Innovation of Solvent Extraction for Metal Separation in Mixed Chloride Media: Case Studies for Different Value Metals

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Summary
Solvent extraction is one of the important unit processes in the commercial production of value metals in metallurgical industry. Process Research ORTECH Inc. (PRO) has developed the innovative mixed chloride-solvent extraction processes for the production of value metals from their different sources such as nickel, cobalt and iron from laterite; titanium, vanadium and iron from ilmenite and concentrates; and copper and iron from chalcopyrite. PRO process uses mixed chloride lixiviant ($HCl+MgCl_2$) to dissolve these metals in solution. The hydrochloric acid (HCl) leaching media provides the opportunity to regenerate the acid by pyrohydrolysis, while the presence of magnesium chloride ($MgCl_2$) in the lixiviant enhances the activity of the hydrogen ion by orders of magnitude, making the lixiviant very aggressive and resulting in high recoveries of these metals. The developed process flowsheets are innovative, environmentally friendly and economically attractive.

Introduction

Demand of base metals including iron, titanium, vanadium, cobalt, nickel and copper is tremendously increasing for the development of science and technology in the world. Meanwhile the number of new ore bodies, and the easily exploited ore, are gradually decreasing. Moreover, a rising awareness of environmental protection has lead to more and more difficulty with the smelting process. On the contrary, chloride hydrometallurgy is emerging as an alternative process for the production of base metals [1-4]. Chloride chemistry is complex and quite different from corresponding other systems including sulfate. The solubility of metal chlorides is generally higher than their corresponding sulphate salts. The solubility of $CuSO_4.5H_2O$ is about one fifth that of $CuCl_2.2H_2O$, while nickel and ferrous chlorides are also more soluble than their sulphate counterparts. This allows the use of more concentrated solutions [5]. Also, the activity of water is <<1 in concentrated magnesium chloride solutions, and the activity of the hydrogen ion, H^+ (or H_3O^+) increases rapidly with chloride concentration [6]. This enhances the leachability of minerals in mixed chloride solutions resulting in increased base metals recovery.

Process Research ORTECH Inc. (PRO) has been at the forefront of technological development of chloride metallurgy and PRO's patented mixed chloride technology has been applied to the recovery of several value metals including base metals from laterite and sulfide ores, titanium dioxide from ilmenite ores, rare earth elements (REE) from alumino-silicate ores, platinum group metals (PGM) from sulfide ores and gold from refractory ores [7-15]. In this paper, application of PRO's mixed chloride technology for the recovery of iron, cobalt and nickel from laterite ore, iron, titanium and vanadium from ilmenite ore, and iron and copper from sulfide ore is described.

Recovery of Iron, Cobalt and Nickel from Laterite Ores

Lateritic ores are formed by prolonged weathering of ultramafic rocks and its use for production of nickel is gradually increasing [16]. Typical mineralogical profile of nickel laterite ore bodies is as described below [17, 18]:

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i. Overburden: This zone contains low nickel values (< 0.8% Ni) and is discarded.
ii. Limonitic ore zone: This zone contains ~1.2-1.7%Ni, ~ 40% Fe and ~1-4% MgO. Hydrometallurgical processes are used to extract nickel from limonitic ore zone. High pressure acid leach (HPAL) process is used for high iron (> 35 % Fe) limonitic ores.
iii. Saprolitic ore zone: This zone contains ~1.7 to 2.3% Ni and low iron (< 15% Fe). Pyrometallurgical smelting processes are used to produce ferronickel or matte from saprolytic ores.
iv. Base rocks: This zone contains <0.5%Ni and it is not economic to extract nickel from base rocks.

In some ore bodies, the saprolitic ore profile is either absent or too trace. In ore bodies with rich saprolytic ore zone, the limonitic ores may be stockpiled and stored for later treatment till the higher grade saprolitic ore zone is exhausted.

