The plasma manufacturing of titania pigment and nano-titania in a pilot plant

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Synopsis
The establishment of a pilot plant for the continuous production of titania pigment and nano-titania is discussed. The plant was designed, constructed and operated on the Necsa site. The TiO₂ production capacity is 7–10 kg.h⁻¹ by the reaction of TiCl₄ and O₂ at >1000°C. Liquid TiCl₄ is sprayed under pressure into a plasma reactor where it evaporates and reacts with O₂ to form TiO₂. Process optimization has allowed for continuous production without any clogging or blockages. The primary advantage of the plasma-assisted process is the possibility to recover and recycle the chlorine values in high yield as Cl₂ for use in the manufacture of TiCl₄. The HCl formed in most conventional fossil-fuelled processes makes Cl₂ recovery and recycling much more difficult. Particle size distribution analysis of the fine, white product revealed a d₅₀ = 125 nm. The raw product consisted of 60% rutile that could be increased to 80–100% rutile by post-annealing. The specific surface area (SSA) of the pigment was 8–20 m²·g⁻¹ (BET). According to the CIE colour index the ‘whiteness’ (L*>95) of the plasma-produced pigment was better than that of several commercially available pigments. The particle size could be manipulated by controlling the TiCl₄ feed rate, gas flow rates, and the particle quench rate and residence time. Nano-sized TiO₂ powders with a particles size (d₅₀) as small as 50 nm were also successfully produced in this way.

Introduction

In this article, the manufacturing of a primary TiO₂ pigment and the manufacturing of nano-titania by a plasma process from TiCl₄ on pilot-plant scale is described, as well as a process for the recovery of the liberated chlorine values as Cl₂ gas. The scaleability and preliminary techno-economics of establishing such a process in South Africa is also briefly discussed.

South Africa is blessed with huge resources of titanium-bearing minerals (estimated at about 145 million tonnes) occurring mainly in the form of ilmenite (FeTiO₃) and rutile (TiO₂) found in heavy mineral beach sands off the east and west coasts of South Africa. Ilmenite accounts for about 90% of titanium mineral production in South Africa. Richards Bay Minerals (RBM) is the world’s largest producer of titania-ferrous slag (>1 million tonnes per annum). Namakwa Sands produce about 250 000 tonnes per annum, containing about 85% TiO₂. Unfortunately, these products are mainly exported from South Africa without further beneficiation or local value-addition. Consequently, the South African government has launched several initiatives over the past few years to establish a bigger local beneficiation industry. These include the Advanced Metals Initiative (AMI) of the Department of Science and Technology (DST) for the manufacture of titanium and zirconium metal, the Titanium Beneficiation Initiative (TBI) of the Department of Trade and Industry (the dti) and several related projects sponsored by the Innovation Fund of South Africa.

Nano-sized and pigment-grade titanium dioxide (TiO₂) are widely used in sunscreens, paints and fillers. The titanium values in titania ores and slags are generally accessed by means of carbo-chlorination, yielding TiCl₄. The TiCl₄ is purified by distillation and subsequently oxidized to yield a TiO₂, which is suitable as a primary pigment grade. Subsequent surface treatment of these particles, usually with a zirconium compound, resulted in a final pigment.

The conventional oxidation process for the production of pigment-grade TiO₂ is carried out in a methane flame reactor according to Reaction [1]:

\[ TiCl₄ + 1.5O₂ + CH₄ \rightarrow TiO₂ + 4HCl + CO \]  \[ \text{[1]} \]

The formation of HCl in Reaction [1] is confirmed by thermodynamic equilibrium calculations. Plasma-assisted oxidation of TiCl₄ with O₂ according to Reaction [2], however, allows the direct recovery of chlorine values from the off-gas in the form of Cl₂:

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\[ \text{TiCl}_4 + O_2 \rightarrow \text{TiO}_2 + 2\text{Cl}_2 \]  \[\text{(2)}\]

The recovered Cl\(_2\) can be recycled to the front-end of the carbo-chlorination process with the consequent benefits to effective waste management and overall process economics.

Another advantage of the plasma process is that the plasma reactor can be designed to control the particle size of the product by varying the operating conditions. A pilot plant capable of producing 7–10 kg.h\(^{-1}\) TiO\(_2\) from TiCl\(_4\) has been accordingly designed and built at Nesca, as will be described below.

