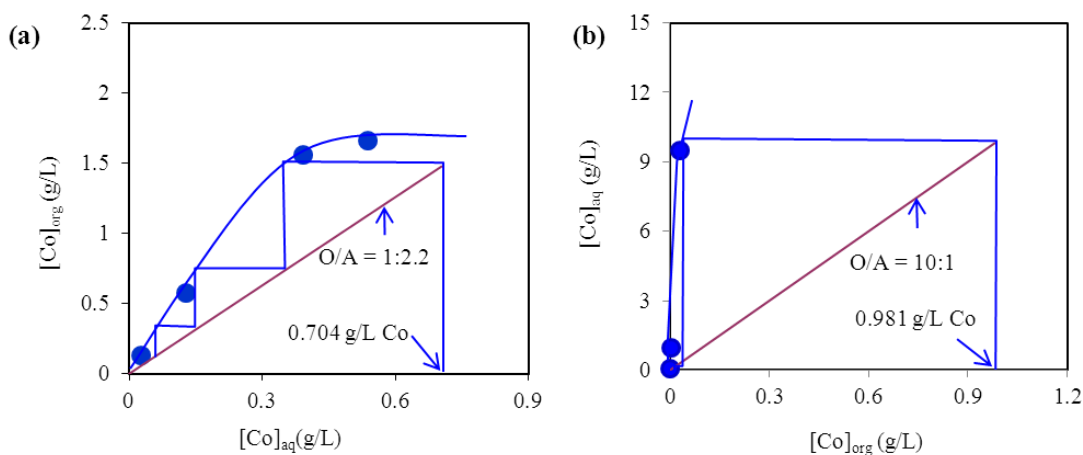

Figure 3 The McCabe–Thiele isotherms for Co2+ (a): extraction isotherm and (b): stripping isotherm [1, 2]
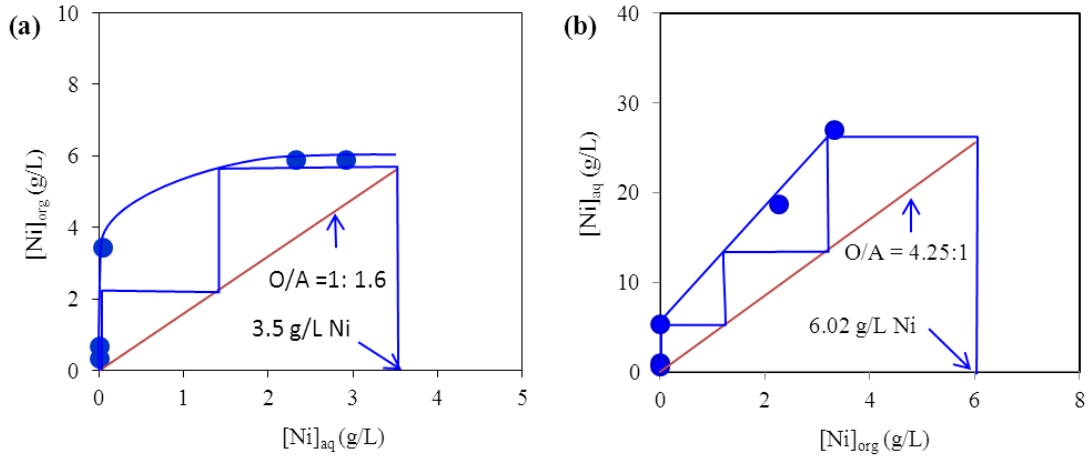
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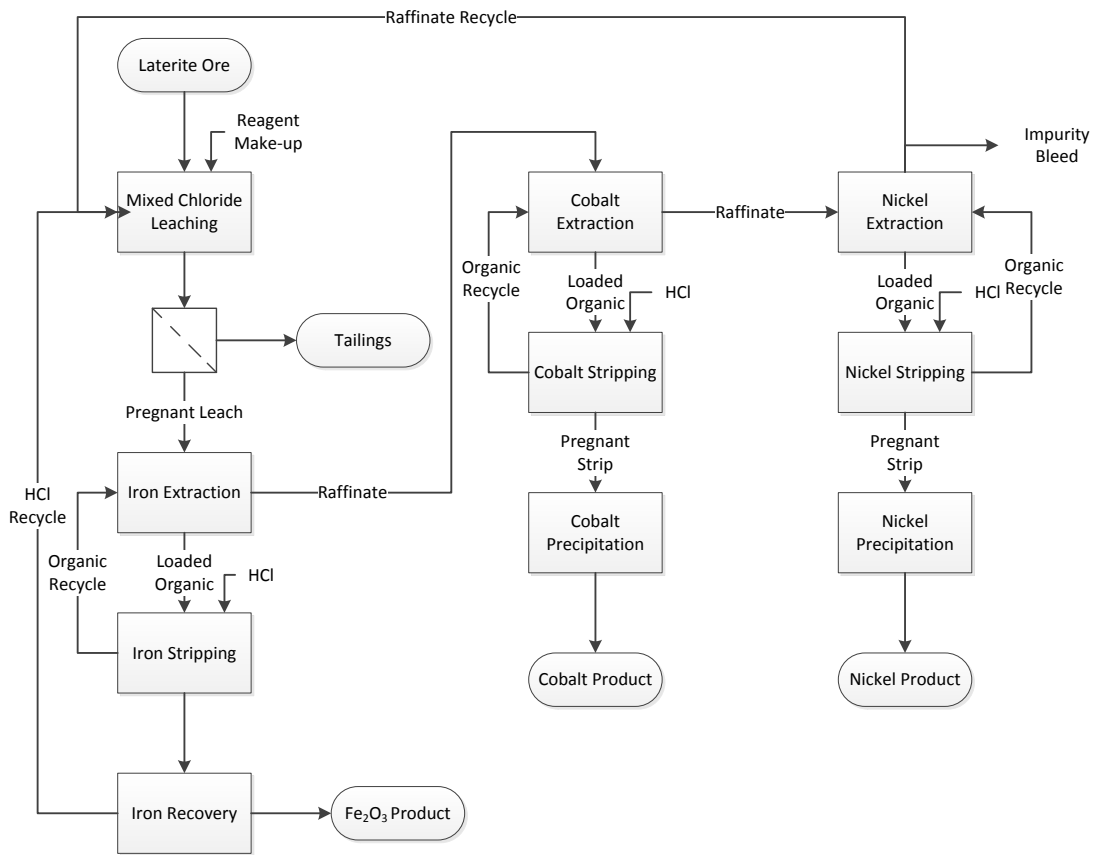Figure 4 The McCabe–Thiele isotherms for Ni2+ (a): extraction isotherm and (b): stripping isotherm [2]

