

# Ilmenite for pigment and metal production

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## Abstract

Low-grade ilmenite can be leached with concentrated HCl at atmospheric pressure and at 80°C. After filtration to separate insoluble matter the solution containing  $\text{TiO}^{2+}$  and  $\text{Fe}^{2+}$  is heated to precipitate titanium hydroxide and recover HCl. The titanium hydroxide is then calcined to synthetic rutile containing 95+% $\text{TiO}_2$  while  $\text{FeCl}_2$  is subjected to oxyhydrolysis or fluidized bed to recover HCl and  $\text{Fe}_2\text{O}_3$ . The process naturally can be applied to high grade ilmenite. It bypasses electric furnace process which applies only to high grade ilmenite and is superior to the sulfuric acid process which is highly pollutant. The product of this process can be used to prepare the white pigment as well as titanium metal.

## Introduction

The major titanium minerals are rutile,  $\text{TiO}_2$  and ilmenite,  $\text{FeTiO}_3$  (Figure 1 and 2). Rutile is easy to process to titanium metal or  $\text{TiO}_2$  pigment by the chlorination method while ilmenite is more complicated because of its high iron content. Since the world reserves of titanium are 90% in the form of ilmenite and only 10% in the form of rutile, the treatment of ilmenite is evidently an important question in metallurgy [1,2].

Ilmenite deposits may be massive as in Province of Quebec (Figure 3) or as black sands (Figure 4) associated with magnetite, monazite, and other valuable minerals which are separated by physical methods (Figure 5). In the first magnetic separation a weak magnet is used to separate magnetite while in the second magnetic separation a high-intensity magnet is used to separate ilmenite.



Figure 1. Museum sample of rutile, ~ 90 %  $\text{TiO}_2$

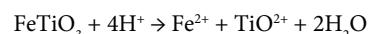


Figure 2. Museum sample of ilmenite,  $\text{FeTiO}_3$  (59.4 %  $\text{TiO}_2$ ).

## Early methods for pigment production

### Sulfuric acid method

In 1916, the Titanium Pigment Corporation of Niagara Falls, New York and the Titan Company of Norway simultaneously began commercial production of this new white pigment. Then, the principal white pigments used in paints were white lead, zinc white, and lithopone. In this method ilmenite was treated with concentrated  $\text{H}_2\text{SO}_4$  at 110–120°C to form ferrous and titanyl sulfates:



The reaction is conducted in large concrete tanks lined with acid resisting brick (Figure 6), heated by direct injection of high pressure steam or in a pug mill (Figure 7) [3]. 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  $\text{TiO}_2$  and 250–300 g/L  $\text{FeSO}_4$  was concentrated under vacuum at 10°C



Figure 3. A sample of massive ilmenite of Quebec.

**Key words:** HCl leaching, Magpie process, synthetic rutile, oxyhydrolysis, electric furnace, chlorination, sulfuric acid process

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Figure 4. Black beach sands as in India.

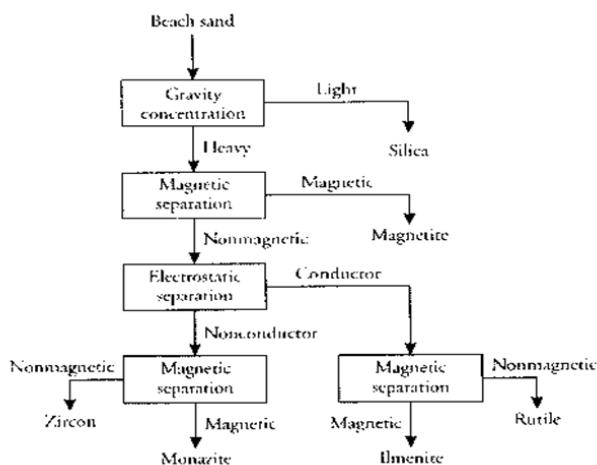


Figure 5. Beneficiation of black sands to recover its valuable components.