Process description

The conversion of TiCl\(_4\) to TiO\(_2\) according to Reaction [2] is carried out in a plasma system at temperatures above 1 000ºC. Activation energy for the reaction is supplied by a 30 kW (nominal) plasma torch operating on nitrogen as plasma gas. The process is presented schematically in Figure 1. The cylindrical reactor is 0.5 m in diameter and consists of five main sections, totalling 3 m in height (Figure 2). It is constructed on two levels to allow operator access to all sections. The total height of the plant is about 6 metres and the footprint of about 4 metres includes all of the ancillary equipment, the plasma power supply, utilities, off-gas treatment and scrubbers.

The reactor sections have the following functions:

➤ The plasma torch is mounted at the top of the evaporation chamber. The hot plasma gas evaporates and superheats the TiCl\(_4\) droplets
➤ The TiCl\(_4\) vapour then enters the mixing zone where it is diluted with nitrogen shielding gas and mixed with oxygen. Allowance has been made to introduce additional nitrogen for temperature control
➤ TiCl\(_4\) vapour and oxygen react in the upper reaction zone to form TiO\(_2\) vapour and Cl\(_2\)
➤ The lower reaction zone allows the residence time required for vapour condensation and TiO\(_2\) particle coagulation
➤ Particle growth is controlled by quenching the reaction mixture within milliseconds to below 600ºC by means of a cold gas that is introduced through a height-adjustable quench probe.

The particle-laden off-gas mixture is cooled in a heat exchanger and the TiO\(_2\) collected in a cyclone and bag filter arrangement. Chlorine is separated from the off-gas stream by selective adsorption in a suitable zeolite from which it can be recovered by desorption as Cl\(_2\) gas. Any residual is finally removed by scrubbing with 20% KOH solution. The cleaned off-gas (mainly nitrogen) is vented to atmosphere.

The reactor is assembled from several steel sections. A suitable graphite lining is inserted in the evaporating zone and structural ceramics in the reaction zones. Reactor and system parts not lined with graphite or ceramic are constructed from water-cooled stainless steel or aluminium.

Process optimization

Usually, industrial TiO\(_2\)-pigment manufacturing reactors are prone to clogging. Precipitation of solid, fine TiO\(_2\) begins immediately upon mixing of TiCl\(_4\) and O\(_2\) and extensive agglomeration of the particles follows. Modification of the original plasma reactor design decreased the clogging significantly and continuous production rates of 7–10 kg.h\(^{-1}\) can now be maintained easily. The modifications consisted of changing the reactor-lining geometry and inner diameters and the addition of nitrogen in a configuration that creates vortex flows in the direction of the reactor outlet.

Specialized equipment for collecting the product contributes greatly to the efficiency of the pilot plant. The cyclone removes more than 90% of the product and the product can be collected continuously by means of a double
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Al₂O₃ and SiO₂ are usually the main contaminants in TiO₂ pigment and influence the crystal and coating properties for pigment applications. The levels of Al₂O₃ (0.08%) and SiO₂ (0.50%) measured in the product are well below the acceptable limits of 4% and 2% respectively. Impurities that have a detrimental effect on the colour (or whiteness) of TiO₂ pigment (V, Fe, Cr, Ni, Cu, Mn, Zr, Zn, P) amounted to a total of less than 0.1%. It must be appreciated that the purity of the final product is highly dependent on the purity of the TiCl₄ feed. In this project, distilled TiCl₄ was used. The low values of especially the Fe, Cr, and Ni indicate very little corrosion of the stainless steel parts of the equipment and consequent contamination of the final product.

SEM analysis (Figure 4) shows that the TiO₂ particles are agglomerated, which helped with the removal of the particles from the product gas stream by the cyclone and filter bags.

