

1 Introduction

Titanium dioxide (TiO_2) is a white powder with high opacity, brilliant whiteness, excellent covering power and resistance to colour change. These properties have made it a valuable pigment and opacifier for a broad range of applications in paints, in the paper industry, in fibers, cosmetics, sunscreen products, toothpaste, foodstuffs, optical coatings, beam splitters and anti-reflection coatings. It is also used as support catalyst. Its use as a humidity sensor and high-temperature oxygen sensor is under consideration. Titanium dioxide is also a starting material for titanium metal production. Titanium metal is applied in construction projects, aircraft, spacecraft, turbine engines and missiles. The metal is also used in the chemical industry (Alemany *et al.*, 2000; Barksdale, 1966; Mellor, 1960; Nielsen and Chang, 1996; Samuel *et al.*, 2005; Stamper, 1970; Stanaway, 1994).

Titanium dioxide is manufactured from naturally occurring *rutile* (TiO_2), *ilmenite* (FeTiO_3) and *leucoxene* minerals, as well as from titanium slag, upgraded slag and synthetic rutile. Rutile is an impure form of titanium dioxide, whereas ilmenite contains titanium combined with iron as a compound oxide. Leucoxene is an altered form of ilmenite. Although common throughout the world, these minerals are most readily exploited in Australia, the US, India, South Africa and Mozambique. Other titanium minerals with no commercial importance at present are *perovskite* (CaTiO_3), *sphene* [$\text{CaTi}(\text{SiO}_4)\text{O}$] and *anatase* (TiO_2) (Afonso and Marques, 1993; Barksdale, 1966; Habashi, 1997; Nielsen and Chang, 1996).

Two routes are currently exploited industrially to retrieve titanium dioxide from its ores. The sulfate route applies sulphuric acid to convert titanium into a soluble sulfate form. Titania is crystallized the sulfate solution obtained. Titania is then calcined and further processed. In the chloride process, titania ore is converted into titanium tetrachloride using chlorine. Titanium tetrachloride is then burned to produce titania (Barksdale, 1966; Doan, 2003; Lahiri *et al.*, 2006; Nielsen and Chang, 1996; Toromanoff and Habashi, 1985).

The sulfate process produces high quantities of iron sulfate by-product which is not readily saleable. The chloride process can be viewed as a solution for the iron sulfate problem. However it needs high quality feedstock. High titanium slag and synthetic rutile are the preferred feedstocks. The production of slag and synthetic rutile entails high energy consumptions which can be associated with greenhouse gases production. Both processes are unable to deal with radioactive impurities in the ore. They are also unable to use a large variety of titanium minerals (Doan, 2003; Jha *et al.*, 2005; Hollit *et al.*, 2003; de Matos *et al.*, 2002).

There is a need to convert the existing methods to ecologically and environmentally friendly and cost-effective methods. Aspects of concern are the corrosion and toxicity problems caused by the acids that have to be disposed of (Berksdale, 1966; Doan, 2003; Nielsen and Chang, 1996). Other limitations are related to the cost of titania pigments; for instance, they amount to 30% of the total mineral costs in the paper industry although they make up only 3% of all the minerals used. According to Cole (2001), because of global demand, the price of titanium dioxide will continue to increase and it is likely that consumption will soon reach production capacity. This situation will consequently trigger further increases in the price of titanium dioxide. There is, therefore, a need to develop new extract titanium dioxide from the most abundant raw material, ilmenite.

We propose here a new route that will enable the sulfate process to deal with a vast range of titanium minerals that are, until now, not used as ores for titania production. Minerals such as anatase, titanomagnetites, titanohematites and pseudobrookite can be included in this class. The new route has the potentiality of dealing with radioactive impurities as well.

Modification of the de Wet process, zircon processing, combined with the sulfate process could make it possible to use a wide variety of titania ores (de Wet, 1999). The process uses the known alkaline fusion reaction of ilmenite to produce alkaline titanates (Richter and Elizabeth, 1933). The alkaline titanates are then hydrolysed with water and diluted mineral acids to

produce hydrous titanium. The hydrous titania produced in this way is reacted with sulphuric acid to titanyl sulfate.

1.1 Aim of the Study

The aim is to establish and optimise an alternative route to the traditional sulfate route. The new method will enable the sulfate process to treat ores previously considered economically untreatable, such as anatase (90–95% TiO₂), titanomagnetites [Fe(Ti)Fe₂O₄] and other low-grade ilmenites with high contents of calcium and magnesium (Yuan *et al.*, 2005).

It is also important to note that the traditional sulfate route is inappropriate for ores with high levels of chromium, vanadium and niobium because they impart colour to the pigment. High levels of calcium and phosphate are also stated to hinder proper crystal development in the sulfate route (Stanaway, 1994).

1.2 Methodology

The proposed route consists in fusing ore with an alkali compound. The identity of the fused products was verified by X-ray diffraction (XRD). After fusion, the fused product was subjected to a leaching process. The leachate was subjected to an acid hydrolysis and the hydrolysate was reacted with sulphuric acid. The product was dissolved in water and unreacted solids were filtered out. The aqueous solution was subjected to elemental analysis by inductively coupled plasmamass spectrometry (ICP-MS) for iron and titanium determination. Accessory characterisation techniques such as scanning electron microscopy (SEM) and Fourier transform infra-red spectrometry (FT-IR) were used.

Three steps in the process were optimised: fusion, leaching and sulfation. Temperature, time, mole ratio and particle size were the parameters tested for fusion optimisation by evaluating the yield in function of these parameters. For leaching time, the temperature and solid:liquid ratio were the parameters considered, while for sulfation the amount of acid was the sole parameter analysed.

1.3 Rationale

According to Pong *et al.* (1995), for a process to be commercially acceptable, it should be environmentally benign, result in minimal chemical loss through recycling, be able to use all grades of ores, produce manageable intermediate products and be economically favourable.

Existing commercial processes are either environmentally unfriendly or are costly, generate high levels of waste or products that need to be recycled, or are unable to process low-grade ores, as well as ores such as anatase, perovskite and sphene (Bulatovic and Wislouzyl, 1999; Cole, 2001; Hsu *et al.*, 1993; Nielsen and Chang, 1996; Yuan *et al.*, 2005). There are unexploited important reserves of *anatase* (Brazil) and *perovskite* (Colorado, US) due to the lack of, for instance, economical methods of extraction (Nielsen and Chang, 1996).

Generally, low-grade titaniferrous ores are submitted to a slagging process. However, this process faces an uncertain future due to its higher energy consumption and greenhouse gas emissions. In addition, slagging is unable to treat radioactive ores, since the radionuclides remain in the solid solution during the slagging process. With increasingly stringent environmental policies on radionuclides content, further treatment has to be conducted to reduce this content. This will result in additional production costs (Aminesh *et al.*, 2005; Habashi, 1997; Lahiri *et al.*, 2006; Nielsen and Chang, 1996).

Alkaline earths and rare earth impurities are not eliminated during the slagging process. Both the alkaline hearths and silica clog the fluidising bed in the chlorination process. Rare earths such as Cr_2O_3 , V_2O_5 and Nb_2O_5 degrade pigment properties (Aminesh *et al.*, 2005; Habashi, 1997; Hollitt *et al.*, 2002; Lahiri *et al.*, 2006; Nielsen and Chang, 1996).

The route presented in this work has the following advantages:

- reduces the time consumed in the traditional digestion process
- addresses the concerning problem of acid disposal, reducing the amount of acid required for digestion
- has the ability to process all types of titaniferrous ores (Mellor, 1960; Nielsen and Chang, 1996).

1.4 References

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2 Literature Review

2.1 Titanium Minerals and Ores

Titanium occurs chiefly in two forms, ilmenite and rutile. Those are the two commercial minerals. Other natural occurring titanium minerals are listed in Table 8 (Grey and Reid, 1975; Murphy and Frick, 2006; Pownceby *et al.*, 2008; Teufer and Temple, 1966).

Table 1: Non-commercial natural occurring titanium minerals

Mineral	Formula	TiO ₂ , %	Characteristics
Anatase	TiO ₂	95 – 100	Rutile polymorph. It forms blue or black tetragonal crystals. Is formed by alteration of titanium minerals
Brookite	TiO ₂	95 – 100	It is a rare orthorhombic polymorph of rutile, originated by ilmenite minerals alteration
Pseudorutile	Fe ₂ Ti ₃ O ₉ (Fe ₂ O ₃ .3TiO ₂)	60 – 65	Also known as arizonite is an altered ilmenite with properties resembling rutile. It crystalizes in hexagonal form.
Altered ilmenite	FeTiO ₃ -FeTiO ₉	53 – 70	This term is used for alteration with composition between ilmenite and pseudorutile. Is optically homogeneous and amorphous
Leucoxene		70 – 100	It is an altered form of all titanium containing minerals with high content of TiO ₂ . They are optically distinguished from rutile and anatase by their internal reflection.
Titanite (sphene)	CaTiSiO ₅	40	Is a reddish brown, gray, yellow, green or red gem. Occurs as accessory mineral in various rocks and minerals
Perovskite	CaTiO ₃	58	Is a relatively rare accessory mineral. It occurs as accessory mineral in metamorphic and igneous rocks.
Ulvospinel	FeTiO ₄	36	Is a black, brown to reddish brown accessory mineral in igneous rocks. Occurs commonly in titaniferous magnetite iron ores, in kimberlites, in strongly reduced iron-bearing basalts, among others.
Pseudobrookite	Fe ₂ TiO ₅	33	It is a rare mineral with thin needle acicular prismatic crystals. Is associated with pyroxenes, hornblende, tridymite, topaz, hematite and bixbyite. Is dark black mineral.
Titanomagnetite	(Fe, Ti) ₃ O ₄	0 – 34	Is a homogeneous cubic mineral with Fe ₂ O ₃ as dominant phase. It contains above 5% TiO ₂ . It is a solid solution of ulvospinel and magnetite.
Titanohematite	(Fe, Ti) ₂ O ₃	0 – 30	Is a solid solution of hematite-ilmenite. It has a light-gray to white appearance. Has lower reflectance.

There is also a set of minor titanium naturally occurring minerals listed in Table 2 (Mackey, 1994). These minerals are not of economic importance.

Table 2: Minor titanium bearing naturally occurring minerals

Mineral	Formula	Mineral	Formula
Anosovite	Ti ₃ O ₅	Hydrorutile	TiO ₂ ·xH ₂ O
Chrictonite	(Ca,Ln,Ac) _{2-x} (Ti,Mg,Al,Fe,Tr) ₂₁ O ₃₈	Kalkowskyn	Fe ₂ Ti ₃ O ₉
Knopite	(Ca,Ti, Ce ₂)O ₃	Doetlerite	TiO ₂
Pyrophanite	MnTiO ₃	Fulvite	TiO
Mananilmenite	(Fe,Mn)TiO ₅	Geikielite	MgTiO ₃
Picroilmenite	(Mg,Ge)TiO ₅	Tielite	AlTiO ₃
Yttrocraosite	YTh ₂ Ti ₄ O ₁₁		

2.1.1 Rutile

Rutile is a titania (TiO₂) polymorph. It is the most common naturally occurring titania mineral. The other two are anatase and brookite. Large reserves of anatase exist in Brazil and these are in the process of being developed for commercial use (de Matos *et al.*, 2002; Nielsen and Chang, 1996; Paixão and de Mendonça, 1979).

Brookite possesses an orthorhombic structure and transforms spontaneously to rutile at around 750 °C. Anatase presents as a tetragonal structure and it changes to rutile at 915 °C. Rutile is the more stable form and presents as a densely packed anatase structure (tetragonal); see Figure 1. Anatase has a density of 3.899 g/cm³, while rutile has a density of 4.250 g/cm³ (Farrell, 2001).

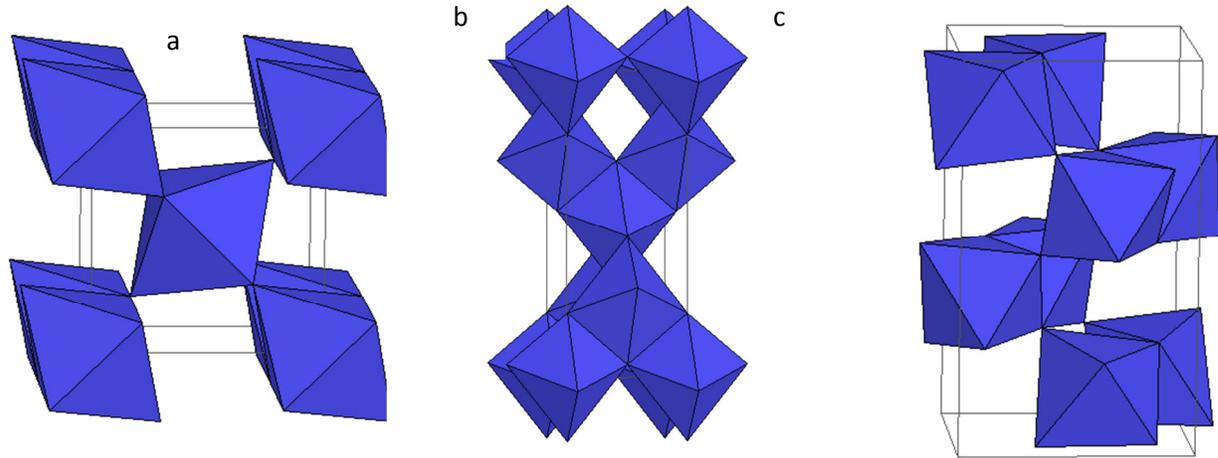


Figure 1: Crystal structure of rutile (a), anatase (b) and brookite (c)

Rutile is the end product of ilmenite and other titanium bearing minerals alteration. The alteration path involves the oxidation of iron to ferric state and progressively leaching out the iron in the ilmenite (Grey and Reid, 1975). It is found in mineral sands, occurs as an accessory mineral of high pressure and high temperature igneous rocks in placers. Is diamagnetic and it can be easily separated from the paramagnetic and ferromagnetic fraction of the heavy mineral, although rutile samples with high iron content can exhibit paramagnetic behaviour owing to losses in magnetic separation (Meinhold, 2010).

2.2 Ilmenite

Ilmenite is an iron-black or steel-grey mineral commonly found as accessory to igneous and metamorphic rocks. It is composed by 36.8% iron, 31.6% titanium and 31.6% oxygen. This corresponds to 52.6% TiO_2 , ideally. In practice the percentage of iron is higher than the presented due, either by partial substitution of titanium by iron or other elements or by the presence of Fe_2O_3 as impurity. Moreover the ferrous iron in ilmenite structure is partially oxidized to ferric state (Grey and Reid, 1975; Murphy and Frick, 2006).

