

# Review of titanium feedstock selection for fluidized bed chlorinators

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Titanium tetrachloride ( $\text{TiCl}_4$ ) is the basic raw material for the production of titanium dioxide ( $\text{TiO}_2$ ) pigment and titanium (Ti) metal. Worldwide, around 3.5 Mt of  $\text{TiO}_2$  pigment is produced annually by the chloride process, consuming in the region of 4.5 Mt of titania feedstock. Titania feedstock is chlorinated in the presence of a carbonaceous reductant at temperatures of approximately  $1000^\circ\text{C}$  for the production of  $\text{TiCl}_4$ .

Mintek has been associated with research work on titania feedstock since the early 1970s. The DC arc smelting process for production of titania slag from ilmenite was jointly developed and patented by Mintek and Anglo American. This technology is successfully used on a commercial scale at the Tronox-operated plants in South Africa. Over the years, Mintek has been working on various aspects of the chlorination of titania feedstock. Feedstock such as titania slag, synthetic rutile, upgraded slag, ilmenite, and rutile have all been evaluated in Mintek's laboratory-scale chlorination facility. Chlorination kinetics of various species present in the feedstock as well as the hydrodynamic properties of various titania feedstock materials, for example the effect of density and particle size on the quantity of blowovers from the chlorinator, have been investigated.

This paper provides a review of the characteristics of the titania feedstock used in industrial fluidized bed chlorinators, the effects of the chlorination kinetics of various species on the chlorinator bed composition, and the impact of the metal chlorides produced on the downstream operations in the production of  $\text{TiCl}_4$ . The information from the review may be useful for selecting titania feedstock for the production of  $\text{TiCl}_4$  using fluid bed chlorination technology.

## INTRODUCTION

Titanium dioxide is the most widely used white pigment in the coating industry. It has high brightness and a very high refractive index. It efficiently scatters visible light, thereby imparting whiteness, brightness, and opacity when incorporated into a coating.  $\text{TiO}_2$  is also an effective opacifier and is widely used in applications such as paints, plastics, paper, and ink.  $\text{TiO}_2$  pigment is produced by two commercial processes - the chloride and the sulphate process. The chloride process has become the more dominant process as it produces a superior quality pigment with significantly fewer waste products.

Titania feedstock consisting mainly of ilmenite, rutile, and titania slag is the basic source for the production of  $\text{TiO}_2$  pigment. This paper reviews the effect of selecting various titania feedstocks used in the chlorination process for producing  $\text{TiCl}_4$ , which is an intermediate product in the production of  $\text{TiO}_2$  pigment and Ti metal. In the chlorination process, titania feedstock is chlorinated in the presence of a carbonaceous reductant at temperatures of  $1000^\circ\text{C}$  for the production of titanium tetrachloride ( $\text{TiCl}_4$ ). The effect of various impurities present in the titania feedstock on the operation of the fluid bed chlorinator and the downstream operations in the production of  $\text{TiCl}_4$  is also discussed.

Titania ores occur in both primary magmatic and secondary placer deposits. Shoreline placer or beach sand deposits are by far the largest titanium deposits. Titanium is generally bonded to other elements in nature and occurs primarily as an oxide. Ilmenite is the most abundant titanium mineral. The other common titanium minerals from which  $\text{TiO}_2$  is extracted include rutile, anatase, altered ilmenite, leucoxene, and titanomagnetite. The  $\text{TiO}_2$  content depends on the source and extent of weathering of the mineral. The other major constituents include iron oxides ( $\text{FeO}$ ,  $\text{Fe}_2\text{O}_3$ ),  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{CaO}$  and silica. (Tittle *et al.*, 1973). Rutile ore extracted from natural deposits is too impure to be used directly as a pigment and is thus further processed. Ilmenite, the main titania ore, can be used directly in the chlorination process for manufacturing of  $\text{TiO}_2$  pigment or upgraded to produce either titania slag or synthetic rutile, which may then be used as a titania feedstock in the chlorination process.

