Iron Removal and Recovery in the Titanium Dioxide Feedstock and Pigment Industries

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Titanium and iron are closely related in nature. Therefore, for both environmental and economic reasons, the fate of iron may be very crucial for the titanium extraction industry. Smelting of ilmenite to produce titania slag allows for the recovery of iron as high purity pig iron. However, in the production of synthetic rutile from ilmenite sands, iron is returned to the mine site as a fine oxide/hydroxide residue. Some projects to recover iron from these residues never reached the industrial scale. In the titanium dioxide (TiO$_2$) pigment industry, iron is deported as sulfate or chloride salt, which is usually neutralized and rejected at a considerable cost. In the past few years, ferrous sulfate heptahydrate (or copperas) and iron chloride have found a few applications, but still the demand for these iron salts is not enough to cover the production volumes. The review of some new processes currently under development clearly shows that iron recovery is essential for the long-term viability of any new ilmenite upgrading or TiO$_2$ pigment production process.

INTRODUCTION

Contrary to some popular belief, the titanium industry is not dominated by the production of titanium metal and alloys, but rather by the production of titanium dioxide (TiO$_2$) pigment. Production statistics[1] show that, in 2007, over 5.7 million tonnes of TiO$_2$ units in titanium feedstock were converted to TiO$_2$ pigment, while only 324,000 tonnes of TiO$_2$ units in titanium feedstock were converted to titanium metal. In fact, even the titanium metal industry is linked to some extent to the TiO$_2$ pigment industry.

Titanium dioxide pigment is produced industrially by two major pro-

How would you...

...describe the overall significance of this paper?

As environmental regulations become more stringent and as the public becomes more concerned about the environmental burden of all human activities, the non-ferrous metals extraction industry has to find ways to minimize its environmental impact. This paper offers an overview of how iron is removed — and in some cases recovered as a valuable product — in the titanium feedstock and pigment industries.

...describe this work to a materials science and engineering professional with no experience in your technical specialty?

The titanium feedstock and pigment industries are faced with serious economic and environmental challenges with the removal of iron from ilmenite (FeTiO$_3$), which is the main titanium mineral resource. Smelting of ilmenite to titania slag allows for the recovery of most of the iron. However, in other process routes, which are reviewed in this paper, iron is mostly lost as an oxide/hydroxide impurity that must be treated and discarded at a significant cost.

...describe this work to a layperson?

Iron is a very common impurity in the non-ferrous metals extraction industry. In most cases (e.g., production of zinc, aluminum, etc.), iron is lost in residues which are expensive to treat and discard. Titanium dioxide is mostly produced from ilmenite, a titanium-iron oxide, through several process routes. However, only smelting at high temperatures allows for the recovery of iron. In other ilmenite processing routes, which are reviewed in this paper, iron is mostly lost. The loss of iron is a significant financial and environmental issue.

cesses[2] with long histories: the sulfate process, which was invented at the beginning of the 20th century, and the chloride process, which was invented around 1950. The latter produces titanium tetrachloride (TiCl$_4$) as an intermediate product. Titanium tetrachloride is also the start material for the production of titanium metal by magnesiothermic reduction (the Kroll process[3]). Some titanium metal producers purchase TiCl$_4$ from TiO$_2$ pigment producers, while others produce their own TiCl$_4$ using the same chlorination technology as in the chloride process.

Titanium is the ninth most abundant element and the seventh most abundant metal in Earth's crust.[4] However, the production of TiO$_2$ pigment and the production of titanium metal are energy and labor intensive. Moreover, the titanium extraction industry—from mining to final product—creates significant emissions to the environment.

According to a 1999 survey of European pigment plants,[5] the production of one tonne of TiO$_2$ equivalent in pigment requires 24 to 45 GJ (average 35 GJ, or 35×10^9 joules) of energy in the sulfate process, or 17–29 GJ (average 24 GJ) of energy in the chloride process. According to another cradle-to-gate life-cycle analysis,[6] the crude energy requirements for the sulfate process range between 70 and 100 GJ/t TiO$_2$ in the final product, while the crude energy requirements for the chloride process range between 100 and 110 GJ/t TiO$_2$ in the final product. In terms of emissions, the sulfate process generates about 5 tonnes CO$_2$ and 0.5–5 tonnes of solid waste per tonne TiO$_2$ in the final product.[6,7] The chloride process generates about 4 tonnes CO$_2$ and 1–2.5 tonnes of solid waste per tonne TiO$_2$ in the final product.[6,7] The produc-

tion of one tonne of titanium metal requires 361 GJ of energy and generates 35.7 tonnes equivalent of CO_2 and 16.9 tonnes of solid waste.[8]

The common way to reduce the impact of TiO_2 and titanium metal production on energy consumption and emissions to the environment is to improve the existing extraction processes or to look for alternative ones. Another way to reduce that impact is to make more products out of the same titanium mineral resources.