Ilmenite has a hexagonal structure similar to corundum, Al_2O_3 . In ilmenite structure iron octahedral layers alternate with titanium octahedron layers. The two octahedrons share the edge oxygen atoms, Figure 2. Titanium oxygen bonds are strong and are difficult to break. Due to that ilmenite alteration occurs in the iron layers, affecting ilmenite magnetic properties. Ilmenite has a density of 4.7 to 4.8, hardness of 5.5 to 6.0 Moh. Pure crystals melt at $1392\text{ }^\circ\text{C}$ (Aguet *al.*, 2001; Murphy and Frick, 2006; Wechsler and Prewitt, 1984).

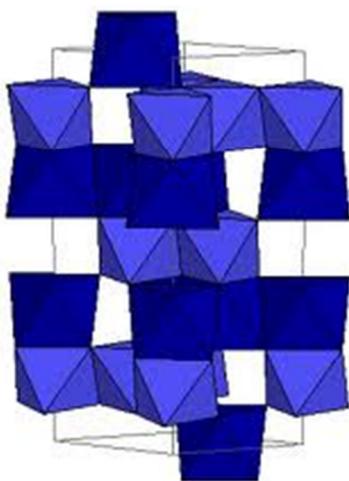


Figure 2: Crystal structure of ilmenite.

Ilmenite occurs in heavy mineral sands (HMS). HMS's possess specific gravity above 4.0. Heavy minerals concentrate in placers as a result of intense wind and waves. The most important minerals economically in HMS are ilmenite and its alteration products, indicated in Table 1, rutile, zircon, and monazite. A list of other minerals commonly associated with HMS is presented in Table 3 (Powncebyet *al.*, 2008).

Generally ilmenite is the main component in HMS deposits. However its chemistry is altered by the presence of impurities in its composition. Titanium and iron, in ilmenite lattice (Figure 2), can be substituted by elements such as magnesium, manganese, chromium and cobalt (Aguet *al.*, 2001; Powncebyet *al.*, 2008). Other elements can be incorporated in ilmenite crystals. These

elements include aluminium, silicon, thorium, phosphorus and chromium, typically. These alterations in ilmenite composition bring difficulties in processing of such ores and reduce its market value (Pownceby *et al.*, 2008).

Table 3: Minerals associated with HMS and their typical impurities

Mineral	Ideal formula	Typical impurities	Specific gravity
Ilmenite	FeTiO ₃	Mg, Mn, V, Nb, Fe ³⁺	4.7-4.8
Rutile	TiO ₂	Nb, Ta, Sn, Fe	4.2-5.5
Pseudorutile	Fe ₂ Ti ₃ O ₉	Mg, Mn, Fe ³⁺ , Cr, OH ⁻ , (H ₂ O, Al ₂ O ₃ , SiO ₂) ¹	3.3-3.8
Zircon	ZrSiO ₄	Hf, Fe, Al, U, Th	4.6-4.7
Monazite	CePO ₄	La, Y, Ca, Th, U, Al, Fe ³⁺	5.0-5.3
Spinel ²	Fe ²⁺ Cr ₂ O ₄ - chromite	Mn, Zn, Fe ³⁺	5.1
	Fe ²⁺ Al ₂ O ₄ - hercynite		4.4
	MgCr ₂ O ₄ - magnesiochromite		4.4
	MgAl ₂ O ₄ - spinel		3.5
	Fe ²⁺ ₂ TiO ₄ - ulvospinel		4.8
	Fe ²⁺ Fe ³⁺ ₂ O ₄ - magnetite		5.2
Garnet ³	Fe ²⁺ ₂ Al ₂ Si ₃ O ₁₂ - almandine	Ca, Mn, Mg, Ti, Cr, Fe ³⁺ , OH ⁻	3.5-4.3
Staurolite	Fe ²⁺ ₂ Al ₉ Si ₄ O ₂₃ (OH)	Fe ³⁺ , Mg, OH ⁻	3.7-3.8
Tourmaline	NaFe ²⁺ ₃ Al ₆ Si ₆ B ₃ O ₂₇ (OH) ₄ - schorl	Mg, Mn, Li, F ⁻	3.0-3.2
Sillimanite (kyanite – high P polymorph)	Al ₂ SiO ₅	Fe ³⁺	3.2-3.3 (3.5-3.6)
Goethite	FeO.OH	Si, Mn ³⁺ , Al	~ 4.3
Quartz	SiO ₂	Al, Fe ³⁺ , Ti	2.6-2.7

P – pressure

¹ commonly co-precipitated with, or adsorbed during weathering

² general name for a group of minerals with formula AB₂O₃

³ garnets are group of silicates that has been as gems, with general formula X₃Y₂(SiO₄)₃, where X can be Ca²⁺, Fe²⁺ or Mg²⁺, and Y Al³⁺, Fe³⁺ or Cr³⁺. The most common in the group are with aluminium in Y site (pyralspite) and with calcium in X site (ugrandite)

Ilmenite can occur in two types of igneous rocks. In rocks related to massif anorthosites and in layered mafic intrusions. The former are of less commercial interest due to extensive intergrowth of ilmenite with magnetite. Anorthosite deposits are characteristically hosted in alkaline rocks rendering ilmenite with high contents of alkaline oxides such as CaO and MgO. Ores from such deposits are suitable for sulfate processing only. They can be also used in the chloride process after alkaline oxides removal (Murphy and Frick, 2006).

Sedimentary deposits are a result of weathering and erosion of titanium minerals from igneous and metamorphic rocks, followed by fluvial transportation and deposition in river beds and coastal shorelines. This process also results in ilmenite alteration and formation of high-grade titanium minerals (Murphy and Frick, 2006).

2.2.1 Titanium Minerals Occurrence

According to US Geological Survey (2010) 95% of the titanium minerals consumption was used in TiO₂ production. The remaining was used in titanium metal production. Australia is the world leader in titanium minerals supplier. Other countries include China, Norway, Canada, South Africa, India, United States and Ukraine. Mozambique is reported to hold half of the total African reserves. In 2010 the world production totalled seven million metric tons for ilmenite and leucosene, while rutile totalled 710 thousands of metric tons (Gambogi, 2010; Murphy and Frick, 2006).

2.2.2 Mining

Large titanium reserves are in the form of anatase and titanomagnetite. These reserves correspond to 50% of the total world reserves. Currently, these are not economically workable under current technologies (Habashi, 1997; Murphy and Frick, 2006).

Ilmenite and rutile are the two mineral sources of titanium with commercial importance. The preferred ilmenite concentrate must contain 50 to 60% of titania. Lower grades are also used. For pigment production, the ore content of chromium oxide and vanadium pentoxide must be 0.2 and 0.5% or less respectively. The mining method depends on the type of ore and on its size. For sand deposits, a concentration of 5 to 7% in TiO_2 is required for economic exploitation. Dredging is used in large scale operation while dry mining is used in small scale operations or where there is no sufficient water available, in hard rock operations or if the clay content is high (Habashi, 1997; Murphy and Frick, 2006; Stamper, 1970).

Sand with 1 to 10% of heavy minerals is usually wet dredged and sieved. The slurry is pumped to a wet concentrator. The concentrator and dredge are both in pool of water and are moved as the operations proceed. The concentrator removes silica, by gravity concentration. The obtained product has a concentration of 90 to 98% in heavy minerals. The separated silica and rocks separated are returned to the mined area while part of the water is recovered and reused (Habashi, 1997; Murphy and Frick, 2006; Stamper, 1970).

Dry mining operations are conducted in the conventional way, involving scrapers, excavators and trucks. For rock mining a primary blasting and the rock is transported for crushing and subsequent separation operations (Murphy and Frick, 2006).

Ilmenite is magnetically and conductively separated from the enriched sand. Leucoxene and other weathered ilmenite fractions are recovered in high-intensity magnetic separators. Rutile

is separated from zircon electrostatically. A small portion of ilmenite comes from hard-rock deposits (Habashi, 1997; Murphy and Frick, 2006).

2.3 Synthetic Feedstock

Environmental pressure on waste disposal has led to an increasing demand for materials with higher titania contents. The synthetic materials are a result of the removal of iron from ilmenite or titanomagnetite (Habashi, 1997; Stanaway, 1994). Feed stocks are classified according to their suitability to either sulfate or chloride process (Murphy and Frick, 2006):

Chloride-grade feed stocks:

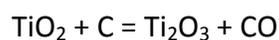
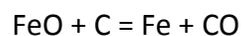
Chloride-grade ilmenite, typically 60% TiO₂
 Leucoxene, typically 75% to 91 % TiO₂
 Rutile, typically 95% TiO₂
 Chloride-grade slag, typically 86% TiO₂
 Upgraded slag (UGS), typically 95% TiO₂
 Synthetic rutile (SR), typically 90% to 93% TiO₂

Sulfate-grade feed stocks:

Sulfate-grade ilmenite, typically 44% to 57% TiO₂
 Sulfate-grade slag, typically 75% to 80% TiO₂

2.3.1 Titanium slag

The process is conducted at 1 650 to 1 700 °C. The extent of rutile formation in slagging has to be limited, especially in the slag to be used in the sulfate process. It is also important to maximize the formation of phases with composition M₃O₅. These phases are soluble in sulphuric acid. The main reactions occurring in the process are

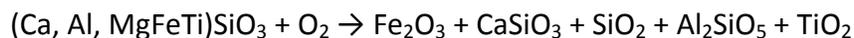


Anthracite or coke is used as reducing agent. As the process proceeds and FeO concentration diminishes the operating temperature has to be raised. FeO acts as a fluxing agent. Due to that FeO removal is limited to up to 90%. Impurity oxides are also partially reduced to metal (Habashi, 1997; Murphy and Frick, 2006). The so produced slag is mainly composed by pseudobrookite and a glassy silicate. The pseudobrookite is a solid solution of iron and titanium oxides with the general formula (van Dyk, 1999).

A relatively new process that enables production of chloride grade slag (UGS) was developed by Canadian QIT⁴. The process was developed to improve Canadian ilmenite, with relatively high concentrations of alkaline oxides. These oxides are less amenable to acid leach. In this process the slag is initially oxidized in order to convert all Ti(III) in Ti(IV) and Fe(II) to Fe(III) as shown in the following equation (Borowiec *et al.*, 1998; van Dyk, 1999).



The aim of the oxidation process is to reduce the content of pseudobrookite phase (M_3O_5) and increase rutile proportion. Apart from the major rutile phase with minor M_3O_5 phase there is a glassy silicate phase. This phase decomposes into wollastonite (CaSiO_3) and tridymite (SiO_2) due to Fe(II) to Fe(III) oxidation according to the reaction (Borowiec *et al.*, 1998; van Dyk, 1999; van Dyk *et al.*, 2004).



During the oxidation process iron migrates to the surface of titania slag particles and into the pores perimeter. This makes it easier to leach it out (van Dyk, 1999; van Dyk *et al.*, 2004). The oxidized slag is then reduced. The aim here is to convert all the iron into the ferrous state. In the reduction stage besides FeO, rutile, pseudobrookite with reduced concentration of MgO and a solid solution of ilmenite-geikielite (MgTiO_3).

⁴ Quebec Iron and Titanium

Finally the reduced slag is leached with dilute HCl solution under pressure, washed and calcined. The resulting slag has a 95% content of TiO_2 , while MgO, CaO, Cr_2O_3 , and V_2O_5 amount typically to 0.67%, 0.08%, 0.06%, and 0.35% respectively (Borowiec *et al.*, 1998; van Dyk, 1999).

2.3.2 Synthetic rutile

Economic reserves of natural rutile (95% TiO_2) are rare compared with ilmenite reserves. Natural rutile is the favourite feedstock for the chloride process. Its advantage includes its bulk density, low trace element content and low iron content (Habashi, 1997; Murphy and Frick, 2006; Stanaway, 1994).

Several processes for converting ilmenite into synthetic rutile (85–96% TiO_2) have been developed to overcome its high price and scarcity. All the processes entail the reduction of Fe^{3+} using carbon or hydrogen. In some cases ilmenite is activated by oxidation prior to reduction. Reduced ilmenite containing Fe^{2+} is preferably treated with hydrochloric acid or diluted sulphuric acid under pressure (Habashi, 1997; Murphy and Frick, 2006). The two most important technologies are: the Becher process (A) and the Benelite process (B) (Murphy and Frick, 2006).

A. The Becher Process

It was developed to upgrade ilmenite with TiO_2 content around 55% to levels as high as 90%. The process is conducted in a rotary kiln using subbituminous coal as reducing agent at 1 050 °C to 1 150 °C. Iron, coal, and sulphur are introduced into the kiln. The Fe(III) is reduced partial or completely to Fe(II), while part of Ti(IV) is also reduced to Ti(III). Sulphur reacts with manganese and iron forming a complex sulphide phase. This complex phase is removed by sulphuric acid (Murphy and Frick, 2006).

Reduced ilmenite from the kiln is mixed with aerated ammonium chloride solution to dissolve iron. Ammonium ions act as buffer preventing localized high pH values consequently avoiding $\text{Fe}(\text{OH})_2$ precipitation in the rutile matrix. Ammonia ions also complex $\text{Fe}(\text{II})$ ions allowing them to diffuse away from high pH zones. The chloride ions from NH_4Cl help in breaking any passive film that eventually might form during aeration (Farrow *et al.*, 1987; Murphy and Frick, 2006).

The product obtained after ammonium chloride treatment is leached with diluted sulphuric acid to remove manganese and residual iron. The product, synthetic rutile (SR), is washed and dried. The so obtained SR is 90% to 93% in TiO_2 (Farrow *et al.*, 1987; Murphy and Frick, 2006).

The Becher process is unable to deal with impurities such as manganese, magnesium, aluminium, uranium and thorium. These elements are retained in the kiln in the minor pseudobrookite (M_2O_5). This phase is insoluble therefore the impurities remain in the SR. Only manganese is partially removed (de Matos *et al.*, 2002; Doan, 2003; Hollit *et al.*, 2003; Murphy and Frick, 2006; Smith and Castro, 2007).

Other constraining aspect in the Becher process is the higher reduction temperature and the time retention in the rotary kiln. The retention is function of the level of weathered of ilmenite. Extensively weathered ilmenite presents cracks that increase the surface available for CO interaction (Murphy and Frick, 2006).

