Fluid bed chlorination pilot plant at Mintek

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Synopsis

A chlorination pilot plant having capacity to produce 5–10 kg/hr of titanium tetrachloride is in operation at the chlorination facility in Mintek. The bubbling fluid bed chlorination plant can be operated in batch and/or continuous process to study the chlorination kinetics of various feedstocks. The chlorination of titaniferous ores to produce titanium tetrachloride ($TiCl_4$) was carried out during the commissioning of the pilot plant and also as part of the titanium programme carried out at Mintek. $TiCl_4$ is a basic raw material for producing commercial titanium dioxide pigment and titanium metal.

This paper discusses the challenges faced during the commissioning and operation of the chlorination pilot plant. It also discusses the effect on the auxiliary facilities and instrumentation as a result of the harsh operating conditions of +1000°C and use of corrosive gases like chlorine and titanium tetrachloride. It discusses the effect of physico-chemical properties of the titanium tetrachloride and iron chlorides. The effect on the chlorinator refractory lining due to heating and cooling of the chlorinator is also discussed.

Besides the special provisions made during the design of the chlorinator, this paper also discusses the operational experience and possible solutions to be implemented in future.

Keywords
Fluid bed chlorination, titanium ore chlorination, titanium tetrachloride ($TiCl_4$) production using fluid bed technology.

Introduction

Titanium ores occur in both primary magmatic and secondary placer deposits. Shoreline placer or beach sand deposits are by far the largest source of titanium deposits. South Africa has the second largest reserves of titanium ore in the world; most of it is in the form of beach placer deposits located along eastern, southern and north-eastern coasts. Titanium is generally bonded to other elements in nature. It is the ninth most abundant element in the Earth's crust and the seventh most abundant metal[1].

Titanium mineral deposits worldwide are exploited to produce raw materials for the production of titanium dioxide (TiO_2) pigment and titanium metal. Approximately 95% of the titanium mineral deposits are used for the production of TiO_2 pigment. About 3% of the mined titanium ores are used for producing titanium metals[2].

The South African titania industry currently produces rutile, zirconia and titania slag from the smelting of ilmenite. A very small part of the slag product is used for the production of titania pigment for domestic needs, using the sulphate process. The level of beneficiation of raw titania to final products is currently small in South Africa. Beneficiation, of course, adds value to the raw materials and creates employment opportunities.

Mintek is involved in a titanium programme driven by the Department of Science and Technology. Mintek, particularly, is involved in the investigation of methods for the production of $TiCl_4$ and primary sponge metal used in the titanium industry. This programme also intends to develop human capital skills needed in this industry.

TiO_2 pigment is a white powder with high opacity, brilliant whiteness, excellent covering power and resistance to colour change. These properties have made it a valuable pigment and opacifier for a broad range of applications in paints, plastics, inks and paper.

Titanium (Ti) also called 'Space Age metal' is a low density, high strength, corrosion resistant transition metal with a silver colour. Titanium has a higher strength to weight ratio than aluminium or other light metals and is capable of withstanding attacks by acids, most chlorine gas, and common salt solutions. It has fairly low electrical and thermal conductivity. Titanium can readily form alloys with other widely used transition elements, such as iron and aluminium.

Overview of the titanium industry

The titanium industry can be broadly classified in three sections:

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➤ Mineral separation and beneficiation of titanium feedstocks
➤ Manufacturing of TiO_2 pigment
➤ Manufacturing of Ti metal and its downstream applications.

The feedstock beneficiation industry includes the production of beneficiated products, such as synthetic rutile, titanium slag and upgraded slag. This industry is mostly orientated towards the supply of titanium feedstocks for the production of TiO_2 pigment.

The TiO_2 pigment is made by two commercial processes— – sulphate and chloride. The chloride process has become more dominant process because it produces superior pigment with significantly fewer waste products.

The flow charts in Figures 1a and 1b illustrate, in simplified form, the two processing routes for TiO_2 pigment production.

The $TiCl_4$ produced in the chloride process is also a raw material for the Ti metal production. Presently, the Kroll process is used mainly for commercial production of the Ti metal.

The Kroll process is carried out in a sealed steel reactor, in the absence of oxygen. Argon is used as a substitute atmosphere as it will not react with the vessel or its content. It involves reduction of $TiCl_4$ with magnesium to form $MgCl_2$ and Ti metal.

