A New Process to Upgrade Ilmenite to Synthetic Rutile

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A NEW PROCESS TO UPGRADE ILMENITE TO SYNTHETIC RUTILE

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ABSTRACT

Ilmenite occurs in black sand at the mouth of great rivers as in India, or as massive deposits like in Quebec Province in Canada. It is unsuitable for processing into pigment or for metal production because of its high iron content and its low grade. Pyrometallurgical and hydrometallurgical methods have been developed to cope with this problem which resulted in the production of two commercial products that became known as synthetic rutile and Sorelslag. Attempts are also underway to produce TiO₂ pigment directly from ilmenite. This report presents a newly developed process called the Magpie process, which enables the production of high-grade synthetic rutile (over 95% TiO₂) from low grade ilmenite (10-12% TiO₂). Naturally, if such process is applied for low-grade ore it can be applied with advantage to high grade material as well.

KEYWORDS

Hydrochloric acid, oxy-hydrolysis, Magpie process, leaching, titanium dioxide, ferric oxide, vanadium
INTRODUCTION

The world reserves of titanium are 90% in the form of ilmenite, FeTiO$_3$, and only 10% in the form of rutile, TiO$_2$. The treatment of rutile to produce metallic titanium or TiO$_2$ pigment is relatively simple (Figure 1). Because of its high iron content (30-50%), the treatment of ilmenite is evidently more complex (Barksdale, 1966), (Sibum et al., 1997) and (Habashi, 1993).

![Figure 1 – Production of titanium or TiO$_2$ pigment from rutile](image)

Ilmenite deposits may be massive as in Quebec Province or as black sands associated with magnetite, monazite, and other valuable minerals which are separated by physical methods.

EARLY METHOD OF PROCESSING ILMENITE

In the early method of TiO$_2$ pigment manufacture from ilmenite the ore was treated with concentrated H$_2$SO$_4$ at 110–120°C to form ferrous and titanyl sulfates:

$$\text{FeTiO}_3 + 4\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{TiO}^{2+} + 2\text{H}_2\text{O} \quad (1)$$

The solidified mass produced in the reactor at the end of the reaction was then discharged from the reactor by dissolution in water or dilute acid. After removing the insoluble residue by filtration, the solution containing 120–130 g/L TiO$_2$ and 250–300 g/L FeSO$_4$ was concentrated under vacuum at 10°C to crystallize FeSO$_4$$\cdot$7H$_2$O which was then centrifuged. Titanium oxide is then precipitated from solution by dilution and seeding resulting in the formation of dilute H$_2$SO$_4$ for disposal (Figure 2) (Habashi, 1996). Although this process has a disposal problem of the dilute acid and ferrous sulphate and is no longer used by modern plants, it is still used by the largest titanium pigment producer in the world located in Salvador, Brazil because the waste material is disposed of in the ocean which is dispersed by the tide.

Because of the pollution problems associated with the disposal of dilute sulphuric acid and FeSO$_4$, iron in the ore is now separated at an early stage. This is achieved in two ways; pyrometallurgical and hydrometallurgical routes.
Figure 2 – The early method for treating ilmenite for TiO₂ production

SEPARATION OF IRON BY PYROMETALLURGICAL ROUTE

The pyrometallurgical method was developed in 1950s (Habashi, 2002). The ore was mixed with a certain amount of anthracite which was just enough to reduce the iron oxide component of the ore, then charged in an electric furnace at 1650°C where iron oxide is reduced to metal while titanium is separated as a slag. The reactions taking place during reduction are the following:

\[ \text{FeTiO}_3 + \text{C} \rightarrow \text{Fe} + \text{CO} + \text{TiO}_2 \text{(slag)} \]  
\[ \text{Fe}_2\text{O}_3 + 3\text{C} \rightarrow 2\text{Fe} + 3\text{CO} \]

This method is used by the QIT Fer et Titan Incorporation at its plant in Sorel near Montreal and at Richards Bay in South Africa, at the Zaporozhye in the Ukraine and in Japan. Titanium slag is mainly iron magnesium titanate, \((\text{Fe,Mg})\text{Ti}_4\text{O}_{10}\), and a small amount of silicates; typical analysis is 70-85% TiO₂. The slag is high in titanium and low in iron and is therefore preferable to ilmenite in manufacturing TiO₂ pigment or titanium metal.
The hydrometallurgical route was developed in 1960s and involved leaching of iron from ilmenite and obtaining a residue rich in titanium (90–95% TiO$_2$) known as “synthetic rutile”. In this method, high-grade ilmenite is decomposed in autoclaves by 20% HCl at 120°C and 200 kPa; iron is solubilized as ferrous chloride leaving a solid containing about 93% TiO$_2$ (Figure 4):

$$\text{FeTiO}_3 + 2\text{H}^+ \rightarrow \text{TiO}_2 \text{[impure]} + \text{Fe}^{2+} + \text{H}_2\text{O}$$

