

INNOVATIVE PROCESSES FOR THE RECOVERY OF GOLD AND BASE METALS

By

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ABSTRACT

Chloride metallurgy is emerging as an alternative process for the production of base metals. Process Research ORTECH Inc. (PRO) has been at the forefront of technological development of chloride metallurgy. PRO's patented mixed chloride technology has been applied to the recovery of several products including titanium dioxide from ilmenite ores, REE from alumino-silicate ores, base metals and PGM from sulfide ores, gold from refractory ores and base metals from laterite ores. This paper will describe the application of PRO's mixed chloride technology for the recovery of gold from refractory ores and base metals from lateritic ores. PRO process uses mixed chloride lixiviant (HCl+MgCl₂) to bring base metals in solution. The HCl leaching system provides the opportunity to regenerate the acid by pyrohydrolysis, while the presence of MgCl₂ in the lixiviant enhances the activity of the hydrogen ion by orders of magnitude, making the lixiviant very aggressive. This results in high recoveries of base metals. Base metals are separated from pregnant leach solution (PLS) successively using innovative solvent extraction steps. Overall, the process flowsheet is efficient, environmentally friendly and economically attractive.

INTRODUCTION

Chloride metallurgy is emerging as an alternative process for the production of base metals⁽¹⁻¹⁰⁾. Chloride chemistry is complex and quite different from corresponding sulfate systems. The solubility of metal chlorides is generally higher than their corresponding sulphate salts. The solubility of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is about one fifth that of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, while nickel and ferrous chlorides are also more soluble than their sulphate counterparts. This allows the use of more concentrated solutions⁽¹¹⁾. Also, the activity of water is $\ll 1$ in concentrated magnesium chloride salt solutions, and the activity of the hydrogen ion, H^+ (or H_3O^+) increases rapidly with chloride concentration as shown in Figure 1⁽¹²⁾. 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 products including titanium dioxide from ilmenite ores, REE from alumino-silicate ores, base metals and PGM from sulfide ores, gold from refractory ores and base metals from laterite ores⁽¹³⁻²⁶⁾. The application of PRO's mixed chloride technology for the recovery of gold from refractory ores and base metals from lateritic ores is described below.

PROCESSING OF GOLD ORES

Gold ores can be divided into non-refractory and refractory ores. Recovery of gold is simpler for non-refractory gold ores compared to that for refractory gold ores. As the grade of non-refractory gold ores is falling across the globe and reserves are depleting, the interest in the treatment of refractory gold ores is increasing⁽²⁷⁻³⁰⁾.

Non-Refractory Gold Ores

Non-refractory gold ores contain free gold particles in a relatively inert matrix. Non-refractory gold ores include placer, free milling and oxidized ores. Nearly 95% of the gold from non-refractory gold ores can be recovered by gravity concentration and/or direct cyanidation.

