Mechanical activation and physicochemical factors controlling pyrometallurgical, hydrometallurgical, and electrometallurgical processing of titanium ore: A review

by H.C.S. Subasinghe[1] and A.S. Ratnayake[1]

Affiliation:

1Department of Applied Earth Sciences, Faculty of Applied Sciences, University, Passara Road, Badulla, Sri Lanka.

Correspondence to:
A.S. Ratnayake

Email:
as_ratnayake@uwu.ac.lk

Synopsis

In this study, we review the role of mechanical activation in the pyrometallurgical, hydrometallurgical, and electrometallurgical processing of titanium feedstock. Mechanical activation has been shown to decrease the activation energy of chemical reactions, thus enhancing process efficiency and product quality by reducing processing time and energy consumption. Pyrometallurgical processing is energy-intensive and time-consuming. Hydrometallurgy is costly, requires high-grade feed material, and generates toxic waste. Waste generation and process complexity are the major drawbacks of electrometallurgy and solvent extraction. Bioleaching *via* a mechanically activated pyrometallurgical process can be identified as an alternative method, but the lengthy processing time is the major disadvantage. Mechanically activated titanium concentrate can be used in a finely tuned combined metallurgical process to overcome the challenges and drawbacks in these technologies.

Keywords
ilmenite, synthetic rutile, titanium metal, pyrometallurgy, hydrometallurgy, electrometallurgy, mechanical activation.

Introduction

Titanium is the ninth most abundant element in the Earth's crust (Das *et al.*, 2013), and is known to be the metal of the 21st century. Titanium-rich heavy minerals such as ilmenite (40–80% TiO_2), leucoxene (>65% TiO_2), and rutile (approx. 95% TiO_2) are the major titanium minerals used to produce refined TiO_2 and titanium metal (Haverkamp, Kruger, and Rajashekar, 2016; Kothari, 1974; Shi *et al.*, 2022; Zhu, Zhang, and Cheng, 2011; Subasinghe *et al.*, 2022). About 95% of the annual global production of rutile (both natural and synthetic) is utilized to produce high-quality white TiO_2 pigments, while the rest is mainly used in the production of titanium metal (Gázquez *et al.*, 2014). Titanium dioxide is characterized by properties such as high transparency to visible light, iridescence, and high UV absorption. TiO_2 therefore has diverse applications such as in pharmaceuticals, advanced ceramics, paints, porcelains, and rubber (Elsner, 2010; Subasinghe and Ratnayake, 2021; Subasinghe and Ratnayake, 2022). The photocatalytic activity of TiO_2 has been used in advanced applications such as photovoltaic cells, gas sensors, purification filters, and electro-ceramics (Bai *et al.*, 2014; Wang and Lin, 2010). Titanium metal finds applications in the aerospace industries, and biomedical engineering such as prosthesis (Elsner, 2010; Subasinghe and Ratnayake, 2021). Titanium minerals cannot be directly used in any of these applications. Consequently, it is essential to upgrade/process titanium ores into refined TiO_2 and/or titanium metal.

Ilmenite smelting was first reported in the late 19th century in New Jersey, USA, and the production of titanium alloys was initiated in 1906 (Morley, 1981). Titanium white pigments were first produced a couple of years later, replacing the toxic Pb and Zn white paint pigments (Brooks, 2000). Since then, several routes have been developed for the conversion of low-grade titanium ores into synthetic rutile *via* chemical, physical, physicochemical, and thermochemical techniques (Nguyen and Lee, 2018; Zhang, Zhu, and Cheng, 2011). Processing high-grade feedstock (natural rutile) generates less waste compared to low-grade feedstock such as ilmenite and leucoxene (Subasinghe *et al.*, 2022) and is the preferred feedstock in the titanium mineral processing industry. However, ilmenite and leucoxene became prominent feed materials
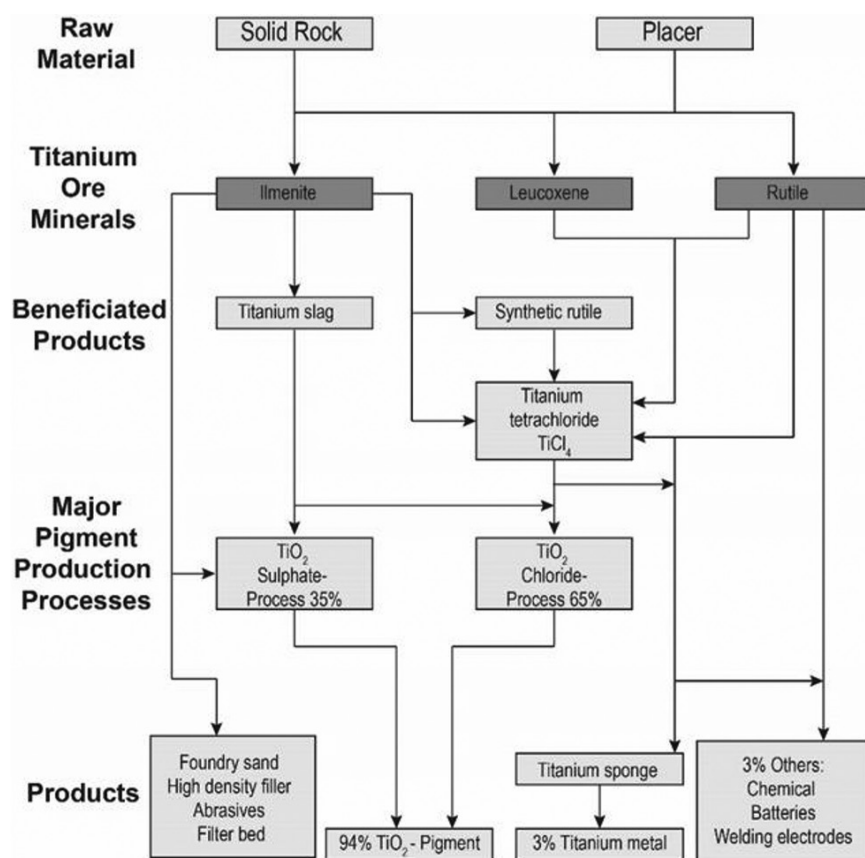
Mechanical activation and physicochemical factors

Figure 1—Schematic flow sheets of the chloride and sulphate processes through to the manufacture of end products (after Elsner, 2010)

to cater to the surging demand for titanium and its compounds due to the scarcity of natural rutile (Subasinghe and Ratnayake, 2021; Wang and Yuan, 2006).

Commercial production of TiO₂ and titanium metal follows distinct routes (Figure 1). Nevertheless, all routes require titanium ores to be upgraded, -usually consuming large amounts of energy and utilizing concentrated acids (Gázquez *et al.*, 2014; Takeda, Ouchi, and Okabe, 2020).

This study is intended to fill the gap in the recent literature between titanium metallurgical processes and the role of mechanical activation in each method. We outline the controlling factors in hydrometallurgical, pyrometallurgical, and electrometallurgical processes to upgrade/refine titanium ores and discuss the significance of mechanical activation for each of the processing techniques (Table I).

Role of mechanical activation

Initial mechanical activation, with or without the addition of reductants, can be advantageous for upgrading titanium ores to synthetic rutile and titanium metal. This step influences the efficiency, product quality, waste generation, and cost of subsequent unit operations. Milling increases the reaction rates by (Amade et al., 2009; Baba *et al.*, 2013; Begin-Colin *et al.*, 1994; Ren, Yang, and Shaw, 2000; Sasikumar *et al.*, 2007; Subasinghe and Ratnayake, 2021; Tao et al., 2012; Tromans and Meech, 2001; Wei *et al.*, 2009; Welham and Llewellyn, 1988):

➤ Increasing the specific surface area
➤ Breaking down crystalline structure (*i.e.*, grain boundary disordering, polymorphic transformations, and creation of

defects such as Schottky, Frenkel, or Wadsley defects along crystallographic shear planes)
➤ Promoting chemical reactions (*i.e.*, mechanochemical reactions with order-disorder reactions and phase transformations, especially in oxides)
➤ Promoting surface amorphization.

The X-ray diffraction patterns of activated and unactivated ilmenite are similar, with no new phases forming during mechanical activation (Li *et al.*, 2008; Li, Liang, and Wang, 2008b; Sasikumar *et al.*, 2004, 2007; Shojaei *et al.*, 2014; Tan, Hu, and Zhang, 2011; Wang *et al.*, 2010; Wei *et al.*, 2009; Wu *et al.*, 2011a; Zhang *et al.*, 2010). However, ilmenite milled with sulphur as a reducing agent shows weak reflections from new phases formed during attrition (Chen *et al.*, 1996; Subasinghe and Ratnayake, 2021). Ball milling can induce alteration of the lattice structure (*i.e.*, rearrangement of grains and increments of strain). In this case, ilmenite peaks in the diffractogram become broadened with diminished intensities (Shojaei *et al.*, 2014).

Milling conditions

Grinding is the main method for the mechanical activation of titanium ore. Milling parameters are thus significant for effective and efficient grinding with the minimum possible energy consumption. For example, a lower ball-to-powder ratio results in less efficient grinding and longer grinding times (Begin-Colin *et al.*, 2000). Planetary, attritor, and vibration mills are different types of ball mills based on the movement of balls and vials (Zhang, Zhu, and Wang, 2008). Impact, chipping, and abrasion are key mechanisms for the deformation of particles in these milling

Mechanical activation and physicochemical factors

Table I

Common titanium ore processing techniques, their features, advantages, and drawbacks (Nurul, 2016; Zhang, Zhu, and Cheng, 2011)

Process	Pyro-treatment	Leaching	Advantages	Disadvantages	References
Pre-treated using a pyro-technique					
Becher sulphate process	Iron oxidized to Fe_2O_3 and reduced to metallic Fe at 1200°C	(a) NH_4Cl/O_2 (b) 0.5 M H_2SO_4	Can handle diverse titanium ore feeds	Multi-step iron conversions and leaching high energy consumption Emission of CO_2	Zhang *et al.*, (2011)
Murso process	Similar to Becher process, but fluidized beds used for conversion	20% HC	Improved efficiency using fluidized beds Easier HCl recycle than sulphate system	Similar to Becher process	Zhang *et al.*, (2011); Nurul (2016)
Laporte process	Lower temperatures for iron conversion to FeO with controlled CO_2 pressure	18% HCl with a bed contactor	Does not form fine TiO_2 particles Ease of leaching FeO	Similar to Becher process in spite of lower temperature used	Zhang *et al.*, (2011)
Benelite process	Iron conversion to Fe(II) carbon Thermic-reduction	18–20% HCl	Simple one-step conversion of iron	Limited titanium ore types as the feed	Zhang *et al.*, (2011); Nurul (2016)
Austpac process	Magnetization of for higher 800–1000°C	25% (w/w) HCl needed for leaching	Magnetic separation >97% TiO_2	Higher acidity remaining magnetic iron	ilmenite at
Dunn process	Selective chlorination of iron in ilmenite with Cl_2	N/A	Cl_2 recycle by oxidation of $FeCl_2$ to Fe_2O_3	Handling highly corrosive Cl_2	
The Kataoka process (in Japan)	Iron conversion to ferrous form	H_2SO_4	H_2SO_4 less corrosive than HCl Low leaching temperature	Large amounts of iron sulphate wastes	
Direct leaching					
Altair process	N/A	(a) HCl digestion (Fe, Ti) (b) Reduction of iron to ferrous state by iron power (c) Solvent extraction (SX) of Ti (d) SX of impurities	Recycling of all chlorides;. Small loss in iron oxide and in digestion residue	Multi step metal leaching, conversion, and separation	Verhulst *et al.*, (2003)
BHP Billiton improved sulphate process	N/A	(a) Concentrated H_2SO_4 (Fe, Ti) (b) Ferrous sulphate crystallization| (c) SX of Ti	99% TiO_2 Reduced waste; Produces clean gypsum; better selectivity by SX (higher product purity)	Increased process complexity Recycle of large volume of diluted acid solution	Roche, *et al.*, (2004); Zhang *et al.*, (2011)

techniques (Kurlov and Gusev, 2007; Wu *et al.*, 2018; Zhang, Zhu, and Wang, 2008, 2013). The median particle size (d_{50}) and the specific surface area are generally used to assess the effectiveness of ball milling. The main milling parameters are rotation speed (r/min), size of balls, ball material (wear resistance and hardness), ball-to-powder mass ratio, milling time, medium of milling, filling ratio, milling container, additives/reducing agents, and milling atmosphere (*e.g.*, vacuum, airtight, ambient air, or inert gas) (Table II). The selection of the milling parameters varies substantially based on feed materials (Zhang, Zhu, and Wang, 2008). However, trace contamination can occur from the balls and vials (Dworkin *et al.*, 2018; Zhang *et al.*, 2013).

Although the conditions listed in Table II have been used in successful bench-scale experiments, they are rarely reported to have been incorporated on an industrial scale, due to the lack of scale-up optimized process parameters for both hard-rock and placer ilmenite.

Milling time and particle size

Increased milling time decreases the particle size and increases the effective surface area. However, the rate of particle size reduction gradually decreases with time. The formation of composites can be initiated by using additives/reducing agents, during milling. Subasinghe and Ratnayake (2021) demonstrated the effect of milling time and particle size on the reduction of ilmenite. Nanoparticles were produced by ball milling a mixture of ilmenite, sulphur, and vein graphite in the weight ratio of 4:0.5:0.5 for 6 hours at room temperature.