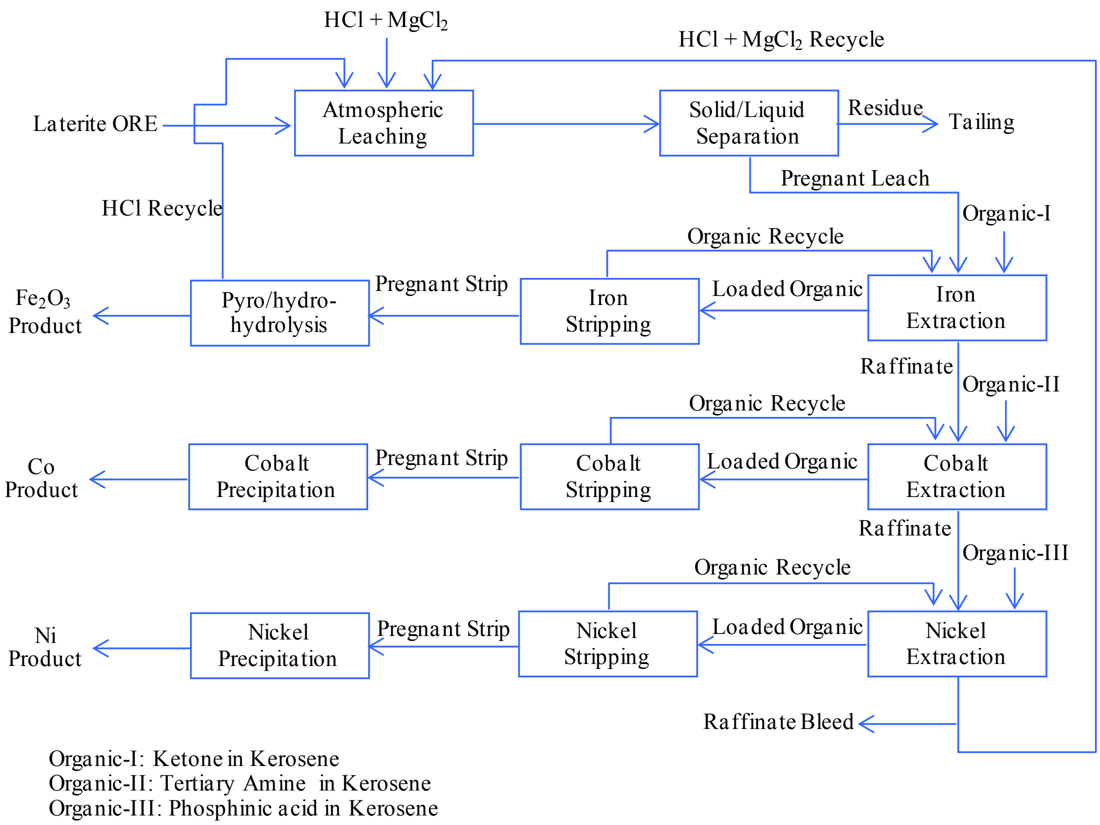

Fig. 1 *PRO mixed chloride process flowsheet for the recovery of Fe, Co and Ni from lateritic ores [7].*

PRO Laterite Process

Based on chloride hydrometallurgy, a innovative mixed chloride process has been developed by Process Research Ortech Inc. (PRO), which is applicable to both high and low iron laterite ores [7]. The process flowsheet is shown in Fig. 1 [7], which involves novel leaching and solvent extraction separation steps. This process is efficient and environmentally friendly. The salient features of the PRO Laterite Process are as follows:

i. Leaching: Leaching is conducted in mixed chloride media to dissolve Fe, Ni, Co and Mg in solution.

ii. Solvent Extraction: Solvent extraction steps are carried out for successive extraction and stripping of Fe, Co and Ni to obtain high purity concentrated pregnant strip solutions of Fe, Co and Ni, respectively.
iii. Precipitation: Precipitation of Ni and Co from respective high purity concentrated pregnant strip solutions is conducted by the addition of MgO generated by pyrohydrolysis.
iv. Pyrohydrolysis:
   a. Fe_2O_3 is produced and HCl is regenerated by the pyrohydrolysis of the iron chloride rich pregnant strip solution.
   b. MgO is produced and HCl is regenerated by the pyrohydrolysis of the bleed stream from the magnesium chloride containing raffinate of the nickel solvent extraction stage. MgO thus produced can be used for pH control as well as precipitation of Ni and Co from their respective pregnant strip solutions. Excess MgO produced can be sold.
v. Recycling: HCl and $MgCl_2$ are recycled to leaching stage.

