

SELECTIVE RECOVERY OF TITANIUM DIOXIDE FROM LOW GRADE SOURCES

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Abstract

There are a number of readily available, large reserves of titanium dioxide bearing minerals from which the titanium dioxide cannot currently be economically recovered via current commercial recovery processes due to:

- The grade of titanium dioxide being too low, resulting in uneconomic, large effluent or by-product generation rates, or
- The presence of contaminants that cannot be handled by commercial processes.

A novel, two-step process has been developed to selectively extract titanium dioxide and overcome the limitations of the current commercial processes.

In the first step, titanium oxides are carbo-thermally reduced in the presence of nitrogen at about 1250°C to produce titanium nitride. The titanium nitride is then selectively chlorinated at temperatures as low as 200°C to produce titanium tetrachloride. The titanium tetrachloride can then be converted to titanium dioxide or titanium metal via conventional processes.

The process has been successfully demonstrated on a continuous bench scale which confirmed the operability and selectivity of the process.

The process is the first fundamentally new route in about fifty years to recover titanium values. 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).

Introduction

There are a number of readily available, large reserves of titanium dioxide bearing minerals from which the titanium dioxide cannot be recovered economically via current commercial processes due to:

- The grade of titanium dioxide being too low, resulting in uneconomic, large effluent or by-product generation rates, or
- The presence of contaminants that cannot be handled by commercial processes.

Specific examples of such resources include:

- Titanium bearing slag from steel production plants using titaniferous magnetite as feedstock (i.e. Highveld Steel and Vanadium Corporation¹ and New Zealand Steel²)
- Titanium resources containing too much chromite for use in the chloride process
- Titanium slag that is too fine for use in the chloride process

- Perovskite (CaTiO₃) resources in Colorado³.

The main problem with utilizing a low-grade resource is the amount of chemical wastes produced per unit of pigment of produced. If a TiO₂ bearing feedstock containing 80% TiO₂ is use, the amount of other components that could potentially react with the TiO₂ liquefaction substance (sulphuric acid or chlorine) is 250 kg/t TiO₂ contained. If in comparison a feedstock containing 25% TiO₂ is used, this increases to 3 t/t TiO₂ contained, or 12 times more.

With such low-grade feed, it also becomes uneconomical to transport the feedstock because the mass of material that has to be transported per ton of TiO₂ increases almost four fold. Such a feed therefore has to be processed at source and if the source is at an inland location, the final effluent and waste disposal measures have to comply with inland regulations where it is unacceptable to release even neutralised salt water into fresh water resources.

It is conceivably possible to recover and sell by-products co-recovered from the feedstock. However, the sheer volume of such by-products and the number of such different by-products makes this a daunting undertaking.

In order to overcome the above-mentioned difficulties and the limitations of current commercial processes to utilize low-grade feed, a selective, two-step process was developed to extract titanium¹.

In the first step, titanium oxides are carbo-thermally reduced in the presence of nitrogen at about 1250°C to produce titanium nitride. The titanium nitride is then selectively chlorinated at temperatures as low as 200°C to produce titanium tetrachloride. The titanium tetrachloride can then be converted to titanium dioxide or titanium metal via conventional processes.

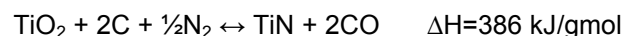
Process Fundamentals

General

Highveld Steel and Vanadium Corporation uses titaniferous magnetite as feed for their steel plant in Witbank. The slag produced in their plant typically contains 22 to 32% titanium dioxide⁴. The selective chlorination process has been demonstrated with this slag.

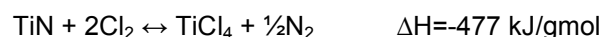
The selective chlorination process is a two-step process. In the first step, TiO₂ is reduced in the presence of nitrogen to form titanium nitride, via the following reaction:

Reaction 1:



The titanium nitride is then chlorinated selectively at low temperature to produce titanium tetrachloride:

Reaction 2:

