



# Nitriding of ilmenite and high-grade slag fines

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## Synopsis

Titanium bearing resources can selectively be chlorinated at temperatures below 200°C if the TiO<sub>2</sub> in the feed is nitrided before chlorination. However, the nitriding reaction is highly endothermic, requires highly reducing conditions, is only thermodynamically favourable at elevated temperatures, and is affected by mass and heat transfer restrictions. At the required processing conditions, problems might also be experienced with sintering and with melting of slag forming components in the raw materials.

A test programme was undertaken to study the effects of raw material type, temperature, gas composition, bed depth, carbon to raw material ratio and residence time in order to simulate conditions required for scaling up a nitriding process.

In contrast to previous experience with low-grade titanium-bearing slag containing about 30% TiO<sub>2</sub>, ilmenite and chlorinateable slag do not form melting phases under the studied nitriding conditions and hardly sintered at all. Both feed materials can readily be nitrided with conversions in excess of 90% at temperatures around 1300°C and using bituminous coal as reducing agent with fixed carbon in excess of 1.1 times the stoichiometric requirement. The conversion decreases as the bed depth of the feed material increases and the N<sub>2</sub>/CO ratio in the gas decreases.

Analysis of the relative rates of mass and heat transfer into the reacting beds of ilmenite and slag showed that the heat transfer rates are more limiting than the mass transfer rates. In order to increase the throughput that can be achieved in a kiln, it would be necessary to take special measures to enhance the heat transfer rates into the mass of reacting material. One such a measure is to pre-form the mass of reacting material into thin-walled, hollow brick shapes prior to introducing it into a kiln.

Depending on bed depth, temperature and N<sub>2</sub>/CO ratio, required residence times in the high temperature zone of the kiln can vary between about 6 and 10 hours.

## Keywords

Titanium dioxide, titanium nitride, carbo-thermic, reduction, ilmenite, slag, tunnel kiln, residence time.

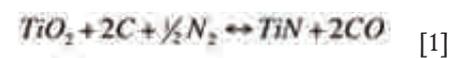
## Introduction

CSIR (Council for Scientific and Industrial Research) together with HSVC (Highveld Steel and Vanadium Corporation) and Anglo American Corporation previously developed a process to selectively extract TiO<sub>2</sub> from low-grade slag produced by HSVC<sup>1,2</sup>. The technology basically entails two steps, namely to first nitride the TiO<sub>2</sub> in the feed at about 1300°C to TiN and to then chlorinate the TiN

selectively at relatively low temperatures (about 200°C) to TiCl<sub>4</sub>.

After purification, the TiCl<sub>4</sub> produced would be suitable for the production of TiO<sub>2</sub> pigment and/or titanium metal.

The two main reactions of the process are:



$$\Delta H_{25^\circ\text{C}} = 386 \text{ kJ / gmol}$$

and



$$\Delta H_{25^\circ\text{C}} = -477 \text{ kJ / gmol}$$

The conceptual process and the underlying theory were described by Van Vuuren and Stone<sup>2</sup>.

The key advantages of the process include:

- ▶ Processing of minerals or slags that can not be processed economically via the current sulphate or chloride routes
- ▶ Highly selective extraction of titanium dioxide, resulting in less chemical waste
- ▶ Significantly lower chlorination reactor temperatures (200°C vs. 900°C)
- ▶ Significantly lower chlorination reactor volumes (more than an order of magnitude)
- ▶ Significantly lower gas volumes to be handled in the chlorination process (more than an order of magnitude).

Comparative techno-economic studies indicated that it might be more economic to use either ilmenite or high-grade slag such as so-called chloride grade (CG) slag fines or sulphate grade (SG) slag as feedstock instead of low-grade HSVC slag because of the high capital cost of the kilns required for nitriding of the feed and because of the large volume of waste arising from the use of low grade slag. In this regards, even though very little material apart from iron and titanium is chlorinated, in

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terms of current South African legislation, the slag passing through the chlorination process that is not chlorinated, will be regarded as hazardous waste and will have to be disposed of as such.

The objective of this work was to determine the effect of nitriding process conditions on the conversion of the  $TiO_2$  in ilmenite and chloride grade slag fines to TiN in order to be able to estimate the size of an industrial tunnel kiln that would be required for the process.

The main reason for considering a tunnel kiln (or rotary hearth furnace) rather than rotary kilns or fluidized beds is the endothermicity of the reaction and highly reducing conditions required. It is not practical to supply the necessary heat for the reaction by partial combustion of the reducing agent because combustion to only carbon monoxide is inefficient and in the presence of carbon dioxide, the nitriding reaction becomes unfavourable. Supplying heat indirectly via hot surfaces is simpler when the hot surfaces are stationary, as in a tunnel kiln, and also not in contact with the material being processed in order to cope with any sintering that may occur at the high temperatures required.

### Experimental

#### Nitriding experiments

The experiments were done in a muffle furnace as shown on Figure 1. The reaction vessel consisted of a large silicon carbide (SiC) crucible inside an electrically heated, top-loaded furnace. Molybdenum (Mo) crucibles made of a thick-walled Mo tube and a Mo disc at the bottom was supported inside graphite crucibles which were installed on a graphite pedestal inside the SiC crucible. The Mo tube had an inside diameter of 19.2 mm and a wall thickness of about 5 mm.