Mintek is involved in the investigation of methods for the production and purification of  $\text{TiCl}_4$  from various titania feedstocks – this is one of the components of the titanium beneficiation programme driven by the South African Department of Science and Technology. As a result of this work, Mintek has established a knowledge base in the chlorination of titania feedstock. Feedstocks such as titania slag, synthetic rutile, upgraded slag, ilmenite, and rutile have been evaluated in Mintek's laboratory-scale chlorination facility. Chlorination kinetics and hydrodynamic properties of these titania feedstock have been evaluated. Mintek has published literature on the study of chlorination kinetics and behaviour of various species present in the titania feedstock. A laboratory-scale chlorination set-up and a fluid bed chlorination pilot plant (Kale *et al.*, 2010) at Mintek are used extensively to conduct the research activities.

## PRODUCTION OF TITANIUM TETRACHLORIDE BY THE CHLORIDE PROCESS

### Process

The production of  $\text{TiCl}_4$  used for  $\text{TiO}_2$  pigment or Ti metal involves chlorination of titania feedstock in a bubbling fluid bed chlorinator using petroleum coke as a reductant. Bubbling fluid bed chlorination technology is widely used commercially for the chlorination of titania feedstock due to its high rate of heat and mass transfer.

A schematic of the chloride process is shown in Figure 1. The mixture of titania feedstock and petroleum coke is fed into the chlorinator bed, where chlorine gas and oxygen are used to fluidize the chlorinator bed and maintain the desired operating conditions. The process operates at high temperatures, typically between 900 and 1100°C. The fluid bed chlorinator is lined with silica/alumina-based refractory in order to withstand the harsh operating conditions.

Various elemental species present in the titania feedstock are chlorinated at different stages, depending on the reactor conditions and their individual thermodynamic properties and chlorination kinetics. The metal chlorides formed in the chlorinator either leave the chlorinator as gaseous chlorides or accumulate in the chlorinator, depending on their individual boiling points and the operating conditions of the chlorinator. The lower boiling point metal chlorides leave the chlorinator and are condensed in the first condenser.

The condensed metal chlorides are treated before being discarded as waste. The treatment involves neutralization with lime. The  $\text{TiCl}_4$  from the chlorinator is condensed in a separate stream in the main condenser and collected as liquid. The liquid  $\text{TiCl}_4$  contains impurities that are removed by a complex proprietary process involving chemical treatment and distillation. The purified  $\text{TiCl}_4$  may then be further oxidized to produce  $\text{TiO}_2$  pigment.