Chlorine recovery

One of the main advantages of the plasma process is the formation of Cl₂ instead of the problematic and very corrosive HCl as in the case of conventional methane combustion processes. Chlorine can be recovered from the off-gas and recycled with the consequent benefits for process economics and waste minimization. This was demonstrated experimentally by diverting a portion of the process off-gas stream for pigment applications. The levels of Al₂O₃ (0.08%) and SiO₂ (0.50%) measured in the product are well below the acceptable limits of 4% and 2% respectively. Impurities that have a detrimental effect on the colour (or whiteness) of TiO₂ pigment (V, Fe, Cr, Ni, Cu, Mn, Zr, Zn, P) amounted to a total of less than 0.1%. It must be appreciated that the purity of the final product is highly dependent on the purity of the TiCl₄ feed. In this project, distilled TiCl₄ was used. The low values of especially the Fe, Cr, and Ni indicate very little corrosion of the stainless steel parts of the equipment and consequent contamination of the final product.

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through a zeolite bed followed by a trap containing a 10% KI/starch solution. The solution in the trap remained clear as long as the zeolite capacity was not exceeded, indicating that Cl₂ had been adsorbed quantitatively. Titration and mass balance calculations showed that >95% of the Cl₂ was recovered by desorption from the zeolite bed.

Nano-titania

SEM analyses revealed particle-size d₅₀ values of 50–250 nm for TiO₂ produced in several experiments under different conditions in the pilot plant (Figure 4). Observed trends show an increasing particle size with increasing TiCl₄ feed rate. This is consistent with an increased TiCl₄:N₂ mass ratio, which means that less dilution of TiCl₄ in the reactor gases and consequently resulting in the formation of larger particles. It was also found that the nozzle size and the position of the TiCl₄ spray nozzles have a significant influence on the particle size as well as the quench rate of the product-gas mixture and effective residence time of particles in the reactor. In general, the higher the quench rate, and the shorter the residence time, the smaller the particle size. Therefore, nano-titania can also be produced on this plasma pilot plant by careful selection and controlling of the process parameters.

Scale-up and economic factors

There is no technical reason why this process cannot be scaled up to a production plant. Plasma processes can be scaled modular, which has the advantage that the production plant capacity can gradually be increased according to market growth and demand. Plasma systems in the order of 450 kW were being run successfully at Necsa. The auxiliary pigment plant equipment is standard in the titania pigment industry.

A preliminary techno-economic evaluation for a 100 000 tonnes per annum TiO₂ pigment plant has indicated a favourable internal rate of return (IRR) and return on Investment (ROI). The economics are positively influenced by the potential direct recovery and recycling of gaseous chlorine instead of HCl. No techno-economic comparison was made between the plasma-based and conventional flame processes. Nano-titania can achieve very high selling prices, up to several thousand dollars per kilogram, depending on characteristics and applications. It is, however, a very smaller market in terms of volume than that of the titania pigment market. No techno-economic study was done on the nano-titania part of this project at this stage.

Conclusions and recommendations

A primary pigment grade TiO₂ was successfully produced on a plasma pilot plant. TiO₂ particles with a d₅₀ of 125 nm were continuously produced at rates of 7–10 kg.h⁻¹ without any clogging of downstream process equipment. Specialized equipment and innovative reactor and pilot plant design allow for control over experimental parameters and conditions. The white TiO₂ product revealed properties conforming to the basic specifications for a primary titania pigment. Plasma parameters can be changed to manipulate the particle size and it was demonstrated that nano-titania can also be produced on the same pilot plant. Parameters that can be changed in order to achieve this are:

➤ The TiCl₄ feed rate
➤ The spray nozzles size and configuration
➤ The dilution of the TiCl₄ with the plasma gas and
➤ The quench rate of the product-gas mixture.

The plasma oxidation of TiCl₄ by O₂ in the above-mentioned pilot plant allows for the successful recovery of Cl₂ for recycling, which will contribute greatly to waste
minimization and the overall economics of a fully integrated commercial plant. Preliminary techno-economic evaluation for such a pigment titania plasma plant showed a favourable IRR and ROI.

The following approach is recommended for further development of the process:
➤ Proving operability and reliability of the present pilot plant facility by continuous production runs of 24 hour duration
➤ Scale-up to at 100 kg.h\(^{-1}\) capacity
➤ Refinement of the techno-economic evaluation
➤ Further exploration of nano-titania opportunities.

Finally, it was proved that it is possible to establish a plasma titania pigment plant and a nano-titania plant in South Africa, fulfilling the South African government ideal for more local beneficiation and value adding of our minerals.

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