

Production of titanium tetrachloride (TiCl₄) from titanium ores: A review

Hossein Bordbar, Ali Akbar Yousefi*, Hossein Abedini

Iran Polymer and Petrochemical Institute, P.O Box 14965-115, Tehran, Iran

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ABSTRACT

Titanium (Ti) is the ninth most abundant element on earth. The titanium mineral ores are widely distributed in different parts of the world. The two main ores of titanium include rutile (TiO₂) and ilmenite (FeO.TiO₂). It is aimed to provide the readers with an insight to the main processes currently employed to extract and recover titanium tetrachloride (TiCl₄) from different titanium ores. Due to the crucial importance of TiCl₄ catalyst in the synthesis and polymerization of polyolefins, the present work examines the literature and developments made in the processing of ilmenite and rutile ores for the extraction of TiCl₄. The attention has been paid to the chlorination processes and the main parameters affecting the recovery of TiCl₄. Different approaches developed to date are reviewed. Different processes, reaction mechanisms and conditions as well as the kinetic models developed for extraction and purification of TiCl₄ in fluidized bed reactors are also reviewed. A literature survey on the combined fluidized bed reactor systems developed for achieving a high-grade synthetic rutile via selective chlorination of low-grade titanium ores having high metal oxides content such as magnesium oxide (MgO) and calcium oxide (CaO) is also reported. Different strategies adopted to avoid agglomeration process during the extraction process are discussed too. **Polyolefins J (2017) 4: 149-173**

Keywords: Titanium; rutile; ilmenite ore; extraction; TiCl₄; chlorination; fluidized bed.

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INTRODUCTION

Titanium, a low density metallic element, was discovered in 1790 and its mass production was started in 1945. Various applications are known for titanium, however, its industry has been faced with difficulties in production yet, which must be overcome [1]. In 1948, some mines and laboratories produced few pounds of titanium. The commercial debut of titanium was in 1950 [1]. Main properties of titanium (Ti) metal include extreme stiffness, lightweight, and high resistance against corrosion. It is therefore used in various fields such as aerospace, marine and chemical plant materials, as well as in the production of other products (glasses, golf clubs, etc.) [2, 3]. The strength to weight ratio of titanium is higher than that of aluminum or other light metals. It can withstand the attack of acids, chlorine gas and salt solutions. The electrical and thermal conductivities of titanium are low [3]. The alloys of titanium with other transition metals have widespread applications and are good alternatives for iron and aluminum. Titanium is the ninth most abundant element on earth [4, 5]. It is a promising metal and can be used as a general metal in the future. Despite the abundance of its resources, the production volume of titanium is low due to the high production cost and low yield of the commercial titanium reduction process [3-5]. A survey on the use of titanium in various fields shows that almost 95% of titanium is used in production of white TiO₂ pigment, which is subsequently used in paint, plastic and paper industries [3]. Owing to its unique characteristics, titanium dioxide also has high potential applications in environmental purification, gas sensors, and in photovoltaic cells [3]. Titanium tetrachloride (TiCl₄) is an intermediate, which is used in production of TiO₂ pigment and titanium sponge [5-8].

The discovery of Ziegler-Natta catalysts is one of the most important discoveries in chemistry in the last century [9]. The catalyst which is used for polymerization of olefins reduces the activation energy of polymerization process which, in turn, accelerates the reaction and allows the polymerization to proceed even under mild conditions. In 1953, Karl Ziegler discovered the titanium tetrachloride (TiCl₄)-based catalyst and diethylaluminum chloride [(C₂H₅)₂AlCl]

as a co-catalyst and used them for production of high density polyethylene (HDPE) via polymerizing ethylene monomer at room temperature. Moreover, this catalyst was used by Giulio Natta for polymerization of propylene monomer to a polypropylene (PP) product [10, 11, 12]. Karl Ziegler and Giulio Natta won Nobel Prize for their respective discoveries in the field of polymers 50 years ago in 1963 [13, 14]. The discovery of Ziegler-Natta catalysts led to a new concept in the world of polymers. Since then, remarkable progress has been made in the field of catalytic olefin polymerization of polyolefins through simplifying the production process and by eliminating deactivation, solvent evaporation and polymer purification stages. The current polymerization industry is utilizing the Ziegler-Natta catalysts as the most popular ones for polyolefins production [13, 14]. Due to the crucial importance of TiCl₄ catalyst in the synthesis and polymerization of polyolefin materials, the present work reviews the literature and presents the developments made in processing of ilmenite and rutile ores for the extraction of TiCl₄. It was aimed to give the major processes currently utilized for extraction and recovery of TiCl₄. The different methods proposed and developed to the date are reviewed.

TITANIUM EXTRACTION

Titanium ores

Titanium ores minerals are distributed all over the world. Rutile (TiO₂) and ilmenite (FeO.TiO₂) are two principal ores of titanium, which have metallic luster [1]. Rutile is a reddish-brown colored substance and the chief source of titanium, with hardness of 6-6.5 (in Mohs' scale) and a specific gravity of 4.18-4.25 [1, 15]. It is usually composed of up to 10% iron in the form of iron oxides. Naturally, rutile is usually dark-red or black, nevertheless, it can be found in other colors such as brown, yellow, green or violet. Rutile ore grade gives a yellow or pale-brown streak. For production of titanium, there are diverse types of rutile with larger amounts of iron, but they are not as favorable as the high-purity rutile [1]. Some minor ores include nigrine, ilmenorutile, seyenite, brookite, and anatase [1, 15].

The second important ore of titanium is ilmenite with theoretically 52.7% TiO₂ [1, 15]. However, the il-

menite minerals vary in TiO_2 content from 40 to 60%. Its hardness is about 5-6 (in Mohs' scale) and its specific gravity is 4.3-5.5 [15]. The color is usually black and gives a brownish-red to black streak. Ilmenite has a slight magnetic property. The composition of the mineral varies in terms of the limits of the following four minerals: crichtonite, geikielite, pyrophanite and senaite [1, 15]. The chemical composition of ilmenite ores for the main sources in the world are presented in Table 1 [1].

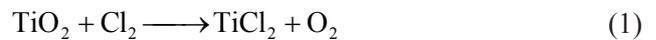
Extraction process

Generally, rutile and ilmenite ores are treated separately. The principal method in titanium ores treatment is to produce a concentrate of mineral via conventional mineral beneficiation techniques [1, 15]. The ore is first crushed and ground. Then, magnetic separation is used for iron (magnetite) removal. For separation of silica, silicate and aluminate the gravity (Hymphrey spiral, tabling, filtering, drying, etc.) and flotation methods are used. The zircon and other ingredients are usually removed by electrostatic separation, and high-grade TiO_2 can be obtained from the beach sand [1]. Concentrates can be treated by different ways depending on the request, either pure titanium dioxide as pigment or metallic titanium (Figure 1).

Extraction from rutile

Owing to its high titanium content and low levels of impurities, natural rutile has been used as preferred feedstock for the production of titanium dioxide pig-

ment. Figure 2 depicts the production of titanium from rutile [16]. There are four important processes developed for the manufacture of titanium from natural rutile [1, 17-69]: (1) the iodide process [1, 25-38, 66, 67], (2) the Kroll process [1, 47, 48], (3) a continuous process developed at Batelle Memorial Institute [39-46], and (4) electrowinning of titanium. Kroll process is currently used for commercial production of titanium [1, 47, 48], and involves three major steps. In the first step, the chlorine gas (Cl_2) is used for chlorination of titanium ore in a carbon-saturated atmosphere, which is then followed by the purification of titanium chloride (TiCl_4) produced during the chlorination. In the second step, the TiCl_4 is reduced by a magnesium (Mg) reductant which produces sponge of titanium and magnesium chloride (MgCl_2) as products. The third step includes the recovery of MgCl_2 and its conversion to Mg and Cl_2 by molten salt electrolysis. These products are then returned to the chlorination and reduction processes, respectively. Efficient circulation of Mg and Cl_2 is a characteristic of Kroll process [1, 47, 48]:



The free-energy change is usually negative [1]. However, the addition of carbon to the titanium oxide promotes the reaction in the forward direction [1]:



Table 1. Chemical composition of ilmenite ores (in %) [1].

Composition	North and South America			Europe			Asia		Africa		Australia	
	U.S.A	Canada	Brazil	Norway	U.S.S.R	Portugal	India	Malaysia	Senegal	Sierra Leone	West Coast	East Coast
TiO_2	43-50	35-73	48-61	37-44	44	52.2	52.2	51-54	54-56	42.3	52-55	45-55
FeO	35-39	31-33	26-27	32-36	32.4	42.1	9-26	35-38	7-14	28.0	20-23	28-33
Fe_2O_3	1.6-13.8	20.0	14-15	11-13	16.9	-	12-27	3-6	28-30	25.0	15-19	1.5-5
SiO_2	1.4-3.0	0.8-4.0	1.4	0.6-3	1.84	0.27	0.9-1.4	0.5-1.11	0.9-1.3	-	1.41	1.20
Al_2O_3	0.2-1.21	1.05-1.7	0.25	0.85-1.8	0.2	0.29	1.0-1.11	1.09	0.50	-	0.25	1.0
P_2O_5	0.07-1.01	Trace	-	0.01-0.2	0.15	0.03	0.17-0.26	0.09	0.14-0.15	-	0.15	-
ZrO_2	0.05-0.55	-	0.25-0.3	0.3-1	-	-	0.60-2.1	-	2.37	-	0.08	-
MgO	0.6-2.35	1.0-2.0	0.3-0.35	1.6-3	2.76	0.03	0.65-1.01	0.21	1.90	-	0.01	-
MnO	0.1-0.52	0.03-0.04	0.1-0.2	0.2-0.3	0.72	5	0.40-0.48	3.5	1.32	-	1.44	1.25-1.5
V_2O_5	0.05-0.27	0.2-0.36	0.06-0.2	0.2-0.3	0.09	0.09	0.03-0.26	0.04	0.27	0.38	0.13	0.23-1.0
Cr_2O_3	0.02-0.27	0.15	0.1-0.5	0.03-0.07	0.02	0.02	0.03-0.26	0.02	0.23	Trace	0.03	1.84-4.9
Rare earth oxide	0.08	0.07	0.08	0.068	0.07	-	0.08	0.079	0.06	-	0.089	0.12