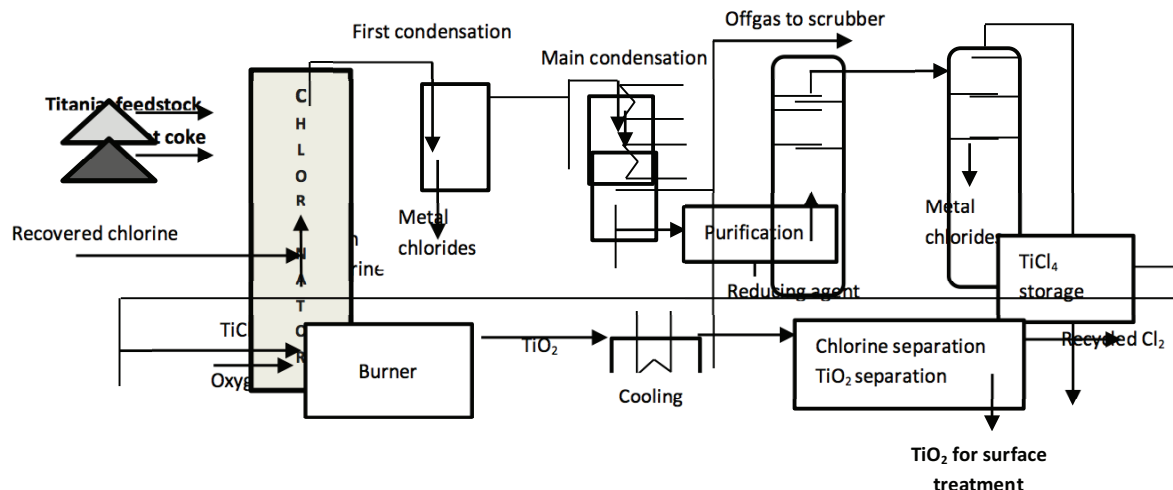


Figure 1. Schematic flow diagram of the chloride process.

### Titania Feedstocks and their Upgrading

Titania feedstock is commercially available in the form of ilmenite, titania slag, rutile, synthetic rutile, and upgraded slag. Ilmenite and natural rutile are natural resources, while synthetic rutile and titania slag are obtained by the processing of ilmenite and upgraded slag (UGS) is obtained by further processing of the titania slag. Typical compositions of titania feedstock are tabulated in Table I.

Minerals separation plants utilize screening, magnetic separation, and electrostatic and gravity separation circuits to separate valuable minerals from the non-valuable minerals and produce different grades of ilmenite, rutile, and zircon products. The  $\text{TiO}_2$  content of commercially available ilmenite can vary from 40% to 60%.

Iron oxide is the major impurity present in ilmenite, and can range from 30 to 50% by mass. Ilmenite also contains various impurities such as  $\text{SiO}_2$ ,  $\text{Cr}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ ,  $\text{MgO}$ ,  $\text{MnO}$ ,  $\text{CaO}$ , and the radioactive elements U and Th. The composition of the impurities varies widely, depending on the source and geographical location of the ilmenite deposits. Some of these impurities occur as discrete minerals (for example  $\text{ZrO}_2$  and  $\text{SiO}_2$ , which are found as  $\text{ZrSiO}_4$ ). Particles of this mineral find their way into concentrates of rutile and ilmenite. Many impurities occur in solid solution in the principal phase (rutile, ilmenite, or  $\text{M}_3\text{O}_5[\text{ss}]$  of slag). Examples include iron and niobium in rutile,  $\text{MnO}$  and  $\text{MgO}$  in ilmenite, and  $\text{MnO}$  and  $\text{Al}_2\text{O}_3$  in pseudobrookite ( $\text{M}_3\text{O}_5$ ) solid solution [ss] (Bessinger *et al.*, 1997).

Table I. Typical chemical composition (wt%) of various titania feedstocks that Mintek has evaluated.

Oxide	Feedstock			
	Ilmenite	Rutile	Ti Slag	UGS
TiO <sub>2</sub>	60.1	95.0	86	94.8
Fe <sub>2</sub> O <sub>3</sub>	26.3	0.6	-	2.4
FeO	10.4	-	8.9	-
SiO <sub>2</sub>	0.7	1.4	1.7	2.1
V <sub>2</sub> O <sub>5</sub>	0.2	0.3	0.4	0.5
MnO	0.4	0.01	1.2	0.1
MgO	0.4	0.05	1.0	1.1
CaO	0.04	0.05	0.3	0.2
ZrO <sub>2</sub>	0.2	0.08	0.1	<0.01
Al <sub>2</sub> O <sub>3</sub>	0.6	0.3	0.8	0.5
Cr <sub>2</sub> O <sub>3</sub>	0.1	0.35	0.01	0.08
Nb <sub>2</sub> O <sub>5</sub>	<0.01	0.4	<0.01	<0.04
U+Th (ppm)	<150	<50	<50	<50

Natural rutile is mined from various deposits and is mostly associated with ilmenite mining. The TiO<sub>2</sub> content in natural rutile can range from 90 to 97%. The iron content can vary between 0.5 to 2 %. SiO<sub>2</sub> and ZrO<sub>2</sub> are the major impurities associated with rutile.

