

# A literature review of titanium metallurgical processes

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## ABSTRACT

Various titanium metallurgical processes have been reviewed and compared for titanium dioxide and titanium metal, mainly focusing on the future development of hydrometallurgical processes. It is recognised that ilmenite is becoming increasingly important due to the rapid depletion of natural rutile. Many processes are commercially used or proposed to upgrade ilmenite to synthetic rutile. Most of these processes involve a combination of pyrometallurgy and hydrometallurgy and are generally expensive.

The commercialised thermo-chemical chloride processes such as Kroll and Hunter processes are batch operations and need higher grade natural rutile or upgraded synthetic rutile and slag as the feed and the involvement of cost sensitive chlorination and thermo steps. Many improvements for the thermo-chemical processes have been made, but they hold little potential for significant cost reductions beyond current technology. The development of the electro-chemical processes for direct reduction of  $\text{TiO}_2$  and electro-slag as feed material and *in-situ* electrolysis has achieved some success. However, some challenging issues such as redox cycling, feeding, kinetics, control heat balance have to be resolved before scaling-up to commercial applications.

Direct hydrometallurgical leach processes are advantageous in processing abundant ilmenite ores, low energy consumption and produce sufficiently high quality of pigment grade  $\text{TiO}_2$  products for a wide range of applications and major demand. Novel BHP Billiton sulphate processes have been developed to improve leaching strategies, separation of metals by solvent extraction, reduced wastes and recycling acids, and very promising for commercial applications in future. Direct chloride leaching processes have been investigated intensively, featuring purification by solvent extraction and reclaiming HCl by hydrolysis or pyrohydrolysis. Caustic leach with high selectivity and titanium dioxide nano-technology has also been developed. Further development of direct leaching ilmenite coupled with solvent extraction for titanium pigment and metal production, is recommended.

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## 1. Introduction

### 1.1. Titanium occurrence and resources

Titanium is the ninth most abundant element in the earth's crust and the fourth most abundant element (Knittel 1983; Minkler and Baroch 1981). Its elemental abundance is about five times less than iron and 100 times greater than copper, yet for structural applications titanium's annual use is 200 times less than copper and 2000 times less than iron. Its commercial production commenced in 1948 driven by the demand from the aircraft industry. World titanium sponge metal production reached 166,000 metric tons in 2008 (Gambogi, 2009a, 2010). The main titanium-containing minerals are rutile, ilmenite and leucoxene (Table 1). Ilmenite supplies about 91% of the world's demand for titanium minerals and the world's ilmenite production reached 5.19 million metric tons in 2009 (Gambogi, 2009b, 2010).

In the 1950s, titanium deposits containing 30% rutile were common. However, by 1981, the content had decreased to less than 1% rutile (Minkler and Baroch 1981). Ilmenite, not only found in beach sands, but also in hard rock deposits, has quite extensive reserves: about 1300 million tons. There is no doubt that ilmenite as the most important titanium resource will continue to dominate the titanium industry in the future.

Ilmenite ( $\text{FeO} \cdot \text{TiO}_2$  or  $\text{TiFeO}_3$ ) contains 40–65%  $\text{TiO}_2$ , depending on its geological history. Leucoxene ( $\text{Fe}_2\text{O}_3 \cdot n\text{TiO}_2$ ) is a natural alteration product of ilmenite, typically containing more than 65%  $\text{TiO}_2$ . Table 1 lists the most common titanium minerals and their chemical compositions (Barksdale 1966; Rhee and Sohn 1990; Whitehead 1983). Rutile contains about 95%  $\text{TiO}_2$  and is the most titanium-rich mineral. Its deposits are often found in coastal areas such as beach sands, and are the simplest to mine and concentrate in a form adaptable for metal production.

### 1.2. Titanium products, usages and process overview

The most widely used titanium product is titanium dioxide ( $\text{TiO}_2$ ), being as pigment, as filler in paper, plastics and rubber industries and

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**Table 1**  
Titanium minerals and their chemical compositions.

Mineral	Composition	TiO <sub>2</sub> content (%)
Rutile	TiO <sub>2</sub> (tetragonal, twinned)	~95%
Anatase	TiO <sub>2</sub> (tetragonal, near octahedral)	~95%
Brookite	TiO <sub>2</sub> (orthorhombic)	~95%
Ilmenite	FeO·TiO <sub>2</sub>	40–65%
Leucoxene	Fe <sub>2</sub> O <sub>3</sub> ·nTiO <sub>2</sub>	>65%
Arizonite	Fe <sub>2</sub> O <sub>3</sub> ·nTiO <sub>2</sub> ·mH <sub>2</sub> O	—
Perovskite	CaTiO <sub>3</sub>	—
Geikielite	MgTiO <sub>3</sub>	—
Titanite or sphene	CaTiSiO <sub>5</sub>	—
Titaniferous magnetite	(Fe·Ti) <sub>2</sub> O <sub>3</sub>	—

as flux in glass manufacture. Only about 6% is used to produce metallic titanium (Rosebaum 1982). The major sources of TiO<sub>2</sub> are from:

- Natural rutile. After a series of concentration of beach sands through gravity concentration, electrostatic separation to remove non-conducting zircon materials and magnetic separation to separate magnetic ilmenite, the rutile concentrate containing about 95% TiO<sub>2</sub> is used as TiO<sub>2</sub> raw material directly (Kahn, 1984).
- Synthetic rutile. There are a few processes to remove the iron from ilmenite to produce synthetic rutile which typically contains about 92% TiO<sub>2</sub>.
- High titanium slag. Ilmenite is smelted in an electric arc furnace to produce pig iron and high titanium slag which typically contains about 85–90% TiO<sub>2</sub>.

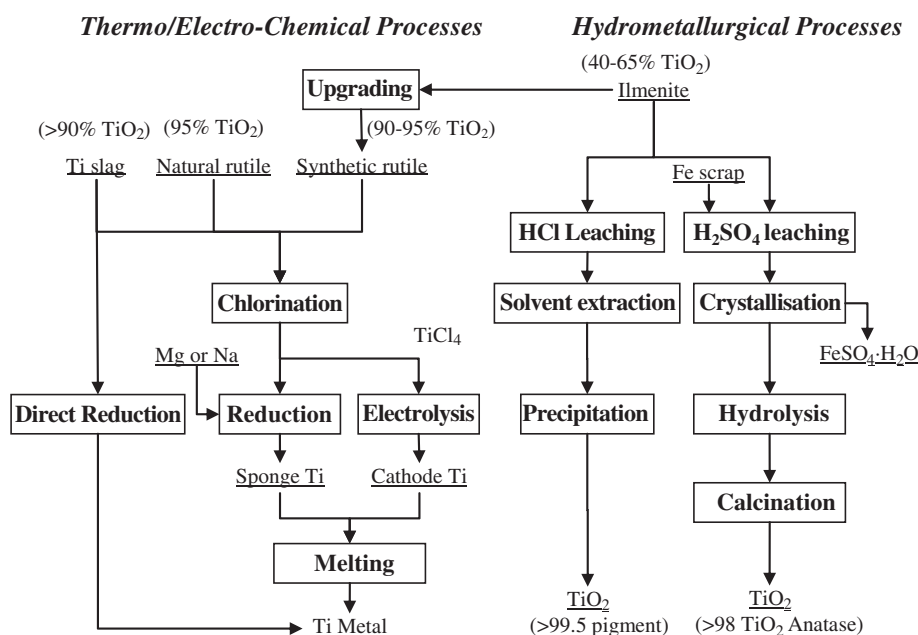
The biggest consumer of TiO<sub>2</sub> is the pigment industry. Unusual optical properties appear when the average particle size of TiO<sub>2</sub> is reduced to <100 nm, including high transparency to visible light and high UV absorption (Ellsworth et al. 2000). Nano-particles of TiO<sub>2</sub> also cause some components of visible light to be reflected and refracted differentially, leading to the phenomenon of iridescence. Nano-particles of TiO<sub>2</sub> have found applications in cosmetics, porcelains and ceramics industries as coating material and additives. Nano-particles of titanium oxide have received great attention recently for their potential applications in catalysis and as photo-electrochemical material. The

high photo-catalytic activity of titanium oxide by irradiation of visible light has been rapidly developed in recent years (Sakatani et al. 2002; Sakatani and Koike, 2003, 2004).