Figure 5 Mixed-chloride process flowsheet for the recovery of Fe, Co and Ni from laterite [1, 2]
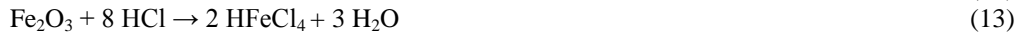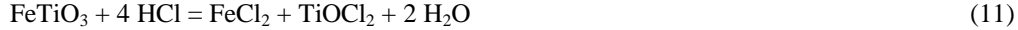
The extractants used in this study are highly selective for Ni^{2+}, Co^{2+} and Fe^{3+} (Table 2), which results in high purity pregnant strip solutions and consequentially high purity Ni, Co and Fe products. Depending on the market value of the product, Ni and Co can be recovered from their respective pregnant strip solutions in different forms such as carbonate and oxide. The developed flowsheet for the recovery of Ni, Co and Fe from laterite is shown in Figure 5 [1, 2]. The use of $MgCl_2$ in the lixiviant and LIX 63 (5, 8-diethyl-7-hydroxy-6-dodecanone) 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. Hydrochloric acid and Fe_2O_3 can be produced from the pregnant strip solution of Fe^{3+} by pyrohydrolysis, which is a

commercially proven process. The process offers many advantages: (i) direct extraction of nickel from cobalt raffinate at lower pH (0.5 − 2.5) without adding any neutralization reagents, (ii) conversion of ferric chloride to Fe_2O_3 and production of concentrated HCl, which is recycled to the leach step, and (iii) recycling of $MgCl_2$ in the nickel raffinate to the leaching stage. A nickel laterite demonstration plant of 1000tpa in capacity is currently being planned in Asia.