The SiC crucible was covered with a flat SiC tile with a hole through which  $N_2$  and CO were introduced and another hole through which a Pt/Rh thermocouple was inserted to measure the temperature inside the SiC crucible.

The Mo tube arrangement was used to minimize any diffusion of  $N_2$  or CO through the walls of the crucible in order to measure the effect of bed depth on the conversion of titanium dioxide under conditions where all the gas has to enter or leave the bed through the top of the bed, as would be the case in a large tunnel kiln where the feed material would be moved through the kiln in the form of a bed supported on kiln cars.

The temperature of the furnace was controlled using a PID-controller coupled to a Pt/Rh thermocouple on the outside of the SiC crucible.

The raw material (ilmenite or chloride slag and coal) was intimately mixed before loading it into the Mo crucibles.

After loading the mixtures of feed into the Mo crucibles the crucibles were loaded into the SiC crucible or muffle, and the muffle and furnace were closed.

Nitrogen was introduced through a vertical inlet on top of the furnace, flushing the atmosphere inside the muffle and the furnace switched on and heated according to a set temperature program. In cases where the effect of dilution of the  $N_2$  with CO was determined, introduction of CO started once the temperature in the furnace reached about 800°C. In such cases the atmosphere inside the SiC crucible was set by the ratio of  $N_2/CO$  fed to the crucible.

The furnace was programmed to heat up linearly to the desired maximum temperature over four hours and to then maintain the temperature at the set maximum temperature for the required time. After that, the furnace switched off and cooled down naturally. The power to the furnace was not sufficient to maintain the set linear heating rate to the maximum temperature and the desired maximum temperature was reached only after about 4½ hours.

Cooling down of the furnace was initially very rapid, but as the temperature dropped, the cooling rate dropped significantly. Whereas the nitriding reaction occurs only at temperatures above about 1200°C, the slow cooling at lower temperatures did not materially affect the time at which the samples were soaked at maximum temperature.

Two  $TiO_2$  feeds were used, i.e. ilmenite and CG slag fines. The analyses of these materials are given in Table I and II.

The particle size of the ilmenite ranged between 46 and 212  $\mu m$  with an average of 117  $\mu m$ .

Ninety per cent of the chloride grades slag fines are smaller than 70  $\mu m$  and the  $d_{50}$  is about 30  $\mu m$ .

Duff coal was used as reducing agent. The proximate, ultimate and ash analyses of the coal were measured by the SABS and are given in Tables III and IV.

The particle size distribution of the coal was measured by screening and is given in Figure 2.

For all experiments, the chosen base reaction conditions were addition of coal to  $TiO_2$  feed giving a stoichiometric ratio of fixed carbon to oxygen bound to iron and titanium of 1.3, a nitrogen flow rate of 1 L/min under atmospheric pressure

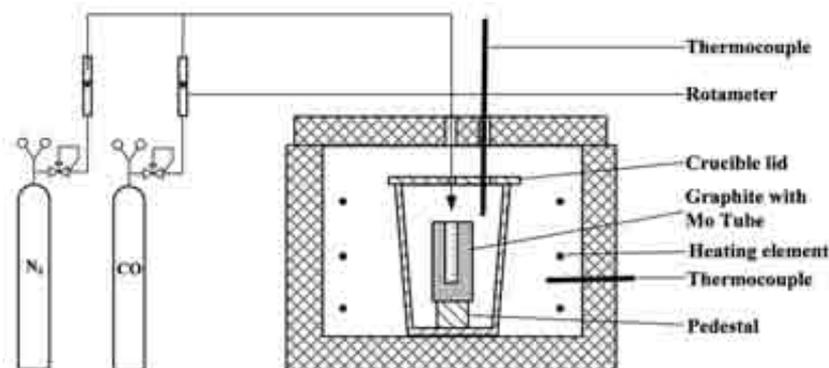


Figure 1—Schematic representation of the nitriding apparatus

## Nitriding of ilmenite and high-grade slag fines

Table I

Chemical composition of Hillendale Ilmenite (unroasted)

Component	TiO <sub>2</sub>	FeO	Fe <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	ZrO <sub>2</sub>	MgO	CaO	Al <sub>2</sub> O <sub>3</sub>	P <sub>2</sub> O <sub>5</sub>
Mass%	48.4	36.2	12.3	0.44	0.08	0.5	0.02	0.27	0.01
Component	Cr <sub>2</sub> O <sub>3</sub>	Nb <sub>2</sub> O <sub>5</sub>	V <sub>2</sub> O <sub>5</sub>	C	MnO	Others	Moisture		
Mass%	0.09	0.12	0.25	0.1	1.068	37 ppm	<1		

Table II

Typical chemical composition of chloride grade slag fines

Component	Ti as TiO <sub>2</sub>	Ti <sub>2</sub> O <sub>3</sub>	Tot. Fe as FeO	Met. Fe	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	CaO	MgO	MnO
Mass%	86.5	26	10	0.2	1.25	2	0.15	0.68	1.85