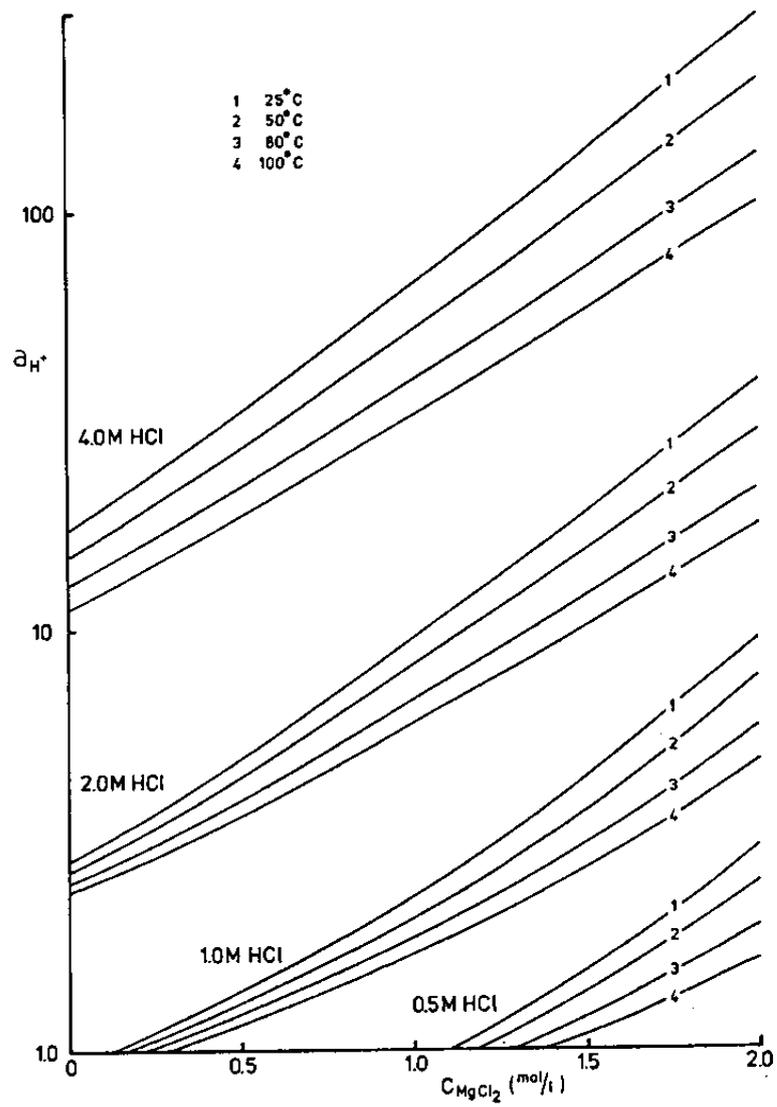


Figure 1: Effect of MgCl₂ Concentration on the Activity of H⁺ in HCl Solutions⁽¹²⁾

The treatment options for non-refractory gold ores include 1) gravity separation, 2) crushing and cyanidation (heap/vat) and 3) crushing/grinding, gravity concentration/flotation followed by cyanidation (CIP/CIL) as shown in Figure 2⁽³¹⁾.

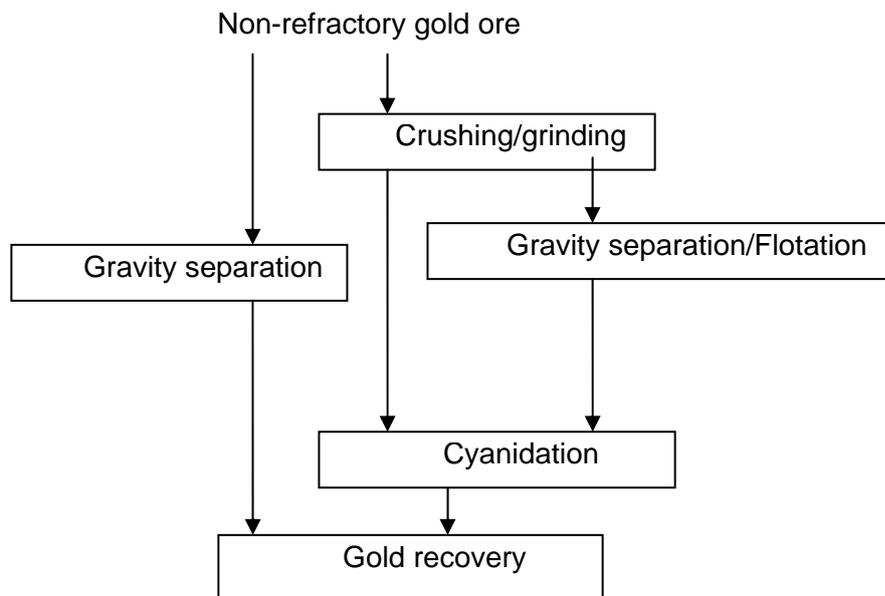


Figure 2: Processing of non-refractory gold ores.

Refractory Gold Ores

If gold extraction by conventional cyanidation process is less than 80% even after fine grinding, then gold ore is considered refractory⁽³²⁾.

There are mainly two constituents responsible for the refractory behavior of ores:

- 1) sulfides, silicates, tellurides, antimonides and selenides
- 2) carbonaceous matter

Refractory behavior of the first type can be divided further in chemical and physical refractoriness. When gold is combined with other elements in compound form such as tellurides (AuTe_2 – calaverite), antimonides (AuSb_2 – aurostibnite) and selenides (Ag_3AuSe_2 – fischesserite), it causes chemical refractoriness. When gold particles are finely disseminated in a matrix such as sulfides or silicates or exist as solid solution, it causes physical refractoriness. The treatment of refractory gold ores is more complex than non-refractory gold ores. The treatment process options for refractory gold ores are shown in Figure 3⁽³³⁾.