In nature, titanium is regularly associated with iron. Ilmenite ($FeTiO_3$) is the most common titanium mineral and it is relatively abundant. Hence, iron can be a significant byproduct in the titanium extractive industry. Recovering iron from titanium resources results in a significant reduction in residue generation. Indirectly, the recovery of iron from titanium resources causes a reduction in greenhouse gas (GHG) emissions and in the energy consumption per tonne of final product.

The ensuing text is an overview of the titanium extractive industry and the fate of iron that is associated with titanium source materials.

THE FATE OF IRON IN THE TITANIUM FEEDSTOCK INDUSTRY

The term titanium feedstock covers a wide variety of natural or industrial titanium resources that can be used as feed material by TiO_2 pigment and titanium metal producers. As shown in Figure 1, the natural titanium feedstock can be ilmenite or rutile (TiO_2). Natural rutile is rarer and can be mined only from heavy mineral sand deposits. Ilmenite, on the other hand, is much more abundant and exists in two forms: either as hard rock ilmenite (massive ilmenite) or as ilmenite sand obtained from heavy mineral placer deposits. Other industrial titanium feedstocks include titania slag, upgraded titania slag (UGS™), and synthetic rutile (SR).

Smelting of Rock Ilmenite

Rock ilmenite is found in massive igneous deposits in Eastern Canada, Norway, and China. Its content in TiO_2 is relatively low (30–50 wt.%), but its iron content is relatively high (30–50 wt.%). In massive igneous deposits,
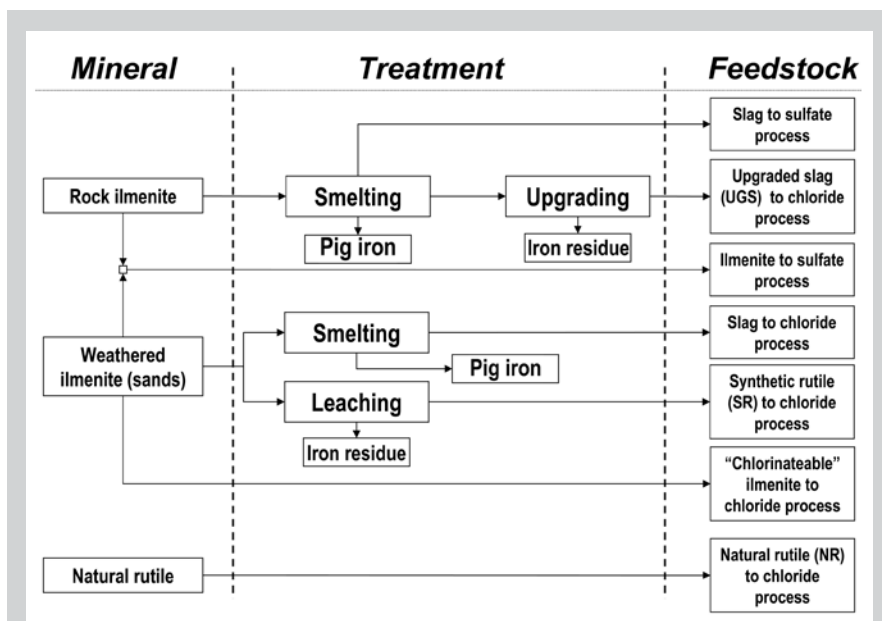

Figure 1. The pathway from titanium mineral resources to titanium feedstock.

ilmenite forms intergrowths with hematite (Fe_2O_3) and may be called hemoilmenite.[9,10] Titanium and iron also form ulvöspinel (Fe_2TiO_4), which is often found together with magnetite (Fe_3O_4) and ilmenite in a series of solid solutions and intergrowths known as the titanomagnetites ($Fe_{3-x}Ti_xO_4$).[11] The titanomagnetites have a low TiO_2 content (3–25 wt.%), but they can be an important iron, titanium, and vanadium resource.[12]

Rock ilmenite is usually reduced with coal in electric furnaces to produce pig iron and a titaniferous or titania slag that contains about 80 wt.% TiO_2 (Figure 2). The slag produced by smelting of rock ilmenite is sold to TiO_2 pigment producers that use the sulfate process, hence the name sulfate slag. The sulfate slag cannot be used in the chloride process, because it contains significant amounts of impurities like alkali earth oxides (CaO and MgO), which can cause severe processing problems.[13]

Ilmenite smelting poses some unique challenges.[14,15] The melting temperature of titaniferous slags is typically around 1,650°C and sometimes higher. In addition, the titaniferous slags are extremely corrosive to all known refractory bricks that are used in electric furnaces. Therefore, the reduction furnace is usually protected by freeze lining, (i.e., the furnace walls are cooled by water running through the furnace cell and a part of the slag solidifies on

the refractory bricks, thus protecting them).[16,17]

For nearly 60 years now, Rio Tinto Fer et Titane or RTFT (formerly QIT-Iron and Titanium Inc.) has been producing sulfate slag by smelting rock ilmenite from its Lac Tio deposit in Allard Lake, Quebec, Canada. RTFT is using nine electric furnaces to produce about 1.1 million tonnes of slag and about 960,000 tonnes of hot metal (liquid iron) per year. The ore from Lac Tio contains about 33 wt.% TiO_2 and 37 wt.% Fe. The ore ("run-of-mine") is upgraded by gravity separation, roasting, and magnetic separation to about 38 wt.% TiO_2 and 42 wt.% Fe.

