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RECOVERY OF GOLD AND TITANIUM DIOXIDE

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ABSTRACT

The growing concerns on process efficiency, escalating operating and capital costs along with environmental and social concerns of using conventional technology for extracting gold and titanium dioxide demand an in-depth understanding of the fundamentals and a broader understanding of the various process steps involved. This will allow development of efficient process flowsheet for product recovery and compliance with regulatory guidelines. This paper will discuss our recent developments in mineral processing and hydrometallurgical technologies to recover gold and titanium dioxide from a wide range of feed materials including ores, concentrates and tailings.

Keywords: Mineral Processing, Hydrometallurgical Technologies, Gold, Titanium Dioxide

INTRODUCTION

The need for mining and metallurgical industries to be sustainable requires them to be innovative in their applications of existing technologies, avail of opportunities to apply proven applicable technologies from other industries and evaluate the role of emerging technologies in their process application. The growing concerns on process efficiency, escalating operating and capital costs along with environmental and social concerns of using conventional technology demand an in-depth understanding of the fundamentals and a broader understanding of the various process steps involved. This will allow development of efficient process flowsheet for product recovery and compliance with regulatory guidelines. The process flowsheet generally involves reactions in both aqueous and non-aqueous media. Development of any flowsheet requires a clear understanding of 'Solution Chemistry' and its influence on the efficient removal of the desired elements and compounds. Effects of parameters such as pH, oxidation potential, 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 process technological development. Having developed a proprietary atmospheric chloride leach process technology for the treatment of sulfide ores, PRO further developed the technology for the production of high purity titanium dioxide from ilmenite ore (Lakshmanan et al. 2002a, Lakshmanan et al. 2002b, Lakshmanan et al. 2004, Lakshmanan et al. 2010a,

Lakshmanan et al. 2010b). Titanium dioxide is used in paints, plastics, rubber, paper, inks, textiles and a number of other miscellaneous applications. The demand for the pigment grade TiO_2 has been growing at 3.0% on an average and this invites for the development of innovative and cost effective processes. The current commercially available processes are not designed to recycle the reagents and thereby discharge the effluents into the environment causing an environmental concern. Currently nanosize TiO_2 is being investigated for application in cosmetics industry. Inorganic sunscreens mainly use TiO_2 or ZnO particles, which reflect and scatter ultra-violet light. TiO_2 nanomaterial is also finding application in smart construction materials and coatings as photo-catalytic converter. Nano TiO_2 can catalyze to dissociate NO_x gases and other automotive emissions, thereby reducing the smog in urban centers. After the construction material is exposed to sunlight or ultra-violet light, TiO_2 is photo-activated and degrades the pollutants. Dye-sensitized TiO_2 is being investigated for production of clean energy. PRO is also working with Barrick to develop an economic flowsheet for double refractory gold ores.

RECOVERY OF GOLD

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 (Scheiner, Lindstrom and Henrie, 1971, Guay, and Peterson, 1973, Guay, 1980, and Jackson, 1982)

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. 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 1 (LaBrooy, Linge and Walker, 1994).

Refractory Gold Ores

If gold extraction by conventional cyanidation process is less than 80% even after fine grinding, then gold ore is considered refractory (Guay, 1981).

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

- 1) sulfides, silicates, tellurides, antimonides and selenides
- 2) carbonaceous matter (Iglesias and Carranza, 1994).

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 2 (Iglesias and Carranza, 1994).

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 (Nyavor and Egiebor, 1992). 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. Barrick and Process Research Ortech Inc. are working together to address some of the challenges associated with double refractory gold 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.

RECOVERY OF TITANIUM DIOXIDE

TiO₂ 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 TiCl₄, which is later reacted with oxygen to form TiO₂. 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 TiO₂ is for the pigment in paint industry. The technical specifications for making pigment grade TiO₂ 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 Process for TiO_2 Production

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 3. 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.

Bench Scale Testwork

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 the recovery of titanium. Laboratory-scale leaching experiments were carried out using a solution of hydrochloric acid and magnesium chloride as a lixiviant under atmospheric pressure at 70-73 °C for 4 hours. The extraction of titanium as high as 96.9% was achieved for a solid loading of 8.8 % and HCl level 1.4 times of stoichiometric amount and MgCl_2 concentration at 300 g/L. At stoichiometric concentrations of hydrochloric acid, magnesium chloride appeared to have significant effects on extraction of titanium. The effects of magnesium chloride in increasing extraction of titanium were most pronounced at concentrations of hydrochloric acid that were greater (1.2x and 1.4x) than the stoichiometric amount required for extraction of titanium and iron. With an increase in

magnesium chloride concentration, titanium extraction reached maxima of 79% and 96.9% at HCl levels of 1.2 times and 1.4 times the stoichiometric amount, respectively. At the highest concentrations of $MgCl_2$ that were tested, the $MgCl_2$ concentrations were near the solubility limits in the solutions used. Thus, the results indicate that there is an optimal range of concentrations of both hydrochloric acid and magnesium chloride for the extraction of titanium and iron from the ore into solution. At hydrochloric acid level of 1.4 times the stoichiometric amount, the optimal magnesium chloride concentration was 300 g/L.