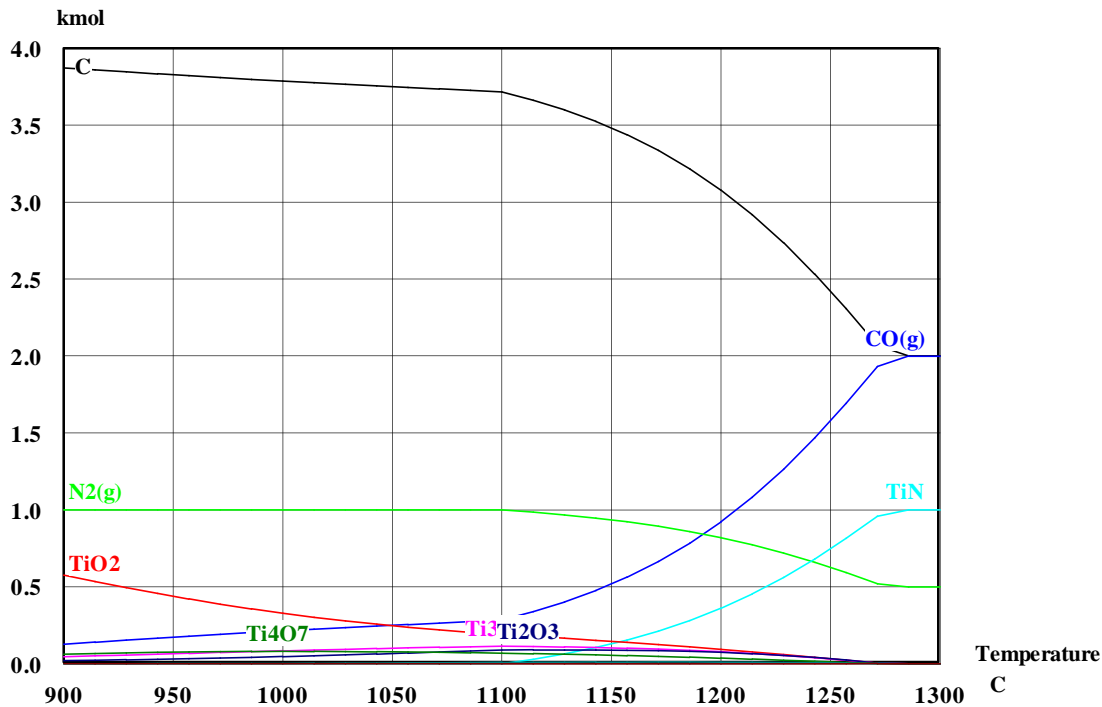


Nitriding

The carbo-thermal reduction of TiO₂ in the presence of nitrogen to form TiN is a strongly endothermic reaction, requiring temperatures of 1250°C to 1300°C and highly reducing conditions.

A simplified indication of the equilibrium composition of the material as a function of temperature is shown in Figure 1 below. The figure shows the equilibrium composition as a function of temperature if 1 kmol of TiO_2 is reacted with a 100% excess of carbon (4 kmol) and nitrogen (1 kmol).

Figure 1: Equilibrium Composition during Nitriding



The mineralogical form of the titanium oxide species affects the thermodynamic equilibrium of the reaction. Calcium titanate, CaTiO_3 (Perovskite) is more stable than magnesium titanate MgTiO_3 , (Geikilite) which is more stable than titanium dioxide or ilmenite (FeTiO_3). Higher temperatures are therefore required to convert these mineral compared to rutile (TiO_2), but that can be partially offset by enriching the reducing atmosphere with nitrogen. Experimentally it was found that at 1300°C residence times in the order of 6 hours were sufficient to ensure high conversion of the titanium species in slag to titanium nitride for the envisaged scale-up conditions.

It can be expected that different reductants would have different reactivities. However, experimentally the effect on titanium conversion was small. It is suspected that the nitriding of the titanium oxides occur via carbon monoxide rather than a direct reaction between the oxide, carbon and nitrogen and that the CO_2 formed in this way is then reduced by carbon in close proximity to the slag particles. Furthermore it is believed that the nitriding reaction rate of the titanium oxides with CO and N_2 is slower than that of the reaction of carbon with CO_2 . The reaction rate-limiting step is therefore the reaction of the titanium oxides with CO and N_2 , and is virtually independent of the reductant source, as observed.