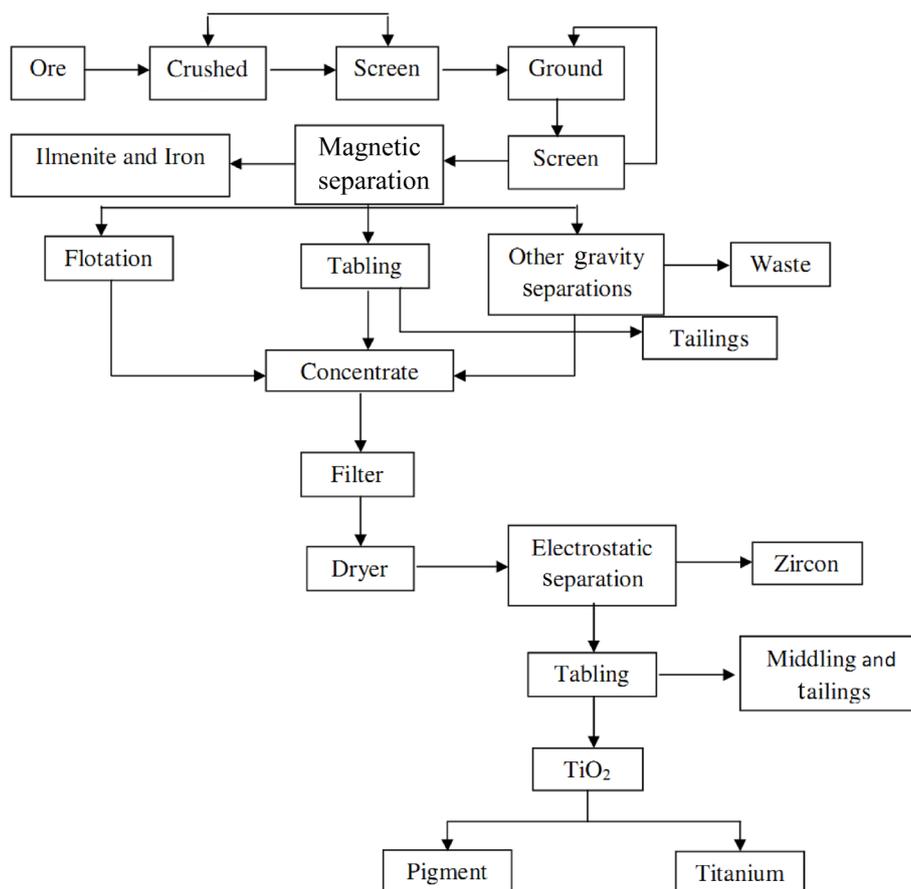


Figure 1. Processing flow sheet of rutile [1].

The reaction is positive. The overall free-energy change and efficiency of the process are controlled by the negative free-energy of formation of carbon monoxide [1]. The conversion of TiO₂ to TiCl₄ upon the reaction with C₁₂/C takes place in two stages: 50% of conversion is by the external reaction in the following form:



and 50% is converted through the internal reaction:



The C₁₂/C free-energy formation controls the sign and magnitude of the free-energy changes. TiCl₄ is a colorless liquid boiling at 136°C and is present in vapor form at the working temperature [1-4]. The liquid TiCl₄ is reduced through the following reaction:



Although Kroll process is the leading process in the field of titanium production, it suffers from being a batch-type process [1, 47, 48]. The ore contains impurities such as iron (Fe) and a substantial extent of chloride wastes, such as iron chlorides (FeCl_x, x = 2, 3), therefore, the chlorination process is preferred.

Extraction from ilmenite ore

Extensive ilmenite ores are found in various parts of the world (Table 1) and significant attention has been paid to remove the different impurities such as iron, chromium, vanadium, etc in order to upgrade these deposits and to obtain synthetic rutile (TiO₂). The latter is then used for pigment and a source of titanium tetrachloride for production of titanium metal either by Kroll process or by electrolysis [42]. The ilmenite ores are usually composed of 40-60% TiO₂ and iron oxide as the other major component. The two oxides are combined with each other to form a chemical compound with a spinel form [1, 42]. Upgrading

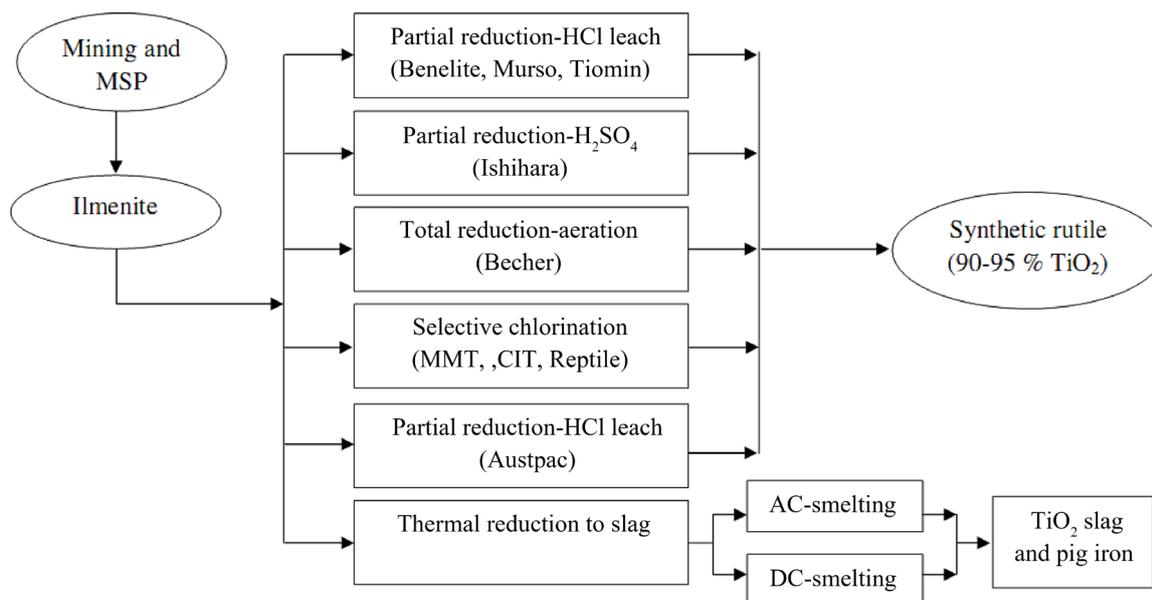


Figure 2. Various technologies (commercial and development) available for upgrading ilmenite [70, 71].

the mineral to rutile before being utilized as TiO_2 is of a vital importance. No applicable physical method is proposed to separate Fe from TiO_2 in ilmenite. A chemical attack is necessary for upgrading [1, 42]. The major processes which are currently used for beneficiation are as follows:

- Smelting with coal or coke in an electric furnace [1, 18, 19, 33, 59, 64, 65].
- Selective chlorination of ilmenite by means of hydrochloric acid or combined chlorine and carbon monoxide operation at high temperatures and pressures [1, 17, 20, 25, 31, 32, 36, 43, 50, 67, 56, 62, 63, 65].
- Sulfidization of ilmenite by H_2SO_4 , H_2S , sodium sulfide with carbon or sulfur vapor at elevated temperatures under pressure [1, 37, 38].
- Reducing iron oxide with a catalyst in the solid-state and subsequent extraction of the oxide in the form of slurry [1, 22, 23].

Commercial processes for upgrading ilmenite include electro-smelting for production of titania-rich slag and the synthetic rutile process, which involves leaching of the iron fraction. Various commercial and developing technologies are available for upgrading of ilmenite (Figure 2) [70, 71].

Ilmenite reduction via solid-state reaction

Titania (TiO_2) as a slag is produced by smelting ilmenite

with coke in an electric furnace. Numerous papers have been published about the commercial technique of slag preparation [1, 18, 19, 59, 64, 65]. However, the U.S Bureau of Mines has proposed a procedure for producing synthetic rutile from ilmenite [33]. A schematic chart for production of titania-rich slag for obtaining synthetic rutile is shown in Figure 3. First, the ilmenite is reduced by carbon (coke or coal) in an electric furnace to obtain pig iron and titania-enriched slag [33]. A glassy slag is formed by utilizing phosphorous pentoxide as a flux. The major impurities such as oxides of Fe, Al, Mg, Mn, Ca and Si are dissolved in the slag. The rutile (TiO_2) crystals with the size of 5-150 microns formed in slag are heated to 800-1550°C. However, TiO_2 crystals of highest purity are formed above 1300°C. The crystals of TiO_2 generated at 800°C had the size of 5 microns. Temperature increase up to 1500°C gave rise to an increase in the rutile crystals' size to 150 microns. These crystals were large enough to be recovered from the slag. The slag was crushed and ground to 100-325 mesh to obtain TiO_2 crystals [1, 33]. To dissolve the glassy slag, the ground mass was treated with 8.5% phosphoric acid solution at 50°C. The TiO_2 crystals obtained from leached slag were removed by tabling. The TiO_2 content was 94.4-96.8%, whereas the recovered titanium was 77-88%. The ground slag's particle size had an important role in leaching. Fine grinding (325-mesh

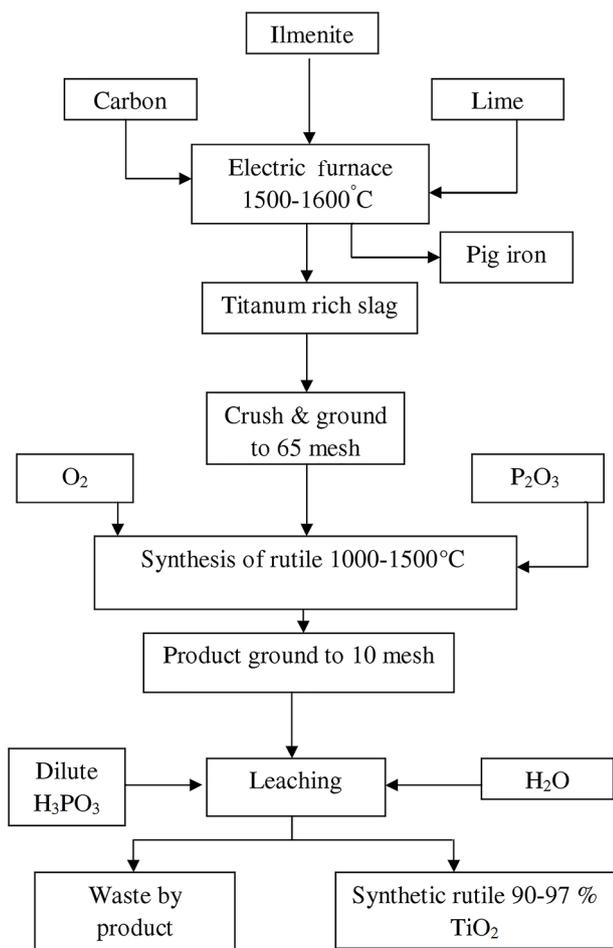
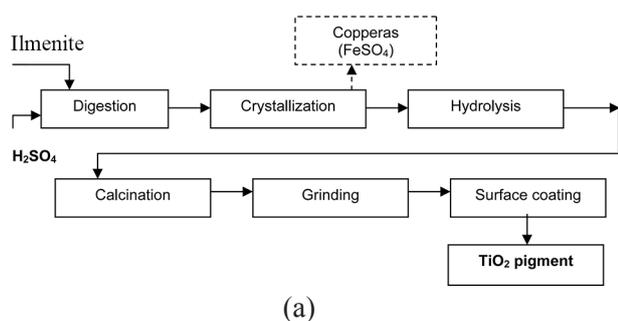


Figure 3. Production of synthetic rutile from ilmenite [1].

particle size) reduced the recovery of TiO₂. Purity of synthetic rutile concentrates was controlled by temperatures of P₂O₅ fluxing. TiO₂ content of the slag increased as the fluxing temperatures were increased. Fluxing could be performed at 1400°C, however, at 1500°C the size of rutile crystals increased. The efficiency of this method for recovering synthetic rutile from ilmenite was more than 90% [33].