Table III

Proximate and ultimate analyses

Component	Ash	Volatiles	Moisture	Total S	Total C	H	N
Mass%	14.22	22.83	3.55	1.74	69.24	3.47	1.58

Table IV

Ash analysis

Component	SiO <sub>2</sub>	MnO	P <sub>2</sub> O <sub>5</sub>	SO <sub>3</sub>	Na <sub>2</sub> O	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	TiO <sub>2</sub>	CaO	MgO	K <sub>2</sub> O
Mass%	42.5	0.017	0.438	0.288	0.031	33.6	8.12	2.13	1.23	0.337	0.404

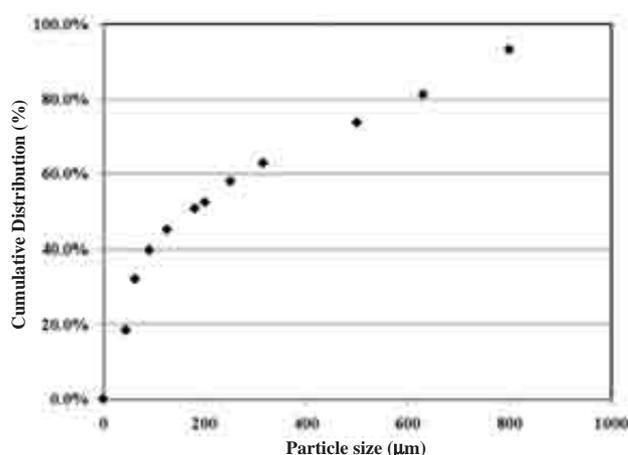


Figure 2—Coal particle size distribution

(about 0.85 bar in Pretoria) and a working temperature of 1350°C. Except for the specific variable being investigated, these parameters remained constant.

### Chlorination apparatus

It is difficult (if not impossible) to measure the extent of nitriding of TiO<sub>2</sub> accurately by chemical analysis since the product of nitriding may be in the form of a carbo-nitride. It is also more important to know how much chlorinateable reduced titanium species formed instead of how much of a specific form of reduced titanium.

The amount of reduced titanium species that can be chlorinated at low temperatures can readily be determined experimentally.

Chlorination of samples of nitrided material was done in a 1200 mm long quartz tube with an internal diameter of 28 mm, placed in a horizontal electric tube furnace. The experimental set-up is shown in Figure 3. A sample of titanium nitride was contained in an alumina boat and heated to a desired temperature in the furnace hot zone. Nitrogen was passed through the tube to flush all the air out of the tube before heating the sample to prevent oxidation of the TiN sample. When the desired experimental temperature was reached, excess chlorine was introduced with the nitrogen.

The temperature at which most of the chlorination runs was done was 400°C.

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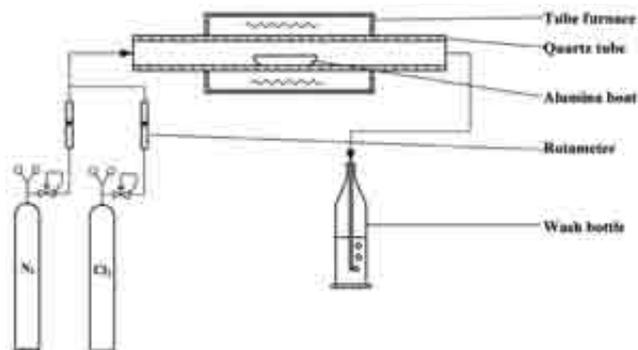


Figure 3—Schematic representation of chlorination apparatus

Table V

**Bulk densities and TiO<sub>2</sub> mass fractions of feed mixtures**

Stoichiometric ratio	Ilmenite	CG slag fines		
	Mass fraction (%)	Density (kg/m <sup>3</sup> )	Mass fraction (%)	Density (kg/m <sup>3</sup> )
R= 0.9	73.8	2120	71.3	
R=1.1	69.8	2050	67.1	1580
R=1.3	66.2	1890	63.3	1750

Although the chlorination temperature used was relatively high, the chlorination reaction rate was relatively low and experimental times of about 7 hours had to be used to achieve repeatable results for the conversions of iron and titanium. This is much longer than the approximately 1 hour found by Adipuri *et al.*<sup>3</sup> who studied the chlorination of titanium oxycarbonitride pellets suspended in a chlorine-containing gas stream and in work by the CSIR<sup>2</sup> on the chlorination of nitrided slag powder suspended in liquid TiCl<sub>4</sub> under pressure.

A possible explanation for the difference with findings of Adipuri *et al.* is that the titanium oxycarbonitride used by them contained no iron whereas the materials used in this study contained iron. The first specie that is chlorinated in the mixture is iron, which is chlorinated to FeCl<sub>2</sub>. If the rate of chlorination of FeCl<sub>2</sub> is low, the FeCl<sub>2</sub> is not removed from the rest of the material and covers it to form a protective layer, preventing contact between chlorine and the rest of the sample, thus retarding further chlorination. When the FeCl<sub>2</sub> is chlorinated to FeCl<sub>3</sub> it boils off, exposing the rest of the sample to chlorine. Note that FeCl<sub>3</sub> has a boiling point of 315°C whereas FeCl<sub>2</sub> has a much higher boiling point than the reactions conditions (1023 vs. 400°C).