3.2   Recovery of Titanium and Vanadium from Ilmenite

Titanium (Ti) is the 9th most abundant element in the earth's crust and forms a very stable oxide, titanium dioxide. TiO_2 is an essential component of paints and is also increasingly used in plastics, rubber, paper, inks, textiles and other applications. There has been a growing interest in the use of vanadium in renewable energy applications for batteries. There is also the potential for a large-scale use of vanadium for grid-level storage of power in a safe manner using Vanadium Redox Batteries (VRB). Ilmenite is the most abundant titanium dioxide-bearing ore containing 40–65% TiO_2, depending on its geological history. It also contains vanadium and other elements such as magnesium, manganese, aluminum, calcium and silicon. There are two commercial processes for the production of TiO_2 from ilmenite ore/concentrate, the sulphate process and the chloride process. Both of these processes have several environmental challenges; the sulphate process suffers from large-scale generation of acidic and solid waste as well as toxic emissions and the chloride process suffers from CO_2 and other toxic emissions. These processes have not been designed to recycle the reagents and discharge the effluents into the environment causing an environmental concern. An innovative atmospheric mixed-chloride leaching process (CTL Process) has been developed for the recovery of titanium, vanadium and iron from ilmenite. The CTL (Canadian Titanium Limited) process is protected by several patents [13, 14, 17 − 19].

Mixed-chloride (HCl + $MgCl_2$) leaching tests were carried out with an ilmenite ($FeTiO_3$) ore containing 26.8 wt % Ti, 35.8 wt % Fe, 0.12 wt % V and 0.03 wt % Cr under atmospheric pressure at 70°C for 4 hours. Extraction of titanium as high as 96.9% was achieved for a solid loading of 8.8 %, HCl level 1.4 times the stoichiometric amount required to solubilize the targeted elements and $MgCl_2$ concentration at 300 g/L. Extraction mechanisms of Ti, V and Fe from ilmenite can be written by the following reactions (11 − 13):

$$FeTiO_3 + 4\ HCl = FeCl_2 + TiOCl_2 + 2\ H_2O \qquad\qquad (11)$$
$$V_2O_4 + HCl = VOCl_2 + H_2O \qquad\qquad (12)$$
$$Fe_2O_3 + 8\ HCl \rightarrow 2\ HFeCl_4 + 3\ H_2O \qquad\qquad (13)$$

One of the major innovations was the finding that with the enhanced H^+ ion activity in the lixiviant due to the addition of $MgCl_2$, enabled the leaching of ilmenite with a lower concentration of HCl at about 70°C. The resultant pregnant leach liquor was subjected to solvent extraction of iron with a high molecular weight ketone in *Exxal™ 13* tridecyl alcohol and Exxsol™ D80 [1, 2, 23]. Iron was stripped from the loaded organic with dilute acid solution. The pregnant strip solution can be used in pyrohydrolysis to produce Fe_2O_3 and 6N HCl which can be recycled to the leaching stage.

The raffinate of iron extraction was subjected to solvent extraction of Ti^{4+} with a suitable extractant in *Exxal™ 13* tridecyl alcohol and Exxsol™ D80. Various organophosphorus extractants, neutral extractants and amine extractants can be used for the Ti^{4+} solvent extraction [22]. Tri-alkyl phosphine oxide (TRPO-Cyanex 923) is one of the most important extractants, which was used for selective extraction of titanium over vanadium and other metals from iron raffinate at a specified concentration of acid [22]. The McCabe–Thiele extraction isotherm for Ti is shown in Figure 6a. Titanium was stripped from the loaded organic phase with dilute acid, while the regenerated organic phase was recycled to the extraction stage. The solvent extraction process developed for the CTL process is extremely selective and results in very pure Ti-rich strip liquor with mg/L levels of impurities. Hydrated titanium dioxide was produced from the Ti-rich pregnant strip liquor by thermal precipitation at 85−95°C followed by calcination to produce TiO_2. The process of titanium solvent extraction, precipitation and calcination are shown in the following reactions (14 − 16):

$$TiOCl_2 + 2TRPO = TiOCl_2 .2TRPO \qquad\qquad (14)$$
$$TiOCl_2\ \ + 2H_2O = TiO_2.H_2O + 2\ HCl \qquad\qquad (15)$$
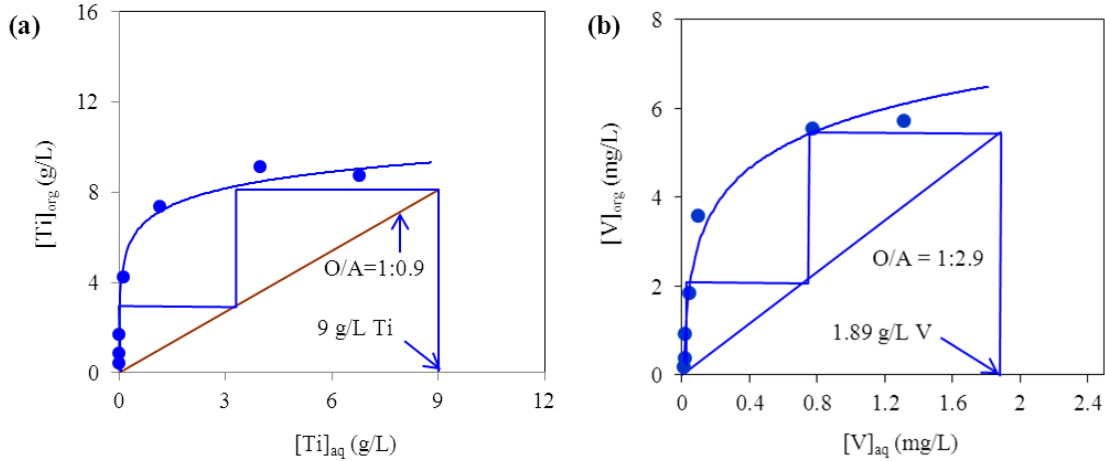$$TiO_2.H_2O = TiO_2 + 2H_2O \qquad\qquad (16)$$