In a series of comparative experiments, to illustrate the effect of concentration of hydrochloric acid in the absence of $MgCl_2$, a series of leaching experiments were conducted on another ilmenite ore with mesh size of -100 that contained 26.8 wt % of Ti, 35.8 wt % of Fe, 0.03 wt % of Cr and 0.12 wt % of V. The results show low titanium extraction of less than 20% from the tested ilmenite ore in the absence of magnesium chloride, even though concentration of hydrochloric acid was as high as 8 N and amount as high as 3.83 times the stoichiometric amount for a solids loading of 5 wt %. It is obvious that the use of a mixed chloride lixiviant of hydrochloric acid and magnesium chloride offers advantages in extracting titanium from ilmenite ore in terms of high recovery. It also permits recycling of hydrochloric acid, magnesium chloride and magnesium oxide in the process. The use of magnesium chloride allows lowering of hydrochloric acid concentration to no more than 20% (mass ratio). This permits use of azeotropic distillation by pyrohydrolysis of recycle solutions without the addition of substantial amounts of fresh hydrochloric acid, thereby avoiding disposal of excess hydrochloric acid, which is an environmental problem. In addition, the use of lower concentration of hydrochloric acid will tend to result in lower extraction of impurities or gangue from the ore, and thus decrease the burden downstream for the removal of impurities.

The solution purification was carried out using solvent extraction separation steps and consisted of two different stages of extraction in a counter current mode. In the first stage iron removal was carried out and in the second stage titanium was extracted. The strip solution obtained from the second stage solvent extraction was used to precipitate titanium dioxide. The barren solution was used for reagent recovery and the regenerated leach

liquor was recycled. Nano-sized rutile TiO_2 powder was produced by controlling thermal precipitation conditions.

Pilot Scale Testwork

Titanium extraction pilot plant run was carried out to obtain the design criteria for capital and operating cost estimates, samples for market evaluation and data for environmental needs. The pilot plant run was performed on an ilmenite feed material from Quebec, Canada, assaying 14.4 % Ti, 41.9 % Fe, 0.06 % Cr and 0.12 % V.

The pilot plant included unit operations for leaching, solid-liquid separation, solution purification and titanium extraction by SX and thermal precipitation. The three leach tanks in the leach circuit were set up in a cascading fashion to allow the slurry to flow co-currently from one tank to the next. The slurry from the third tank was discharged into a barrel and then filtered in a 12-in. plate and frame filter press. The pregnant liquor obtained after filtration was used for SX. During leaching, the acid addition was maintained at 1600 kg/t and residence time was maintained at 4 hours in the leach circuit.

SX and thermal precipitation circuit was run continuously for 100 cycles under steady state conditions. Tri Butyl Phosphate (TBP) was used with moderator (Exal10) and diluent (CF231) in the ratio of 15/15/70 % by volume to extract Fe^{+3} impurities from the leach liquor. Alamine 336 was combined with moderator (Exal10) and diluent (CF231) in the composition of 15/15/70 % by volume to remove Fe^{+2} and Fe^{+3} from TBP raffinate. Cyanex 923 was combined with moderator (Exal10) and diluent (CF231) in the ratio of 20/15/65 to extract titanium. The titanium concentration in the final strip liquor was analyzed to be ~17 g/L, which was used for thermal precipitation of TiO_2 .

TiO₂ Product Quality

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 TiO_2 is produced by thermal precipitation from the Ti-rich strip liquor. Rutile TiO_2 is produced after drying and calcinations of the precipitate. Figure 4 shows the XRD pattern of the rutile TiO_2 produced. The distinct sharp and narrow peaks indicate a crystal structure of rutile formed at ambient temperature. Figure 5 shows the morphology of the nano-sized TiO_2 with

particle size of 20-40 nm. The purity of the TiO_2 products obtained is shown in Table 1. Such materials can find application in knowledge-based industries such as production of catalysts for energy application and photolytic decomposition of smog producing toxic emissions from automobiles.