High conversions can be obtained under laboratory conditions. However, at the temperatures required for high conversions (+90%), the solid material is close to its melting point. The material becomes soft and sticky, and sintering and agglomeration of material occurs.

Developing scaleable continuous nitriding step posed many difficulties e.g:

- The high processing temperatures required

- The large scale at which a commercial process would have to operate (In the order of 100 000 tpa per reactor)
- The energy for the reaction must be provided indirectly in order to maintain sufficiently reducing conditions in the nitriding reactor,
- Melting and accretion formation, and
- Limited mass transfer rates of nitrogen into the bulk volume of feedstock being processed and of carbon monoxide out of the bulk volume.

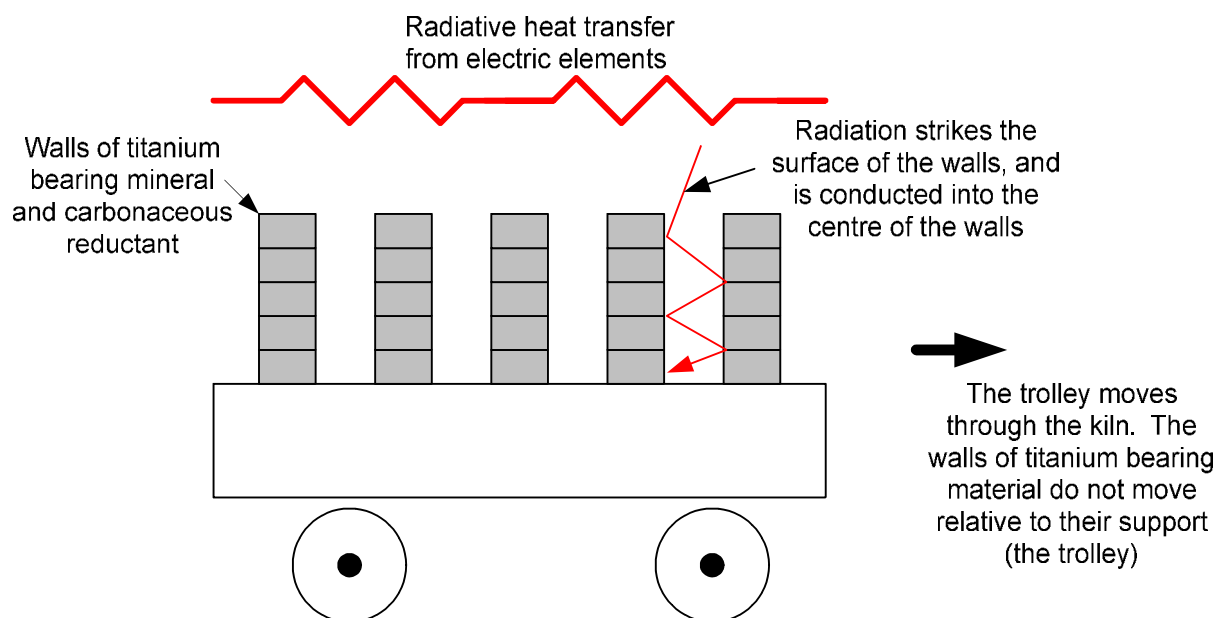
A large number of different furnace configurations were considered, i.e. rotary kilns, fluidised beds, direct resistance rotary kilns, shaft furnaces, electric arc furnaces, top hat furnaces and finally tunnel kilns. In conventional furnaces such as rotary kilns, the soft material sticks to the walls of the kiln, and the kiln eventually needs to be shutdown to remove accretions that build up in the kiln. Agglomeration in moving beds such as fluidised bed reactors causes the beds to slump.

The only kiln type that satisfied all the physical and scale-up requirements was an indirectly heated tunnel kiln. Various novel aspects of using a tunnel kiln in the envisaged mode were required in order to overcome various scale-up problems^{5,6}.

The suitability of a continuous tunnel kiln was demonstrated through various batch experiments and demonstrations simulating a batch of material moving through a tunnel kiln. The tests include laboratory scale experiments on a gram and on a kilogram scale, 100 kg batch operation and finally about 15 tons of materials were processed successfully in ca 400 kg batches.

