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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 TiO_2 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% TiO_2) from low grade ilmenite (10-12% TiO_2). 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).

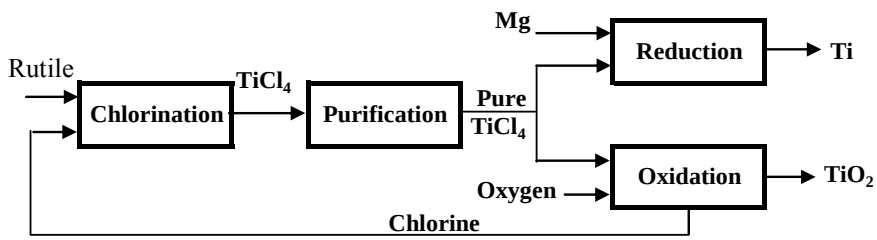

Figure 1 – Production of titanium or TiO_2 pigment from rutile

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_2SO_4 at 110–120°C to form ferrous and titanyl sulfates:

$$FeTiO_3 + 4H^+ \rightarrow Fe^{2+} + TiO^{2+} + 2H_2O \quad (1)$$

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 $FeSO_4 \cdot 7H_2O$ which was then centrifuged. Titanium oxide is then precipitated from solution by dilution and seeding resulting in the formation of dilute H_2SO_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.

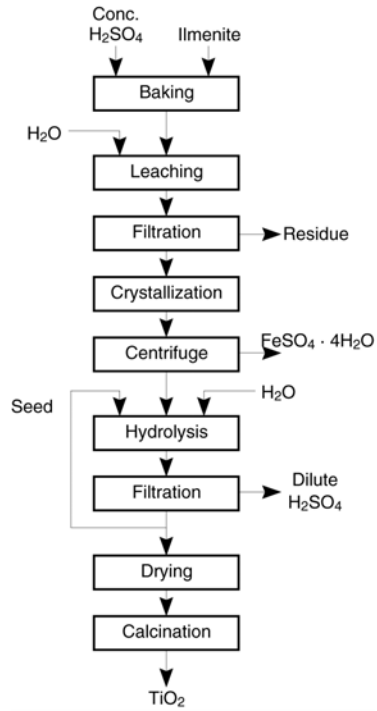

Figure 2 – The early method for treating ilmenite for TiO_2 production

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:

$$FeTiO_3 + C \rightarrow Fe + CO + TiO_{2(slag)} \quad (2)$$

$$Fe_2O_3 + 3C \rightarrow 2Fe + 3CO \quad (3)$$

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, $(Fe,Mg)Ti_4O_{10}$, and a small amount of silicates; typical analysis is 70-85% TiO_2. The slag is high in titanium and low in iron and is therefore preferable to ilmenite in manufacturing TiO_2 pigment or titanium metal.

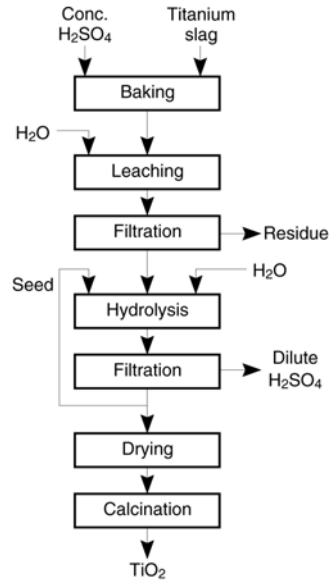

Figure 3 – Leaching of titanium slag for production of TiO_2 pigment

SEPARATION OF IRON BY HYDROMETALLURGICAL ROUTE

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):

$$FeTiO_3 + 2H^+ \rightarrow TiO_2\ [\text{impure}] + Fe^{2+} + H_2O \tag{4}$$

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_2O_3 by oxy-hydrolysis:

$$2FeCl_2 + 2H_2O + {}^1/_2O_2 \rightarrow Fe_2O_3 + HCl \tag{5}$$

This is the same technology that is used for treating pickle solution.