CONCLUSIONS

Gold ores can be divided into non-refractory and refractory ores. Non-refractory gold ores contain free gold particles in a relatively inert matrix. Nearly 95% of the gold from non-refractory gold ores can be recovered by gravity concentration and/or direct cyanidation. The treatment of refractory gold ores is more complex than non-refractory gold ores. 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, which is followed by neutralization and cyanidation. Double refractory gold ores contain both sulfides and carbonaceous matter. The processing of double refractory gold ores presents a major challenge to gold producers.

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 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.

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FIGURE CAPTIONS

Fig 1 - Processing of non-refractory gold ores.

Fig 2 - Processing of refractory gold ores

Fig 3 - The flowsheet developed for the production of TiO_2

Fig 4 - X-ray diffraction pattern of TiO_2 showing 100 % rutile crystal structure

Fig 5 - Morphology of TiO_2 sample

TABLE CAPTIONS

Table 1 - Composition of TiO_2 products made in the test (wt %)

FIGURES

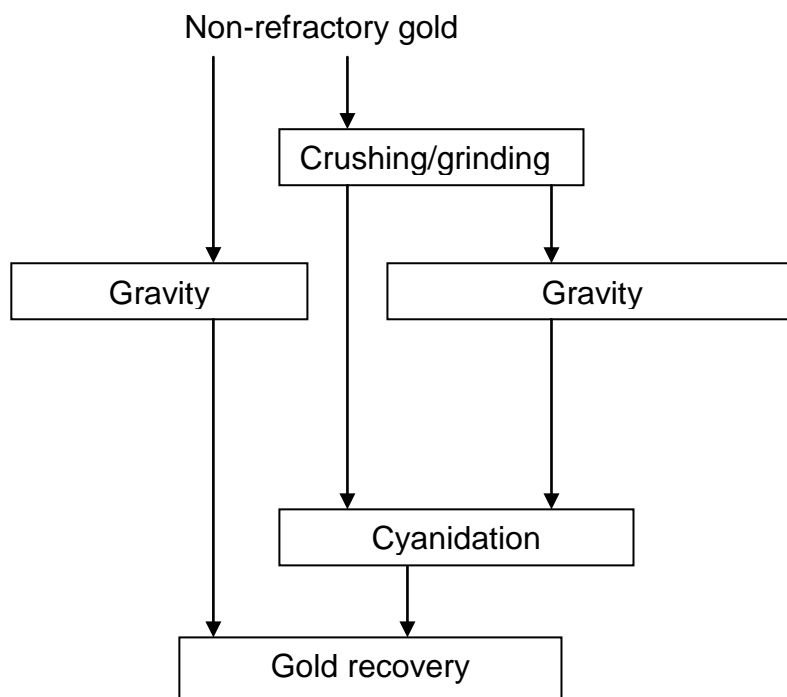


Fig 1 - Processing of non-refractory gold ores.