The processes for production of pigment grade TiO<sub>2</sub> and titanium metal are schematically presented in Fig. 1. There are two processes to manufacture titanium pigment: the sulphate process and the chloride process. The two processes differ in both their chemistry and raw material requirements (Hamor 1986). Because the chloride process has some advantages over the traditional sulphate process in cost and waste management, it has dominated the pigment industry in recent times. However, unlike the sulphate process, in which low-grade titanium raw material is acceptable, the chloride process needs a high grade of rutile (Rosebaum, 1982). The growing titanium metal industry also relies on high grade rutile. All these make the upgrading of ilmenite to synthetic rutile more and more important. However, the upgrading processes are generally expensive due to the involvement of multi steps of energy sensitive thermo reductive conversions and leaching to remove iron impurities.

Titanium metal is commercially produced by thermo chemical reduction processes using TiCl<sub>4</sub> as feed material. The low efficiency and high energy consumption in the batch operations make the thermo chemical processes rather expensive. Electro chemical reduction and direct reduction process for TiO<sub>2</sub> in molten CaCl<sub>2</sub> to produce pure titanium metal and its alloy have been developed in recent years as a potential alternative to the conventional commercial processes (Chen et al., 2000, 2001; Fray, 2001; Ono and Suzuki 2002; Suzuki 2007; Suzuki et al. 2003). However, difficulties in eliminating redox cycling and in handling very reactive dendritic products.

In the next decade, global demand growth for TiO<sub>2</sub> is expected to continue to increase at an average rate of about 3% annually (Gambogi, 2009a, 2009b, 2010). Growth higher than the average is expected to occur in the Asia region. China in particular is expected to lead world growth in production and consumption. However, the proliferation of small TiO<sub>2</sub> pigment plants using the sulphate-route in China was expected to recede as environmental concerns rise. TiO<sub>2</sub> production capacity in China is expected to double, reaching 1 Mt/yr by the end of the decade. In the next several years, prices for TiO<sub>2</sub> pigment are expected to rise because of increasing costs for chlorine, coke, caustic soda, and energy. Growth in aerospace, defence, and industrial uses will



**Fig. 1.** A schematic of processes for the production of Ti metal and pigment TiO<sub>2</sub>.

strongly influence the demand for titanium metal for the foreseeable future. Based on the announced capacity expansion plans, by 2015, world-wide capacities would be expected to reach 350,000 t/yr (Gambogi, 2009a, 2009b, 2010).

In recent years, direct hydrochloric leaching and solvent extraction (SX) hydrometallurgical processes have been developed to produce pigment grade  $\text{TiO}_2$  (>99.5%) and titanium metal through conventional fused electrolysis (Duyvesteyn et al., 2001a, 2002; Lakshmanan et al., 2001, 2002, 2004a, 2004b, 2005a, 2005b; Lakshmanan and Sridhar 2002; Puvvada et al. 2003; Verhulst et al., 2002, 2003). Improved sulphate processes and caustic leach processes have also been developed. Hydrometallurgical processes will become more and more important due to its low energy requirement compared to the conventional thermo and electro chemical processes.

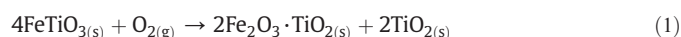
This review briefly summarises the conventional thermo and electro chemical processes and highlights the ilmenite processing and the production of titanium dioxide and metal through hydrometallurgical routes. Various processes for titanium production are compared in terms of their technical feasibility, economics and product quality, aiming at identifying promising processes and directions in future development for fully hydrometallurgical processes.

## 2. Upgrading ilmenite to synthetic rutile

There are a number of commercialised or proposed processes to produce synthetic rutile or high grade titanium slag from ilmenite as feed for the chloride process. These processes involve a combination of thermal oxidation and reduction by roasting, leaching and physical separation steps. Iron is converted to soluble ferrous or elemental forms by reduction at high temperatures followed by acid leaching to obtain synthetic rutile ( $\text{TiO}_2$ ) products. The process features are summarised in Table 2 and discussed subsequently.

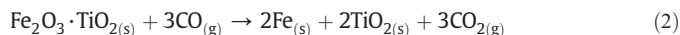
An industrial process for upgrading ilmenite to synthetic rutile is typically represented by the Becher process (Bracanin et al. 1980; Cassidy et al., 1986; Farrow et al. 1987; Hoecker, 1994; Reaveley 1980). The ilmenite contains 40–65% titanium as  $\text{TiO}_2$ , with the rest being iron oxide. The Becher process removes the iron oxide, leaving a residue of synthetic rutile, which contains more than 90%  $\text{TiO}_2$ . A schematic flowsheet comprising four major steps: oxidation, reduction, aeration and acid leach is shown in Fig. 2.

Oxidation involves heating the ilmenite in a rotary kiln with air to convert the iron in ilmenite to iron oxides:



This allows for the use of a wide range of ilmenite materials with various Fe(II) and Fe(III) forms for subsequent step.

Reduction is performed in a rotary kiln with pseudobrookite ( $\text{Fe}_2\text{O}_3 \cdot \text{TiO}_2$ ), coal and sulfur mixture at >1200 °C to reduce iron oxide to metallic iron:



The metallic iron is oxidised and precipitated from the solution as a form of slime in the aeration “rusting” step in large tanks with 1% ammonium chloride solution at 80 °C. The finer iron oxide is then separated from the larger particles of synthetic rutile.



Once the majority of the iron oxide is removed, the residual iron oxide is leached using 0.5 M sulfuric acid and separated from the synthetic rutile.

Another commercial process, the Benelite process, employs carbon thermo-reduction for conversion of other iron forms to ferrous state and is then separated by leaching with 18–20% HCl. Fluidised beds are used in the Murso process (Sinha, 1972, 1975) for the thermo-conversions, where the pre-oxidation of ilmenite is carried out in a fluidised bed in a temperature range of 900–950 °C, and the hot oxidised ore is transferred into another fluidised bed where ferric ion is reduced by a reducing agent (for example,  $\text{H}_2$  gas). The product from the second fluidised bed is then leached with about 20% HCl at 108–110 °C. The remaining HCl acid is regenerated after the magnetic separation of the solid synthetic rutile from the leach solution

In the Laporte process, the ore is pre-oxidised in a fluidised bed at about 950 °C (Robinson et al. 1977) followed by reductive roasting in a rotary kiln using coal as reductant at ca 900 °C. The incomplete reduction of iron to the ferrous state without metallisation is achieved by the appropriate choice of equipment, temperature and reductant. There is a sufficient  $\text{CO}_2$  partial pressure developed to prevent the formation of metallic iron due to the reaction:



The roasted ore is so reactive that a single stage leach with 18% HCl at atmospheric pressure for 3.5 h is all that is needed, yielding a product of the same overall particle size range as the starting ore. A bed contactor is used for leaching to prevent the formation of very fine particles from the soft feedstock. It is claimed that the discharged ore is free of fine  $\text{TiO}_2$  particles.

