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# Effect of carbon particle on the degree of chlorination of natural rutile

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## ABSTRACT

Titania-containing feedstock is the basic raw material in the production of titanium dioxide (TiO<sub>2</sub>) pigment by either the sulphate or the chloride route. Mintek has been involved in the processing of titania-containing feedstocks since 1969 and has various patents and publications on the production of pig iron, titania slag and chlorination of titania-containing feedstocks.

Mintek is equipped with a chlorination facility comprising a semi-pilot and laboratory-scale fluid bed chlorinators. The laboratory-scale chlorinator, an 80mm diameter quartz reactor, is a versatile reactor used for the study of the chlorination kinetics of various feedstocks at various conditions of temperature, gas and feed compositions and hydrodynamics.

Carbochlorination trials of rutile were conducted in the above bubbling fluid bed reactor. Calcined petroleum coke (Petroleum coke) was used as a reductant source for the chlorination trials. The tests were carried out in comparable conditions keeping the operating conditions similar and varying the particle size distribution of the reductant in order to investigate the effect of reductant particle size on the chlorination rate of the specific natural rutile. The chlorination of 300 g of rutile in the presence of 90 g of calcined petroleum coke was carried out at a single temperature of 1000° C and constant reaction time of 30 minutes using a chlorination gas comprised of 7 and 3 Nl/min for Cl<sub>2</sub> and CO, respectively.

This paper discusses the results of the above investigation. The chlorination of rutile is very much affected by the particle size distribution of the petroleum coke.

**Keywords: Chlorination, Titanium feedstock, Fluidization, Reductant particle size effect**

## 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 reserve 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.

Titanium mineral deposits are mined to produce raw materials for the production of titanium dioxide (TiO<sub>2</sub>) pigment and titanium metal. Approximately 95% of the titanium ores mined is used for the production of TiO<sub>2</sub> pigment whilst about 3 % is used for the production of titanium metal.

TiO<sub>2</sub> pigment is a white powder with high opacity, brilliant whiteness, excellent hiding power and resistance to colour change. These properties have made it a valuable pigment and opacifier for a broad range of applications in paint, plastic, ink and paper.

The TiO<sub>2</sub> pigment is produced by two commercial processes – sulphate and chloride. The chloride process has become the most dominant process as it produces superior quality pigment with significantly fewer waste products. The chloride process consists in the chlorination of titania feedstock to produce TiCl<sub>4</sub> which is further purified and oxidized into TiO<sub>2</sub> pigment. The above chlorination is carried out in a fluid bed reactor at high temperatures of 1000 – 1050° C using chlorine gas in the presence of carbon as a reductant. The resulting product is mainly composed of iron and titanium chlorides. The high melting metal chlorides mainly consisting of iron chlorides are condensed in a cyclone separator whilst the low boiling point metal chlorides, mainly TiCl<sub>4</sub> are condensed down the line using TiCl<sub>4</sub> scrubbing towers and chilled condensers.

Mintek, a global leader in mineral and metallurgical innovations, is involved in the investigation of methods for the production and purification of TiCl<sub>4</sub> which is one of the components of the titanium beneficiation programme driven by the South African Department of Science and Technology.

## APPARATUS AND SETUP DESCRIPTION

### *Chlorination reactor*

An 80mm diameter quartz reactor is used as a bubbling fluid bed reactor. Porous quartz frit placed at the bottom of the reactor acts as a distributor plate. The frit used is a pore 2 type which has an average opening of 40 to 90 micron. The distributor plate enables the gas to flow through and fluidize the solid particles in the reactor. Gases enter through the pores of the distributor plate and fluidize the solids placed on it. A highly expanded gas solid expansion forms strictly above the distributor; the dispersion divides into many little bubbles and emulsion phases few millimetres above the plate. The bubbles grow rapidly by coalescence as they rise upwards and finally burst on the surface of the bed.

A silica thermowell protrudes through the frit into the reactor (Figure 1); this enables to measure the temperature of the bed. A 'K' type thermocouple is used for measuring the temperature. The temperature controller of the electrically heated furnace is connected to the thermocouple that reads the temperature in the burden of the fluid bed reactor. This helps in maintaining the set temperature inside the reactor.