Commercial production of titanium tetrachloride— principles and operating philosophy

Commercial $TiCl_4$ production involves fluid bed chlorination of titanium feedstock using carbon as a reductant. The process operates at high temperatures of 1000–1050°C and uses chlorine gas for chlorination of titaniferous ores/slags. The high melting metal chlorides formed are condensed in a cyclone separator. The low boiling point metal chlorides,

mainly $TiCl_4$ are condensed down the line using $TiCl_4$ scrubbing towers and chilled condensers. The liquid $TiCl_4$ contains impurities that are separated by a distillation process.

The process generally starts with the heating of the reactor and the raw materials using coal/coke, air/oxygen. Once the reaction temperature of around 1025°C is attained, the Cl_2 gas replaces air and starts reacting with the reduced metal oxides. The temperature in the chlorinator is maintained between 1000°C and 1050°C.

Mixtures of metal chlorides leave the chlorinator in gaseous form. High boiling point metal chlorides like iron chloride condense in the range of 150°C to 200°C. Iron chloride precipitates out as solid powder and settles in the condenser. The gaseous mixture of $TiCl_4$, carbon monoxide (CO), carbon dioxide (CO_2), N_2 and unreacted Cl_2 pass further to the shell and tube condenser. $TiCl_4$ condenses out in the condenser where sub-zero temperatures are maintained. The non condensable gases like CO_2, CO, unreacted Cl_2 and N_2 leave the condenser and are scrubbed in a caustic scrubber.

This purification process of $TiCl_4$ is quite complex: it involves chemical treatment and a distillation operation.

Major reactions

$$2C + O_2 = 2CO \qquad [1]$$

$$FeO + Cl_2 + CO = FeCl_2 + CO_2 \qquad [2]$$

$$TiO_2 + 2Cl_2 + 2CO = TiCl_4 + 2CO_2 \qquad [3]$$

At reaction temperatures of around 1000°C the equilibrium shifts towards the CO formation as indicated in Reaction [1]. This CO acts as a reductant in reducing the metal oxides as indicated in Reaction [2] and Reaction [3] and helps the chlorination of metals to form metal chlorides.
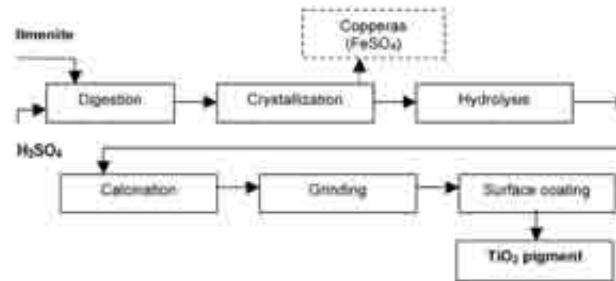

Figure 1a—TiO_2 manufacturing by sulphate process
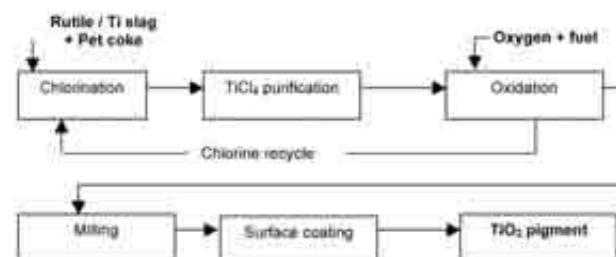
Figure 1b—TiO_2 manufacturing by chloride process

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Chlorination pilot plant at Mintek

It was attempted to incorporate the above principles and concept philosophy in the in-house design of the pilot plant chlorinator at Mintek.

Major equipments used in pilot plant

Chlorinator

A 1.8 metre tall and 250 mm diameter bubbling fluid bed reactor is used for chlorination of the ores. The reactor is refractory lined internally in order to withstand the severe chlorination conditions of 1050°C and chlorine atmosphere. The refractory also helps to reduce the heat loss and maintain the reaction temperature. Though the reactions occurring in the chlorinator are exothermic, the shell heat losses are high due to the high surface area associated with the small scale of the operation.

A distributor plate is cast into the bottom of the chlorinator, which allows the gas to flow through the distributor plate and keeps the solid particles (Ti slag and petroleum coke) in even suspension.