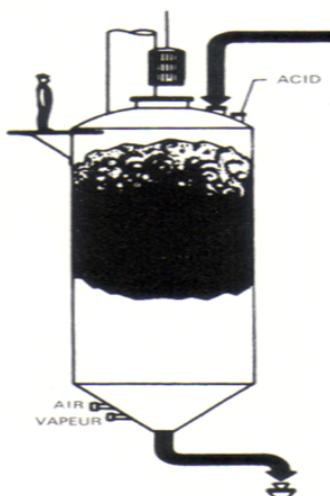


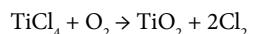
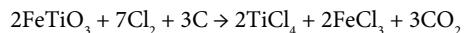
Figure 6. Large concrete tanks lined with acid resisting brick.

to crystallize  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  which was then centrifuged. Titanium oxide is then precipitated from solution by dilution and seeding resulting in the formation of dilute  $\text{H}_2\text{SO}_4$  for disposal (Figures 8 and 9). However, the largest producer of pigment in Salvador, Brazil still uses this technology because it disposes the waste products in the ocean which are removed by the tide.

### Chlorination method

DuPont in USA [4] produces the pigment since 1950 by direct chlorination of ilmenite ore, separation of products by fractional

distillation, then oxidation of  $\text{TiCl}_4$  (Figure 10):



The problem of this process is recovery of chlorine from ferric chloride or marketing the large amounts of this co-product.

### Separation of iron

Because of the pollution problems associated with the disposal of dilute sulfuric acid and  $\text{FeSO}_4$ , iron in the ore is separated at an early stage. This is achieved in two ways: by electric furnace and by hydrometallurgical routes.

### Electric furnace process

The electric furnace method was developed in 1950s [5]. 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  $1650^\circ\text{C}$  where iron oxide is reduced to metal while titanium is separated as a slag (Figure 11). The reactions taking place during reduction are the following:

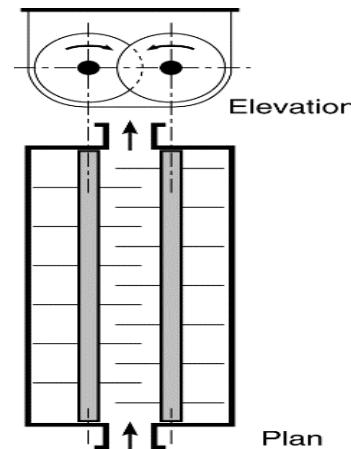


Figure 7. Heated pug mill.

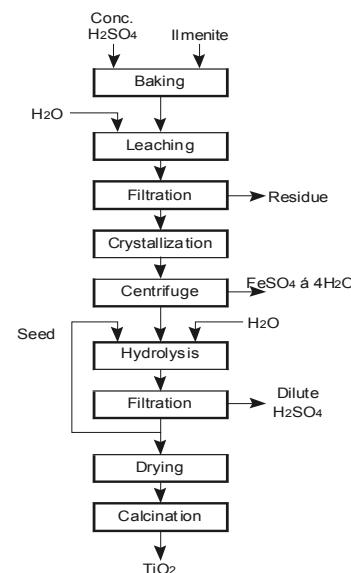
Figure 8. Production of  $\text{TiO}_2$  pigment by the sulfuric acid process.

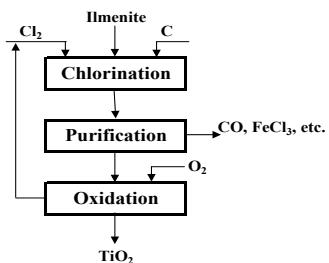
Figure 9. Titanium white, ~ 100%  $\text{TiO}_2$ .

Figure 10. Simplified Du Pont process for pigment production from ilmenite.