Figure 6 The McCabe–Thiele isotherms for (a): Ti extraction isotherm and (b): V extraction isotherm

After adjustment of pH to levels of about 0-0.1 with MgO, the raffinate from titanium extraction was subjected to selective solvent extraction of V over other metals with Cyanex 923 in *Exxal™ 13* tridecyl alcohol and Exxsol™ D80. The McCabe–Thiele extraction isotherm for V is shown in Figure 6b. Stripping of vanadium was performed by contacting the loaded organic phase with 1.0−2.0 M of HCl at 35−40 °C. Vanadium pentoxide (V_2O_5) was recovered from V-rich strip liquor by hydrolysis followed by calcination. Extraction of vanadium with TRPO can be shown by the following reaction (17):
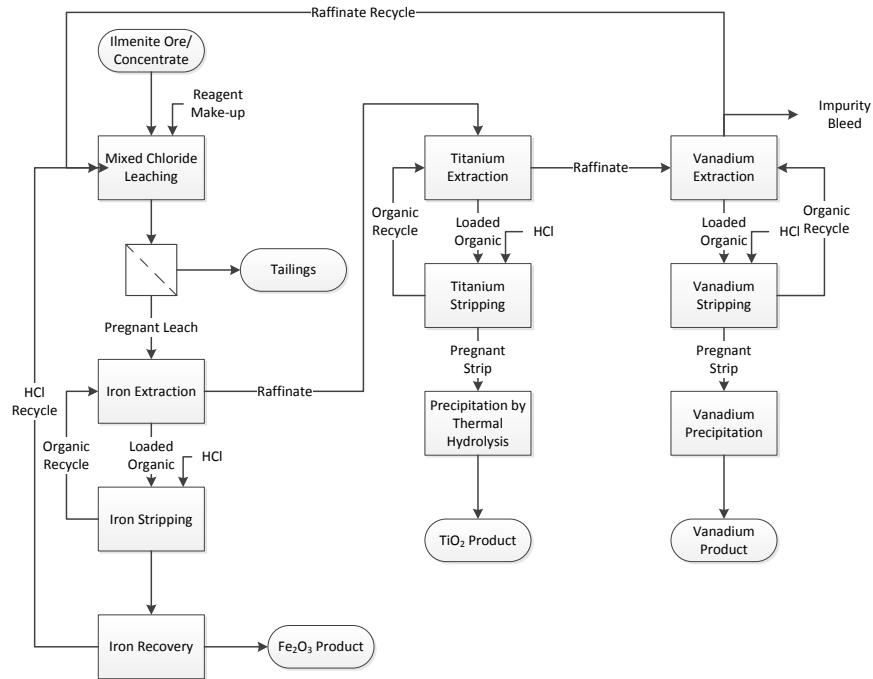
$$VOCl_2 + TRPO = VOCl_2 \cdot TRPO \tag{17}$$

Figure 7 Mixed chloride process (CTL process) flowsheet for the recovery of titanium, vanadium and iron from ores/concentrates [22, 37]

The process has several advantages including: (i) the use of $MgCl_2$ with HCl in the leaching stage which allows lowering of the hydrochloric acid concentration. This permits the use of the azeotropic HCl solution

produced by pyrohydrolysis without the need to add substantial amounts of concentrated HCl, thereby avoiding disposal of excess chloride bearing solutions which is an environmental problem; (ii) the use of a lower concentration of HCl results in lower extraction of impurities or gangue from the ore, and thus decreases the downstream burden for the removal of impurities; and (iii) the process produces less environmental waste due to closed loop operation with recycling of reagents (Figure 7). It is noted that solvent extraction process steps have been incorporated into processes to separate titanium and vanadium from iron and other impurities to enable the use of low grade ilmenite as feed materials.