PRO Testwork

Tests were conducted with a laterite ore having a composition of 0.76% Ni, 0.11% Co and 42.61% Fe. Optimum leach recoveries of Ni, Co and Fe in PRO's proprietary mixed chloride lixiviant were 97.8%, 89.4% and 97.7%, respectively. After solid/liquid separation, the pregnant leach solution went through a series of solvent extraction separation steps to sequentially extract Fe, Co and Ni from the solution using different organic extractants. Loaded organics were stripped using dilute acidic solutions to generate high purity pregnant strip solutions of Fe, Co and Ni individually. The solvent extraction separation steps developed by PRO are highly selective for the target metals, which results in high purity pregnant strip solutions and consequentially high purity Fe, Co and Ni products. Iron oxide and magnesium oxide can be produced from respective solutions by pyrohydrolysis, which will also regenerate the hydrochloric acid. Pyrohydrolysis is a commercially proven process. PRO has developed a novel hydrothermal hydrolysis process that can be used to regenerate the hydrochloric acid and produce high purity iron oxide and magnesium oxide. PRO's hydrothermal hydrolysis process is more economical than pyrohydrolysis process as hydrothermal hydrolysis process runs at a much lower temperature.

Comparison of PRO Laterite Process with Commercial Processes

There are three commercial processes for the recovery of nickel from lateritic ores: Pyrometallurgical process, Caron process and High Pressure Acid Leach (HPAL) process [16]. The Pyrometallurgical process involves drying, calcining and smelting of entire ore body at successively higher temperatures and therefore is energy intensive. The Caron process involves ore drying followed by selective reduction of nickel, leaching with ammonia solution and nickel carbonate precipitation from pregnant leach solution. Nickel carbonate is decomposed to produce nickel oxide, which is then reduced to form nickel metal. In contrast, HPAL process involves high pressure leaching with H_2SO_4 followed by counter-current decantation and neutralization. Different options exist for purification of nickel containing solutions and separation of nickel and cobalt with solvent extraction, followed by electrowinning of nickel. A comparison of PRO laterite process with commercial processes is shown in Table 1.

Table 1 *A comparison of PRO Laterite Process with commercial processes.*

	Pyrometallurgical Process	Caron Process	HPAL Process	PRO Laterite Process
Ores that can be treated	Med-high Ni (1.8-2.5%), low-med Fe (10-20%) ores	Low Ni (1.2-1.5%), high iron (>40%) ores	Low Ni (1.2-1.5%), high iron (>40%) ores	Both low Fe and high Fe ores
Ni recovery	~ 95%	~ 75%	~ 95%	> 90%
Co recovery	None	< 50%	~ 95%	> 90%
Fe recovery	No	No	No	Yes
Mg recovery	No	No	No	Yes
Capital cost	High	Medium	High	Low
Operating cost	High	Medium	High	Medium
Energy requirement	High (due to water removal from ore and high temperature processing)	High (due to water removal from ore and high temperature processing)	Low (no water removal from ore and low temperature process)	Medium (no water removal while pyrohydrolysis needed for acid regeneration adds energy cost)
Reagents	Not recycled	Not recycled	Not recycled	Recycled
Residue	High volume	High volume	High volume	Low volume
Environmental	Slag disposal	Residue disposal containing NH_3	Higher residue disposal	Inert residue
Sulphur price	No effect	No effect	Very dependent	No effect
Fuel price	High effect	Medium effect	Lower effect	Medium effect
Byproduct credit	None	None	None	Fe_2O_3 and MgO credit

Recovery of Iron, Titanium and Vanadium from Ilmenite

The main raw material for TiO_2 production is the mineral ilmenite ($FeO.TiO_2$), which is conmonly found in the mineral sand beache. It also occurs as hard rock. In the processing of mineral sands, rutile ore is also recovered. Rutile ore is essentially TiO_2 and is used for the production of TiO_2 pigments by the chloride process.