Synthetic rutile is produced by roasting the ilmenite, followed by treatment of the roasted ilmenite with hydrochloric acid or sulphuric acid to remove iron and other impurities, thereby increasing the TiO<sub>2</sub> content. Typically, synthetic rutile contains in the region of 90 to 93% TiO<sub>2</sub>. Other impurities present in synthetic rutile depend on the geographical source of the ilmenite deposit.

Titania slag is produced by the smelting of ilmenite. The iron is removed from ilmenite as pig iron, thereby increasing the TiO<sub>2</sub> content of the remaining slag. Typically the TiO<sub>2</sub> content of the slag can be in the range of 80 to 90%. The iron content in the slag can vary from 5 to 15%. Upgraded slag is produced by further treating the titania slag to increase the TiO<sub>2</sub> content to 90–95% by roasting and leaching out the impurities with hydrochloric acid.

## IMPACT OF VARIOUS PARAMETERS ON THE CHLORINATION REACTION

### Process Economics

Titania feedstock is a major cost in the production of TiO<sub>2</sub> pigment, contributing around 40–45% of the total variable cost for a chloride route pigment plant (Adams, 2003). Selection of an appropriate titania feedstock is therefore a critical factor affecting the profitability of the TiO<sub>2</sub> pigment business. There is a significant difference in the price of various titania feedstocks – typical titania feedstock containing about 85% TiO<sub>2</sub> is about 2.5 times the price of ilmenite, for example. Natural rutile, synthetic rutile, and UGS are almost five times the price of ilmenite. Cost considerations therefore play a major role in the selection of an appropriate feedstock for the chloride process.

The economics of feedstock selection is further affected by selection of technology used for certain types of feedstock. A plant using ilmenite as a feedstock needs to be designed to cater for the higher quantity of iron chlorides produced in the chlorinator. Due to the lower TiO<sub>2</sub> content (typically about 60%) in ilmenite, a larger quantity of feedstock is required to produce a ton of TiCl<sub>4</sub>; hence, the raw material handling facility and wrap-around process plant will be significantly larger than that of a chlorination plant using titania slag or rutile as feedstock. As can be seen in Table II, approximately 850 kg of ilmenite is required to produce a ton of TiCl<sub>4</sub>, as compared to 530 kg of rutile. A plant using ilmenite as a feedstock will therefore be required to handle 60% more raw material than a plant handling rutile as feedstock. Higher material handling requirements will lead to increased wear and tear of equipment, and higher capital and maintenance costs. The overall footprint of a production facility using ilmenite will be larger compared to a plant using rutile as feedstock to produce the same quantity of TiCl<sub>4</sub>. This will result in a higher capital investment for a TiCl<sub>4</sub>-producing facility using ilmenite as a feedstock. The quantity of chlorine required will be significantly greater due to the chlorine consumed for chlorinating the iron impurities in ilmenite. The quantity of iron chloride waste generated will also be significantly higher, hence using the comparatively cheaper ilmenite feedstock will result in higher waste treatment and waste disposal costs. As a result, many chloride process plants use a blend of feedstock to increase the TiO<sub>2</sub> content to 88–92% to optimize their operations.

Table II. Titania feedstock required to produce one ton of TiCl<sub>4</sub>.

Ilmenite	850 kg
Rutile	530 kg
Ti Slag	600 kg
UGS	530 kg

### Operational Challenges

The various impurities present in the titania feedstock play an important role in the production of TiCl<sub>4</sub> in a bubbling fluid bed chlorinator (van Dyk, 1999). These impurities also affect the quality of TiO<sub>2</sub> pigment (in most cases adversely). In order to produce a high-quality TiO<sub>2</sub> pigment, the impurities in TiCl<sub>4</sub> must be removed to as low as <50 ppm.