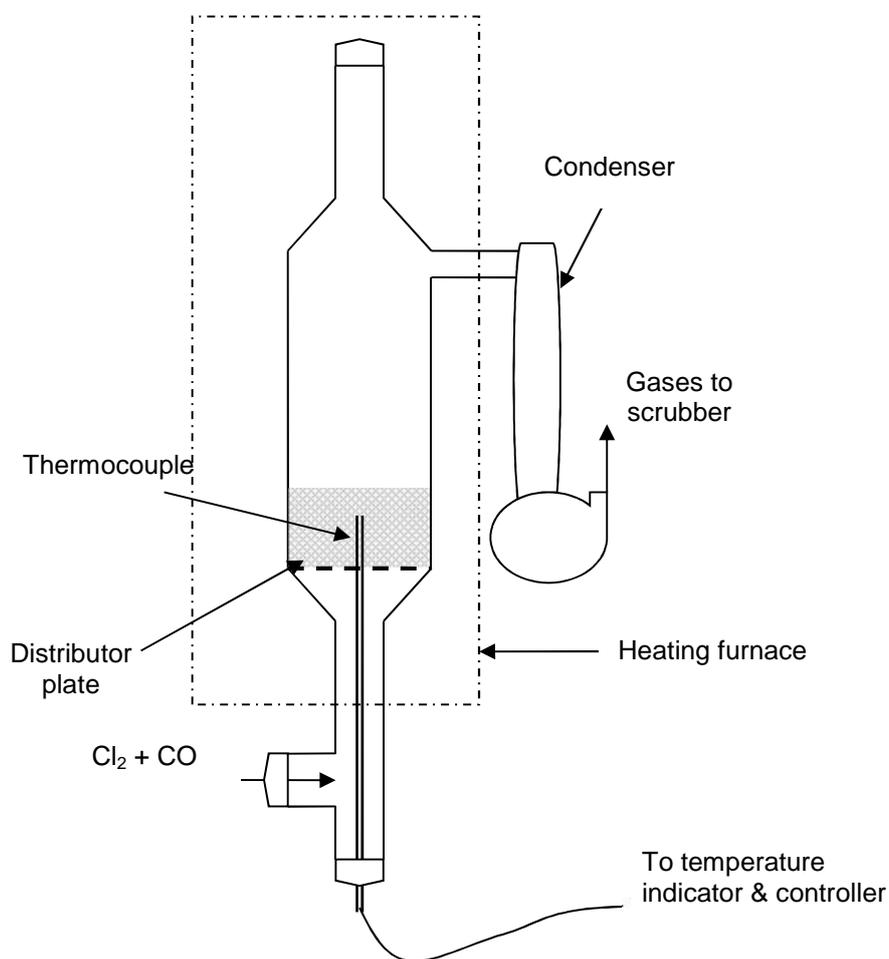


Fig 1 – Laboratory setup for carbochlorination

The crossover duct protrudes out of the furnace and is connected to a condenser. The high boiling point metal chlorides are condensed in the condenser whilst uncondensed gases are vented off to the caustic scrubber. The blowovers from the reactor are collected in the condenser. Gases enter the bottom of the reactor through a flexible tube suitable for chlorine. All gas flows are controlled and measured using variable area gas flow rotameters.

Cl<sub>2</sub>, Ar & CO gases are used from gas cylinders; a pressure regulator is used to maintain constant pressure of the gases.

### *Condenser and scrubber*

Metal chlorides comprising mainly of TiCl<sub>4</sub> are condensed in a jacketed silica condenser cooled with a coolant fluid that can reach a temperature down to 0°C. The liquid TiCl<sub>4</sub> is collected in the glass flask connected to the bottom of the condenser. This liquid also entrains and dissolves the solid metal chlorides that are condensed on the surface of the condenser.

The uncondensed gases mainly consisting of unreacted chlorine, CO, CO<sub>2</sub>, TiCl<sub>4</sub> and other metal chlorides are extracted and scrubbed in a caustic scrubber.