An alternative to overcome this is to operate above 1 200 °C. At this temperature a phase composed by impurities is formed on ilmenite crystals. This phase can be leached in a series of acid leaching steps, taking away manganese, magnesium, thorium, and uranium. A borate salt is used as flux agent to reduce the reaction temperature and form a glassy phase. This process, although successful is costly and there is a threat of acid disposal (Murphy and Frick, 2006).

B. The Benilite Process

In the Benelite process ilmenite containing typically 54 to 65% in TiO_2 is heated up to 870 °C in a rotary kiln mixed with fuel oil. Fuel oil is used as reducing agent to convert Fe(III) to Fe(II). Reduced ilmenite is digested with 18 – 20% at 140 °C. Fe(II) is dissolved as FeCl_2 , while TiO_2 is left in solid state. TiO_2 are water washed and calcined. The final product has 94% of TiO_2 . The FeCl_2 is recovered in later stage and HCl concentrated for reuse (Gambogi, 2010; Murphy and Frick, 2006).

Synthetic feed stocks such as synthetic rutile and titanium slag are available for titania production. The production of slag or synthetic rutile is aimed at ameliorating the environmental burden of waste disposal in the direct use of ilmenite, which is the most abundant and viable source of titania. Although these synthetic feed stocks partially solve the immediate problem of iron waste, such procedures are unable to deal with radioactive and other impurities that are of environmental concern, such as lead and chromium. Such impurities are at present simply discharged. In future, additional costs for waste treatment will exert pressure on the price of the product (de Matos *et al.*, 2002; Doan, 2003; Hollit *et al.*, 2003; Murphy and Frick, 2006; Smith and Castro, 2007).

On the other hand, slagging involves high energy consumption and greenhouse gas emissions (Jha and Dattatray, 2005; Mahmoud *et al.*, 2004; Murphy and Frick, 2006). There is a need to develop new processes that will be able to use a number of raw materials with less and/or recyclable waste. Moreover, the waste generated must not constitute any environmental threat.

2.4 Titanium Processing Technology Overview

There are currently two industrial processes for titania production: the sulfate process and the chloride process. The sulfate process uses low-grade raw materials (ilmenite or titania slag), while the chloride process requires comparatively higher grade and more expensive raw material (natural or synthetic rutile, leucoxene and titania slag) (Gambogi, 2010; Murphy and Frick, 2006).

2.4.1 The Sulfate Process

Dried ilmenite or slag (labelled “titanium ore” in Figure 3) is pulverised and mixed with concentrated sulphuric acid. Water or steam is injected to initiate the reaction (Figure 3). The main reaction can be described by the following equation.

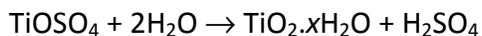


The cake is allowed to mature (1–12 h) and dissolved in water or recycled dilute sulphuric acid. The temperature must be maintained at 85 °C to avoid premature hydrolysis. Ferric ions in solution are reduced to the ferrous state but a small proportion of titanous ions must also be reduced to the titanous state (Ti^{3+}), preferentially, to ensure the reduction of ferric species.

The solution is filtered to remove solids. The filtrate is cooled under vacuum, precipitating FeSO_4 as copperas (ferrous sulfate – $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$). Copperas is used in sewage water treatment and as raw material for iron oxide pigment. Alternatively, the filtrate can be roasted to Fe_2O_3 and SO_2 , thereby recovering sulphuric acid (Habashi, 1997; Lynd and Lefond, 1975).

The final solution is thermally hydrolysed to TiO_2 , according to the reaction below. For higher yields, TiO_2 nuclei are added. Hydrous titania is collected and washed with weak acid. The

product is bleached with acid and mixed with zinc or aluminium powder. The titania is finally dried, calcined and processed (Habashi, 1997).



Spent acid (20–28% H_2SO_4) is concentrated to 70–80% and reused. In another approach, the spent acid is neutralised with lime. Alternatively, the spent acid can be used in the fertiliser industry. The process is summarised in Figure 3 (Habashi, 1997).

Some concerning aspects in this process are listed below for each of the processing steps:

- a. **Preliminary drying.** Preliminary drying of the ore is required to avoid premature reaction due to the heat of hydration of H_2SO_4 . Drying increases energy consumption.
- b. **High acid consumption.** From 2.4 to 3.5 tons of concentrated H_2SO_4 are required to produce a ton of TiO_2 . The acid is discharged as spent acid (6–9 tons). This high volume of spent acid in some cases is simply neutralised and discharged to the environment (Lynd and Lefond, 1975).
- c. **Time consumption.** The whole process can take more than 32 hours (German Federal Environmental Agency, 2001).
- d. **Productivity.** The sulfate process is a batch one and, as indicated before, is a time-consuming process, which implies poor productivity.
- e. **Environment.** The sulfate process impacts negatively on the environment, due mainly to the huge amounts of pollutants that are discharged into the environment. This includes not only the sulphuric acid already mentioned, but also the disposal of iron by-products and the emission of TiO_2 , SO_2 and volatile organic compounds.

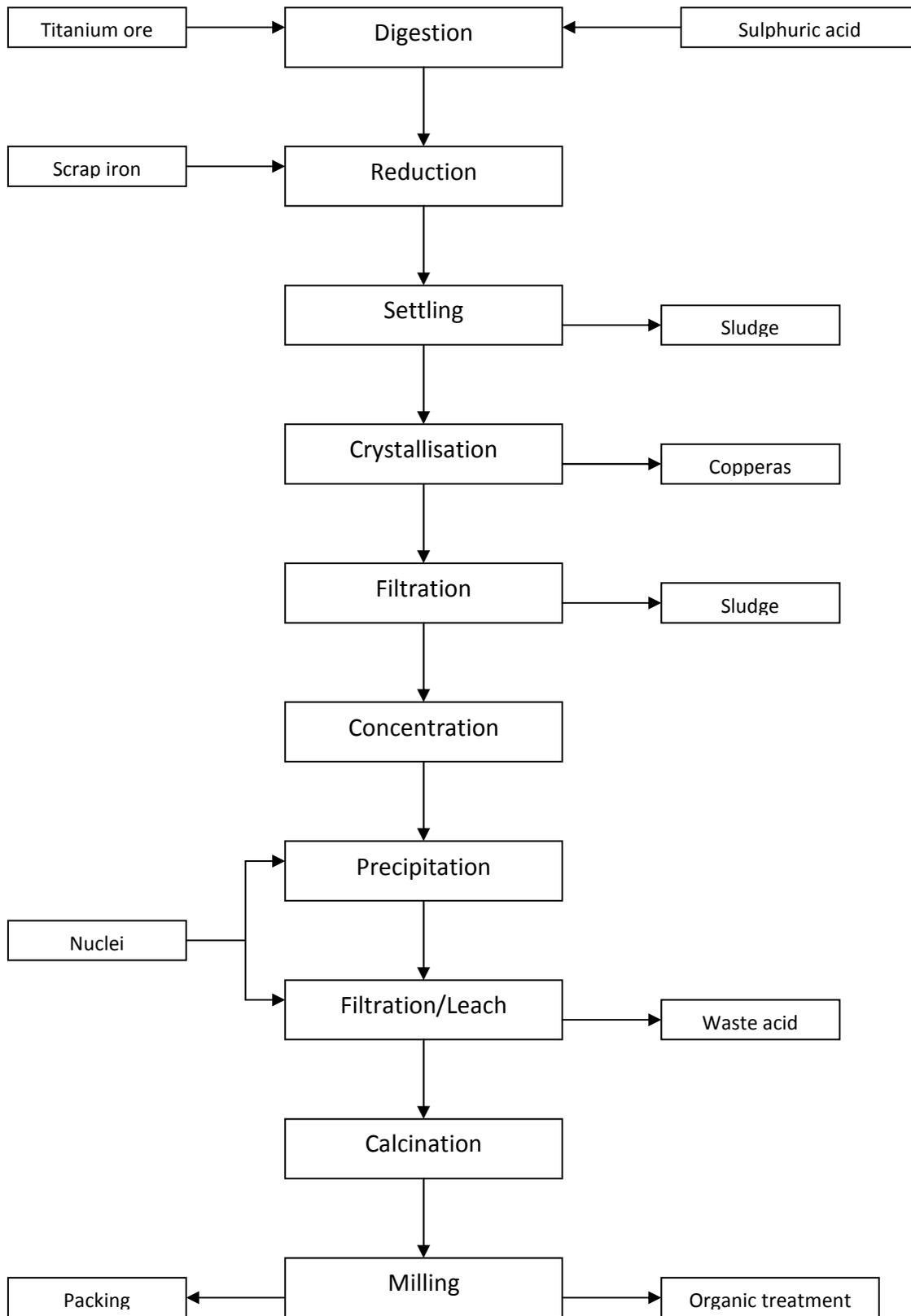
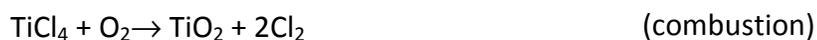


Figure 3: The sulfate process

Part of the titanium sulfate by-product crystallised as copperas is used in water treatment plants and sewerage, as well as in the production of iron oxide pigments. The remainder is disposed of. Attempts to recover sulphur and iron have proved to be technologically, economically or ecologically impracticable. The quantities of iron by-products generated also raise questions concerning their marketability and selling prices (German Federal Environmental Agency, 2001; Lynd and Lefond, 1975).

2.4.2 The Chloride Process

The chloride process (Figure 4) uses mostly slag, rutile, synthetic rutile and, rarely, ilmenite or leucoxene as raw materials. Calcined petroleum coke is used as reducing agent. This coke has low ash content and low volatiles content. This is a continuous process and the main reactions are as given below (Habashi, 1997):



The chlorination process is conducted at 1 000 °C. Under these conditions, most of the metal chlorides are gaseous. However, the magnesium and calcium chlorides are liquid and clog the chlorination surface bed. Their content in the raw material must not exceed 1% and 0.2% respectively as oxides. SiO₂ must also be kept within certain limits (1.5%) as it coats mineral grains and reduces their reactivity. All the raw materials must be dry to avoid losses of chlorine as HCl. The conversion rate in this process is high, 98–100% for chlorine and 90–100% for TiO₂ (Habashi, 1997; Lynd and Lefond, 1975; Stanaway, 1994).

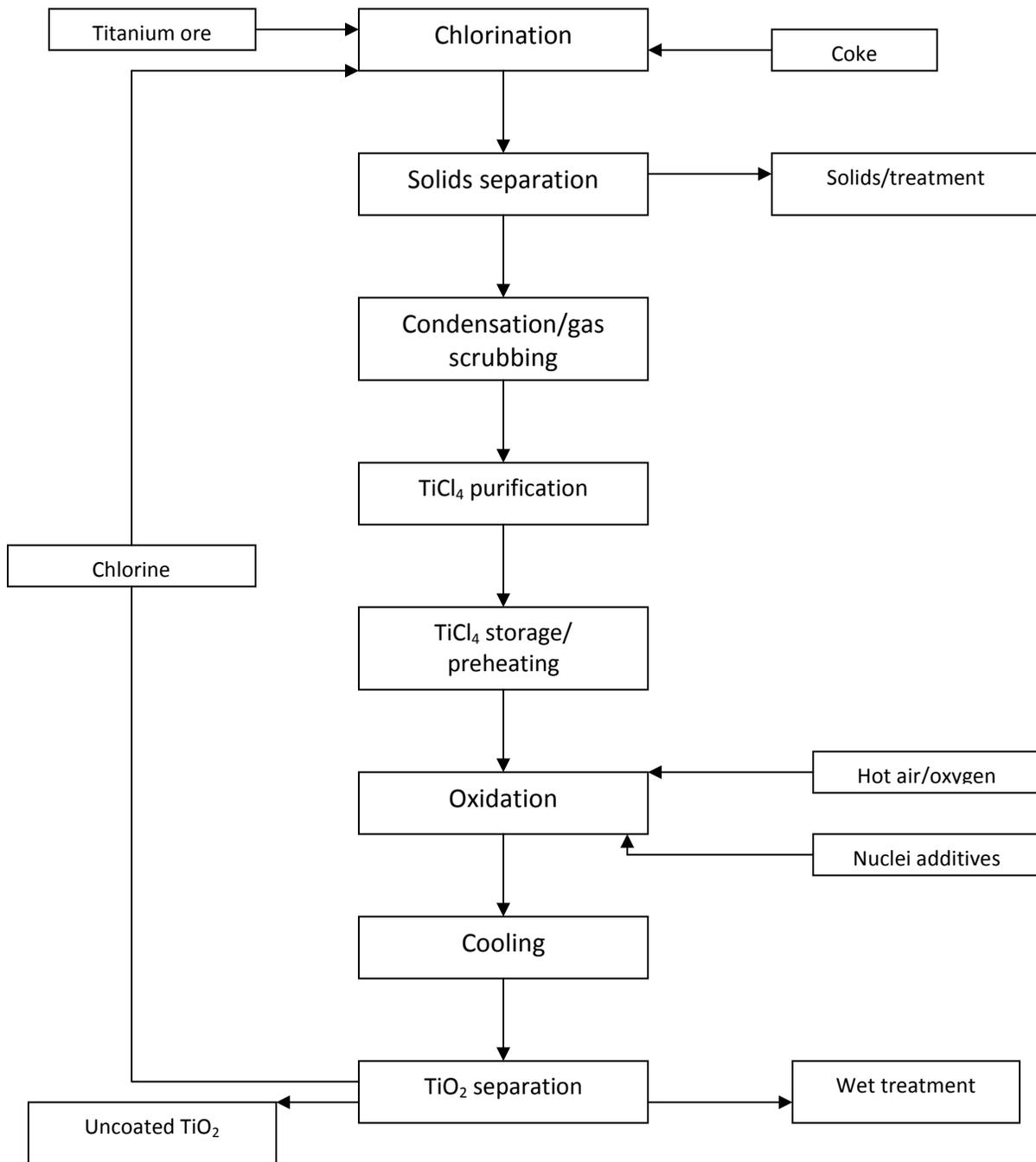


Figure 4: The chloride process

TiCl₄, together with other gaseous metal chlorides, combustion gases and residual TiO₂, SiO₂ and petroleum coke, are discharged from the reactor and cooled, by adding cold TiCl₄, to a

temperature just above the boiling point of TiCl_4 . Most of the chlorides condense, are separated from the residual solids and are then dissolved in water. This solution is used in wastewater treatment as precipitation agent, provided it contains mainly FeCl_2 . If the solution has a different composition, it is neutralised with lime and discharged (Habashi, 1997; Lynd and Lefond, 1975).