In the case of the prior work of the CSIR, the reaction was done in a medium of liquid TiCl<sub>4</sub> that allowed dissolution of the FeCl<sub>2</sub> preventing the formation of a protective layer.

The conversions of iron to FeCl<sub>3</sub> and of titanium species to TiCl<sub>4</sub> in a number of samples were calculated from the mass losses of the nitrided samples during chlorination and the chemical analyses (determined by UIS Analytic (Pty) Ltd) of the nitrided samples before and after chlorination. The conversions of titanium measured in this way were then correlated with the mass loss of samples experienced during nitriding, which allowed calculation of the conversion of the titanium in the feed materials to TiN from the fractional mass loss during nitriding.

Separate correlations for different feed mixtures of TiO<sub>2</sub> source and coal were determined in this way.

### Results and discussion

Table V gives the mass fraction of TiO<sub>2</sub> feed and the bulk densities of the different mixtures tested.

The total tons of TiO<sub>2</sub> that can be converted per hour in a given kiln is:

$$M = LWh\rho_{\text{feed}}m_{\text{feed}}X_{\text{TiO}_2}F/t_{\text{oxid}} \quad [3]$$

Preliminary conceptual designs of a tunnel kiln that would be suitable on a large scale for a TiO<sub>2</sub> nitriding process indicated that if the feed through the kiln is heated up in three hours, then kept at a maximum temperature for six hours and afterwards cooled in about three hours, sufficient heat can be transferred to the reaction mixture to satisfy the energy requirement of the endothermic reactions. Most of the experiments were therefore done to determine if a time of six hours at a selected maximum temperature is adequate to also provide sufficient time for the relevant reactions and diffusional processes to occur.

Only one type of coal was used in the tests because in prior unpublished work, it was found that the carbon source used had little effect on the process provided the carbon particle size is less than about 200 μm. It was also previously found that the type of carbon has little effect on the rate of the process.

The various parameters studied were:

- ▶ Type of TiO<sub>2</sub> feed (ilmenite and CG slag fines)
- ▶ Ratio of fixed carbon in the coal to the stoichiometric requirement (0.9, 1.1 and 1.3)
- ▶ Maximum temperature (approximately 1225, 1275 and 1325°C)
- ▶ Time at maximum temperature (6 and 8 hours)
- ▶ Bed depth (25, 50, 75 and 100 mm)
- ▶ CO/N<sub>2</sub> ratio (0 and 1.0).

## Nitriding of ilmenite and high-grade slag fines

Figure 4 is a photograph of ilmenite, nitrided in a graphite crucible. No sintering of the bed of material was observed, which has a direct impact on the kiln design. In prior work on low grade slag from Highveld Steel and Vanadium Corporation, significant sintering occurred and a kiln concept was developed to cope with this sintering (Van Vuuren *et al.*<sup>4</sup>) The effect of sintering was actually used to form relatively thin-walled blocks of reacting materials that allows for faster diffusion of nitrogen into the mass of reacting solids. In the case of ilmenite and CG slag fines, the positive benefit that was derived from the sintering effect of HSVC low-grade slag will be more difficult to achieve and more binder material will have to be used to achieve the same effect. It was concluded that with a non-sintering reaction mass, it might be better to simply use a deeper bed of material.

When a deeper bed of material was reacted (i.e. a 75 mm deep bed) a deposit of fine carbon and nitrided product formed on the rim of the crucible (see Figure 5). This was caused by particles being carried out of the bed of reacting material by volatiles and product gas flowing out of the bed of reacting material. The deeper the bed, the more gas formed and hence the more fine particles were carried out of the bed. Although the amount of particles carried out are very small, it would probably be advisable in an industrial kiln not to heat at a faster rate in order to avoid losses of feed material and undesired deposition of fine solids in areas of low gas flow.

Figure 6 shows the effect of bed depth and maximum temperature on the average  $TiO_2$  conversion when beds of ilmenite were nitrided using a  $CO:N_2$  ratio of one, a stoichiometric carbon ratio of 1.3 and a reaction time of 6 h at maximum temperature. As can be seen, the extent (and hence the rate) of nitriding increased substantially with temperature.



Figure 4—Nitrided ilmenite

It is interesting that at lower temperature (1229°C) the conversion of  $TiO_2$  was virtually independent on the bed depth, whereas at higher temperatures the average conversion became a strong function of bed depth. If the rate of reaction is the rate limiting step and mass transfer rates are much faster than the reaction rate, the conversion of  $TiO_2$  would be independent of bed depth, whereas if the diffusion of  $N_2$  into the bed and  $CO$  out of the bed is rate limiting relative to intrinsic reaction rates, the average conversion would be a strong function of bed depth. In actual fact in the extreme of the latter case, the profile of  $TiO_2$  conversion through the bed would be in the form of a reaction front moving through the bed and the average conversion as a function of bed depth would vary with the inverse of the total bed depth.

In view of the change of the profiles of  $TiO_2$  conversion with temperature, it is concluded that at the lower temperature, the conversion of  $TiO_2$  is limited by the intrinsic reaction rates, whereas at higher temperatures, the intrinsic reaction rate becomes faster and the mass transfer rates become increasingly important as the bed depth increases.