Each RTFT furnace is a big rectangular structure equipped with six electrodes in line operating with AC current. The total power load at each RTFT furnace varies between 50 MW and 70 MW. Iron is tapped near the furnace bottom, while titania slag, which is lighter than liquid iron, is tapped from the upper part of the furnace. All of the titanium and a portion of the iron end up in the slag in pseudobrookite–karrooite crystal structures[9] of the type $X^{3+}_2TiO_5$–$Y^{2+}Ti_2O_5$ where X is a trivalent metal like Ti, Al, V, Cr, etc., and Y is a divalent metal like Mg, Fe, or Mn.

About one third of RTFT's hot metal is cast into pigs to be sold as high-purity pig iron (HPPI). Due to its very low manganese, sulfur, and phosphorus content, HPPI is one of the best materi-

als for the production of ductile iron, which finds unique high-tech applications such as in the construction of wind generators, in motor block castings, etc. The rest of RTFT's hot metal is converted to iron powders, steel billets, and steel powders. The share of each iron product is dictated by the market demand. For example, in 2008, the high price of HPPI made the company produce more of that product and less of the other iron products (steel and powders).

About half of the slag tapped from the RTFT furnaces is sold as feedstock for the sulfate process. The rest is further upgraded to a high-grade titanium feedstock by thermal treatment and pressure leaching in HCl media.[18,19] The upgraded slag contains 94.5 wt.% TiO_2 and has a very low content of magnesium and calcium, and virtually no radionuclides. It is thus one of the best feedstocks for the chloride process (and for titanium metal producers). In the UGS process, iron, magnesium, aluminum, and calcium are converted into a stable oxide residue by pyrohydrolysis of spent chloride solutions. The main phase in this oxide is a spinel of the type $X^{2+}Y^{3+}_2O_4$, where X = Mg, Fe, etc. and Y = Fe, Al, etc.[9] About 0.2 tonnes of spinel residue is produced per tonne of UGS product. Overall, in the RTFT metallurgical complex, more than 90% of the iron from ilmenite is recovered in various metal products.

In Norway, the former Tinfos Titan & Iron (TTI) smelter (now part of the Eramet group) in Tyssedal treats rock ilmenite from the nearby Tellnes mine to produce about 200,000 t/a of sulfate slag and about 110,000 t/a HPPI. (The Tellnes mine is also unique in that it produces rock ilmenite concentrate of 45 wt.% TiO_2, which is sold as feedstock to sulfate TiO_2 pigment plants.[10]) In the TTI smelter,[20] ilmenite is pelletized with bentonite and then pre-reduced to its metallic state in a rotary kiln. The pre-reduced ilmenite is then fed into one circular AC open-arc furnace with three self-baking Söderberg electrodes. The 40 MW furnace is similar to the furnaces used for the production of ferroalloys.

In China, a titanium concentrate is produced from the vast vanadium-bearing titanomagnetite deposits of Panzhihua (Sichuan Province). The Panzhihua ilmenite has a very high content of magnesium and calcium.[21] Nonetheless, because of the high demand for TiO_2 feedstock and iron in China, Chinese ilmenite smelters are expanding their production capacity, some with the help of Western engineering firms.[22] These smelters are producing only sulfate slag—and probably pig iron—for the local Chinese market.

Smelting of Ilmenite Sand

As mentioned above, ilmenite sand is mined from placer deposits along with rutile (TiO_2), zircon ($ZrSiO_4$), monazite ($(Ce, La, Y, Th)PO_4$), and other heavy minerals. Vast ilmenite sand deposits exist in the coasts of Australia, South Africa, and Madagascar. Sand ilmenite is also found in Florida, India, Malaysia, Vietnam, and elsewhere. A significant portion of iron in ilmenite sand is present in the trivalent state, while the TiO_2 content may exceed significantly the TiO_2 content of stoichiometric $FeTiO_3$ (52.6 wt.% TiO_2). This is due to natural iron oxidation and dissolution; hence the term altered or weathered ilmenite. One alteration phase is pseudorutile, which has an ideal composition of $Fe_2Ti_3O_9$ (40 wt.% Fe_2O_3, 60 wt.% TiO_2,). The TiO_2 content of altered ilmenite may exceed 60 wt.% and be as high as 90 wt.%. In that case the alteration product is called leucoxene, but leucoxene is not a distinct mineral phase; it is rather a mixture of rutile or anatase (TiO_2 polymorphs) and iron oxides.