3.3 Recovery of Gold from Ores, Concentrates and Tailings

The interest in the treatment of complex gold ores (refractory and doubly refractory gold ores) is increasing across the globe due to the eventual depletion of easily extractable gold ores. Recovery of gold from complex ores is a major challenge for the gold mining industry. Depending upon the type of ore, the ground/comminuted ore or concentrate prepared by gravity separation or flotation, undergoes one or combination of several of the following treatments: (i) roasting, (ii) attrition milling, (iii) atmospheric oxidative leaching, (iv) pressure oxidative leaching or (v) bacterial leaching. Leaching is generally followed by neutralization. This is followed by cyanidation and further processing for gold recovery. In most cases, Fe is removed by precipitation prior to Au recovery. More stringent regulations for controlling the environmental pollution by cyanide bearing streams and solid wastes have resulted in increased interests towards alternative lixiviants such as thiosulphate, thiourea and halides [12, 38 - 43]. Among these approaches, chloride leaching has some advantages including higher dissolution rate of gold and non-polluting character.

An innovative atmospheric mixed-chloride leaching process has been developed for the recovery of gold from gold-bearing complex ores, concentrates and tailings [12]. The process consists of crushing/grinding, gravity separation/flotation to produce a concentrate. Depending on the type of ore, the concentrate can be roasted to remove sulfur and other toxic elements including arsenic. The concentrated/roasted sample is then subjected to leaching with the lixiviant containing HCl and $MgCl_2$ at atmospheric pressure in an oxidizing condition. The leach slurry is subjected to a liquid/solid separation step to produce pregnant leach solution and subsequent solvent extraction steps to recover gold from the pregnant leach liquor. For example, a gold-bearing material containing 3.48 kg/t of gold was subjected to mixed chloride leaching with a lixiviant of 4N HCl, 225 g/L $MgCl_2$, at a temperature of 90^oC and pulp density of 10% solids to bring Au into solution. In addition to Au, Fe was also brought into solution. The leaching time and the oxidation reduction potential were 4 h and 1150 mV, respectively. The leaching mechanism of Au can be shown by the following reaction (19):
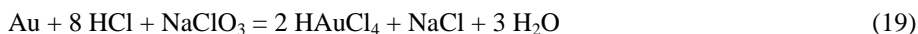
$$Au + 8\ HCl + NaClO_3 = 2\ HAuCl_4 + NaCl + 3\ H_2O \qquad (19)$$

Table 3 Results on solvent extraction of Au with a patented oxime at ambient temperature [12]

	Au (mg/L)		Fe (mg/L)
	Aqueous phase	Organic phase	Aqueous phase
Pregnant leach solution	1.49	0	18030
(i) Au extraction at the O/A of 1:1	0.48	1.01	17710
(ii) Au extraction at the O/A of 1:3	0.83	1.99	17910
Selective stripping of Fe followed by Au from loaded organic phase of (ii)			
(iii) Fe stripping at the O/A of 7:1	<0.1	1.99	2178
(iv) Fe stripping at the O/A of 7:1	<0.1	1.99	350
(v) Au stripping at the O/A of 7:1	11.69	2.25	<0.1

About 98% Au was leached under these conditions. The pregnant leach solution was subjected to selective recovery of Au over Fe by solvent extraction process steps. The gold can be extracted with different extractants such as oxime, crown ether, phosphinic acid, ester or oxide, tertiary amines and quaternary ammonium salts with a modifier and a diluent [12]. Among these extractants, the oxime has high selectivity of Au over Fe under certain conditions. Results of Au extraction with a patented oxime from a pregnant leach solution containing about 225 g/L $MgCl_2$ and about 1.5 N HCl are shown in Table 3 [12]. In the presence of high concentration of Fe (18030 mg/L),

approximately 68% Au is extracted with this organic solution in one contact at the O/A of 1 at ambient temperature, while less than 1.8% of Fe is co-extracted. The gold loaded organic phase was contacted with an aqueous phase containing dilute acid for the selective removal of Fe prior to stripping of Au with thiosulphate. Subsequent stripping tests were carried out at the O/A ratio of 7:1 at ambient temperature. The stripping results of Fe and Au are also shown in Table 3. Results suggest that all co-extracted Fe is stripped by a two stage stripping with dilute acid, while the concentration of Au in the Fe stripped solution is less than 0.1 mg/L, which is below the detection limit of the ICP (inductively coupled plasma) method used for Au. Meanwhile, about 84% of Au is stripped from the loaded organic phase with dilute thiosulphate solution in one contact at the O/A ratio of 7:1.