Several studies have focused on the mechanical activation of titanium ores followed by acid leaching (Nguyen and Lee, 2018; Zhang, Zhu, and Cheng, 2011). In this regard, prolonged milling to decrease the crystallite size improved the leaching efficiency of ilmenite (Shojaei *et al.*, 2014; Wei *et al.*, 2009). The improvement of leaching efficiency can occur due to the hindrance of lattice structure by mechanical activation (Li *et al.*, 2008; Li,

Mechanical activation and physicochemical factors

Table II

Summary of detailed milling conditions

Rotation speed (r/min)	Ball size (φ, mm)	Ball material	Mill material	Ball-to-powder ratio (BPR)	Milling time	Milling atmosphere	References
	Approx. 15 mm	Hardened steel (Fe-Cr)	Stainless steel	40.0:1.0	3 min–3 h	Argon	Begin-Colin *et al.* (1994)
	25.4	Hardened steel	Stainless steel		100–200 h	Room temperature	Chen *et al.* (1996)
	25.4	Hardened steel	Stainless steel		100–200 h	Room temperature static vacuum or air	Chen (1997)
	25.4	Stainless steel	Stainless steel	24.0:1.0	15 min–200 h	Room temperature vacuum	Welham and Llewellyn (1988)
1420	15	Steel (Fe-13% Cr) or alumina	Steel (Fe-13% Cr) or alumina	40.0:1.0, 30.0:1.0, 20.0:1.0, 10.0:1.0	5 min–1.5 h	Air	Begin-Colin *et al.*, (2000)
600	4.76	Tungsten carbide (WC)		60.0:1.0	1.5–48 h	Argon	Ren *et al.*, (2000)
200	20	Agate	Agate	4.0:1.0	30 min–4 h	Ambient	Sasikumar *et al.*, 2004; (2007)
200	10 and 5	Hardened steel	Stainless steel	20.0:1.0		Air	Li *et al.*, (2008)
200	10 5	Hardened steel		40.0:1.0	4 h	Vacuum	Li, *et al.*, (2008)
	8	Alumina	Alumina	2.0:1.0	30 min–4 h	Room temperature in air	Amade *et al.*, (2009)
300	20, 10, and 6	Agate	Polytetrafluoroe-thylene (PTFE)	10.0:1.0	2–8 h		Wei *et al.*, (2009)
200	20, 10, and 5	Steel balls	Stainless steel	20.0:1.0	2 h	Air	Wang *et al.*, (2010)
300	20, 10, and 6	Agate	Polytetrafluoroe-thylene (PTFE)	10.0:1.0	2–8 h	Room temperature in air	Zhang *et al.*, (2010)
300	20 and 10	Agate		10.0:1.0	2 h	Room temperature vacuum	Tan *et al.*, (2011)
200	20, 10, and 5	Steel	Stainless steel	20.0:1.0	2 h	Air	Wu *et al.*, (2011a)
165	25.4	Hardened steel	Stainless steel		50 h	Room temperature argon	Tao *et al.*, (2012)
250, 350 450	6 and 10	Stainless steel		20.0:1.0	1–6 h	Argon	Chen *et al.*, (2015)
180	20	Silicon nitride	Agate	10.0:1.0	30 h		Shahien *et al.*, (2015)
500	10 and 5	Zirconium	Zirconium ceramic	10.0:1.0 ceramic	1–6 h	Room temperature in airtight conditions	Wijewardhana *et al.*, (2021), Subasinghe *et al.*, (2021)

Liang, and Wang, 2008; Zhang *et al.*, 2010). Li, Liang, and Wang (2008) demonstrated that high-energy ball milling increases iron dissolution and the subsequent hydrolysis of titanium by HCl. However, the filterability of reactive slurries is a major drawback with fine-grained particles. Milling time can be adjusted to obtain suitable particle sizes for solid-liquid separation (Li, Liang, and Wang, 2008).

Pyrometallurgy in titanium ore processing

Solid-state reactions such as oxidation and reduction occur at elevated temperatures (Bordbar, Yousefi, and Abedini, 2017; Nguyen and Lee, 2018; Zhang, Zhu, and Cheng, 2011). However, thermal treatments do not yield only pure products (Kothari, 1974). In this case, a mixture of TiO_2 and elemental iron (usually referred to as slag in titanium ore processing) is obtained. These pyrometallurgical processing routes employ combinations of thermal oxidation and reduction by roasting, leaching, and physical separation (Zhang, Zhu, and Cheng, 2011). During these processes, iron is converted

to the soluble ferrous or elemental form by thermal reduction in a pre-treatment step (Nguyen and Lee, 2018; Zhang, Zhu, and Cheng, 2011), and the ore is subsequently acid-leached to obtain synthetic rutile (TiO_2) (*e.g.*, Kataoka and Yamada, 1973).
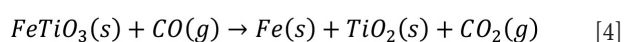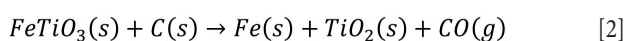
Common reducing agents

Several authors have highlighted the benefits of reducing agents during the high-energy ball milling of titanium ores (Chen et al., 1996, 2013a); Chen, Tang, and Xiao, 2015; Shahien *et al.*, 2015; Wijewardhana, Subasinghe, and Ratnayake, 2021). For example, ilmenite undergoes sulphurization reduction (Equation [1]) with the formation of pyrite (FeS_2) during prolonged milling in the presence of sulphur at room temperature (Chen *et al.*, 1996; Subasinghe and Ratnayake, 2021). Chen *et al.* (1996) also claimed that milling ilmenite with sulphur for 200 hours successfully produces TiO_2 at room temperature. Recently, Subasinghe and Ratnayake (2021) reduced the milling time to 6 hours by optimizing the ilmenite to sulphur ratio. Chen *et al.* (1996) obtained pure TiO_2

Mechanical activation and physicochemical factors

powder by sulphurization reduction followed by selective leaching using HCl. Shahien *et al.* (2015) isolated the Fe and Ti phases as elemental Fe and TiO_2 using carbothermic reduction, and leached the product to remove iron and produce pure TiO_2. Wijewardhana, Subasinghe, and Ratnayake (2021) and Subasinghe and Ratnayake (2021) optimized parameters such as grinding, and carbothermic and sulphurization reduction conditions.

$$2FeTiO_3(s) + 4S(s) \rightarrow 2FeS_2(s) + 2TiO_2(s) + O_2(g) \quad [1]$$
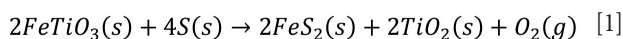
Various carbon sources (flake graphite, crystalline vein graphite, coal, anthracite, carbon black powder, activated carbon, and carbonized waste coconut shells) have been successfully used in the carbothermic reduction of ilmenite (Amer, 2002; Chen *et al.*, 2013, 2015; Shahien *et al.*, 2015; Subasinghe and Ratnayake, 2021; Tao *et al.*, 2012; Tripathy, Srinivasan, and Mehrota, 2012 ; Wang *et al.*, 2008; Wijewardhana, Subasinghe, and Ratnayake, 2021). However, the initiation of carbothermic reduction during ball milling was not observed in these investigations. Subsequent thermal treatments have produced TiO_2 *via* carbothermic reduction of ilmenite (see Equations [2]–[4]) (Chen *et al.*, 1996, 2013a; Merk and Pickles, 1988; Run *et al.*, 2017; Shahien *et al.*, 2015; Thripathy *et al.*, 2012; Wang and Yuan, 2006; Welham, 1996; Zhao, 1990).

$$FeTiO_3(s) + C(s) \rightarrow Fe(s) + TiO_2(s) + CO(g) \qquad [2]$$

$$C(s) + CO_2(g) \rightarrow 2CO(g) \qquad [3]$$

$$FeTiO_3(s) + CO(g) \rightarrow Fe(s) + TiO_2(s) + CO_2(g) \qquad [4]$$

Interestingly, Subasinghe and Ratnayake (2021) obtained more promising results using commercially available sulphur and crystalline vein graphite (Figure 1).

Significance of reducing agents

The reducing agents (sulphur and carbon) improve results during pyrometallurgical processes. A sufficient mass (according to stoichiometric or weight ratios) should be added to complete the reduction (Chen *et al.*, 1996; Shahien *et al.*, 2015; Subasinghe and Ratnayake, 2021). Chen *et al.* (1996) used an ilmenite to sulphur ratio of 6:2.5 in the milling process to produce TiO_2 at room temperature. A mixture of graphite and titanium dioxide was used to observe polymorphic transformations and powder characteristics during high-energy ball milling (Ren, Yang, and Shaw, 2000). The authors observed the transformation of anatase to rutile and srilankite, and amorphization of TiO_2.

In addition to polymorphic transformation, TiO_2 and graphite particles, and crystallite refinement, agglomeration of fine particles, and mixing of TiO_2 and carbon on a nanometre scale were observed. Ilmenite and carbon were mixed at the stoichiometric ratio of 4:1 to provide sufficient carbon for completing ilmenite reduction (Shahien *et al.*, 2015; Tao *et al.*, 2012). Carbonized coconut shells mixed with ilmenite in the ratio of 1:4 have also served as a successful reducing agent (Wijewardhana, Subasinghe, and Ratnayake, 2021). Subasinghe and Ratnayake (2021) also used ilmenite with sulphur and vein graphite in three different weight ratios. A combination of ilmenite, sulphur, and vein graphite in the ratio of 4.0:0.5:0.5 produced the best results.

Oxidation and reduction during thermal treatment

In industrial practice, oxidation involves high-temperature thermal treatment in a rotary kiln in the presence of air or oxygen to convert iron in titanium ore to iron oxides (Tan, Hu, and Zhang, 2011). Oxidation enhances the reactivity of titanium minerals (Janssen and Putnis, 2011; Sarker, Rashid, and Kurny, 2006; Zhu, Zhang, and Li, 2014). The preferred oxidation products are haematite and rutile. However, the increase in crystallite size of haematite and rutile above 800°C decreases the interfacial surface area (Zhu, Zhang, and Li, 2014), which may decrease the efficiency of subsequent leaching. According to Vásquez and Molina (2012), oxidation of titanium ore at 800–1050°C increases the proportion of pseudobrookite. The oxidation rate increases gradually with temperature, and ilmenite can be completely oxidized above 800°C, as shown in Equation [5] (Zhu, Zhang, and Li, 2014).

$$4FeTiO_3(s) + O_2(g) \rightarrow 2Fe_2O_3 \cdot TiO_2(s) + 2TiO_2(s) \quad [5]$$
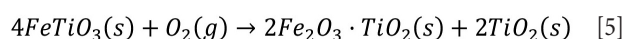
The reduction of titanium ore is relatively cheap to carry out, and is thus preferred in the industry. Titanium ore is heated in the presence of a reducing agent as described above. Numerous investigators have reported the successful reduction of titanium ore using either solid or gaseous reductants such as H_2 and CO, or mixtures of both (Bordbar, Yousefi, and Abedini, 2017; Kothari, 1974; Merk and Pickles, 1988). Several techniques have been commercialized to reduce titanium ore; for instance, smelting in electric furnaces to yield titania-enriched slag and pig iron (Bordbar, Yousefi, and Abedini, 2017), removal of Fe, Mg, Si, and Mn oxides using vacuum carbothermic reduction (Run *et al.*, 2017), and microwave heating (Wang *et al.*, 2014). Zhao (1990) described the carbothermic reduction of titanium ores using four steps: (i) diffusion of CO into porous grains, (ii) reaction of CO with ilmenite to produce TiO_2 and Fe, (iii) migration of Fe from the unreacted core towards the grain boundaries, and (iv) formation of Fe nuclei and their subsequent growth. Zhao (1990) used three stages (induction, acceleration, and deceleration) to demonstrate the mechanism of conversion of ilmenite to Fe and TiO_2. The coalescence of Fe particles retards the rate of reduction (Zhao, 1990). Moreover, the annealing environment (vacuum, air, or inert gas) is also important for the reduction reactions (Merks and Pickles, 1988). However, the major disadvantage of oxidation and reduction pretreatments is the intense energy consumption (Vásquez and Molina, 2008).

Temperature and time

Temperature and time of thermal treatment (*e.g.*, annealing, sintering, smelting, roasting) are important parameters in pyrometallurgical processes (Merks and Pickles, 1988; Run *et al.*, 2017; Wang *et al.*, 2014; Zhang and Ostrovski, 2001, 2002; Zhao, 1990). The temperature and time of pretreatment determine the amount and concentration of acid required and energy consumption during post-treatments such as leaching. Mechanical activation/grinding of ilmenite ore before heat treatment considerably reduces the annealing temperature and time (Subasinghe and Ratnayake, 2021). Moreover, the purity and crystallinity of the end-products depend on temperature and time of thermal treatment, whereas mechanical activation has produced better results (Subasinghe and Ratnayake, 2021). For example, high-purity TiO_2 crystals can be formed by thermal treatment above 1300°C. The crystal size of rutile increases with increasing temperature (Bordbar, Yousefi, and Abedini, 2017; Subasinghe and Ratnayake, 2021; Zhang *et al.*, 2011). Thermal treatments oxidize Ti^{3+} to Ti^{4+} with increasing temperatures from 1000°C to >1500°C (Zhang *et al.*, 2011). It is also claimed that the grain size and volume fraction of rutile depend on melting temperature, heating

Mechanical activation and physicochemical factors

time, and cooling rate. In this case, the rutile phase is precipitated rapidly during high-temperature treatment. The grain sizes are subsequently increased during the isothermal heating time and cooling stages (Zhang et al., 2011).