Reduction roasting, in which iron in ilmenite is reduced to ferrous forms followed by sulphuric acid leaching, has been employed in the Kataoka process in Japan (Kataoka and Yamada 1973). In this process, hydrated titanium dioxide is added to the leaching solution as seeds to increase the rate of precipitation of titanium salts and to improve the removal of iron. This also allows the separation of iron from the ore at

**Table 2**  
Summary of upgrading ilmenite to synthetic rutile.

Process	Pyro-treatment	Leaching	Advantage	Disadvantages
The Becher sulphate process	Iron oxidised to $\text{Fe}_2\text{O}_3$ and reduced to metallic Fe by at 1200 °C	(a) $\text{NH}_4\text{Cl}/\text{O}_2$ (b) 0.5 M $\text{H}_2\text{SO}_4$	Allowing diverse ilmenite ores feed	Multi step iron conversions and leaching High energy consumption Emission of $\text{CO}_2$
The Murso process	Similar to the Becher process, but fluidised beds for the conversion	20% HCl	Improved efficiency by using fluidised beds Easier HCl recycle than sulphate system	Similar to the Becher processes
The Laporte process	Lower temperatures for iron conversion to FeO with controlled $\text{CO}_2$ pressure	18% HCl with a bed contactor	Free of formation of fine $\text{TiO}_2$ particles Ease for leaching FeO	Similar to the Becher processes in spite of lower temperature used
The Benelite process	Iron conversion to Fe(II) forms by carbon thermo-reduction	18–20% HCl	Simple one step conversion of iron	Limited ilmenite types as the feed
The Austpac process	Magnetisation of the ilmenite at 800–1000 °C	25% (w/w) HCl	Magnetic separation for higher >97% $\text{TiO}_2$	Higher acidity need for leaching remaining magnetic iron form
The Dunn process	Selective chlorination of iron in ilmenite with $\text{Cl}_2$	-	$\text{Cl}_2$ recycle by oxidation of $\text{FeCl}_2$ to $\text{Fe}_2\text{O}_3$	Handling highly corrosive $\text{Cl}_2$
The Kataoka process (in Japan)	Conversion to ferrous form	$\text{H}_2\text{SO}_4$	Less corrosive using $\text{H}_2\text{SO}_4$ than HCl Low leaching temperature	Produce large iron sulphate wastes

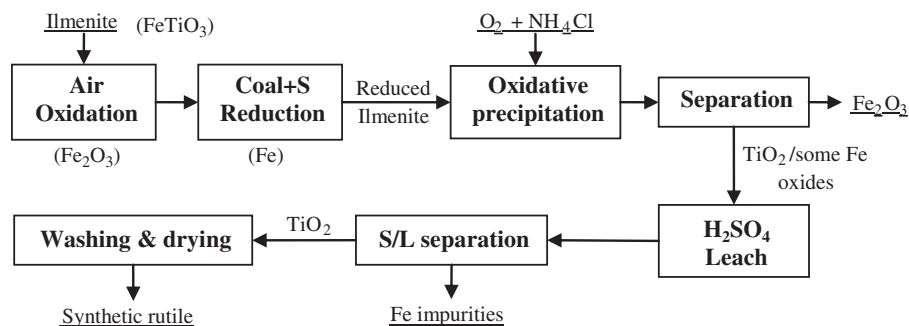
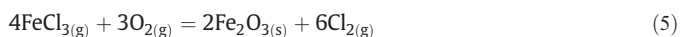


Fig. 2. A schematic of the Becher process (based on Cassidy et al., 1986).

lower temperature and at a sulphuric acid concentration that makes the construction of the reactors economical. More than 95%  $\text{TiO}_2$  content in the ilmenite can be recovered.

While most processes produce synthetic rutile with 93%  $\text{TiO}_2$ , in the Austpac process the synthetic rutile product contains >97%  $\text{TiO}_2$  (Walpole and Winter 2002). Ilmenite ore is roasted at temperatures between 800 and 1000 °C to selectively magnetise the ilmenite, so that gangue minerals may be easily removed by magnetic separation. Roasting also activates the iron component of the ilmenite so that iron leaching is enhanced. Iron and other impurities are removed by leaching in 25% (w/w) HCl. The resultant solids are then filtered, washed and calcined. The product is subjected to a last stage magnetic separation and a synthetic rutile containing >97%  $\text{TiO}_2$  is obtained.

A different thermo-conversion was proposed in the Dunn process (Kahn 1984 and Minkler and Baroch 1981). The principle of this proposed selective chlorination process is that iron in ilmenite is more readily chlorinated than titanium. Excess ilmenite in the fluidised bed prevents the chlorination of titanium because any titanium that chlorinates will react with iron oxide to form titanium dioxide. The iron chloride gas leaving the fluidised bed reacts with oxygen to form  $\text{Fe}_2\text{O}_3$  and  $\text{Cl}_2$  gas for recycle as described in the following equation (Dooley 1975):



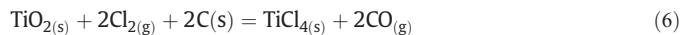
The reactivity of ilmenite ore during leaching with hydrochloric acid was greatly enhanced by reduction in solution using metallic iron (Mahmoud et al. 2004). Similar results were obtained by El-Hazek et al. (2007). The addition of a small amount of iron powder (0.1 kg iron powder for 1 kg ilmenite ore) was proved to largely enhanced the leaching rates of both iron and titanium. When the solid/liquid ratio was increased from 1/20 to 1/8, complete dissolution of both iron and titanium was achieved in 1.5 h with iron powder addition compared with 2.5 h under similar other leach conditions with no iron powder addition.

A direct leaching process for upgrading Rosetta ilmenite concentrate (40–47%  $\text{TiO}_2$ ) into synthetic rutile without thermo-treatment step was investigated by Lasheen (2005). A high acid concentration (high ilmenite/acid molar ratio), and reduction with metallic iron facilitated the removal of iron from the mineral lattice and avoid titanium dissolution. Without addition of a reductant, iron leaching efficiency did not exceed about 55% when using concentrated HCl (12 M) with an S/L ratio of 1:5 at 90 °C for 8 h although almost complete insolubilisation of titanium was realized. Addition of metallic iron raised the recovery to 89%  $\text{TiO}_2$ . It is clearly evident that addition of a reductant is necessary to reduce the Fe(III) forms to the Fe(II) soluble forms. A remaining total iron content of less than 7%  $\text{Fe}_2\text{O}_3$  is most probably due to complex mineralogical composition resulting from the existence of the three fundamental solid solution series in the  $\text{FeO}$ – $\text{Fe}_2\text{O}_3$ – $\text{TiO}_2$  ternary system (Lasheen 2005): (a)  $\text{FeO}$ – $\text{Fe}_2\text{O}_3$ – $\text{Fe}_2\text{TiO}_4$ : magnetite–ulvo–spinel series

(b)  $\text{Fe}_2\text{O}_3$ – $\text{FeTiO}_3$ : hematite–ilmenite series (c)  $\text{Fe}_2\text{TiO}_5$ – $\text{FeTi}_2\text{O}_5$ : pseudobrookite series.

### 3. Thermo and electro chemical processes

In the commercialised thermo chemical processes, the chloride system is used to produce a purer  $\text{TiO}_2$  and titanium metal employing more complicated technology (Fig. 1). First, synthetic rutile or high grade titanium slag is obtained from upgrading the ilmenite ores and is then purified by chlorination at an elevated temperature (900–950 °C) to obtain pure titanium tetrachloride ( $\text{TiCl}_4$ ):



The  $\text{TiCl}_4$  is separated from impurities by condensation and distillation. However the separation of  $\text{TiCl}_4$  from  $\text{VOCl}_3$  is difficult due to their close boiling points and needs special treatment by adding mineral oil,  $\text{H}_2\text{S}$  gas, or copper metal. Three commercial processes are used in the world to produce  $\text{TiCl}_4$  on a commercial scale (Minkler and Baroch 1981), namely fluidised bed process (most widely used), shaft furnace process and chlorination in a molten salt bath (former U.S.S.R. and Japan). These processes involve the use of petroleum coke and gaseous chlorine, which is capital intensive, resulting in the formation of dioxins, furans, and other deleterious persistent organic pollutants (Lakshmanan et al. 2004a). After the oxidation of the titanium tetrachloride at high temperature to produce titanium dioxide, a reduction stage is used to convert the purified titanium dioxide to obtain titanium sponge, which is further purified and melted using a number of techniques to obtain titanium metal. The wastes produced by the chloride process are more environmentally acceptable for disposal than the sulphate processes. However, the thermo chloride process needs higher grade feedstock (>90%  $\text{TiO}_2$ ): natural or synthetic rutile or high grade titanium slag.

