

APPLICATION OF MIXED CHLORIDE TECHNOLOGY FOR THE RECOVERY OF TiO₂ AND BASE METALS

V.I. Lakshmanan, R. Sridhar, and R. Roy*

Process Research Ortech Inc.
2350 Sheridan Park Drive
Mississauga, ON L5K 2T4

(*Corresponding author: rroy@processortech.com)

Increasingly attention is being paid to the efficiency of separation steps, as it leads to improved product recovery and environmental compliance. An understanding of aqueous chemistry is very important for this purpose. The paper will discuss the use of chloride technology to recover Ni, Co and TiO₂ from a variety of feed materials. The flowsheets developed are efficient and environmentally friendly.

INTRODUCTION

The development of flowsheets requires a clear understanding of ‘Solution Chemistry’ and its influence on the efficient removal of the desired elements and compounds. For innovative process flowsheet development, increasingly attention is being paid to the efficiency of separation steps, as it leads to improved product recovery and environmental compliance. The process flowsheet generally involves reactions in aqueous media. An understanding of aqueous chemistry is very important for this purpose. Effects of parameters such as pH, e.m.f., concentration, nucleation, co-precipitation, temperature, organic and ionic concentrations need to be considered for innovative process development.

Process Research ORTECH Inc. (PRO) has been at the forefront of technological development of chloride metallurgy. Chloride metallurgy is emerging as an alternative process for the production of base metals [1-10]. PRO has been developing process flowsheets based on a mixed chloride lixiviant consisting of HCl and MgCl₂. The HCl leaching system was chosen as it is possible to regenerate the acid by pyrohydrolysis. The mixed chloride system was chosen because the presence of MgCl₂ in the lixiviant enhances the activity of the hydrogen ion by orders of magnitude [11]. This makes the lixiviant very active as seen in Figure 1. PRO has applied its patented mixed chloride technology to develop flowsheets for the recovery of base metals from laterite [12-14], sulphide [15-17] and ilmenite ores [18-24], which will be described in the following sections.

BASE METAL RECOVERY FROM LATERITE ORES

Laterite ores can be classified as low iron, medium iron, and high iron. The low iron (<15 % Fe) ores, which are mostly saprolytic in nature, contain 1.7- 2.3% Ni and are treated by pyrometallurgical smelting processes to produce ferronickel or matte. More recently, the medium iron deposits (15-30 % Fe) are treated by mini blast furnaces in China to produce low grade ferronickel, nickeliferous iron or matte. High pressure leach using sulphuric acid has been considered the best option for high iron (> 35 % Fe) limonitic ores. However, with increasing world demand for sulphur due to requirements in the fertilizer industry in growing economies, these processes may not remain cost effective. A selective reduction – mixed chloride leach process developed by PRO can provide an alternative option.

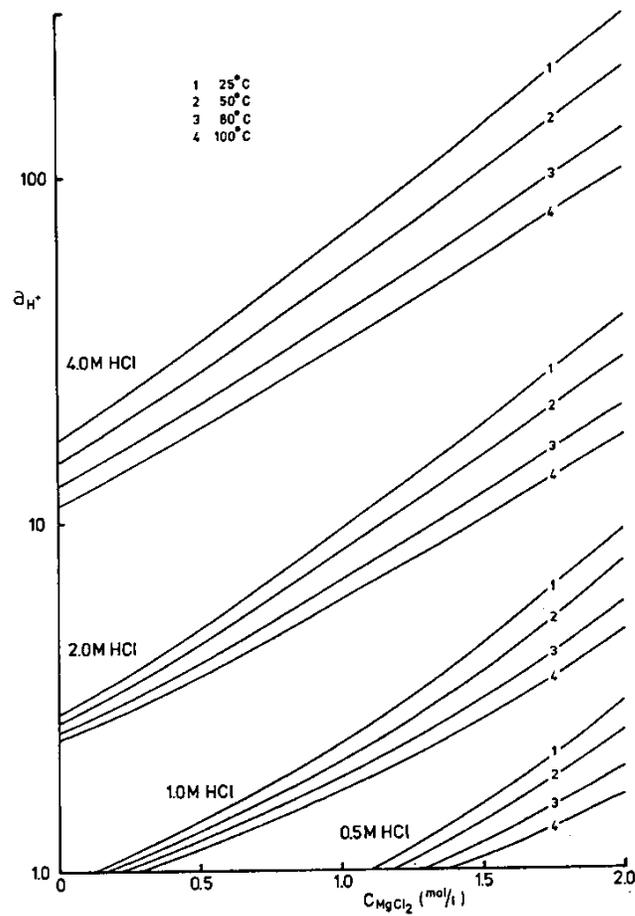


Figure 1 – Effect of MgCl_2 concentration on the activity of H^+ in HCl solutions; from [11]

