Environmental impact of ilmenite from mines to product.

Bachelor Thesis in mechanical engineering

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Cover: Raw ilmenite ore. (Lavinsky, n.d.)

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Abstract

Currently titanium is considered scarce, thus it is imperative to effectives the current use of titanium rich ores such as ilmenite. Based on a review of the gathered information, calculation and flowcharts a probable solution for the effectivization of ilmenite usage is by combining flows of two existing ilmenite processes. The effect of which will make ilmenite usage more sustainable and in turn better for the environment. Oxygen carrier aided combustion (OCAC) and titanium dioxide (TiO_2) production are two processes that could potentially be combined. The outcome of the combined process is that greater amount of waste in mass is accumulated overall both in the ilmenite processes and emissions from transportation. However, less titanium ends up as waste in combined flow in comparison to the singular flow. Further studies are needed in order to establish if the reduction in usage of titanium outweighs the increase of overall emissions from a sustainability frame of reference.

Sammandrag

För närvarande anses titan vara knappt, så det är absolut nödvändigt att effektivisera den nuvarande användningen av titanrika malmer som ilmenit. Baserat på en genomgång av den samlade informationen, beräkningen och flödesscheman är en sannolik lösning för effektivisering av ilmenit användning genom att kombinera flöden av två befintliga ilmenit processer. Effekten av detta kommer att göra användningen av ilmenit mer hållbar och i sin tur bättre för miljön. Oxygen carrier aided combustion (OCAC) och titandioxid (TiO_2) produktion är två processer som kan potentiellt kombineras. Resultatet av den kombinerade processen är att större mängd avfall i massa samlas totalt sett både i ilmenit processerna och utsläpp från transporter. Mindre titan hamnar dock som avfall i kombinerat flöde jämfört med singelflödet. Ytterligare studier behövs för att fastställa om minskningen av användningen av titan uppväger ökningen av de totala utsläppen från en hållbarhetsram.

Acknowledgements

We would like to express our appreciation towards Pavelta Knutson, Martina Petranikova Fredrik Lind and Bo Leckner. Their constant counseling, resource and kindness allowed the makings of this project. A special mention towards Pavleta Knutsson, our supervisor and mentor, for having the patience and strength of helping us through the struggle of the current pandemic. We would also like to mention our family and friends that motivated us through this remarkable journey.

Hussein Abbas & James Andrén, Gothenburg, June 2021

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Abbreviations

C	Carbon
CFB	Circulating fluidized bed
Cl	Chlorine
Cl_2	Chlorine gas
CO	carbon monoxide
CO_2	Carbon dioxide
Fe	Iron
Fe_2+	Ferrous ion
Fe_3+	Ferric ion
$FeTiO_3$	Ilmenite
Fe_2TiO_5	Pseudobrookite
$Fe_2(SO_4)_3$	Ferric sulphate
H	Hydrogen
H_2O	Water
HCl	Hydrochloric acid
H_2SO_4	Sulphuric acid
LCA	Life-cycle analysis
NH_4Cl	Ammonium chloride
O_2	Oxygen
OCAC	Oxygen carrier aided combustion
S	Sulphur
TiO_2	Titanium dioxide
Ti	Titanium
$TiCl_4$	Titanium tetrachloride
$TiO\ (OH)_2$	hydrous titanium oxide
$TiOSO_4$	Titanium oxide sulphate

1 Introduction

1.1 Background

The current society consumes more and more products, and the result is more emissions and depletion of resources. One such resource that is currently being depleted is titanium, which is an element constituent in the mineral ilmenite (European Commission, 2017). As a result of the observed scarcity of titanium and ilmenite, effective use of the mineral is imperative. Currently 95% of ilmenite is used by industries to produce titanium dioxide (*Titanium Statistics and Information*, 2021). Ilmenite is either used directly as feed stock for titanium dioxide ($\mathrm{TiO_2}$) production processes or it is pre-treated to produce titanium slag and synthetic rutile that are further used as feed stock (Middlemas et al., 2015).

There are two main processes that are used today for $\mathrm{TiO_2}$ production, namely the chloride and sulphate method. The chloride method used for producing titanium dioxide is more energy intensive due to the need for ore pre-treatment. The sulphate method uses ilmenite directly as feed stock and does not require pre-treatment. However, the chloride process is potentially more environmentally friendly because it is performed as a closed system, which prevents leakage of gas products or reactants, e.g., chlorine (Cl_2), which can be harmful to the environment. In the sulphate method one does not recycle the acid which leads to higher material waste flows and thus a greater impact on the environment. Oxygen carrier aided combustion (OCAC),), represents a new technique used for heat and electricity production using fluidized bed technology. In OCAC conventionally used silica sand is replaced with ilmenite as bed material. As a result, in addition to the $\mathrm{TiO_2}$ production industry, more ilmenite is needed as a resource, and further amounts of waste in form of deactivated ilmenite that is landfilled (Gyllén, A. 2019).

According to EU waste management hierarchy developed within the Waste Framework Directive *(Waste Framework Directive, 2021),* disposal/landfill is considered as the least environmentally friendly solution. As the existing solution for recirculating ilmenite and its reuse are not sufficient to totally avoid waste streams in form of deactivated ilmenite, an additional solution can possibly be is to investigate the deactivated ilmenite as a potential source for production. The latter option is considered as possible as the deactivated ilmenite still contains relatively high levels of Ti in its mineral structure. Such a solution would allow to unite the two separate flows of ilmenite (for $\mathrm{TiO_2}$ production and for OCAC) into a single flow of ilmenite where the mined ore is first used for heat and power production and the deactivate material is further used as a resource for the TiO_2 production. In order to achieve singular flow, the mineral needs to go from the mine to fluidized bed boiler and then further to production. The thesis will focus primarily on analysing the flow of ilmenite on a high-level overview and low-level. The low-level will focus on the processes and usage of ilmenite while the high-level will focus on the distribution from the mines to the different production facilities. Because of the changes in the flow of ilmenite to a single flow, in-depth material analysis, as well as analysis on transportation and distribution of ilmenite are needed which are not included in the scope of the present thesis.

1.2 Aim

The present thesis aims to unite two processes that are totally separated today and to find a way to optimize the material flow of ilmenite so that a circular economy for ilmenite use can be reached. The obtained data from the thesis can be used as a building block to further support the development of synergies between processes as more sustainable solutions in industries.

1.3 Limitation

This thesis will not include a physical model. The results given in the thesis are based on current theories, models, reports/interview. Most of the information gathering was done on distance due to the pandemic situation of covid-19. Even contacting various companies or researchers was done in distance form through email or phone call. Most of the calculations on the flow chart were based on chemical process calculation without taking in considerations of process losses. Thus, in the present's thesis no impurities in the raw material or alternative reaction pathways have been considered. Material “waste” generated from the flow chart of processes are considered waste in the thesis. The thesis does not consider for further recycle and reuse of material waste generated. This is to keep the thesis focused on the ilmenite processes. Assumption is made due to limited (no)access to a laboratory or facility for research due to covid-19.