The Hunter process is the pioneering process developed in 1887 to reduce  $\text{TiCl}_4$  to titanium metal in a molten sodium bath. It was later replaced by the cheaper Kroll process for commercial production in 1940 to reduce  $\text{TiCl}_4$  in molten magnesium at 900 °C (Table 3). The main disadvantages of the Kroll process are the use of  $\text{TiCl}_4$  as raw material and the long process route including batch steps, resulting in low efficiency, high energy consumption and high cost, and electrochemical conversion of  $\text{MgCl}_2$  to magnesium metal for recycling (Jackson and Dring 2006). Since then, numerous investigations have been reported and several alternative processes have been developed, including better reactor design, omitting cooling step between the  $\text{TiCl}_4$  reduction with vacuum distillation, the development of a diaphragmless cell to enhance the current efficiency in electrolysis processes to regenerate  $\text{MgCl}_2$ .



**Table 3**  
Processes for reduction of tetrachloride to titanium metal.

Process	Features	Advantage	Disadvantage	Reference
The Hunter and Kroll processes (Thermo)	Molten Na or Mg as the reductant	Ti product with less oxygen content and metallic impurities; lower costly using Mg than Na reduction	Labor-intensive batch process; heterogeneous exothermic reactions; low productivity	Fuwa and Takaya 2005; Ikeshima 1985; Nagesh et al. 2004
Electrolysis processes	KCl–LiCl electrolyte graphite anode; steel cathode; TiO <sub>2</sub> feed	Fewer steps; continuous operation; No TiCl <sub>4</sub> and metallic involvement; cheaper than thermo-chemical	Redox cycling and handling very reactive dendritic products	Anon. 1983; Chen et al. 2000; van Vuuren et al. 2005
ESE processes (direct electro)	Graphite anode; Cu cathode; molten CaF <sub>2</sub> –CaO–TiO <sub>2</sub>	Direct reduction from TiO <sub>2</sub> slag; potential for continuous operation	Difficult to control the heat balance and CO evolution	Cardarelli 2003; Takenaka et al. 1999
OS process (direct electro)	TiO <sub>2</sub> powder cathode graphite rod anode Ca reductant and molten CaCl <sub>2</sub>	Direct reduction from TiO <sub>2</sub> powder as feed in a single cell	Existence of free carbon contaminating the Ti product by the formation of TiC	Ono and Suzuki 2002; Suzuki et al. 2003; Suzuki 2007
FFC process (direct electro)	Pre-formed porous TiO <sub>2</sub> pellet as the cathode; inert anode for O <sub>2</sub> evolution; molten CaCl <sub>2</sub> phase	Simple, rapid and better current efficiency; potential continuous operation	Slow O <sub>2</sub> diffusion; costly for the TiO <sub>2</sub> pellet feed; long time for removing the waste CaCl <sub>2</sub> after the electrolysis	Chen et al., 2000, 2001; Fray, 2001

A continuous metallothermic TiCl<sub>4</sub> reduction process producing titanium powder seems to be the best route to reduce the cost of producing final titanium products (van Vuuren 2009). Researchers at Commonwealth Scientific and Industrial Research Organisation (CSIRO) developed a low temperature industrial process (TiRO process) for production of titanium metal (Table 4). The TiRO reaction takes place in an operating window that is conducive to a fluidised bed reactor. Deura et al. (1998) attempted to inject the TiCl<sub>4</sub> gas to the molten MgCl<sub>2</sub> salt to produce titanium powder, and Elliott (1998) reported to circulate the molten salt (the TiLAC process). To increase the production efficiency and energy efficiency, TiCl<sub>2</sub> was tested as the feed material (Takeda and Okabe, 2006). Alternative processes were also reported, including the production of titanium alloys, production of titanium ingots, carbonitrothermic reduction method, fluorotitanate process, and calcium reduction process (Table 4). Unfortunately, the thermo-chemical processes, such as the Kroll and Hunter processes, hold little potential for significant cost reductions beyond current technology.

Electrochemical technique is regarded as one of the key technologies to significantly reduce the cost of titanium. The Timet and D–H titanium production of pilot quantities of electrolytic titanium has been developed (Table 3). Major advantages of electrochemical extraction are reduced energy consumption, automation, and continuous production. However, the electrolysis process suffers from difficulties in eliminating redox cycling and in handling very reactive dendritic products, which has hindered its success in commercialisation (Chen et al. 2000).

Recently, a direct electro-chemical reduction technique shows tremendous promise to reduce the cost of titanium production. The direct reduction process accomplishes the production in one single step (Suzuki et al. 2003). The production cost would be largely reduced if TiO<sub>2</sub> can be used as a feed material without use of chlorination for the TiCl<sub>4</sub> intermediate. Several direct reduction processes have been developed, including Electro-slag electrolysis processes (ESE), the OS Process and the Fray–Farthing–Chen (FFC) process, with their own features (Table 3). In comparison, the FFC process features better efficiency, but the requirement for pre-formation of TiO<sub>2</sub> pellets is one of the main drawbacks. In

these regard, the direct reduction with powdered TiO<sub>2</sub> as the feed material could be an alternative in the scale-up.

#### 4. Hydrometallurgical processes

In the thermo-chloride process, the production of pigment grade titanium dioxide from ores involves roasting and leaching to obtain an intermediate product of synthetic rutile with 90–95% TiO<sub>2</sub>. Hence further purification such as chlorination is required to produce a pigment-grade titanium dioxide, which makes the process complicated and adds costs to the process. To solve this problem, direct leaching–purification processes have been developed to obtain pigment grade titanium dioxide without the production of intermediate synthetic rutile. Titanium dioxide nano-technology has also been developed. The process features are compared in Table 5.

##### 4.1. H<sub>2</sub>SO<sub>4</sub> leaching processes

The sulphate process was the first commercialised technology to convert ilmenite to titanium pigment. In the sulphate process, ilmenite (40–60% TiO<sub>2</sub>) and/or titanium slag (72–87% TiO<sub>2</sub>) is digested with sulphuric acid to form water soluble sulphates (titanyl sulphate TiOSO<sub>4</sub> and iron sulphates). Metallic iron scrap is used to reduce the ferric iron to ferrous iron which otherwise will co-precipitate with TiO<sub>2</sub> and contaminate the product. The solution is then cooled down to crystallise the iron as ferrous sulphate heptahydrate (FeSO<sub>4</sub>·7H<sub>2</sub>O). To this point, the process is in the “black stage”. The solution is then subjected to hydrolysis and the resultant solids are subjected to calcination to produce anhydrous TiO<sub>2</sub>. This is so-called the “white stage”. It uses simple technology and lower grade and cheaper raw materials to produce a form of pigment called anatase (tetragonal, near octahedral), which is preferred over the pigment from the chloride process for use in papers, ceramics and inks. However, the traditional sulphate processes produce lower quality products for most applications and large quantities of waste iron sulphate. Therefore, it generally has higher production costs for

**Table 4**  
Improved thermo processes.

Process	Features	Reference
The TiRO process	Continuous, low temperature Ti metal product	Brooks et al. 2007; Doblin and Wellwood 2007; Wellwood and Doblin 2008
The TiLAC process	Circulating the molten salt	Elliott 1998
Ti alloy and ingots processes	Production of Ti alloys or ingots	Hayes et al. 1984; Hiatt 1990; Ikeshima 1985; Minkler and Baroch 1981
Carbonitrothermic reduction	Alternative reductants or reagents	Hiatt 1990
Fluorotitanate process		
Calcium reduction		