The bubbling fluid bed chlorinator is typically operated at temperatures around 900°C to 1100°C. At these temperatures, most of the volatile metal chlorides (M<sub>x</sub>Cl<sub>y</sub>, having boiling points below the chlorinator operational temperature) formed as a result of the reaction between chlorine and the titania feedstock will leave the chlorinator in gaseous form. The gas stream from the chlorinator is cooled to a temperature that permits selective separation of various undesired metal chlorides by condensation. The melting and boiling points of various metal chlorides are therefore critical when designing the condenser. Table III shows the boiling and melting points of various metal chlorides formed during the chlorination of titania feedstock.

The physical properties of titania feedstock can also affect the operation of bubbling fluid bed chlorinators. Particle size, density, and sphericity of the particles are important parameters for the design of an industrial chlorinator. Different titania feedstocks have appreciably different particle size distributions. As can be seen from Table IV, titania slag has particle size distribution from 850 µm to below 75 µm, while rutile and ilmenite has a particle size from 300 µm to below 75 µm.

Studies on the behaviour and hydrodynamic properties of the particles in a fluid bed chlorinator have shown that finer particles have a tendency to elutriate from the chlorinator. The particle size of the titania feedstock has an effect on the terminal velocity of the particles. According to calculated terminal velocity values, particles finer than 75 µm will be highly susceptible to entrainment and elutriation from the chlorinator (Moodley *et al.*, 2012). It is therefore important to limit the quantity of fine particles in the titania feedstock. The elutriation of particles from the chlorinator makes these

particles unavailable for chlorination, and is a direct loss of TiO<sub>2</sub> value. The elutriated material from the chlorinator also adds to the cost of solid waste disposal.

Table III. Boiling and melting points of various metal chlorides (Wikipedia).

Metal oxides	Metal chlorides	Melting point °C	Boiling point °C
Al <sub>2</sub> O <sub>3</sub>	AlCl <sub>3</sub>	180 (sublimes)	180
CaO	CaCl <sub>2</sub>	772	1935
Cr <sub>2</sub> O <sub>3</sub>	CrCl <sub>3</sub>	1152	1300
Fe <sub>2</sub> O <sub>3</sub>	FeCl <sub>3</sub>	306	316
MgO	MgCl <sub>2</sub>	714	1412
MnO	MnCl <sub>2</sub>	654	1225
Nb <sub>2</sub> O <sub>5</sub>	NbCl <sub>5</sub>	204.7	248.2
SiO <sub>2</sub>	SiCl <sub>4</sub>	-68.4	57.6
TiO <sub>2</sub>	TiCl <sub>4</sub>	-24	136.4
V <sub>2</sub> O <sub>5</sub>	VOCl <sub>3</sub>	-76.5	126.7
ZrO <sub>2</sub>	ZrCl <sub>4</sub>	331 (sublimes)	331

Table IV. Particle size distributions for various titania feedstocks.

Particle size (µm)	Ilmenite (wt%)	Rutile (wt%)	Ti slag (wt%)
+850	-	-	1.2
-850+600	-	-	18.7
-600+425	-	-	23.2
-425+300	-	-	19.5
-300+212	1.7	2.0	15.8
-212+150	29.3	19.4	8.7
-150+106	54.9	49.0	7.7
-106+75	10.7	28.0	3.5
-75	3.4	1.5	1.6

### Chlorinator Bed De-fluidization

Metal chlorides with boiling points higher than the operating temperature of the chlorinator will tend to remain and accumulate in the chlorinator bed. If the melting point of these metal chlorides is below the chlorinator operating temperature, then these metal chlorides will affect the fluidizing properties of the chlorinator bed. From Table III, it can be seen that CaCl<sub>2</sub>, MgCl<sub>2</sub>, MnCl<sub>2</sub>, and CrCl<sub>3</sub> will remain in the chlorinator bed as liquids. These metal chlorides may cause particle agglomeration and clumping in the chlorinator bed, resulting in the de-fluidization of the bubbling fluid bed and associated reduction in heat and mass transfer. This will ultimately lead to gas channelling, and

unreacted chlorine and oxygen gas will leave the chlorinator. This may cause additional operational problems in the downstream process. The reduced heat transfer will lead to a drop in temperature of the chlorinator bed, slowing the rates of the chlorination reactions.