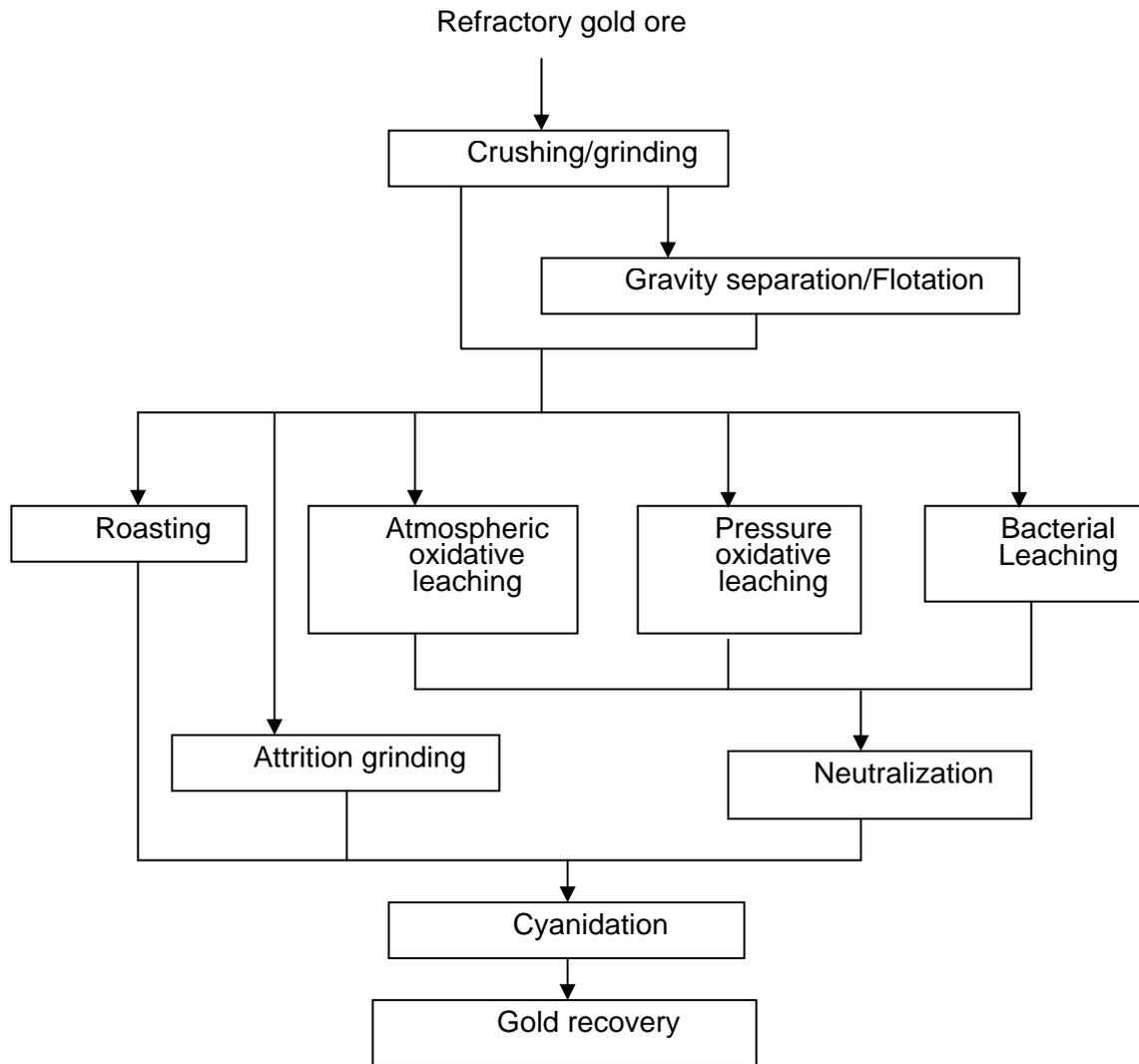


Figure 3: Processing of refractory gold ores

The ore is first crushed and ground and may undergo concentration using gravity separation or flotation. Depending upon the type of ore, the crushed/ground ore or concentrate may undergo one of these treatments: 1) roasting, 2) attrition milling, 3) atmospheric oxidative leaching, 4) pressure oxidative leaching or 5) bacterial leaching. Leaching is generally followed by neutralization. This is followed by cyanidation and further processing for gold recovery.

Double Refractory Gold Ores

An ore body is called double refractory, if it contains both sulfides and carbonaceous matter⁽³⁴⁾. The carbonaceous matter may be present as organic carbon or elemental carbon. Organic carbon may be in the form of hydrocarbons, humic acids and other organic substances, while the elemental carbon may be graphitic or amorphous. Graphitic carbon is the main source of carbonaceous matter in double refractory gold ores presenting serious challenges in the recovery of gold during leaching. The processing of double refractory gold ores presents a major challenge to gold producers. As with refractory gold ores, double refractory sulfide ores can be oxidized to decompose the sulfide matrix thereby liberating gold and making the disseminated gold amenable to leaching. The oxidizing pre-treatment processes may include the conventional roasting, pressure oxidation, chlorination and bacterial oxidation as described in the previous section. In case of double refractory gold ores, however, one needs to deal also with the preg-robbing behavior of the carbonaceous matter. The carbonaceous matter needs to be either removed or passivated before cyanidation.

There are several approaches that are being investigated to deal with the preg-robbing behavior of the carbonaceous matter. These methods include flotation, addition of blanking agents, roasting and competitive loading onto commercial activated carbon. Flotation of carbonaceous matter may be an option, if the amount of gold associated with carbonaceous matter is low. In that case,

carbonaceous matter may be floated and discarded. Further processing can then be done by one of the processes discussed above for refractory gold ores.