Possible catalysts for the carbothermic reduction of titanium ores

Carbothermic reduction of ilmenite is not preferred in the industry due to time requirements and high energy consumption. However, the addition of catalysts during mechanical activation could decrease the activation energy of reactants during heat treatment and subsequent leaching processes. Several studies have focused on enhancing the rate of solid-state reactions to reduce energy consumption and speed up the process. Alkalis, chlorides, carbonates, and oxides have been found to increase the rate of reduction of iron oxide (Barnes and Pickles, 1988; Lv et al., 2017; Singh, Kishor, and Mankhand, 2018; Taylor, 1976). Specifically, the alkali carbonates of Group 1A elements in the periodic table have been shown to increase the reaction rates of titanium ore with gases such as CO_2 and CO by increasing the fluidity of the charge (Rao, Adjorlolo, and Haberman, 1982). Singh, Kishor, and Mankhand (2018) used sodium carbonate as a catalyst for the carbothermic reduction of ilmenite. Similarly, Wijewardhana, Subasinghe, and Ratnayake (2021) used powdered seashells (calcium carbonate) during milling as a possible catalyst to enhance the rate of carbothermic reduction of ilmenite. Future research should investigate better catalysts for use during mechanical activation for sulphurization and carbothermic reduction of titanium ore.

Effect of impurities and ore grade on reduction

The physical and chemical characteristics and mineralogy of titanium ores significantly affect the rate of reduction reactions (Ismail, Amarasekera, amd Kumarasinghe, 1983; Merks and Pickles, 1988, 2008; Sasikumar et al., 2004; Wang and Yuan, 2006; Welham, 1996; Welham and William, 1999; Zhang and Ostrovski, 2001). For example, the presence of manganese impurities (Mn >1.24 wt.%) in titanium ores reduces the rate of carbothermic reduction (Wang and Yuan, 2006; Wang et al., 2008). Zhang and Ostrovski (2001) investigated the effect of different Fe and TiO_2 contents on the rate of reduction. The authors suggest that higher Fe contents increase the reduction rate at the induction stage. In contrast, magnesium oxide (MgO), manganese oxide (MnO), calcium oxide (CaO), and silica inhibit reduction (Merks and Pickles, 1988). The reduction rate of titanium ores is controlled by the grade and impurity level of the feedstock, and thus the purity of synthetic rutile produced using mechanical activation and pyrometallurgical routes is questionable. Mechanical activation/fine grinding followed by magnetic and gravity separation would yield a higher grade concentrate.

Hydrometallurgical processes

Extraction or leaching using solutions (liquid phases) is referred to as hydrometallurgical processing. Pyrometallurgical processes are also followed by hydrometallurgical steps to extract pure TiO_2 and titanium metal. There are several hydrometallurgical processes used in the titanium industry (Figure 2).

Acid leaching

HCl and H_2SO_4 are the most commonly used acids for upgrading and purification of titanium ores. However, the leachability of titanium ore using weaker acids such as oxalic acid and citric acid has also been studied (Table III). Mahmoud, Afifi, and Ibarhim (2004) classified acid leaching of titanium ores into five process routes:
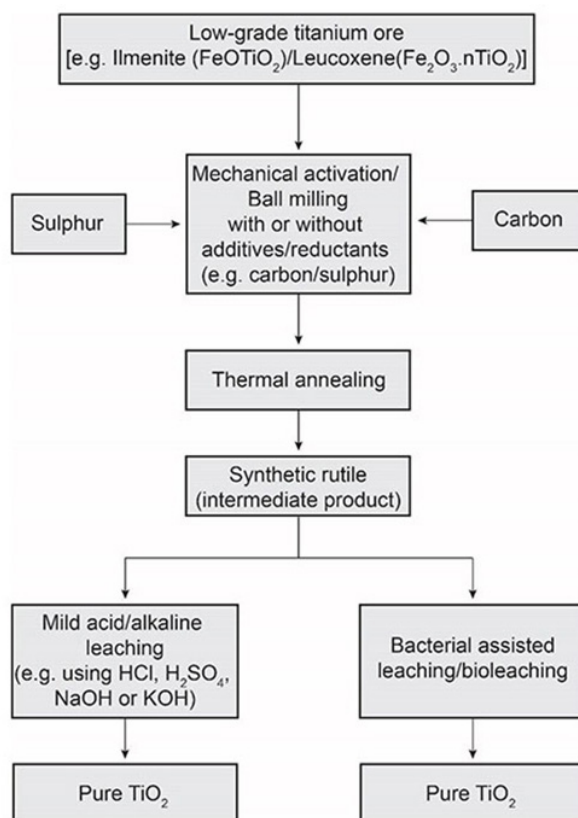

Figure 2—Schematic showing the most environmentally friendly methods of pigment-grade titanium dioxide production

Mechanical activation and physicochemical factors

(i) Smelting followed by H_2SO_4 or HCl leaching at elevated temperatures
(ii) Reduction of titanium ore followed by acid leaching
(iii) Reduction of iron in ilmenite to metallic iron followed by corrosion with oxygen and ammonium chloride
(iv) Oxidation of titanium ore followed by reduction and HCl leaching
(v) Roasting and magnetic separation followed by HCl leaching.

Almost all of these processes have been successful in the production of TiO_2 and/or titanium metal using direct leaching techniques (Figure 3). However, there are both advantages and disadvantages to these processes (Table III), most of which can be circumvented by mechanical grinding before acid leaching.

Leaching time and temperature are significant variables affecting product quality. Therefore, future research should focus on the kinetic modelling of mechanically activated titanium ore to investigate the leaching models. If ball-milled titanium ore follows the shrinking core model during leaching, the effectiveness and process efficiency could be raised (Kuppusamy and Holuszko, 2022).

Factors such as temperature, concentration of acid, particle size, and solid to liquid ratio also affect the leaching kinetics, efficiency and quality of products (Nguyen and Lee, 2018; Zhang, Zhu, and Cheng, 2011). However, HCl and H_2SO_4 are consumed in dissolving impurities. Therefore, only part of the acid is used to break the strong covalent bonds of titanium minerals. This reduces the economic feasibility at an industrial scale. Simple initial

Table III

Commonly followed strong and weak acid leaching techniques

| Process	Advantages	Disadvantages	References
HCl leaching	High efficiency Easy regeneration and recyclability of HCl Both cost and waste management Regeneration of acid through pyrohydrolysis Excellent impurity removal capability Fast leaching rate Acid regeneration technology	Corrosion of the production equipment Requires a high-grade titanium raw material Pyrohydrolysis is energy-intensive High capital cost for process equipment due to the use of concentrated HCl Problem in solid/liquid separation	Zhang *et al.* (2010) Middlemas, Fang, and Fan (2013) Jia *et al.* (2014)
H_2SO_4 leaching	Less corrosion of production equipment Reusability of the discharged H_2SO_4 waste Use of low-grade titanium ore Low capital investment and low energy consumption	Less efficiency in removing impurities Difficulty in treatment of crude iron (II) sulphate and of the waste acid solution Large volume of waste requiring treatment and disposal Slow leaching rate Large quantities of waste iron sulphate and diluted sulphate acid	Zhang and Nicol (2010) Wu *et al.* (2013) Jia *et al.* (2014)
Weak acid leaching	Low acid concentration Highly selective for Ti over Fe Reasonable liquid to solid ratio Less corrosive action	Requires high energy High cost of acid	Nayl, Awwawad, and Aly (2009a)
Caustic leaching	Higher leaching selectivity for Ti over Fe Mild atmospheric leach conditions at low temperature	Need to transform titanate to to hydrous TiO_2 in acidic solution Recycling of large amount of alkaline solution High energy consumption	Zhang, Zhu, and Cheng (2011)
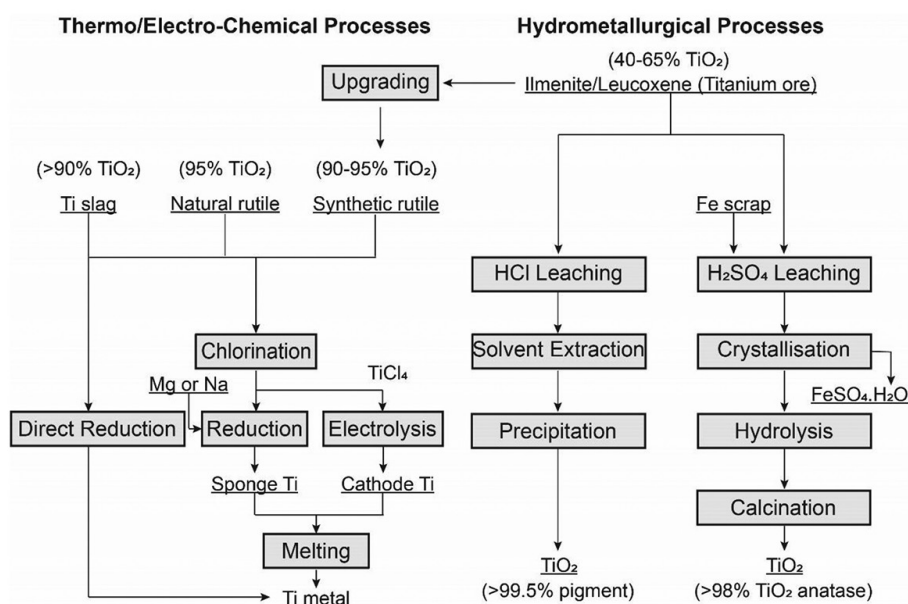
Figure 3—Most common commercial processes of titanium metal and titanium dioxide pigment production (after Zhang, Zhu, and Cheng, 2011)

Mechanical activation and physicochemical factors

leaching with dilute HNO_3 can be used to dissolve the impurities, thus reducing the consumption of HCl and H_2SO_4 (Figure 4). A brief comparison of the advantages and disadvantages of common hydrometallurgical methods is summarized in Table IV.

H_2SO_4 leaching

H_2SO_4 leaching dissolves titanium minerals to form Ti(VI) and SO_4^{2-}/ HSO_4^- complexes, such as $TiOSO_4$, $TiO(SO_4)_2^{2-}$, $TiO(SO_4)_4^{6-}$, and $Ti(OH)_3HSO_4$ (Nayl and Aly, 2009). Han, Rubcumintara, and Fuerstenau (1987) reported that a distinctive product layer of $TiOSO_4$ and $FeSO_4$ is formed at higher than 16 M H_2SO_4, and which is soluble in water at 98°C (see Equations [6] and [7]). Jonglertjunya and Rubcumintara (2013) identified a

significant reduction of titanium dissolution in acid concentrations ranging from 12 M to 18 M at 90°C, due to the formation of titanium precipitates. Li, Liang, and Guo (2007) and Li *et al.* (2008) ascertianed that the leaching of titanium is very low in H_2SO_4 solution (concentration range from 10 to 40 wt.%) below 100°C due to the hydrolysis of dissolved titanium. Leach residues can form a compact layer on the surface of unreacted ilmenite at 150°C with sulphuric acid concentration above 40 wt.%, hindering the leaching of iron (Jia *et al.*, 2014).
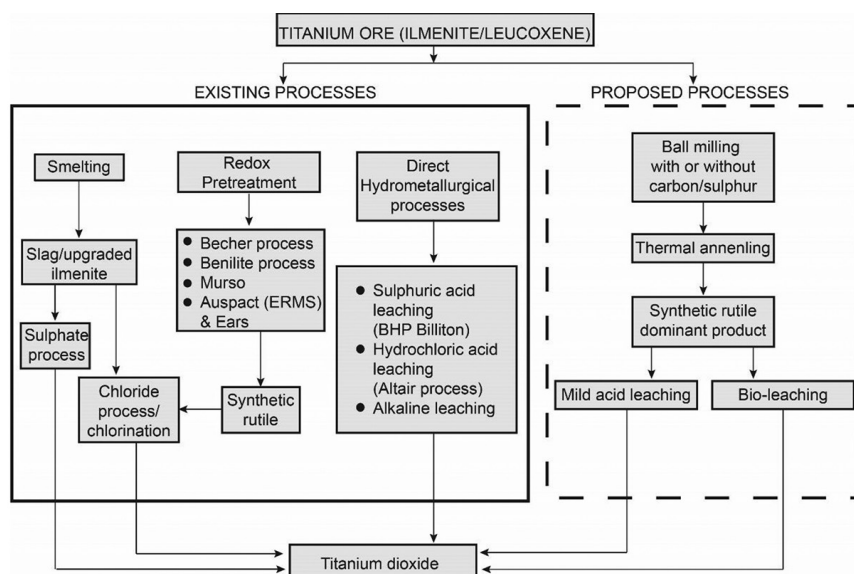
$$FeTiO_3(s) + 2H_2SO_4(aq) \rightarrow FeSO_4(aq) + TiOSO_4(aq) + 2H_2O(l) \quad [6]$$

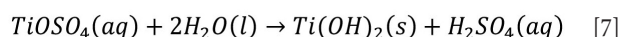$$TiOSO_4(aq) + 2H_2O(l) \rightarrow Ti(OH)_2(s) + H_2SO_4(aq) \quad [7]$$
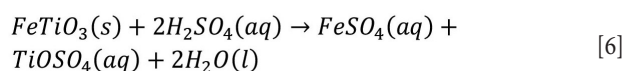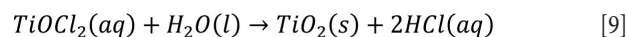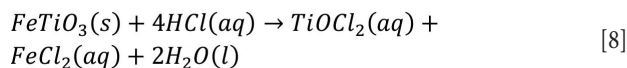

Figure 4—Summary of techniques used to process titanium ore to synthetic rutile (after Nurul, 2016; Nguyen and Lee, 2018; Subasinghe and Ratnayake, 2021)

Table IV

Feed materials, purity of products, advantages and drawbacks of common titanium ore leaching techniques