A large number of investigations have been per-



(a)

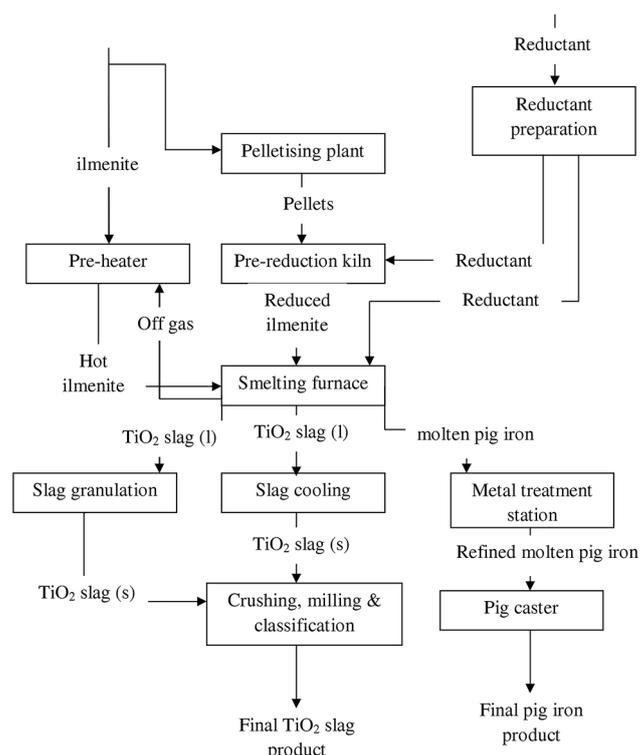
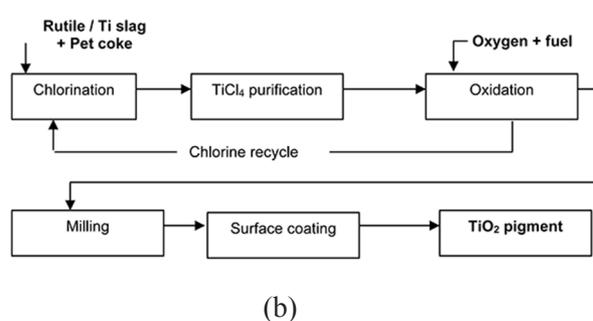


Figure 4. Ilmenite smelting [1, 70].

formed successfully on a laboratory scale for iron reduction from ilmenite. These methods include the use of either solid or gaseous reductants such as carbon, hydrogen, carbon monoxide or mixtures of hydrogen and carbon monoxide [1, 69].

The feedstock beneficiation industry considers the preparation of beneficiated products such as synthetic rutile, titanium slag and upgraded slag. The field is frequently dealing with the supply of titanium feedstocks in order to produce TiO₂ pigment [72].

Two commercial processes used for production of TiO₂ pigment are sulfate and chloride processes [72]. The chloride process is the prevalent process as it generates superior pigment with considerably fewer



(b)

Figure 5. TiO₂ manufacturing by different processes. (a) Sulphate process, and (b) Chloride process [72].

wastes. Simplified flow charts, given in Figures 5a and 5b, illustrate both processing routes for TiO_2 pigment production [72].

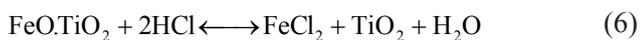
Ilmenite chlorination

Selective removal of iron from ilmenite through chlorination process has been performed by numerous researchers [1, 17, 23, 25, 31, 32, 36, 43, 50, 55-63]. Iron has been removed by the following methods:

- (1) Direct leaching of ilmenite by hydrochloric acid [1, 17, 55, 63] or
- (2) Selective chlorination with C and CO at 500-800°C which gives rise to a product containing 55-90% TiO_2 [1, 50, 55].

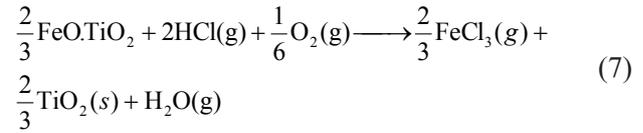
The chlorination of ilmenite in a fluidized-bed reactor using a mixture of Cl_2 , CO and CO_2 at 800-1100°C has been investigated by a number of workers [25, 31, 32, 43, 56]. Doraiswamy et al. [31] extracted 97% of iron with 1% TiO_2 loss using a mixture of CO- Cl_2 ratio of 1.6 at 900°C. Dunn [32] prepared an artificial rutile containing 97-98% TiO_2 having just 0.7% iron at 900-1000°C by applying a CO- Cl_2 mixture. Chlorination at elevated temperatures produced TiCl_4 . A continuous chlorinating process of iron oxides at lower temperatures 800-950°C and of titanium at 1100°C in the presence of a mixture of CO- Cl_2 was developed by Frey [36]. Bergholm [25] prepared chlorinated ilmenite using a CO- Cl_2 - CO_2 mixture at 900°C. The oxidation process was applied to the produced iron chloride, and chlorine was regenerated for recirculation. A two-stage fluidized-bed reactor was used by Hughes and Arkless [43]. The treatment of ilmenite with a CO- Cl_2 mixture at 800°C was performed in the first reactor, resulting in the formation of iron-chloride vapor from iron oxide. On the second bed, the vapor was passed through and oxidized to ferric oxide, regenerating chlorine.

The following reaction shows the direct chlorination of ilmenite with hydrogen chloride gas:



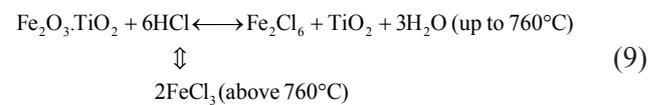
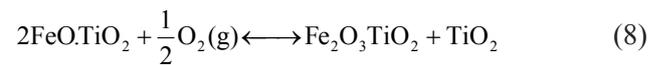
The generation of FeCl_2 , a liquid of low volatility, leads to some difficulty in the upgrading process. However, in the presence of oxygen or air FeCl_2 turns into FeCl_3 which has a high vapor-pressure, and re-

moves most of the iron from the rutile [1, 46]. The reaction can be represented as follows:



The ferric chloride vapor is produced by this reaction and the chlorine can be regenerated.

The research conducted on Kerala beach sand [62] for upgrading ilmenite demonstrated that ilmenite chlorination at 800°C by hydrogen-chloride gas alone resulted in the removal of most of the impurities which yielded a rutile product. Utilizing air-HCl or air- Cl_2 gas mixtures gave rise to vanadium removal by 99% and 40-50% of chromium removal from ilmenite and a product with 95-97% TiO_2 . A flow diagram of chlorination of ilmenite upon the action of air or O_2 is displayed in Figure 6.



Rabie et al. [56] successfully upgraded ilmenite upon the action of a CO- Cl_2 gas mixture within a fluidized bed reactor at 700-1000°C. The effects of CO- Cl_2 ratio, concentrate particle size, and temperature were studied. The chlorination process increased with increasing temperature, particle size reduction and in-

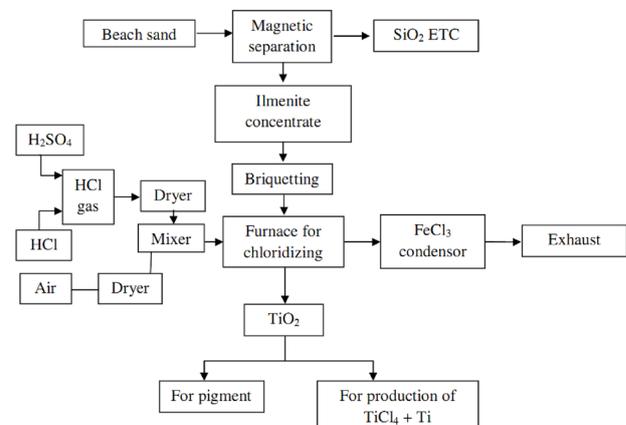
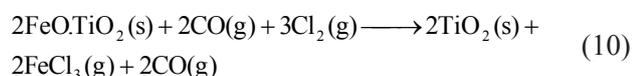


Figure 6. Schematic flow diagram showing chlorination of ilmenite in the presence of an air-HCl mixture [1].

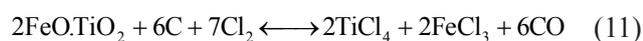
creasing CO-Cl₂ ratio at about 1.3-1.4. The iron was removed in the form of ferric-chloride vapor which leaved a titania-enriched residue. The related reaction is given below:



No iron and manganese were present in the product but chromium and vanadium were only partly removed. The schematic chart of chlorination within a fluidized bed is depicted in Figure 7.

COMMERCIAL PRODUCTION OF TITANIUM TETRACHLORIDE

From the preceding discussions, it comes out that selective chlorination upgrades of ilmenite can be employed at a satisfactory level for subsequent use for conversion of TiO₂ removal to TiCl₄ removal [1, 66-78]. In a patent by DuPont [1], TiCl₄ was prepared from ilmenite via total chlorination at 850-1050°C:



Commercial TiCl₄ is produced by fluidized bed chlorination of rutile or titanium feedstock using carbon as reducing agent. The process is performed at 1000–1050°C and the chlorination of titaniferous ores/slugs is carried out by chlorine gas. In the case of rutile, the chlorination process may be represented by the following reactions:

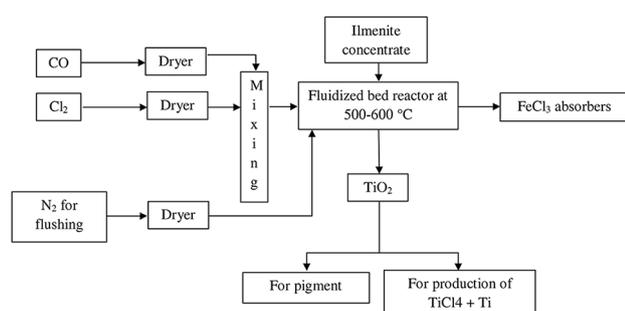
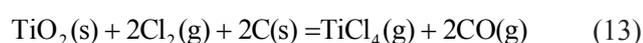
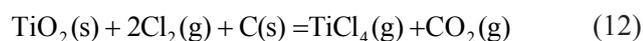


Figure 7. Schematic flow diagram showing chlorination of ilmenite in fluidized bed [1].



Reactions 12 and 13 are exothermic whereas reaction 14 is endothermic.

The produced metal chlorides are condensed in a cyclone separator. The metal chlorides of low boiling point such as TiCl₄ are condensed down the line using chilled condensers. The liquid TiCl₄ is composed of impurities that are usually removed by distillation [1].