The treatment of double refractory gold ores is very challenging and there is a need for economical and practical methods to treat these ores. Fundamental understanding of ore mineralogy, solution chemistry along with a deeper knowledge of the limitations of various chemical and thermal processing methods are key considerations in development of a robust solution.

Features of PRO Gold Technology

Process flowsheet developed by PRO for treatment of refractory/double refractory gold ores is shown in Figure 4⁽³⁵⁾. The flowsheet consists of crushing/grinding, gravity separation/flotation to produce a concentrate, roasting of calcine, leaching of calcine in PRO's proprietary lixiviant and solvent extraction separation process for recovery of gold from the pregnant leach solution (PLS).

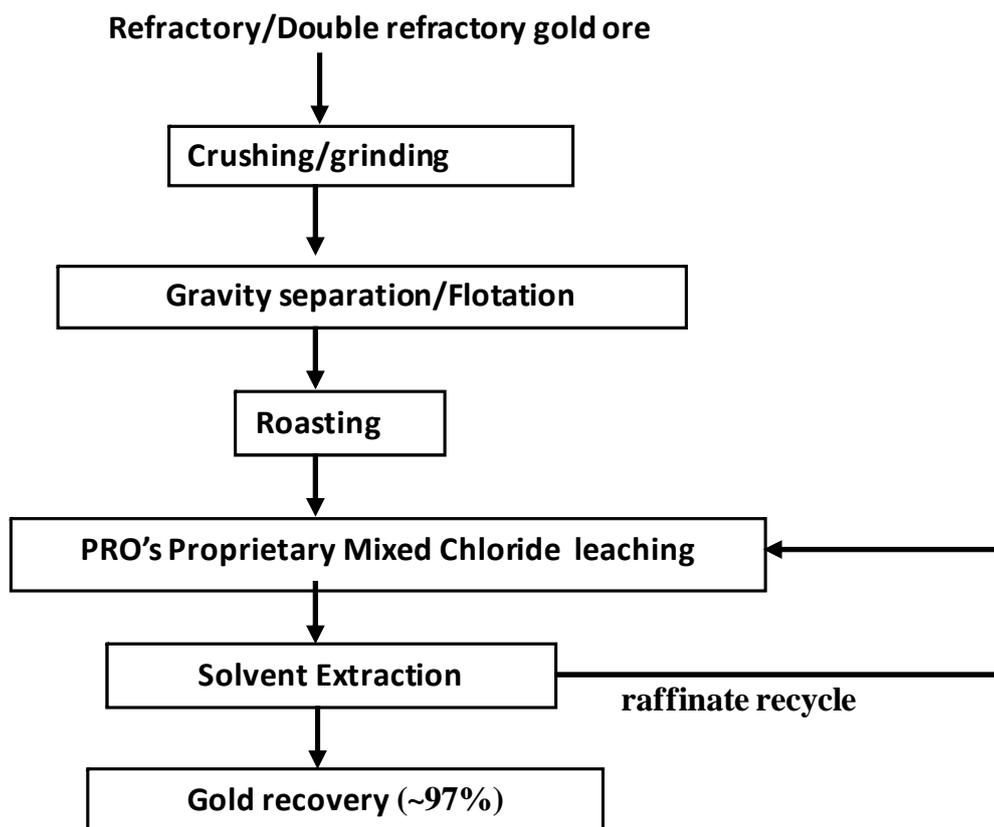


Figure 4: PRO process flowsheet for treatment of refractory/double refractory gold ores⁽³⁵⁾

PRO process is environmentally friendly as no cyanidation is involved and reagents are recycled. PRO's proprietary technology can be applied in jurisdictions where use of cyanide is not permitted. In addition, PRO process results in higher gold recovery compared to commercial processes and this will provide an economically and environmentally attractive alternative to commercial processes.

PROCESSING OF LATERITE ORES

Lateritic ores are formed by prolonged weathering of ultramafic rocks and its use for production of nickel is gradually increasing⁽³⁶⁾. Typical mineralogical profile of nickel laterite ore bodies is as described below⁽³⁷⁻³⁸⁾:

- 1) Overburden: This zone contains low nickel values (< 0.8% Ni) and is discarded).
- 2) 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 using sulphuric acid may be used for high iron (> 35 % Fe) limonitic ores.

- 3) 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 saprolitic ores.
- 4) 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, not present or too trace for economical extraction, in which case nickel is extracted from the limonitic ore zone. In ore bodies with rich saprolitic ore zone, the limonitic ores may be stockpiled and stored for later treatment till the higher grade saprolitic ore zone is exhausted.