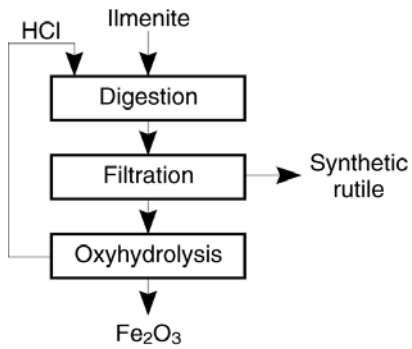

Figure 4 – Production of synthetic rutile from high grade ilmenite ore

Table 1 – Production plants for synthetic rutile

Process	Process steps	By-products	Producer and location
Benilite Corporation of America	Partial reduction to Fe(II), digestion with HCl solution, calcination	$FeCl_2$ pyrolyzed to Fe_2O_3 and HCl	- Kerr McGee, Mobile, USA - Kerala, Minerals and Metals Ltd., Chavara, Kerala - Indian Rare Earths, Orissa, India
Western Titanium	Oxidation to Fe(III), reduction to Fe, digestion with $FeCl_2$, with air oxidation	Iron hydroxides	- Associated Minerals Consolidated Cael, Australia - AMC, Narngulu, Australia
Lurgi	Reduction to Fe, digestion with air blowing, hydrocyclone separation, calcination	Iron hydroxides	- Westralian Sand Ltd., Capel, Australia
Ishibara Sangyo Kaisha	Reduction to Fe(II), digestion with H_2SO_4, calcination	$FeSO_4$ solution reacted with NH_3 to form ammonium sulfate and iron hydroxide	- Ishibara, Yokkaichi, Japan
Dhrangadhra Chemical Works	Reduction to Fe(II)/Fe, digestion with HCl, calcination	Iron chloride solution	- Dhrangadhra Chemical Works Ltd., Suhupuram, Tamil Nadu, India

PRODUCTION OF PIGMENT DIRECTLY FROM ILMENITE

Two processes are under development for the production of a pigment grade TiO_2 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 % TiO_2 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 TiO_2 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 pyro-hydrolysis 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.

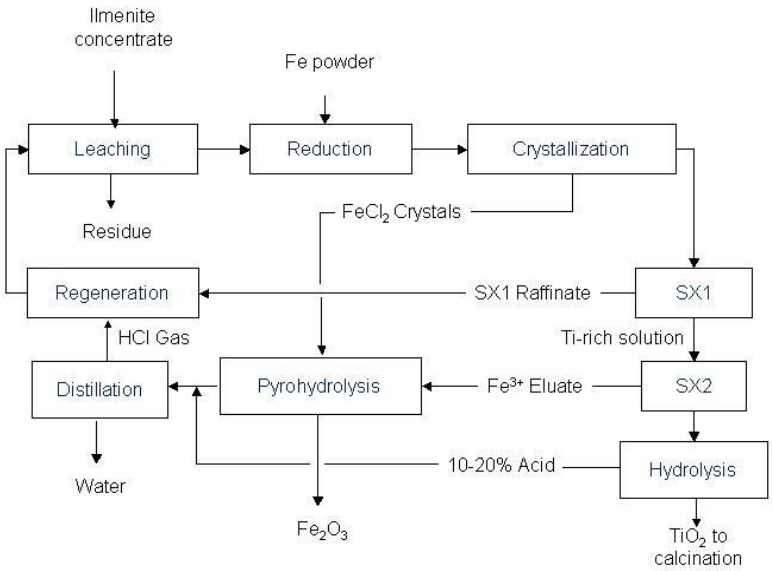

Figure 5 – Simplified flowsheet of Altair process

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 Fe_2O_3 while the solution containing titanium is treated to recover pigment grade 99.8% TiO_2. Hydrochloric acid generated during the recovery of Fe_2O_3 and TiO_2 is collected for recycle.