Ilmenite sand can be smelted in electric furnaces just like rock ilmenite[23] (Figure 2). The slag from ilmenite sand has a higher TiO_2 content (about 85 wt.% or higher) and a relatively low content of impurities like magnesium and calcium. As such, the slag from ilmenite sand smelting can be used in the chloride process for pigment production. Ilmenite sand can be also used for the production of synthetic rutile (SR) via the Becher process, which is described in the next section.

Richards Bay Minerals (RBM), a company affiliated with RTFT, has been producing titaniferous slag in South Africa from ilmenite sand since 1977.[24] The RBM ilmenite sand concentrate is first roasted in two three-stage fluidized bed roasters to change the magnetic susceptibility of ilmenite. The roasted ilmenite is highly magnetic and it is easily separated from chromium-containing minerals by low-intensity magnetic separation. The roasted ilmenite is then fed into four AC open-arc furnaces similar to those used by RTFT. The feed to the RBM furnaces has a higher TiO_2 content than the feed to the RTFT furnaces. Hence RBM is producing a slag containing about 85 wt.% TiO_2 and very little MgO and CaO. That slag is called chloride slag, because it can be used as feedstock by TiO_2 pigment producers that use the
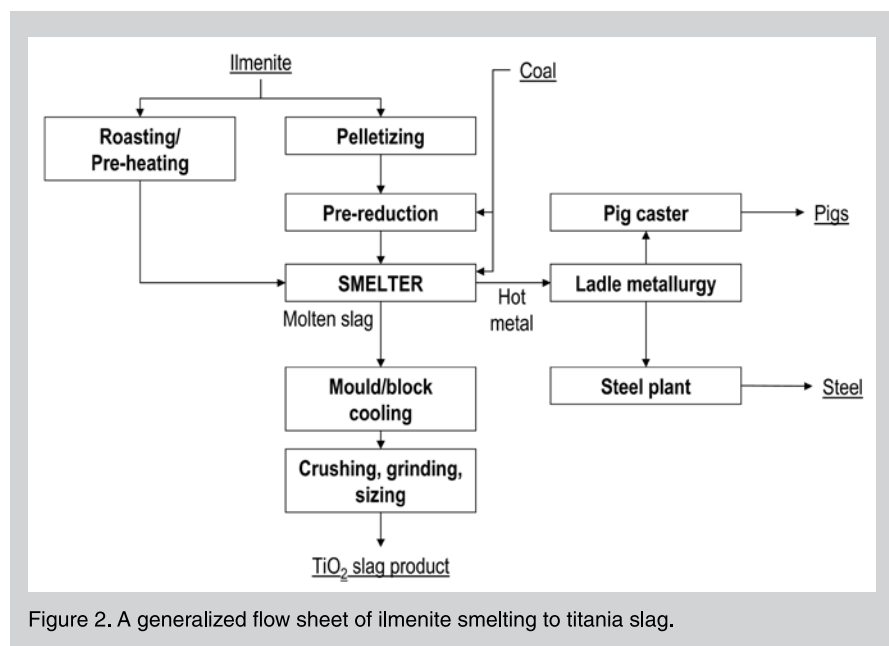

Figure 2. A generalized flow sheet of ilmenite smelting to titania slag.

chloride process. In the RBM plant, all iron produced is converted to pig iron. The plant capacity is about one million tonnes slag and 550,000 tonnes pig iron.

Exxaro is another company that produces chloride slag and pig iron by smelting ilmenite sand. What makes Exxaro different from RBM and RTFT is that it is using DC plasma arc furnaces, each equipped with one hollow pre-baked graphite electrode. This is a newer technology developed in the 1990s in collaboration with Mintek. The first two DC plasma arc furnaces were commissioned in Namakwa on the SW coast of South Africa in 1994. They have a maximum power load of 25 MW and 35 MW, and their combined capacity is 200,000 t/a chloride slag and 120,000 t/a pig iron.[25] Exxaro's KZN plant on the SE coast of South Africa has two DC plasma arc furnaces of maximum power load 36 MW each and a combined capacity of 250,000 t/a chloride slag and 145,000 t/a pig iron.[26]

Synthetic Rutile from Ilmenite Sands

Ilmenite sands are also converted to high grade titania feedstock without smelting, but through oxidation/reduction at solid state and leaching in acid media (Figure 1). The end product of such treatment is called synthetic rutile (SR) because it has a crystal structure similar to natural rutile and a TiO_2 content of about 90 wt.% or more. One SR process is the Becher process, which was developed in the 1960s and 1970s for the treatment of ilmenite sands from Western Australia. Another SR process is the Benilite or BCA process, which was invented in the United States in the 1970s, but is now used by a few plants in India and Malaysia.