1.4 Specification of issues under investigation

There are three questions that the thesis addresses. Those three are:

- Potential solutions for sustainability regarding future ilmenite usage?

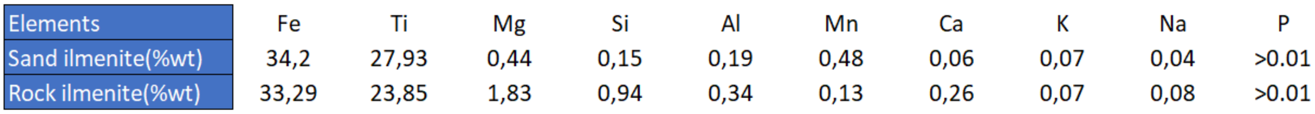
- Emissions and energy usage from current and future processes of ilmenite?
- Current ilmenite emission and improvements regarding that?

2 Theoretical backgrounds

This chapter will go through the data and information collected for the thesis. The chapter includes description of ilmenite as a mineral- structure, global consumption, and production. The chapter also goes through the most common application of ilmenite and alternative application as an oxygen carrier. This part will also explain the principles of LCA (Life Cycle Assessment), which is commonly used method to determine the environmental impact of a process by looking at the included material energy flows. The results are used to determine the sustainable use of ilmenite.

2.1 Ilmenite as a mineral – structure, global consumption and production

Ilmenite was discovered in 1790s by William Gregor who treated it using hydrochloric acid in order to dissolve the contained in ilmenite iron oxide. After further treatment, Gregor discovered also the presence of titanium dioxide (TiO_2) (Reck & Richards, 1999). Ilmenite is found in nature either as sand ilmenite or rock ilmenite where both are denoted by the dominating in them chemical phase – $FeTiO_3$. The difference between the two materials is that sand ilmenite has been exposed to weathering and is therefore more eroded than the rock ilmenite that is mined and crushed prior to use.



Elements	Fe	Ti	Mg	Si	Al	Mn	Ca	K	Na	P
Sand ilmenite(%wt)	34,2	27,93	0,44	0,15	0,19	0,48	0,06	0,07	0,04	>0.01
Rock ilmenite(%wt)	33,29	23,85	1,83	0,94	0,34	0,13	0,26	0,07	0,08	>0.01

Table 1. *Elemental composition of sand and rock ilmenites, Corcoran et al. (2018)*

Comparing the two ilmenites elemental composition (seen in table 1) (Corcoran et al., 2018) we can see in table 1 that sand ilmenite has a higher titanium (Ti) content in proportion to the iron (Fe) content than the rock ilmenite. One of the most common modern use of ilmenite in production is to create pigment. Titanium dioxide pigment production is reliant on the Ti content of the mineral and thus sand ilmenite could potentially be more beneficial for the production of pigment. The usage of ilmenite for pigment production started in 1916 to produce titanium dioxide for white pigment and has since been the primary use of ilmenite (*About Us – KRONOS Ecochem*, n.d.). Further subchapters will explore further the current production of ilmenite and the consumption of ilmenite in the form of TiO_2 production.

2.1.1 Production

Ilmenite is mined in most parts of the world, as seen in figure 1 where its largest producers are China, South Africa, and Australia. In the majority of cases the production of ilmenite is correlated with the amount of ilmenite in reserves. However, this is not true for all the countries extracting ilmenite. According to Mohapatra et al. (Mohapatra, 2015) the reason that India, a country with a large ilmenite reserves, does not have a large production, is due to a lack of awareness. This could very well be true for the other countries with unextracted reserves of ilmenite such as Brazil.

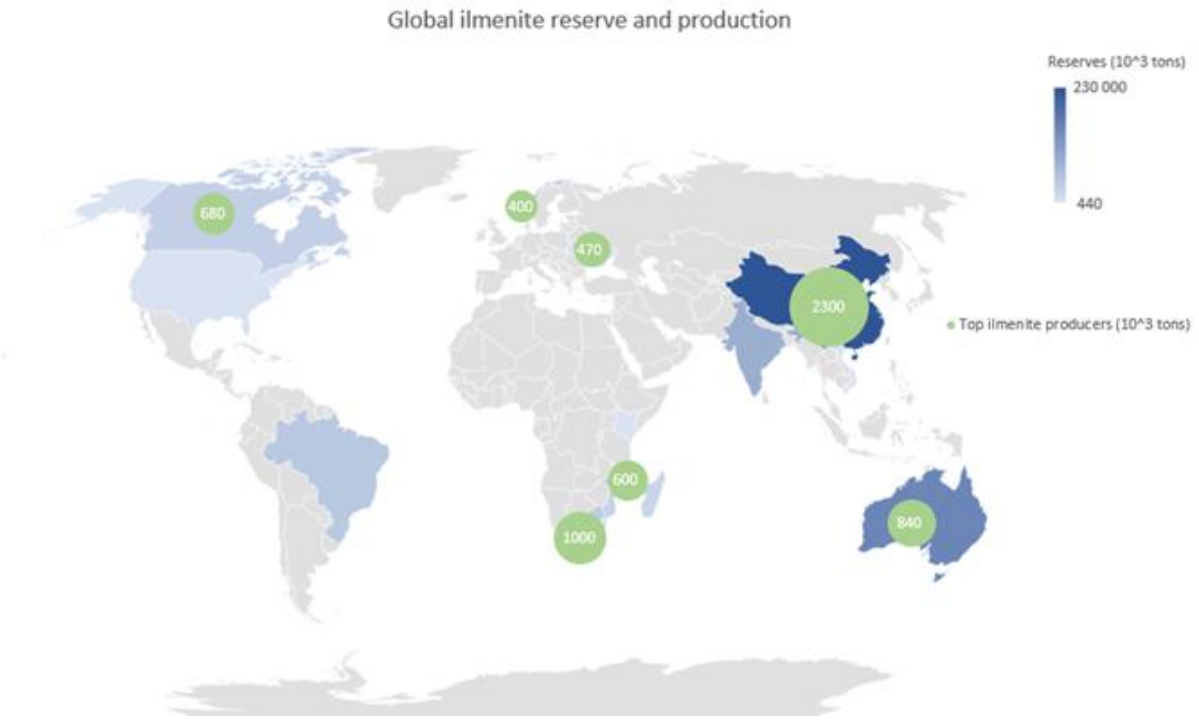


Figure 1. *Global ilmenite reserve and production*

Note. The data is from TITANIUM MINERAL CONCENTRATES (USGS, 2021)