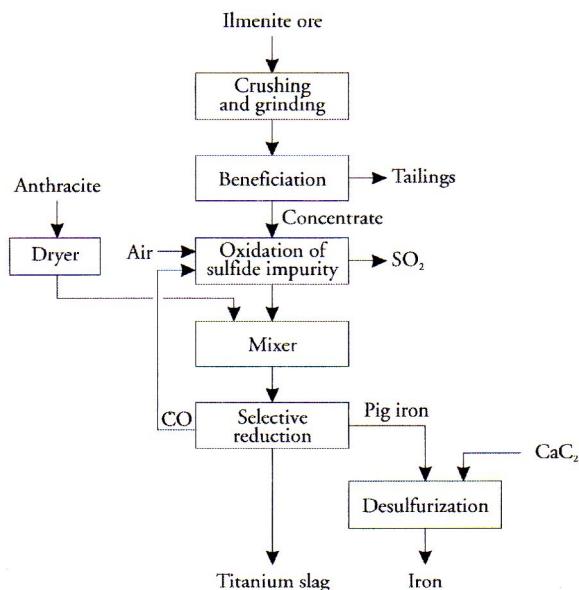
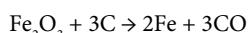
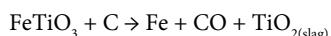


Figure 11. Electric furnace process for iron separation.



This method is used by the Rio Tinto QIT at its plant in Sorel near Montreal and at Richards Bay in South Africa. It is also used in the Soviet Union at Zaporozhye (Ukraine) and in Japan.

Titanium slag is mainly iron magnesium titanate,  $(\text{Fe}, \text{Mg})\text{Ti}_4\text{O}_9$ , and a small amount of silicates; typical analyses is 72–85% total  $\text{TiO}_2$ . A small amount of  $\text{TiO}_2$  is reduced to  $\text{Ti}_2\text{O}_3$ . The reduction of the iron oxides is not taken to completion so that some iron oxide is left in the slag to decrease its melting point. Melting point of  $\text{TiO}_2$  1840°C and ilmenite 1435°C.

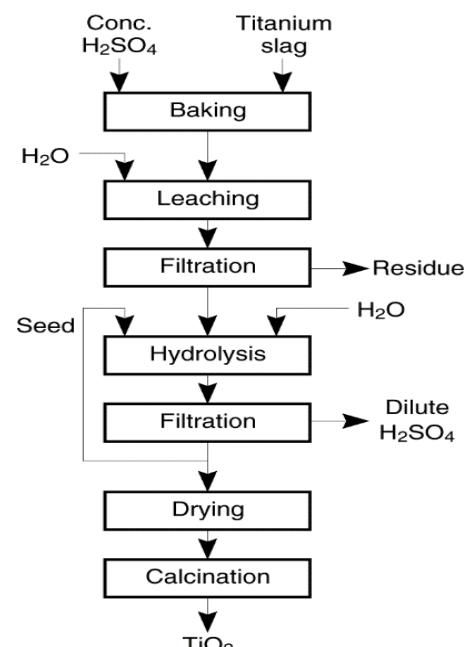
The slag is high in titanium and low in iron (Figure 12) and is therefore preferable to ilmenite in manufacturing  $\text{TiO}_2$  pigment or titanium metal. However, the slag produced in Quebec is not suitable for chlorination because of its high impurity level — about 16.6% as compared to about 6% in other slags [6]. These impurities will not

only consume unnecessary amounts of chlorine but also will create a disposal problem. Furthermore, some of these impurities, e.g., calcium and magnesium will interfere with the chlorination process itself which is conducted at 800°C by forming a molten phase ( $\text{CaCl}_2$  m.p. 770°C,  $\text{MgCl}_2$  m.p. 708°C).

For these reasons, titanium slag was used only for making pigment by the sulfuric acid process [7]. The slag was treated in the same way as ilmenite with the exception that no separation of ferrous sulfate was necessary because the bulk of iron was already separated by reduction in the earlier step (Figure 13). The sulfuric acid treatment process of the slag, however, still suffered from the disposal problem of the waste acid and as a result it was abandoned in the 1980s and replaced by a new technology based on upgrading the slag to 94.5%  $\text{TiO}_2$  by leaching away most of the impurities by  $\text{HCl}$  under pressure to render it suitable for chlorination.