PRO process is presented in Figure 2 and employs the following innovative steps:

1. Selective reduction of nickel in preference to the iron by reducing gases produced by combusting fuel with sub-stoichiometric air, followed by leaching in mixed chloride media requiring lower acid requirement than the atmospheric leaching processes developed at PRO earlier [14] with no reduction step. Efficient design of the selective reduction step will increase nickel and cobalt recovery to $\sim 95\%$ and lower the fuel requirement. The development of biomass based energy in the mining areas may lower the process costs. PRO is working on these initiatives now.
2. Recycle of the acid by pyrohydrolysis of the magnesium chloride produced in the process. High sustainability due to minimal effluent production because of recycling.

3. Production of a leach residue with excellent settling properties avoiding the problems encountered in solid/liquid separation in high pressure leach processes.
4. Production of a MgO by-product which could pay for the fuel required in the acid regeneration pyrohydrolysis step.

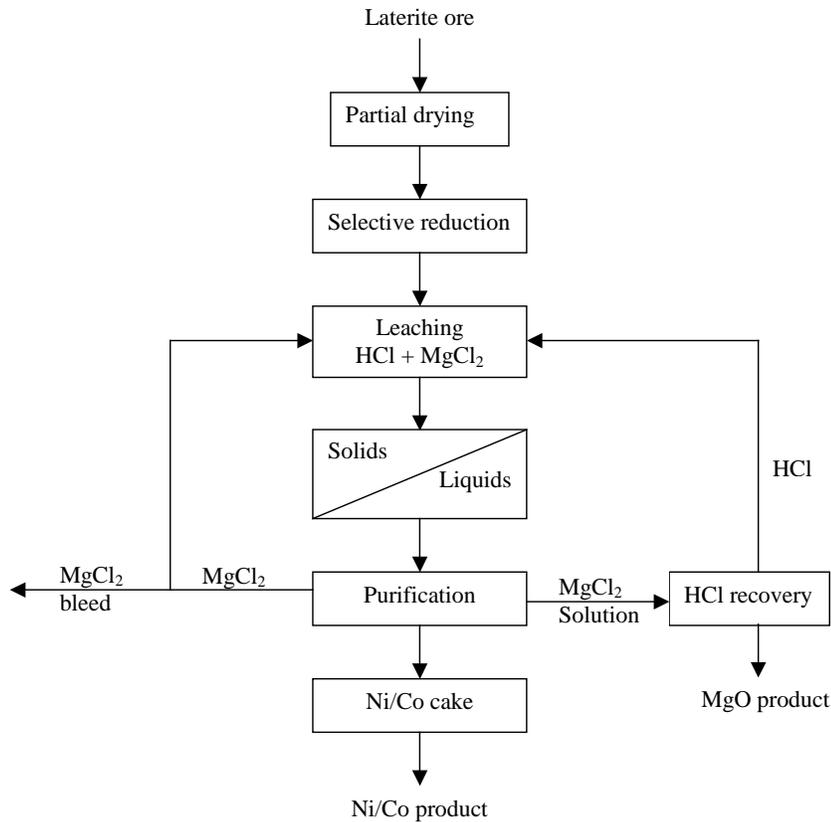


Figure 2– Process Research Ortech's flowsheet for treatment of laterite ores

Figure 3 shows the free energy of formation of oxides of nickel, cobalt and iron. It can be seen that due to the lower stability of the oxides of nickel and cobalt compared to that of iron it should be thermodynamically possible to reduce nickel and cobalt in preference to iron selectively. The selective reduction has to be carried out at an oxygen potential such that nickel and cobalt is in their reduced state but iron is in oxide state. The oxygen potential can be defined by the CO/CO₂ ratio in the gas stream used for reduction. This is because the CO/CO₂ ratio defines the oxygen potential according to:



The relationship between CO/CO₂ and the stability of the phases in the Ni-Fe-O system is shown in Figure 4. Ideally, the reduction should be carried out in region 1 in Figure 4. The figure indicates that the highest reduction potential is obtained when CO/CO₂ = 40/60. In this region the Ni will be as metal with iron as magnetite. This is a simplified analysis of the thermodynamics as in real practice the activities of nickel and iron in the metallic phase comes into play and hence 100% selectivity cannot be achieved in plant practice and some reduction of iron cannot be avoided, especially when high nickel reduction and recovery is desired.