## **EXPERIMENTAL WORK**

### **Sample preparation**

A sample of natural rutile with a TiO<sub>2</sub> content of 93% was used in all the trials. Detailed chemical composition of the rutile ore is tabulated in Table 1. The particle size distribution of rutile is given in Table 2. In order to reduce the effect of blowovers, a rutile sample with particle size distribution between 300 micron and 106 micron was used for all the test work as finer particles less than 106 micron have a tendency of blowing out of the reactor.

Table 1 – Chemical composition of rutile

Elements	mass %
TiO <sub>2</sub>	93.04
FeO	1.20
SiO <sub>2</sub>	1.60
V <sub>2</sub> O <sub>5</sub>	0.90
Cr <sub>2</sub> O <sub>3</sub>	0.20
CaO	0.05
Al <sub>2</sub> O <sub>3</sub>	0.08
MnO	0.05
MgO	0.20

Table 2 – Physical properties of as received rutile

Particle size	mass %	Density
Micron		
-300 + 212	1.5	4.09
-212 + 150	20	4.15
-150 + 106	46	4.20
-106 + 90	22	4.20
-90 + 75	9	4.21

Calcined petroleum coke was used as a reductant, the chemical composition of petroleum coke is tabulated in Table 3. In order to study the effect of petroleum coke particle size distribution on the degree of chlorination, four different size ranges were selected: -5000 + 1400 micron; -1400 + 850 micron; -850 + 425 micron; and -425 + 212 micron. The selection of the petroleum coke particle size ranges was based on the fact that particles more than 5000 micron in size are difficult to fluidize while less than 200 micron sized particles will blow out of the reactor.

Table 3 – Composition of petroleum coke

Elements	mass %
Fixed carbon	99.3
Moisture	0.05
Volatile matter	0.3
Ash	0.4

## Procedure

The main objective of the trials was to study the effect of the reductant particle size on the chlorination rate of natural rutile. In order to conduct a comparative study of the degree of chlorination, similar operating conditions were maintained in all the trials whilst only varying the reductant particle size. To maintain a constant ore to reductant ratio, 300 g of rutile and 90 g of petroleum coke were used in all the trials. The operating temperature inside the reactor was maintained at 1000° C.

Each test followed a batch procedure. The reactor, charged with 300 g of rutile and 90 g of petroleum coke was secured in the electrically heated furnace. Argon gas was used to fluidize the bed inside the reactor during the heating period of the reactor to the reaction temperature. Once the fluidized bed burden reached the reaction temperature of 1000°C, the argon gas flow was replaced by the reactive gas composed of Cl<sub>2</sub> and CO. The Cl<sub>2</sub> flow was maintained at 7Nl/min whilst CO flow was at 3Nl/min.

The chlorination time for each test was 30minutes. After this stipulated time, the Cl<sub>2</sub> and CO flows were turned off and the power to the furnace was switched off. Argon gas was then used to flush the chlorides and cool the reactor. The material from the side arm and condenser was collected, washed and dried. The dried material was calcined at 1000° C to burn off the carbon; this material was basically the reactor blowovers. The residue from the reactor was collected and heated in a furnace at 1000°C. This was done to ensure that all the carbon was burnt off and mass of rutile was noted. From the mass recorded, the degree of chlorination was calculated using Equation 1 below.

$$\varepsilon = \frac{[\omega_i - (\omega_o + \omega_b)]}{\omega_i} * 100 \quad [1]$$

- ε = degree of chlorination (%)
- ω<sub>i</sub> = initial mass of rutile
- ω<sub>o</sub> = final mass of rutile
- ω<sub>b</sub> = mass of blowovers

## RESULTS AND DISCUSSION

### *General observations*

The rutile material mixed with petroleum coke fluidized well in the fluid bed reactor. When chlorine was introduced in the reactor at the operating temperature of 1000°C, brown dense fumes were first generated in the condenser. The fumes became light with time and turned white eventually. The chlorinated material from the reactor was yellowish in colour. The chlorinated rutile particles became finer as can be seen in Table 4.