**Table 5**  
Comparison of sulphate processes with chloride processes.

Process	Feed	Product	Advantage	Disadvantage
Traditional sulphate leaching process	Natural ilmenite (>44 TiO <sub>2</sub> ) Ti slag (78% TiO <sub>2</sub> )	Anatase (>98% TiO <sub>2</sub> ) (for papers, ceramics and inks)	Processing low grade ilmenite; low capital cost; low energy consumption; simple technology	High H <sub>2</sub> SO <sub>4</sub> consumption; large iron sulphate waste and dilute H <sub>2</sub> SO <sub>4</sub> production
BHP Billiton improved sulphate process	Diverse ilmenite ores; Fe scrap reductant	>99% TiO <sub>2</sub> with solvent extraction; >97% with crystallisation	Reduced waste; producing clean gypsum; better selectivity by SX to produce purer products	Increased process complexity
Thermo chloride processes	>90% TiO <sub>2</sub> natural or synthetic rutile or high grade Ti slag	Pigment grade products (>99.5% TiO <sub>2</sub> ); Ti metal	Recycle use of HCl reagent Suitable for larger scale Purer products Waste more environmentally acceptable	Recycling large volume of dilute acid solution Need for higher grade feed; more corrosive high energy consumption; complicated technology
Chloride leaching process	Natural ilmenite and Ti slag	>99.5% TiO <sub>2</sub>	More complete HCl acid recycle; lower cost for waste and more environmental acceptable; higher purity products	Higher capital costs for equipment and construction; higher requirement for operation and maintenance skill
Caustic process	Natural ilmenite and Ti slag	>99.3% TiO <sub>2</sub>	Higher leaching selectivity for Ti over Fe; mild leach conditions at low temperature and atmosphere	Need for transformation of titanate to hydrous TiO <sub>2</sub> in acidic solution; recycling of large amount of KOH solution and energy consumption

expensive acid treatment than the chloride process. A typical conventional sulphate process involves the following reactions:

#### Leaching



#### Ferric reduction



#### Ferrous sulphate crystallisation



#### Titanyl sulphate precipitation



#### Hydrolysis



#### Calcination



In a patent process by Watanable and Sei (1988), the recovery of titanium from sulphuric acid solutions containing mainly titanium and iron comprises (a) adding NaCl or the like to the solution and extracting iron as chloride complex with one or more organic extractants from the group of oxygen-containing organic solvents and alkylamines, (b) extracting titanium from the raffinate from (a) into the organic phase as chloride complex with one or more organic extractants from the group of alkylphosphoric acids and alkylarylphosphoric acids, (c) stripping the resultant organic solution with an aqueous solution containing NH<sub>4</sub><sup>+</sup> or K<sup>+</sup> together with HF, and then (d) adding NH<sub>3</sub> gas, NH<sub>4</sub>(OH) or KOH to the aqueous solution to form a precipitate such as (NH<sub>4</sub>)<sub>2</sub>TiF<sub>6</sub> or titanium hydroxide. Titanium halides and alkoxides can be produced from the precipitate.

Researchers at BHP Billiton Innovation Pty invented an improved sulphate process for production of titania (Roche et al. 2004). The process, as shown in Fig. 3, features:

- (i) The use of at least a part of raffinate from solvent extraction step as the leach solution for the leaching step to maximizes the effective use of acid in the process. This also controls the concentration of iron in the circuit.

- (ii) The use of the depleted leach liquor allows a reduction or complete elimination of the production of waste acidic effluents and/or their neutralization products such as 'brown gypsum'; and allows recuperation of heat and also eliminates energy intensive acid recovery and evaporative concentration steps.
- (iii) Precipitation of iron sulphate can be confined to one step to simplify downstream processing of the iron sulphate.
- (iv) Selective solvent extraction (SX) step with organic systems such as trioctylphosphine oxide (TOPO) and butyl dibutylphosphonate to separate titanium from impurities of iron, chromium, manganese and niobium.
- (v) Due to the solvent extraction step, the titania produced has a very high purity (>99%).
- (vi) The use of a reductant such as metallic iron, Ti(III) salts, SO<sub>2</sub>, thiosulphate, etc. to makes it possible to use less concentrated sulphuric acid than is required for the conventional sulphate process.

In another patented process developed BHP Billiton researchers (Roche, et al. 2005), crystallisation of titanil sulfate step is used as an alternative to solvent extraction to produce TiOSO<sub>4</sub> crystals which is then dissolved and hydrolysed to form a solid phase containing hydrated titanium oxides followed by calcining the solid phase and forming titania. In the hydrolysis step, the crystal growth in the reactor could be controlled under temperature, residence time and solution concentration to produce coarse hydrated titanium oxides with a particle size of at least 0.005–0.01 mm or fine hydrated titanium oxides with a particle size of less than 0.0005 mm, suitable for a wide range of further processing. Compared to the use of solvent extraction technique in the process, the crystallisation is simpler, but the final synthetic product is less pure with about 97% TiO<sub>2</sub>. Both flowsheets have been tested to a continuous pilot stage.

Further research and development by the BHP Billiton researchers resulted in an alternative involvement of a reduction roasting step to reduce ferric iron to ferrous iron in the ilmenite by a reducing gas at a controlled temperature range to avoid formation of rutile that is unleachable under the conditions of leaching step (Stuart et al. 2005). It may also comprise a mixture of hydrogen, carbon monoxide, and/or methane, and another suitable gas such as inert gas and/or carbon dioxide. This reductive pre-treatment step make the leaching efficiency is comparable to that using the iron scrap, but high recoveries of titania with low acid consumption in the leaching step. However, a high

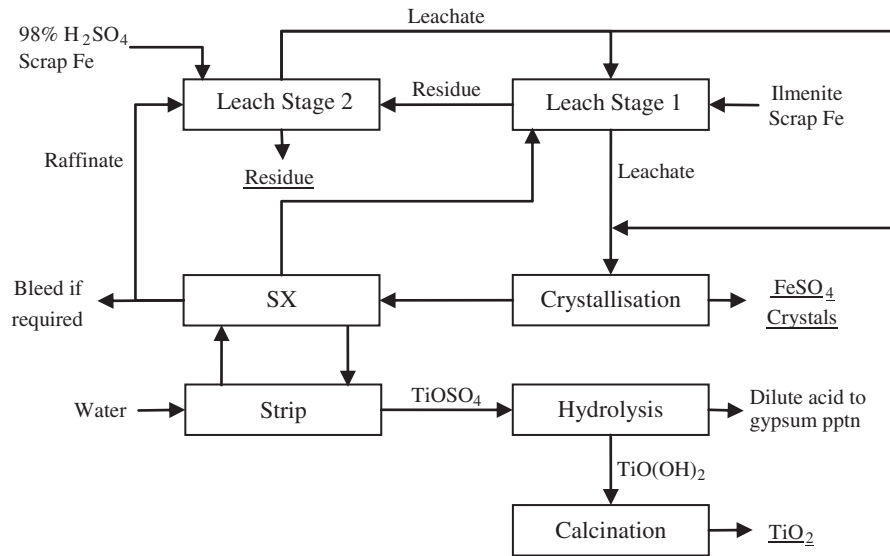


Fig. 3. Flowsheet of an improved sulphate process (based on Roche et al. 2004).

temperature (450–700 °C) has to be used to make the reduction occur, which may result in sensitive energy consumption.

Recent research work by the researcher in BHP Billiton has led to a new finding that the presence of titanyl sulphate particulate can act as a seed resulting in premature precipitation of the dissolved titanyl sulphate during the leach step and is one of the major factors in preventing the achievement of high extraction rates (Stuart et al. 2010). The newly developed flowsheet is characterised by a filtering leachant

for the leach step to substantially remove the titanyl sulphate particles from the leachant prior to supplying the leachant to the leach step (Fig. 4). It was also found by the inventors that the co-precipitated ferric iron with titanyl sulphate tended to be carried forward to downstream processing steps to adversely affect the product quality. A ferric reduction step is used with a suitable reductant such as Ti<sup>3+</sup> species, SO<sub>2</sub> gas, zinc dust, scrap iron, etc. A bleaching step is used after the hydrolysis of TiO(OH)<sub>2</sub> to reduce chromophores into their soluble