### Hydrometallurgical route

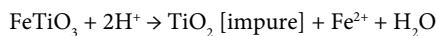
The hydrometallurgical route was developed in 1960s and involved leaching of iron from ilmenite and obtaining a residue rich in titanium (90–95%  $\text{TiO}_2$ ) known as “synthetic rutile” [8]. In one case, the Altair

Figure 12. Ground titanium slag,  $\text{FeTi}_4\text{O}_{10}$  (70-80%  $\text{TiO}_2$ ).Figure 13. Leaching of titanium slag for production of  $\text{TiO}_2$  pigment, now obsolete.

process, a pigment grade  $\text{TiO}_2$  was obtained. All these processes use an oxyhydrolysis process for treating ferrous chloride to get HCl for recycle and  $\text{Fe}_2\text{O}_3$  as a by-product.

### High-pressure method

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 95%  $\text{TiO}_2$  which has the chemical analysis to rutile that us why it called synthetic rutile (Figure 14):



Low grade ilmenite cannot be treated by this method since all silicates and insoluble matter will contaminate the product. The synthetic rutile is then treated by chlorine to prepare  $\text{TiCl}_4$  from which  $\text{TiO}_2$  or titanium metal are obtained without pollution problems. The process is used in the USA, England, Japan, Taiwan, and Australia. Oxyhydrolysis could be conducted in a variety of ways as described below.

### Atmospheric process

In 2014 it was found by Magpie Incorporation in Canada [9] that low grade ilmenite can be dissolved at 80°C with concentrated HCl at atmospheric pressure. After filtration to remove insoluble matter, the solution is distilled to recover HCl and to hydrolyse titanyl ion to  $\text{TiO}_2$ . After filtration, the residue is calcined to produce synthetic rutile (Figure 16):

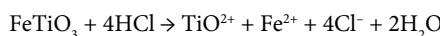


Figure 14. Synthetic rutile (~95%  $\text{TiO}_2$ ).

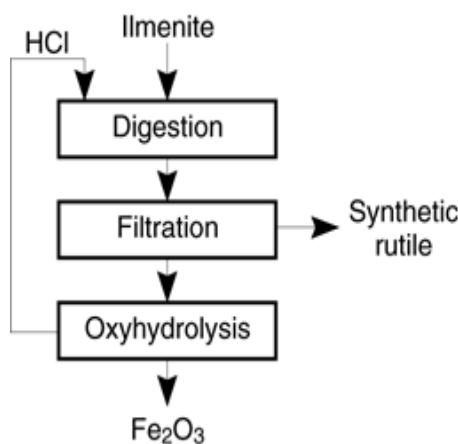
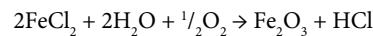


Figure 15. Production of synthetic rutile from ilmenite.

It is evident that the new leaching technology at ambient pressure is superior to the old electric furnace smelting-autoclave upgrading.

### Oxyhydrolysis

Ferrous chloride solution is regenerated to HCl and  $\text{Fe}_2\text{O}_3$  by oxyhydrolysis:



It is the same technology that is used for treating pickle solution. Two methods are used

### Fluidized-bed oxyhydrolysis

In a fluidized-bed reactor the ferrous chloride solution is introduced onto a large bed of hot ferric oxide where heating is provided by the hot fluidizing combustion gases (Figure 17). As the combustion gas flows through the well agitated bed of oxide it quickly reaches thermal equilibrium with the bed. The solution is fed on top of the bed of oxides. The liquid feed wets the outer layer of the hot oxide particles and is quickly evaporated to form an onion-like layer of new solid oxide on top of the existing oxide, thereby producing dense homogeneous particles.