In the proposed nitriding process, milled slag and reductant are mixed and extruded into thin-walled hollow blocks. The blocks are stacked onto kiln cars and then processed in a tunnel kiln. The shape of the blocks is optimised to enhance radiative heat transfer to the material; conductive heat transfer inside the material and diffusive mass transfer inside the material; (see Figure 2).

Figure 2: Simplified Tunnel Kiln Schematic



The titanium mineral bearing blocks do not move relative to their support (the kiln cars). As the material heats up, it softens and sinters. Under oxidizing conditions the slag melt, but under reducing conditions, as the TiO_2 is converted to carbide or nitride, the slag becomes much stiffer, to be more like clay rather than a flowing liquid. The softening limits the practical height of the blocks. Because the blocks do not move relative to their support as they are moved through the furnace, they retain their shape throughout the process preventing the formation of large lumps of material or accretion to the walls of the furnace.

Chlorination

The main process problem of the second step is the prevention of temperature runaways due to the high exothermicity of the reaction. Two reactor types that have excellent heat transfer characteristics are fluidised beds and slurry reactors of which slurry reactors are superior for the specific application. The main advantage of a slurry reactor for highly exothermic reactions between a gas and a solid is that the gas liquid mass transfer rate becomes limiting as the temperature increases preventing the reaction to run away.

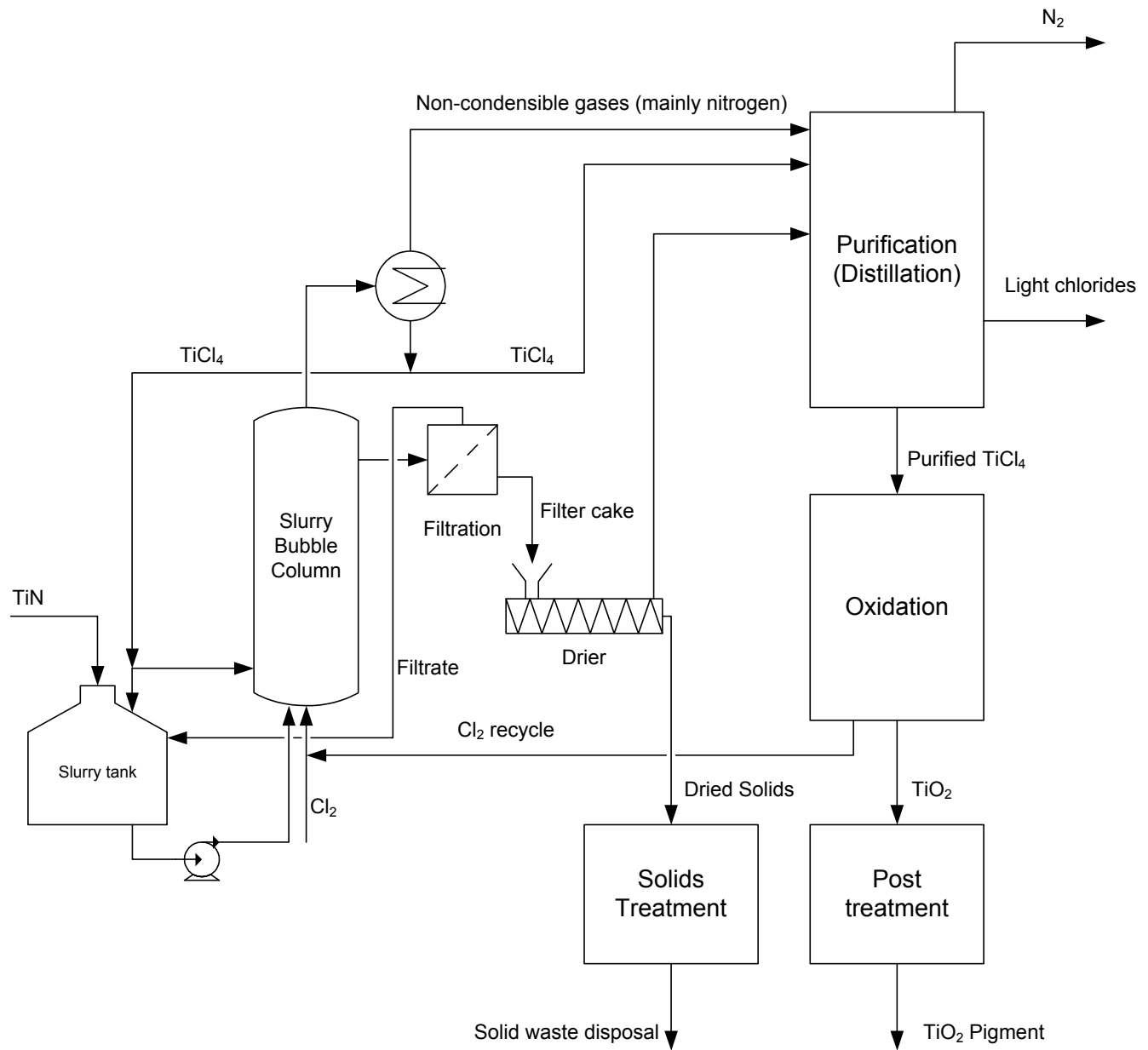
In slurry reactors additional heat can also be removed by evaporation of some of the liquid.