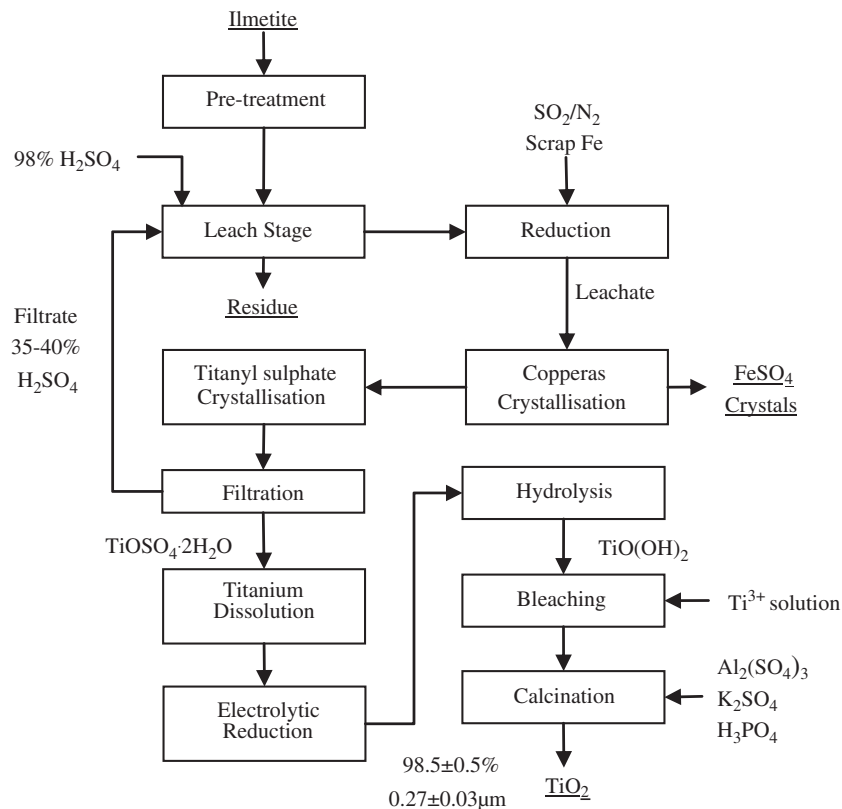
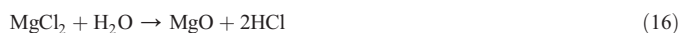
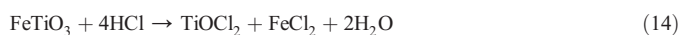


Fig. 4. A schematic flowsheet recently developed by BHP Billiton researchers (based on Stuart et al. 2010).

forms. In calcination step, additives of a mixture of  $K_2SO_4$ ,  $ZnO$  and  $H_3PO_4$  are used to control the growth of the rutile crystals to be in the range of  $0.27 \pm 0.03 \mu m$ . The final rutile product obtained is  $98.5 \pm 0.5\%$   $TiO_2$ .

#### 4.2. HCl leaching processes

A direct leaching process with concentrated HCl was developed by Berkovich (1975) to dissolve at least 80% of the titanium and iron in the ilmenite ore. Ferric ions were reduced to ferrous ions by  $SO_2$  and the resultant  $FeCl_2$  was crystallised and separated. The titanium chloride in the solution was hydrolysed, precipitated, further purified and calcined as pigment grade  $TiO_2$  (at least 99.5%). The conversion of  $Fe(III)$  to  $Fe(II)$  is essential in view of the affinity of  $TiO_2$  for  $Fe(III)$  and the difficulty in separating  $Fe(III)$  from  $TiO_2$ . A small excess of a reductant is also useful to reduce some  $Ti^{4+}$  to  $Ti^{3+}$ . Due to the greater affinity of  $Ti^{3+}$  for oxidation, as compared to  $Fe^{2+}$ , the presence of a small quantity of  $Ti^{3+}$  in the solution decreases the tendency for  $Fe^{2+}$  ions to later oxidise to  $Fe^{3+}$  and possibly contaminate the later-formed  $TiO_2$  (Berkovich, 1975). Leaching and reduction proceed according to Eq. (14) for the subsequent separation of iron by conventional hydrolysis or solvent extraction. Pyrohydrolysis is a distinct feature of the chloride leaching process to recover  $TiO_2$  and  $MgO$  reagents, and simultaneously recover HCl for recycle based on the reactions (15) and (16):



In another patent by Thomas (1985), a dilute acid leach was used ahead of strong acid leach (25% HCl) to eliminate some easily dissolvable impurities. After ferrous chloride crystallisation and chlorination, the  $TiCl_4$  was hydrolysed to obtain pigment grade  $TiO_2$ . It was found that alcohols such as methanol, ethanol and ethylene glycol all substantially increased the leaching rate of ilmenite in mixed HCl–alcohol solutions (Girgin and Turker 1986).

A process for the production of pigment-grade  $TiO_2$  using chloride media was developed (Lakshmanan et al., 2001, 2002, 2004a, 2004b, 2005a, 2005b; Lakshmanan and Sridhar 2002; Puvvada et al. 2003). The process involves the leaching of the ore or concentrate with a hydrogen halide solution at temperature greater than  $90^\circ C$  (Fig. 5). The resultant leach solution is subjected to solvent extraction of iron with TBP and D2EHPA in kerosene. The iron is then stripped from the organic phase and subjected to pyrohydrolysis to recover iron as iron oxides. The raffinate has a concentration of less than 50 mg/L Fe, and is treated to precipitate  $TiO_2$  by addition of water. The solution rich in titanium chlorides is then hydrolysed, with calcium or magnesium chlorides, to precipitate titanium oxyhydrate which is then converted to  $TiO_2$  through calcination with elevated temperatures of  $700$ – $1000^\circ C$  in the presence of air and/or oxygen.

Alternatively, the titanium in the leach solution is extracted by an organic phase, which is subjected to fractional distillation (Lakshmanan et al., 2004a, 2004b). The organic phase is so selected that they have different boiling points to that of the titanium halide in the leachate by an amount that permits separation by fractional distillation, typically a higher or lower boiling point than that of the titanium tetrachloride by  $30^\circ C$ . The selected organic phase is phosphine oxides or esters and tertiary or quarternary ammonium chlorides, which are stable with respect to the titanium halide. Stripping the titanium halide from the organic phase is achieved by heating to volatilise the titanium tetrachloride, which is then condensed (Fig. 6). From the tetrachloride solids, titanium metal can be electrowon using the fused salt electrolysis technique. The advantage of this process is to ensure environmental acceptance at low costs and to produce titanium and other products of high purity.

A method providing cost-effective extraction of titanium from titanium-bearing ore or concentrates was reported by Lakshmanan et al. (2005a and 2005b). The first step is leaching the ore at atmospheric pressure with a lixiviant containing a chloride and hydrochloric acid in a temperature range of less than  $85^\circ C$ . The concentration of the hydrochloric acid is at least 20% to allow titanium to be leached and remain in solution. The preferred chloride is magnesium chloride to enhance the extraction of titanium. The lixiviant may contain an oxidant, e.g. chlorate salts or chlorine. The redox potential (Eh) of the solution is controlled at least 350 mV in combination with the control of chloride concentration for leaching metal values.

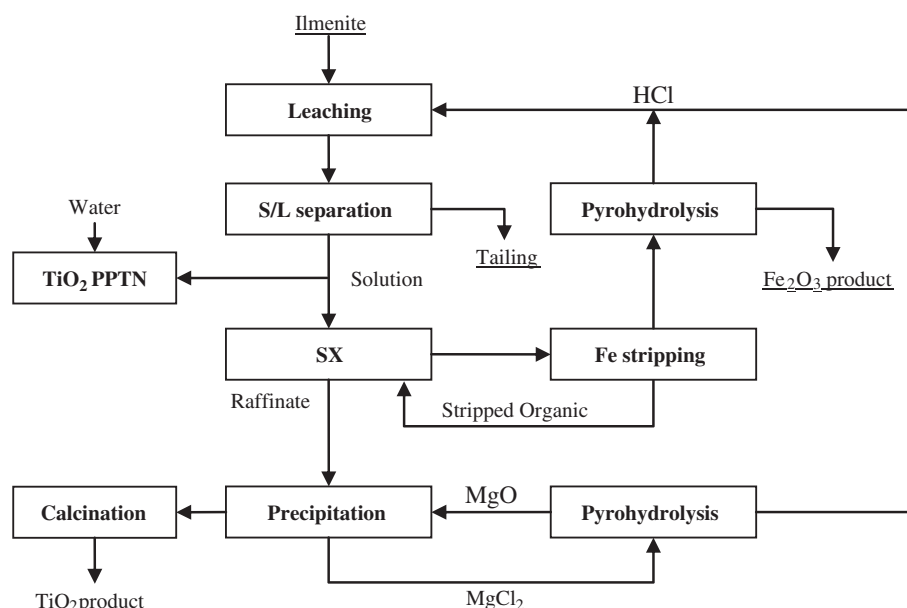


Fig. 5. A process flowsheet for pigment-grade  $TiO_2$  (based on Puvvada et al. 2003).