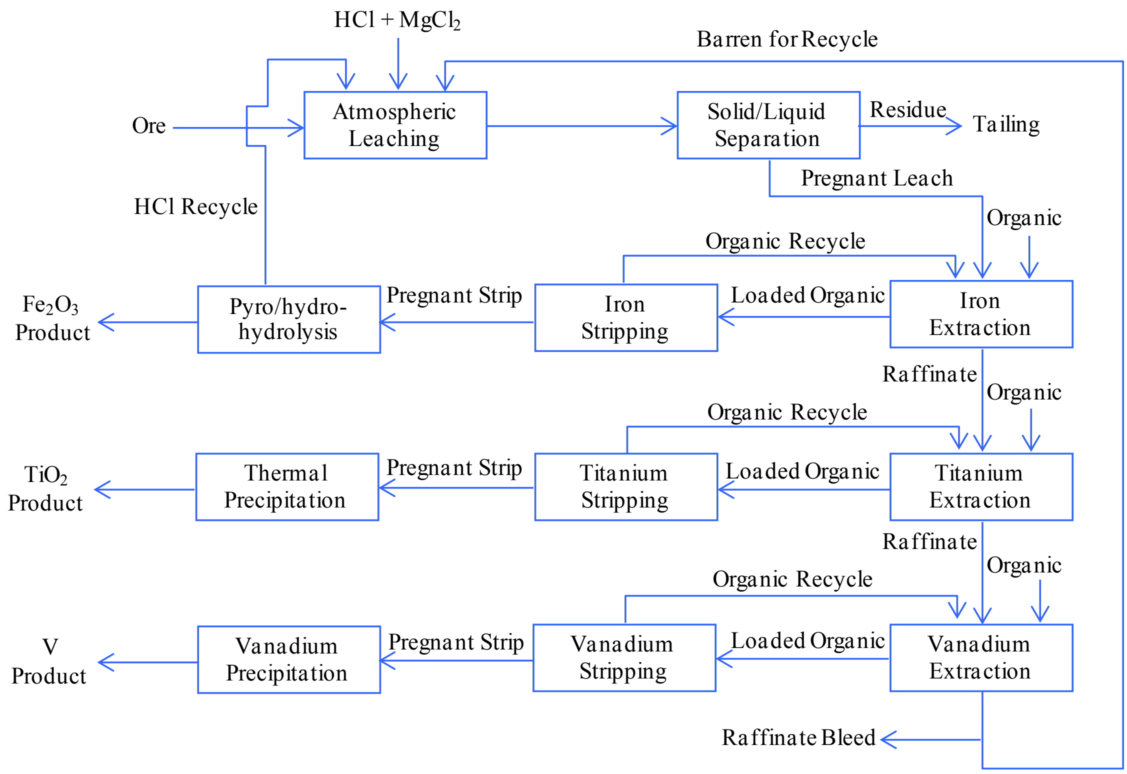

Fig. 2 *The process flowsheet for the production of Fe, Ti and V oxides from ore [12, 15].*

PRO Process

PRO has developed a proprietary mixed chloride Canadian Titanium Limited (CTL) process for the recovery of Fe, Ti and V from ilmenite concentrate [12,14, 15]. The process flowsheet is shown in Fig. 2 [12, 15]. This process consists of atmospheric mixed chloride leaching of ilmenite ore to bring Fe, Ti and V in solution. After solid-liquid separation, pregnant liquor is subjected to solvent extraction steps for subsequent extraction of Fe, Ti and V with different organic extractants followed by stripping and precipitation for product recovery.

PRO Testworks

An ilmenite ore containing 22.8 wt.% of Ti, 38 wt.% of Fe, 0.13 wt.% of Cr_2O_3, 4.69 wt.% of SiO_2 and 2.82 wt.% of MgO with a mesh size of –100 was used as feed material for extraction of iron, titanium and vanadium with a solution of hydrochloric acid and magnesium chloride as a lixiviant under atmospheric pressure at 70-73 ºC for 4 hours. The results show that extraction of Fe and Ti was achieved as high as 84.4% and 96.9%, respectively, for a solid loading of 8.8 %, 1.4 times of stoichiometric amount HCl and 300 g/L of $MgCl_2$. Then, the slurry was filtered to separate the pregnant leach liquor from residue.