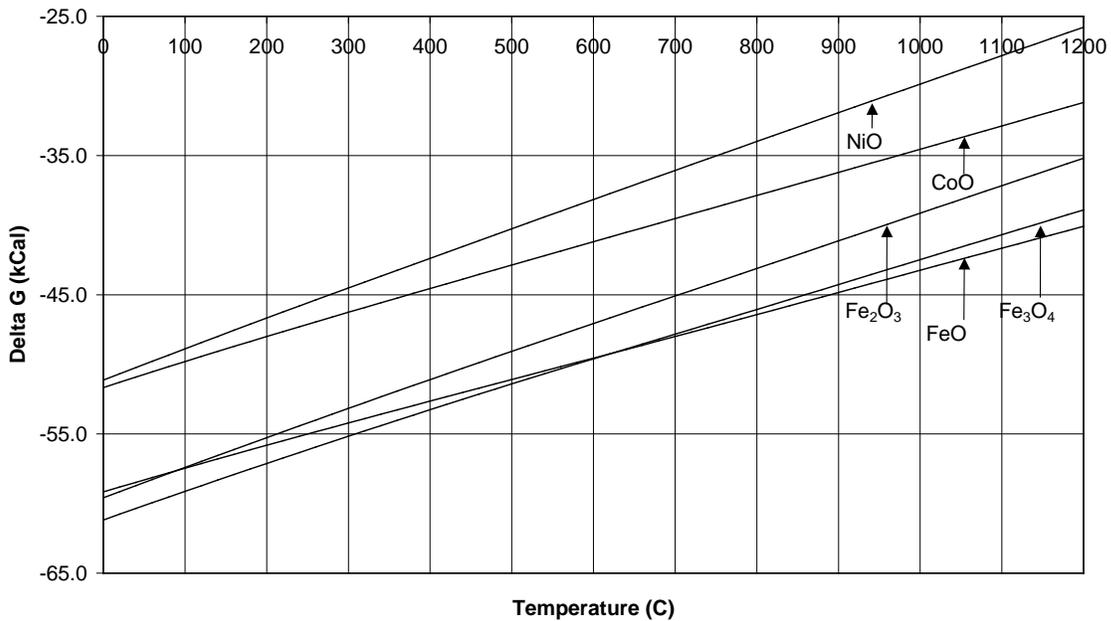


Figure 3 – Free energy of oxides [25]

The laterite ores always contain magnesium oxide, which will dissolve during the acid leach and will later be recovered as MgO during pyrohydrolysis. It is estimated that the value of the MgO could pay for the fuel used for the pyrohydrolysis in a typical limonite operation using this process. This is an added advantage of adopting a mixed chloride media system for leaching. Series of experiments carried out with HCl–MgCl₂ mixtures indicated that the optimum level of MgCl₂ is about 250 to 350 g/l in the lixiviant.

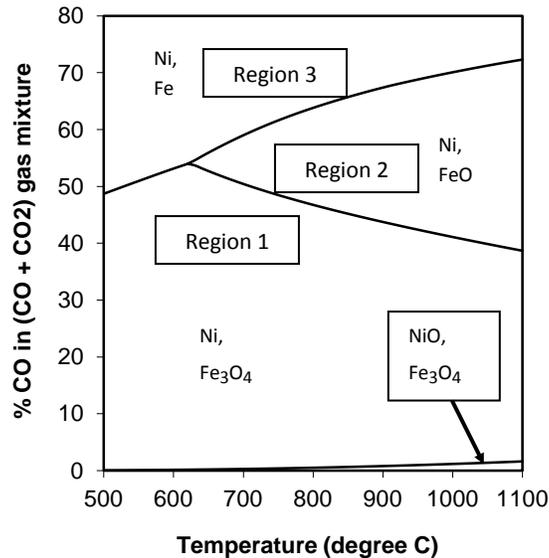


Figure 4 – Stability of metallic and oxide phases at different CO/CO₂ ratios

BASE METAL RECOVERY FROM SULPHIDE ORES

PRO has also developed a process for the recovery of base metals and PGMs from sulfide ores. This process has several advantages over the pyrometallurgical technologies used for base metals and PGM recovery from sulfide concentrates. The pyrometallurgical technologies are capital intensive and also suffer from scaling limitations. There are problems with SO₂ emission and PGM reports to the anode slime resulting in long delay in value recognition.