In the Becher process[11,27,28] (Figure 3), the ilmenite sand is treated with coal and recycled char in a rotary kiln at temperatures reaching 1,200°C so that the iron in ilmenite is reduced almost completely to its metallic form. The coal used is sub-bituminous coal from Western Australia. This coal has a high content of volatiles, but apparently it has high combustion efficiency and allows for a controlled temperature profile throughout the rotary kiln.
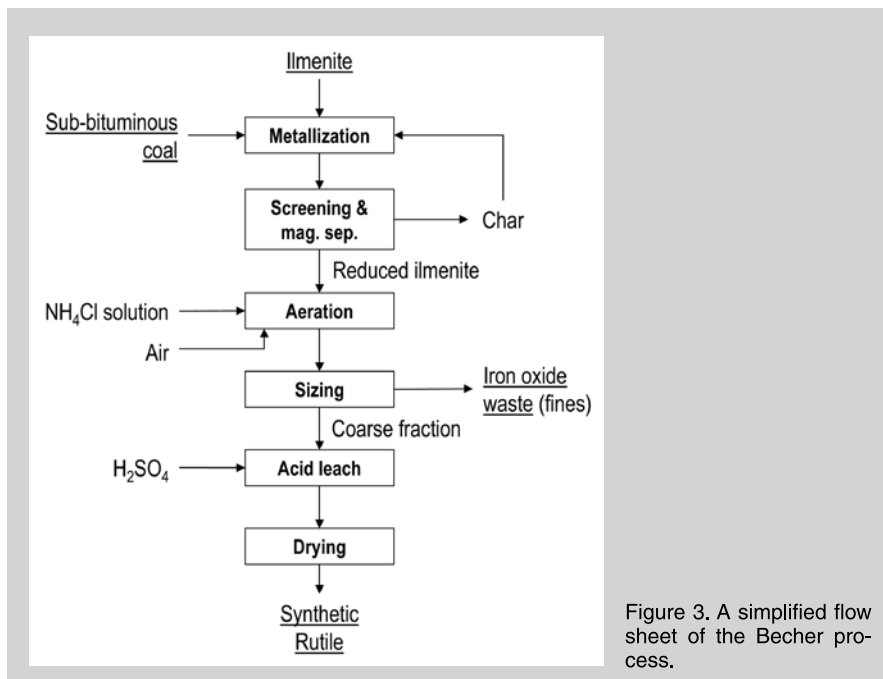

Figure 3. A simplified flow sheet of the Becher process.

Elemental sulfur is added into the rotary kiln to capture manganese in a sulfide phase that can be easily leached in the subsequent leaching step.[29] Also, a borate flux may be added upon metallization to convert radionuclides (uranium and thorium) into leachable borate phases.[30]

The reduced ilmenite goes through screening and magnetic separation to remove the residual char, which is recycled back to the rotary kiln. The reduced ilmenite is then fed into a cascade of tanks, where it is leached with 1.0–1.5 wt.% NH_4Cl aqueous solution at 65–75°C for 12–16 h. The tanks are aerated so that the iron in the reduced ilmenite is oxidized and precipitates as a fine iron oxide/hydroxide. The fine iron oxide/hydroxide is separated from the coarser synthetic rutile by hydrocyclone sizing. An additional leach in 0.4 wt.% H_2SO_4 may be used to raise the TiO_2 content of SR to about 93 wt.%

Three plants are presently using the Becher process, all of which are located in Western Australia. In North Capel, Iluka operates two rotary kilns[31,32] with a combined capacity of 290,000 t/a SR. Until recently, Iluka's Narngulu plant[31] also had two rotary kilns in operation with a combined capacity of 220,000 t/a SR. However, in fall 2008, Iluka announced that it will idle one of its kilns in Narngulu because it lacks suitable feed material. Tiwest operates one SR

plant at Chandala[33] with just one rotary kiln, which through several upgrades has reached a capacity of 225,000 t/a SR.

The iron hydroxide residue from the Becher process is rich in iron (60 wt.% Fe), but extremely fine with an average particle size of 1 to 10 μm. Ward[34] simulated in laboratory the production of this residue and found that it may have a highly variable mineralogical composition; depending on the aeration rate and the agitation speed, the residue may contain magnetite, lepidocrocite (γ-FeOOH), goethite (α-FeOOH), hematite, or a mixture of these phases. The Becher plants produce 0.7 to 0.95 tonnes of iron residue per tonne SR. That residue is thickened, dried, or filtered, and returned to the mine site. Several attempts were made in the past to use this residue as feedstock for the production of pig iron or direct reduced iron (DRI), but apparently none of them went beyond the pilot stage.