Temperatures are measured at various points across the chlorinator. There are three temperature measuring probes in the fluid bed area. In ideal conditions when the chlorinator is well fluidized, the three temperatures are in a very close range. Three other probes are located at different points above the fluid bed to measure the temperature in the freeboard area and the temperature of gases leaving the chlorinator.

Iron chloride condenser or space cooler

The iron chloride condenser is made of steel and designed to allow separation of the iron chlorides from gases due to cooling of the gases and reducing the velocity of the gases.

Gases from the chlorinator enter the condenser tangentially from side. The temperature of the gases drops down to around 200°C in the condenser. Iron chlorides, solidifies (condenses) at this temperature. The condenser also provides a large cross-sectional area which leads to a drop in velocity of the gases and allows the solid iron chloride particles to separate from the $TiCl_4$ gas. Solid iron chlorides are collected from the bottom of the condenser.

$TiCl_4$ condenser

A shell and tube condenser is used to condense the $TiCl_4$. A chiller is used to circulate coolant to maintain sub-zero temperature in the condenser. $TiCl_4$ gas condenses as liquid at this temperature and is collected in a $TiCl_4$ storage tank. Two condensers are connected in series in order to condense most of the $TiCl_4$. Uncondensed gases along with non condensable gases like CO, CO_2, Cl_2 and N_2 leave the condenser and are scrubbed in the caustic scrubber to remove the residual chlorine.

The main design features were:

➤ *Chlorine cylinders and storage*—a number of chlorine cylinders operate in parallel. This was designed from experience of chlorine handling.
➤ *Chlorinator*—the chlorinator was designed using the data obtained from hot and cold laboratory trials. This data provided the cross-sectional area and the

disengagement height of the reactor. In practice, the height of the reactor should be more than the disengagement height. The concept of using carbon and oxygen as a heat source (instead of plasma) was studied on a laboratory-scale chlorinator.

➤ *Separation of iron chlorides from $TiCl_4$*—the gases from the chlorinator are cooled and expanded in the air-cooled space cooler.
➤ *Condensation*—the $TiCl_4$ gas is condensed in a series of condensers maintained at sub-zero temperature with the circulation of glycol.
➤ *Scrubbing of the unreacted gas*—this is primarily done in a small scrubber using a caustic soda solution.
➤ *Measurement of the bed temperature*—because of the intermittent operation of the pilot plant, it is difficult to adopt the industrial practice. Contact thermocouples were placed in the reactor at three levels in the bed.

The process followed for $TiCl_4$ production in the pilot plant is presented schematically in Figure 2.

Operation of the chlorination plant at Mintek

The plant was operated in a batch process where a mixture of 10 kg titaniferrous ore and petroleum coke was fed to the chlorinator and the temperature was raised to around 1025°C using air and oxygen (O_2). The quantity of reductant added was far more than the stoichiometric requirement. It is usually in the range of 25% by weight of Ti slag present in
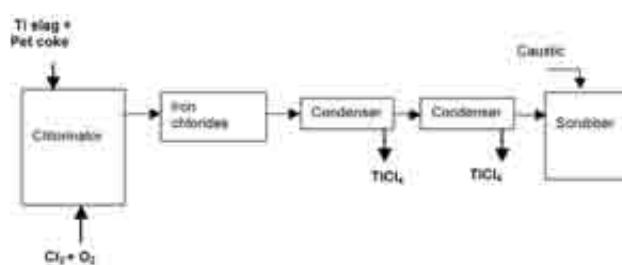

Figure 2—Process flow diagram for $TiCl_4$ production at Mintek pilot plant

Figure 3—Chlorinator and iron chloride condenser at Mintek pilot plant
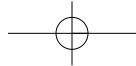
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the fluid bed. Petroleum coke, when reacting with oxygen, provides the necessary energy required to maintain the reaction temperature and also acts as a reductant to reduce the metal oxides present in the Ti slag.

The ratio of oxygen/nitrogen flow rates were regulated to maintain the temperature in the chlorinator between the range of 1000°C to 1050°C. The total gas flow rates were adjusted to maintain a superficial velocity between 0.13 and 0.15 m/s.

The operating temperatures were constantly monitored with three thermocouple probes placed in the fluid bed and regulated by changing the ratio and flow rate in the mixture of inlet gas.

For any unexpected surges, pressure would be safely released through the pressure release disk placed in the freeboard of the reactor.

Cold commissioning and system integrity

The cold commissioning was carried out to assess the integrity of the system, the pressure drop and the cold fluidization using air. This led to some modification to the design.