TiCl_4 is cooled and separated from the gases. The liquid TiCl_4 is refined by the addition of a reducing agent and distillation in order to eliminate vanadium. Vanadium, even in trace amounts, gives a yellow colour to the pigment. Small amounts of AlCl_3 are added to the purified TiCl_4 , prior to oxidation, to disrupt the TiO_2 lattice. This prevents paints from chalking. TiCl_4 is then burned to TiO_2 in oxygen. Thereafter, the TiO_2 is finally processed to obtain the desired qualities (Habashi, 1997; Lynd and Lefond, 1975).

The chloride process is less harmful to the environment compared with the sulfate process. Like the previous process, the chloride process emits volatile organic compounds that can cause cancer or vomiting and are also responsible for ozone production. Excess ozone causes permanent lung damage.

Chlorine itself is highly corrosive and poisonous. Special reaction vessels are therefore required. The reaction conditions are said to be less flexible and reaction occurs at high temperature (Barton, 1916).

One of the most hampering aspects in the chloride process is the need for raw material with a high titania content. FeCl_3 does not have a commercial value and would result in a waste of chlorine. So, for the chloride process there is a need to pre-treat the most abundant source, ilmenite, resulting in additional production costs (Clark, 1968).

Another aspect of concern is related to the inability of the process to produce anatase-type pigment. The chloride process produces only titania of rutile modification (Loughbrough, 1992).

Both the chloride and sulfate processes release particulate pollution as titania dust to the atmosphere. According to the US Environmental Protection Agency (EPA, 2010), one-third of the titania dust inhaled remains in the lungs and can cause lung damage.

Both processes also result in waste sludge that can contaminate local groundwater, resulting in acute toxicological effects or chronic effects such as kidney and liver disease (EPA, 2010).

2.4.3 Surface Crystal Treatment

This procedure is common to the sulfate and chloride processes and is aimed at producing specific properties in the titania crystals required in some applications.

The base pigment is dispersed in water, milled and classified. The desired particle size for pigment applications is approximately $0.2 \mu\text{m}^5$. In order to improve characteristics such as better dispersion, gloss and durability, the titania crystals are coated with aluminium oxide and silica. Zirconia (ZrO_2) is also used as coating material (Qiu and Starr, 2007). This treatment minimises the photocatalytic activity of titania. The coating process is carried out by selective precipitation via time/temperature pH cycles. Coated particles are dried and micronized in organic solvents (Figure 5) (Habashi, 1997; Lynd and Lefond, 1975).

⁵DuPont brochure on coatings (Titanium dioxide for coatings). Available at <http://www2.dupont.com/home/en-us/index.html>

2.5 Other Processes

Several other processes for titanium recovery have been described in the literature without, however, much attention being paid to commercial use. They are regarded as cumbersome, low yield and involving high energy consumption in general (George and Mohan Das, 1985).

2.5.1 Direct leaching

In direct leaching, titaniferous material is leached in order to selectively dissolve iron and other impurities, enriching its titanium content. In some recent modifications, however, titanium is dissolved instead of iron (Liu *et al.*, 2006). The influencing parameters are acid concentration, temperature, particle size, stirring speed, additives, ratio of ore to acid and pre-treatment.

A concentrate with 90% TiO₂ and 0.8% Fe₂O₃, after leaching of ilmenite (41% TiO₂) at 110 °C, using 20% HCl, for 5 h, was reported (Mahmoud *et al.*, 2004). Iron powder was added at the proportion of 0.1 g per gram of feed. Impurity levels were reported to be 0.12% in total for colouring (MnO₂, Cr₂O₃ and V₂O₅) and 0.08% for chlorine-consuming (CaO, MgO, Al₂O₃) impurities. The process, however, was unable to deal with SiO₂ as 5.8% in the product was reported (Mahmoud *et al.*, 2004).

Using 80% KOH solution, Liu *et al.* (2006) reported solubilisation of 80–85% of titanium at 220 °C with a 7:1 alkali:ilmenite mass ratio.

Iron powder promotes the reduction of Fe³⁺ to Fe²⁺. An extension to Ti⁴⁺ - Ti³⁺ reduction is desirable. Titanous ions are believed to have a role in the dissolution of ferric ions (Ibrahim *et al.*, 2003). Ibrahim *et al.* (2003) found approximately 10% iron powder to be optimum, while Lasheen (2005) reported 7%.

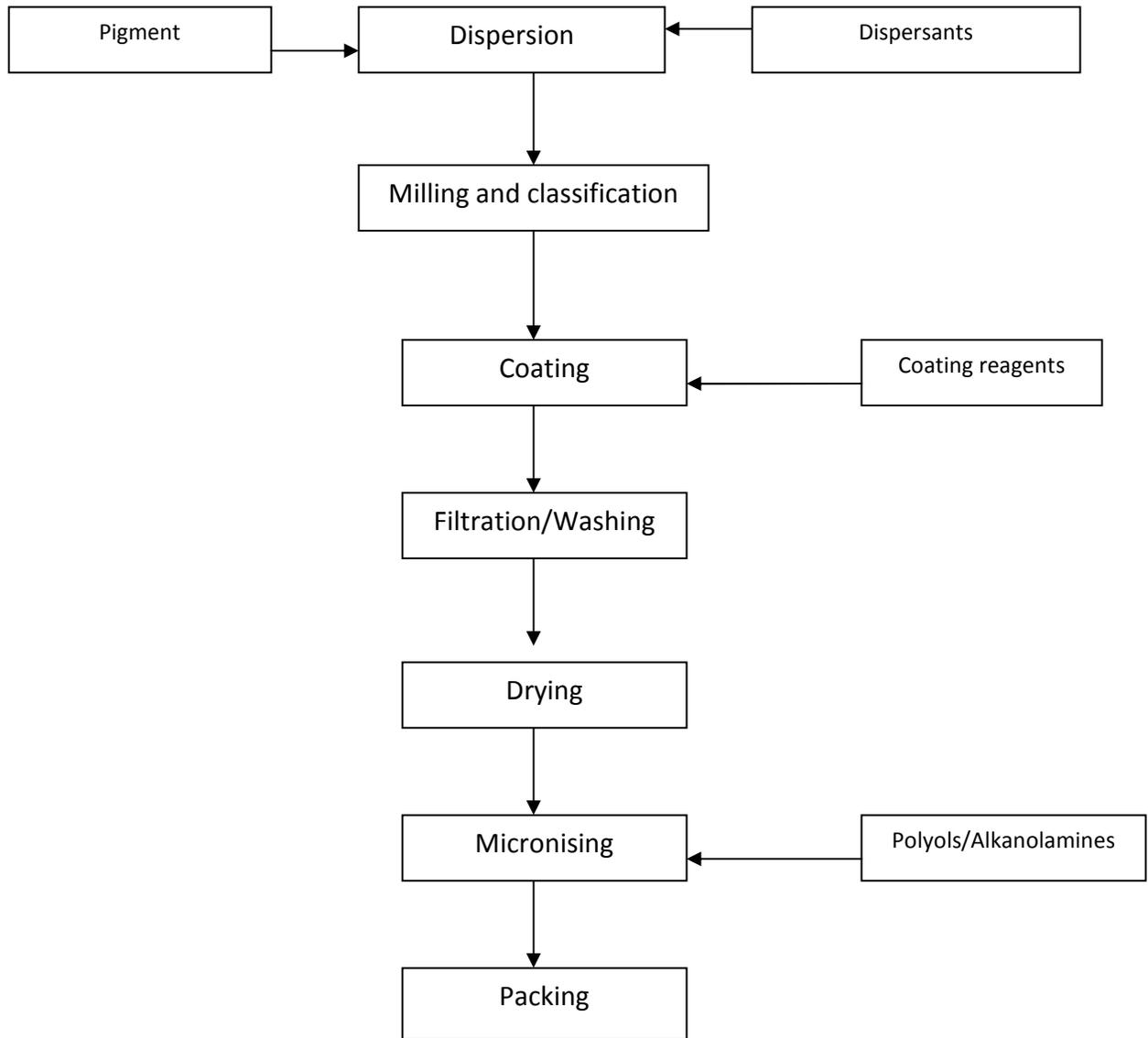


Figure 5: Surface treatment

Oxidation prior to reduction was found to enhance the rate and extent of leaching. Optimum temperatures were reported to be 950 and 850 °C for oxidation and reduction respectively (Sarker *et al.*, 2006; Sinha, 1984).

Ball milling is reported to improve leaching since it reduces particle size and produces particle strain. Combined milling and leaching is said to be very effective (Li *et al.*, 2006b and 2007).

Alcohol solutions were found to lower leaching temperature (Girgin and Turker, 1986). Girgin (1990) found the mixture HCl – CH₃OH to exert a stabilising effect on titanium ions preventing them from hydrolysing (compared to HCl – H₂O and HCl – H₂O – CH₃OH).

Direct leaching can provide concentrates with TiO₂ content as high as 90% (Mahmoud *et al.*, 2004). The main parameters are particle size, acid concentration, temperature, stirring time and speed, acid:ilmenite ratio, presence of additives, as well as pre-treatment.

It was established that ilmenite must be pre-treated, oxidised and reduced (950 and 850 °C respectively) in order to obtain better results. This increases energy consumption. In addition, 10% of iron must be added to the feed. The optimum leaching temperature is about 100–110 °C. Various values for the ilmenite:acid ratio are presented in the literature, although higher ratios seem to be beneficial.

George and Mohan Das (1985) indicated as disadvantageous aspects the need for concentrated solutions of the leachant, extensive leaching times and excessive amounts of leachants, among others. It is important to note that the leaching procedure is intended to produce an intermediate feedstock for pigment processing.

On the other hand, this procedure is unable to tackle the problem of waste in the titanium industry. Iron is leached out as iron chloride or sulfate. In addition, the method is incapable of eliminating or immobilising radioactive impurities and is therefore susceptible to environmental criticism.

2.5.2 Reduction and leaching

In this approach iron in ilmenite is reduced to the elemental state. The elemental iron is then leached out with HCl, leaving TiO_2 as a residue. In some modifications, however, iron reduction is conducted up to the ferrous state. Various reducing agents are used, the most common being hydrogen, coal, coke, carbon monoxide and natural gas. Dilute HCl and H_2SO_4 are the most common leachants, but FeCl_2 solution is also used.

Preferentially, ilmenite is oxidised prior to reduction. The oxidation process is intended to make the ore composition uniform. Natural ores contain a mixture of different oxides, giving rise to different rates of reduction and sometimes, to a lesser extent, of iron dissolution. Oxidation reportedly produces lattice strain, which enhances leaching (George and Mohan Das, 1985; Sarker *et al.*, 2006).

El-Tawil *et al.* (1996) roasted ilmenite with carbon in the presence of Na_2CO_3 . The addition of Na_2CO_3 was aimed at increasing the reduction rate and coarsening the iron. The optimum amount was found to be 20% to the feed. Roasting was conducted at 1 000–1 200 °C for 0.5–3 h.

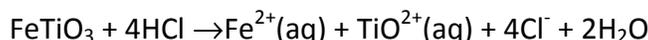
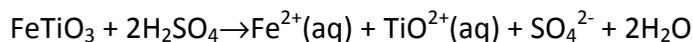
Sinha (1984) and George and Mohan Das (1985) reported 850 °C to be the optimum reduction temperature, although Zhang *et al.* (2007) reported 1 300 °C. For oxidation the optimum was reported to be approximately 950 °C (George and Mohan Das, 1985; Sinha, 1984).

Kucukkaragoz and Eric (2006) found the first stage of the reaction to comprise Fe^{3+} reduction to Fe^{2+} and Fe and the formation of Fe_3C , as well as the reduction of Ti^{4+} to Ti^{3+} . The second stage encompasses the reduction of Ti^{3+} to Ti^{2+} and eventually the formation of the TiO_{1-x} oxygen-deficient phase (Kucukkaragoz and Eric, 2006).

This process produces TiO_2 feedstock to both chlorination and sulfation. George and Mohan Das (1985) pointed out the ability of the process to be commercially exploited, the use of coal as reductant and energy source, and the flexibility to operate in a continuous fashion as the main advantages. The fact that two stages are involved is the only disadvantage they pointed out (George and Mohan Das, 1985). The inability to tackle environmental issues is another disadvantage that should be added. The sole purpose in all the work reported on this process was to extract iron and enrich the TiO_2 content. Impurities such as Al, Si and P, as well as radionuclides, are not mentioned. In reducing roasting, chromium forms chromite species, which are not leachable and remain in the residue as pointed out by Tathavadkar and Jha (2004).

2.5.3 Dissolution

Dissolution techniques involve the solubilisation of both iron and titanium, using mineral acids, generally. The solvents mainly used are hydrochloric and sulphuric acid. The reaction in each case can be described by the following equations:



The most influential parameters are acid concentration, particle size, ratio of ilmenite to acid, temperature, stirring speed and additives. These individual parameters will now be reviewed since the proposed method relies partially on the dissolution reaction.

Extended milling also improves ilmenite dissolution in mineral acids. According to Welham and Llewellyn (1998) milling has the effect of reducing the particle size and in the crystallite size. This is considered to enhance the mass transport phenomenon by increasing the number of grain boundaries.

A. Effect of acid concentration

Ilmenite dissolution, in general, increases with acid concentration. Han *et al.* (1987) observed a maximum at 14 M with H₂SO₄. This was attributed to the peaking of H⁺ ion concentration at this acid concentration. In concentrated solutions, TiOSO₄ and FeSO₄ tend to cover the surface of the crystals, hindering further reaction. In dilute solutions, the products are dissolved, leaving the surface available for further reaction (Han *et al.*, 1987). Li *et al.* (2007), however, observed a steady situation while working with dilute acid solutions. Dissolved Ti did not change with time in weaker solutions and in the case of 20% solution, the Ti in solution even dropped (Li *et al.*, 2007).

El-Hazek *et al.* (2007), using HCl as solvent, reported 12 M as the optimum. Lower concentrations, 7 M HCl, resulted in the dissolution of much of the Fe, while Ti remained in approximately half of the Fe dissolved. Hydrolysis of TiO₂²⁺ was suggested as the reason for this (El-Hazek *et al.*, 2007). Van Dyk *et al.* (2002) reported conflicting results. Quoting an earlier work from Hussein *et al.* (1976) they report dissolution of mainly iron by HCl, while from Jackson and Wadsworth (1976) it was reported dissolution of both titanium and iron (van Dyk *et al.*, 2002).