At the beginning of the process, the reactor and the raw materials are heated by using coal/coke and air/oxygen. At the temperatures near 1025°C, the Cl₂ gas replaces air and reacts with the reduced metal oxides. The chlorinator temperature is usually kept between 1000°C and 1050°C. The gaseous mixtures of metal chlorides leave the chlorinator. Metal chlorides with high boiling points like iron chloride condense at 150°C to 200°C. Iron chloride precipitates out in the form of solid powder and settles in the condenser. The gaseous mixture of TiCl₄, CO, CO₂, N₂ and unreacted Cl₂ pass further and enter the shell and tube condenser. TiCl₄ condenses out in the condenser where is maintained at subzero temperatures. The non-condensable gases such as CO₂, CO, unreacted Cl₂ and N₂ leave the condenser and are scrubbed in a caustic scrubber. The process of extraction and purification of TiCl₄ is a highly complex process, and involves chemical treatments and distillation operations.

Bergholm [25] studied the chlorination of titania feedstocks with carbon and CO and found that the presence of carbon significantly improved the reaction rate.

Dunn [32] investigated the chlorination of rutile with carbon and carbon monoxide and reported that small amounts of CO did not affect the reaction rate significantly. However, CO in large amounts tended to have a sharp negative effect on the reaction kinetics. The effect became more serious as the carbon particle size decreased and the authors suggested that the CO was absorbed onto the carbon surface which, in turn, did not allow the other reagents to reach the surface. Dunn [32] also proposed a mechanism for the chlorination of TiO₂ in the presence of C and studied the effects of temperature, TiCl₄, Cl₂ concentration and titania and carbon surface area on the chlorination reaction rate. The obtained results were as follows:

- (1) Titanium tetrachloride concentration helped to chlorinate titania, but the chlorine concentration had a little effect on the reaction rate.
- (2) The amount of carbon and its geometrical surface area were linearly related to the reaction rate for concentrations up to about 20wt% above which the reaction rate became progressively less dependent on the carbon surface area.
- (3) The partial pressure of chlorine was only a minor variable in determining the reaction rate.
- (4) The presence of $TiCl_4$ catalyzed the reaction and greatly increased the reaction rate while simultaneously a decrease in chlorine content did not significantly affect the rate.
- (5) Large internal surface area and voids did not improve the reaction rate [32]. The chlorination rates for natural rutile and beneficiated ilmenite in the carbon/chlorine reaction were substantially the same; although their chlorination rates in the carbon monoxide/chlorine reaction differed by an order of magnitude.
- (6) Commercial practice confirmed that the use of inactive carbons such as petroleum cokes did not favor the conversion of CO_2 to CO , a reaction that occurred with a negligible rate at these temperatures and in the presence of chlorine and chlorides [32].

Barin and Schuler [75] studied the impact of solid carbon on the TiO_2 chlorination in the presence of Cl_2 and $CO-CO_2-Cl_2$ gas mixtures. They used discs of rutile and graphite. In the presence of carbon, the rate of chlorination of TiO_2 was observed to be 40 to 50 times faster than that without carbon. The acceleration of the chlorination rate was attributed to the kinetic effect of solid carbon and took place even when TiO_2 and C were separated by the gas phase [75]. Barin and Schuler [75] found that the initial rate of reaction was greatest for TiO_2 -C contact and decreased with increasing TiO_2 -C initial separation, l_0 . For those cases in which $l_0 \leq 30 \mu m$, the reaction rate at first decreased and then, after an initial reaction time period, reached a constant value [75]. Due to removal of TiO_2 and C by the reaction, the separation l_0 attained a certain value denoted as the critical separation, L . For $l_0 > L$ no kinetic influence of carbon was observed on the TiO_2 chlorination, and the chlorination rate was the same

as in the absence of carbon. In these experiments, L was found to be approximately $40 \mu m$. According to these observations, the authors suggested that activated chlorine species were formed on the carbon surface and desorbed into the gas phase [75]. If these species do not recombine to form stable molecules they reach the TiO_2 surface and there react [75]. The acceleration of the TiO_2 chlorination with decreasing TiO_2 -C separation was attributed to the restricted range of the active gas species. Chlorination experiments conducted in a closed reaction tube demonstrated that the rate increase due to solid carbon was approximately inversely proportional to the total pressure of the gas phase at constant temperature, as was the case for the mean free path of the gas molecules [75].

In the case of impact of solid carbon, Robson et al., Black-Wood and Cullis, and Kol'tsov et al. demonstrated that Cl_2 was chemisorbed at active sites on the carbon surface and formed C-Cl complexes which, according to Kol'tsov et al., were subsequently dissociated and desorbed into the gas phase above 673 K [75].

Studies made by Vyachkeleva and Ketov and by Vasyutinskii and Berezhko on the Cl_2 -Ni, and Cl_2 -Ti reactions in the presence of solid carbon also showed that activated chlorine species were generated on the carbon surface [75]. These species which were in the form of Cl atoms or Cl containing radicals or activated Cl_x molecules accelerated the chlorination of the metals under investigation. Vasyutinskii and Berezhko proposed that active chlorine molecules formed on the carbon surface move towards the Ti-C interface where they react to form titanium chloride [75].

Bonsack and Schneider [76] chlorinated a low-grade titaniferous slag over the temperature range of 550-1100°C and prepared titanium tetrachloride. The carbon reactivity employed for the chlorination process had a strong effect on the chlorination rates. The use of a lignitic char increased chlorination rates, whereas petroleum lowered the reaction rates [76]. Utilizing bituminous coke resulted in intermediate chlorination rates. Above 700°C, the mass transfer was a key parameter controlling the chlorination reaction rate. Chlorine was completely reacted in 2.5 s at 1100°C using slag/char feedstocks of 7-mm median particle diameter, with 10 to 25wt% excess of carbon and 15

to 20wt% excess of slag [76].

Den Hoed and Nell [77] pointed out increased degree of chlorination with increasing carbon content, but levels off at 15% carbon. At carbon levels lower than 15wt%, availability of carbon was the rate limiting step. However, when the stoichiometric condition was exceeded the reaction continued [77]. Dunn [73, 74] found that reaction rate increased linearly with carbon content up to 25wt%.

Den Hoed and Nell [77] also investigated the impact of CO on the reaction rate with carbon in the bed. They showed that the absence of CO only slightly decreased the reaction rate. According to Den Hoed and Nell [77], satisfactory rates of chlorination were attained at 1000°C in a vigorously fluidized bed containing 20% solid carbon and 35% Cl₂. They also compared the chlorination results of coke with those of more reactive carbons such as carbon black and activated carbon and found that the reductant reactivity had a small effect on the reaction kinetics.

Feedstock requirements for the chloride process

The feedstock requirements are dependent on the chlorination and purification processes and their ability to dispose of the waste streams produced from the process. It is estimated that about thirteen kilograms less waste is generated for every percentage point increase in TiO₂ feedstock [78].

The feedstock requirements for chlorination process are as follows [70, 71]:

- CaO and MgO content of the feedstock is normally restricted to 0.2 and 1.2%, respectively, because these substances create chlorides (CaCl₂ and MgCl₂) of high boiling points (Figure 8) which can liquefy in the chlorinator and cause operational problems such as stickiness and defluidization. CaO is also problematic because it reduces TiO₂ chlorination by forming CaO.TiO₂ [79].
- Limitations have been imposed on the SiO₂ content. This is because certain forms of silica (i.e. alpha quartz) do not react in the chlorinator, but merely accumulate on the bed and must be periodically removed. The more SiO₂, the more frequent the bed drains and the greater the plant down-times are. SiO₂ also coats the TiO₂ particles and prevents the reaction with chlorine [80].

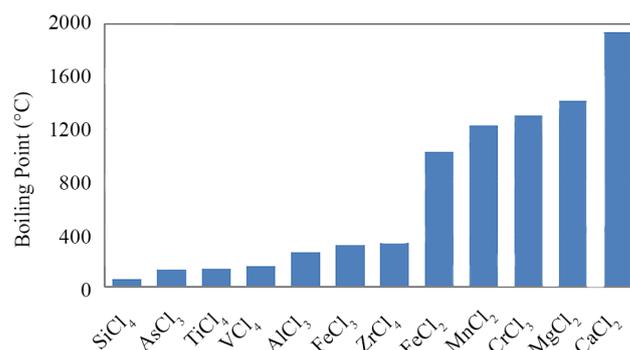


Figure 8. Boiling points of metal chlorides [70].

- Low FeO is favorable in order to minimize waste generation (i.e. iron chlorides) and chlorine consumption.
- Arsenic contents must be low. Although, arsenic chlorinates readily, it is difficult to separate from TiCl₄ because their boiling points are nearly the same (Figure 8).
- Low levels of uranium and thorium are required for both sulfate and chloride routes due to environmental considerations.
- Aluminum is undesirable because compared to other metals it consumes chlorine at a higher rate. Aluminum trichloride is soluble in TiCl₄ and causes corrosion problems in the plant because it attacks carbon steel.
- The feedstock is required to have adequate grain size and bulk density to minimize blow over in the chlorinator. Slag and rutile have an advantage over synthetic rutile since the latter has a porous structure [80]. Coarser particles are required for chloride process because, this decreases entrainment and blow over.

Selective chlorination

During the chlorination process of ilmenite, both iron and titanium are usually chlorinated under the action of reductant material. Efforts have been made to prevent the complete chlorination through adding a controlled amount of reducing agents or via a proper selection of a chlorinating gas. The two-stage process for production of TiCl₄ involves the chemical beneficiation of ilmenite by selective chlorination of its iron oxides which yields a titanium-rich residue in the first step which is chlorinated to produce TiCl₄ in the second step. Research works on this subject dealt with

chlorination in a conventional boat in tube setup or a static bed using a briquetted charge [80, 81]. These processes had the common difficulties including channeling, sintering, hanging, stratification and poor temperature distribution. In addition, chlorine can be consumed to some extent by the binding agent, and the briquettes have a propensity to disintegrate in the reactor with the loss of binder. These problems can be largely addressed through utilization of a fluidized bed. Numerous publications on the fluidized bed chlorination of ilmenite reveal chlorine as a fluidizing gas with or without C, CO, CCl_4 , and TiCl_4 , etc [81]. A very high temperature for chlorination reaction is usually required when chlorine gas is used. It was claimed that the usage of a selective gaseous chlorinating agent such as hydrogenchloride gas could be an attractive alternative owing to the following reasons [81]:

- Preferred chlorination via HCl gives rise to an uncontaminated product
- Selective chlorination by using HCl can be performed at significantly lower temperature (900°C) than the temperature needed for chlorine alone (1200°C)
- If HCl is synthesized in the reactor itself, engineering difficulties of attaining high temperatures can be solved
- Gaseous substances, such as H_2 and Cl_2 , are inexpensive by-products of the caustic chlorine industry
- Process economics is likely to favor downgrading of H_2 and Cl_2 to HCl.