In the Benilite or BCA process[35,36] (Figure 4), ilmenite is reduced with heavy oil to 80–95% ferrous iron in a rotary kiln at about 850°C. The reduced ilmenite is subjected to pressure leaching with concentrated hydrochloric acid solutions to produce SR. Leaching is carried out batchwise in rotary digesters with 18–20% HCl at 145°C for several hours. The spent acid from leaching is sent to spray pyrohydrolysis, where HCl is regenerated and iron
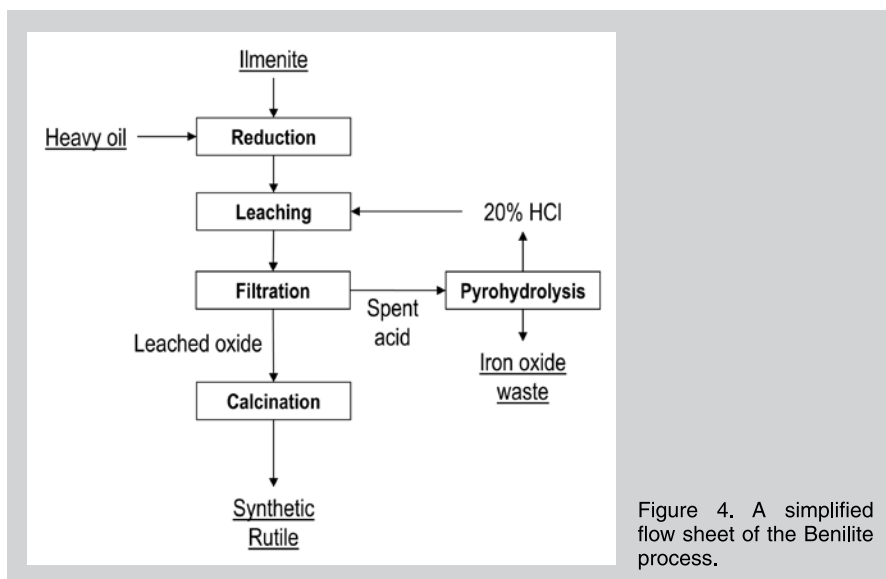
Figure 4. A simplified flow sheet of the Benilite process.

converts to fine hematite residue.[2] The leached solids are filtered, washed, and calcined at about 850°C.

The Benilite process can give SR containing more than 95 wt.% TiO_2. However, the process is rather costly, mostly due to the high cost of acid regeneration. The biggest Benilite plant was the Kerr–McGee one in Mobile, Alabama. That plant, which had a capacity of 140,000 t/a SR, was closed in 2003. Now the process is used by some small plants in India (The Kerala Minerals and Metals, Cochin Minerals and Rutile, and DCW) and Malaysia (TOR Minerals Malaysia). Two of these Benilite plants (The Kerala Minerals and Metals and DCW) have announced capacity increases, with the excess iron to be sold as $FeCl_3$ salt for wastewater treatment plants.

THE FATE OF IRON IN THE TITANIUM DIOXIDE PIGMENT INDUSTRY

Iron in the Sulfate Process

The sulfate process for the production of TiO_2 pigment (Figure 5a) accounts roughly for half of the global TiO_2 capacity. The sulfate process history is longer than that of the chloride process. For several decades, the highly acidic residues generated by the process were dumped almost untreated. Nowadays, this practice has ceased, but the neutralization or the regeneration of sulfuric acid has added significant process costs. As a result, the sulfate process has been on the decline, yet in the last four to five years it has seen a revival due to a rapid capacity expansion in China.[1]

The sulfate process[2] essentially consists of a digestion step, where the titanium feedstock is digested batchwise with concentrated sulfuric acid and dissolved into water for a few hours; a crystallization step, where some iron may be removed as sulfate salt; and a hydrolysis step, where the purified digestion liquor is heated with steam to convert the dissolved titanium into titanium oxyhydroxide ($TiO(OH)_2$) precipitate. After washing and bleaching with reducing agents, the titanium oxyhydroxide is calcined to pure TiO_2 in a rotary kiln. The calciner product is ground to submicrometer size in Micronizer mills and treated with more additives to obtain the final pigment quality.

The fate of iron in the sulfate process depends on the feedstock used. If ilmenite is used as feedstock, then the digestion liquor (black liquor) is rich in Fe^{3+}. Hence, iron scrap is added to reduce most of Fe^{3+} into Fe^{2+} and to obtain a solution containing 16–20 wt.% $FeSO_4$. From that solution, most of the iron is recovered by vacuum crystallization as ferrous sulfate hydrate ($FeSO_4·7H_2O$) salt, or copperas. The rest of the iron ends up as a hydroxide residue upon the neutralization of waste acid. If slag is used as feedstock, then the black liquor contains only 5–6 wt.% $FeSO_4$ and the crystallization of copperas is not required. In that case, all iron is removed by neutralization of the waste acid.

Depending on the iron content of the feedstock, the amount of copperas generated may exceed four tonnes per tonne of TiO_2 in pigment. For many years, copperas was a process residue. This salt can also be used in the production of fertilizers and animal food, as coagulant for wastewater treatment plants, or as cement additive for the stabilization of chrome contained in the cement. However, the quantities of copperas produced exceed the demand and significant quantities of this salt end up stockpiled or in landfills.