The accumulation of these metal chlorides in the chlorinator bed must be controlled by periodic draining of the bed. The disposal of the solid metal chlorides containing material from the chlorinator bed is also a concern due to their toxicity issues. Hence, while selecting the titania feedstock it is important to make sure that the total content of CaO and MgO is below 1% (Cong *et al.*, 2006).

### **Chlorinator Refractory Lining**

The high operating temperatures (between 900°C and 1100°C), together with the use of chlorine, makes it necessary to use a refractory brick lining inside the chlorinator for protecting the walls of the vessel. The refractory bricks used are typically silica/alumina-based. Over time, the refractory brick lining becomes worn and eventually needs replacement. Replacement is an expensive exercise, and involves manually removing the old refractory bricks and replacing them with new ones. The new refractory bricks need curing time, and as a result the entire operation leads to appreciable downtime, which can be more than a week.

Typically, the life of the refractory brick lining in the chlorinator can vary between 9 months and 24 months, depending on the operational parameters of the chlorinator and the type of impurities present in the feedstock. Damage to the refractory lining occurs mainly as a result of mechanical erosion, thermal shock, and chemical corrosion. In typical chlorinators, the titania feedstock and petroleum coke mixture is fed horizontally into the vessel over the chlorinator bed using a transporting gas at high pressure. The abrasive nature of the titania feedstock then causes mechanical erosion of the refractory lining. If ilmenite is used as a feedstock, the quantity of material fed into the chlorinator is significantly higher than when using rutile feedstock. This may lead to more severe mechanical erosion of the refractory brick lining. Some manufacturers have opted for a vertical feeding system in order to address the issue of erosion caused by the horizontal feeding of feedstock into the chlorinator.

Ferrous and ferric chloride formed by the chlorination of iron in the feedstock are a major source of chemical corrosion of the refractory bricks. Iron chlorinates vigorously compared to the TiO<sub>2</sub> in the feedstock (den Hoed *et al.*, 2003). The higher iron content of the titania feedstock may therefore lead to increased chemical corrosion of the refractory bricks. Although silica-based refractory is well known for its corrosion-resistance properties, it undergoes phase changes in the chlorinator, especially in the presence of iron at high temperature. This may lead to additional corrosion problems in the refractory lining.

The chlorinator bed needs to be drained periodically due to the accumulation of impurities in the bed. The draining disturbs the normal chlorinator operation, and leads to changes in chlorinator conditions such as temperature. This temperature variation imparts thermal shock to the refractory brick lining, adversely affecting its performance and increasing the likelihood of a lining failure.

### **Impact of Minor Impurities**

Various minor impurities such as vanadium, niobium, alumina, and silica have significant impact on the chlorinator and downstream operations.

The silica and zirconia in the titania feedstock accumulate in the chlorinator bed due to the unfavourable chlorination kinetics of these species compared to iron oxide and titania (den Hoed *et al.*, 2003). Over time, the accumulation of silica and zirconia leads to changes in the bed composition. A critical point is reached when the percentage of these two components in the chlorinator bed leads to chlorine leaving the chlorinator without reacting, a phenomenon commonly referred to as 'chlorine slip' in the TiO<sub>2</sub> pigment industry. To mitigate this behaviour, once the silica content in the bed reaches a critical level of above 45%, the chlorinator bed is drained and replaced with fresh titania feedstock. Draining involves operational downtime, resulting in production loss. Frequent bed

draining also affects the temperature inside the chlorinator and imparts thermal shock to the refractory lining. The higher the SiO<sub>2</sub> and ZrO<sub>2</sub> content in the titania feedstock, the more frequently the bed will need to be drained.