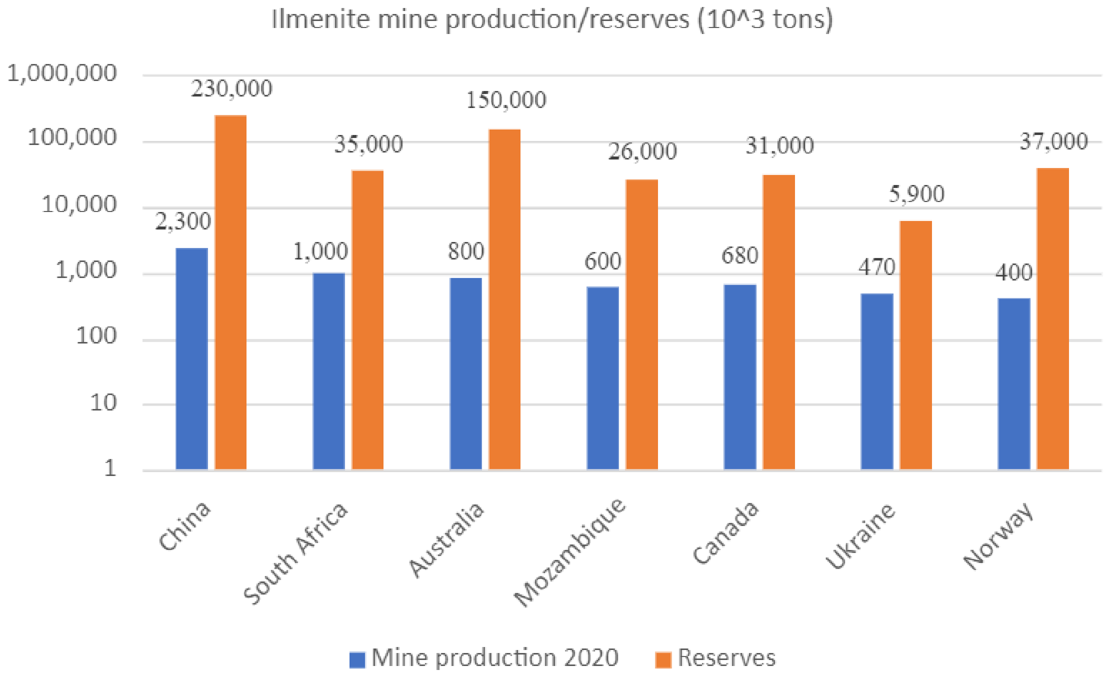


Figure 2. This diagram demonstrates a combination of mine production in 2020 and reserves for leading countries in ilmenite reserves.

Note. The data is from TITANIUM MINERAL CONCENTRATES (USGS, 2021)

The figures above (Figure 1 and 2) show where the leading countries in mine production and ilmenite reserves are located, and how much ilmenite they are producing. More detailed data for the leading countries on recent ilmenite increase/decrease, associated worldwide companies, mine settlement, and processing plants for ilmenite production is briefly explained down below:

China- The largest ilmenite reserve in the world is in Sichuan province of southwest China. This ilmenite reserve is registered to be over 90% of Chinas ilmenite resources and more than 35% of the world ilmenite reserve (Chen & Xiong, 2015). China is the leading producer of ilmenite yielding up to 2300 000 tons in 2020 (Gambogi, 2021).

Australia- The second-largest ilmenite reserve in the world is located in Australia, with an approximated reserve of 150-million-ton ilmenite (Gambogi, 2021). Australia exports fresh ilmenite to around 25 countries including China, United States and Saudi Arabia (*Mineral Sands*, 2018). The leading company in Australia is Tronox and owns 6 production facilities, there of them are operating mines. The first mine is located in Cataby western Australia and the second mine one in Murray Basin, Australia (Global Locations – Tronox, 2021). In 2019 the Cooljarloo Mine located in Cataby, had a life span of 8.5 year and was expected to produce 200 000 t/yr of chloride-grade ilmenite (Bedinger, 2020). Chandala Processing plant in western Australia is where the produced ilmenite is transported for processing (Global Locations – Tronox, 2021).

South Africa- In 2017 Mineral Commodities Ltd.'s produced 217 000-ton ilmenite concentrate, and in 2020 the amount of ilmenite concentrate increased drastically with a value of one million tons (Bedinger, 2020). Some of the mine settlements in South Africa is owned by the American chemical company Tronox Ltd.

In KwaZulu-Natal (KZN) on the east coast of South Africa, Tronox Ltd. owns a Fair breeze mine and in 2015 the first payload of titanium-rich ore was conveyed. Tronox possesses another mine located in Namakwa, South Africa (Global Locations – Tronox, 2021), the main purpose of this mine is to produce titanium dioxide feedstock, both these mines contain a total amount of 54.7 Mt heavy minerals. In 2017 Tronox decreased its reserve at the mines located in KwaZulu-Natal and Namakwa by 5.9 % (Bedinger, 2020). Tronox Ltd. Is an American chemical company, with worldwide production facilities, and most of the ilmenite produced in South Africa is distributed to American TiO_2 production facilities (Global Locations – Tronox, 2021).

Mozambique- In 2017 Kenmare Resources plc produced 998 000 t of ilmenite with an increase of 11 % compared to 2016, due to developed dredge and dry mining techniques. Recently Mozambique production decreased to 600 000 tons (Bedinger, 2020).

Canada-Recently Argex Titanium located in Quebec was developing a new form of technology for production of chloride-based TiO_2 pigments and the total production development should be observed by 2020. The new developed production produced 840 000-ton ilmenite in 2020 (Bedinger, 2020).

Ukraine- In 2017 Velta LCC produced 215 000 tons of ilmenite concentrate from Byrzulivske Mine, and in the same year Velta LLC and the Commercial Metals Co. signed a memorandum to build a mine at the Likarivske deposit in the Kirovohrad region that was planned to produce 217 000 t/yr of ilmenite. Recently Ukraine production increased to 417 000 tons (Bedinger, 2020).

Norway- Tellnes mine is one of the biggest titanium/ilmenites mine in Europe and has an estimated annual production of 550 000 tons of ilmenite. Norway produces 5% of the total ilmenite production in the world and has 15% of the total ilmenite reserves in the world. In 2020 Norway's ilmenite production have somewhat decreased to 400 000 tons (KORNELIUSSEN et al., 2000).

Most of the ilmenite produced from the reserves mentioned above is distributed to countries with TiO_2 production facilities. The next subchapter 2.1.2 will introduce prominent consumers of ilmenite and distribution to the leading TiO_2 production facilities.

2.1.2 Consumption

Around 95% of all the ilmenite consumption globally goes to the production of titanium pigment that is used in industries for plastic, paint, paper, etc. Titanium dioxide pigment consumption has an increase of 4.1% per year and the usage of titanium dioxide is closely tied to the living standard of the country (Mineral Sands Industry Information, 2019).