Biswas and Mondal (1987) found hydrofluoric acid (HF) to be the most effective dissolution agent. They determined the optimum concentration as 6.4 M at boiling point, at a 1:20 solid:liquid ratio. They reported that after 5 h, 81% Ti had dissolved and 26% of Fe. Hansen and Traut (1989) and Olanipekun (1998) found the leaching rate to be linearly dependent on HF concentration and that Ti leached much faster than Fe, independent of the stirring speed. The dissolution rates were found to be consistent with the reaction-controlled kinetic model (Hansen and Traut, 1989; Olanipekun, 1998).

B. Effect of particle size

It is commonly accepted that the leaching rate is inversely affected by particle size, i.e. the larger particles will dissolve slowly compared with the fine ones (Han *et al.*, 1987; Hansen and Traut, 1989; El-Hazek *et al.*, 2007; Olanipekun, 1999).

It is important to note, however, that this effect is also related to slurry density. El-Hazek *et al.* (2007) found that leaching rate was inversely related to slurry density. Working with 12 M HCl they were able to dissolve 92% of titanium at 1/20 slurry density (molar acid/ilmenite ratio). Using a slurry solids-to-liquid ratio of 9/1 only 11% of titanium was dissolved. Apparently this is also connected to the acid concentration as well as to titanium concentration in solution. Lower acid concentrations ($[\text{H}_3\text{O}^+] < 0.5 \text{ M}$) coupled with high titanium concentration ($[\text{Ti(IV)}] > 10^{-3} \text{ M}$) lead to titanium polymerization, reducing therefore titanium solubility, due to lower mobility of polymerized titanium species formed in solution (Nabivanets and Kudritskaya, 1976; van Dyk *et al.*, 2002).

The particle size can also play a role on slurry density effect. Lower densities (higher liquid:solid ratios) particle size will not affect the dissolution process, whereas at higher densities it does.

C. Effect of ilmenite to acid ratio

Li *et al.* (2006b) reported a positive influence when the ratio of ilmenite to acid (w/w) increased from 1:1.4 to 1:1.6 (0.1 increments). Above that point no increase was observed (Li *et al.*, 2006b). El-Hazek *et al.* (2007) reported similar behaviour. Sasikumar *et al.* (2007), however, did not observe any effect (ratios of 1:10 and 1:100).

The critical factor here is acid (H_3O^+) and titanium (Ti(IV)) concentration in solution as was observed by Nabivanets and Kudritsakaya (1976) and van Dyk (2002). Polymerisation leads to

reduced diffusion of titanium species in solution. The polymerisation can lead eventually to TiOCl_2 precipitation, depending on Cl^- and Ti(IV) concentration in solution.

D. Effect of temperature

In all three systems, $\text{HCl} - \text{FeTiO}_3$, $\text{HF} - \text{FeTiO}_3$ and $\text{H}_2\text{SO}_4 - \text{FeTiO}_3$, reported results show an increase in the rate and extension of dissolution. Biswas and Mondal (1987) reported this finding in the $\text{HF} - \text{FeTiO}_3$ system, while Olanipekun (1999) and El-Hazek *et al.* (2007) reported it in the HCl system.

El-Hazek *et al.* (2007) observed a maximum reaction at $80\text{ }^\circ\text{C}$ (98% Ti) and suggested that this should be considered the optimum for the reaction. Their results indicate a decreasing reaction with a further increase in temperature due to Ti polymerisation and hydrolysis enhancement without affecting iron (El-Hazek *et al.*, 2007).

Li *et al.* (2006b) reported an increase up to $120\text{ }^\circ\text{C}$. Using 100% H_2SO_4 , 80% Ti was dissolved after 2 h. A decline was observed due to hydrolysis afterwards. Li *et al.* (2007), using dilute solutions (5–20% H_2SO_4), found that iron dissolution increased with temperature while the percentage of Ti decreased.

E. Effect of stirring speed

Tushida *et al.* (1984) and Olanipekun (1999) found ilmenite dissolution to be independent of stirring speed, using 11.4 M HCl at $70\text{ }^\circ\text{C}$, a 1:69 ilmenite:acid mole ratio, and 7.2 M HCl at $70\text{ }^\circ\text{C}$, respectively.

Jonglertjuania and Rubcumintara (2012) studied the leaching of ilmenite in sulphuric acid (4 M) at $90\text{ }^\circ\text{C}$, using three different stirring speeds (250, 500 and 750 rpm). They obtained the best results at 750 rpm (14.5% of titanium). They attributed this direct relation between titanium

dissolution and stirring speed to the turbulence created in the leaching area. The higher the intensity of the turbulence, the higher the dissolution rate was.

Nayl *et al.* (2009) leaching ilmenite treated with KOH with 6 M sulphuric acid at 150 °C concluded that above 375 rpm the dissolution rate was independent on the stirring speed. The study was conducted on 105 – 74 µm ilmenite on the range of 50 to 500 rpm.

F. Effect of additives

Duncan and Metson (1982) reported Ti dissolution to be seriously affected by additives, attributing this to the chemistry of Ti ions in solution.

Girgin (1990) found better results using HCl in CH₃OH compared with aqueous solutions with or without CH₃OH added. It was then indicated that HCl – CH₃OH exerted a stabilising effect on Ti ions.

Ibrahim *et al.* (2003) found iron powder addition to be beneficial in ilmenite leaching. This was later confirmed by Mahmoud *et al.* (2004) and Lasheen (2005).

2.5.4 Oxidative roasting/fusion

Ilmenite is fused with an alkaline and/or an alkaline earth metal compound to produce, mainly, oxides of iron and titanium. The metal impurities can be in the oxide form or not. The fused product is subjected to selective leaching or complete dissolution of both iron and titanium, followed by separation methods.

In earlier developments, ilmenite was fused with alkali metal compounds or hydroxides in the presence of reductants. The product was leached with dilute mineral acid or water. The residue was calcined to give titania (Barksdale, 1966; George and Mohan Das, 1985).

Sadykhov *et al.* (1994) investigated the effect of Na₂O on the reduction of low-titanium titanomagnetite ore by hydrogen at 700 – 1 200 °C. They found that Na₂O was used mainly to bind SiO₂ into aluminosilicates, while FeO, MgO and CaO were displaced from the silicate phase. Excessive amounts of Na₂O as well as low temperatures (≤ 900 °C) resulted in the formation of bronzes. Higher temperatures (≥ 1 100 °C) favoured sodium titanates (Sadykhov *et al.*, 1994).

In a subsequent report, Sadykhov *et al.* (1998) studied the effect of aluminosilicates such as nepheline (NaAlSiO₄) and albite (NaAlSi₃O₈), and other phases such as MgAl₂O₄, anosovite (Me³⁺TiO₅.MgTi₂O₅, Me³⁺= Fe, Al, or Mn), titanium lovingerite isostructural, Ca(Fe, Mn, Mg)₈Ti₁₃O₃₈ and titanium bronzes Na₂(Fe, Mn)₂Ti_nO_{2n+4} (6 ≤ n ≤ 8), as well as free rutile on autoclave leaching with sulphuric and hydrochloric acid (25–45% H₂SO₄, 180–200 °C). Vanadium was selectively extracted by roasting with soda. They found albite and titanium bronzes to be inert. Titanium bronzes did decompose at much more severe conditions (65–75%, 220 °C). Bronzes are a series of sodium iron titanates with general formula Na_xTiO₂ or Na_{4+x}Ti_{5-x}O₁₂ (Nalbandyan *et al.*, 1998; Reid and Sienko, 1967). An insoluble phase was released, TiO₂.0,1Fe₂O₃.1,3SO₃ (Sadykhov *et al.*, 1998).

El-Tawil *et al.* (1996) applied Na₂CO₃ in the reduction of ilmenite ore in carbon. They observed an enhancement in ilmenite reduction efficiency. A maximum metallisation of 85% at 1 200 °C using 30% Na₂CO₃ was reported. The rest of the iron was accommodated in sodium iron titanates (El-Tawil *et al.*, 1996).

Biswas *et al.* (1996) roasted ilmenite ore with salt-water vapour and leached the product with HCl. Yields of 73%, 96% (NaCl), 35%, 56% (Na₂SO₄) and 87%, 71% (NaNO₃) were achieved for titanium and iron respectively. The roasting was conducted at 800 °C (885 °C for Na₂SO₄), for 90 min, for NaNO₃ and Na₂SO₄ (75 min for NaCl) and a ratio of 0.67 ilmenite to salt for NaCl (Biswas *et al.*, 1996).

De Matos *et al.* (2002) used anatase to produce artificial ilmenite to enable it to be used in current processing methods. They roasted anatase ore with Na_2CO_3 or K_2CO_3 . No reducing agents were used to avoid iron solubilisation. The fusion was intended to convert aluminium, silicon and phosphorus into soluble forms. The fused product was leached with alkaline solution ($\text{pH} \approx 10$) for 60 min at 60–90 °C. The leached cake was calcined at 900–1 300 °C for 20 to 60 min. The calcined product was again leached with HCl or H_2SO_4 ($> 50 \text{ g/l}$) for 20–240 min at 60–90 °C. The final product, artificial ilmenite, contained 50% TiO_2 and 41% Fe_2O_3 as reported, which corresponded to 100% and 94% recoveries respectively. Impurity metal valuables (Al_2O_3 , P_2O_5 and SiO_2) were reported to be recoverable from the leach liquor (de Matos *et al.*, 2002).

Borowiec *et al.* (2003), in a process claimed to be appropriate for ores with substantial contents of iron, manganese, chromium, vanadium, aluminium, silicon and alkaline earths, oxidised slag at 950 °C to decompose silicate glassy phases. The oxidised slag was afterwards reduced at 700 °C for 30 min, to reduce only iron. The calcined and subsequently reduced slag was leached with mineral acid at 125 °C under pressure. The final product was washed and calcined again at 600–800 °C (Borowiec *et al.*, 2003).

Hollit *et al.* (2003) applied the fusion method to remove radioactive impurities. They fused titaniferous ore with alkali metal compounds and boron, such as borax, caustic soda, soda ash and silica, at temperatures less than 1 300 °C for 4 h. The product was cooled slowly in order to avoid crystallisation. The alkali metal compounds were added in order to ensure the formation of glassy phases, while borax was added to avoid the formation of alkali ferric titanates and sodium titanate bronzes (NaTiO_3). Phosphorus compounds can also be used for this purpose. In cases where the titaniferous material proved to contain such components, no additive was used. Alkali ferric titanates and sodium titanate bronzes are reportedly not amenable to leaching. The solidified phase was leached with acid or alkali solution. A product with a 96% TiO_2 content was reported (Hollit *et al.*, 2003).

Jha *et al.* (2010) mixed titaniferrous ore with Na_2CO_3 or K_2CO_3 , or the mixture of both, CaO (1–4%) and alumina (20%). The mixture was roasted at 950 °C for 120 min. The roasted mass was leached with hot water at 80 °C for 40 min. The residue was persistently washed until pH 7 was achieved. As impurities (Fe, Al, Nb, U, Th and rare earths) may be precipitated as hydroxides from the leachate, the pH was adjusted by adding ammonium salts. Controlled precipitation was conducted by bubbling CO_2 or by organic acid addition. The solid titania residue was leached with 5% HCl at 70 °C for 10 min. It was then washed with dilute acid solution. The leachate solution was found to contain Nb, U, Zr and REE. The solid residue was dried and mixed with NaHSO_4 or NaHCO_3 and roasted at 300 °C in air for 1 h. The roasted residue was then water leached at 80°C for 30 min and washed until pH 7 was achieved. The final residue was dried (Jha *et al.*, 2005).

Lahiri *et al.* (2006) fused ilmenite with Na_2CO_3 in stoichiometric proportions at 873–1173 K for 4 h. The fused ilmenite was leached with water for 30 min. The authors reported the formation of Na_2TiO_3 and Na_4TiO_4 in the fused product at 600 and 700 °C respectively. Na_2CO_3 was also reported to be present in the fused product. The conversion achieved was around 50% (Lahiri *et al.*, 2006).

In another modification, Jha and Thatavadkar (2009) alkali roasted a titaniferrous ore with alumina and calcium oxide sources. The roasted material was leached in water or alkali solution (to enhance selectivity in leaching). The residue was leached with acid to remove CaO and Al_2O_3 . The residual solid was essentially TiO_2 . Further purification was effected by fusing it with NaHSO_4 or NaHCO_3 , followed by water leaching. TiO_2 with 95% purity was reported. Metal contaminants (Al_2O_3 , CaO, V_2O_3 , Fe_2O_3 and Cr_2O_3) were recovered from the leaching aqueous solution by acidification (Jha and Thatavadkar, 2010).

In recent years, the focus of studies on oxidative roasting has been on extracting impurities such as aluminium, chromium, silicon, phosphorus, vanadium, calcium and magnesium, as well as radionuclides (uranium and thorium), among others. These impurities are converted into soluble forms and can therefore be leached out, leaving the material free of their hazardous effect. Some of these impurities have been the deterrents for using some of the ores (Jha *et al.*, 2005; de Matos *et al.*, 2002; Nielsen and Chang, 1996; Smith and de Castro 2007).

The fusion product can be selectively leached with either alkali or acid. In this approach the product is intended to be processed further, to be used as a feedstock for currently used techniques. This implies additional steps which will result in a costly end-product.

The main intention with slagging is to separate iron from ilmenite. Other impurities remain in the slag (Hollit *et al.*, 2003; Jha *et al.*, 2005; de Matos *et al.*, 2002; Smith and de Castro, 2007). There is also uncertainty about slagging due to its high power consumption and greenhouse gas emissions (Jha *et al.*, 2005). In addition, with increasingly stringent environmental regulations regarding radioactive levels in spent liquors, wastes and pigment-containing products, there will be increasing pressure on the pigment producers to use feed stocks with lower radionuclide contents (Doan, 2003).

Another interesting feature of the fusion/roasting process is the possibility of producing phases that can be regarded as radionuclide immobilisers. Zirconolite $[(Ca, Fe, Y, Th)_2(Fe, Ti, Nb)_3Zr_2O_7]$ and hiarnite $[(Ca, Mn, Na)_2(Zn, Mn)_5(Sb, Ti, Fe)_2O_{16}]$ are such phases (de Hoog and van Bergen, 1997; Jha *et al.*, 2005).

However, the aforementioned methods are affected mainly by the following disadvantageous aspects:

- Multiple steps are involved in these methods.

- The fusion temperatures are considerably higher, bearing in mind that they are intended to pre-treat the raw material.

In some approaches a pre-treated (slag) feedstock was used. This simply means that the challenging problems related to slag production, as indicated earlier, remain.