The proposed flow sheet is shown in Figure 5. The salient features include leaching of the sulfide concentrates at 90-100 °C in recycled HCl/MgCl₂ mixture with an oxidant. In a first stage leach, base metals are recovered and elemental sulfur is liberated from hydrogen sulfide formed during this leaching stage. Base metals are recovered from leach solution by proven hydrometallurgical methods. Sulfur is removed as H₂S and is converted to elemental sulfur in a Claus reactor. Other steps include solvent extraction of copper, removal of impurities such as Fe, As, Sb and Bi in two or three stages using lime and recycled magnesia from the pyrohydrolysis step, removal of Ni-Co as hydroxides and regeneration of the leachant by pyrohydrolysis. Precious metals can be recovered during second stage leach using proven separation

technologies, or alternatively, leach residue containing PGMs can be sold as is. The flowsheet has been developed based on the fundamental understanding of ore mineralogy, aqueous chloride chemistry and a deeper understanding of chemical processing methods.

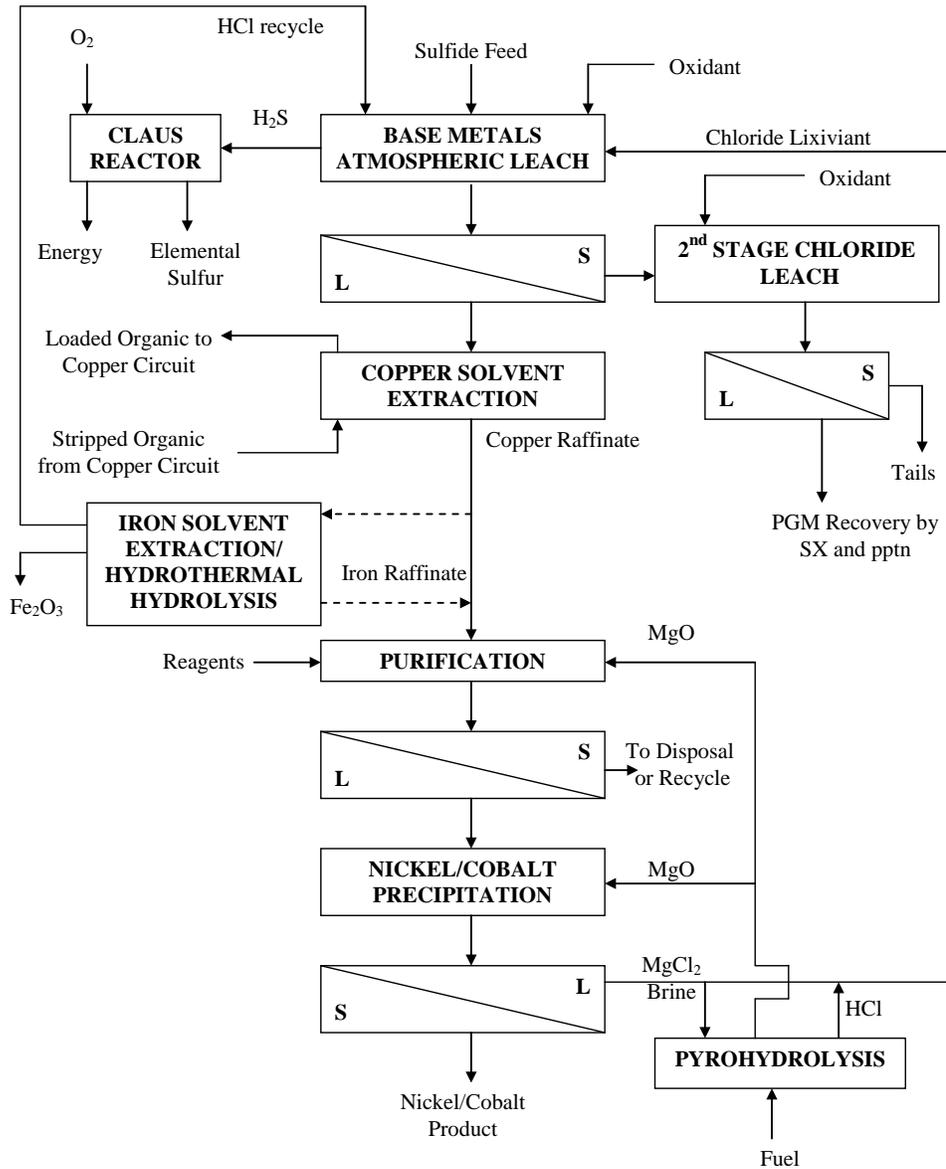


Figure 5: The flowsheet developed for the treatment of sulfide ores

The use of high strength chloride brine, in particular magnesium chloride, has certain advantages in leaching, e.g. high H^+ activity and low water activity. Some advantages of this process are: (a) elimination of harmful SO_2 emissions; (b) recovery of sulfide sulfur as elemental