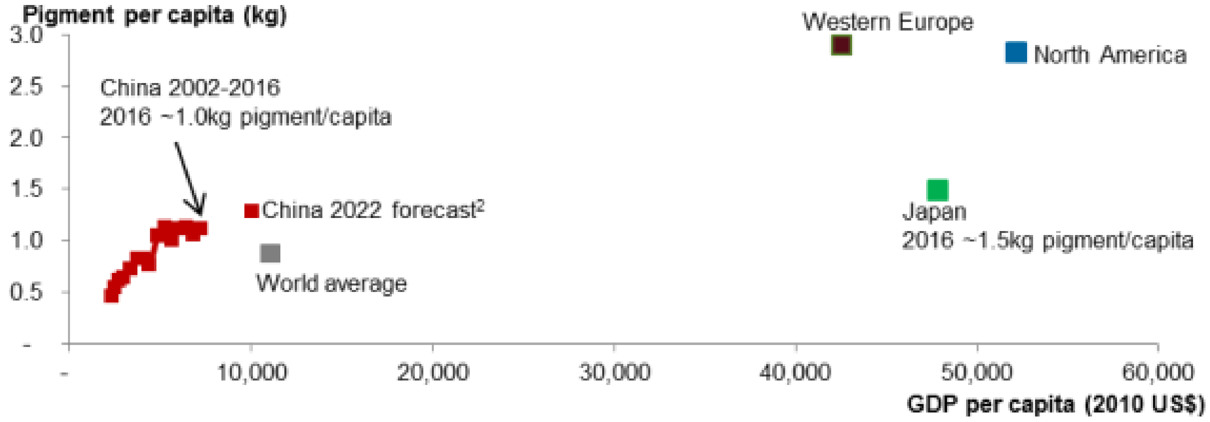


Figure 3. *GDP (Gross Domestic Product) per capita and pigment per capita*

(Mineral Sands Industry Information, 2019)

Countries with more consumer-based goods use a higher degree of titanium dioxide per capita (Figure 3). The leading consumer and producer of titanium pigment globally is China (Mineral Sands Industry Information, 2019). Despite the high level of production and consumption of pigment China is still consuming less titanium pigment per capita than geographic locations with higher living standards such as North America, Western Europe, and Japan. This could be due to multiple factors such as abundance in domestic resource of ilmenite or the rate of increase of consumption. For most cases the high standard of living leads to a higher TiO_2 production, as we can see in Figure 4,

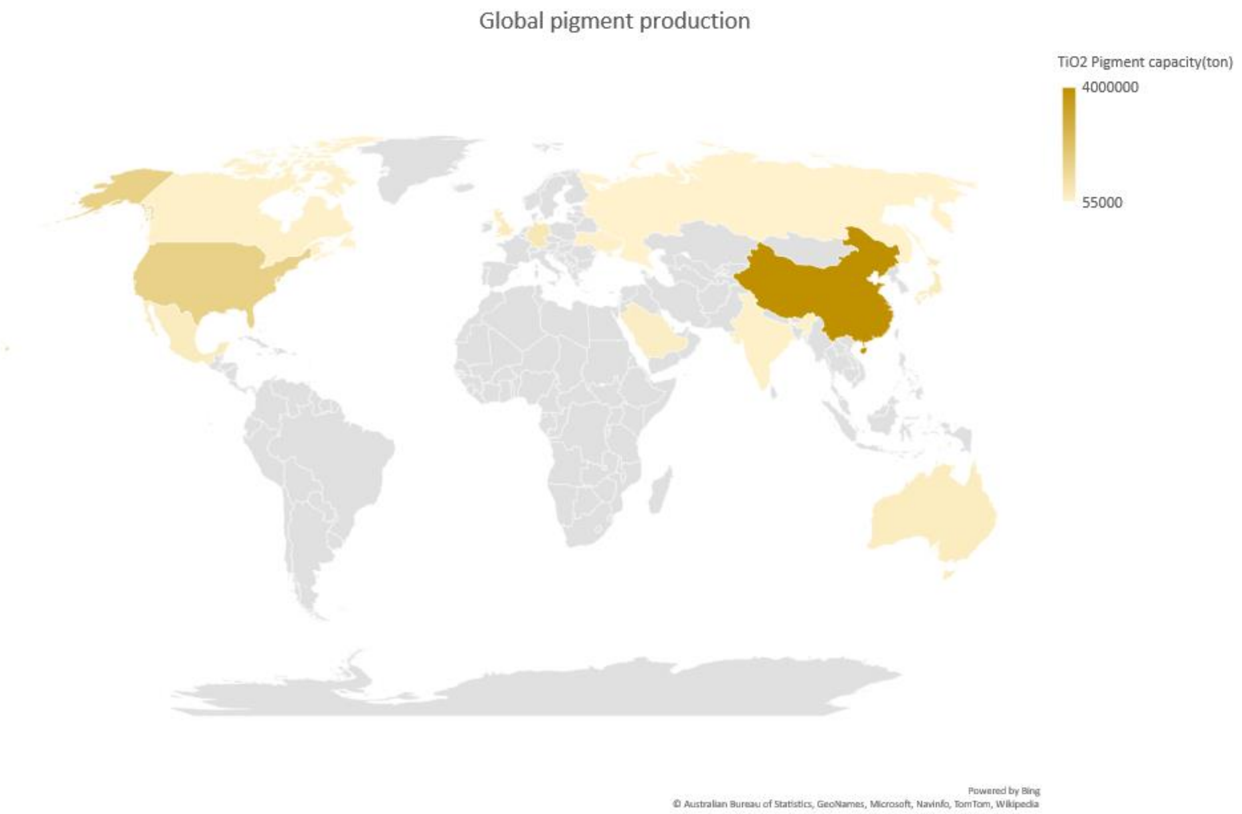


Figure 4. Global capacity of TiO_2 pigment production, and countries coloured with stronger contrast have the leading production.

Note. The data is from TITANIUM AND TITANIUM DIOXIDE (USGS, 2021)

where the leading countries in TiO_2 production are located, and how much TiO_2 they are producing. The more detailed data for each leading country about TiO_2 production increase/decrease, fresh ilmenite distribution, worldwide companies and production facilities and recent news about production facilities is briefly explained down below:

China- According to a titanium dioxide market analyst Artikol, Chinas titanium dioxide has increased by 11% in 2017. During 2017 the Chinese government had a lasting closure of pigment plants that produced lesser than 300,000 t/yr of TiO_2 pigment capacity, as a part of Environment Protection Law. That resulted with 42 active pigment plant in the end of 2017 and the top 10 TiO_2 pigment producers provided 65% of the total pigment production in that year. Lomon Billions Group Co. Ltd is the top producer of TiO_2 pigment in China with an estimate capacity of 705 000 t/yr (Bedinger, 2020). All Lomon Billions production facilities are located in China, within five districts (*Global Presence*, 2021). To maintain TiO_2 pigment production, China imports ilmenite mainly from Australia (*Mineral Sands*, 2018).