Hot commissioning

This was done to assess the temperatures across the chlorinator, the pressure drop, and the integrity at high temperature. This was generally done by partially combusting the carbon contained in the solid feed mixture using air and oxygen.

It was also done to calibrate the thermocouples using contact and optical pyrometers and to define the operating parameters of the chlorination reactor at the required superficial gas velocity of 0.13 to 0.15 m/s.

Chlorination

On successful hot commissioning, chlorine was used to carry out the chlorination tests. This was also done to assess the condensation of metal chlorides in the space cooler and condensers.

Results achieved in Mintek pilot plant and challenges

$TiCl_4$ was produced with a low efficiency during the operation of the pilot plant. This could be explained by the size of the plant and various technical challenges faced during the operation of the pilot plant. These challenges are discussed here. This discussion does not include a number of minor modifications carried out during cold and hot commissioning to improve the integrity of the plant.

$TiCl_4$ produced at Mintek

A typical analysis of main impurities of the crude $TiCl_4$ produced in the pilot plant is given in Table I.

The high percentage of vanadium (V) is due the fact that V is present in the Ti ore chlorinated and also due to the fact that $TiCl_4$ and vanadium oxychloride ($VOCl_3$) have close boiling points. Hence, the $VOCl_3$ condenses along with $TiCl_4$. $TiCl_4$ has a boiling point of 136°C whereas $VOCl_3$ has a boiling point of 127°C[3]. Alumina (Al) is present in the form of aluminium chloride ($AlCl_3$).

Pressure build-ups

During the chlorination reaction it was observed that the pressure increased to unacceptable levels in the chlorinator so that the operation had to be stopped.

The iron chloride leaves the chlorinator in gaseous form as the temperature in the chlorinator is around 1000°C. The gas temperature in the air-cooled box drops to around 200°C and its velocity is significantly decreased (expansion), allowing the iron chloride to condense out as solids. It was observed that some of the iron chloride does not settle and gets carried away out of space cooler and blocks the lines to the $TiCl_4$ condenser. This happened principally in the elbows of the pipes where feed carry-over was deposited and some iron chloride was condensed. This leads to increasing pressure in the chlorinator.

The condensed iron chloride particles are very fine and do not settle easily. They pass through the condenser and agglomerate on the cold pipes, resulting in blockages. The space cooler reduces the velocity of the gases but is not able to provide efficient capture of the condensed iron chloride particles.

A catch pot was designed and installed after the air-cooled box to provide a high condensation surface area on Raschig rings for the iron chloride. This reduced the occurrence of blockages. Providing additional surface area inside the space cooler is envisaged to improve the separation of the iron chloride from the $TiCl_4$ gas. This will require some other modification in order to maintain an acceptable pressure drop across the system.

Chlorinator fluid bed temperature measurement and wear of the thermocouples

Temperature measurements of the fluid bed were carried out with temperature probes. These probes are K-type thermocouples placed in thermowells that protrude into the chlorinator. These probes regularly failed during the chlorination process and this resulted in chlorine leaks from the chlorinator.

The extreme conditions of temperatures higher than 1000°C and chlorine atmosphere make the temperature measurement very difficult. Adding to the above conditions is the abrasive nature of the Ti slag that erodes the thermowell, exposing the thermocouple that is destroyed immediately by contact with the chlorine. Various grades of stainless steel were used for fabricating the thermowell without success. A non-contact temperature measuring device was considered. The idea was ruled out as one of the requirements was the availability of a clean measuring surface for the infrared

Table I

Typical chemical analysis of impurities present in crude $TiCl_4$

Impurity	Parts per million (ppm)
Al	680
Fe	550
V	1910

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radiation. The condensing iron chloride on the cold surface will not provide the required clean surface. The normal ceramic thermowell did not last long due to thermal shock.

Only a special grade ceramic can withstand the severe conditions in the chlorinator fluid bed such as a ceramic thermowell with high alumina content. This will be tested.

Fluidization and sintering in the chlorinator fluid bed

During the initial heating of solid particles with a mixture of air and oxygen the fluid bed sometimes tend to defluidize. Sintering in a fluid bed causes defluidization. If this happens, the chlorinator has to be stopped, cooled down, and cleaned.