Commercial Processes for the Treatment of Lateritic Ores

There are three commercial processes for the extraction of nickel from lateritic ores: Pyrometallurgical process, Caron process and High Pressure acid Leach (HPAL) process. The flowsheet for all three commercial processes is shown in Figure 5⁽³⁶⁾. The Pyrometallurgical process is used for saprolitic ores with high nickel values to produce ferronickel and matte with 25 to 75% Ni content. The flowsheet for pyrometallurgical processing of lateritic ores consists of ore drying followed by calcination/reduction in a rotary kiln. The calcine from the rotary kiln is smelted in an electric furnace with carbon as reductant followed by refining or conversion to produce ferro-nickel or matte. The process involves drying, calcining and smelting of entire ore body at successively higher temperatures and therefore is energy intensive.

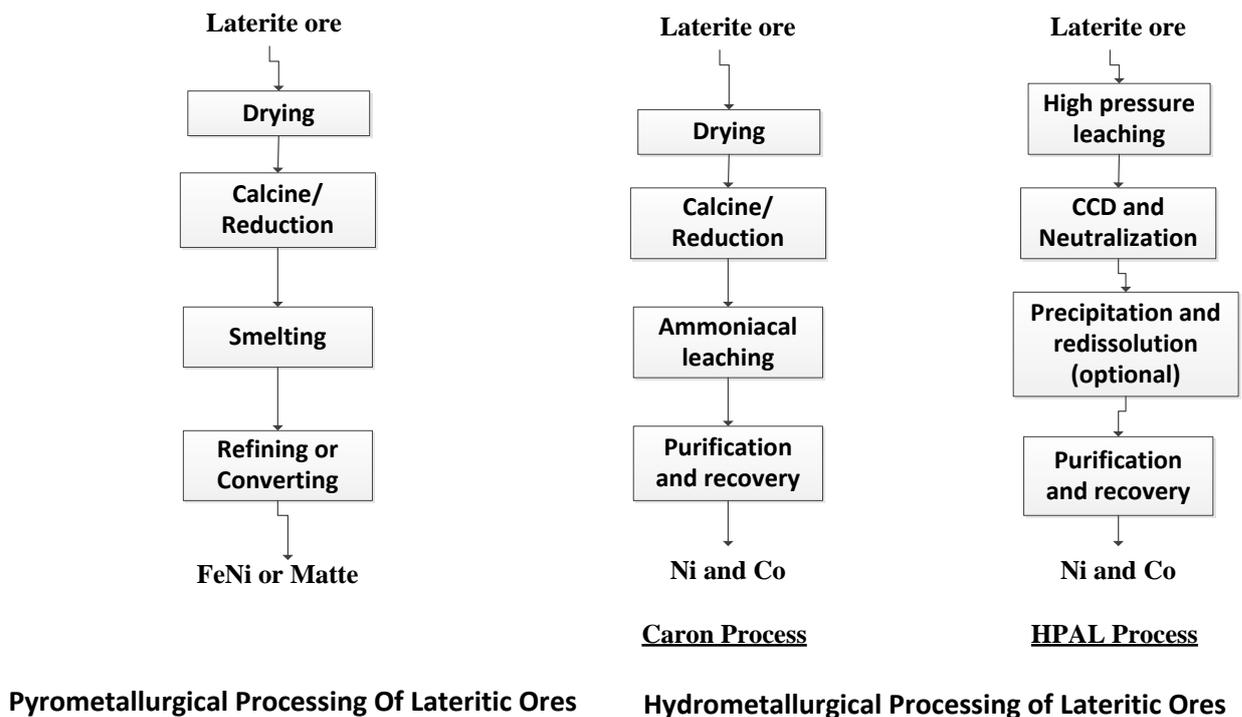


Figure 5: Commercial processes for the treatment of lateritic ores⁽³⁶⁾

The Caron process is used either for limonitic ores or for mixtures of limonitic and saprolitic ores and involves ore drying followed by selective reduction of nickel. This is followed by leaching in an ammoniacal solution to bring metals in solution. After solid liquid separation, basic nickel carbonate is precipitated from pregnant leach solution. Basic nickel carbonate is decomposed to produce nickel oxide, which is then reduced to form nickel metal.

High Pressure Acid Leach (HPAL) processes are used to treat the high iron limonitic ores. The HPAL process involves high pressure leaching followed by counter-current decantation (CCD) and neutralization. Different options exist for purification of nickel containing solutions and separation of nickel and cobalt including solvent extraction, followed by electrowinning of nickel. The economics of HPAL process is highly dependent on sulfur prices, as sulfur prices determine the sulfuric acid prices. The acid requirement for high iron limonitic ores is typically about 30 to 40 weight percent of

the ore weight depending on the MgO content⁽³⁹⁾. A few years ago the sulfuric acid prices rose to \$200 per ton and the economics of the new plants became questionable at those prices. Though market has corrected itself, sulfuric acid prices could spike again. This has provided an incentive for the development of an alternate process less dependent on sulfuric acid.