Process	Feed	Products	Advantages	Disadvantages
Traditional sulphate leaching process	Natural ilmenite (>44 TiO_2) Ti slag (78% TiO_2)	Anatase (>98% TiO_2) (for papers, ceramics, and inks)	Processing low grade ilmenite Low capital cost Low energy consumption Simple technology	High H_2SO_4 consumption Large amounts of iron sulphate waste and dilute H_2SO_4
BHP Billiton improved sulphate process	Diverse ilmenite ores Fe scrap reductant	>99% TiO_2 with solvent extraction, 97% with crystallization	Reduced waste, produces clean gypsum Better selectivity by SX, purer products	Increased process complexity Large volume of dilute acid solution needs recyling
Thermo chloride processes	>90% TiO_2, natural or synthetic rutile, or high-grade Ti slag	Pigment grade products (>99.5% TiO_2) Ti metal	Recycle use of HCl reagent Suitable for larger scale Purer products Waste more environmentally acceptable	Need for higher grade feed More corrosive, high energy consumption Complicated technology
Chloride leaching process	Natural ilmenite and Ti slag	>99.5% TiO_2	More complete HCl acid recycle Lower cost for waste, and more environmental acceptable Higher purity products	Higher capital costs for equipment and construction Higher degree of operational and maintenance skill
Caustic process	Natural ilmenite and Ti slag	>99.3% TiO_2	Higher leaching selectivity for Ti over Fe Mild leach conditions at low temperature and ambient atmosphere	Need for transformation of titanate to hydrous TiO_2 in acidic solution Recycling of large amount of KOH solution High energy consumption

# Mechanical activation and physicochemical factors

HCl leaching

Samal (2011) found that the leaching efficiency of titanium is lower than that of iron at low acid concentrartions such as 2.5 M HCl due to the precipitation of $TiOCl_2$ (Equations [8] and [9]).

$$FeTiO_3(s) + 4HCl(aq) \rightarrow TiOCl_2(aq) + FeCl_2(aq) + 2H_2O(l) \quad [8]$$

$$TiOCl_2(aq) + H_2O(l) \rightarrow TiO_2(s) + 2HCl(aq) \quad [9]$$

El-Hazek *et al.* (2007) suggested that leaching with high acid concentrations such as 12 M at 80°C is needed to suppress the hydrolysis of titanium at a high solid to liquid ratio of 1/20. The dissolution of titanium and iron increases with increasing acid concentration (Das *et al.*, 2013; El-Hazek *et al.*, 2007; Middlemas, Fang, and Fan, 2013; Olanipekun, 1999). The leach liquor of the pretreated titanium slag leached with 0.75–1.5 M HCl at 50°C is quite turbid and difficult to filter (Middlemas, Fang, and Fan, 2013). Clear filtrate and less finely suspended particles can be obtained at HCl concentrations above 1.5 M. However, precipitation occurs in this solution after only a few days (Middlemas, Fang, and Fan, 2013). Consequently, the hydrolysis of dissolved titanium occurs at either low acidity or low temperature (*e.g.*, 1.5 M and 50°C).
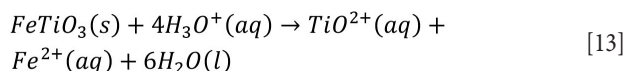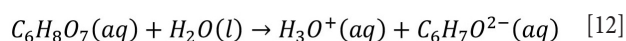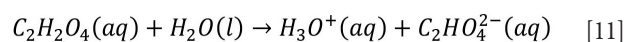
The effect of HCl concentration on the selective leaching of iron over titanium from ilmenite has been reported in the literature (Gireesh *et al.*, 2015; Guo *et al.*, 2014; Lasheen, 2005; Liu *et al.*, 2015; Mahmoud, Afifi, and Ibarhim, 2004). Iron is almost completely dissolved in 30 wt.% HCl under reducing conditions, but titanium dissolution is negligible (Mahmoud, Afifi, and Ibarhim, 2004). In addition, 20 wt.% HCl is a suitable acid concentration for the selective leaching of iron. Therefore, it enhances the TiO_2 content in the residue (Guo *et al.*, 2014). Liu et al. (2015) also indicated that the recovery of TiO_2 in the residue increased with increasing acid concentration from 200 to 240 g/L. Consequently, HCl concentrations higher than 220 g/L can be used to obtain a product containing more than 92% TiO_2. The leaching efficiency of iron also increased as the acid concentration increased from 2 M to 12 M, but the solubility of TiO_2 seemed to be negligible in this acid concentration range (Gireesh *et al.*, 2015; Lasheen, 2005). Furthermore, TiO_2, HCl, and MgO ($MgCl_2$ is added to increase the chloride ion concentration to enhance titanium and iron leaching) can be recovered *via* pyrohydrolysis/high-temperature hydrolysis. The recovered HCl is recyclable as shown in Equation [10] (Zhang, Zhu, and Cheng, 2011).

$$MgCl_2(s) + H_2O(l) \rightarrow MgO(s) + 2HCl(aq) \quad [10]$$
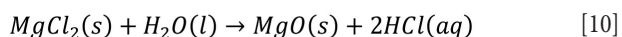
HCl is generally more efficient than H_2SO_4 in terms of titanium dioxide purity and recovery (Jia *et al.*, 2014; Mehdilo and Irannajad, 2012; Razieh, 2014; Sasikumar *et al.*, 2004). In addition, HCl can be easily recovered from waste, making it more advantageous than H_2SO_4 (Mehdilo and Irannajad, 2012). However, the corrosion of production equipment is less with H_2SO_4 in comparison to HCl (Jia *et al.*, 2014).

Dissolution of titanium ore with weaker acids

Titanium ores can also be leached using weaker acids such as oxalic ($C_2H_2O_4$) and citric ($C_6H_8O_7$) acid (Jonglertjunya and Rubcumintara, 2013; Kordzadeh-Kermani *et al.*, 2020; Nayl, Awwad, and Aly, 2009a; Nayl and Aly, 2009). The reactions are as indicated in Equations [11][13].

$$C_2H_2O_4(aq) + H_2O(l) \rightarrow H_3O^+(aq) + C_2HO_4^{2-}(aq) \quad [11]$$

$$C_6H_8O_7(aq) + H_2O(l) \rightarrow H_3O^+(aq) + C_6H_7O^{2-}(aq) \quad [12]$$

$$FeTiO_3(s) + 4H_3O^+(aq) \rightarrow TiO^{2+}(aq) + Fe^{2+}(aq) + 6H_2O(l) \quad [13]$$
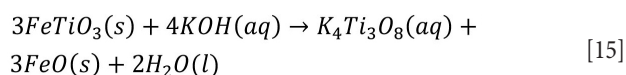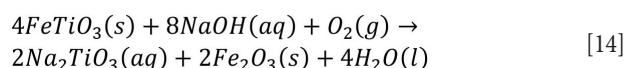
Both oxalic and citric acid are able to leach titanium, and citric acid provides effective results at low concentrations with the same physical conditions (Jonglertjunya and Rubcumintara, 2013). However, the leaching efficiencies of hydrochloric and oxalic acid are low compared to sulphuric and citric acid for lower grade ore (Jonglertjunya and Rubcumintara, 2013). Titanium leached more than iron under optimum conditions due to the precipitation of Fe(III) and Fe(II) at 90°C (Jonglertjunya and Rubcumintara, 2013). In contrast, the leaching efficiency of titanium gradually declines at temperatures above 150°C with 80 wt.% oxalic acid due to titanium hydrolysis (Nayl, Awwad, and Aly, 2009).

Although the leaching efficiency of sulphuric acid is high for low-grade ore, Jonglertjunya and Rubcumintara (2013) suggest citric acid as a better reagent due to lower acid consumption and lower leaching of iron. In addition, Nayl, Awwad, and Aly (2009) suggest oxalic acid as the most favourable reagent for the dissolution of pre-treated titanium ore due to the selectivity for titanium over iron. Oxalic acid is less corrosive, and the liquid/solid ratio is also reasonable. However, higher costs for oxalic acid and higher energy requirements compared with HCl and H_2SO_4 are the main disadvantages (Nayl, Awwad, and Aly, 2009).

Alkaline/caustic leaching

Alkaline/metal hydroxide/caustic leaching is also used to process titanium ores. Ilmenite is decomposed in an alkaline medium such as concentrated KOH or NaOH under atmospheric pressure to obtain an intermediate product with lower iron and higher titanium concentrations as shown in Equations [14] and [15], (Han *et al.*, 2021; Nguyen and Lee, 2018; Zhang, Zhu, and Cheng, 2011).

$$4FeTiO_3(s) + 8NaOH(aq) + O_2(g) \rightarrow 2Na_2TiO_3(aq) + 2Fe_2O_3(s) + 4H_2O(l) \quad [14]$$

$$3FeTiO_3(s) + 4KOH(aq) \rightarrow K_4Ti_3O_8(aq) + 3FeO(s) + 2H_2O(l) \quad [15]$$

Amer (2002) developed a method to dissolve titanium from mechanically activated Rosetta ilmenite (a prominent deposit located in Egypt) using sodium hydroxide. About 90% of the titanium could be leached under optimum conditions of 0.3 M NaOH, 200°C, 90 minutes, and an oxygen partial pressure of 10 bar (Amer, 2002). Subsequently, several researchers have prepared TiO_2 from titanium slag using alkaline leaching and obtained intermediates (*e.g.*, Na_2TiO_3 and $K_4Ti_3O_8$) with high titanium and low iron contents (Han *et al.*, 2021; Liu *et al.*, 2006; Qi *et al.*, 2005; Xue *et al.*, 2009). For example, the intermediate product ($K_4Ti_3O_8$) can be hydrolysed in acid (HCl and H_2SO_4) of pH 2.0 at 25°C for 1 hour. The resulting hydrous TiO_2 is calcined at 400°C to obtain well-crystallized anatase (TiO_2) with a purity of 99.3% (Zhang, Zhu, and Cheng, 2011). Alkaline leaching is usually used for the dissolution of titanium from raw ilmenite or hydrolysed titania after the removal of iron (Wu *et al.*, 2011a, 2011b). Finely powdered titanium slag can be completely dissolved with 10 M NaOH at a NaOH to TiO_2 ratio of 4:1 at a temperature of 220°C to obtain $Na_4Ti_3O_8$. This intermediate has been acidified and subjected to cation exchange in the pH range <1.20 at 100°C to form TiO_2 (Zhang *et al.*, 2009).
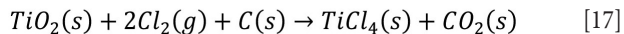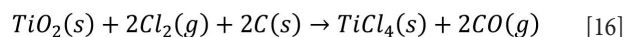
Mechanical activation and physicochemical factors

$NH_3.H_2O$ has also been employed along with H_2O_2 as an oxidizing agent to provide O_2^{2-} ions (O_2^{2-} reacts with titanium to form peroxide (TiO_3^{2-}) and pertitanate (TiO_6^{2-}) groups) for dissolving titanium from hydrolysed titania (Wu *et al.*, 2011a, 2011b). However, the final TiO_2 obtained was less pure due to the presence of SiO_2 (Wu *et al.*, 2011a). In this case, Wang *et al.* (2010, 2013) proposed two-step alkaline leaching (re-leaching the first filtrate to dissolve SiO_2) and leaching with a mixture of NaOH and H_2O_2, respectively to obtain titanium precursors with less SiO_2.

Interestingly, the alkaline leaching processes require less energy than conventional methods of titanium ore processing (Zhang, Zhu, and Cheng, 2011). These processes can be carried out at comparatively low temperatures and pressures.

Thermochemical reduction and dissolution

Chlorination at elevated temperatures (900–950°C) is the major commercialized thermochemical process for producing pure titanium tetrachloride ($TiCl_4$) (Equations [16] and [17]). This method is also employed to produce high-purity TiO_2 and titanium metal from titanium slag or synthetic rutile (Zhang, Zhu, and Cheng, 2011). Thermochemical processing was initiated immediately after the beginning of ilmenite smelting at end of the 19th century. For example, the Hunter process (reduction of $TiCl_4$ in an inert atmosphere with sodium at 1000°C and re-leaching the salt with dilute HCl) was developed in 1887 to produce titanium metal via reduction of $TiCl_4$ in a molten bath of sodium (Zhang, Zhu, and Cheng, 2011).

$$TiO_2(s) + 2Cl_2(g) + 2C(s) \rightarrow TiCl_4(s) + 2CO(g) \quad [16]$$

$$TiO_2(s) + 2Cl_2(g) + C(s) \rightarrow TiCl_4(s) + CO_2(s) \quad [17]$$

The Kroll process, in which $TiCl_4$ obtained by carbochlorination is purified and reduced with magnesium, followed by electrolysis of $MgCl_2$ to recycle Mg, is now industrially mature (Fatollahi-Fard and Pistorius, 2017). This method was introduced in 1940 to replace Hunter process, and is relatively cheap compared with the Hunter process. The Kroll process reduces $TiCl_4$ at 900°C in molten magnesium (Nagesh *et al.*, 2004). However, production of the $TiCl_4$ feed material is capital intensive due to the use of petroleum coke and chlorine gas, and quite environmentally unfriendly due to the release of dioxins, furans, and bulky organic pollutants (Jackson and Dring, 2006). Several studies have been carried out incorporating modifications to overcome these drawbacks using thermochemical reduction and dissolution (Zhang, Zhu, and Cheng, 2011). However, cost reduction of these thermochemical processes (the, Hunter and Kroll processes) remains a challenge.

There are three commercially established technologies to produce $TiCl_4$, namely the fluidized bed process (most prominent), shaft furnace process, and chlorination in a molten salt bath (used in Japan and the former USSR). These thermochemical processes require high-grade feed material (over 90% TiO_2) from natural/synthetic rutile or high-grade titanium slag (Zhang, Zhu, and Cheng, 2011). However, the wastes generated in these processes are more disposable than those generated by the sulphate processes.