George and Mohan Das (1985) indicated energy consumption, the corrosive nature of the melt and low yields as, essentially, the major drawbacks for development of the fusion process on a commercial scale. It is worth pointing out that the average fusion temperature is comparable to that of slagging. The slagging process also involves dealing with the corrosiveness of chlorine gas, as well as of alkali in chlorine gas production. The major challenging aspect is therefore the improvement of recovery levels. However, the fusion procedure does tackle, as established, the challenging aspect of radioactive waste (de Hoog and van Bergen, 1997; Jha *et al.*, 2005).

2.5.5 Remarks on Titania Technology

It seems obvious from the brief review presented in this chapter that the titanium industry is surrounded by environmental and operational challenges. Although on the one hand, the chloride process presents a partial solution to the iron waste problem presented by sulfate process, on the other hand the process itself is faced with high energy consumption and highly corrosive reactants, leading to a short life-time for the equipment. Furthermore, there is the already indicated problem of greenhouse gas emissions and the inability to eliminate or immobilise radioactive impurities (Jha *et al.*, 2005; Hollit *et al.*, 2003; de Matos *et al.*, 2002). The chloride process as it now operates is unable to treat different types of raw material (Habashi, 1997; Murphy and Frick, 2006; Pong *et al.*, 1995).

It was pointed out that in a considerable number of titania applications the anatase form is preferable. The chloride process is incapable of producing pigments with anatase crystal

structure, i.e. incapable of anatase modification (Loughbrough, 1992; Murphy and Frick, 2006). This reality means that the sulfate route will continue coexisting with the chloride one. The task now is to reduce the environmental burden of the sulfate process, as well as to make it more economically viable, producing in a cost-effective way. In addition, it has to be updated in manner that will enable it to deal with most, if not all, types of ore. This is the main goal of the investigation presented here.

2.6 Phase Diagrams

The alkali fusion reaction of ilmenite can produce a mixture of alkali titanates and alkali iron titanates. The relative proportion of different phases is dependent on the mole ratio of ilmenite to alkali, temperature and reaction time. Alkali phases releasing proportionally high quantities of titanium are preferred.

2.6.1 System $\text{Na}_2\text{O}-\text{TiO}_2$

Sodium titanates have been extensively investigated due to their applicability in photocatalysts, fuel cell electrolytes, ion exchange processes, ceramic capacitors, as dielectric resonators in microwave oscillator band pass filters, reinforcing agents of plastic, oxygen sensors and as adiabatic materials. Some are effective in the separation of radioactive nuclides (Meng *et al.*, 2004; Ramírez-Salgado *et al.*, 2004). Nevertheless, there is controversy regarding the phases occurring in this system (Bamberger and Begun, 1987; Hill *et al.*, 1985; Mitsuhashi and Fujiki, 1985; Nalbandyan, 2000).

Most of the titanates can be grouped into two series, namely $\text{Na}_2\text{Ti}_n\text{O}_{2n+1}$ and $\text{Na}_4\text{Ti}_n\text{O}_{2n+2}$. For the previous series ($\text{Na}_2\text{Ti}_n\text{O}_{2n+1}$) compounds with $n = 1-9$ are known or merely reported, while

for the latter series only compounds with $n = 1, 3, 5$ and 9 are reported (Clearfield and Lehto, 1988).

The partial phase diagrams published by Bouaziz and Mayer (1971) and Gicquel *et al.* (1972) seem to have been commonly approved (Figure 6) (Bamberger and Begun, 1987; Glasser and Marr, 1979; Roth *et al.*, 1981). These include the Na_2TiO_3 (α and β), $\text{Na}_8\text{Ti}_5\text{O}_{14}$, $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_2\text{Ti}_6\text{O}_{13}$, Na_4TiO_4 and $\text{Na}_6\text{Ti}_2\text{O}_7$ phases. Previous literature, however, included Na_2TiO_3 and $\text{Na}_2\text{Ti}_2\text{O}_5$, as reported in the reference literature (Gmelins Handbuch, 1951).

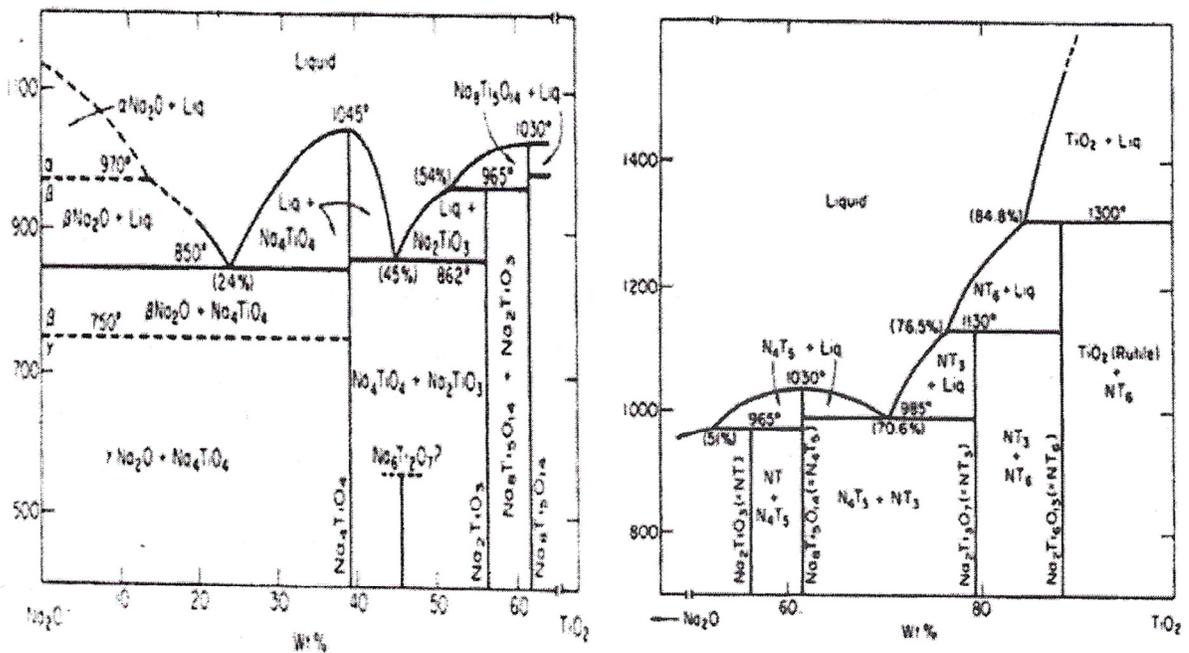


Figure 6: Na₂O – TiO₂ phase diagrams (Bouaziz and Mayer, 1971; Gicquel *et al.*, 1972)

Anderson and Wadsley (1961) identified the phase they obtained by fusing Na₂CO₃ and TiO₂ (1:2 mole ratio) at 1 300 °C as Na₂Ti₃O₇. The same phase was reported to have been produced hydrothermally (Watanabe, 1981). Ramírez-Salgado *et al.* (2004) reported the synthesis of

$\text{Na}_2\text{Ti}_3\text{O}_7/\text{Na}_2\text{Ti}_6\text{O}_{13}$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}/\text{TiO}_2$ mixtures by the sol-gel method using alkoxide precursors.

Plumley and Orr (1961) claimed to have produced $\text{Na}_2\text{Ti}_6\text{O}_{13}$ by metatheses of $\text{K}_2\text{Ti}_6\text{O}_{13}$ with NaCl. In fusing the mixture of Na_2CO_3 and TiO_2 (1:6 mole ratio) at 1 300 °C, Anderson and Wadsley (1962) reported the production of $\text{Na}_2\text{Ti}_6\text{O}_{13}$. The same result was claimed by Anderson and Wadsley (1962) on heating $\text{Na}_2\text{Ti}_3\text{O}_7$ (950 °C). Sauvet *et al.* (2004) reported the production of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ by the sol-gel method. $\text{Na}_2\text{Ti}_3\text{O}_7$ was found to decompose into $\text{Na}_2\text{Ti}_6\text{O}_{13}$ upon heating, as previously observed by Anderson and Wadsley (1962) (Sauvet *et al.*, 2004). Watanabe (1981) and latterly Seo *et al.* (2004) reported the hydrothermal synthesis of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ from TiO_2 and NaOH solutions at mild temperatures (between 250 and 350 °C).

Belyaev and Golovanova (1962) studied the system $\text{Na}_2\text{O} - \text{TiO}_2 - \text{V}_2\text{O}_5$ and identified Na_2TiO_3 , $\text{Na}_8\text{Ti}_5\text{O}_{14}$ and $\text{Na}_2\text{Ti}_3\text{O}_7$ in the $\text{Na}_2\text{O} - \text{TiO}_2$ side of the system, by X-ray diffraction. Belyaev and Belyaeva (1965) found $\text{Na}_8\text{Ti}_5\text{O}_{14}$ along with Na_2TiO_3 in the NaCl- Na_2TiO_3 - TiO_2 system. They also suggested the existence of $\text{Na}_2\text{Ti}_3\text{O}_7$ in this system.

Batygin (1967), studying the formation of titanates from NaOH+ TiO_2 mixtures, concluded that the XRD data attributed to metatitanate (Na_2TiO_3) was, in fact, that of $\text{Na}_8\text{Ti}_5\text{O}_{14}$. This observation was later supported by Glasser and Marr (1979). Batygin (1967), in the same report, heated Na_2TiO_3 and observed the broadening of the lines $d = 2.25$ and 2.60 , giving an indication of the formation of $\text{Na}_8\text{Ti}_5\text{O}_{14}$.

Batygin (1967) identified the product of 1:2 mole ratio ($\text{Na}_2\text{O}:\text{TiO}_2$) fusion at 700 °C (for prolonged times) as $\text{Na}_2\text{Ti}_2\text{O}_5$, since the XRD pattern did not show similarities to known titanates. He also reported that, on heating, dititanate ($\text{Na}_2\text{Ti}_2\text{O}_5$) transforms into $\text{Na}_8\text{Ti}_5\text{O}_{14}$. It was pointed out that this finding had prevented other researchers from producing $\text{Na}_2\text{Ti}_2\text{O}_5$

(Batygin, 1967). Belyaev *et al.* (1970) described the formation of $\text{Na}_2\text{Ti}_2\text{O}_5$ along with $\text{Na}_8\text{Ti}_5\text{O}_{14}$ and $\text{Na}_2\text{Ti}_4\text{O}_9$ as an intermediate stage in the formation of Na_2TiO_3 in mixtures of Na_2CO_3 with TiO_2 (1:1 mole ratio). Bouaziz and Mayer (1971) expressed some concern about the existence of $\text{Na}_2\text{Ti}_2\text{O}_5$.

According to Batygin (1967), the XRD pattern assigned to sodium pentatitanate ($\text{Na}_2\text{Ti}_5\text{O}_{11}$) in the ASTM⁶ index, allegedly taken from Plumley and Orr (1961), belongs to a mixture of pentatitanate and hexatitanate, since it was recorded from a mixture in which $\text{Na}_2\text{Ti}_6\text{O}_{13}$ was the dominant phase. Glasser and Marr (1979) indicated that the pattern under debate belonged to the mixture of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$. This ultimate correction was rejected by Bamberger and Begun (1987). They tried to synthesise $\text{Na}_2\text{Ti}_5\text{O}_{11}$ as reported by D'Ans and Löffler (1930), using mixtures of Na_2CO_3 and TiO_2 (1:2) at 1 100 °C and cooling slowly. A mixture of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_8\text{Ti}_5\text{O}_{14}$ was obtained. Trials with 1:5 mixtures at 900 °C produced mixtures of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ (Bamberger and Begun, 1987).

Wadsley and Mumme (1968) reported isolation of $\text{Na}_2\text{Ti}_7\text{O}_{15}$ crystals after heating a mixture of $\text{Na}_2\text{C}_2\text{O}_4$, Al_2O_3 and TiO_2 (1:1:2 mole ratios). They believe that $\text{Na}_2\text{Ti}_7\text{O}_{15}$ and $\text{Na}_2\text{Ti}_8\text{O}_{17}$ cannot be obtained by a single oxides mixing and heating experiment. The sole prediction was $\text{Na}_2\text{Ti}_8\text{O}_{17}$. $\text{Na}_2\text{Ti}_7\text{O}_{15}$ was believed to result from the decomposition of $\text{Na}_2\text{Ti}_6\text{O}_{13}$, according to the following equation (Wadsley and Mumme, 1968):



Belyaev *et al.* (1970) established the nature of an intermediate phase initially denominated by β -titanate as $\text{Na}_4\text{Ti}_3\text{O}_8$. This phase decomposes into $\text{Na}_8\text{Ti}_5\text{O}_{14}$ and $\text{Na}_2\text{Ti}_3\text{O}_7$ (Belyaev *et al.*, 1970). Furthermore, as indicated previously, they found $\text{Na}_8\text{Ti}_5\text{O}_{14}$, $\text{Na}_2\text{Ti}_2\text{O}_5$ and $\text{Na}_2\text{Ti}_4\text{O}_9$ to be intermediates in Na_2TiO_3 formation. Surprisingly, $\text{Na}_2\text{Ti}_4\text{O}_9$ (sodium tetratitanate) is indicated as one of the intermediates without any supporting substantiation in the text. Dion *et al.* (1978),

⁶ American Standards and Testing Materials

however, reported the preparation of $\text{Na}_2\text{Ti}_4\text{O}_9$ by metatheses of $\text{Ti}_2\text{Ti}_4\text{O}_9$ with NaCl . Later, Akimoto and Takei (1989b) reported this from mixtures of Ti_2O_3 and Na_2O , and Watanabe (1981) reported the hydrothermal synthesis of $\text{Na}_2\text{Ti}_4\text{O}_9$ from TiO_2 and NaOH at 250–350 °C. Sun *et al.* (2002) observed that $\text{Na}_2\text{Ti}_4\text{O}_9$ hydrothermally produced decomposes into $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ at 900 °C.

Belyaev (1976) analysed sodium metatitanate formation from $\text{Na}_2\text{CO}_3/\text{TiO}_2$ mixtures. He concluded that the reaction proceeded via successive reactions of Na_2CO_3 and TiO_2 with $\text{Na}_2\text{Ti}_2\text{O}_5$, $\text{Na}_4\text{Ti}_3\text{O}_8$ and $\text{Na}_8\text{Ti}_5\text{O}_{14}$ intermediates. The reaction of Na_2CO_3 with $\text{Na}_8\text{Ti}_5\text{O}_{14}$ was indicated to be the determinant stage. According to Belyaev (1976), $\text{Na}_8\text{Ti}_5\text{O}_{14}$ possesses a compact layer which is resistant to Na^+ and O^{2-} diffusion.