As explained in the previous sections (3.1 and 3.2), the Fe can be extracted from the raffinate of Au with ketone in *Exxal™ 13* tridecyl alcohol and Exxsol™ D80, followed by stripping with dilute HCl solution [1, 2, 23]. The pregnant strip solution of Fe can be processed by pyrohydrolysis to produce Fe_2O_3 and HCl, which can be recycled to the leaching stage. A mixed-chloride process flowsheet for the recovery of Au from gold-bearing materials is shown in Figure 8 [12]. This process has several advantages such as (i) it is environmentally friendly as no cyanidation is involved and it can be applied in jurisdictions where use of cyanide is not permitted, (ii) selective extraction of Au from the pregnant leach solution followed by stripping, precipitation and calcination avoid the use of cyanide, (iii) this route offers economic advantage by eliminating the cyanide ion in subsequent management of process effluents and solid wastes, and (iv) minimizes reagent costs by recycling HCl and iron raffinate to the leaching stage.
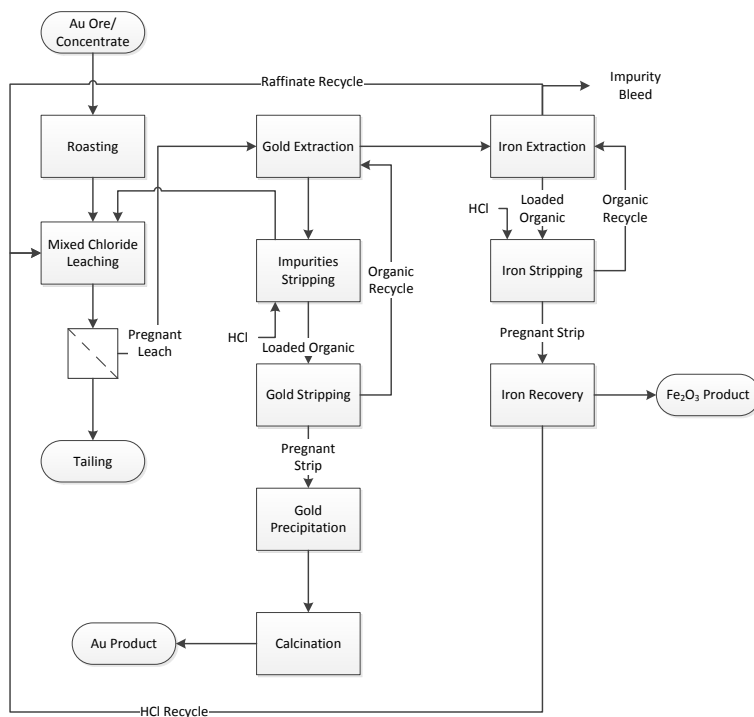

Figure 8 Mixed-chloride process flowsheet for the recovery of gold from gold-bearing materials [12]

4   Conclusions

Innovative atmospheric mixed-chloride hydrometallurgical processes have been developed for the recovery of value metals such as nickel and cobalt from low grade laterites; titanium and vanadium from ilmenite; aluminum from bauxite, and gold from gold-bearing complex ores and concentrates. Leaching of these ores and concentrates were conducted with mixed chloride lixiviant containing HCl and $MgCl_2$ at atmospheric pressure and varying temperature between 70°C to 90°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 subsequent solvent extraction process steps with organic phase containing commercially available extractant,

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modifier and diluent. The mixed-chloride processes have several advantages over the current conventional processes including:

(i)   increased H^+ activity in the lixiviant by addition of $MgCl_2$ to HCl in the leaching stage which helps to increase metal recovery with a lower concentration of HCl,

(ii)   recovered HCl from the pregnant strip of iron and raffinate from the final solvent extraction stage are recycled back to the leaching stage, which 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, compared to other processes that operate at a pH of 5-6 [2],

(iv)   the chloride route offers economic advantage by eliminating treatment of cyanide ions in subsequent process effluents and solid waste treatment in the recovery of gold,

(v)   recoveries of nickel, titanium, aluminum and gold are about 99%, 96.9%, 98% and 97%, respectively,

(vi)   developed processes have simplified flowsheets which are closed loop and thus environmentally more friendly.

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