Table 4 – Particle size distribution of chlorinated rutile

Particle size	Rutile	Test 1	Test 2	Test 3	Test 4
Micron	mass %				
-300 + 212	2	2	3	-	-
-212 + 150	30	35	18	19	21
-150 + 106	68	30	36	38	32
-106 + 90	-	15	18	15	12
-90 + 75	-	14	19	18	15
-75	-	4	6	10	20

### *Effect of reductant particle size*

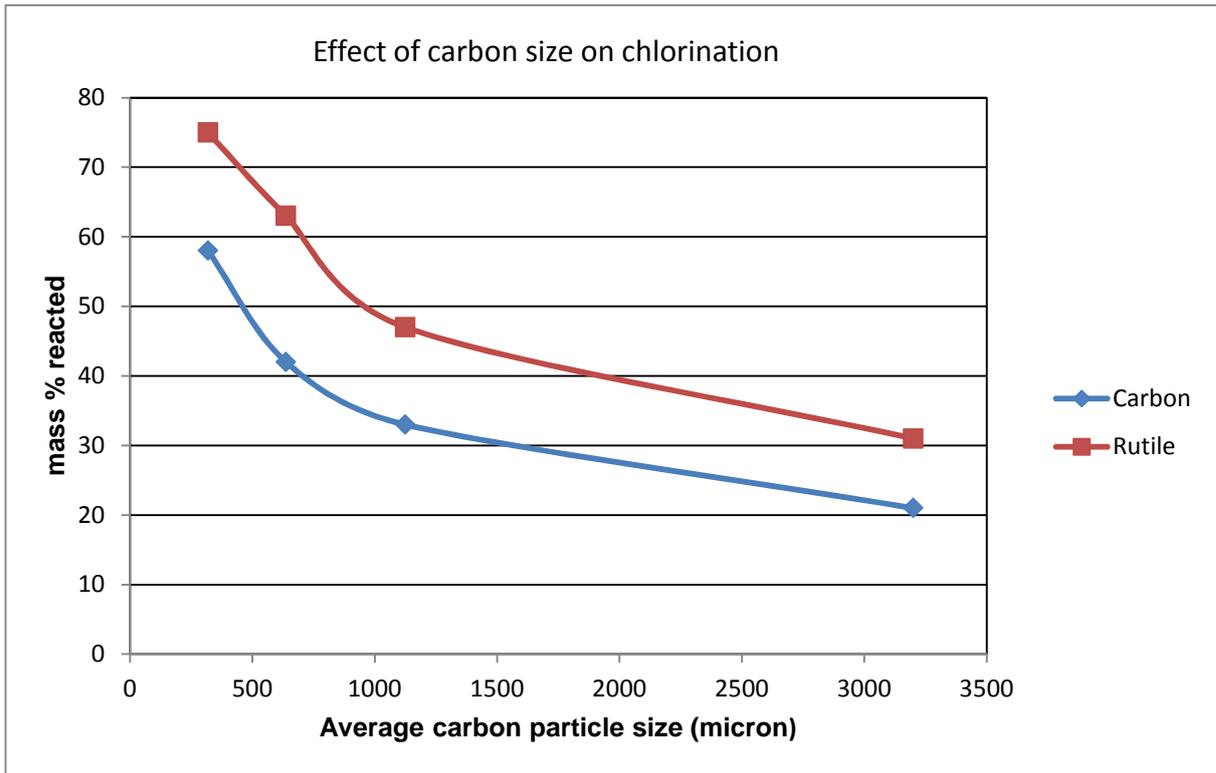
Experiments to evaluate the effect of reductant particle size on the degree of chlorination of natural rutile sample were conducted according to the above procedure.

The results are summarised in Table 5 and depicted in Figure 2. The average results of the mass balance were considered. As expected, the petroleum coke blowovers increased with the decrease of particle size. It was observed that the chlorination rate increased with the decrease of petroleum coke particle size.

Table 5 – Chlorination mass balance for rutile

	Petroleum coke particle size (micron)	Blowovers		Rutile chlorinated		Petroleum coke consumed	
		Petroleum coke (g)	Rutile (g)	Mass (g)	mass %	Mass (g)	mass %
1	-5000 + 1400	-	0.8	93	31	18.5	21
2	-1400 + 850	0.9	1	141	47	29.5	33
3	-850 + 425	2.5	1.3	189	63	37.5	42
4	-425 + 212	2.8	1.5	226	75	52.5	58

Fig 2- Rutile, Petroleum coke mass loss



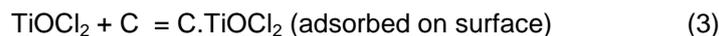
The highest degree of chlorination was observed when petroleum coke of particle size in the range between 425 micron and 212 micron was used. About 75% of the rutile was chlorinated whilst about 58% of petroleum coke was consumed in the reaction. Higher surface area available for finer petroleum coke particles may be one of the contributing factors to the higher chlorination rate of the rutile.