Figure 5—Material blown out of the crucible

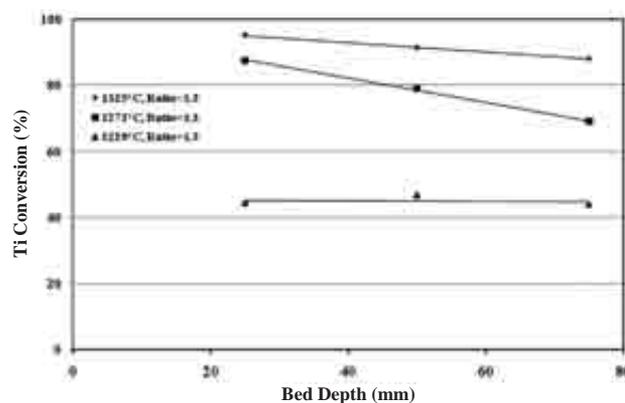


Figure 6—Nitriding of ilmenite using a  $CO/N_2$  ratio = 1

## Nitriding of ilmenite and high-grade slag fines

Figure 7 illustrates the effect of bed depth, temperature and stoichiometric ratio on  $TiO_2$  conversion. At first glance it appears that increasing the stoichiometric ratio from 1.1 to 1.3 has a significant effect on  $TiO_2$  conversion. However, the concentration of  $TiO_2$  in the bed of reacting material in the mixture with a stoichiometric ratio of 1.1 is 14% higher than in the bed with a stoichiometric ratio of 1.3. A large part of the difference is therefore simply caused by the larger amount of  $TiO_2$  in the case of the bed with the lower carbon feed.

The relatively larger difference between the conversions achieved for different ratios of carbon used at 1275°C and the weak effect of bed depth on the conversion of  $TiO_2$  at a stoichiometric ratio 1.1, suggests that at lower temperatures (relative to 1325°C) and lower carbon concentrations, the intrinsic reaction limits the overall rate of reaction.

The effects of temperature and bed depth on the  $TiO_2$  conversion of CG slag fines are shown in Figure 8. The conversions achieved were slightly lower than that of ilmenite at similar conditions. However, the concentration of  $TiO_2$  in the reacting beds of CG slag fines were more than 50% higher than that in the ilmenite beds (about 960 kg/m<sup>3</sup> vs. 610 kg/m<sup>3</sup>). This result together with the fact that for both raw materials the conversions achieved for 15 mm deep beds were not 100% and the conversions achieved for 50 mm deep beds were well in excess of 50% of that achieved for 25 mm deep bed, indicates that at temperatures as high as 1325°C both intrinsic reaction rates and mass transfer rates affect the overall conversion.

Figure 9 shows the effect of temperature and bed depth on the nitriding of CG slag when the time at maximum temperature is increased to 8 hours. As can be seen, the average conversions increased by about 10% compared to the conversions achieved over six hours. For a bed depth of 50 mm the conversion is virtually complete after 8 hours at 1314°C.

A couple of experiments were done to study the effect of the  $CO:N_2$  ratio. It was for example found that when pure  $N_2$  was used to nitride a bed of coal and ilmenite with a stoichiometric ratio of 1.3, for 6 hours at 1325°C, beds of 25, 50 and 75 mm were fully nitrided. Similarly, beds of CG slag were fully nitrided after 8 hours. At a lower  $CO:N_2$  ratio, the  $N_2$

concentration is higher and the rate of  $N_2$  diffusion into the beds of reacting material is higher, resulting in higher conversions compared to that achieved at a higher  $CO:N_2$  ratio.

Although an increase in  $N_2$  concentration results in higher conversions, it will not be practical to operate the process in a virtually pure  $N_2$  atmosphere because of excessive  $N_2$  consumption. A better way to utilize the effect of a higher  $N_2$  concentration in a real tunnel kiln, would be to feed the  $N_2$  into the kiln in a countercurrent manner to the movement of the solid material through the kiln.

An interesting difference between the nitriding of ilmenite and the nitriding of CG slag is that in the case of ilmenite, all the iron in the beds of reacting material were fully reduced to metallic iron before any substantial degree of titanium nitriding occurred. This was not so with the nitriding of CG slag. For example, when the conversion of  $TiO_2$  reached a level of about 50%, the iron reached a conversion of only about 75% to metallic iron.