sulfur, which can be used as a source of energy; (c) environmental friendliness due to recycling of the chloride lixiviant, thereby eliminating effluent treatment steps; and (d) use of excess energy from the Claus reactor for the pyrohydrolysis step.

Extraction of 98 % Ni, 98 % Fe, 96 % Co and 98 % Cu was achieved by using Cl_2 as an oxidant. It was seen that the sulfate level in the leach solution was less than 0.023 g/L, which amounted to more than 99% of sulfide sulfur being removed as hydrogen sulfide.

RECOVERY OF TITANIUM DIOXIDE

TiO_2 is currently produced using either a chloride process or a sulphate process from either ilmenite, rutile or titanium slag. Chloride process uses reaction of chlorine with titanium in the feed material to form TiCl_4 , which is later reacted with oxygen to form TiO_2 . The sulphate process uses leaching with sulfuric acid to bring titanium in solution. Hydrated titanium dioxide is precipitated from the solution and calcined to make titanium dioxide. The main application of TiO_2 is for the pigment in paint industry. The technical specifications for making pigment grade TiO_2 are very strict, and require extreme control of other transition metal elements, which can make the color of pigment off-white and unacceptable. The process developed by Process Research Ortech will be a third processing route for making pigment grade TiO_2 . The process is capable of treating low grade ores and ores containing Mg, V or Cr economically, and may lead to the processing of ilmenite ore bodies previously considered not viable.

PRO proprietary process consists of leaching ilmenite ore/concentrate in a HCl-MgCl_2 lixiviant thereby bringing Ti, Fe, V and other metals in solution. After solid-liquid separation, pregnant liquor is subjected to Stage 1 solvent extraction for iron removal. This results in Fe-rich preg strip, which can be subjected to pyrohydrolysis for the production of iron oxide and regeneration of acid for recycle and Fe-deficient raffinate. This raffinate is subjected to Stage 2 solvent extraction for titanium extraction. Ti-rich preg strip from Stage 2 solvent extraction is subjected to thermal hydrolysis for precipitation of TiO_2 . Ti-deficient Raffinate from Stage 2 solvent extraction is subjected to Stage 3 solvent extraction for vanadium extraction. V-rich preg strip can be further processed to make V_2O_5 and the final raffinate is recycled to leaching circuit after adjusting the acid concentration. The process flowsheet is shown in Figure 6. The process flowsheet has been developed based on the fundamental understanding of ore mineralogy,

aqueous chloride chemistry and solvent extraction separation steps. Organic extractants were chosen based on their ability to selectively extract iron, titanium and vanadium from aqueous chloride solutions to obtain high quality end products.

Solvent extraction process developed by PRO is extremely selective and results in highly pure Ti-rich strip liquor with ppm level impurities of other elements. Hydrated TiO₂ is produced by thermal precipitation from the Ti-rich strip liquor. Rutile TiO₂ is produced after drying and calcinations of the precipitate. Precipitation and calcinations conditions can be controlled to produce anatase TiO₂ as well. Process conditions can be controlled to produce nano-sized TiO₂ with particle size of 20-40 nm as well as particles in the range of 250-300 nm for application as pigment. PRO has produced high purity TiO₂ powder that meets the specifications of pigment users.

CONCLUSION

Chloride metallurgy is emerging as an alternative process for the production of base metals. PRO has applied its patented mixed chloride technology to develop flowsheets for the recovery of base metals from laterite, sulphide and ilmenite ores.

PRO process for recovery of base metals from laterite ores consists of selective reduction followed by leaching in mixed chloride media. Efficient design of the selective reduction step will increase nickel and cobalt recovery to ~ 95% and lower the fuel requirement.