United States- United States have the second largest TiO_2 production in the world, with leading production facilities owned by American chemical companies like Tronox, Ltd and Chemours Co. Tronox is an American chemical with the second largest TiO_2 production facility in the United States and in 2017 produced 225 000 ton of TiO_2 (Bedinger, 2020). Tronox owns mine and production facilities mainly in United States, United Kingdom Australia, South Africa, China and Brazil, and the largest TiO_2 production facility owned by Tronox is called Hamilton Pigment Plant and located in the United States (Global Locations – Tronox, 2021).

The Chemours Co. is also an American chemical company with partners in China, this company fixate on titanium dioxide and overall titanium technologies and have around 25 production facilities (including Mexico, China and Canada) for TiO_2 worldwide (*Chemours Global Reach and Locations Worldwide*, 2021). In 2017 Chemours Co produced 340 000 ton of chloride processed TiO_2 (*Mineral Sands*, 2018).

United States have relations with the Saudi Arabian chemical company Cristal Global (*Cristal Global | RISI Technology Channels*, 2017). This company owns a TiO_2 manufacturing facility in the United States and have the second largest TiO_2 production facility in the United States and in 2017 produced 250 000 ton of TiO_2 (Global Locations – Tronox, 2021) and ilmenite mine sites in Brazil and Australia. Cristal Global mine site and production facilities is later owned by Tronox Ltd. (*Cristal Global | RISI Technology Channels*, 2017)

Germany- The largest TiO_2 production facilities in Europe are located in Germany and the facilities is owned by a Norwegian chemical company Kronos Worldwide, Inc. This worldwide company owns production facilities in five countries: United States, Canada, Belgium and Germany. Norway's largest mine Tellnes distribute ilmenite to those five countries (About Us – KRONOS Ecochem, n.d.). In 2020 Germany produced 472 000-ton TiO_2 pigment (USGS, 2021).

Figure 5 introduce a moderately accurate demonstration of fresh ilmenite distribution from the largest ilmenite producers to worldwide leading TiO_2 production facilities, based on the acquired information and sources above. Some of the countries have detailed and accurate information except distribution from Brazil and ilmenite import to Saudi Arabia, that resulted with logical assumption. This logical assumption is based on Saudi Arabian production facility in United States, where the nearest mine site of ilmenite reserves for the production facility is in Brazil and owned by the Saudi Arabian company Cristal global and the American chemical company Tronox Ltd (*Cristal Global | RISI Technology Channels*, 2017).

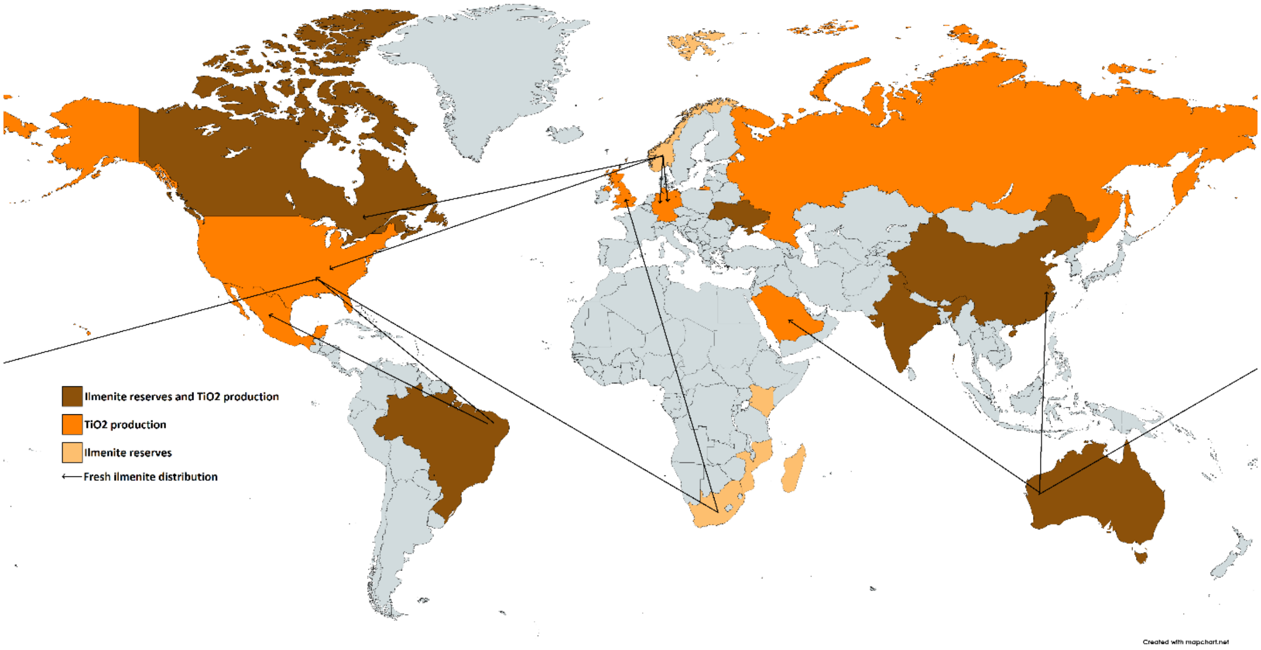
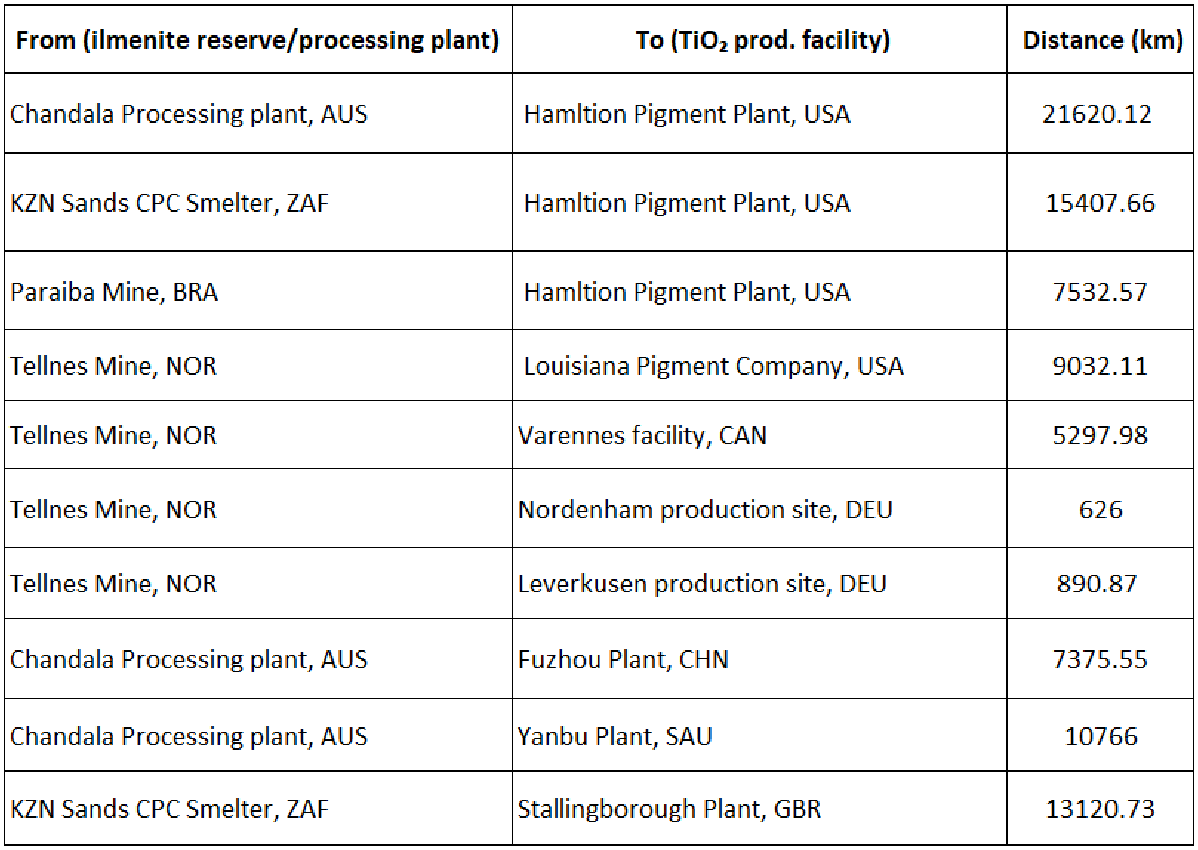