The liquid phase selected for the slurry reactor is the titanium tetrachloride product itself. Whereas the boiling point of titanium tetrachloride is only 136°C and the required reaction temperature a bit higher, a pressurised slurry reactor is required.

In order to feed the material into the pressurised slurry reactor, the nitrated blocks of feed are milled, and mixed with liquid TiCl_4 at atmospheric pressure and temperature to form a slurry (see Figure 3). The slurry is pumped into a reactor, operating at temperatures between 200°C and 300°C . Gaseous chlorine is also fed into the reactor. Elevated pressures (in the region of 6 to 20 bar depending on the temperature of the reactor) are required to keep liquid TiCl_4 in the reactor.

At these low temperatures, only the reduced mineral species are chlorinated. Iron forms FeCl_2 and FeCl_3 ; titanium nitride and titanium carbides form TiCl_4 and nitrogen or carbon and reduced vanadium species form VCl_4 and VOCl_3 . CaO , MgO , SiO_2 and Al_2O_3 species hardly reacts at all. Typical conversions measured for these were in the order of 1.5%.

Figure 3: Selective Chlorination Process



Slurry exiting the reactor consists mainly of TiCl₄ liquid and unreacted solid feed material. At the lower temperature range (200°C to 300 °C), FeCl₃ remains in the solid phase, although some of it dissolves in the TiCl₄. The solids are separated from the liquid by filtration, and dried. The filtrate can be used to make-up fresh slurry.

Reaction at 200°C also simplifies the materials of construction, as SS316 can be used as the reactor material instead of expensive high nickel alloys such as Inconel.

A pilot plant with a design solid feed rate of 10 kg/h was built to demonstrate the process. The maximum design temperature was 290°C and the maximum design pressure 30 bar.

Although feeding and tapping a slurry of finely milled slag in titanium tetrachloride into and out of a pressurized system posed many operational problems on the small scale used, continuous operation and excellent control of the process was successfully demonstrated.

In order to generate more data to determine the intrinsic rates of reaction of the system, the test facility was operated in a batch mode.

The experimental procedure to determine the reaction rates were as follow:

- A batch of dilute slurry was loaded into the stirred reaction vessel at room temperature and atmospheric pressure.
- The system was then pressurized with nitrogen and heated to the desired operating temperature.
- Once the desired operating temperature was reached, chlorine was fed continuously directly into the slurry in the reactor at an excess flow rate to ensure that the reaction rate was limited by intrinsic reaction rates rather than by gas liquid mass transfer rates.
- Samples of the slurry were withdrawn at different time intervals, quenched, filtered and analysed.

The data collected was interpreted in terms of shrinking core model and the rate of conversion was found to be a strong function of temperature and a weak function of chlorine partial pressure.

It was found that appreciable reaction rates could be achieved at temperatures as low as 200°C and system pressures as low as 6 bar⁷.

Waste treatment

The solid residue from the chlorination process contains chlorides and it therefore has to be treated to make it safe for disposal. Treatment of the solid waste requires relatively standard methods, but these were nevertheless tested in a continuous bench-scale pilot plant in order to confirm the suitability of the processes and to determine the final waste disposal requirements.