Small amounts of ZrCl<sub>4</sub> formed in the chlorinator leave the chlorinator bed, as ZrCl<sub>4</sub> sublimates at 301°C. The ZrCl<sub>4</sub> reacts with the organic polymers used for purification of crude TiCl<sub>4</sub> and forms a coating on the TiCl<sub>4</sub> distillation trays. This reduces the heat and mass transfer and hence the performance of the distillation column.

Alumina in titania feedstock reacts with chlorine and leaves the vessel in gaseous form along with TiCl<sub>4</sub> and other metal chlorides. AlCl<sub>3</sub> is highly corrosive and may cause damage to equipment used in the downstream operation. To eliminate the presence of AlCl<sub>3</sub> in the downstream operation, TiCl<sub>4</sub> producers use a variety of proprietary techniques in order to remove AlCl<sub>3</sub> from the gaseous stream leaving the chlorinator. Some TiCl<sub>4</sub> is lost in the process of removing AlCl<sub>3</sub>, and hence higher quantities of alumina in the feedstock will result in increased losses of TiCl<sub>4</sub> associated with the removal of AlCl<sub>3</sub>.

Niobium in the titania feedstock reacts with chlorine, producing niobium pentachloride (NbCl<sub>5</sub>), which must be condensed and removed from the operation before it reaches the water-cooled condensers. If it is not removed, NbCl<sub>5</sub> forms a scale over the surfaces in the heat exchangers, affecting the efficiency of the units. This scaling needs periodic cleaning, the frequency of which increases with higher niobium content in the feedstock.

Vanadium in the feedstock is chlorinated to form vanadium oxychloride (VOCl<sub>3</sub>), which has a boiling point of 127°C, close to the boiling point of TiCl<sub>4</sub> (134.4°C). The VOCl<sub>3</sub> therefore condenses with TiCl<sub>4</sub> in the product stream. Vanadium causes severe colour and brightness problems in the TiO<sub>2</sub> pigment. As can be seen in Table V, it is recommended that the V content in the purified TiCl<sub>4</sub> product should be less than 10 ppm. Vanadium compounds are removed from TiCl<sub>4</sub> by proprietary chemical treatments and careful distillation control. Titania feedstock with lower vanadium content is therefore preferred in order to reduce the cost of purification of crude TiCl<sub>4</sub> and improve the quality of TiO<sub>2</sub> pigment.

Table V. Typical composition of commercial TiCl<sub>4</sub> (<http://KMML.com>)

TiCl <sub>4</sub> (%)	V (ppm)	Fe (ppm)	Al (ppm)	Si (ppm)
>99.5	<10	<5	<20	<50

Radioactive elements such as U and Th are present in different quantities in various titania feedstocks. The high operating temperature of above 1000°C in the chlorinator will result in some U and Th leaving the chlorinator and precipitating in the condenser along with other undesirable metal chlorides (<http://v.pl.3.eu-norm.org/index.pdf>). These metal chlorides are mixed with water and neutralized (typically with lime). Neutralization precipitates all the radionuclides and the level of neutralization will determine the losses to the effluent stream. In the case of complete neutralization stream the U and Th will end up in the solid waste stream. Higher levels of U and Th in the feedstock will therefore lead to higher values of radionuclides in the solid waste, and hence it is desirable to control the U and Th levels in the feedstock as per the specific solid waste disposal requirements for the TiO<sub>2</sub> production site.



## CONCLUSION

The selection of titania feedstock for the production of  $\text{TiO}_2$  using chloride technology is a complex process. Major criteria affected by the selection are:

- Process plant design
- Economics of the process due to differences in price of feedstocks and various impurities present
- Loss in production due to process and equipment downtime
- Waste treatment and solid waste disposal cost
- Quality of the  $\text{TiO}_2$  pigment product.

Process design is very much dependent on the type of feedstock used for production of  $\text{TiO}_2$  pigment. A plant using ilmenite (60%  $\text{TiO}_2$ ) as feedstock will have a larger footprint compared to a plant using rutile (95%  $\text{TiO}_2$ ) for the same production capacity.