Figure 5. Fresh ilmenite distribution to worldwide TiO_2 production facilities, and the arrows indicate the fresh ilmenite distribution from prominent ilmenite mines/processing plants.

Note. The data is from various mentioned sources above.



From (ilmenite reserve/processing plant)	To (TiO_2 prod. facility)	Distance (km)
Chandala Processing plant, AUS	Hamltion Pigment Plant, USA	21620.12
KZN Sands CPC Smelter, ZAF	Hamltion Pigment Plant, USA	15407.66
Paraiba Mine, BRA	Hamltion Pigment Plant, USA	7532.57
Tellnes Mine, NOR	Louisiana Pigment Company, USA	9032.11
Tellnes Mine, NOR	Varennes facility, CAN	5297.98
Tellnes Mine, NOR	Nordenham production site, DEU	626
Tellnes Mine, NOR	Leverkusen production site, DEU	890.87
Chandala Processing plant, AUS	Fuzhou Plant, CHN	7375.55
Chandala Processing plant, AUS	Yanbu Plant, SAU	10766
KZN Sands CPC Smelter, ZAF	Stallingborough Plant, GBR	13120.73

Table 2. Typical distances within the distribution of ilmenite

Note. The data is from the sources mentioned above.

Table 2 shows in a more detailed form the distances between ilmenite reserves/processing plant to production facilities from the map chart in Figure 5.

The production facilities enumerated in Figure 5 and Table 2 use different processes to produce pigment, and which seems to be dependent on the location in the world the production facilities are situated. The two main processes as mentioned previously are chloride method and sulphate method. Which will be further discussed in more details in next chapter.

2.2 Production processes for ilmenite

Titanium dioxide pigment production is the most common use of ilmenite. The chloride and sulphate process are the two most common ways to process ilmenite to TiO_2. The main difference between the two processes when it comes to the raw material is that the sulphate method uses ilmenite directly as feedstock, while the chloride method requires a Ti concentrated feed-stock. To obtain a Ti concentrated feedstock, ilmenite in the chloride method needs to be pre-treated into a titanium slag or synthetic rutile with concentration that ranges between 90-95% TiO_2.

2.2.1 Pre-treatment

Ilmenite material is pre-treated differently depending if it is rock ilmenite or sand ilmenite and resulting also in different yields (Filippou & Hudon, 2009). Rock ilmenite is smelted while sand ilmenite can both be smelted or leached in order to generate highly concentrated feed stock. When smelting rock ilmenite using electrical furnaces a titanium slag is obtained with concentration of 70-90 wt %. This slag can, however, not be used in the chloride process because of impurities from minerals (MgO and CaO) that are problematic when using the chloride process (Filippou & Hudon, 2009). Thus, the slag needs to be furthered treated through a UGS (upgraded slag) process where the impurities are removed by thermal treatment and by leaching with hydrochloric acid (HCl). The result of the upgrade is a slag with 95 wt% concentration which can be further used in the chloride method (Gázquez et al., 2014).

Sand ilmenite can yield either titanium slag or synthetic rutile, the former through smelting and the latter through leaching. The ilmenite that is melted uses an electric furnace, where it yields a slag with 85 wt % concentration with low amount of impurities and can thus be used in the chloride method with no further treatment.

Synthetic rutile is commonly produced from ilmenite by two pre-treatment methods called Benilite and Becher process (Filippou & Hudon, 2009) and has a similar composition to natural rutile (U.S. Environmental Protection Agency, n.d.). In the Becher process the ilmenite is placed in a rotary kiln at 1200°C in order to reduce the iron ions to their metallic form. After screening and using magnetic separators to detach ilmenite from the char, the ilmenite rich fraction is then exposed to ammonium chloride (NH_4Cl) solution in order to oxidise and separate the iron from the ilmenite and to produce synthetic rutile. In the Benilite process the ilmenite is placed in a kiln at 850-1100 °C while being exposed to heavy oil. The ilmenite is then leached using 20% hydrochloric acid (HCl) and after being filtered it is subjected to calcination which purifies the obtained product and produces synthetic rutile. Titanium slag is produced by smelting the ilmenite mineral to separate the iron from the titanium. The titanium slag or synthetic rutile is then used in the chloride process as feed stock to produce.

2.2.2 Chloride process

Figure 6 demonstrate a simplified flow of the chloride process with the main processes mentioned.