Treatment of the solid waste firstly entails leaching of soluble chlorides (e.g. FeCl₃) from the solid waste. Some lime is then added before disposal of the solid waste.

Treated solid residue were subjected to acid rain tests and it was found that due to the large volume of waste envisaged the waste would be classified as hazardous and a type H:H mono-landfill site would be required.

The pH of leachate from the solids treatment step is increased stepwise to precipitate the oxides or hydroxides of the various metal salts present in the leachate. These oxides will be recycled for co-disposal with the washed solids residue.

It is envisaged that a commercial plant will require an electrolysis unit to produce make-up chlorine from both fresh NaCl and NaCl formed from the neutralisation of solid chlorides with NaOH.

Process Advantages

The selective chlorination route has the following advantages over the conventional chlorination route:

- The process unlocks the potential of reserves that can currently not be exploited economically via the sulphate or chloride routes.
- The process results in highly selective extraction of titanium dioxide, resulting in less chemical waste

- By using waste as feed, pristine beaches that are the source of much of the ilmenite used today, can be conserved in their natural state.
- The process does not require higher value metallurgical reductants such as coke or anthracite to reduce ilmenite as required in commercial arc furnace technology – low grade duff is adequate
- Significantly lower chlorination reactor temperatures (200°C vs 900°C), resulting in cheaper materials of construction.
- Significantly lower chlorination reactor volumes (more than an order of magnitude)
- Significantly lower gas volumes to be handled and treated than in the commercial chloride process (more than an order of magnitude).
- No reductant (petroleum coke) is required in the chlorination reactor

The major disadvantages of the process are the following:

- The entire process route is novel and has not been proven commercially.
- The high capital cost and energy requirements of the nitriding step result in the process being uneconomic compared to conventional chlorination if conventional synthetic rutile is used as a feedstock.
- Whereas the low-grade feed considered would typically contain a relatively low percentage of TiO₂, a large volume of final waste residue has to be treated and disposed.
- Recovering all the TiCl₄ from the un-reacted residue requires larger equipment compared to the conventional chloride route because of the significantly larger volume of residue from which the TiCl₄ has to be separated when using low-grade feed.

Techno Economics

The techno economic viability of a world-scale (100 000 tpa), green fields project in an inland venue using waste slag at no cost has been estimated and found to give an internal rate of return that is higher than the hurdle rate typically required in the chemical industry.

A direct financial comparison with current commercial processes is not easy because a new project based on current technologies and feed stocks would optimally be placed in a different part of the world than a project based on low grade feed stocks to which this process apply. Different manpower costs, feed stock costs, energy costs, product transport costs, investment incentives, custom duties etcetera apply which all impact on the economies of such projects. The issue therefore becomes more a matter of whether a specific project is economically viable or not, rather than whether one technology is better than the other.

As a rough guide, the main driver for a project based on the new technology is the availability of a waste feed stock at virtually no costs. The waste has to be processed in a high temperature kiln to render it suitable for chlorination and the cost of that can readily be estimated for specific circumstances. Subsequent to that the nitrided product would be chlorinated in a process that has some major cost saving advantages, but this would be partially offset by an additional solid liquid separation step to recover all the TiCl₄ from the waste residue before disposal of the residue. A first test for the economic viability of a project based on the new selective process is therefore whether titanium nitride can be produced from a specific feed stock at a total cost, including the reward of capital, of less than the cost of commercially traded synthetic rutile or chloride grade slag which averages at about \$400/ton.

Economic analyses indicated that the nitriding process can deliver a nitrided product that is indeed cheaper per ton of titanium contained than that of synthetic rutile (assuming a zero value for the slag prior to milling). The net

result is that the selective chlorination process is believed to deliver the cheapest TiCl_4 in the world if waste slag is used as a feed.

Conclusions

- A novel, selective process to recover TiO_2 from low-grade waste sources had been developed and demonstrated up to a continuous bench-scale (10 kg/h) level.
- Techno economical analyses of a potential project based on the technology showed that the project could be the lowest cash-cost producer of TiCl_4 in the world.
- In addition to economic and process advantages, the principle of using waste contributes to sustainable production and conservation of the environment.

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