The difference in the price of feedstock is a major criterion in raw material selection. The low price of titania feedstock often comes with the associated cost of technological challenges and operational issues. If the technological challenges and operational issues are effectively managed, the low price of feedstock may constitute an advantage for producing the  $\text{TiO}_2$  pigment at low cost.

The effect of physical properties such as particle size distribution of the titania feedstock should be considered when evaluating the fluid bed chlorinator operation. Finer particles below  $75\ \mu\text{m}$  have a tendency to elutriate from the chlorinator, leading to loss of titanium values and additional cost of treating the solid waste.

Impurities like iron present in the titania feedstock lead to operational challenges resulting from damage caused to the refractory brick lining in the chlorinator. Any decrease in the lifetime of the refractory lining decreases the availability of the chlorinator for production of  $\text{TiCl}_4$ , while also incurring additional operating costs.

Minor impurities such as  $\text{SiO}_2$  and  $\text{ZrO}_2$  that accumulate in the chlorinator bed lead to more frequent draining of the chlorinator bed. This reduces the availability of chlorinator and causes thermal shock to the refractory lining.  $\text{CaO}$  and  $\text{MgO}$  in the titania feedstock lead to the formation of high-boiling-point chlorides that remain in the liquid form in the chlorinator bed at the operating temperature of the chlorinator. If the content of  $\text{CaO} + \text{MgO}$  is higher than 1%, the metal chlorides formed will cause defluidization of the chlorinator bed and adversely affect the chlorinator operation.

The scaling caused by metal chlorides such as  $\text{NbCl}_5$  and  $\text{ZrCl}_4$  on the surfaces of heat exchangers and distillation columns may result in lower production efficiencies. The presence of these impurities, even in small quantities, therefore plays a major role in the operational problems in the production of  $\text{TiO}_2$  pigment and reduces the production capacity of the plant. The direct loss of  $\text{TiCl}_4$  associated with removal of  $\text{AlCl}_3$  from the chlorinator product stream is proportional to the amount of  $\text{Al}_2\text{O}_3$  in the titania feedstock, hence lower  $\text{Al}_2\text{O}_3$  content in the feedstock is desirable.

Higher quantity of impurities in titania feedstock will in general result in higher waste treatment and solid waste disposal costs. Hazardous impurities such as radionuclides end up in the solid waste – this can be a critical factor in deciding the suitability of titania feedstock. Hence, it is important to consider the U+Th content in the titania feedstock.

Impurities such as vanadium should be removed to concentrations below 10 ppm in the final product, as they can impart colour to the  $\text{TiO}_2$  pigment. The higher the content of  $\text{V}_2\text{O}_5$  in the titania feedstock, the greater the quantity of treatment chemicals required for the removal of V from the  $\text{TiO}_2$  pigment.

It is anticipated that a better understanding of the impact of various impurities titania feedstocks will help operators and businesses to make informed decisions in the selection of which feedstock to choose, and in optimizing the design and operation of their process plants for TiCl<sub>4</sub> production.

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## **Aditya Kale**

Chief Engineer  
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MS - Materials Science and Engineering; B.Tech - Chemical Engineering. Twenty years of versatile industrial experience in production, process development, technical sales and research activities. Worked for organizations like Heubach Colours, India; Cristal, Saudi Arabia and Mintek, South Africa.

Hands on experience in production of phthalocynine pigments, aluminium hydroxide, titanium dioxide pigment and technical due diligence for technologies. Evaluated various grades of titania feedstock for industrial chlorinators. Associated with technical sales and market development for activated carbon regeneration technology.

Involved in various process development activities from lab scale to commercial scale production with specialization in high temperature fluid bed chlorination technology. Exposure to industrial fluid bed chlorinator operations, evaluation of various ilmenite beneficiation processes, and techno commercial activities. Working with Mintek, since 2007 and coordinating the minerals beneficiation cluster at Pyrometallurgy division.