Solvothermal/hydrothermal conversion

Solvothermal and hydrothermal techniques are closely associated. They only differ in their precursor solutions (Zhang, Zhu, and Cheng, 2011). Several authors have used hydrothermal conversion to decompose titanium minerals into iron and titanium using acidic or alkaline solutions (Li, Wang, and Li, 2016; Manhique, Focke,

and Madivate, 2011; Nayl *et al.*, 2009a, 2009b; Nayl and Aly, 2009; Xiong *et al.*, 2013). In particular, the minerals are decomposed to obtain solid or liquid phase TiO_2 using sulphuric acid solution (Li, Wang, and Li, 2016; Sui and Zhai, 2014; Xiong *et al.*, 2013). Xiong *et al.* (2013) decomposed ilmenite with 80–85 wt.% H_2SO_4 at 150°C, followed by leaching with water to obtain titanium sulphate. The major drawbacks of this method can be summarized as the requirement for highly concentrated 80–85 wt.% H_2SO_4 (Xiong *et al.*, 2013), energy for heating (Sui and Zhai, 2014), and generation of toxic gases such as H_2S, SO_2, and SO_3 (Baba *et al.*, 2013). However, titanium minerals are successfully decomposed at optimum conditions of 13.5 M H_2SO_4, at 160°C for 2 hours to yield titanium with minimal generation of unfriendly by-products (Li, Wang, and Li, 2016).

Titanium dissolution has been observed in concentrated KOH under atmospheric pressure. In this method, potassium titanate and iron oxide are obtained (Liu *et al.*, 2006; Nayl and Aly, 2009). In addition, Baba *et al.* (2013) reported that NaOH is a better roasting agent than Na_2CO_3 in terms of the capacity for Na_2O generation for reacting with titanium minerals to form $NaFeTiO_4$, Na_2TiO_3, $NaFeO_2$, and $NaFeTi_3O_8$. Moreover, this method enhances the leaching efficiency of titanium using sulphuric acid, enabling complete dissolution to be achieved (Baba *et al.*, 2013).

Solvothermal techniques can be employed to synthesize titanium-based nanomaterials (Xie and Shang, 2007). These methods have some merits over other synthetic processes, such as the use of mild chemical conditions at relatively low temperatures and the formation of non-agglomerated nanomaterials (Zhan, Zhu, and Cheng, 2011).

Biohydrometallurgical process

In this method, titanium minerals are leached using microorganisms such as bacteria and fungi. Jonglertjunya and Rubcumintara (2013) compared acid leaching and bioleaching in terms of titanium and iron extraction. The experimental results indicated very low iron and titanium dissolutions even after 35 days of leaching in both pure (A. niger, P. citrinum, and B. megaterium) and mixed (A. niger and P. citrinum) culture media (Jonglertjunya and Rubcumintara, 2013). Besides, Acidithiobacillus ferrooxidans (A. ferrooxidans), an iron oxidizing bacterium and Pseudomonas mendocina (P. mendocina), an iron scavenging bacterium have been used to extract titanium from ilmenite (Navarrete *et al.*, 2013). Bioleaching is thus less effective due to very low iron and titanium dissolutions even after extensive leaching times. However, the combination of pyrometallurgy and biohydrometallurgy would be the best solution to enhance productivity while being environmentally acceptable. In this regard, bioleaching should effectively incorporate mechanical activation of raw ore for better results. Metal scavenging bacteria would attack smaller particles more rapidly than coarser particles. This will also increase efficiency and decrease leaching times. Therefore, practicing this on a large scale is likely to produce better results than traditional bioleaching techniques. Moreover, the titanium mineral processing industry can test such alternative methods for their suitability in terms of reaching the United Nations Sustainable Development Goals.

Factors controlling hydrometallurgical process
Acid concentration

The literature suggests that leaching recovery gradually increase with increasing acid concentration (Jonglertjunya and Rubcumintara, 2013; Nayl, Awwad, and Aly, 2009a; Nayl and Aly,

Mechanical activation and physicochemical factors

2009; Sasikumar et al., 2007; Zhang and Nicol, 2010). For example, dissolved titanium is hydrolysed in the presence of 10–40% H_2SO_4, which has an adverse effect on the leaching process (Li, Liang, and Guo, 2007, Li et al., 2008). In addition, the leaching of iron and titanium in pre-treated titanium ore increases considerably with HCl concentrations up to 9 M (Nayl and Aly, 2009).

Temperature

The leaching rate of ilmenite using sulphuric acid is extremely sensitive to reaction temperature. Titanium and iron are dissolved simultaneously by concentrated sulphuric acid, and the leaching recoveries of these metals increase with temperature (Nayl et al., 2009; Sasikumar et al., 2007; Zhang and Nicol, 2010). Titanium and iron can be separated in the leaching process (using dilute H_2SO_4) by controlling reaction temperature (Jia et al., 2014; Li, Liang, and Guo, 2007). Leaching of iron increased with temperature using 20% H_2SO_4, while that of titanium decreased due to the instability of titanium in the solution at high temperatures (Li, Liang, and Guo, 2007). Jia et al. (2014) also reported that most of the iron from Panzhihua (the main deposit located in Sichuan, southwest China) ilmenite was selectively leached using 20% H_2SO_4 at 150°C, while leaching of Ti was less than 1%. Hydrolysis of the dissolved titanium ion occurs simultaneously during leaching at 125–200°C, resulting in a decrease in the leaching efficiency of titanium (Jia et al., 2014).

The leaching of titanium and iron from ilmenite using HCl increases significantly as the temperature increases from 25 to 80°C (Das et al., 2013; El-Hazek et al., 2007; Lasheen, 2005). High leaching efficiency of ilmenite was obtained at higher temperatures (>80°C). However, several drawbacks can be identified, such as increased loss of HCl vapour and hydrolysis of dissolved titanium (Das et al., 2013; Tao et al., 2012). El-Hazek et al. (2007) and Lasheen (2005) reported low leaching efficiencies of iron and titanium at room temperature due to the low reactivity of ilmenite. Nevertheless, the leaching recovery of iron increased more rapidly than that of titanium as the temperature increased from 20 to 50°C, owing to the partial hydrolysis of titanium. The mobility of ions increases with temperature, enhancing the interaction between reactants in solids and liquids (Gireesh et al., 2015). However, reaction temperatures above 100°C adversely affect the leaching of titanium due to high polymerization and hydrolysis of titanium without affecting iron (El-Hazek et al., 2007). Leaching temperature is quite important for the production of high-purity TiO_2 using moderate (pH 3–5) HCl concentrations (Guo et al., 2014; Lasheen, 2005; Liu et al., 2015; Mahmoud, Afifi, and Ibarhim, 2004; Razieh, 2014; Tao et al., 2012). The leaching of iron rapidly increased with enhanced temperature up to 90°C using 4 M HCl, leaving most TiO_2 in the residue at any temperature (Lasheen, 2005). The hydrolysis reaction of $TiOCl_2$ is known to be greatly enhanced at higher temperatures. Consequently, the recovery of TiO_2 from the ilmenite residue using a moderate HCl concentration increases with temperature (Guo et al., 2014; Liu et al., 2015; Mahmoud, Afifi, and Ibarhim, 2004; Razieh, 2014). Middlemas, Fang, and Fan (2013) reported that the dissolved titanium can react with water to form insoluble hydrates such as orthotitanic acid, $Ti(OH)_4$ or $TiO_2.2H_2O$ at low temperatures (25–80°C), and metatitanic acid, $Ti(OH)_2$ or $TiO_2.H_2O$ at higher temperatures (80–110°C).

Ultrasound (>16 kHz) can also be used to reduce leaching time and temperature. Specifically, the reaction rate is enhanced due to high frequency, wave intensity, duration of ultrasound irradiation, and the physical characteristics of the lixiviant and nature of titanium ore (Narayana et al., 1997; Swamy et al., 1995).

The reduction of chlorine content during the leaching of titanium-bearing minerals is another advantage of using ultrasound (Narayana et al., 1997).

Contact time

Long contact times between the solution/acid and the feed material increase the dissolution of iron (El-Hazek et al., 2007; Gireesh et al., 2015; Jia et al., 2014; Li, Liang, and Guo, 2007, Li et al., 2008; Li, Liang, and Wang, 2008; Nayl and Aly, 2009; Samal, 2011). Nevertheless, hydrolysis of dissolved titanium delays the leaching process (Li, Liang, and Guo, 2007; Zhang, Zhu, and Cheng, 2011). Moreover, the production of H^+ during the hydrolysis of titanium ions enhances the ionic strength and the reactivity of the acid. In this regard, the dissolution of iron becomes rapid (Zhang et al., 2010). The literature reveals that the percentage dissolution of iron and the enhancement of TiO_2 in the residue increases with time (Li, Liang, and Wang, 2008b; Mahmoud, Afifi, and Ibarhim, 2004; Razieh, 2014). However, minimizing the contact time between acid (both HCl and H_2SO_4) and feed material by adjusting the other parameters would add more economic benefits (Zhang, Zhu, and Cheng, 2011).

Effect of particle size

Several researchers describe how the ilmenite particles break down during reduction/oxidation as a result of the separation of the iron from the TiO_2. A decrease in particle size increases the effectiveness of leaching. The leaching of titanium increases at particle sizes below 150 μm and mostly decreases above >200 μm (El-Hazek et al., 2007; Mehdilo and Irannajad, 2012; Samal, 2011). The reduction of particle size increases the effective surface area and enhances the leaching activity (El-Hazek et al., 2007; Samal, 2011). The dissolution of iron and titanium occurs generally for any particle size in the presence of HCl (van Dyk, Vegter, and Pistorius, 2002). Fine particles show faster reaction rates (El-Hazek et al., 2007; Nurul, 2016). However, reduction of particle size to less than 105 μm weakens iron dissolution (Nayl, Awwad, and Aly, 2009; Nayl, Ismail, and Aly, 2009; Nayl and Aly, 2009).

Additives and catalysts

Reducing agents have been found to improve leaching efficiency (Nguyen and Lee, 2018). The effect of additives and catalysts can be summarized as follows.

(i) The leaching of titanium increases, and that of iron decreases, with increasing $FeSO_4$ (addition of Fe^{2+} ions) concentration during H_2SO_4 leaching (Jia et al., 2014)

(ii) The presence of Ti(III) ions and SO_2 gas in sulphuric acid reduces iron (III) in titanium minerals via a redox reaction and aids dissolution of titanium (Zhang and Nicol, 2010)

(iii) Addition of metallic iron powder increases titanium leaching efficiency via reduction of iron(III) during HCl leaching

(iv) The HCl leaching efficiency of titanium ores depends on the chloride ion concentration, and the effect has been found to be in the order $CaCl_2$ > $MgCl_2$ > NaCl (Das et al., 2013)

(v) The presence of sulphate ions in HCl solution also increases the efficiency of iron dissolution (Gireesh et al., 2015)

(vi) Leaching efficiency increases in the presence of hydrogen peroxide (H_2O_2) and ultraviolet (UV) light (Jayaweera et al., 2011).

Mechanical activation and physicochemical factors

However, the increment of iron powder also increases acid consumption (El-Hazek *et al.*, 2007). The presence of 6% iron powder enhances iron dissolution in HCl solution, and increases TiO$_2$ content (Lasheen, 2005). Furthermore, the presence of sulphates/sulphate ions such as CaSO$_4$, MgSO$_4$, Na$_2$SO$_4$, and K$_2$SO$_4$ during HCl leaching enhances the purity of titanium. Specifically, monovalent metal sulphates (Na$_2$SO$_4$ and K$_2$SO$_4$) are less effective than divalent metal sulphates (CaSO$_4$ and MgSO$_4$). Moreover, an excess of reducing agents might reduce Ti(IV) to Ti(III) and decrease the tendency of Fe(II) ions to be oxidized to Fe(III) (Mahmoud, Afifi, and Ibarhim, 2004).

Oxidation and reduction of titanium ore during hydrometallurgical processing

Oxidation induces micro-cracks, and micro-pores. Therefore, it enhances the rate of leaching at 1000°C (Grey *et al.*, 2007; Sarker, Rashid, and Kurny, 2006; Zhu, Zhang, and Li, 2014). However, oxidation at 900–1000°C significantly decreases the leaching efficiency due to the formation of pseudobrookite (Zhu, Zhang, and Li, 2014). Oxidation below 800°C has little effect on iron dissolution, as the solubility of ferric iron is low during acid leaching (Janssen and Putnis, 2011).

Titanium ore upgrading processes such as the Becher process employ iron oxidation followed by reduction (Farrow, Ritchie, and Mangono, 1987). Methods such as the Murso process oxidize titanium ore in fluidized beds at temperatures ranging from 900 to 950°C (Sinha, 1973), and the ferric iron formed is reduced using a reducing agent such as H$_2$ gas. Similarly, in the Laporte process titanium ore is pre-oxidized in a fluidized bed at 950°C and reduced in a rotary kiln using coal at 900°C (Robinson *et al.*, 1977). Iron is oxidized according to Equation [5] followed by reduction (see Equation [18]) in a rotary kiln with a mixture of pseudobrookite (Fe$_2$O$_3$·TiO$_2$), coal, and sulphur at >1200°C to convert iron oxide to metallic iron (Zhang, Zhu, and Cheng, 2011).

$$Fe_2O_3 \cdot TiO_2(s) + 3CO(g) \rightarrow 2Fe(s) + TiO_2(s) + 3CO_2(g) \qquad [18]$$
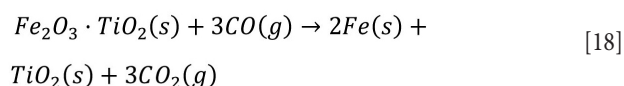
The produced metallic iron is re-oxidized (see Equation [19]) and precipitated as a slime in large vessels using 1% ammonium chloride solution at 80°C during the aeration 'rusting' step (Zhang, Zhu, and Cheng, 2011).

$$4Fe(s) + 3O_2(g) \rightarrow 2Fe_2O_3(s) \qquad [19]$$
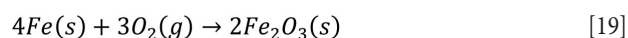
Electrometallurgical/electrochemical processes

Electrometallurgical/electrochemical processing (i.e., use of electrical energy to extract metals by electrolysis) of titanium minerals became more common in the 21st century due to the invention of electro-deoxidization in molten salt in 2000 (Liu *et al.*, 2012). Several studies have focused on producing titanium metal and alloys *via* electrometallurgical routes (Table V). Disadvantages such as low productivity and lengthy times required for impurity removal could be circumvented by mechanically grinding the titanium ore. This would simultaneously increase the recovery of TiO$_2$ in products.