The main selective reaction of oxidized ilmenite around 800°C is [81]:



Lakshmanan et al. [82] in their kinetic study of ilmenite chlorination with CO and Cl_2 mixture in a fluidized bed concluded that the surface reaction is the slowest rate controlling step. Dunn [73, 74] studied chlorination of TiO_2 bearing materials (including ilmenite) by CO and Cl_2 and found that the bed weight loss, either fluidized or packed, versus time of reaction resulted in a straight line plot. Similar mechanism is likely to hold when HCl is used as the chlorinating agent. AthaVale and Altekar [81] studied the effect of process variables and reaction mechanism in both batch and continuous fluidized bed reactors. A 9.5 kcal per

mole activation energy was obtained for the kinetic and geometric constants at $600\text{-}850^\circ\text{C}$. Various combinations of hold up and solid feed rates revealed that higher iron oxide conversions were obtained either via reduction of the feeding rate of solid or through increasing the holdup of the column. It was concluded that the process should be carried out in not more than three stages.

Deventer [83] reported selective chlorination of ilmenite. It was claimed that the ilmenite selective chlorination was not possible under equilibrium conditions at 1200 K and 1 atm from the thermodynamics point of view in the presence of carbon. Considering the occurring this process in practice implied the requirement for non-equilibrium conditions [83]. Batch experiments carried out between 915 and 970°C in a horizontal tube furnace revealed that the selective chlorination kinetics were controlled by diffusion of iron through a product layer of TiO_2 which was formed from the outside of a particle. An about 4% titanium weight loss happened in the form of volatiles during chlorination process. Chlorination easily removed calcium and manganese impurities to a lesser extent, with no removal of aluminum, niobium and magnesium [83]. A partial removal of vanadium and silicon happened. Matsuoka and Okabe [84] used selective chlorination in the Ti-Fe-O-Cl system for iron removal from titanium ore. They used the thermodynamic analysis of the chlorination process prior to the experimental work [84]. The iron in the titanium ore was selectively chlorinated via reacting low-grade titanium ore (ilmenite) and metal chloride (MCl_x , $\text{M}=\text{Mg}$, Ca, etc.) at 1100 K under nitrogen atmosphere. The result of this reaction was a low-iron titanium ore and iron chloride (FeCl_x) [84]. The reaction between FeCl_x and metallic titanium at 1100 K under an argon atmosphere recovered chlorine as TiCl_4 .

Burger et al. [78] used value-in-use calculations to show that the production cost of high-grade slag is more than the savings realized at the pigment plant, based on certain cost and plant assumptions.

Zheng and Okabe [85] carried out a study on the removal of iron from titanium ore by selective chlorination by means of metal chlorides (MCl_x , $\text{M}=\text{Mg}$, Ca, etc.). A schematic representation of the plant used for the selective chlorination of titanium ore is depicted in

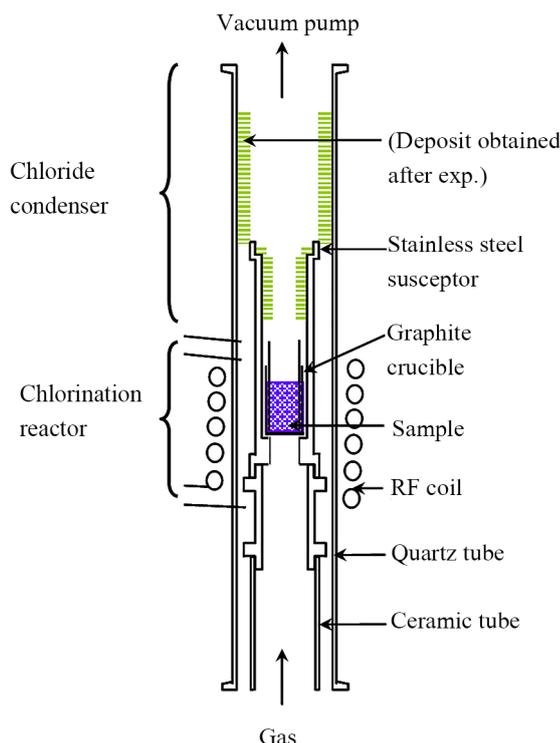
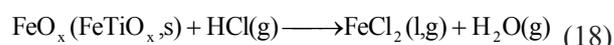
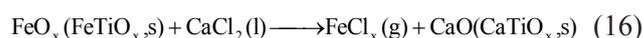


Figure 9. Experimental apparatus for the selective chlorination of titanium ore using MgCl₂ or CaCl₂ + H₂O as a chlorine source [85].

Figure 9 [85]. The titanium ore (ilmenite) reacted with metal chlorides (and water vapor) in a graphite crucible operating at 1023-1293 K. After removing iron through selective chlorination, a low iron content titanium ore was achieved. The iron chloride gas (FeCl_x)

by-product was recovered through condensation process. These researchers applied the preform reduction process (PRP) based on the calciothermic reduction of titanium oxide contained in the feed preform to directly obtain titanium powder from the recovered titanium ore [85]. Metallic titanium powder with purity higher than 99% was achieved upon the reduction of preform containing titanium ore by calcium vapor at 1273 K.

The selective chlorination mechanism was explained by the following reactions:



For direct removal of iron from ilmenite, Kang and Okabe [86] investigated selective chlorination process using magnesium chloride (MgCl₂) as chlorinating agent. HCl gas produced from the MgCl₂/titanium ore mixture reacted with the iron present in the titanium ore placed in the other crucible to produce TiO₂ [86]. The iron present in the titanium ore of the titanium ore/MgCl₂ mixture reacted with MgCl₂, and MgTiO₃ and MgO were achieved. Upon the chlorination process, 97% TiO₂ was obtained directly in a single step

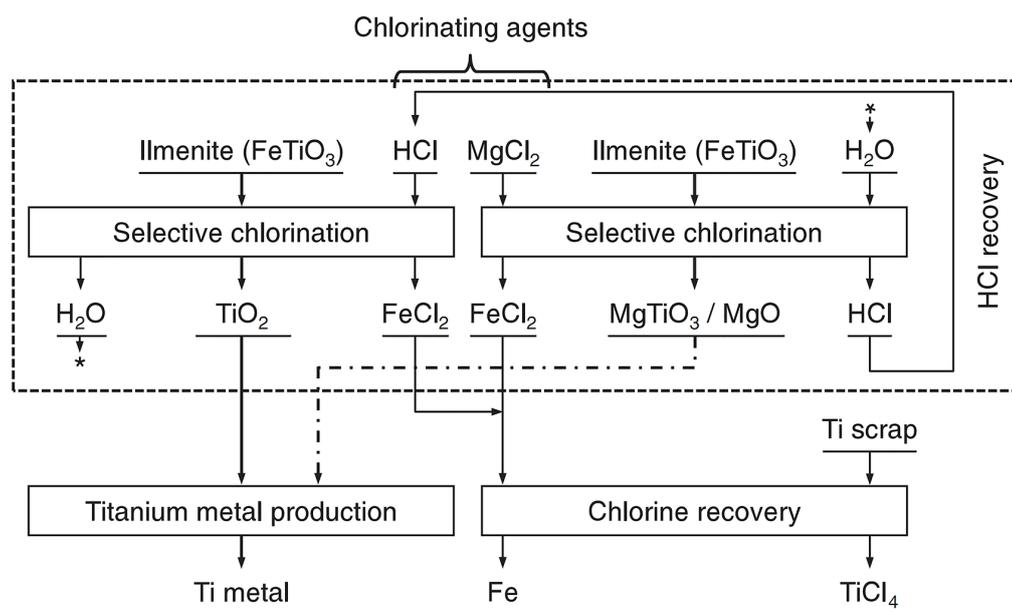


Figure 10. Flow diagram of the selective chlorination process using magnesium chloride [86].

from the low-grade titanium ore with 51% TiO_2 [86]. Chart of the selective chlorination process is shown in Kang and Okabe [87] investigated a selective chlorination process using calcium chloride (CaCl_2) as the chlorine source. Iron in the titanium ore was selectively removed in the form of iron chlorides via reaction of the titanium ore in the two crucibles with either HCl produced from CaCl_2 or CaCl_2 itself at 1100 K (827°C) [87]. Titanium dioxide (TiO_2) of about 97% purity was directly obtained via a single step from titanium ore containing 51% TiO_2 . Flow diagram of the selective chlorination process is shown in Figure 11.

Kang and Okabe [88] used carbo-selective-chlorination method using titanium tetrachloride (TiCl_4) as a chlorinating agent for the direct production of high-grade titanium dioxide (TiO_2) from titanium ore (Ti ore). These researchers set Ti ore and carbon powder in a gas-tight quartz tube that was then placed in a horizontal furnace at 1100 K to react with TiCl_4 . Under certain conditions, the iron present in the titanium ore was removed in the form of iron chloride (FeCl_2), and a product with 98% TiO_2 was obtained [88]. Figure 12 shows the process for the Ti smelting according to carbo-selective-chlorination. Kang and Okabe [120] claimed several advantages for the carbo-selective-chlorination using TiCl_4 [88]. According to Figure 12:

- (1) The carbo-selective-chlorination process can read-

ily be adapted into the Kroll process as a large amount of TiCl_4 is circulated in the current Ti smelting process.

- (2) Cl_2 gas can be collected from the chloride wastes produced, because they are produced in a dry form not containing any water.
 - (3) The problems such as chlorine loss and pipe clogging commonly encountered in current chlorination process can be decreased when this process is used for the pretreatment of low-grade TiO_2 feed [88].
 - (4) Production of low amount of acid aqueous waste solution as no concentrated acid is required for removing iron from Ti ore.
 - (5) The mixture of the ore and carbon powder can be supplied directly to the current chlorination process.
 - (6) One can obtain high-grade TiO_2 directly from the low-grade Ti ore through a one step process [88].
- For production of synthetic rutile, Guo et al. [89] upgraded titanium slag containing high Ca and Mg by a process of oxidation-reduction-high gradient magnetic separation-acid leaching. The effects of roasting temperature, time and magnetic field intensity on removal of impurities were investigated. Optimized oxidation condition was found to be 1000°C for 15min. Under this condition the anosovite was converted to rutile

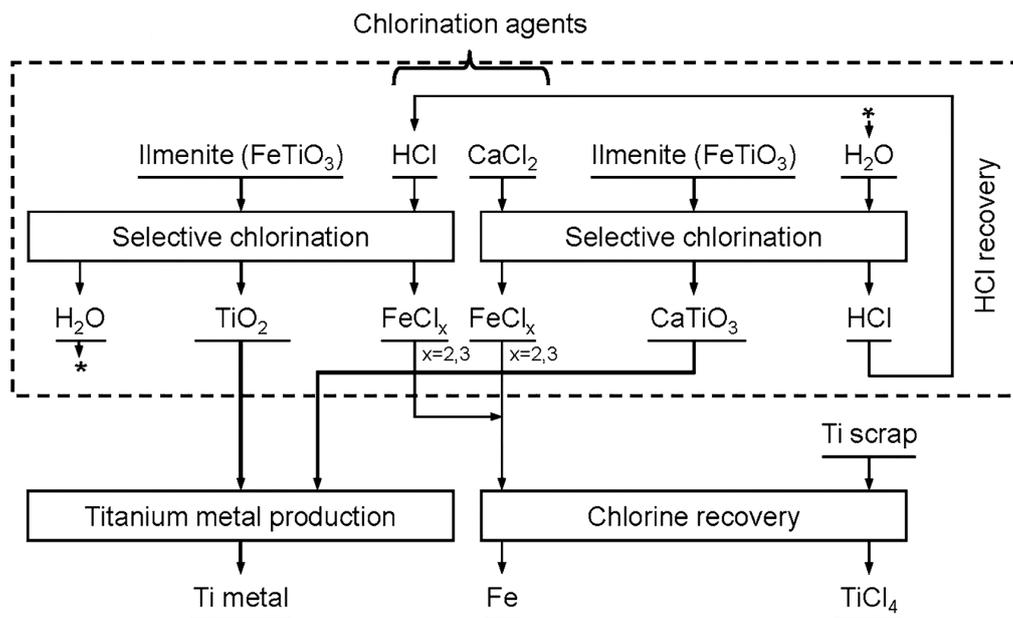


Figure 11. Flow diagram of the selective chlorination process using magnesium chloride/calcium chloride [87].