Iron in the Chloride Process

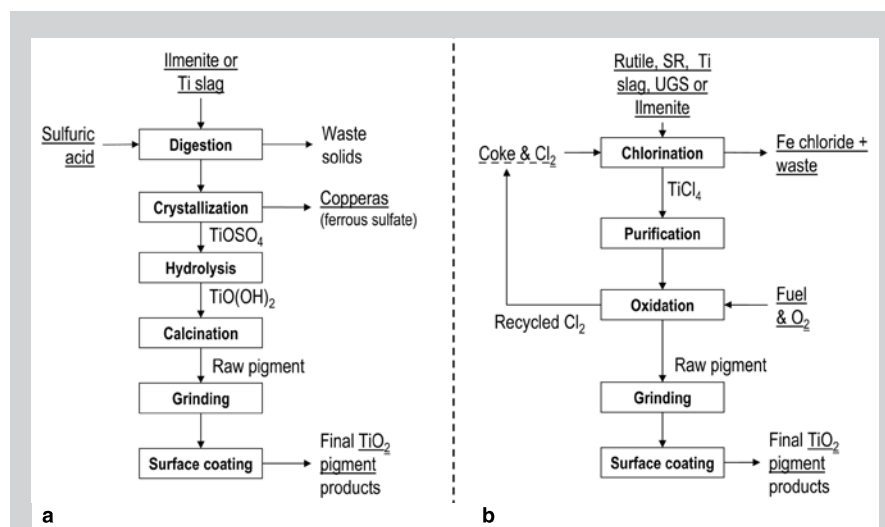The chloride process[2] (Figure 5b) does not generate as much solid waste

Figure 5. Simplified flow sheets of (a) the sulfate process, and (b) the chloride process for the production of TiO_2 pigment.

as the sulfate process.[13] However, the residues from this process are highly soluble chloride salts, which can be more detrimental to the environment.

In the chloride process, the titanium feedstock is chlorinated into $TiCl_4$ gas with petcoke and chlorine gas inside a fluidized bed reactor at about 1,100°C. With the exception of silica, all the other impurity elements are also converted into gaseous chlorides. The impurity chlorides condense as a solid chloride mixture as the off-gases from chlorination are cooled with recirculating liquid $TiCl_4$ to about 200–250°C. The $TiCl_4$ does not condense at such temperatures. It is captured as crude liquid $TiCl_4$ by cooling the off-gases at temperatures below 0°C. The crude liquid $TiCl_4$ is purified by chemical treatment and distillation. The purified $TiCl_4$ is finally oxidized with oxygen at temperatures above 1,500°C to give pure TiO_2 and chlorine gas, which is recycled back to chlorination. The oxidizer product is ground, treated with additives, and dried to pigment.

Iron follows the other impurities as a chloride salt. The impurity chlorides are usually dissolved into a weak HCl solution, and then neutralized for disposal. In one chloride plant in the United States, the chloride salts are not neutralized, but they are injected into deep exhausted oil wells.

Essentially, all iron in the feedstock used by the chloride process is lost as waste. Depending on the feedstock used the amount of solid waste generated by the chloride process may vary between 0.1 and 0.7 tonnes per tonne of TiO_2 in pigment.[5] Chloride plants that use ilmenite as feedstock produce much more solid waste than those that are using high-grade feedstock such as natural rutile, slag, SR, or UGS. Occasionally, some chloride plants recover and sell an iron chloride solution for wastewater treatment, but the amount of iron recovered seems to be rather limited.

NEW CONCEPTS

In the past two to three decades, several new concepts were put forth to overcome some economic and environmental problems that are inherent in the industrial routes for the production of TiO_2 pigment or titanium metal. Most of these new concepts were aimed at the production of high quality feedstock from low-cost ilmenite concentrate. However, some researchers have also tried to produce TiO_2 pigment directly from low-cost ilmenite, albeit at a cost and environmental impact significantly lower than those of the sulfate and the chloride processes.

Of all these concepts, none was ever developed beyond the pilot stage. To the authors' knowledge, only two concepts are still under development, the Austpac process and the Altair process. These concepts are discussed below. Other concepts that have been more-or-less abandoned are reviewed elsewhere.[13,36]

The Austpac Process

The Austpac process[37] has been an attempt to produce high-quality synthetic rutile or pigment directly from ilmenite. The final product is indeed high-grade SR with a TiO_2 content of 97 wt.% or greater, but not of TiO_2 pigment quality.

The high TiO_2 content of the final product is achieved by 'enhanced roasting and magnetic separation' (ERMS) combined with 'enhanced acid regeneration' (EARS). Roasting enhances the magnetic properties of ilmenite. Magnetic separation of the roasted ilmenite with powerful rare earth (RE) magnets gives a magnetic fraction with higher TiO_2 content. That fraction is subjected to leaching under atmospheric pressure conditions with superazeotropic hydrochloric acid (25 wt.% HCl). The regeneration of superazeotropic acid is

achieved by crystallization of the spent acid and fluidized bed pyrohydrolysis of the crystallizer salts. Rutile is nonmagnetic; thus a final magnetic separation can improve the SR grade even more.

The residue of acid regeneration consists of iron oxide pellets. Austpac has tested the iron oxide pellets as feedstock for the production of direct reduced iron (DRI). In 2008, the company completed a test program in a 3,000 t/a SR demo plant. However, it seems the DRI tests in particular were so successful that, in the immediate future, the company will focus its efforts into the production of DRI from waste pickle liquors from steel plants.