PRO Laterite Process

A new innovative process based on Chloride hydrometallurgy has been developed by Process Research Ortech Inc. (PRO), which is applicable to both high and low iron laterite ores⁽⁴⁰⁾. The process flowsheet as shown in Figure 6 involves novel leaching and solvent extraction separation steps and 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 bring Fe, Ni, Co and Mg in solution.
- II. **Solvent Extraction:** Innovative solvent extraction steps are carried out for successive extraction and stripping of Fe, Ni and Co to obtain high purity concentrated preg strip solutions of Fe, Ni and Co, respectively.
- III. **Precipitation:** Precipitation of high purity Ni and Co products from respective high purity concentrated preg strip solutions of Ni and Co is conducted by the addition of MgO generated from pyrohydrolysis.
- IV. **Pyrohydrolysis:**
 - a. Fe₂O₃ is produced and HCl is regenerated by the pyrohydrolysis of the iron chloride rich preg strip solution.
 - b. MgO is produced and HCl is regenerated by the pyrohydrolysis of the bleed stream from the magnesium chloride containing raffinate from the nickel solvent extraction stage. MgO thus produced can be used for pH control as well as precipitation of Ni and Co compounds from their respective preg strip solutions. Excess MgO produced can be sold.
- V. **Recycling:** HCl generated by pyrohydrolysis is recycled to leaching stage.