Glasser and Marr (1979) were unable to produce $\text{Na}_2\text{Ti}_2\text{O}_5$, $\text{Na}_2\text{Ti}_5\text{O}_{11}$ and $\text{Na}_2\text{Ti}_7\text{O}_{15}$ as reported earlier (*Gmelins Handbuch*, 1951). These authors claim to have crystallised $\text{Na}_6\text{Ti}_2\text{O}_7$ from melts containing 46–48% mol of TiO_2 as bright green crystals. Hill *et al.* (1985), however, identified these green crystals as $\gamma\text{-Na}_2\text{TiO}_3$ by electron microprobe analysis. $\text{Na}_2\text{Ti}_2\text{O}_5$ and Na_2TiO_3 were reported to have been produced from mixtures of TiO_2 powder and 4 N NaOH solutions for 10 h at 1 020 and 1 080 K respectively (Mitsuhashi and Fujiki, 1985).

Watanabe *et al.* (1979) reported the synthesis of $\text{Na}_2\text{Ti}_9\text{O}_{19}$ by hydrothermal means, using TiO_2 gel with NaOH aqueous solution, at 450–600 °C. Watanabe (1981) also reported hydrothermal synthesis of $\text{Na}_2\text{Ti}_9\text{O}_{19}$ at 250–530 °C. The product was identified by electron microprobe analysis and single-crystal XRD.

Werthmann and Hoppe (1984) claim to have synthesized a new titanate, $\text{Na}_4\text{Ti}_5\text{O}_{12}$, from mixtures of TiO_2 and Na_2O at 1 000 °C in an Au crucible after 6 days of fusion. Nalbandyan *et al.* (1998) determined the existence conditions of $\text{Na}_4\text{Ti}_5\text{O}_{14}$. They found it to decompose at 900–950 °C into $\text{Na}_2\text{Ti}_3\text{O}_{14}$ and $\text{Na}_8\text{Ti}_5\text{O}_{14}$. Nalbandyan (2000) later determined the unit cell

parameters of $\text{Na}_4\text{Ti}_5\text{O}_{14}$. He concluded that the XRD pattern previously attributed to disputed $\text{Na}_2\text{Ti}_2\text{O}_5$ belonged, in fact, to $\text{Na}_4\text{Ti}_5\text{O}_{14}$ (Bamberger and Begun, 1987; Bouaziz and Mayer, 1971; Glasser and Marr, 1979). Avdeev and Kholkin (2000) resolved the crystal structure of $\text{Na}_4\text{Ti}_5\text{O}_{12}$.

Bamberger and Begun (1987) admitted Na_4TiO_4 , α , β and γ Na_2TiO_3 , $\text{Na}_8\text{Ti}_5\text{O}_{14}$, $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$ as the only existing phases in the system $\text{Na}_2\text{O} - \text{TiO}_2$. They considered the existence of phases such as $\text{Na}_2\text{Ti}_2\text{O}_5$, $\text{Na}_4\text{Ti}_3\text{O}_8$ and $\text{Na}_6\text{Ti}_2\text{O}_7$ as an artefact. They failed to produce $\text{Na}_2\text{Ti}_2\text{O}_5$ as previously described by other researchers (Mitsuhashi and Fujiki, 1985). According to Bamberger and Begun (1987), the product previously denominated $\text{Na}_2\text{Ti}_2\text{O}_5$ was, in fact, a mixture of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_8\text{Ti}_5\text{O}_{14}$, identified by Raman spectroscopy. In their review, Bamberger and Begun (1987) point out some questionable cards on the powder diffraction file, namely the Na_2TiO_3 , $\text{Na}_4\text{Ti}_{0.3}\text{O}_{2.6}$ and $\text{Na}_2\text{Ti}_5\text{O}_{11}$. They considered the typing of $\text{Na}_4\text{Ti}_{0.3}\text{O}_{2.6}$ in that card as a typographical error since the original reference indicated $\text{Na}_4\text{Ti}_3\text{O}_8$ (considered by Bamberger and Begun not to exist).

Clearfield and Lehto (1988) reacted NaOH with anatase or titanium isopropoxide via hydrothermal reaction and reported $\text{Na}_4\text{Ti}_9\text{O}_{20} \cdot x\text{H}_2\text{O}$, based on the neutron activation analysis and XRD pattern of the product.

Yang *et al.* (2003) concluded that the nanotube synthesised hydrothermally from mixtures of TiO_2 and NaOH solutions was $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$, based on the XRD pattern from powder diffraction files (JCPDS)⁷. Tsai and Teng (2006) claim to have identified $\text{Na}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ after hydrothermally processing mixtures of TiO_2 and NaOH solutions, based on the XRD patterns. These researchers support their claim through the determination of the unit cell parameters.

⁷ Joint Committee on Powder Diffraction Standards

2.6.2 System $\text{Na}_2\text{O-TiO}_2\text{-Fe}_2\text{O}_3$

The phase diagram published by Li *et al.* (1971) and included in the reference book *Phase Diagrams for Ceramists* (Roth *et al.*, 1981) presents NaFeTiO_4 , $\text{NaFeTi}_3\text{O}_8$ and $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ ($0.90 \geq x \geq 0.75$) (Figure 7).

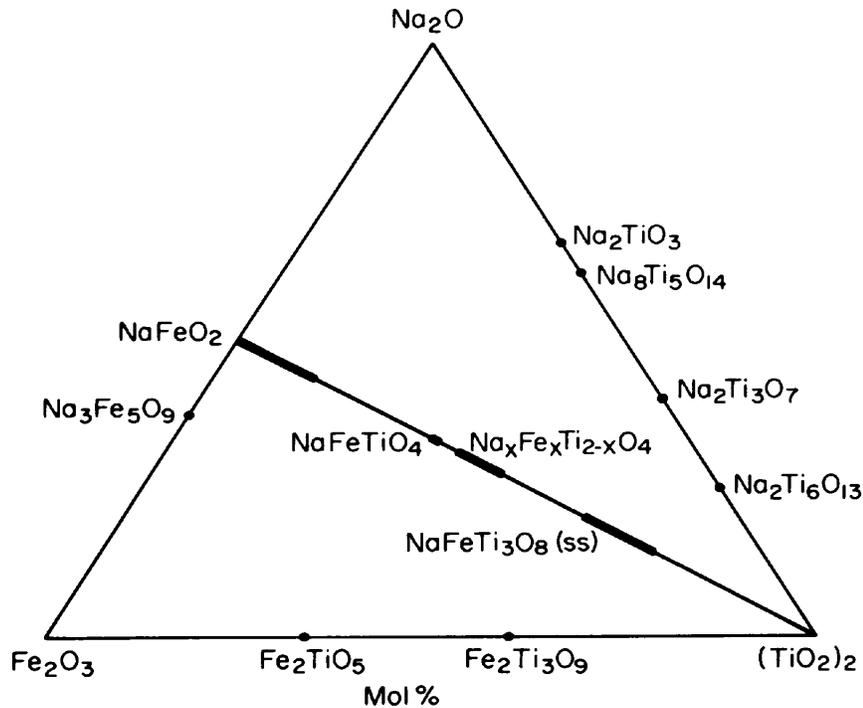


Figure 7: $\text{Na}_2\text{O} - \text{Fe}_2\text{O}_3 - \text{TiO}_2$ phase diagram (Li *et al.*, 1971)

Wadsley (1964) found crystallographic similarity between freudenbergite ($\text{Na}_2\text{Fe}_2\text{Ti}_7\text{O}_{18}$) and Na_xTiO_2 . Freudenbergite is a titaniferous mineral present in alkali syenite rock.

Bayer and Hoffmann (1965) reported six structures in the series $\text{Na}_x\text{Fe}_x\text{Ti}_{8-x}\text{O}_{16}$. Attempts to replace completely sodium ions with potassium led to the formation of a compound resembling priderite.

Mumme and Reid (1968) reported the preparation of $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ ($0.75 \leq x \leq 0.90$) by melting NaFeTiO_4 at 1 000 °C. They found $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ to be structurally related to NaFeTiO_4 . NaFeTiO_4 is an isotype of CaFe_2O_4 .

Foley and MacKinnon (1970) roasted ilmenite (FeTiO_3) with soda ash (Na_2CO_3) at 860 °C and observed $\text{Na}_x\text{Fe}_x\text{Ti}_{8-x}\text{O}_{16}$ ($1.20 \leq x \leq 2.00$), $\text{Na}_x\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$ ($0.67 \leq x \leq 1.00$) and $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ ($0.75 \leq x \leq 0.90$), based on the XRD patterns. $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ was only obtained at 1 040 °C. They found that the phases obtained were readily interconvertible. The excessive iron was found to be accommodated in $\alpha\text{-Fe}_2\text{O}_3$ and titanium in single titanates, mainly Na_2TiO_3 . Equilibrium products were found to be dependent only on the Na:Ti ratios.

Akimoto *et al.* (2004) reported the synthesis of a new member of the series $\text{Na}_{2+x}\text{Fe}_x\text{Ti}_{4-x}\text{O}_9$ ($x = 0.65$) from a mixture of Na_2CO_3 , Fe_2O_3 and TiO_2 at 1 000 °C. The structure was found to consist of large tunnels in the *b*-axis with three types of Na atom.

Biswas *et al.* (1996) roasted ilmenite with salt water vapour (NaCl , NaNO_3 and Na_2SO_4). They suggest that roasting with NaCl led to the formation of $\text{Na}_4\text{FeTiO}_5$, based on the optimum ratio of $\text{FeTiO}_3:\text{NaCl}$. This suggestion could not be confirmed by XRD. For NaNO_3 and Na_2SO_4 , NaFeTiO_4 was observed along with an unknown phase, suggested to be $\text{NaO}_{0.5}.\text{FeO}_{1.5}.\text{TiO}_2$ on the basis of XRD analysis. The optimum ratio suggested $\text{NaO}_{0.5}.\text{FeO}.\text{TiO}_2$. According to these authors, the latter is not stable thermodynamically, unlike the former.

Kuhn *et al.* (1996) studied the effect of extracting sodium on the formation of substructures on the composition $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ ($0.75 \leq x \leq 0.90$). They were able to produce crystals with sodium contents ranging from 0.58 to 0.87. For starting material with a sodium content of $x = 0.79$, the upper level of extraction was found to be 0.30. In studying the effect of sodium removal, they found that the *a* parameter increased correspondingly, while the *b* parameter increased only slightly. The volume of the cell did not, mostly, change partly because of irregular changes in the *c* parameter (Kuhn *et al.*, 1997).

El-Tawil *et al.* (1996) applied Na_2CO_3 in slag production. They carbon-reduced ilmenite in the presence of Na_2CO_3 at 1 000 to 1 200 °C for periods up to 180 min. $\text{Na}_{0.9}\text{Fe}_{0.9}\text{Ti}_{1.1}\text{O}_4$, $\text{NaFeTi}_3\text{O}_6$, $\text{Na}_2\text{Fe}_2\text{Ti}_3\text{O}_{10}$, as well as the single titanates Na_2TiO_3 , Na_4TiO_4 , $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_8\text{Ti}_5\text{O}_{14}$ were observed. The single titanates were found to be temperature dependent. At lower temperature (1 000 °C) $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_8\text{Ti}_5\text{O}_{14}$ were present, while Na_2TiO_3 , Na_4TiO_4 and $\text{Na}_8\text{Ti}_5\text{O}_{14}$ were observed between 1 100 and 1 200 °C. Sodium iron titanates were observed in all experiments. $\text{NaFeTi}_3\text{O}_6$ was present after extensive roasting periods, equal to or above 2 h (El-Tawil *et al.*, 1996).

2.6.3 Comments on the phase diagrams

The available phase diagrams on the Na_2O - TiO_2 system, from Bouaziz and Mayer (1971) and Gicquel *et al.* (1972), indicate the existence of Na_2TiO_3 (α and β), $\text{Na}_8\text{Ti}_5\text{O}_{18}$, $\text{Na}_2\text{Ti}_3\text{O}_7$, $\text{Na}_2\text{Ti}_6\text{O}_{13}$ and Na_4TiO_4 . In addition, $\text{Na}_2\text{Ti}_2\text{O}_5$ and $\text{Na}_6\text{Ti}_2\text{O}_7$ are mentioned.

Later literature reported the following phases: $\text{Na}_2\text{Ti}_4\text{O}_9$ (Akimoto and Takei, 1989b; Belyaev *et al.*, 1970; Dion *et al.*, 1978; Watanabe, 1981), $\text{Na}_2\text{Ti}_7\text{O}_{15}$ (Wadsley and Mumme, 1968), $\text{Na}_4\text{Ti}_3\text{O}_8$ (Belyaev *et al.*, 1970), $\text{Na}_2\text{Ti}_9\text{O}_{19}$ (Watanabe *et al.*, 1979; Watanabe 1981), $\text{Na}_4\text{Ti}_5\text{O}_{12}$ (Werthmann and Hoppe, 1984), γ - Na_2TiO_3 (Hill *et al.*, 1985) and $\text{Na}_4\text{Ti}_9\text{O}_{20}$ (Clearfield and Lehto, 1988). $\text{Na}_2\text{Ti}_8\text{O}_{17}$ was predicted (Wadsley and Mumme, 1968).

There seems to be consensus regarding the existence of members $n = 1, 3, 4, 6, 7$ and 9 in the $\text{Na}_2\text{Ti}_n\text{O}_{2n+1}$ family, while $n = 8$ has been predicted. With regard to the missing members ($n = 2$ and 5), although they are reported in literature, their existence is still surrounded by a certain amount of controversy (Bamberger and Begun, 1987; Glasser and Marr 1979; Hill *et al.*, 1985; Nalbandyan, 2000).

Batygin (1967) reported $\text{Na}_2\text{Ti}_2\text{O}_5$ to be stable below 800 °C and to transform to $\text{Na}_4\text{Ti}_5\text{O}_{14}$ above that temperature. He indicated the instability of $\text{Na}_2\text{Ti}_2\text{O}_5$ as the difficulty faced by other researchers in attempting to produce $\text{Na}_2\text{Ti}_2\text{O}_5$. Belyaev *et al.* (1970) found $\text{Na}_4\text{Ti}_5\text{O}_{14}$ to be one of the intermediates in Na_2TiO_3 formation (850–950 °C). Later Glasser and Marr (1979) and Bamberger and Begun (1987) were unable to produce $\text{Na}_2\text{Ti}_2\text{O}_5$, suggesting the improbability of its existence. This was supported by Nalbandyan (2000) who indexed to $\text{Na}_4\text{Ti}_5\text{O}_{12}$ the XRD pattern previously attributed to $\text{Na}_2\text{Ti}_2\text{O}_5$, and by Avdeev and Kholkin (2000) who resolved the crystal structure of $\text{Na}_4\text{Ti}_5\text{O}_{12}$.