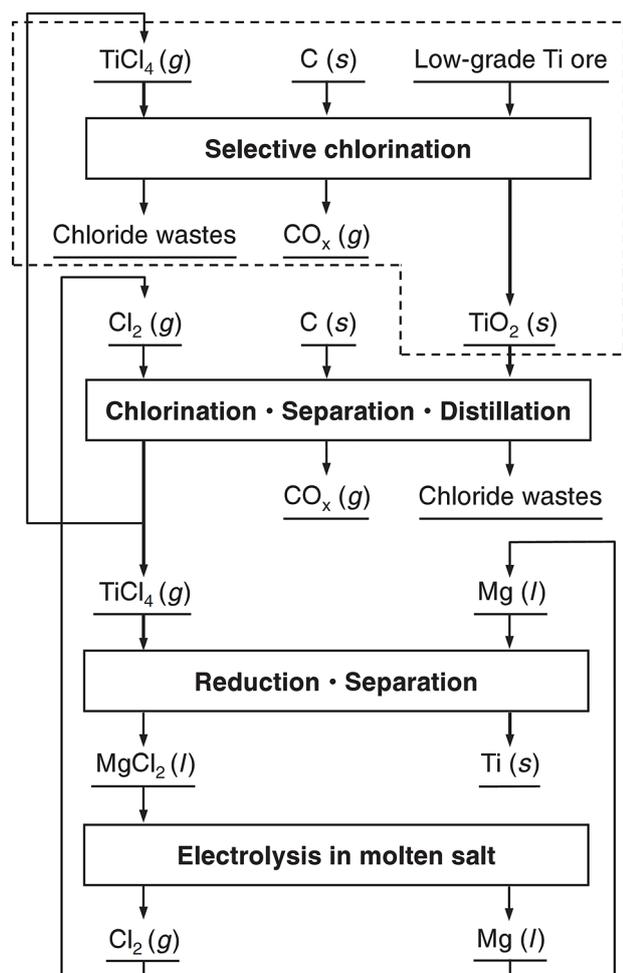


Figure 12. Flow diagram for new titanium smelting adopting the selective chlorination process using titanium tetrachloride [88].

and pseudobrookite, however, it was difficult to remove Mg [89]. After the reduction and acid-leaching of tailings, the grade of TiO₂ products was improved to more than 6.72%.

Yang et al. [90] investigated the process of microwave oxidizing roasting of high titanium slag to produce synthetic rutile. The results showed that the microwave roasting process of high titanium was divided into three stages, FeTi₂O₅, A-TiO₂ and R-TiO₂ as main phases correspondingly. Different dielectric constants of three phases led to a periodic decrease in heating rate of high titanium slag microwave roasting which resulted in the cracks and holes formation on the surface of high titanium slags, promoting the oxidation of high titanium slag [90].

Dmitriev et al. [91] studied the ores and concentrates of the Kachkanarsky deposit of low-titanous

and high-titanous. The reducibility, durability and softening and melting temperatures of metallurgical iron ore raw materials were studied in vitro [91]. The chemical analysis of low titanium and high titanium concentrates led to this conclusion that the chemical composition (vanadium and titan) of high vanadium concentrate of Mainmine of the Gusevogorsky deposit was similar to that of the concentrate of the actually Kachkanarsky deposit [91]. The possibility of processing of such concentrates under the scheme “blast furnace–converter” and scheme “metallization–electrosmelting” was demonstrated [91].

Mechanism, kinetics and modeling

Dunn [73, 74] proposed a mechanism for the high temperature chlorination of titanium bearing minerals:



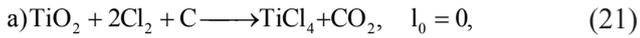
Which accounts for its autocatalytic characteristics. An equilibrium is established at the rutile (titania) surface between titanium tetrachloride and titania which react to form a gaseous moiety composed of oxygen and chlorine gases as a titanium oxychloride [73, 74].



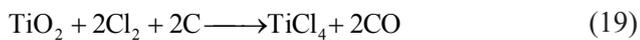
This species is present at a small but significant partial pressure and serves as the transporting species for the titanium and oxygen values to diffuse through the gaseous boundary layer surrounding the rutile surface. The titanium oxychloride is then transported rapidly by eddy diffusion to the gaseous boundary layer surrounding the carbon and diffuses through it to reach the carbon surface where it gives up its oxygen and receives chlorine to convert to titanium tetrachloride and to form carbon oxides [73, 74]. This mechanism implies an autocatalytic role for titanium tetrachloride since the equilibrium will be influenced by the concentration of TiCl₄. It implies further that both carbon and titania surfaces are involved although the internal surfaces are not involved. The exterior surfaces alone are reactive because the rate limiting diffusion is through gas boundary layers which surround and hence are proportional to the boundary layer surface area [73, 74].

Barin and Schuler [75] proposed a kinetic reaction model to provide a quantitative description for the impact of solid carbon on the TiO₂ chlorination in the presence of Cl₂ and CO-CO₂-Cl₂ gas mixtures using rutile and graphite tablets. A schematic diagram is shown in Figure 13.

The overall reactions corresponding to two cases can be formulated as [75]:



The following simplified steps were considered to define the reaction course: Activated chlorine species are formed on the carbon and desorbed into the gas phase. These species diffuse in the gas phase and because of "three particle collisions" they can partly recombine to form stable molecules and are thus deactivated [75]. The activated chlorine species which reach the TiO₂ surface react to form TiCl₄ and O₂. The O₂ molecules diffuse to the carbon surface and react there to produce CO. The overall reaction was given by:



The activated chlorine species were assumed to be chlorine atoms. The molar chlorination rate as a function of the TiO₂-C separation *l* in μm was given by the following reaction:

$$i_{\text{TiO}_2} = 4.4267 \times 10^4 (l + 12)^{-2} \text{ mol/cm}^2 \cdot \text{s}; \quad l(\mu\text{m}) \quad (22)$$

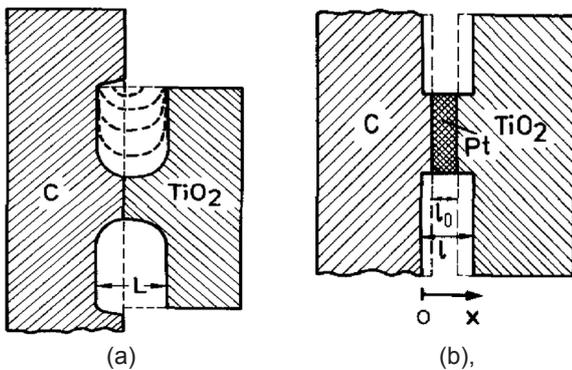
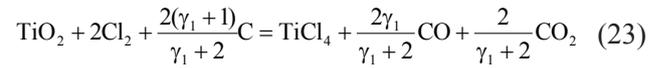


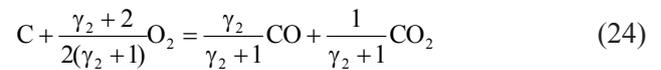
Figure 13. Schematic diagram for the reaction of the tablets with TiO₂-C contact (a) and for given TiO₂-C initial separation (b), *L* represents the maximum separation for influence of carbon [75].

Youn and Park [92] developed a model for fluidized bed chlorination of rutile with coke for production of titanium tetrachloride. The reactions involved in the chlorination of rutile are represented by Eqs. (12)-(14).

Reactions (12) to (14) were combined and expressed by the reaction represented by Eq. (25) [125]:



Where γ_1 is the molar ratio of CO to CO₂ in the product gas formed by Reaction (23). The reaction between coke and oxygen was assumed to be represented by Reaction (24) in a form similar to Reaction (23) [92].



Where γ_2 is the molar ratio of CO to CO₂ in the gas product of Reaction (24). The reaction system was divided into compartments whose heights were adjusted to the bubble size at their levels. Each compartment consisted of an emulsion phase, a cloud phase, and a bubble phase [92]. A schematic diagram is shown in Figure 14.

The gas-solid reactions occurred in the emulsion

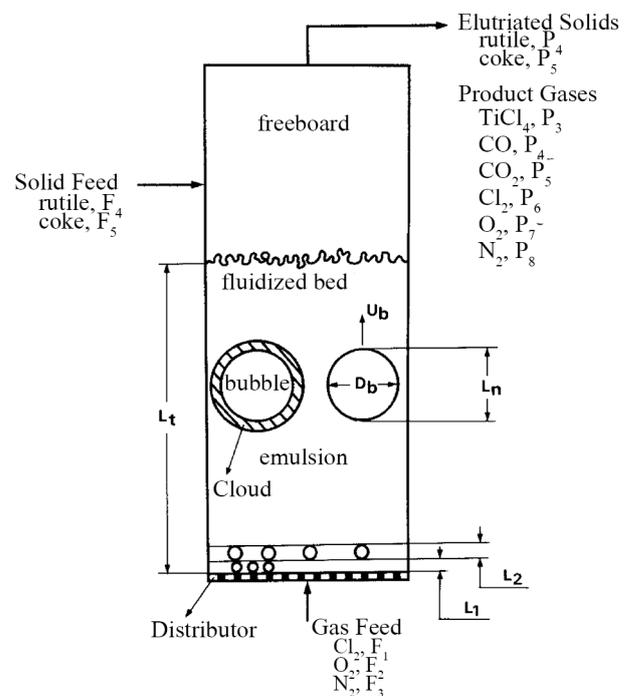


Figure 14. Schematic diagram for the reaction system of the fluidized bed chlorination of rutile [92].

and cloud phases. The following assumptions were made by Youn and Park [92]:

- (1) No resistance against mass transfer was exist between the cloud and bubble phases,
- (2) The voidage within the cloud was the same as that in the emulsion phase.
- (3) For the heat balance, the temperature was uniform throughout the bed and no heat loss occurred from the bed.