This difference might be ascribed to the difference in iron oxide content between ilmenite and slag. In the case of ilmenite, all the iron can be reduced without any of the  $TiO_2$  reacting because as the iron is reduced, pores open in the ilmenite crystal structure that allows the diffusion of  $CO$  into the structure to reduce remaining iron oxide in the crystal. CG

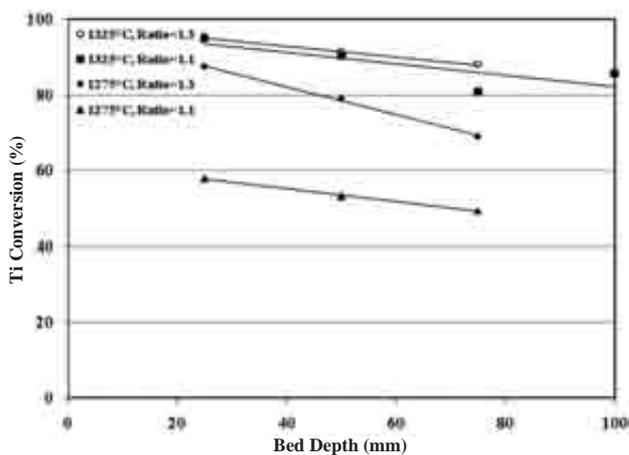


Figure 7—The effect of stoichiometric ratio on nitriding of ilmenite for 6h

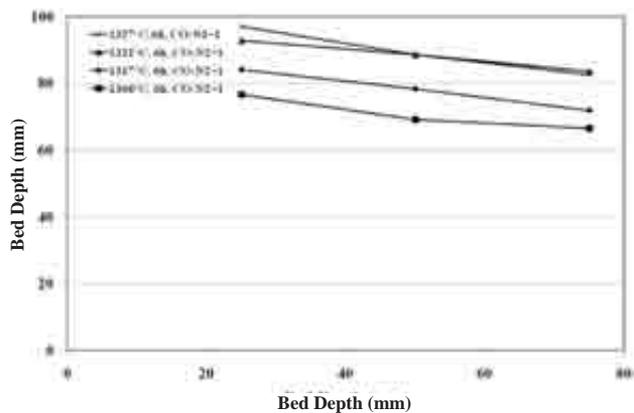


Figure 8—The effect of temperature and bed depth on the nitriding of CG slag fines

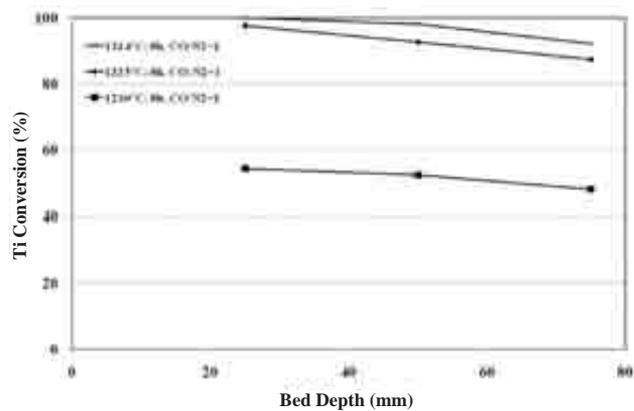


Figure 9—Nitriding of CG slag in 8 hours at maximum temperature

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slag also has a crystalline structure, karrooite<sup>4</sup>, but the FeO to TiO<sub>2</sub> ratio is significantly lower than that of ilmenite so that FeO is more encapsulated by TiO<sub>2</sub>. The result is that as some FeO is reduced, smaller and fewer pores relative to ilmenite open up to allow CO to penetrate into the crystal to reduce the remaining FeO. CO can therefore not penetrate effectively through the CG slag crystal structure until the TiO<sub>2</sub> structure is broken up by the nitriding reaction.

If CG slag is used as feed to a nitriding process, with the view to subsequently remove iron from the material by leaching, it would be imperative to achieve virtually full conversion of TiO<sub>2</sub> to TiN in order to remove the iron efficiently.

### Theory

Although the envisaged nitriding kiln is a very complex system with variations along the length of the kiln, with all the species in the system, with a multitude of solid phases and the gas phase, with mass transfer considerations into the bed of materials and into the particles, with kinetics of different reactions, with heat transfer considerations such as radiation to the bed of material, conduction into the bed of materials and conduction into the bed support material, valuable insight into the system can be gained by simplifications to consider limiting cases.

The experimental programme was designed to investigate one such a limiting case namely the case where mass transfer into the bed of material is limiting.

Whereas the titanium carbo-nitriding reaction is very endothermic, 370 MJ/gmol TiN at 1300°C, it is possible that heat transfer may be more limiting than mass transfer rates.

### Diffusion of nitrogen into the bed controlling

If the following simplifying assumptions are made for the case of mass transfer limited conditions:

- At the high temperatures where nitriding occurs, the titanium species is in equilibrium with the nitrogen and carbon dioxide
- The accumulation of nitrogen in the gas phase is negligible relative to the amount of nitrogen bound to TiN because of the very low molar density of the gas phase
- All the iron oxide is reduced and all the volatiles from the coal are released before the temperature is high enough for titanium dioxide carbo-nitriding to occur
- There are no temperature or concentration differences along the width of the kiln at a specific depth in the bed, the reaction occurs at a horizontal reaction plane parallel to top of the bed and the plane moves downwards as nitrogen diffuses to the plane and is consumed at the plane.