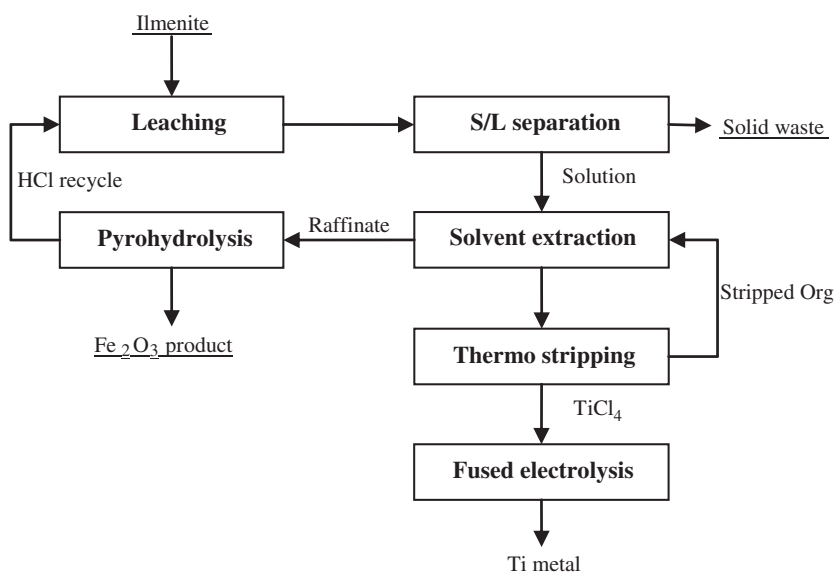


Fig. 6. A conceptual flowsheet for the production of titanium metal from ilmenite feed stock (based on Lakshmanan et al. 2004a).

Duyvesteyn et al. (2001a and 2002) and Verhulst et al. (2002 and 2003) reported a process to produce pigment grade  $\text{TiO}_2$  from ilmenite (Fig. 7). The process comprises (i) leaching the ore with hydrochloric acid to generate a leachate containing titanium and iron chloride and residue, (ii) cooling the solution to form crystals of  $\text{FeCl}_2$  which are separated from the leachate, (iii) extracting titanium together with ferric ions by a first solvent extraction (SX) circuit with phosphine oxide to produce raffinate containing ferrous ions and other impurities, (iv) extracting ferric ions in the second SX circuit with an amine extractant from the loaded strip liquor of the first SX circuit, (v) hydrolysing the raffinate to produce pigment grade  $\text{TiO}_2$ , (vi) pyrohydrolysing/distilling the strip liquor containing ferric ions to produce ferric oxides and reclaiming HCl for leaching. Alternatively, the ferric ions in the leachate could be reduced to ferrous ions electrolytically or by a metal such as iron scrap before the crystallisation of  $\text{FeCl}_2$ . The advantages of the process include: (1) using inexpensive ilmenite as the feed material, (2) using gaseous HCl to enhance leaching kinetics and to produce very pure titanium chloride solution, (3) using solvent extractions to separate titanium from iron and

other impurities, (4) Recovering iron as an oxide of potential commercial value (5) regenerating and recycling substantial gaseous HCl for leaching.

#### 4.3. Caustic leaching processes

A novel process was patented for preparing titanium dioxide from titanium slag in sodium or potassium hydroxide solution by the researchers at Chinese Academy of Science (CAS) (Liu et al. 2006; Qi et al. 2005; Tong et al. 2007; Xue et al. 2009). The ilmenite is decomposed in concentrated KOH or NaOH solution under atmospheric pressure and an intermediate with high in titanium and low in iron is obtained by separation, which can be converted into pigment grade titanium dioxide after further treatment (Fig. 8). The reaction of ilmenite with concentrated KOH solutions led to the formation of potassium titanate ( $\text{K}_4\text{Ti}_3\text{O}_8$ ) and iron oxide could be described by:

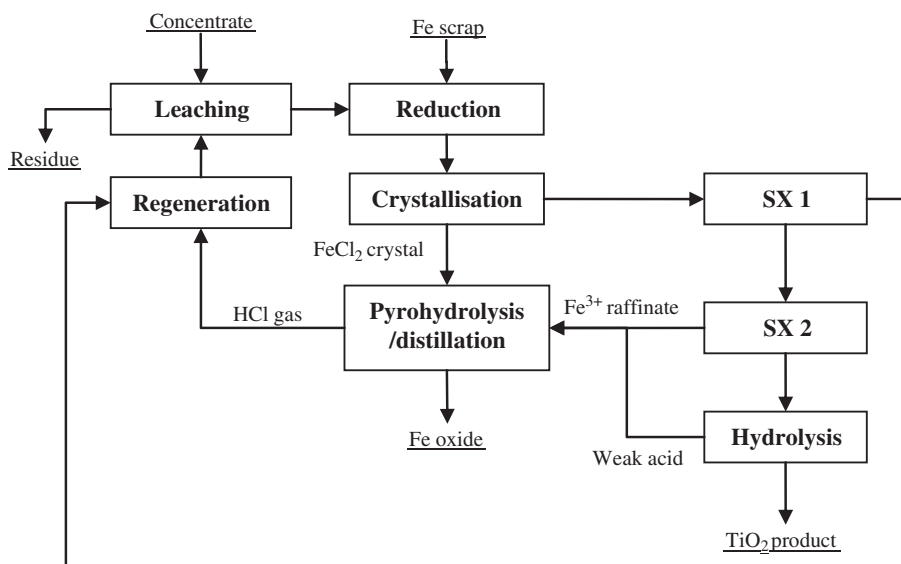


Fig. 7. A schematic flowsheet of the Altair  $\text{TiO}_2$  pigment process (based on Verhulst et al., 2002, 2003).

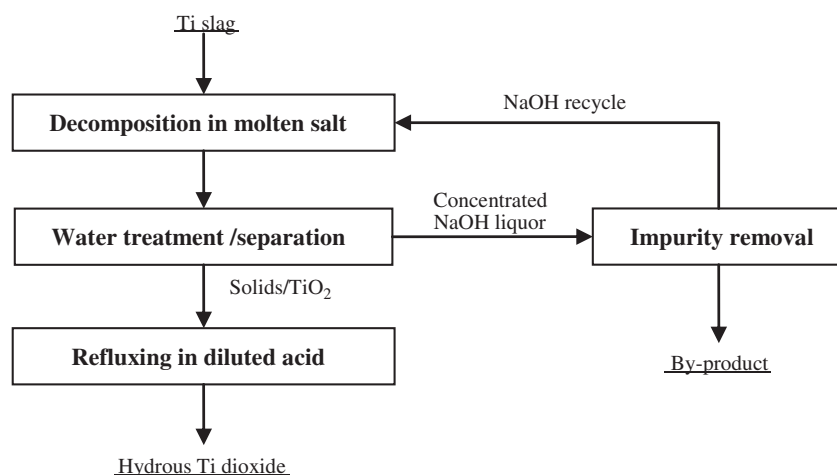


Fig. 8. A schematic flowsheet of the new process for titanium dioxide production (based on Xue et al. 2009).

The phase transformation of potassium titanate was carried out by hydrolysing the potassium titanate in acid solution (pH 2.0) at 25 °C for 60 min. The obtained hydrous titanium dioxide was calcined at 400 °C to form well-crystallised anatase  $\text{TiO}_2$ . Approximately 95–98% Ti in the titanium slag could be extracted under optimal conditions. In addition, the  $\text{TiO}_2$  purity in the product was up to 99.3%.