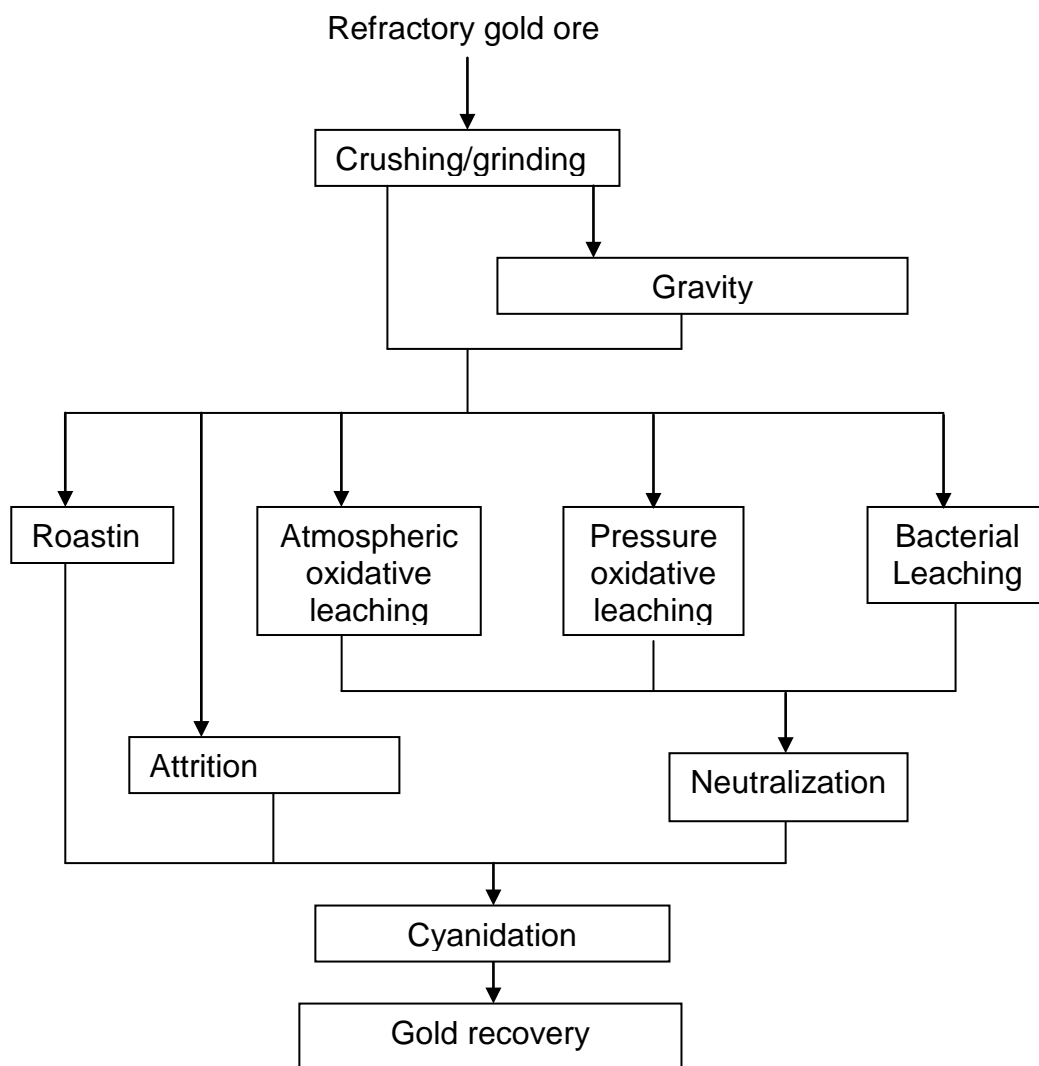


Fig 2 - Processing of refractory gold ores

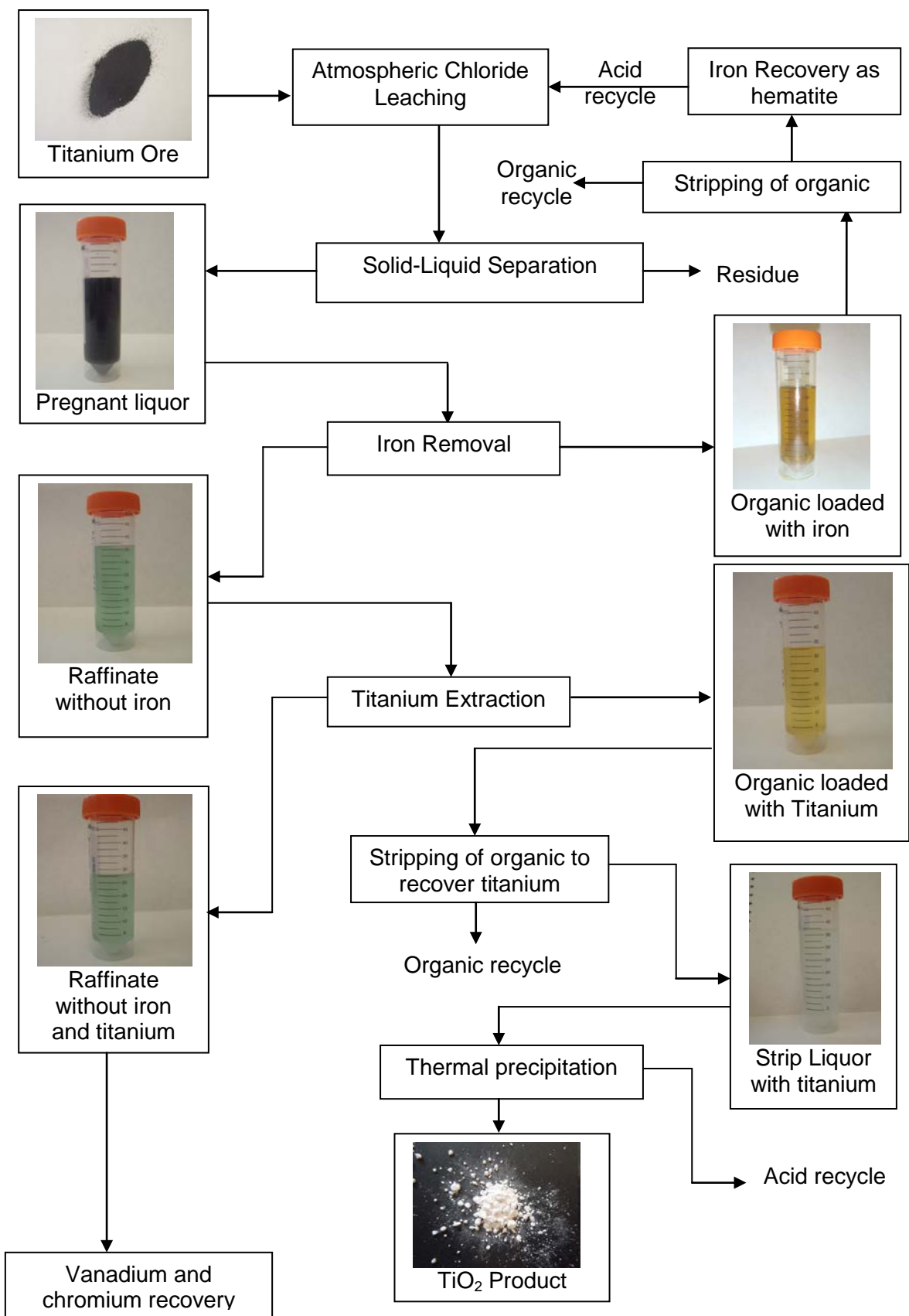


Figure 3 - The flowsheet developed for the production of TiO_2

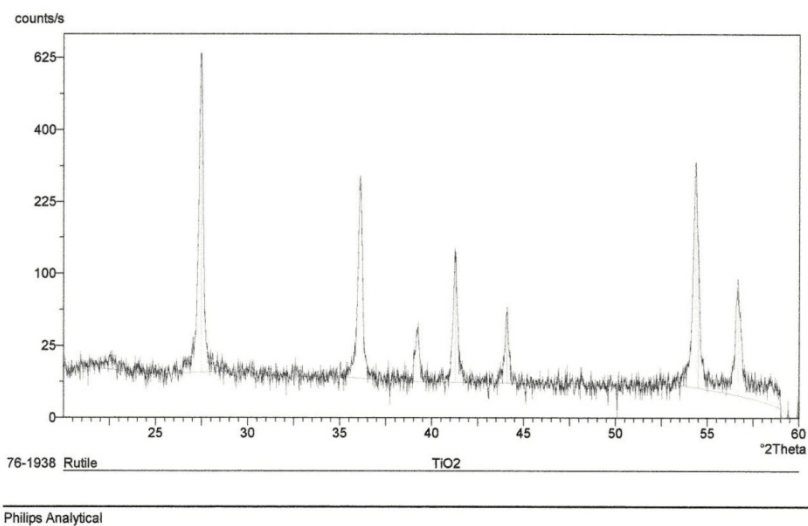


Figure 4: X-ray diffraction pattern of TiO₂ showing 100 % rutile crystal structure

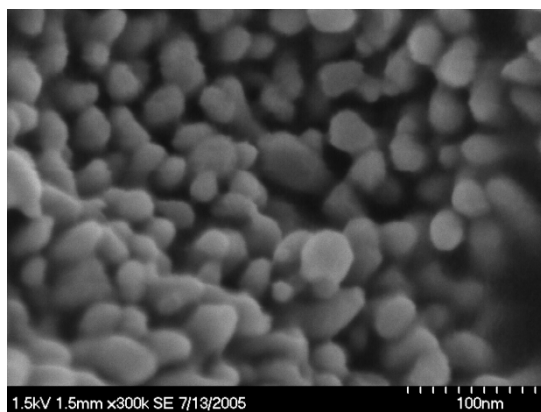


Figure 5: Morphology of TiO₂ sample

TABLES

Table 1 - Composition of TiO₂ products made in the test (wt %)

Element	Al₂O₃	B	Ba	Be	CaO	Cd	Co	Cr	Cu	Fe₂O₃	MgO
%	0.32	<0.01	<0.01	<0.01	0.16	<0.01	<0.01	<0.01	<0.01	0.96	0.33
Element	Mn	Mo	P₂O₅	K₂O	Na₂O	Ni	Pb	SiO₂	TiO₂	V	Zn
%	<0.01	<0.01	-	-	0.13	<0.01	<0.01	3.74	>94.35	<0.01	<0.01