A close carbon-titania contact may play an important role in the carbochlorination of rutile and this is improved as the petroleum coke particle size decreases.

It is believed that there is a rapidly diffusing intermediate gas phase that transports the titanium values from the rutile to the carbon. The mechanism proposed by Dunn (1979b) <sup>[1]</sup> defines the autocatalytic role of  $TiCl_4$ . It states that an equilibrium is established at the rutile surface between  $TiCl_4$  and titania which react to form a gaseous species containing both oxygen and chlorine, known as a titanium oxychloride ( $TiOCl_2$ ).

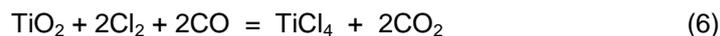


At the carbon surface there will be a number of species vying for space such as chlorine, carbon monoxide and titanium oxychloride. The carbon surface further promotes the chlorination of oxychloride to titanium tetrachloride. The oxygen from oxychloride reacts with carbon to form carbon monoxide.



Equation 3,4 & 5 were proposed by Nell & Den Hoed <sup>[2]</sup>.

The carbon monoxide formed at the carbon surface can participate in further reaction with chlorine as mentioned in Equation 6, particularly in the rutile internal surface which is not involved in the direct carbon chlorine reaction.



Intuitively, increasing the distribution of carbon in the system by decreasing the size particle will increase the probability of all the reaction involving adsorption on solid carbon to occur.

## CONCLUSIONS

The chlorination rate of rutile is very much affected by the particle size of the reductant. The rate seems progressing as the reductant particle size decreases. As can be seen in Figure 2, there is a sharp rise in the degree of chlorination of rutile when the average particle size of carbon is below 1000 micron. For the same ratio of carbon to rutile and fixed chlorination time of 30 minutes and using a similar reactive gas composed of 70% CO and 30% Cl<sub>2</sub>, the degree of chlorination of natural rutile varied from as low as 31% to as high as 75% just by varying the particle size of the reductant.

The maximum degree of chlorination of about 75% for natural rutile was observed when finer reductant of particle size in the range between 425 and 212 micron was used. When reductant of coarse particle size (-5000 + 1400 micron) was used, the degree of chlorination was about 31%. The finer particle size seems to improve the degree of chlorination. Fines of either titania feedstock or reductant are also generated during the chlorination process by various mechanisms including abrasion, breakage, etc. Hence, a fine balance has to be maintained while specifying the particle size of the reductant in commercial chlorinators.

As observed during the test work, the blowovers are negligible when coarse reductant particles are used. For finer reductant particle size (-425 +212 micron) about 2.6% of blowovers was recorded. Considering the commercial scale operations, the feeding of fine reductant has its own issues of material handling and blowovers.

Carbon is probably used more as a reagent than a catalyst in the chlorination of natural rutile. This is evidenced by the amount of carbon consumed during the carbochlorination reaction. It is obvious that the titania and reductant grain surfaces are involved in the chlorination reaction. If the carbon grain surface were missing or very small grain surface were used, e.g. extremely large particle size, the reaction would nearly cease. As stated by Le Roux, low chlorination rates were observed during the chlorination of titania feedstocks in the absence of carbon and in the presence of only CO<sup>[3]</sup>.

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## REFERENCES

1. Dunn, W.E. (1979b). High temperature chlorination of titanium bearing minerals: Part IV. Metall. Trans. B. vol 10B, pp 271.277
2. NELL, J. and Den HOED, P. Carbochlorination of rutile, titania slag and ilmenite in a bubbling fluidized-bed reactor. XII IMPC, Cape Town, 28 September–3October 2003.
3. J.T.Le Roux, "Fluidizedbed chlorination of titania slag" (MSc, University of Pretoria, 2001)