The use of electrical energy in conjunction with chemicals has also focused on reducing the production cost of TiO$_2$ and titanium metal. Most of the electrochemical methods are automated, and thus utilize continuous production lines (Fatollahi-Fard and Pistorius, 2017; Zhang, Zhu, and Cheng, 2011). However, reactive products and associated problems in redox recycling are the main limitations of this method (Chen, Fray, and Farthing, 2000). Consequently, several methods have been introduced for direct reduction, such as Electro-slag electrolysis (ESE) and the Fray–Farthing–Chen (FFC) process. The FFC process, with TiO$_2$ as feed material, is the more efficient. These methods enable the production of titanium metal in one step (Suzuki, Teranuma, and Ono, 2003; Takenaka *et al.*, 1999). The cost of production can be significantly controlled by using well-ground TiO$_2$ as the feed material in these processes.

Conclusions

Pyrometallurgy, hydrometallurgy, and electrometallurgy are prominent methods to cater to the escalating global demand for TiO$_2$ and titanium metal. Mechanical activation (ball milling with or without reductants) of titanium ore is an important method to

---

Table V

Comparison of common electrochemical and thermochemical titanium ore processing techniques

Process	Features	Advantages	Disadvantages	References
Hunter and Kroll processes (thermo)	Molten Na or Mg as the reductant	Ti product with less oxygen content and metallic impurities Lower costs using Mg reduction	Labour-intensive batch process Heterogeneous exothermic reactions Low productivity	Nagesh *et al.*, (2004)
Electrolysis processes	KCl-LiCl electrolyte graphite anode steel cathode TiO$_2$ feed	Fewer steps Continuous operation No TiCl$_4$ and metallic involvement Cheaper than thermochemical	Redox cycling and handling very reactive dendritic products	Chen, Fray, and Farthing, (2000)
ESE processes (direct electro-chemical)	Graphite anode Cu cathode Molten CaF$_2$-CaO-TiO$_2$	Direct reduction from TiO$_2$ slag Potential for continuous operation	Difficult to control the heat balance and CO evolution	Takenaka *et al.*, (1999)
OS process (direct electro-chemical)	TiO$_2$ powder cathode Graphite rod anode Ca reluctant and molten CaCl$_2$	Direct reduction from TiO$_2$ powder as feed in a single cell	Free carbon contaminating the Ti product by the formation of TiC	Suzuki, Teranuma, and Ono, (2003)
FFC process (direct electro chwmical)	Pre-formed porous TiO$_2$ pellet as cathode Inert anode for O$_2$ evolution Molten CaCl$_2$ phase	Simple, rapid, and better current efficiency Potential continuous operation	Slow O$_2$ diffusion Costly for the TiO$_2$ pellet feed Long time required for removing waste CaCl$_2$ after electrolysis	Chen, Fray, and Farthing, (2000)

reduce the activation energy required for interacting with the strong covalent bonding in titanium ores. This increases the efficiency of subsequent metallurgical processes. Pyrometallurgical treatment produces low-purity synthetic rutile (TiO_2) and slag. In this case, an additional leaching step is required to separate synthetic rutile. Two major hydrometallurgical routes, namely the chloride and sulphate processes, have been commercialized.

Low-grade feed material such as ilmenite or leucoxene can be used in sulphate route leaching. However, a greater amount of waste is generated at the expense of high energy requirements. In contrast, the chloride process yields highly pure products with less waste generation. This process requires high-grade feed material such as natural or synthetic rutile or titanium slag. Thermochemical processes such as the Kroll and Hunter processes require high-grade feed material such as $TiCl_4$. Consequently, these processes have proven to be less efficient, even with the existing technology. Electrochemical methods are comparatively feasible. However, the generation of highly concentrated solutions, redox recycling, feeding, and controlling heat balance are the main drawbacks. Direct leaching technologies have proven to be more effective than thermochemical and electrochemical techniques.

The use of combined metallurgical techniques such as pyro- and hydrometallurgy to increase process efficiency and purity of products, and reduce energy consumption and waste generation, should be a future focus of the titanium ore processing industry. Pyrometallurgical processing of mechanically activated titanium ore followed by microbial leaching/biohydrometallurgy can constitute an unconventional method to enhance production while being environmentally friendly.

Acknowledgements

Conflict of interest statement

On behalf of all authors, the corresponding author states that there is no conflict of interest.

References

Amade, R., Heitjans, P., Indris, S., Finger, M., Haeger, A., and Hesse, D. 2009. Defect formation during high-energy ball milling in TiO_2 and its relation to the photocatalytic activity. *Journal of Photochemistry and Photobiology A: Chemistry*, vol. 207. pp. 231–235. https://doi.org/10.1016/j.jphotochem.2009.07.015

Amer, A.M. 2002. Alkaline pressure leaching of mechanically activated Rosetta ilmenite concentrate. *Hydrometallurgy*, vol. 67. pp. 125–133. https://doi.org/10.1016/S0304-386X(02)00164-0

Baba, A.A., Swaroopa, S., Ghosh, M.K., and Adekola, F.A. 2013. Mineralogical characterization and leaching behaviour of Nigerian ilmenite ore. *Transactions of Nonferrous Metals Society of China*, vol. 23. pp. 2743–2750.

Bai, Y., Mora-Sero, I., De Angelis, F., Bisquert, J., and Wang, P. 2014. Titanium dioxide nanomaterials for photovoltaic applications. *Chemical Reviews*, vol. 114, no. 19. pp. 10095–10130. https://doi.org/10.1021/cr400606n

Barnes, C. and Pickles, C.A. 1988. A thermogravimetric study of the catalytic effect of alkali carbonates on the reduction of ilmenite. *High Temperature Technology*, vol. 6. pp. 195–201. https://doi.org/10.1080/02619180.1988.11753400

Begin-Colin, S., Girot, T., le Caër, G., and Mocellin, A. 2000. Kinetics and mechanisms of phase transformations induced by ball-milling in anatase TiO_2. *Journal of Solid State Chemistry*, vol. 149., pp. 41–48. https://doi.org/10.1006/jssc.1999.8491

Begin-Colin, S., Le Caër., G., Mocellin, A., and Zandona, M. 1994. Polymorphic transformations of titania induced by ball milling. *Philosophical Magazine Letters*, vol. 69, no. 1, pp. 1–7. http://dx.doi.org/10.1080/09500839408242430

Bordbar, H., Yousefi, A.A., and Abedini, H. 2017. Production of titanium tetrachloride ($TiCl_4$) from titanium ores: A review. *Polyolefins Journal*, vol. 4. no. 2. pp. 149–173. https://dx.doi.org/10.22063/poj.2017.1453

Brooks, D.R. 2000. Reclamation of land disturbed by mining of heavy minerals. *Reclamation of Drastically Disturbed Lands*, vol. 41. pp. 725–754. https://doi.org/10.2134/agronmonogr41.c29

Chen, Y. 1997. Low-temperature oxidation of ilmenite (FeTiO3) induced by high energy ball milling at room temperature. *Journal of Alloys and Compounds*, vol. 257, no. 1–2. pp. 156–160. https://doi.org/10.1016/S0925-8388(97)00012-1

Chen, G.Z., Fray, D.J., and Farthing, T.W. 2000. Direct electrochemical reduction of titanium dioxide to titanium in molten calcium chloride. *Nature*, vol. 407. pp. 361–363. https://doi.org/10.1038/35030069

Chen, Y., Marsh, M., Williams, J.S., and Ninham, B. 1996. Production of rutile from ilmenite by room temperature ball-milling-induced sulphurisation reaction. *Journal of Alloys and Compounds*, vol. 245. pp. 54–58. https://doi.org/10.1016/S0925-8388(96)02483-8

Chen, G., Song, Z., Chen, J., Peng, J., and Srinivasakannan, C. 2013. Evaluation of the reducing product of carbonthermal reduction of ilmenite ores. *Journal of Alloys and Compounds*, vol. 577. pp. 610–614. https://doi.org/10.1016/j.jallcom.2013.06.038

Chen, M., Tang, A., and Xiao, X. 2015. Effect of carbothermic reduction of ilmenite. *Transactions of the Nonferrous Metals Society of China*, vol. 25. pp. 4201–4206. https://doi.org/10.1016/S1003-6326(15)64070-5

Chen, L., Wen, S., Xu, G., and Xie, H. 2013. A novel process for titanium sand by magnetic separation and gravity concentration. *Mineral Processing and Extractive Metallurgy Review*, vol. 34. pp. 139–150. https://doi.org/10.1080/08827508.2011.623749

Das, G.K., Pranolo, Y., Zhu, Z., and Cheng, C.Y. 2013. Leaching of ilmenite ores by acidic chloride solutions. *Hydrometallurgy*, vol. 133. pp. 94–99. https://doi.org/10.1016/j.hydromet.2012.12.006

Dworkin, J.P., Adelman, L.A., Ajluni, T., Andronikov, A.V., Aponte, J.C., Bartels, A.E., and Burton, A.S. 2018. OSIRIS-REx contamination control strategy and implementation. *Space Science Reviews*, vol. 214, no. 1. pp. 19. https://doi.org/10.1007/s11214017-0439-4

El-Hazek, N., Lasheen, T.A., El-Sheikh, R., and Zaki, S.A. 2007. Hydrometallurgical criteria for TiO_2 leaching from Rosetta ilmenite by hydrochloric acid. *Hydrometallurgy*, vol. 87. pp. 45–50. https://doi.org/10.1016/j.hydromet.2007.01.003

Elsner, H. 2010. Heavy Minerals of Economic Importance. Bundesanstalt für Geowissenschaften und Rohstoffe (BGR). Federal Institute for Geosciences and Natural Resources, Hanover, Germany.

Farrow, J.B., Ritchie, I.M., and Mangono, P. 1987. The reaction between reduced ilmenite and oxygen in ammonium chloride solution. *Hydrometallurgy*, vol. 18. pp. 21–38. https://doi.org/10.1016/0304-386X(87)90014-4

Fatollahi-Fard, F. and Pistorius, P.C. 2017. Comparison of methods for electrochemical iron removal from titanium ores. *Journal of Sustainable Metallurgy*, vol. 3, no. 4. pp. 711–719. https://doi.org/10.1007/s40831-017-0132-6

Gázquez, M.J., Bolívar, J.P., Garcia-Tenorio, R., and Vaca, F. 2014. A review of the production cycle of titanium dioxide pigment. *Materials Sciences and Applications*, vol. 5. pp. 441–458. https://doi.org/10.4236/msa.2014.57048

Gireesh, V.S., Vinod, V.P., Krishnan Nair, S., and Ninan, G. 2015. Catalytic leaching of ilmenite using hydrochloric acid: A kinetic approach. *International Journal of Mineral Processing*, vol. 134., pp. 36–40. https://doi.org/10.1016/j.minpro.2014.11.004

Grey, I., McDonald, K., Fisher-White, M., and de Vries, M. 2007. Hydrogen reduction of preoxidised ilmenite in fluidised bed and packed bed reactors. *Mineral Processing and Extractive Metallurgy*, vol. 116. pp. 209–216. https://doi.org/10.1179/174328507X198717

Mechanical activation and physicochemical factors

Guo, Y., Liu, S., Jiang, T., Qiu, G., and Chen, F. 2014. A process for producing synthetic rutile from Panzhihua titanium slag. *Hydrometallurgy*, vol. 147-148. pp. 134–141. https://doi.org/10.1016/j.hydromet.2014.05.009

Han, K.N., Rubcumintara, T., and Fuerstenau, M.C. 1987. Leaching behaviour of ilmenite with sulphuric acid. *Metallurgical Transactions B*, vol. 18. pp. 325–330.