According to these assumptions, the mass and heat balances were derived. The model predicted the conversion of chlorine, particle size distribution in the bed, composition of the gas product, and reaction temperature. The bubble assemblage model and the population balance were employed to calculate the reactant gas mass transfer rate from the bubble phase to the emulsion phase and size distribution of particles in the bed, respectively [92]. A good agreement was observed between computed and experimental results. Rhee and Sohn [93] studied the chlorination of ilmenite with CO and proposed that the iron in ilmenite reacted with Cl₂ first and the liberated O₂ was removed by carbon monoxide. They claimed that the reaction proceeded rapidly at first but then slowed down. This has been attributed to the formation of high boiling liquid phases which block the particle pores and thereby prevent reacting of the gases with the particle. Jena et al., [94] chlorinated TiO₂ powder and graphite powder (20–25wt%) and proposed the following chlorination mechanisms:



Morris and Jensen [95] investigated the chlorination process of Australian rutile in a CO-Cl₂ and C – Cl₂ system and proposed empirical equations for these systems. These researchers found that the activation energy of C-Cl₂ system (45.2 kJ/mol) was significantly lower than that of CO system (158 kJ/mol). It was reported that coke was a far better chlorination promoter than CO and at 1000°C the chlorination rate

with carbon was 19 times greater than that with CO [95].

Sohn and Zhou [96] investigated the fluidized bed chlorination of natural rutile in CO-Cl₂ mixtures. A rate equation was determined for the temperature range 950°C – 1150°C.

Sohn and Zhou [97] studied the chlorination kinetics of titania slag with chlorine gas and petroleum coke. A rate equation was established in which the effects of temperature, chlorination partial pressure and initial particle size were accounted. The reaction mechanism for the chlorination of rutile, suggested by these experimental observations, can be presented as follows [97]:



where the prime indicates the number of electrons added to the corresponding titanium defects.

As described in Eq (28), the trapped electrons in the oxygen vacancy may be excited at the high temperature and transferred to the Ti in its normal lattice position. Therefore, the Ti can change from the tetravalent state to the trivalent or divalent state according to Eqs. (29) and (30).

Sohn and Zhou [98] proposed a rate equation for the chlorination of beneficiated ilmenite (i.e. synthetic rutile) in a CO, Cl₂ atmosphere. Since synthetic rutile was more porous than the natural rutile, the reaction kinetics for the two feedstocks were expected to be different. The shrinking core model was not applicable for this feedstock, because the pore diffusion simultaneously occurred with the chemical reaction inside the particle.

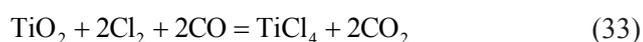
Sohn and Zhou [98] compared the kinetics of beneficiated ilmenite to a previous study of natural rutile. It was found that beneficiated ilmenite chlorinated much faster than natural rutile, mainly due porous nature of synthetic rutile.

Le Roux [99] studied the chlorination rate of titania slag in a fluidized bed reactor. The effects of CO and Cl₂ partial pressures, particle size and temperature

were examined and a rate model was proposed. The model was only valid for the first 20% TiO₂ chlorination.

Nell [100] conducted carbochlorination tests with matched particle-size fractions of rutile, ilmenite and high-titania slag in a small bubbling fluidized-bed reactor. The effects of temperature, the type and proportion of solid reductant in the charge, and the fraction of Cl₂ in the fluidizing gas were investigated. The results revealed the need for solid carbon in the bed if the chlorination was to run at high rates. With solid carbon in the bed, CO supplied with the fluidizing gas did not increase significantly the degree of chlorination after 75 min. Ilmenite was chlorinated more quickly than titania slag did, which, in turn, was chlorinated more quickly than rutile [100]. Rates of chlorination at 1100°C and 1000°C were much the same and significantly higher than that at 900°C. Chlorination was related to increase in the porosity of particle (even for rutile), which was caused by the rapid initial chlorination of FeO and MnO (in ilmenite and slag) and (it is argued) by the chlorination of Ti₂O₃ forming at high-energy surface sites. A reaction mechanism was presented and its validity was confirmed by empirical observations [100].

Kale and Bisaka [99] expressed the following reactions as the major reactions:



According to Eq. (33), at 1000°C the equilibrium shifts towards the formation of CO. The CO acts as a reductant and, as indicated in Eqs. (32) and (33), reduces the metal oxides and promotes the chlorination of metals to produce metal chlorides.

A summary of the reaction condition and rate equations for the above-mentioned studies is illustrated in Table. 2.

Niu et al. [101] investigated the thermodynamics and kinetics of Kenya nature rutile carbochlorination in a fluidized-bed reactor. The calculations on the thermodynamic of TiO₂-C-Cl₂ system showed that tita-

anium tetrachloride and carbon monoxide were stable in the system when C was excess in the solid phase. The appropriate reaction conditions were as follows: reaction temperature 950°C, reaction time of 40 min, carbon ratio of 30wt% of rutile, natural rutile particle size 96 μm, petroleum coke size of 150μm, and chlorine flow 0.036 m³h⁻¹ [101]. Under these conditions, the reaction conversion rate of TiO₂ reached about 95 %. For the TiO₂-C-Cl₂ system, the reaction rate was dependent on the initial radius of rutile particle, density, and the partial pressures of Cl₂. The following empirical equation was obtained for the conversion rate of Kenya rutile in the C-Cl₂ system [101]:

$$\frac{1 - (1 - X_B)^{1/3}}{\theta} = 2548 \exp\left(-\frac{10569}{RT}\right) P_{Cl_2}^{0.9062} d^{-0.9556} \quad (34)$$

Maharajh et al. [102] developed a techno-economic model for quantification of the effect of different feedstocks on the chlorinator, and described and assessed the chlorination process and process variables at steady state. They reported the development of the value-in-use (VIU) model and studies in which the model was used to quantify the effects of using different feedstocks [102]. The VIU concept aims to extract maximum sustainable value through knowledge and understanding of the value chain for the customer and producer. One of the main uses of VIU models is to evaluate product changes against a base case and to determine the financial impact of the change. VIU models can also be used to compare and assess the value of different products in a customer's process [102]. VIU calculations showed that for the given set of assumptions and prices, the value of natural rutile in the chlorinator was 6.7% higher than that of the slag. This was largely due to the chlorine costs, which account for 4.80% of the 6.7% change. Maharajh et al. concluded that although VIU models are a powerful decision-making tool, care must be taken to ensure that the assumptions are valid and regularly updated [102].

Combined fluidized bed

TiCl₄ has been commercially produced mainly by chlorination of high-grade titania feedstock (HGTF) such as rutile and high titanium slag in bubble bed

Table 2. A summary of the reaction conditions and rate equations.

Author	Materials	Temp (°C)	PSD (µm)	Partial Pressure (kPa)	Activation energy (kJ/mol)	Rate Equation
Morris and Jensen [95]	Rutile CO Cl ₂	870-1038	149-177	CO: 25.33-50.65 Cl ₂ : 25.33-50.65	158	$1-(1-X)^{1/3}=6065(P_{CO}P_{Cl_2})^{0.665}\exp\left(\frac{-1.90 \times 10^4}{T}\right)_t$
Morris and Jensen [95]	Rutile Coke Cl ₂	955-1033	149-420	Cl ₂ : 25.33-50.65	45.2	$1-(1-X)^{1/3}=0.294\exp\left(\frac{-10.820}{RT}\right)P_{Cl_2}^{0.692}d_c^{-0.55}\left(\frac{\text{coke}}{\text{ore}}\right)^{0.367}t$
Shon and Zhou [96]	Rutile CO Cl ₂	950-1150	38-250	CO and Cl ₂ : 0.9 - 57	175	$1-(1-X)^{1/3}=2.87 \times 10^4 d_p^{-1}P_{CO}^{0.55}P_{Cl_2}^{0.74}\exp\left(\frac{-2.10 \times 10^4}{T}\right)_t$
Shon and Zhou [97]	Slag (84.6% TiO ₂) Coke Cl ₂	950-1120	53-300	Cl ₂ : 17-86	29	$1-(1-X)^{1/3}=2.93 \times 10^{-4} d_p^{-0.2}P_{Cl_2}^{1.5}\exp\left(\frac{-3488}{T}\right)(t-t_0)$ with $t_0=0.042 \exp\left(\frac{6900}{T}\right)$ and $X=0$ for $0 \leq t \leq t_0$
Shon and Zhou [98]	Beneficiated ilmenite/SR (92% TiO ₂) Coke Cl ₂	900-1050	63-253	CO: 9.6-55.4 Cl ₂ : 9.6-55.4	156	$\lambda \left[\exp\left(\frac{X}{\lambda}\right) - 1\right] - b = 69\exp\left(\frac{-18800}{T}\right)P_{CO}^{0.82}P_{Cl_2}^{1.05}t$ where $b=3.3 d_p^{-0.8}$ and $\frac{1}{\lambda} = 1.32 \times 10^3 d_p^{0.36}\exp\left(\frac{-11700}{T}\right)$
Le Roux [99]	Slag (86-89% TiO ₂) CO Cl ₂	910-950	106-850	CO: 25.8-60.2 Cl ₂ : 8.6-25.8	28.8	$X_T = X_{TiO_2}^{init} + [2.45 \times 10^3 d_p^{-0.14}P_{CO}^{0.84}P_{Cl_2}^{0.47}\exp\left(\frac{-28.8 \times 10^3}{RT}\right)](1 - X_{TiO_2}^{init})$ where $X_{TiO_2}^{init} = 7.9 \times 10^3 P_{CO}^{0.21}P_{Cl_2}^{0.09}N^{1.9}\exp\left(\frac{-66.5 \times 10^3}{RT}\right)t$ and $X_T \leq 0.2$

[102, 103]. The effectiveness of bubble bed in enhancing the conversion of HGTF originates from high rates of heat and mass transfer. However, the total mass content of calcium oxide (CaO) and magnesium oxide (MgO) in HGTF is required to be lower than 0.5%-1.0% in order to reduce the particle agglomeration. This is because the agglomeration may cause gas channel and decrease mass and heat transfer effects [103, 104]. The agglomeration occurs due to the fact that in the temperature range of 1073 K to 1273 K, the calcium chloride (CaCl₂) (melting point, 1045 K) and magnesium chloride (MgCl₂) (melting point, 987 K) formed in the reaction of chlorine with CaO and MgO become liquid and agglomerate the particles. The high titanium slags obtained by smelting in the electric furnace contain 6.0%-9.0% (by mass) CaO and MgO, and cannot be used as materials for bubble bed [104-109]. Being unavailable as high grade materials for bubble bed is a serious concern. As a result, there have

been increased attempts and attentions for developing a new method in which HGTF with high content CaO and MgO can be utilized to produce TiCl₄. Some studies have proposed the addition of some materials such as titanium phosphate into the reactor to form a new infusible matter with CaO and MgO so as to effectively prevent agglomeration. However, the studies on these materials are inadequate as well as recycling of solid material involves the separation of the infusible matters which is a difficult process. Another study suggested the requirement for complex prilling devices to prevent particles from agglomeration by prilling [105-106]. Yang and Hlavacek [106] investigated the chloridized process at a lower temperature range of 573-873 K. To eliminate diffusion effects, sufficient contact between rutile and coke seemed to be important, thus premixing, grinding, briquetting, sintering and porphyzizing were adopted in their studies. In these studies the attention has mainly paid on

the improvement of the reaction conditions and few studies have been reported as far as a commercial process is concerned. Mintek company in South Africa established a pilot-plant using the circulating fluidized bed as a reactor, but it was only an attempt in the development of a new reactor during the last decade. In addition, the high titanium slag used in the experiment still consisted of low-level CaO [0.16% (by mass)] and MgO [0.17% (by mass)] [106]. It is known that the formation of liquid bridge between particles is responsible for the agglomeration during the production of $TiCl_4$. In fact, the agglomeration cannot be formed unless the liquid bridge is strong.