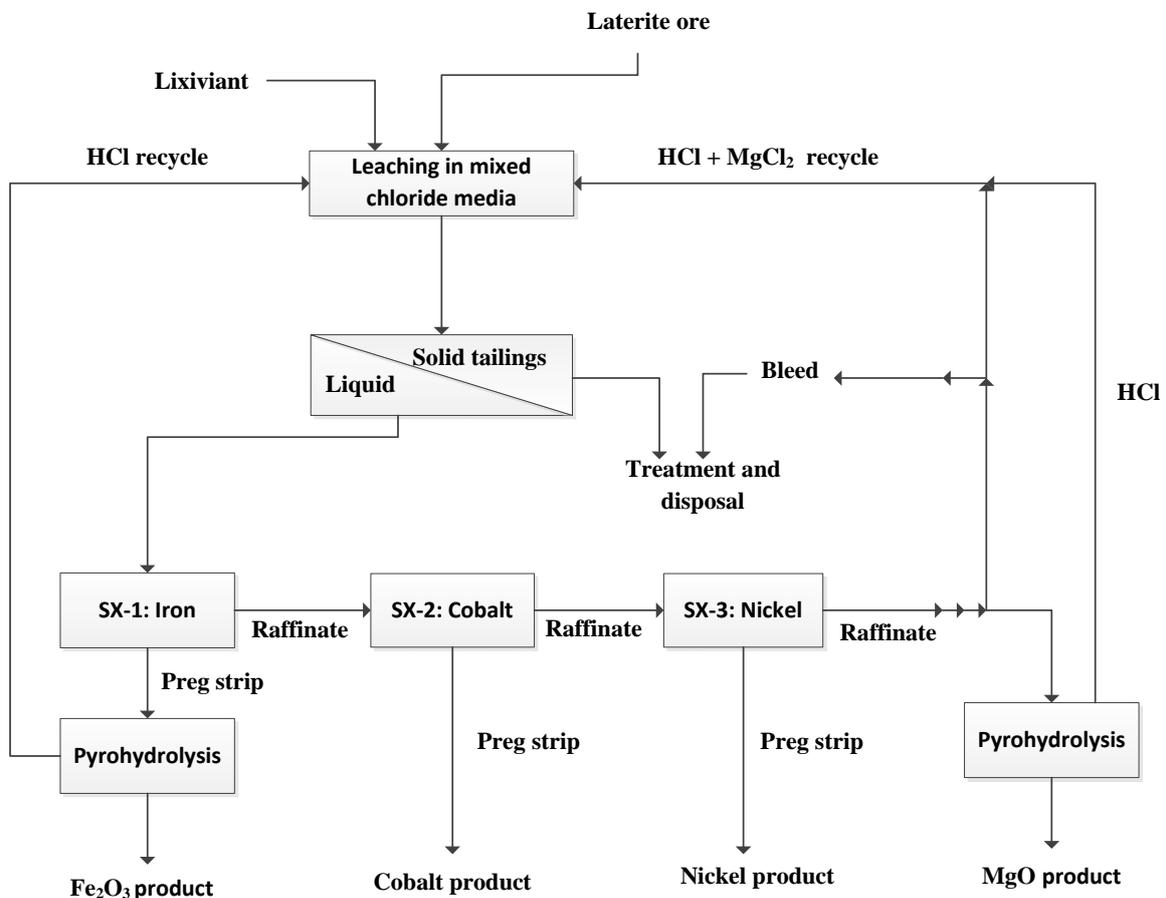


Figure 6: PRO process for treatment of lateritic ores⁽⁴⁰⁾

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 remove Fe, Co and Ni from the solution using organic extractants. Loaded organics were stripped using dilute acidic solutions to generate high purity preg strip solutions of Fe, Co and Ni individually. The extraction isotherms for Fe, Co and Ni are shown in Figures 7, 8 and 9 respectively. The solvent extraction separation steps developed by PRO after extensive testing with different organic extractants are highly selective for the selected elements, which results in high purity preg strip solutions and consequentially high purity Fe, Co and Ni products. Iron oxide and magnesium oxide can be produced from respective preg strip solutions by pyrohydrolysis as shown in Figure 6, which will also regenerate the hydrochloric acid. Pyrohydrolysis is a commercially proven process and pyrohydrolysis units can be designed by commercial vendors based on the preg strip analysis and planned plant output.

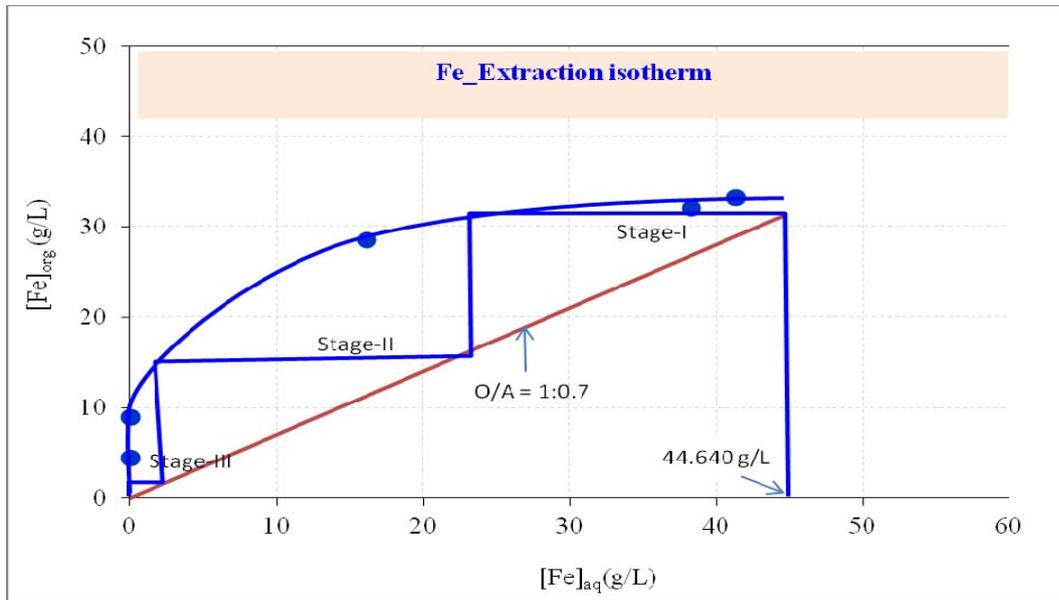


Figure 7: Fe extraction isotherm

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 from the preg strip solutions containing iron chloride or magnesium chloride respectively. PRO's hydrothermal hydrolysis process is more economical than pyrohydrolysis process as hydrothermal hydrolysis process runs at a much lower temperature.