The rate of nitrogen transfer to the reaction plane per unit area is:

$$N_{N_2} = -D_{eff} C_G \frac{dy}{dx} + y(N_{N_2} + N_{CO})$$

But

$$N_{CO} = -4N_{N_2}$$

Therefore

$$N_{N_2} = \frac{D_{eff} C_G}{3h} \ln \left[ \frac{(1+3y_1)}{(1+3y_2)} \right]$$

The rate at which the reaction plane moves away from the top of the bed plane is:

$$\frac{dh}{dt} = \frac{2N_{N_2}}{C_{GS}}$$

Substituting Equation [1] into Equation [2] and integration of the result assuming that carbonitriding begins at time t=0 and that the concentrations of gas at the bed-gas interface and at the reaction plane are constant give:

$$h = 2 \sqrt{\frac{D_{eff} C_G t}{3C_{GS}} \ln \left[ \frac{(1+3y_1)}{(1+3y_2)} \right]}$$

Table VI gives the nitrogen mole fraction in equilibrium with carbon and titanium oxides at different temperatures at an atmospheric pressure of 0.85 bar as calculated using the HSC thermodynamic modelling programme<sup>6</sup> assuming that different titanium oxide species form separate phases.

Considering the reported results in Figures 8 and 9 for the nitriding of 50 and 75 mm deep beds of CG slag fines at >1310°C, it works out the minimum effective diffusion coefficient of nitrogen through the bed of material had to be between 25 and 57% of the gas phase diffusion coefficient of nitrogen in carbon monoxide in order to achieve the measured conversions. For the 50 mm beds, lower minimum coefficients are required than for the 75 mm deep beds, which is what can be expected if the intrinsic kinetics were not infinitely fast.

For porous media, the effective diffusivity is often estimated from the fluid (gas) diffusion coefficient, the bed porosity and the so-called tortuosity:

$$D_{eff} = D_{Gas} \frac{\epsilon}{\tau}$$

In the case of the beds of CG slag fines, the bed porosity after nitriding was in the order of 70%. For packed beds of different materials with a porosity of 70%, the ratio between the porosity and tortuosity is typically between about 0.35 and 0.57. This is quite close to the estimated minimum values, which suggests that even though in the experiments the resistance of the process to the rate of intrinsic reaction kinetics was not negligible at the high temperatures, diffusional mass transfer limitations contributed significantly to the overall resistance. Furthermore, for modelling purposes, this result gives confidence in the adequacy of estimating the effective diffusion coefficient from the bulk gas phase diffusion coefficient and the bed porosity and tortuosity.

Table VI

#### Equilibrium nitrogen gas fraction

Temperature (°C)	1150	1200	1250	1300
N <sub>2</sub> fraction	0.505	0.315	0.089	0.020

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### Conduction in bed controlling

In the limiting case where conduction into a reacting bed material is the rate limiting step and where the rate of diffusion of nitrogen into the bed is infinitely fast and all the reactions are at equilibrium, the reaction will occur at a reaction plane that moves into the bed as heat is transferred to the reaction plane.

The temperature of the reaction plane will be the temperature where the reaction of titanium oxides, carbon and nitrogen will be at equilibrium with the nitrogen in the gas space above the bed. If the fractions of nitrogen and carbon monoxide are both 50%, the temperature of the reaction plane would be about 1150°C as can be seen from Table VI.

Assuming that the sensible heat accumulation is negligible compared to the heat of reaction, the flux of heat transfer to the reaction plane is:

$$Q = \frac{k\Delta T}{h}$$

The velocity at which the reaction plane moves away from the bed-gas interface is:

$$\frac{dh}{dt} = \frac{k\Delta T}{hC_{N_2}\Delta H}$$

Assuming that at time zero the reaction plane is at the top of the bed, integration gives:

$$h = \sqrt{\frac{2k\Delta Tt}{C_{N_2}\Delta H}}$$

In a study on the kinetics of carbothermic reduction reactions under heat transfer control a effective thermal conductivity of 0.53 W/mK for a bed of limestone had been used<sup>8</sup>. This is similar to values predicted by the method proposed by Sih and Barlow<sup>9</sup> for the bed of reaction titania slag.

At 1150°C the heat of reaction of the carbonitriding reaction is 373 MJ/kmol TiN. If a value of 20% more, or 448 MJ/kmol is used instead in order to compensate for the assumption to neglect the effect of the accumulation of sensible heat and for the heat of reaction of the iron present in the CG slag and a temperature difference of 175°C (1325–1150) is assumed, it follows that the rate of reaction under complete heat transfer control is about 1.9 times slower than the rate under complete mass transfer control conditions. If a more realistic reaction plane temperature of say 1225°C is assumed, the achievable heat transfer limited reaction rate is about 2.5 times less than that determined by mass transfer rate limitations.

Furthermore, as already mentioned earlier, even at temperatures as high as 1310°C, the resistances caused by finite intrinsic rates of reactions are not negligible.

It is therefore not possible to simply estimate the throughput that can be achieved in a tunnel kiln from the experiments as described above. An experimental configuration such as that used by Coetsee and Pistorius<sup>10</sup> with a modification to ensure one-dimensional mass transfer as well as one-dimensional heat transfer would be required to realistically simulate by laboratory experiments the achievable

conversions and throughputs of a single bed of material fed through a tunnel kiln.

Assuming a temperature difference of 100°C between the top of the bed and the reaction plane, it follows that a bed of CG slag of about 21 mm deep can be fully nitrided in 6 hours. The throughput that can be achieved in a kiln that is 6 m wide by 100 m long with a nitriding section of 50 m is equivalent to about 0.97 ton TiO<sub>2</sub> per hour.