### Spray roaster oxyhydrolysis

In this type of oxyhydrolysis roaster, the ferrous chloride solution is sprayed into an empty cylindrical vessel, while the required energy

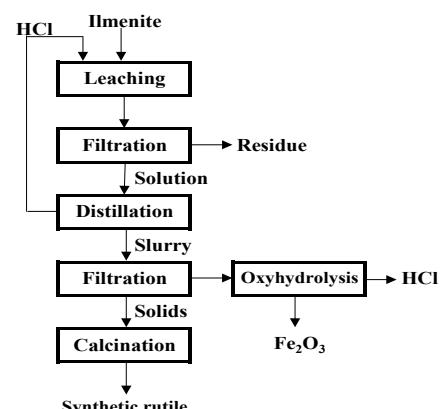


Figure 16. Production of 98+%  $\text{TiO}_2$  from a low-grade ilmenite [Magpie process].

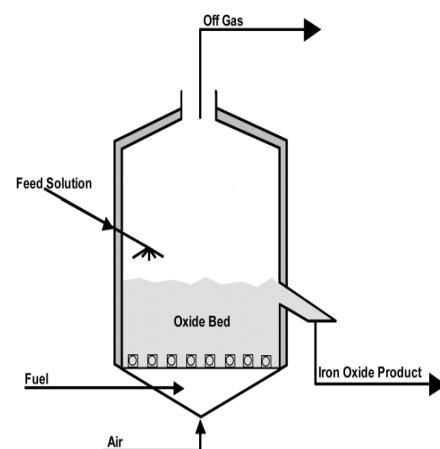


Figure 17. Fluidized-bed reactor for oxyhydrolysis of ferrous chloride

is supplied by the up flow of hot gases generated in the bottom burners (Figure 18). Spray roasters have large diameters to keep the gas velocities low. If the gas velocity is high, too many particles are elutriated with the off-gas, and the product quality and the efficiency of the roaster drop. The off-gas and oxides leave the roaster counter-currently at about 400°C to 500°C. The residence time of the sprayed particles in the high-temperature reaction zone is very short; therefore, very small liquid droplets, which can be quickly heated, should be created by atomization. The fast heat-up results in the formation of a solid oxide crust on the surface of each droplet. As the bulk of the droplet heats, the water content vaporizes and breaks through the oxide shell. Therefore, the spray roasted oxide is composed of very fine "fluffy," hollow spheres.

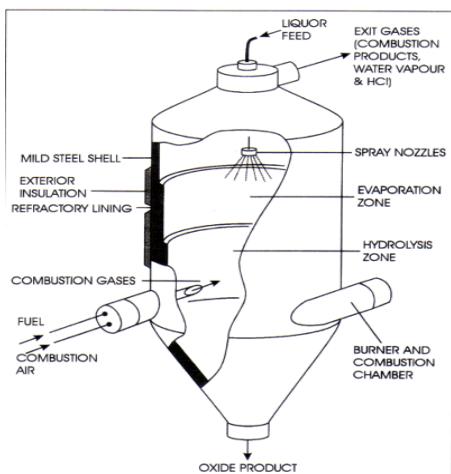


Figure 18. Regeneration of HCl from ferrous chloride solution by oxyhydrolysis in spray roaster.

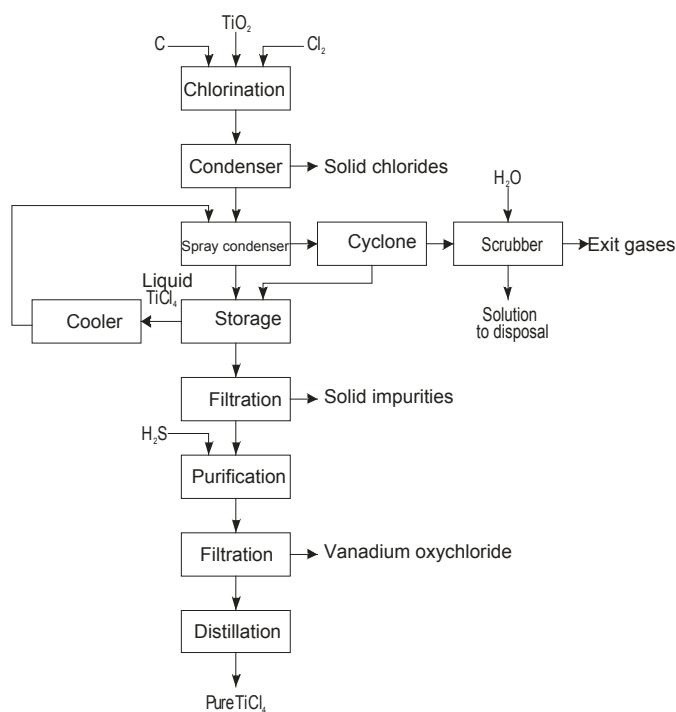


Figure 19. Production of  $\text{TiCl}_4$  from rutile, synthetic rutile, or titanium slag.