Han, J., Zhang, J., Zhang, J., Chen, X., Zhang, L., and Tu, G. 2021. Extraction of vanadium and enrichment of titanium from modified Ti-bearing blast furnace slag. *Hydrometallurgy*, vol. 201. pp. 105577. https://doi.org/10.1016/j.hydromet.2021.105577. https://doi.org/10.1007/BF02656150

Hao, X., Lü, L., Liang, B., Li, C., Wu, P., and Wang, J. 2012. Solvent extraction of titanium from the simulated ilmenite sulphuric acid leachate by trialkylphosphine oxide. *Hydrometallurgy*, vol. 113-114. pp. 185–191. https://doi.org/10.1016/j.hydromet.2011.12.023

Haverkamp, R.G., Kruger, D., and Rajashekar, R. 2016. The digestion of New Zealand ilmenite by hydrochloric acid. *Hydrometallurgy*, vol. 163. pp. 198–203. https://doi.org/10.1016/j.hydromet.2016.04.015

Ismail, M.G.M.U., Amarasekera, J., and Kumarasinghe, J.S.N. 1983. The upgrading of ilmenite from Sri Lanka by the oxidation-reduction-leach process. *International Journal of Mineral Processing*, vol. 10, no. 2, pp. 161–164. https://doi.org/10.1016/03017516(83)90040-6

Jackson, M. and Dring, K. 2006. A review of advances in processing and metallurgy of titanium alloys. *Material Science and Technology*, vol. 22, no. 8, pp. 881–887. https://doi.org/10.1179/174328406X111147

Janssen, A. and Putnis, A. 2011. Processes of oxidation and HCl leaching of Tellnes ilmenite. *Hydrometallurgy*, vol. 109. pp. 194–201. https://doi.org/10.1016/j.hydromet.2011.07.004

Jayaweera, P.M., Jayaweera, P.V.V., Jayasundara, U.L., Jayaweera, C.D., Peiris, G.S., and Premalal, E.V.A.P. 2011. Photo induced reductive leaching of iron from ilmenite in hydrochloric acid solutions. *Mineral Processing and Extractive Metallurgy*, vol. 120. pp. 191–196. https://doi.org/10.1179/1743285511Y.0000000018

Jia, L., Liang, B., Lü, L., Yuan, S., Zheng, L., Wang, X., and Li, C. 2014. Beneficiation of titania by sulphuric acid pressure leaching of Panzhihua ilmenite. *Hydrometallurgy*, vol. 150., pp. 92–98. https://doi.org/10.1016/j.hydromet.2014.09.016

Jonglertjunya, W. and Rubcumintara, T. 2013. Titanium and iron dissolutions from ilmenite by acid leaching and microbiological oxidation techniques. *Asia-Pacific Journal of Chemical Engineering*, vol. 8, no. 3. pp. 323–330. https://doi.org/10.1002/apj.1663

Kataoka, S. and Yamada, S. 1973. Acid leaching upgrades ilmenite to synthetic rutile. *Chemical Engineering*, vol. 80, no. 7. pp. 92–93.

Kordzadeh-Kermani, V., Schaffie, M., Rafsanjani, H.H., and Ranjbar, M. 2020. A modified process for leaching of ilmenite and production of TiO2 nanoparticles. *Hydrometallurgy*, vol. 198. pp. 105507. https://doi.org/10.1016/j.hydromet.2020.105507

Kothari, N.C. 1974. Recent developments in processing ilmenite for titanium. *International Journal of Mineral Processing*, vol. 1. pp. 287–305. https://doi.org/10.1016/0301-7516(74)90001-5

Kuppusamy, V.K. and Holuszko, M. 2022. Sulfuric acid baking and water leaching of rare earth elements from coal tailings. *Fuel*, vol. 319. 123738. https://doi.org/10.1016/j.fuel.2022.123738

Kurlov, A.S. and Gusev, A.I. 2007. Effect of ball milling parameters on the particle size in nanocrystalline powders. *Technical Physics Letters*, vol. 33, no. 10. pp. 828–832. https://doi.org/10.1134/S1063785007100070

Lasheen, T.A.I. 2005. Chemical benefication of Rosetta ilmenite by direct reduction leaching. *Hydrometallurgy*, vol. 76. pp. 123–129. https://doi.org/10.1016/j.hydromet.2004.10.002

Li, C., Liang, B., and Guo, L.H. 2007. Dissolution of mechanically activated Panzhihua ilmenites in dilute solutions of sulphuric acid. *Hydrometallurgy*, vol. 89. pp. 1–10. https://doi.org/10.1016/j.hydromet.2007.04.002

Li, C., Liang, B., Song, H., Xu, J.Q., and Wang, X.Q. 2008. Preparation of porous rutile titania from ilmenite by mechanical activation and subsequent sulphuric acid leaching. *Microporous and Mesoporous Materials*, vol. 115. pp. 293–300. https://doi.org/10.1016/j.micromeso.2008.01.045

Li, C., Liang, B., and Wang, H.Y. 2008. Preparation of synthetic rutile by hydrochloric acid leaching of mechanically activated Panzhihua ilmenite. *Hydrometallurgy*, vol. 91. pp. 121–129. https://doi.org/10.1016/j.hydromet.2007.11.013

Li, Z., Wang, Z., and Li, G. 2016. Preparation of nano-titanium dioxide from ilmenite using sulphuric acid-decomposition by liquid phase method. *Powder Technology*, vol. 287. pp. 256–263. https://doi.org/10.1016/j.powtec.2015.09.008

Liu, X., Hu, M., Bai, C., and Lv, X. 2012. The electro-deoxidation process for ilmenite concentrate in molten salt. *Proceedings of the T.T. Chen Honorary Symposium on Hydrometallurgy, Electrometallurgy and Materials Characterization*. Wang, S., Dutrizac, J.E., Free, M.L., Hwang, J.Y., and Kim, D. (eds). Wiley, Hoboken, NJ. pp. 613–620.

Liu, Y., Qi, T., Chu, J., Tong, Q., and Zhang, Y. 2006. Decomposition of ilmenite by concentrated KOH solution under atmospheric pressure. *International Journal Mineral Processing*, vol. 81. pp. 79–84. https://doi.org/10.1016/j.minpro.2006.07.003

Liu, S., Zhu, K., Xiang, J., and Huang, P. 2015. Upgrading ilmenite by an oxidation-magnetic separation-pressure leaching process. *Bulg Chemical Communicable*, vol. 47. pp. 1118–1123.

Lv, W., Lv, X., Xiang, J., Zhang, Y., Li, S., Bai, C., Song, B., and Han, K. 2017. A novel process to prepare high-titanium slug by carbothermic reduction of pre-oxidized ilmenite concentrate with the addition of Na2SO4. *International Journal of Mineral Processing*, vol. 167. pp. 68–78. https://doi.org/10.1016/j.minpro.2017.08.004

Mahmoud, M.H.H., Afifi, A.A., and Ibarhim, I.A. 2004. Reductive leaching of ilmenite ore in hydrochloric acid for preparation of synthetic rutile. *Hydrometallurgy*, vol. 73. pp. 99–109. https://doi.org/10.1016/j.hydromet.2003.08.001

Manhique, A.J., Focke, W.W., and Madivate, C. 2011. Titania recovery from low-grade titanoferrous minerals. *Hydrometallurgy*, vol. 109. pp. 230–236. https://doi.org/10.1016/j.hydromet.2011.07.008

Mehdilo, A. and Irannajad, M. 2012. Iron removing from titanium slag for synthetic rutile production. *Physicochemical Problems in Mineral Processing*, vol. 48. pp. 425–439.

Merk, R. and Pickles, C.A. 1988. Reduction of ilmenite by carbon monoxide. *Canadian Metallurgical Quarterly*, vol. 27, no. 3. pp. 179–185. https://doi.org/10.1179/cmq.1988.27.3.179

Middlemas, S., Fang, Z.Z., and Fan, P. 2013. A new method for production of titanium dioxide pigment. *Hydrometallurgy*, vol. 131-132. pp. 107–113. https://doi.org/10.1016/j.hydromet.2012.11.002

Middlemas, S., Fang, Z.Z., and Fan, P. 2015. Life cycle assessment comparison of emerging and traditional titanium dioxide manufacturing processes. *Journal of Cleaner Production*, vol. 89. pp. 137–147. https://doi.org/10.1016/j.jclepro.2014.11.019

Morley, I.W. 1981. Black Sands: A History of the Mineral Sand Mining Industry in Eastern Australia. University of Queensland Press, St. Lucia, Qld.

Nagesh, C.R.V.S., Rao, C.S., Ballal, N.B., and Rao, P.K. 2004. Mechanism of titanium sponge formation in the Kroll reduction reactor. *Metallurgical and Materials Transactions B*, vol. 35. pp. 65–74. https://doi.org/10.1007/s11663-004-0097-2

Narayana, K.L., Swamy, K.M., Sarveswara, Rao, K., and Murty, J.S. 1997. Leaching of metals from ores with ultrasound. *Mineral Processing and Extractive Metallurgy Reviews*, vol. 16. pp. 239–259. https://doi.org/10.1080/08827509708914137

Navarrete, J.U., Cappelle, I.J., Schnittker, K., and Borrok, D.M. 2013. Bioleaching of ilmenite and basalt in the presence of iron-oxidizing and iron-scavenging bacteria. *International Journal of Astrobiology*, vol. 12, no. 2. pp. 123–134. https://doi.org/10.1017/S1473550412000493

Mechanical activation and physicochemical factors

Nayl, A.A. and Aly, H.F. 2009. Acid leaching of ilmenite decomposed by KOH. *Hydrometallurgy*, vol. 97. pp. 86–93. https://doi.org/10.1016/j.hydromet.2009.01.011

Nayl, A.A., Awwad, N.S., and Aly, H.F. 2009. Kinetics of acid leaching of ilmenite decomposed by KOH. Part 2. Leaching by H₂SO₄ and C₂H₂O₄. *Journal of Hazardous Materials*, vol. 168. pp. 793–799. https://doi.org/10.1016/j.jhazmat.2009.02.076

Nayl, A.A., Ismail, I.M., and Aly, H.F. 2009. Ammonium hydroxide decomposition of ilmenite slag. *Hydrometallurgy*, vol. 98. pp. 196–200. http://dx.doi.org/10.1016%2Fj.hydromet.2009.04.011

Nguyen, T.H. and Lee, M.S. 2018. A review on the recovery of titanium dioxide from ilmenite ores by direct leaching technologies. *Mineral Processing and Extractive Metallurgy Review*, vol. 40, no. 4. pp. 231–247. https://doi.org/10.1080/08827508.2018.1502668

Nurul, A. 2016. Chemical and electrochemical leaching studies of synthetic and natural ilmenite in hydrochloric acid solution. PhD thesis, Murdoch University, Perth, Western Australia.

Olanipekun, E. 1999. A kinetic study of the leaching of a Nigerian ilmenite ore by hydrochloric acid. *Hydrometallurgy*, vol. 53. pp. 1–10. https://doi.org/10.1016/S0304-386X(99)00028-6

Qi, T., Liu, Y.M., Chu, J.L., Li, H.J. and Li, Z.H. 2005. Preparation of potassium titanate using sub-molten salt method. CN patent 200510059715.5.

Rao, Y.K., Adjorlolo, A., and Haberman, J.H. 1982. On the mechanism of catalysis of the Boudouard reaction by alkali-metal compounds. *Carbon*, vol. 20. pp. 207–212. https://doi.org/10.1016/0008-6223(82)90022-7

Razieh, R. 2014. Production of nanosized synthetic rutile from ilmenite concentrate by sonochemical HCl and H₂SO₄ leaching. *Iran Journal Chemical Engineering*, vol. 33. pp. 29–36. https://dx.doi.org/10.30492/ijcce.2014.10749

Ren, R., Yang, Z., and Shaw, L.L. 2000. Polymorphic transformation and powder characteristics of TiO₂ during high energy milling. *Journal of Materials Science,* vol. 35. pp. 6015–6026. https://doi.org/10.1023/A:1026751017284

Robinson, M., Clamp, F., Mobbs, D.B., and Pearse, R.V. 1977. The Laporte high-efficiency ilmenite beneficiation process. *Advances in Extractive Metallurgy*. Jones, M.J. (ed.). *Institution of Mining and Metallurgy*, London. pp. 89–96.

Roche, E.G., Stuart, A.D., and Grazier, P.E. 2004. Production of titania. WO patent 2004035841-A1.

Run, H., Pengsheng, L., Yuehui, Y., and Jinzhu, Z. 2017. Vacuum carbothermic reduction of Panzhihua ilmenite concentrate: A thermodynamic study. *Mineral Processing and Extractive Metallurgy Reviews*, vol. 38. pp. 193–198. https://doi.org/10.1080/08827508.2017.1281129

Samal, S. 2011. The dissolution of iron in the hydrochloric acid leach of titania slag obtained from plasma melt separation of metalized ilmenite. *Chemical Engineering Researcher Design*, vol. 89. pp. 2190–2193. https://doi.org/10.1016/j.cherd.2011.01.026

Sarker, M.K., Rashid, A.K.M.B., and Kurny, A.S.W. 2006. Kinetics of leaching of oxidized and reduced ilmenite in dilute hydrochloric acid solutions. *International Journal of Mineral Processing*, vol. 80. pp. 223–228. https://doi.org/10.1016/j.minpro.2006.04.005

Sasikumar, C., Rao, D.S., Srikanth, S., Mukhopadhyay, N.K., and Mehrotra, S.P. 2007. Dissolution studies of mechanically activated Manavalakurichi ilmenite with HCl and H₂SO₄. *Hydrometallurgy*, vol. 88. pp. 154–169. https://doi.org/10.1016/j.hydromet.2007.03.013

Sasikumar, C., Rao, D.S., Srikanth, S., Ravikumar, B., Mukhopadhyay, N.K., and Mehrotra, S.P. 2004. Effect of mechanical activation on the kinetics of sulphuric acid leaching of beach sand ilmenite from Orissa, India. *Hydrometallurgy*, vol. 75. pp. 189–204. https://doi.org/10.1016/j.hydromet.2004.08.001

Shahien, M.G., Khedr, M.M.H., Maurice, A.E., Farghali, A.A., and Ali, R.A.M. 2015. Synthesis of high purity rutile nanoparticles from medium-grade Egyptian natural ilmenite. *Journal of Basic and Applied Sciences*, vol. 4. pp. 207–213. http://dx.doi.org/10.1016/j.bjbas.2015.05.013

Shi, J., Qiu, Y., Yu, B., Xie, X., Dong, J., Hou, C., Li, J., and Liu, C. 2022. Titanium extraction from titania-bearing blast furnace slag: A review. *Journal of the Minerals, Metals & Materials Society*, vol. 74. pp. 654–667. https://doi.org/10.1007/s11837-021-05040-y

Shojaei, V., Schaffie, M., Mohebbi, A., and Ranjbar, M. 2014. Upgrading of ilmenite using KOH sub-molten salt process assisted by mechanical activation. *Materials and Manufacturing Processes*, vol. 29. pp. 1284–1288. https://doi.org/10.1080/10426914.2014.941485

Singh, K.K., Kishor, B., and Mankhand, T.R. 2018. Reduction of Manavalakurichi ilmenite by activated charcoal in presence of catalyst. *Transactions of Indian Institute of Metals*, vol. 71, no. 12. pp. 2993–3001. https://doi.org/10.1007/s12666-018-1400-2

Sinha, H.N. 1973. MURSO process for producing rutile substitute. *Titanium Science and Technology*. Springer, Boston, MA. pp. 233–245.