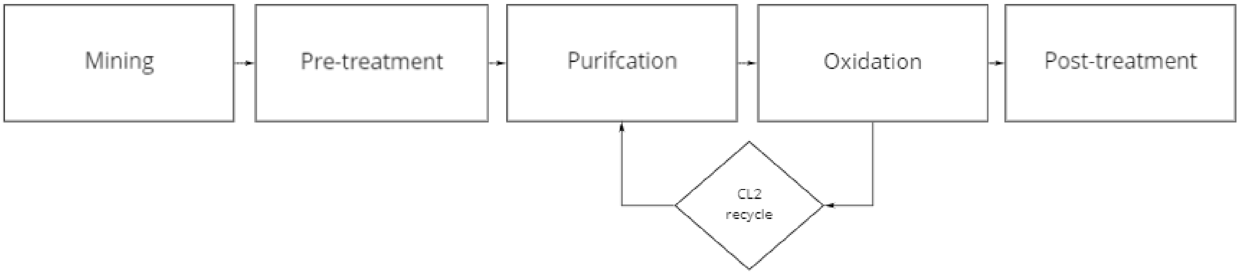


Figure 6. *A simplified flow sheet of the Chloride process*

(Gázquez et al., 2014) and (Reck and Richards, 1999).

Processing the slag/synthetic rutile using the chloride method starts with blending the raw material with gaseous chloride at a temperature of approximately 900 °C– 1000°C (Middlemas et al., 2015) in a fluidized bed reactor with a reducing agent in the form of petroleum coke. One of the gases that are formed from the blend results is titanium tetrachloride ($TiCl_4$) along with the impurities in the form of gaseous chlorides, the exceptions are silica and zirconium which remains accreted in the reactor (Gázquez et al., 2014). The mixture of gaseous metal chlorides is then cooled by using liquid $TiCl_4$ to separate the titanium tetrachloride from the other metal chlorides. The $TiCl_4$ is then liquified by further cooling it and condensing it. The titanium tetrachloride is then oxidized through high temperature oxidation using either a plasma arc furnace or a toluene-fired furnace. The $TiCl_4$ is oxidized at temperatures over 1500°C which results in release of chlorine gas (Cl_2) and the formation of titanium dioxide (TiO_2). The released chloride is recycled back at the start of the process. The titanium dioxide is subjected to hydrolysis to remove residual chloride. The obtained titanium dioxide is post-treated by mill, drying, etc to finalize the production of titanium dioxide pigment. With a prerequisite of pre-treatment, the chloride process will require more energy at 109 MJ/kg compared to the 74 MJ/kg using the sulphate method (Reck and Richards, 1997). The chloride process, however, is a closed system and as seen in Figure 4 the Cl_2 is recycled back to the process. Sulphate process requires fewer specific conditions for ilmenite pre-treatment and use ilmenite directly as feed stock.

2.2.3 Sulphate process

Figure 7 demonstrate a simplified flow of the sulphate process with the main processes mentioned.

Figure 7. *A simplified flow sheet of the Sulphate process*

(Gázquez et al., 2014) and (Reck and Richards, 1999).

The sulphate method uses highly concentrated sulfuric acid for digestion of ilmenite to achieve mixture of sulphate salts mainly consisting of titanyl sulphate, iron sulphate and free acid. The digested mineral is then leached by water and the metallic iron scrap is acquainted into the acid solution to minimize the ferrous iron $Fe^{2+}$and the ferric ion Fe^{3+}. The residue is then cooled by crystallization to remove the iron as $FeSO_4 \cdot 7H_2O$. After the removal, the titanyl sulphate solution $TiOSO_4$ is hydrolysed to accelerate a hydrous titanium oxide ($TiO(OH)_2$). If surplus water is added to the hydrolysis process an increasing amount of mild sulfuric acid is formed and then the obtained solution is hard to recycle. After the hydrolysis process the hydrous titanium oxide is calcinated at 650°C -1000 °C (Middlemas et al., 2015) to produce raw pigment, which is then grinded, and surface coated to produce the final TiO_2 pigment (Zhu et al., 2019).

The two main processes mentioned above are applied for production, which is the primary application of ilmenite. Alternative applications of ilmenite have been discovered in the last decades, where the ilmenite is implemented as bed material for fluidized bed boilers. This subject will be explored further in the next chapter.

2.3 Alternative applications of ilmenite

Ilmenite primary application is for titanium dioxide production. Lately, alternative application of ilmenite has been discovered in nanotechnology and in fluidized beds.

Recently in Chalmers, researchers have developed a new method for combustion of biomass in fluidized beds called Oxygen Carrier Aided Combustion (OCAC). This method is mainly applied in circulating fluidized bed (CFB) systems. This chapter will predominantly focus on OCAC process and how ilmenite as bed material will be influenced by OCAC conditions compared to quartz sand. Furthermore, the chapter will treat also the current developments in waste management for OCAC process in form of magnetic separation. At the end of this chapter alternative application for deactivated ilmenite will be introduced.

2.3.1 Oxygen Carrier Aided Combustion (OCAC) process

Figure 8 demonstrate a simplified flow of the OCAC process with the main processes mentioned.

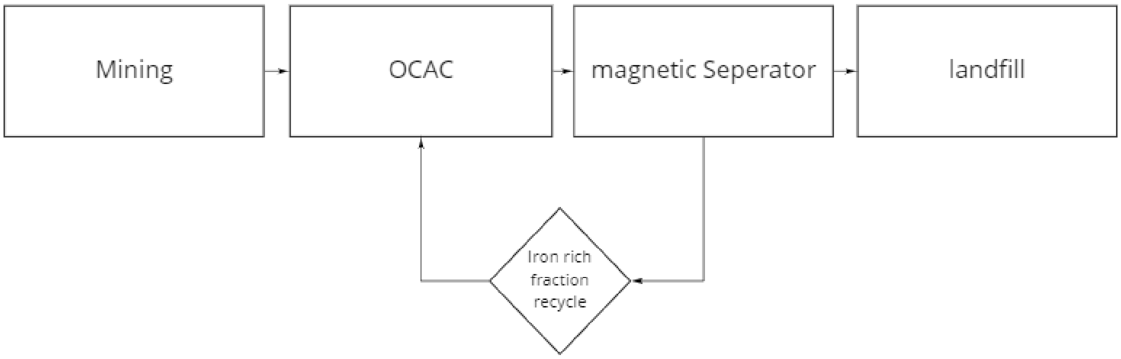


Figure 8. *A simplified flow sheet of OCAC.*

(Gázquez et al., 2014) and (Reck and Richards, 1999).

The Oxygen Carrier Aided Combustion (OCAC) is a process where in the combustor oxygen-carrier bed material are used instead of sand that is used as a conventional bed material (Gyllén et al., 2020). The OCAC process improves the overall efficiency of the combustion process and the conversion rate of the fuel by increasing the mixing and the transport of oxygen between the chosen fuel and the oxidizer (the air). The concept for the efficiency improvement was first applied for chemical looping combustion (CLC) conditions where through the use of oxygen carrier (OC) as an oxidizer for combustion a concentrated CO_2 stream could be emitted that is easy to compress and store (Gyllén et al., 2020). Both the OCAC process and the CLC process is implemented in conventional fluidized bed boilers with various amount of capacity illustrated in Figure 9.