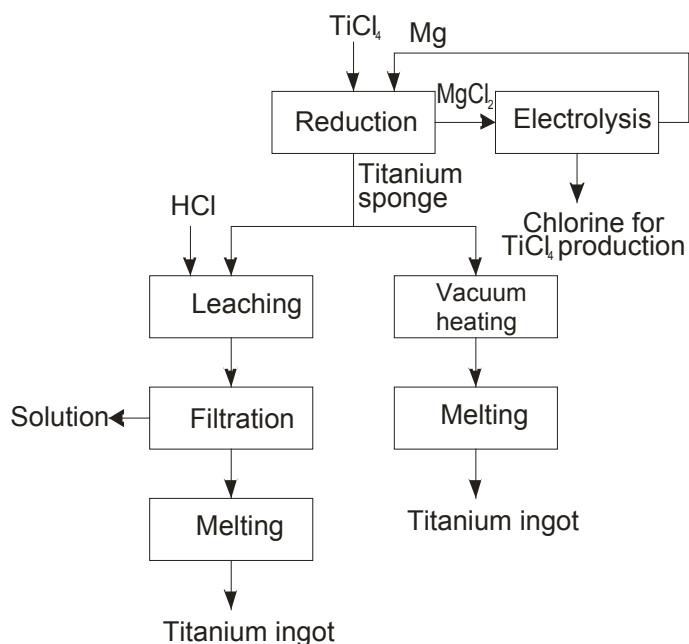


Figure 20. Production of titanium from  $\text{TiCl}_4$ .

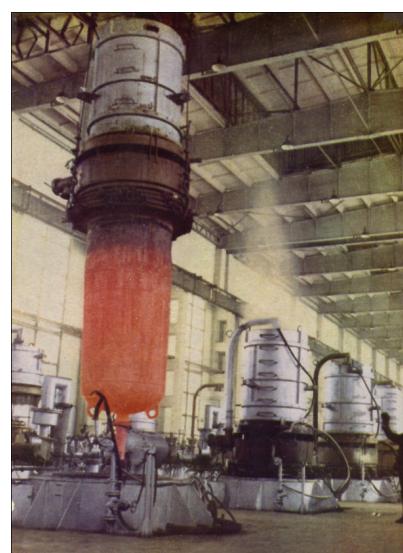
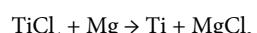
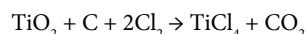


Figure 21. Metallothermic reactor being removed from furnace.

## Production of titanium

Metallic titanium is produced by chlorination of rutile, synthetic rutile, or titanium slag then reduction in a metallothermic reactor of  $\text{TiCl}_4$  by magnesium to titanium (Figures 19 and 20) [10]:



Magnesium chloride is then electrolyzed to get back the magnesium and chlorine for recycle. Figure 21 shows the metallothermic reactor removed from the furnace after reduction from which titanium sponge is recovered (Figure 22).

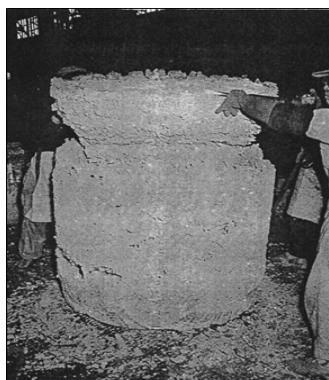


Figure 22. Titanium sponge (top) and MgCl<sub>2</sub> (bottom) removed from the reactor.

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