Solvent extraction was carried out for subsequent extraction of Fe, Ti and V with different organic extractants in kerosene from pregnant leach solution. Three different types of extractants namely acidic organophosphorus, neutral and amine extractants could be used to extract titanium followed by vanadium [12, 15]. Detailed explanation of theses organics is given in the previous studies [12, 14, 15]. Loaded organics were stripped using acidic solutions to generate high purity pregnant strip solutions of Fe, Ti and V individually (Table 2). Iron oxide can be produced from pregnant strip solution by pyrohydrolysis, which will also regenerate the hydrochloric acid. The titanium pregnant strip was used for thermal precipitation of TiO_2, while V was precipitated from its pregnant strip solution by increasing pH. The barren solution was used for reagent recovery and the regenerated liquor was recycled.

Table 2 Results of first stage stripping of Fe, Ti and V from their loaded organics with 0.05M HCl, 1M HCl and 1.5M H_2SO_4, respectively, at the O/A ratio of 1 at room temperature.

Fe			Ti			V		
Concentration (g/L)		Stripping (%)	Concentration (g/L)		Stripping (%)	Concentration (g/L)		Stripping (%)
Organic phase	Pregnant strip		Organic phase	Pregnant strip		Organic phase	Pregnant strip	
37.8	35.6	94	9.8	7.6	78	5.2	4.6	88

Comparison of Ttanium Dioxide Production Processes

TiO_2 is currently produced by either the sulphate process or the chloride process. PRO process is compared with the sulfate process and chloride process in Table 3.

***Table 3** Comparison between TiO_2 production processes.*

	The chloride process	The sulphate process	The CTL process
Raw material ($/ton of feed)	Higher cost ($2000 +)	Lower cost Ilmenite ($300)	Lowest cost Ilmenite ($250)
TiO_2 product ($/ton of TiO_2)	High value ($4500)	Low value ($3500 +)	High value ($4500)
Capex	Highest (including front-end)	Medium	Lowest
Opex	Highest (including front-end)	Medium	Lowest
Environmental	Medium challenges	Major challenges	Environmentally friendly
Flexibility in processing raw material	Limitation (Ca, Cr, Mn, Mg, V, size)	Limitation (Cr, V)	Flexible
Process Condition	High Temp. Chlorination (800-1000 ^{0}C)	High Temp Leaching (140-180 ^{0}C)	Low temp., atmospheric Leaching (70 ^{0}C), precipitation (90 ^{0}C)
Technology	Old	Old	Patented, New
End to end in one location	Not practiced	Possible	Possible
Pigment production	Rutile	Rutile/Anatase	Rutile/Anatase
Commercially Proven process	In practice	In practice	Innovatively applied, will soon be in practice
Environmental challenges	Disposal of iron and other byproduct chlorides	Disposal of large iron sulphate product and dilute acid	Minimum environmental impact, Iron oxide as byproduct
Safety Requirements	High (chlorine at high temperature)	High (High temperature acid digestion)	Low (no pressurized vessel and lower temperature)
chlorine and carbon/carbon containing chemicals at high temperature	Challenges to handle	N/A	N/A
Energy consumption	High	High	Efficient
Sulfur price	No effect	Substantial effect	No effect

Recovery of Iron and Copper from Sulfide Ores

Copper ore is mainly copper sulfide or copper oxide ore. The chalcopyrite concentrates, which account for about 70% of the world's known copper reserves. In the last 10 years, very few grass roots copper smelter-refinery complexes have been built, due to their very high capital cost. In contrast, there has been a gradual increase in the production of copper by leaching-solvent extraction-electrowinning operation, which is now account for about 30% of world copper production. There are a large number of reasons for looking at process alternatives for the smelter-refinery approach. They are: (i) capital cost; (ii) handling of impurities; (iii) precious metals in copper concentrates; (iv) recovery of valuable by-products; (v) use of existing SX-EW equipment; (vi) mine to market optimization; and (vii) overall economics [19, 20].