The synthetic rutile is then treated by chlorine to prepare TiCl$_4$ from which TiO$_2$ or titanium metal are obtained without pollution problems. The process is used in the USA, England, Japan, Taiwan, and Australia. Modifications for this technology were introduced as shown in Table 1. The process is not suitable for low-grade ilmenite because the silicate gangue will remain in the synthetic rutile thus decreasing its tenor in titanium. Ferrous chloride solution is regenerated to HCl and Fe$_2$O$_3$ by oxy-hydrolysis:

$$2\text{FeCl}_2 + 2\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow \text{Fe}_2\text{O}_3 + \text{HCl}$$

This is the same technology that is used for treating pickle solution.
PRODUCTION OF PIGMENT DIRECTLY FROM ILMENITE

Two processes are under development for the production of a pigment grade TiO₂ from ilmenite without the use of chlorine.

Altair Process

The Altair process (Verhulst, et al, 2002, 2003) is under development in USA is based on leaching of ilmenite concentrate containing 52.2 % TiO₂ and 32.8 % Fe in hydrochloric acid to solubilise titanium and iron while silicates and chromites remain in the residue. Iron in solution is then reduced to the ferrous state by addition of iron powder, the solution cooled and filtered to separate ferrous chloride. Titanium in solution is extracted by organic solvent then converted to TiO₂ hydrate by spray hydrolysis at about 600°C, calcined and milled. Water vapor and HCl gas from the spray hydrolyser are condensed in absorption columns. Ferrous chloride crystals are re-dissolved in weak acid and subjected to pyrohydrolysis or spray hydrolysis to generate HCl. The major part of the chloride remains in solution and is
recycled to the digestion operation. Soluble impurities accumulating in the circuit are kept at a tolerable level by bleeding. The bleed stream is combined with the iron chloride crystals and sent to pyro-hydrolysis. Figure 5 shows a simplified flow sheet of the process.

![Simplified flowsheet of Altair process](image)

Figure 5 – Simplified flowsheet of Altair process

Titanium was extracted using Cyanex 923 in Orfom SX-11 as a diluent and with decanol as a modifier to avoid third-phase formation. A high concentration of chloride in the feed is beneficial to increase the loading capacity of the organic phase and to achieve a high concentration of titanium concentrate in the eluate.

**Ortech-Argex Process**

The Ortech-Argex process (Ortech) is being developed in Canada and is based on leaching ilmenite with HCl. After solid-liquid separation the solution is subjected to two solvent extraction steps (Figure 6). The first is to remove iron and the second to recover titanium. Vanadium is then precipitated from the residual solution. The solution containing iron is treated to recover Fe₂O₃ while the solution containing titanium is treated to recover pigment grade 99.8% TiO₂. Hydrochloric acid generated during the recovery of Fe₂O₃ and TiO₂ is collected for recycle.
Figure 6a – Flow sheet of Ortech-Argex process as deduced from the patent
Large deposits of low-grade ilmenite containing about 11% TiO$_2$ are available in the Province of Quebec. Pressure leaching with HCl removes the iron but the product will still be low in titanium because of the large amount of silicates that are not leached. In the new process it was found that leaching at 75°C and at ambient pressure with concentrated HCl results in dissolving all the iron and titanium. After filtration to remove the silicate gangue minerals the solution is subjected to boiling to expel excess HCl. During this operation titanyl hydroxide, TiO(OH)$_2$, precipitates but not the iron. After solid-liquid separation, vanadium can be extracted by organic solvents while ferrous chloride solution is then subjected to oxy-hydrolysis to recover Fe$_2$O$_3$ and HCl. Calcination of titanyl hydroxide results in a product containing 95.8% TiO$_2$ at 93.1% overall recovery (Figure 7). The product has the potential to be used for pigment or metal production by chlorination.
Figure 7 – Magpie process for transforming low-grade ilmenite into synthetic rutile

Figure 8 – Experimental set up for batch leaching tests

Figure 9 – Pilot plant in operation. F. Habashi (left) and E. Bourricaudy. Photo by F. Kamaleddine
CONCLUSIONS

It is believed that the best strategy to process low-grade ilmenite is to produce synthetic rutile because this gives the option of using such product for pigment as well as for metal production by standard technology. No special technology is required to dispose of the iron except the well established oxyhydrolysis. Hydrochloric acid consumption is negligible since it recycled. The Magpie process thus offers an alternative and simple approach to produce synthetic rutile - - the starting material for metal or pigment production.

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