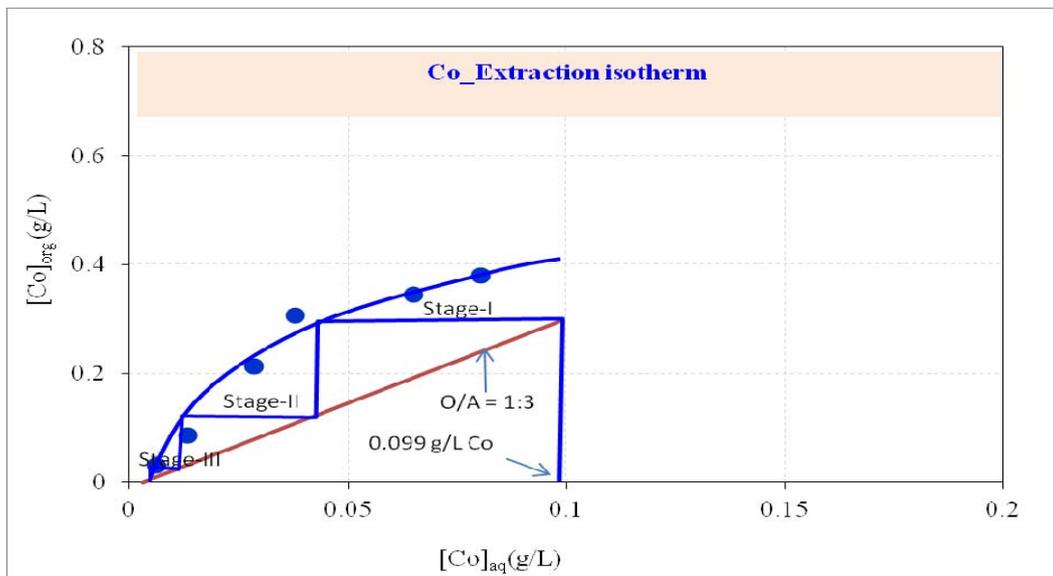


Figure 8: Co extraction isotherm

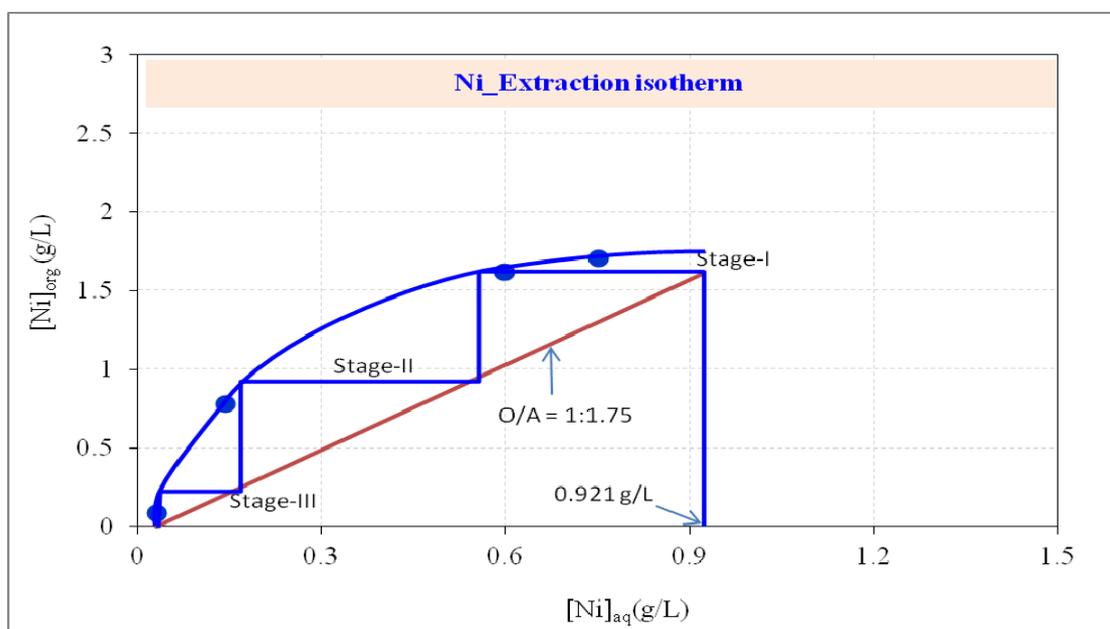


Figure 9: Ni extraction isotherm

Comparison of PRO Laterite Process with Commercial Processes

A comparison of PRO laterite process with commercial processes is shown in Table I.

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 from ore and low temperature process, however pyrohydrolysis needed for acid regeneration adds energy cost)
Reagents	Not recycled	Not recycled	Not recycled	Recycled
Residue amount	High volume	High volume	High volume	Low volume
Environmental	Slag disposal	Residue disposal containing ammonia	High volume residue disposal	Inert residue
Sulphur price	No effect	No effect	Very dependent	No effect
Fuel price	High effect	Medium effect	Lower effect	Medium effect
By-product credit	None	None	None	Fe ₂ O ₃ and MgO credit

CONCLUSION

Innovative processes has been developed for the recovery of gold from refractory ores and base metals from lateritic ores. These innovative processes use mixed chloride lixiviant (HCl+MgCl₂) to bring metals in solution. The presence of MgCl₂ in the lixiviant makes the lixiviant very aggressive, which results in high recoveries of metals. Additional advantage of using mixed chloride lixiviant is the opportunity to regenerate the hydrochloric acid by pyrohydrolysis, which can be recycled to leaching stage. For processing of lateritic ores, innovative solvent extraction steps are used to separate base metals successively from the pregnant leach solution (PLS) and generate high purity preg strip solutions of Fe, Ni and Co individually. The process can treat low grade ores as well as rejects from higher grade ores and is also suitable for slags generated from pyrometallurgical operations during the production of Ni, Cu and Co. The PRO process uses atmospheric leaching and therefore is more economical than HPAL process which uses autoclaves to generate high pressure required for leaching. Overall, the process flowsheet is efficient, environmentally friendly and economically attractive.

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