Cong et al. [109] described a novel approach for producing $TiCl_4$ by chloridizing ores of high CaO and MgO content, in which a combined fluidized bed was used as a reactor to avoid agglomeration between the particles caused by molten $CaCl_2$ and $MgCl_2$. The combined fluidized bed consisted of at least a riser tube and a semi-circulating fluidized bed. The reactor, combined fluidized bed, in which the materials with high-level content of CaO and MgO were chloridized, is shown in Figure 15 [110].

The reactor was consisted of a riser and a semi-cir-

culating fluidized bed (SCFB), and a structure such as riser-SCFB-riser. The breaking up the liquid bridge between the particles by shear force generated from the turbulence was the mechanism of anti-agglomeration in this reactor. In the riser, the premixed solid particles measured by a screw feeder enter into the bottom of the riser. At the same time, the solid particles are fed and pure chlorine, preheated to 773 K, is also introduced into the bottom. The gas velocity of chlorine, ($>5m.s^{-1}$), was higher than both of the terminal velocities of the slag particle and the petrocake particles, and made the particles to be at a pneumatic transport state [110]. Therefore, all particles were transported upwards and heated by an extra-mural electric furnace. The conversion of high titanium slag and chlorine is small through the riser owing to the low temperature and the short residence time. Because of the strong shear force caused by high intensity turbulence that can break up the liquid bridge efficiently, and the low concentration of particles (<0.05 , by volume) with short contacting time between them, no agglomeration occurs in the riser [110]. A distributor is used at the top of the riser, to distribute the gases and particles. In the semi-circulating fluidized bed, the gas velocity is lower than the transport velocity ($u_{tr,c}$) and higher than the transition velocity (u_{cc}) from the bubble fluidization to the turbulent fluidization as shown in Figure 15. Only a part of the particles (large particles) are at turbulent fluidization ($u_{cr} < u_g < u_{tr,r}$), and for the other part of the particles (fine particles), the gas velocity is higher than the transport velocity ($u_{tr,r}$). That is, all of the petrocake particles and large slag particles form a turbulent bed. Meanwhile, a circulating fluidized bed formed by fine slag particles is superposed on the turbulent bed. Such combination is called semi-circulating fluidized bed with a shear force higher than that for the conventional bubble fluidization, especially the slag particles crossing through the entire bed greatly enhance the shear force [110]. Owing to shorter residence time of the slag particles in the semi-circulating fluidized as compared with that in the bubble bed, the slag particles, the source of the liquid $CaCl_2$ and $MgCl_2$, can quickly leave the reaction area. As a result, the propensity of agglomeration would decrease. In addition, both mass transfer rate and heat transfer rate in the semi-circulating fluidized bed are higher than those

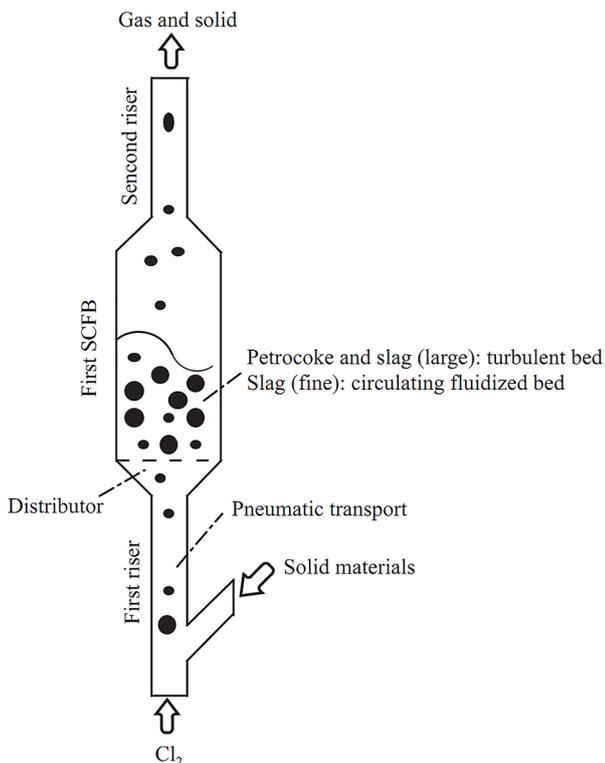


Figure 15. Diagram of the combined fluidized bed [110].

in the bubble bed. Experiments at cold state revealed the more activity and a better anti-agglomeration characteristic of turbulent bed as compared with those in bubble bed [110].

Xu et al. [111] employed two kinds of high titanium slags containing 2.03% and 9.09% CaO and MgO, to investigate the anti-agglomeration effect and the conversion of the materials in the temperature range of 923.15 K - 1073.15 K, gas apparent velocity of 0.7-1.1 m.s⁻¹, and solid materials inlet amount of 4.6-7.0 kg.h⁻¹. A satisfactory anti-agglomeration effect was found in the combined fluidized bed. Moreover, low-temperature chloridization at 923 K or 973 K could produce TiCl₄ and avoid agglomeration.

Yuan [112] proposed a process for comprehensive utilization of complex titania ore (Figure 16). In this process, panzhihua ilmenite concentrate was first reduced in a rotated hearth furnace to produce iron and

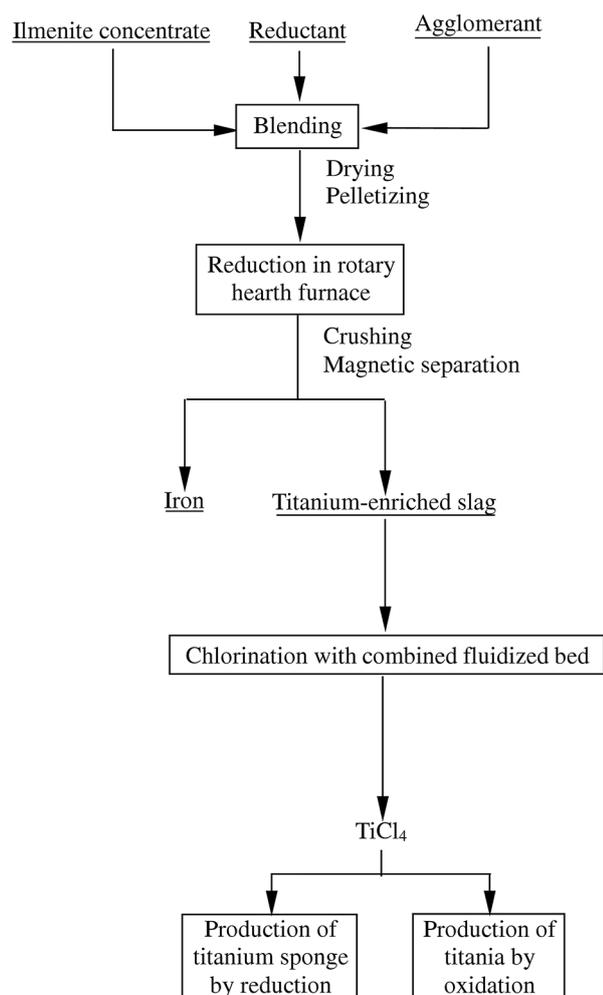
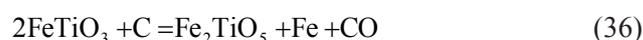
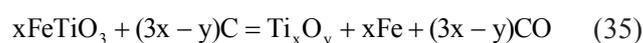


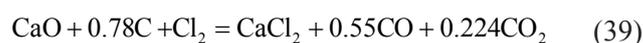
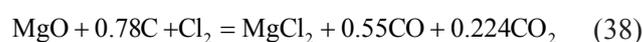
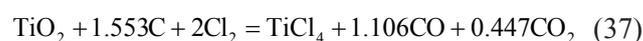
Figure 16. Procedure design of the titanium resource in Panzhihua [112].

titanium-enriched material, then the latter was chloridized in a new combined fluidized bed to produce TiCl₄. Yuan employed the combined fluidized bed consisted of two fast fluidized beds and a turbulent fluidized bed, in which an effective anti-agglomeration effect generated during the chloridizing of materials with high-level CaO and MgO [112].

The reactions are described by Eqs. (37) and (38). Ilmenite may be deoxidized to iron and other titanium compounds such as TiO₂, Ti₃O₅, Ti₂O₃, TiO, Fe₂TiO₅, etc [112].



After the magnetic separation of iron, a titanium-enriched slag was obtained, which can be chloridized using a combined fluidized bed, which accepts materials with high contents of calcia and magnesia. The main reactions are described below, for CO/O₂ ratio of 0.532/0.215 [112].



When titanium tetrachloride is produced, titanium sponge and titanium dioxide can be produced conventionally by reduction and oxidation, respectively.

Shao-Feng et al. [113] investigated the effects of carbon/slag molar ratio, chloride amount and temperature on equilibrium molar ratio (R_{Eq}) of CO to CO₂ for the off-gas produced by carbochlorination of titanium slag. The experimental CO/CO₂ molar ratio (R_{Ex}) of 0.2-0.3 was obtained in the carbochlorination experiment using a novel combined fluidized bed as chlorination reactor. The R_{Ex} was similar to R_{Re} (0.5-1.2) but different from R_{Eq} (≥ 4.3), however, consistent with the R_{Ex} expected for the novel combined fluidized bed [113]. The short retention time (about 1s) of materials in the combined fluidized bed together with carbochlorination of oxide impurities (CaO, MgO and SiO₂) contained in the titanium slag were responsible

for the difference between the R_{Ex} and corresponding R_{Eq} [113].

Yuan et al. [114] conducted a new test in a multi-stage series combined fluidized bed on a pilot scale to solve the agglomeration problem in $TiCl_4$ preparation process. The pilot plant could make full use of titanium slag with a high MgO and CaO content as the feedstock. Up to 90% TiO_2 conversion rate was obtained. The combined fluidized bed was found to have effective anti-agglomeration capability owing to accumulation of $MgCl_2$ and $CaCl_2$ on the surface of unreacted slag [114].

CONCLUSION

Owing to the vital importance of $TiCl_4$ catalyst in polymerization of polyolefin materials, attempt was made in the present work to examine the literature for the developments made in the processing of ilmenite and rutile ores for the extraction of $TiCl_4$. As a result, different chlorination processes involved in the production of $TiCl_4$ were reviewed. The utilized plants, reaction mechanisms and conditions together with the proposed models were reviewed. The recent progresses made in the selective extraction processes of low-grade titanium ores were also reported and discussed.

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