Mixed chloride technology was also applied for the extraction of base metals from sulfide ores. Extraction of 98 % Ni, 98 % Fe, 96 % Co and 98 % Cu was achieved by using Cl₂ as an oxidant. Precious metals can be recovered during second stage leach using proven separation technologies, or alternatively, leach residue containing PGMs can be sold as is.

In another major application of mixed chloride technology currently being tested at pilot scale, PRO has developed a unique hydrometallurgical technology for the extraction of high purity titanium dioxide from ilmenite ores. The process is capable of treating low grade ores and ores containing Mg, V or Cr economically, and may lead to the processing of ilmenite ore bodies previously considered not viable.

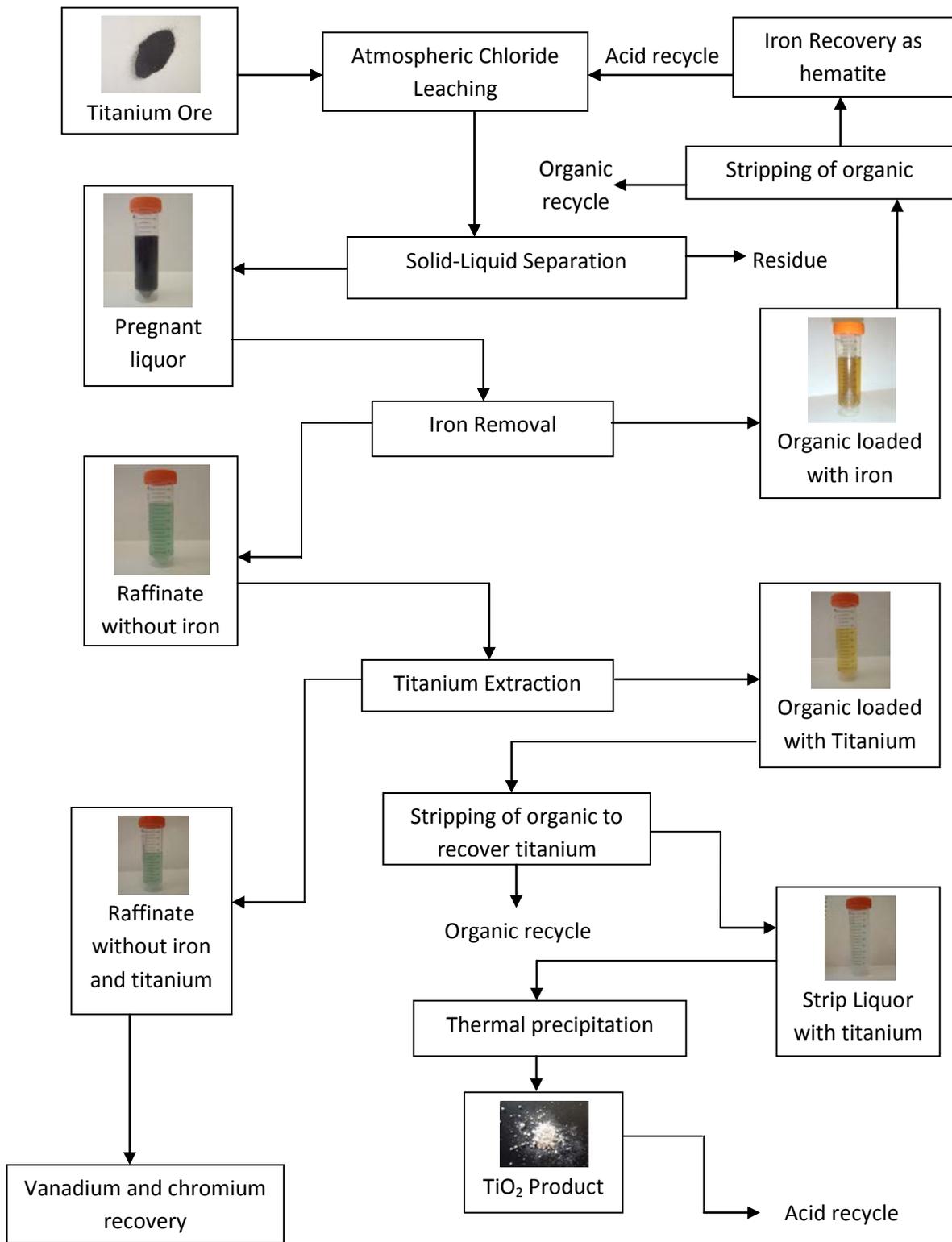


Figure 6 - The flowsheet developed for the production of TiO₂

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