### Radiative heat transfer

The mass and heat transfer resistances due to diffusion and conduction into the bed of reacting material can be reduced significantly if the feed material is shaped into relative thin-walled hollow brick shapes before feeding it into a kiln instead of processing it as a thick bed of powder<sup>4</sup>. However, regardless of how rapidly the nitrogen diffuses or heat is conducted into the mass of reacting material, the heat for the endothermic process still has to be transferred from an external heat source to the material. Much of the preheating of the feed can be done by convective heat transfer, but once the temperatures reached are too high for convenient materials of construction to be used, radiative heat transfer from hot refractory materials such as silicon carbide becomes more practical.

The energy that has to be transferred by radiation to the mass of reacting materials has been estimated by assuming that the feed can be heated convectively to 800°C, where most of the coal would be devolatilized but virtually no reduction of iron or titanium oxides would have occurred and by assuming that the average temperature of the reacting mass of material after nitriding is 1300°C. For CG slag and ilmenite with a fixed carbon stoichiometric feed ratio of 1.3, the energy required it is about 441 and 679 kJ/gmol TiN produced respectively.

Approximating the heat transfer by two infinite planes at constant temperatures, the heat exchanged can be calculated by:

$$\frac{Q}{A} = \frac{\sigma(T_1^4 - T_2^4)}{\frac{1}{\epsilon_1} + \frac{1}{\epsilon_2} - 1}$$

The emissivity of SiC is typically between 0.83 and 0.85<sup>11</sup> and a value of 0.8 is typical for powder beds studied by Sih and Barlow<sup>12</sup>.

Assuming that the hot surface is at 1400°C and the reacting mass at 1300°C, the radiative heat exchange rate is approximately 68 kJ/m<sup>2</sup>. For the estimated energy requirements, the required radiative heat transfer areas to nitride one ton TiO<sub>2</sub> per hour are 35 and 23 m<sup>2</sup> respectively if ilmenite and CG slag is processed. Naturally this can be reduced if the SiC temperature is increased, which is possible, but which is probably unnecessary because of the other transfer rates that have to be enhanced to the same extent as well.

### Conclusions

The preferred process conditions for an industrial-scale operation are approximately as follows:

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- A bed operating temperature of about 1300°C .
- A fixed carbon to ilmenite stoichiometric ratio of 1.1
- An average particle size <200 μm for both coal and TiO<sub>2</sub> feed.

Under mass transfer limited conditions almost full conversion of ilmenite with bed depths of up to 100 mm and CG slag with bed depths of up to 75 mm in 8 hours seems possible. Unfortunately heat transfer rate limitations are more restrictive and the actual depth of beds that can be converted would be in the order of three times less.

By pre-forming the feed material into thin-walled hollow brick shapes, it would be possible to overcome the restrictions of diffusion of nitrogen and conduction of heat into the mass of reacting material, but then radiative heat transfer to the mass of reacting materials to provide the energy for the highly endothermic reactions would become the limiting condition.

It is estimated that under radiation limited conditions the hot radiative heat transfer surface area required is about 35 m<sup>2</sup> per ton TiO<sub>2</sub> nitrided per hour when processing ilmenite and 23 m<sup>2</sup> when processing CG slag. For a 6 m × 100 m long kiln that has a radiative heating section that is 55 m long, it works out that the equivalent of about 9.5 t/h of TiO<sub>2</sub> can be nitrided when processing ilmenite and about 14.6 t/h when processing CG slag fines. The challenges are to reduce the mass and heat transfer limitations in the reacting mass sufficiently to achieve such a high rate of production

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### Nomenclature

A =	area	m <sup>2</sup>
C <sub>G</sub> =	molar concentration of kiln gas	kmol/m <sup>3</sup>
C <sub>B,Ti</sub> =	molar titanium concentration of the bed	kmol/m <sup>3</sup>
D =	diffusion coefficient	m <sup>2</sup> /s
F =	fraction of TiO <sub>2</sub> converted	
ΔH =	heat of reaction	J/kmol
k =	thermal conductivity	W/mK
M =	rate of TiO <sub>2</sub> converted	kg/s
N =	molar flux	kmol/m <sup>2</sup> s
L =	length of kiln	m
W =	width of the kiln	m
h =	height of the bed of feed in the kiln or height of mass nitrided	m
m <sub>Feed</sub> =	mass fraction of TiO <sub>2</sub> feed	
Q =	heat flux	W/m <sup>2</sup>
T =	temperature	K
t =	time	s
t <sub>Total</sub> =	the total residence time in the kiln	s
X <sub>TiO<sub>2</sub></sub> =	mass fraction of TiO <sub>2</sub> in the TiO <sub>2</sub> feed	

x =	distance from the top of the bed	m
y =	nitrogen mole fraction	
ε =	bed porosity	
ε <sub>1</sub> =	emissivity of hot surface	
ε <sub>2</sub> =	emissivity of bed	
σ =	Stefan-Boltzmann constant	W/m <sup>2</sup> K
ρ <sub>Bed</sub> =	the bed density	m
τ =	tortuosity of bed	

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