The Altair Process

The Altair process[38] (Figure 6) is unique as it converts ilmenite directly into TiO_2 pigment in a way significantly different from the sulfate process or the chloride process. The process was invented in the United States in the mid-1990s, but has not reached yet the industrial scale.

The process is rather complex. Leaching with high chloride solutions (>400 g/L Cl^-) at 60–85°C for 3 to 6 h is used to dissolve about 85% of TiO_2 of ilmenite. The leach solution is treated with iron powder to reduce the dissolved ferric iron to below 0.1 g/L. After that, the reduced leach solution goes through a crystallization stage, where most of the iron is recovered as $FeCl_2 \cdot 4H_2O$ salt. The solution, which contains about 25 g/L iron, is further purified by two solvent extraction stag-
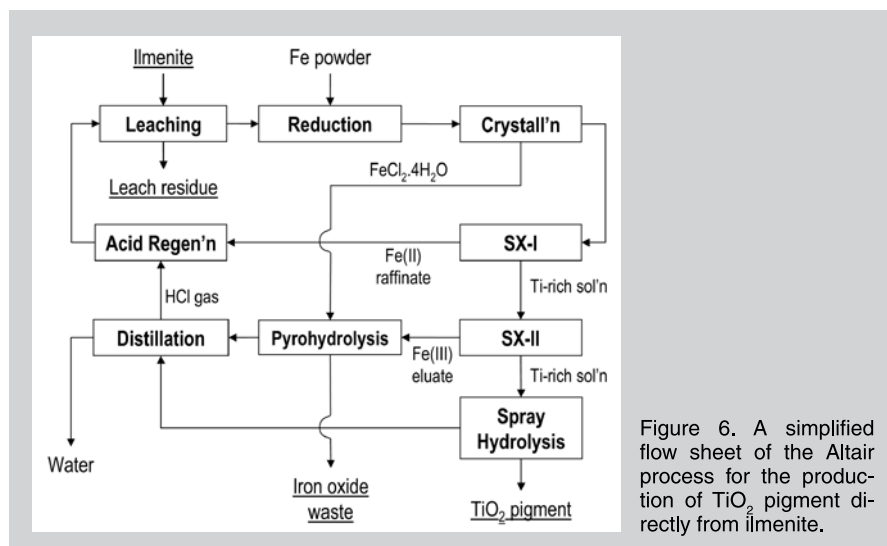
Figure 6. A simplified flow sheet of the Altair process for the production of TiO_2 pigment directly from ilmenite.

es: one with trialkyl phosphine oxide (TOPO) to produce an eluate containing 70 g/L titanium, and another with tertiary amine to remove all Fe^{3+} (which is detrimental to pigment quality) down to a few mg/L. The titanium-rich eluate from the second solvent extraction stage goes through spray hydrolysis at about 600°C to give pure $TiO(OH)_2$, which is further calcined into TiO_2 pigment.

The eluate from the second solvent extraction stage and the $FeCl_2 \cdot 4H_2O$ crystals are fed into a spray roaster where they pyrohydrolyze at 600°C to give an iron oxide waste and HCl gas. The HCl gas is captured into the raffinate from the first solvent extraction stage. The grade of the regenerated acid is boosted at about 25 wt.% HCl solution by pressure swing distillation. The highly concentrated regenerated acid is used for leaching.

The Altair process has the advantage of converting a natural mineral (ilmenite) into a final product (pigment). However, all iron in the ilmenite feed is converted into a waste oxide.

Altair has made a few attempts to convert its technology into an industrial application, but without any success yet. Apparently, Altair is still looking for partners to fund this project.

CONCLUSIONS

The production of TiO_2 offers a unique example of the intricacies and interdependencies in the metal extraction industry. Ilmenite is a low-cost and relatively abundant mineral resource. It can be used as a concentrate in the sulfate process or the chloride process, but most of the iron contained in ilmenite is then lost into the process waste. For the moment, upgrading the TiO_2 feedstock by smelting is the only route that allows for the recovery of most of the iron.

Based on global TiO_2 production data from 2007,[1] the authors of the present article estimate that roughly 1.3 million tonnes of iron or 40% of the total iron contained in TiO_2 mineral resources is not recovered, but it is lost as waste. The recovery of these iron units will reduce the environmental impact of TiO_2 pigment and titanium metal production in terms of waste generated.

Indirectly, the recovery of iron will reduce the GHG charge of TiO_2 pigment and titanium metal.

Clearly the way to go is as sustainable development dictates: a new process whereby the recovery of TiO_2 is complemented by iron recovery so as to minimize waste emissions and to reduce energy consumption. Some new processes under development are aiming at these targets, but they are still far from being financially viable. Therefore, considerable R&D work is needed to bring about a new paradigm in the TiO_2 feedstock and pigment industries.

ACKNOWLEDGEMENTS

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