PRO Process

Process Research ORTECH (PRO) Inc. has been developed an innovation properitory mixed chloride leaching technology for the recovery of Fe and Cu from sulfide ores/concentrates [11]. A tentative process flowsheet is shown in Fig. 3. The main features of this flowsheet include leaching of the ores/concentrates at 90-100 °C in recycled mixed chloride ($HCl+MgCl_2$) with an oxidant. In this leaching stage, Fe and Cu are dissolved and sulphide sulphur is removed as H_2S, which is converted to elemental sulphur in a Claus reactor. Iron and Cu are recovered from leach solution by solvent extraction. Other steps include removal of impurities with lime and production of magnesia and regeneration of HCl by pyrohydrolysis.

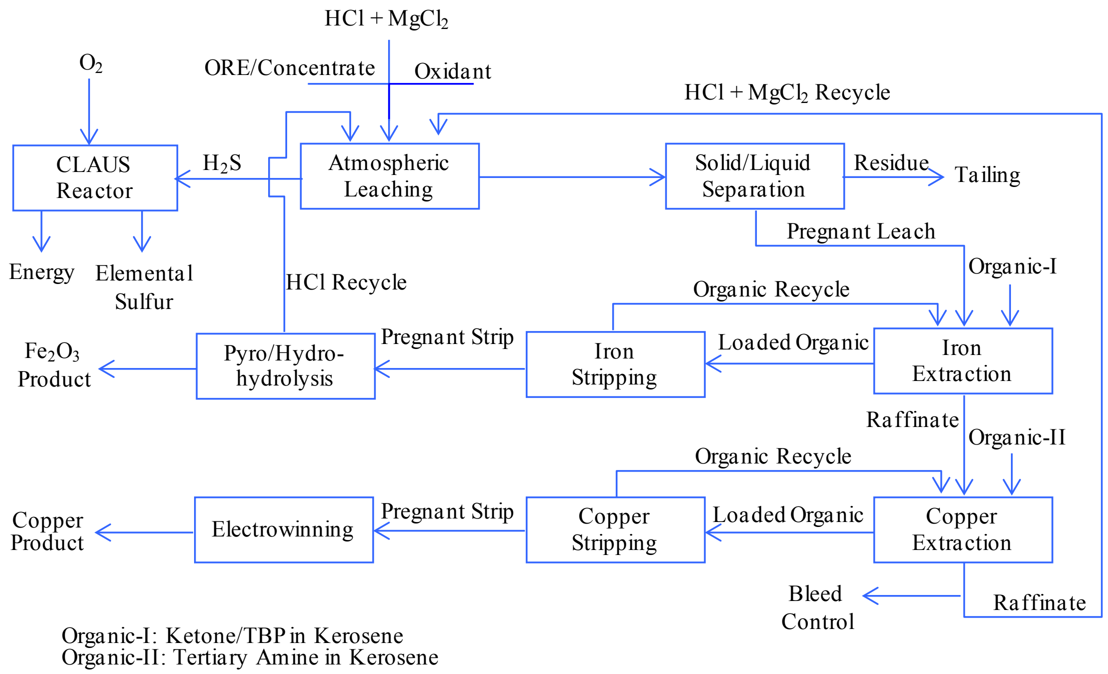

Fig. 3 *A tentative process flowsheet for the production of Fe oxide and Cu from their sulfide ores.*

PRO Testworks

A series of leaching tests were carried out using a copper ore containg 1.275% Cu, 2.61% Fe and 0.93% S and a leach solution of hydrochloric acid (4N) and magnesium chloride, at a total chloride ion concentration of 400 g/L. The leached solution was subjected to a solid/liquid separation followed by subsequent solvent extraction steps for separation and purification of Fe and Cu.

Iron followed by copper could be selectively separated from pregnant leach solution with a organic solvent contained a ketone/tri-butyl phosphate (TBP) and a tertiary amine in kerosene, respectively. Both of the Fe and Cu could be stripped from their loaded organics with a dilute acid. Barren organics could be recycled to the extraction circuits. The raffinate of the Cu extraction circuit can be treated for removal of impurities with lime followed by pyrohydrolysis to recover magnesia and HCl which can be recycled to the leaching stage. Iron oxide and HCl can be produced from Fe pregnant strip solution by pyrohydrolysis. Copper can be recovered from its pregnant strip solution by electrowinning.

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