Recent publications, however, brought back the discussion around the existence of $\text{Na}_2\text{Ti}_2\text{O}_5$ and the reliability of its XRD pattern (Mitsubishi and Fujiki, 1985; Nian and Teng, 2006; Tsai and Teng, 2006; Yang *et al.*, 2003; Zhang *et al.*, 2005). These researchers claim to have identified $\text{Na}_2\text{Ti}_2\text{O}_5$ in the form of either $\text{Na}_2\text{Ti}_2\text{O}_5 \cdot \text{H}_2\text{O}$ or $\text{Na}_2\text{Ti}_2\text{O}_4(\text{OH})_2$. This last structure was previously rejected by Nalbandyan (2000) as the $\text{Na}_2\text{Ti}_2\text{O}_5$ structure, since the compound was obtained either with NaOH or with Na_2CO_3 .

Other disputed phases are $\text{Na}_2\text{Ti}_5\text{O}_{11}$, $\text{Na}_4\text{Ti}_3\text{O}_8$ and $\text{Na}_6\text{Ti}_2\text{O}_7$ (Bamberger and Begun, 1987; Batygin, 1967; Belaev *et al.*, 1970; Belyaev, 1976; Glasser and Marr, 1979; Hill *et al.*, 1985).

For Batygin (1967) the XRD pattern previously attributed to $\text{Na}_2\text{Ti}_5\text{O}_{11}$ was, in fact, that of a mixture of $\text{Na}_2\text{Ti}_5\text{O}_{11}$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$. Glasser and Marr (1979) attributed this pattern to a mixture of $\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{Na}_2\text{Ti}_6\text{O}_{13}$. Nishizawa and Aoki (1985) claim to have observed traces of $\text{Na}_2\text{Ti}_5\text{O}_{11}$ while reacting TiO_2 gel with aqueous NaOH, based on the XRD patterns. For Bamberger and Begun (1987), however, only $\text{Na}_2\text{Ti}_6\text{O}_{13}$ was present, thus indicating that the pattern in question belonged to this phase ($\text{Na}_2\text{Ti}_6\text{O}_{13}$). Despite this controversy, Kokubo and Namakura (2000) reported that, while studying the formation mechanism of apatite on the surface of titanium metal, they observed $\text{Na}_2\text{Ti}_5\text{O}_{11}$. Hedouin and Seguelong (2001) reported $\text{Na}_2\text{Ti}_5\text{O}_{11}$ as one of the phases existing in the pigment they produced. Torres-Martínez *et al.* (2006) in studying the system $\text{Na}_2\text{O}-\text{Li}_2\text{O}-\text{TiO}_2$ after fusing the starting material at 950 °C for 24

h, using different proportions, claim to have observed $\text{Na}_2\text{Ti}_5\text{O}_{11}$ formation, based on the XRD patterns.

Belyaev *et al.* (1970) found the intermediate previously reported as β -titanate to be $\text{Na}_4\text{Ti}_3\text{O}_8$. According to these researchers, it decomposes into Na_2TiO_3 and $\text{Na}_8\text{Ti}_5\text{O}_{14}$. Belyaev (1976) found $\text{Na}_4\text{Ti}_3\text{O}_8$ to be an intermediate in the formation of Na_2TiO_3 . Bamberger and Begun (1987), although they expressed some doubt about the existence of $\text{Na}_4\text{Ti}_3\text{O}_8$, did not report any attempt at producing this phase. Lizuka *et al.* (2005), however, indicate $\text{Na}_4\text{Ti}_3\text{O}_8$ as one of the phases in the exhaust cleaner of their invention.

A search with regard to the $\text{Na}_6\text{Ti}_2\text{O}_7$ phase initially reported by Glasser and Marr (1979) was not fruitful, suggesting that the correction made by Hill *et al.* (1985) is acceptable.

Apart from the previously mentioned there are bronze-type oxides, such as Na_xTiO_2 and $\text{Na}_x\text{Ti}_4\text{O}_8$, (Anderson and Wadsley, 1962; Bayer and Hoffmann, 1965; Wadsley, 1964) and mixed valence oxides, such as NaTi_2O_4 and $\text{NaTi}_8\text{O}_{13}$ (Akimoto and Takei, 1989a; Akimoto and Takei, 1991).

The phase diagram of this system $\text{Na}_2\text{O-TiO}_2\text{-Fe}_2\text{O}_3$ by Li *et al.* (1971) and published elsewhere (Roth *et al.*, 1981) includes NaFeTiO_4 , $\text{NaFeTi}_3\text{O}_8$ and $\text{Na}_x\text{Fe}_x\text{Ti}_{2-x}\text{O}_4$ ($0.90 \geq x \geq 0.75$). Other literature, however, points out the existence of additional phases such as $\text{Na}_2\text{Fe}_2\text{Ti}_3\text{O}_{10}$, $\text{Na}_2\text{Fe}_2\text{Ti}_7\text{O}_{18}$, $\text{Na}_x\text{Fe}_x\text{Ti}_{8-x}\text{O}_{16}$, $\text{Na}_{2+x}\text{Fe}_x\text{Ti}_{4-x}\text{O}_9$ and $\text{Na}_x\text{Fe}_x\text{Ti}_{1-x}\text{O}_2$ (Akimoto *et al.*, 2004; Bayer and Hoffmann, 1965; Foley and Mackinnon, 1970; Wadsley, 1964).

2.7 The Proposed Process

The proposed process is a combination of the De Wet process of zirconia recovery from zircon sands (de Wet, 1999) and the Richter process of making titanium dioxide (Richter and Elizabeth, 1933). The overall process is summarised in Figure 8.

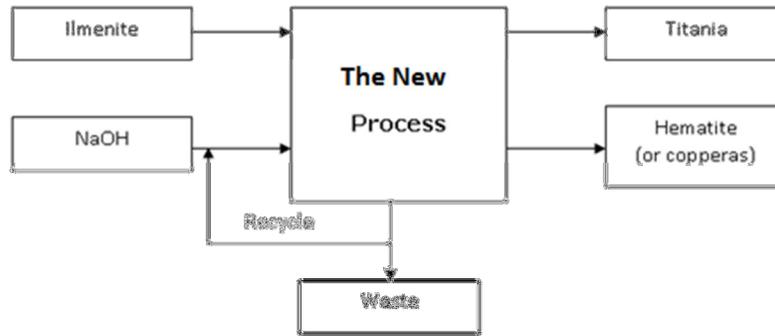


Figure 8: Block diagram of the proposed process of titania recovery using ilmenite ore

In essence, the ore is roasted with an alkali compound, preferably sodium hydroxide or sodium carbonate. The aim is to produce highly soluble species and simultaneously produce radionuclide-immobilising compounds. Zirconolite, $\text{CaZrTi}_2\text{O}_7$, has the ability to be used as radionuclide immobiliser owing to its ability to exist in a wide range of substitutions (de Hoog and van Bergen, 1997). Zirconolite is a potential product of the alkali roasting reaction (Jha *et al.*, 2005). The procedure also provides a method of removing silicon efficiently.

2.7.1 The Richter Process

Richter and Elizabeth (1933) found that when fine ilmenite or rutile is mixed with sodium hydroxide, in the proportion of 2:1 ($\text{NaOH}:\text{TiO}_2$) mole ratio, reacts with formation of sodium titanate. The reaction takes place on the temperature range of 280° to 650 °C. Sodium hydroxide can be replaced by potassium hydroxide but, according to authors, the results are

pure. The addition of carbonated alkali, that is, soda ash was viewed as beneficial (Richter and Elizabeth, 1933). Apparently soda ash acts as fondant in the reaction.

In one particular experiment they mixed equal masses of rutile and sodium hydroxide solution (75%). The mixture was heated, up to 300 °C, in kneading equipment and an equivalent of a quarter of the mass of sodium hydroxide in soda ash was added to the vessel. The mass was transferred to a rotary kiln at 600-650 °C, for 30 minutes. The obtained powder was leached with water allowing to the recovery of much of the soda used in the reaction, 80 to 90%. The residue was then leached with dilute sulphuric acid. Much of the iron contained in the ore and other impurities are said to dissolve in this stage of the process. The crude titania can be purified further by acid washing or by dissolving in sulphuric acid 50% and subsequently hydrolysing thermally. In order to enhance the product purity, Fe(III) must be reduced to Fe(II) (Richter and Elizabeth, 1963).

2.7.2 The de Wet Process

The de Wet process was developed by de Wet (1999) to extract zirconia from zircon sands. The process consists in fusing zircon with sodium hydroxide or soda ash. The intension is to break $ZrO_2 \cdot SiO_2$ bonds. They are thermally and chemically and require aggressive reaction conditions (Farnworth *et al.*, 1980; Nielsen and Chang, 1996; Zeis and Giesekke, 1997). The net reaction in the de Wet process is as following



operating at temperatures above 700 °C (Manhique *et al.*, 2003). The X value has importance on the economy of the process. Higher yields of Na_2ZrSiO_5 in the reaction prevent extensive

recoveries of the alkali used in the reaction. It does not hydrolyze in water. It has to be acid treated in order to release its zirconium content.

The fusion cake obtained at optimum conditions, 2:1 (NaOH:ZrSiO₄) mole ratio for 2 h at 850 °C, is leached with water to dissolve soluble silicates and to hydrolyze sodium zirconates owing to the recovery of alkali. Alkali solution obtained after leaching was then treated with ammonium to precipitate silica. The zirconium containing residue was treated with dilute mineral acid (HCl preferably) to hydrolyze sodium zirconium silicates. The residue from the HCl treatment consists essentially of hydrous zirconia and unreacted zircon. This later residue is dissolved in concentrated H₂SO₄ to produce acid zirconium sulfate tetrahydrate (AZST). The AZST is separated from the residue of unreacted zircon by dissolving it in water and recrystallizing. Zirconia or any other zirconium chemical can be produced from the AZST obtained in this process (Manhique *et al.*, 2003).

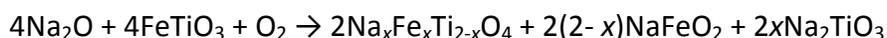
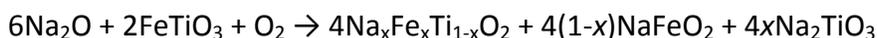
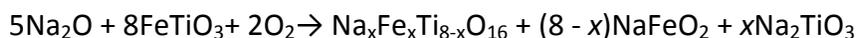
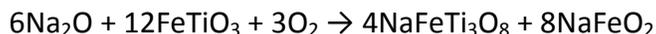
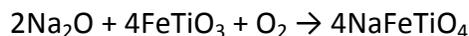
2.7.3 Description of the New Process

The process proposed in this work is aimed to extract titania from titaniferrous minerals. The process relies on the alkali fusion reaction followed by sulfation of the obtained cake. We describe each step and the idea behind it.

A. Fusion

Ilmenite or other titaniferrous mineral is intimately mixed with a sodium containing chemical, preferably NaOH. The aim of the fusion reaction is to produce sodium iron titanates, since they comprise the least sodium hydroxide consuming phases in their formation. The reaction can also produce sodium titanates and sodium ferrates. According to the literature the main sodium iron titanates are NaFeTiO₄, NaFeTi₃O₈, Na_xFe_xTi_{8-x}O₁₆, Na_xFe_xTi_{1-x}O₂ and Na_xFe_xTi_{2-x}O₄ (Foley and MacKinnon, 1970; Mumme and Reid, 1968). Economically the phases containing less

sodium per unit titanium are ideal. The hypothetical reactions for the indicated ternary phases are



The stoichiometry of the first two reactions is 1:1 mole ratio. The following are 5:4, 6:1 and 2:1 (NaOH:FeTiO₃) mole ratio. First reaction does not allow a good alkali recovery. Thus reaction conditions have to be such that NaFeTiO₄ be at minimum levels or, if possible, its formation avoided. However reaction products are a mix of the described phases as was observed by Foley and MacKinnon (1970) and by Biswas *et al* (1996), including sodium titanates and sodium ferrates. The challenge then is to determine optimum conditions for the reaction, i.e., conditions where the desired phases are predominant in the product spectrum.

B. Water leaching

The water leaching process is aimed to hydrolyse the titanates and ferrates in order to recover the NaOH used in the fusion reaction. The less stable sodium iron titanates will also hydrolyse (Biswas *et al.*, 1996). Bronze like titanates are not amenable to water leach. Several impurities also leached out in this stage of the process. Leachate is essentially composed by sodium hydroxide as well as soluble impurities. Temperature, time and slurry density are the important parameters for this step.

C. Acid Leach

This step is intended to leach the least soluble impurities. Most of the impurities are converted into oxides in the fusion step. These oxides are of basic nature therefore soluble in acids producing soluble chlorides (Biswas *et al.*, 1996). Some of the sodium iron titanates are hydrolysed in this stage. The most important parameter in this step is the acid concentration. The acid solution has to be concentrated enough to dissolve impurities. High concentration acid can lead to titanium loss. The idea here is to selectively dissolve impurities and hydrolyse titanium bearing phases in the residue. The hydrolysis reduces the amount of acid to be consumed in the sulfation step. This treatment is effective to remove impurities such as Cr, V, Ca, Zr, Nb, Ce, Nd, U and Th, as was reported by Jha *et al.* (2009) and Jha and Tathavadkar (2010).

D. Sulfation

The residue from the previous step is mainly composed by hydrous titania. Some of the impurities are also present in the residue. The idea here is to dissolve titania containing phases in the residue. Insoluble impurities remain in the residue and can be removed by filtration.

2.7.4 Benchmarks of the Proposed Process

This process reduces the environmental pressure exerted by the traditional sulfate process.

Compared with the traditional sulfate process, it offers:

- (i) reduced operation time
- (ii) low sulphuric acid consumption
- (iii) ability to treat a wide variety of ores
- (iv) reduction of environmental harm
- (v) recyclability of a considerable proportion of the reactants

(vi) no acid disposal

George and Mohan Das (1985) have suggested that rutile production through fusion is hindered by the need for high quantities of alkali, high energy inputs and lower recoveries. We dispute these findings since in our experiments considerably high recoveries were achieved using substoichiometric correlations at comparatively mild operating temperatures.

2.8 References

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