A similar process using caustic leaching for the production of titanium dioxide from titanium slag was reported by Zhang et al. (2009). Almost complete titanium dissolution was achieved when finely ground titanium slag ( $-61 + 51 \mu\text{m}$ ) was reacted with a 10 M NaOH solution using an alkali to  $\text{TiO}_2$  ratio of 4 at 220 °C for 4 h. The hydrothermal product was identified by XRD as  $\text{Na}_4\text{Ti}_3\text{O}_8$ . Titanium dioxide with a rutile structure was obtained by acidification and cation exchange when acid was added at 100 °C in the pH range of  $<1.20$ . The purity of  $\text{TiO}_2$  was  $>99\%$  when HCl was used.

In comparison with the conventional process of upgrading ilmenite, the process with leaching titanium slag in alkaline solutions requires relatively mild reaction conditions and high decomposition rate of titanium slag can be fulfilled under relatively low temperature and atmospheric pressure. Therefore, the energy consumption of this technology is lower than the existing ones.

#### 4.4. Electrochemical reduction and dissolution

Electrochemical techniques have been investigated for the reduction and dissolution of two different ilmenite samples in 450 g/L sulphuric acid solutions at elevated temperatures (Zhang and Nicol 2009). The dissolution of ilmenite ( $\text{FeTiO}_3$ ) is slow at potentials above 0.3 V at

which potentials the dissolution of ilmenite and the reduction of hematite (if present in the ilmenite sample) are the main reactions. At more negative potentials the dissolution of ilmenite increases simultaneously with the reduction of ilmenite to trivalent titanium. Hematite dissolved faster under reductive conditions than ilmenite. Studies of the effect of temperature on the dissolution of ilmenite at low potentials such as 0 V have shown that in the temperature range of 65–95 °C, the activation energy is about 50 kJ/mol and this together with the high ratio of the charge passed to metals dissolved suggests that the rate of the non-reductive dissolution reaction is insignificant under these conditions. This technique is in laboratory research stage and has challenges in energy consumption, dissolution kinetics and selectivity for advancement.

#### 5. Titanium dioxide nano-technology

A hydrometallurgical process was developed for producing ultrafine titanium dioxide from aqueous titanium chloride solutions (Duyvesteyn et al., 2001b, 2001c, 2003). It features hydrolysing the solution via complete evaporation under well controlled temperature to form amorphous titanium oxide followed by further evaporation and spray hydrolysis in a spray dryer (Fig. 9). Nano-sized particles of  $\text{TiO}_2$  could be obtained in a process by adding a chemical control agent including various inorganic salts and organic acids and organic salts, e.g. oxalic acid to the titanium chloride solution (Duyvesteyn et al. 2001c). After hydrolysing, the titanium hydroxide is calcined to the desired form of titanium dioxide, being either anatase or rutile. The titanium dioxide is milled to provide the desired particle size distribution. The advantages

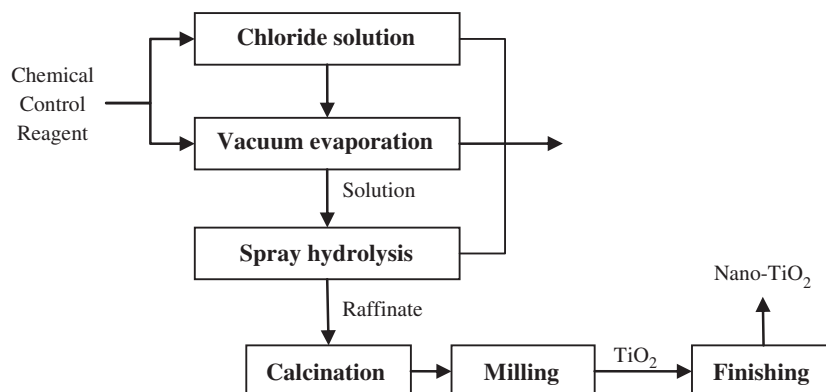


Fig. 9. A schematic flowsheet of processing aqueous solution to ultrafine titanium dioxide pigment (based on Duyvesteyn et al., 2001c).

of the process include a high quality titanium pigment, readily controlled physical and chemical characteristics of the product, and low costs, since dilution of the solution is avoided and the acid can be recycled.

Nano-technology for producing particles of less than 100 nm has developed rapidly in recent years due to their special usage as catalysts. A process has been developed, which comprises the steps of (i) reacting a titanium compound with ammonia in an amount exceeding the stoichiometric amount necessary to convert the titanium compound to a titanium hydroxide or reacting a titanium compound with a base in a pH range of 2–7, to obtain a reaction product, and (ii) calcining the obtained product (Sakatani et al. 2002; Sakatani and Koike, 2003; 2004). The process easily produces titanium oxide, which exhibits high photocatalytic activity under irradiation by visible light, and having an average particle size of <20 nm.

Solvothermal techniques (especially the hydrothermal method) are widely used in the synthesis of the nanoparticles (Xie and Shang, 2007). Unlike most other synthetic processes, the solvothermal synthesis is performed under much milder chemical conditions under relatively low temperatures. Compared to those methods involving calcination and milling, which tend to result in agglomerate formation and degradation of the surface, hydrothermal processing maintains the particles in solution throughout the process so that non-aggregated nanomaterials may be obtained readily. The solvothermal synthesis route is very similar to the hydrothermal route, the only difference is the precursor solution is usually non-aqueous and allows for the precise control over shape, size distribution, crystallinity of titanium dioxide nanoparticles or nanostructure. Some of these experimental parameters may include reaction temperature, reaction time, solvent type, surfactant type and precursor type. Therefore the use of solvothermal synthesis to produce a tailored TiO<sub>2</sub> motif is very advantageous to maximise the TiO<sub>2</sub> usage in applications.

## 6. Conclusions and recommendations

Abundant ilmenite is becoming the main source of titanium. Many processes are commercially used or proposed to upgrade ilmenite to produce synthetic rutile. Most of these processes involve a combination of the technologies of pyrometallurgy, hydrometallurgy and electrometallurgy, and are generally expensive.

The commercialised thermo-chemical chloride processes such as Kroll and Hunter processes need higher grade natural rutile or upgraded synthetic rutile as the feed and chlorination step to produce intermediate TiCl<sub>4</sub> for the production of pigment grade TiO<sub>2</sub> and titanium metal. The thermo-chemical processes are very expensive and energy inefficiency. Although many improvements have been made, the thermo-chemical processes, such as the Kroll and Hunter processes, hold little potential for significant cost reductions beyond current technology. The development of the electro-chemical processes for direct reduction of TiO<sub>2</sub> and electro-slag as feed material and *in-situ* electrolysis has achieved some success. However, some challenging issues such as redox cycling, feeding, kinetics, control heat balance have to be resolved before scale-up to commercial application.

Compared to the thermo-chemical and electro-chemical processes, direct hydrometallurgical leach processes are advantageous in processing abundant ilmenite ores, low energy consumption and produce sufficiently high quality of pigment grade TiO<sub>2</sub> products for a wide range of applications and major demand. The main drawbacks of the conventional sulphate processes are the high consumption of H<sub>2</sub>SO<sub>4</sub> and the production of large amounts of sulphate wastes and high cost for the treatment. BHP Billiton has developed several improved sulphate processes involving leaching strategies, solvent extraction to separate metals and recycling acids, and very promising for commercial applications in future.

Direct hydrometallurgical processes for leaching ilmenite in chloride solutions and the subsequent purification using solvent extraction have been investigated intensively. Reclaiming HCl for recycling by hydrolysis or pyrohydrolysis processes is a significant strategy to reduce operating costs and protect the environment. It is noted that solvent extraction has been incorporated into processes to separate titanium from iron and other impurities to enable the use of low grade ilmenite as feed materials, the elimination of the chlorination for the production of high purity TiO<sub>2</sub>. Novel caustic leaching process established features high selectivity of titanium over iron in leaching step. Titanium dioxide nano-technology for the hydrometallurgical processes has also been developed. Further development of direct leaching ilmenite coupled with solvent extraction for titanium pigment and metal production is recommended.

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