Subasinghe, H.C.S. and Ratnayake, A.S. 2021. Processing of ilmenite into synthetic rutile using ball milling induced sulphurisation and carbothermic reduction. *Minerals Engineering*, vol. 173. pp. 107197. https://doi.org/10.1016/j.mineng.2021.107197

Subasinghe, H.C.S. and Ratnayake, A.S. 2022. General review of titanium ores in exploitation: present status and forecast. *Comunicações Geológicas*, vol. 109. pp. 21–31. https://doi.org/10.34637/aab4-mk81

Subasinghe, C.S., Ratnayake, A.S., Roser, B., Sudesh, M., Wijewardhana, D.U., Attanayake, N., and Pitawala, J. 2022. Global distribution, genesis, exploitation, applications, production, and demand of industrial heavy minerals. *Arabian Journal of Geosciences*, vol. 15. pp. 1–28. https://doi.org/10.1007/s12517-022-10874-0

Sui, L.L. and Zhai, Y.C. 2014. Reaction kinetics of roasting high-titanium slag with concentrated sulphuric acid. *Transactions of the Nonferrous Metals Society of China*, vol. 24. pp. 848–853. https://doi.org/10.1016/S1003-6326(14)63134-4

Suzuki, R.O., Teranuma, K., and Ono, K. 2003. Calciothermic reduction of titanium oxide and in-situ electrolysis in molten CaCl₂. *Metallurgical and Materials Transactions B*, vol. 3. pp. 287–295. https://doi.org/10.1007/s11663-003-0074-1

Swamy, K.M., Sarveswara, Rao, K., Narayana, K.L., Murty, J.S., and Ray, H.S. 1995. Application of ultrasound in leaching. *Mineral Processing and Extractive Metallurgy Reviews*, vol. 14. pp. 179–192. https://doi.org/10.1080/08827509508914124

Takeda, O., Ouchi, T., and Okabe, T.H. 2020. Recent progress in titanium extraction and recycling. *Metallurgical and Materials Transactions B*, vol. 51, no. 4. pp. 1315–1328. https://doi.org/10.1007/s11663-020-01898-6

Takenaka, T., Suzuki, T., Ishikawa, M., Fukasawa, E., and Kawakami, M. 1999. The new concept for electrowinning process of liquid titanium metal in molten salt. *Electrochemistry*, vol. 67, no. 6. pp. 661–668. https://doi.org/10.5796/electrochemistry.67.661

Tan, P., Hu, H.P., and Zhang, L. 2011. Effects of mechanical activation and oxidation-reduction on hydrochloric acid leaching of Panxi ilmenite concentration. *Transactions of the Nonferrous Metals Society of China*, vol. 21. pp. 1414–1421. https://doi.org/10.1016/S1003-6326(11)60875-3

Tao, T., Chen, Q.Y., Hu, H.P., Yin, Z.L., and Chen, Y. 2012. TiO₂ nanoparticles prepared by hydrochloric acid leaching of mechanically activated and carbothermic reduced ilmenite. *Transactions of the Nonferrous Metals Society of China*, vol. 22. pp. 1232–1238. https://doi.org/10.1016/S1003-6326(11)613101

Taylor, 1976. Process for ilmenite ore reduction. US patent 3,966,455.

Tripathy, M., Srinivasan, T., and Mehrota, S.P. 2012. Investigations on reduction of ilmenite ore with different sources of carbon. *IMM Transactions Section C: Mineral Processing and Extractive Metallurgy*, vol. 121, no. 3. pp. 147-155. doi: 10.1179/1743285512Y.0000000007

Tromans, D. and Meech, J.A. 2001. Enhanced dissolution of minerals: stored energy, amorphism and mechanical activation. *Minerals Engineering*, vol. 14. pp. 1359–1377. https://doi.org/10.1016/S0892-6875(01)00151-0

Van Dyk, J.P., Vegter, N.M., and Pistorius, P.C. 2002. Kinetics of ilmenite dissolution in hydrochloric acid. *Hydrometallurgy*, vol. 65. pp. 31–36. https://doi.org/10.1016/S0304-386X(02)00063-4

Mechanical activation and physicochemical factors

Vásquez, R. and Molina, A. 2008. Leaching of ilmenite and pre-oxidized ilmenite in hydrochloric acid to obtain high grade titanium dioxide. *International Journal of Mineral Processing*, vol. 68. pp. 13–21.

Vásquez, R. and Molina, A. 2012. Effects of thermal preoxidation on reductive leaching of ilmenite. *Minerals Engineering*, vol. 39. pp. 99–105. https://doi.org/10.1016/j.mineng.2012.05.003

Verhulst, D., Sabachy, B., Spitler, T., and Prochazka, J. 2003. New developments in the Altair hydrochloride TiO₂ pigment process. *Hydrometallurgy 2003 Proceedings of the 5th International Conference in Honour of Professor Ian M. Ritchie*, Vancouver, BC. Vol. 1. TMS, Warrendale, PA. pp. 565–575.

Wang, J. and Lin, Z. 2010. Dye-sensitized TiO₂ nanotube solar cells with markedly enhanced performance *via* rational surface engineering. *Chemistry of Materials*, vol. 22, no. 2. pp. 579–584. https://doi.org/10.1021/cm903164k

Wang, X., Li, W., Yang, B., Guo, S., Zhang, L., Chen, G., Peng, J., and Luo, H. 2014. Microwave-absorbing of carbothermic reduced products of ilmenite and oxidized ilmenite. *Journal of Microwave Power and Electromagnetic Energy*, vol. 48. pp. 192–202. https://doi.org/10.1080/08327823.2014.11689883

Wang, X., Li, X., Wang, Z., Wu, L., Yue, P., Guo, H., Wu, F., and Ma, T. 2010. Preparation and characterization of Li₄Ti₅O₁₂ from ilmenite. *Powder Technology*, vol. 204. pp. 198–202. https://doi.org/10.1016/j.powtec.2010.07.030

Wang, Y. and Yuan, Z. 2006. Reductive kinetics of the reaction between a natural ilmenite and carbon. *International Journal of Mineral Processing*, vol. 81, no. 3. pp. 133–140. https://doi.org/10.1016/j.minpro.2006.07.010

Wang, Y.M., Yuan, Z.F., Guo, Z.C., Tan, Q.Q., Li, Z.Y., and Jiang, W.Z. 2008. Reduction mechanism of natural ilmenite with graphite. *Transactions of the Nonferrous Metals Society of China*, vol. 18. pp. 962–968. https://doi.org/10.1016/S1003-6326(08)60166-1

Wei, L., Hu, H., Chen, Q., and Tan, J. 2009. Effects of mechanical activation on the HCl leaching behaviour of plagioclase, ilmenite and their mixtures. *Hydrometallurgy*, vol. 99. pp. 39–44. https://doi.org/10.1016/j.hydromet.2009.06.003

Welham, N.J. 1996. A parametric study of the mechanically activated carbothermic reduction of ilmenite. *Minerals Engineering*, vol. 9, no. 12. pp. 1189–1200. https://doi.org/10.1016/S0892-6875(96)00115-X.

Welham, N.J. and Llewellyn, D.J. 1988. Mechanical enhancement of the dissolution of ilmenite. *Minerals Engineering*, vol. 11, no. 9. pp. 827–841. https://doi.org/10.1016/S0892-6875(98)00070-3

Welham, N.J. and Williams, J.S. 1999. Carbothermic reduction of ilmenite (FeTiO₃) and rutile (TiO₂). *Metallurgical and Materials Transactions B*, vol. 30, no. 6. pp. 1075–1081. https://doi.org/10.1007/s11663-999-0113-7

Wijewardhana, T.D.U., Subasinghe, H.C.S., and Ratnayake, A.S. 2021. Value addition to ilmenite using carbonized waste coconut shells: A mechanochemical approach aided with powdered seashells as a rate raiser. *Mining, Metallurgy & Exploration*, vol. 38, no. 3. pp. 1573-1587. https://doi.org/10.1007/s42461-021-00420-z

Wu, F., Li, X., Wang, Z., Wu, L., Guo, H., Xiong, X., Zhang, X., and Wang, X. 2011a. Hydrogen peroxide leaching of hydrolysed titania residue prepared from mechanically activated Panzhihua ilmenite leached by hydrochloric acid. *International Journal of Mineral Processing*, vol. 98. pp. 106–112. https://doi.org/10.1016/j.minpro.2010.10.013

Wu, F., Li, X., Wang, Z., Guo, H., Wu, L., Xiong, X., and Wang, X. 2011b. Preparation of TiO₂ nanosheets and LiTi₅O₁₂ anode material from natural ilmenite. *Powder Technology*, vol. 213. pp. 192–198. https://doi.org/10.1016/j.powtec.2011.07.034

Wu, Z., Liang, Y., Fu, E., Du, J., Wang, P., Fan, Y., and Zhao, Y. 2018. Effect of ball milling parameters on the refinement of tungsten powder. *Metals*, vol. 8, no. 4. pp. 281. https://doi.org/10.3390/met8040281

Xie, R. and Shang, J.K. 2007. Morphological control in solvothermal synthesis of titanium oxide. *Journal of Materials Science*, vol. 42. pp. 6583–6589. https://doi.org/10.1007/s10853-007-1506-0

Xiong, X., Wang, Z., Wu, F., Li, X., and Guo, H. 2013. Preparation of TiO₂ from ilmenite using sulphuric acid decomposition of the titania residue combined with separation of Fe³⁺ with EDTA during hydrolysis. *Advanced Powder Technology*, vol. 24. pp. 60–67. https://doi.org/10.1016/j.apt.2012.02.002

Xue, T., Wang, L., Qi, T., Chu, J., Qu, J., and Liu, C. 2009. Decomposition kinetics of titanium slag in sodium hydroxide system. *Hydrometallurgy*, vol. 95. pp. 22–27. https://doi.org/10.1016/j.hydromet.2008.04.004

Zhang, L., Hu, H., Wei, L., Chen, Q., and Tan, J. 2010. Hydrochloric acid leaching behaviour of mechanically activated Panxi ilmenite (FeTiO₃). *Separation and Purification Technology*, vol. 73. pp. 173–178. https://doi.org/10.1016/j.seppur.2010.03.022

Zhang, P., Jia, D., Yang, Z., Duan, X., and Zhou, Y. 2013. Influence of ball milling parameters on the structure of the mechanically alloyed SiBCN powder. *Ceramics International*, vol. 39, no. 2. pp. 1963–1969. https://doi.org/10.1016/j.ceramint.2012.08.047

Zhang, G. and Ostrovski, O. 2001. Reduction of ilmenite concentrates by methane containing gas: Part I. Effects of ilmenite composition, temperature and gas composition. *Canadian Metallurgical Quarterly*, vol. 40, no. 3. pp. 317–326. https://doi.org/10.1179/cmq.2001.40.3.317

Zhang, G. and Ostrovski, O. 2002. Effect of preoxidation and sintering on properties of ilmenite concentrates. *International Journal of Mineral Processing*, vol. 64, no. 4. pp. 201–218. https://doi.org/10.1016/S0301-7516(01)00055-2

Zhang, S. and Nicol, M.J. 2010. Kinetics of the dissolution of ilmenite in sulphuric acid solutions under reducing conditions. *Hydrometallurgy*, vol. 103. pp. 196–204. https://doi.org/10.1016/j.hydromet.2010.03.019

Zhang, W., Zhu, Z., and Cheng, C.Y. 2011. A literature review of titanium metallurgical processes. *Hydrometallurgy*, vol. 108. pp. 177–188. https://doi.org/10.1016/j.hydromet.2011.04.005

Zhang, F.L., Zhu, M., and Wang, C.Z. 2008. Parameters optimization in the planetary ball milling of nanostructured tungsten carbide/cobalt powder. *International Journal of Refractory Metals and Hard Materials*, vol. 26, no. 4. pp. 329–333. https://doi.org/10.1016/j.ijrmhm.2007.08.005

Zhao, Y. and Shadman, F. 1990. Kinetics and mechanism of ilmenite reduction with carbon monoxide. *AIChE Journal*, vol. 36, no. 9. pp. 1433–1438. https://doi.org/10.1002/aic.690360917

Zhu, Q., Zhang, J., and Li, H. 2014. Influence of phase and microstructure on the rate of hydrochloric acid leaching in pretreated Panzhihua ilmenite. *Particuology*, vol. 14. pp. 83–90. https://doi.org/10.1016/j.partic.2013.08.002

Zhu, Z., Zhang, W., and Cheng, C.Y. 2011. A literature review of titanium solvent extraction in chloride media. *Hydrometallurgy*, vol. 105. pp. 304–313. https://doi.org/10.1016/j.hydromet.2010.11.006 ◆