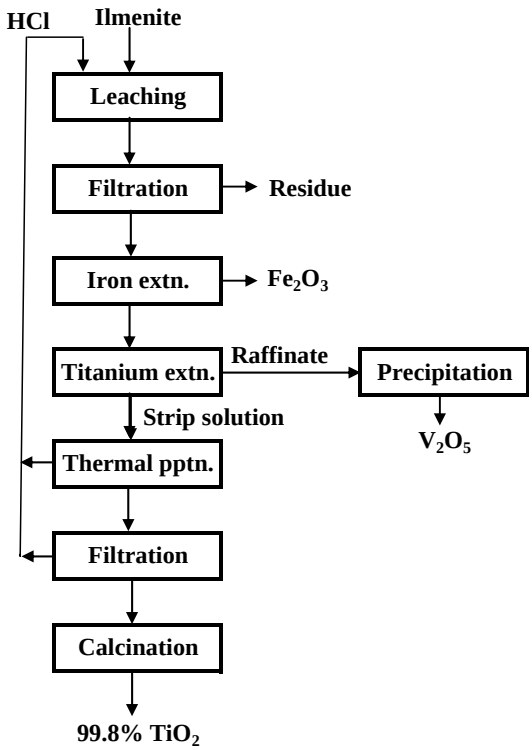

Figure 6a – Flow sheet of Ortech-Argex process as deduced from the patent

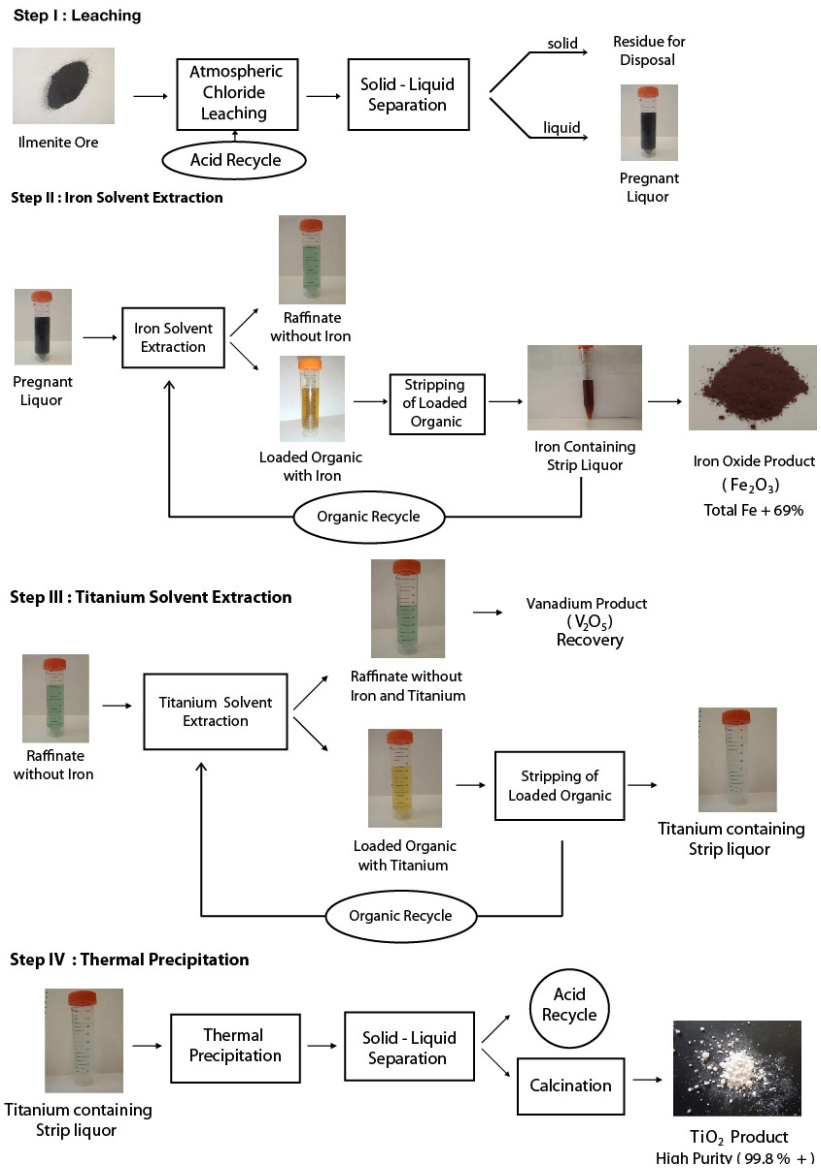

Figure 6b – Flow sheet of Ortech-Argex process as given by the inventors

A NEW PROCESS FOR PRODUCING SYNTHETIC RUTILE FROM LOW-GRADE ILMENITE

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_2O_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.

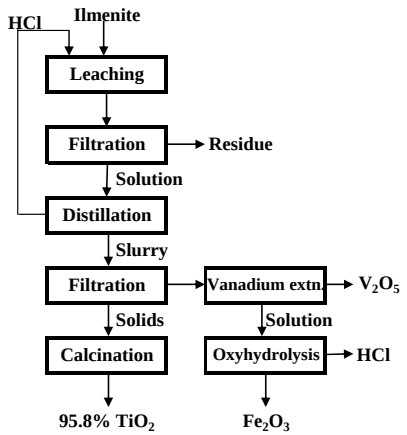

Figure 7 – Magpie process for transforming low-grade ilmenite into synthetic rutile

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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