Sintering also damages the distributor plate as the slag formes bonds with the refractory of the distribution plate that has to be chipped off. It also blocks the holes in the distributor plate, resulting in high pressure drop across the distributor plate.

The blocked holes in the distributor plate holes are cleaned with thin metal rods. This can also increase the size of the holes. An increase in the diameter of the distributor plate holes leads to uneven distribution of the gases, resulting in poor fluidization.

The sintered material removed from the chlorinator contained the particles of petroleum coke and Ti slag trapped in solidified phase of molten Ti slag. The sintered material had a chemical composition different from the Ti slag it was high in Mn, Al and silica.

It was observed that the amount of oxygen in the mixture (air + oxygen) is critical; too much oxygen leads to sintering. The total oxygen content in the air-oxygen mixture should not exceed 40% by volume, as this may lead to hot spots in the fluid bed and cause sintering in the chlorinator. This was implemented throughout the chlorination campaign.

Defluidization of the fluid bed

Pockets of a 'dead zone' are sometimes observed in the fluid bed chlorinator. The 'dead zone' tends to grow and spread over the distributor plate. This leads to sintering and defluidization of the chlorinator. When the three temperatures in the fluid bed start to differ from each other, it gives an indication that the bed is not well fluidized (the three temperature probes in the fluid bed will have temperatures in a close range when the fluid bed is well fluidized).

Petroleum coke (used as a reductant in the process) has sharp edges and is not a good fluidizing material. There is a big difference in the densities of the petroleum coke (1.9 g/cc) and Ti slag (4.1 g/cc). The density difference causes the segregation of the material, resulting in formation of dead spots in the chlorinator. The reason for formation of the dead zones is the excessive quantity of petroleum coke in the chlorinator. If the quantity of petroleum coke is high in the fluid bed, it leads to segregation of the material. The Ti slag is seen fluidizing just around the holes of the distributor plate and the petroleum coke is stagnant.

As per our experience and observations while using the pilot-plant fluid bed chlorinator, the quantity of petroleum coke should not exceed 60% in the chlorinator. A higher proportion of petroleum coke leads to segregation and this tends to defluidize the bed in the chlorinator.

Refractory erosion and reactor integrity

Unreacted gases were seen bypassing the fluid bed in the chlorinator during the initial heating of the material (Ti slag + petroleum coke) with air and oxygen. Flames were observed above the fluid bed area. More oxygen was required to increase the temperature of the fluid bed.

The high alumina refractory lining in the chlorinator developed cracks and the gas passed through the reactor without reacting in the fluid bed. Unlike commercial chlorinators, the pilot-plant chlorinator cannot be operated continuously. The frequent heating and cooling of chlorinator leads to the formation of cracks in the refractory. These cracks lead to gas channelling, i.e. the gases bypass the fluid bed without reacting. Not all the oxygen entering the bottom of the chlorinator passed through the fluid bed; some oxygen passed through the cracks as it has less resistance and reacted with the CO above the fluid bed, resulting in the flame above the fluid bed.

The design of the chlorinator will be changed and provision will be made so that the refractory lining in the fluid bed area can be changed easily without having to reline the entire chlorinator.

Safety

The pilot plant is well equipped to handle hazardous gases like Cl_2 and CO. Gas monitors are placed at critical locations and linked to the scrubber and control system. The plant is provided with various extraction points and fresh air inlet ports. Various interlocking arrangements are provided to ensure safe operation of the plant.

A HAZOP study was conducted and valuable suggestions were identified and implemented during the designing stage.

Special arrangements are made to store Cl_2 and $TiCl_4$. The iron chloride waste is treated in the effluent treatment plant and the unreacted chlorine gas and uncondensed $TiCl_4$ gas are scrubbed in the caustic scrubber.

Conclusion

The design, commissioning and operation of the pilot plant for $TiCl_4$ production has helped Mintek to take a step towards further beneficiation of titanium ore or slag. The experience gained from the pilot plant will be useful for further development of this technology. The pilot plant also plays a vital role in developing human capital skills for $TiCl_4$ production.

Due to small-scale of operations, it is not possible to mimic the $TiCl_4$ gas condensation process as carried out in commercial plants. A more innovative approach should be carried out where the iron chlorides are trapped before reaching the $TiCl_4$ condensers.

The technical challenges faced in the $TiCl_4$ production process helped us in understanding the operational challenges. The recommended solutions should further help in the smooth operation of the pilot plant.

References

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