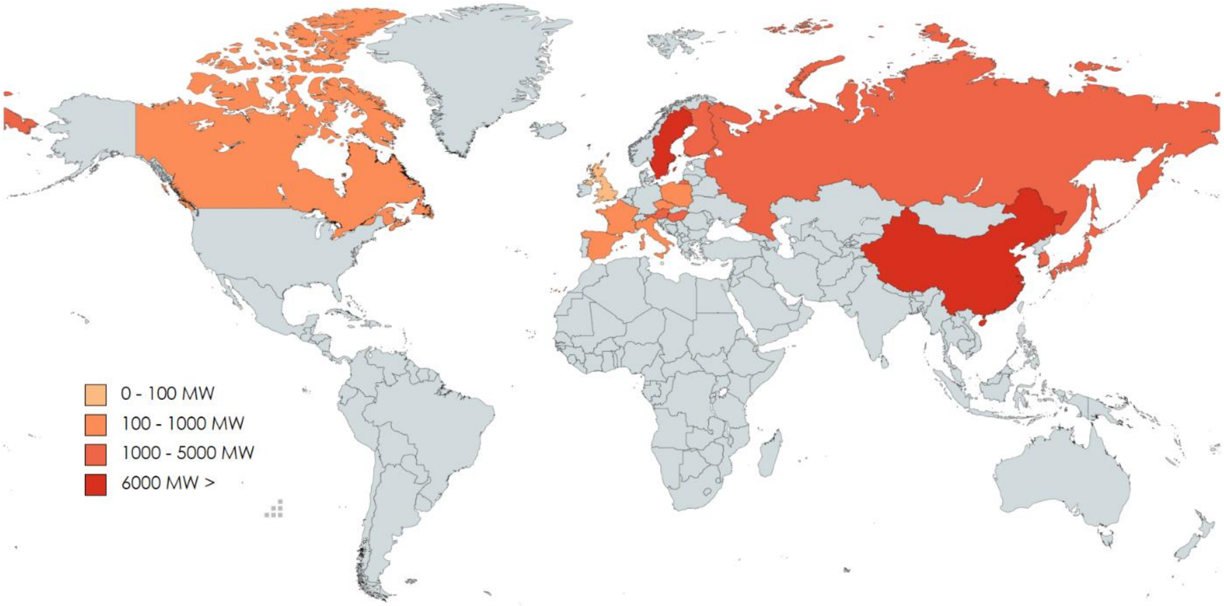


Figure 9. The overall global capacity for fluidized beds boilers for each county, and countries coloured with stronger contrast have the highest overall capacity in bed boilers.

Note. The information for the map chart is gathered from (Leckner, B. 2011) and (Leckner, B. 2017). The data can be seen in Appendix.

The map chart in Figure 9 illustrates the global overall capacity for fluidized bed boilers in 17 countries. The leading counties with highest bed boiler capacity are China, Sweden, Finland, South Korea and Japan. The most conventional type of bed boiler for the OCAC process is the circulating fluidized bed (CFB) boiler (Gyllén, A. 2019), where the OCAC process in this type of bed boiler is further explained in Figure 10.

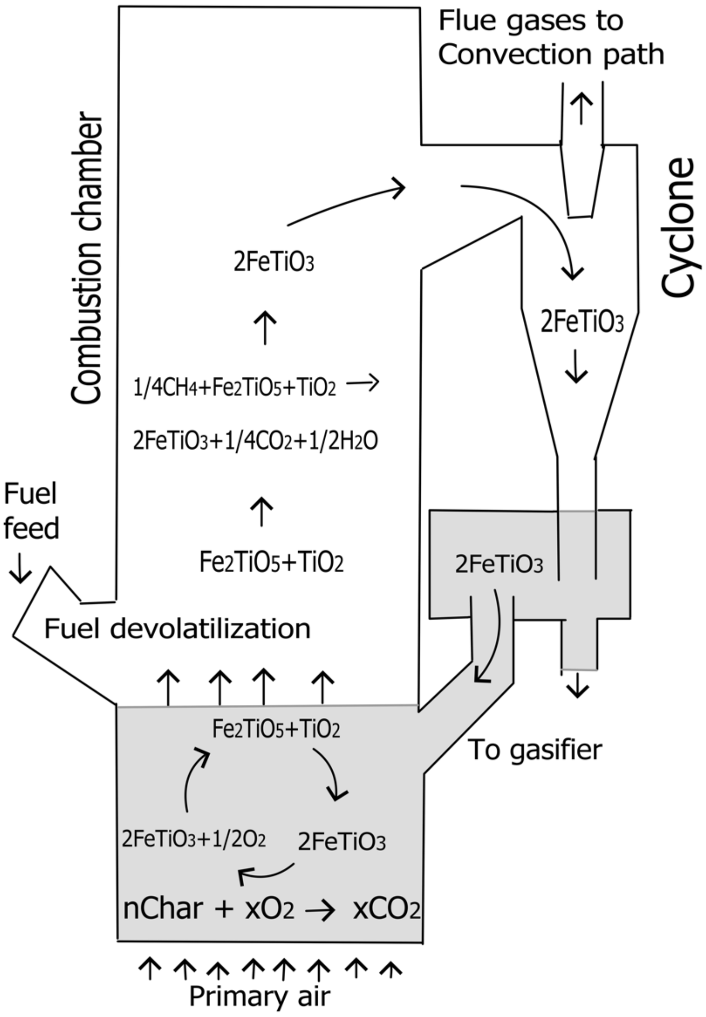


Figure 10. *OCAC process*

Note. Principle of OCAC process (Thunman et al., 2013)

In the OCAC process seen in Figure 10, the preferred bed material ilmenite at a rate of 3 kg/MWh (Lind, F., 2017) is circulated throughout the CFB boiler where the fuel that is fed is usually coal or biomass. The ilmenite circulation starts in the lower part of the combustion chamber, at the air inlet, where the ilmenite undergoes oxidation and then the material is lifted upwards where it is reduced by the fuel. During devolatilization of biomass fuel volatile compounds such as hydrocarbons, CO, CH_4, and H_2 are formed that interact with pseudobrookite and reduce it to ilmenite at the same time as forming CO_2 and H_2O (Thunman et al., 2013). The combustion process is considered as an activation process for ilmenite as more Fe migrates to the surface and is available for redox and oxygen transport. The conversion rate of the bed material evens out after a few cycles, when the ilmenite is activated. Due to different levels of oxidation the mineral can take three forms, the lowest oxidating form being ilmenite (FeTiO3) and the highest being psuedobrookite (Fe2TiO5) (Gyllén, A., 2019) The reduced ilmenite is then transported to the water-cooled cyclone, where the bed material and flue gases in the convection path are separated. The bed material is then transported to the particle distributor, and through the particle distributor - re-circulated back to the combustion furnace. The formed ash during the OCAC becomes eventually either bottom ash or fly ash. The bottom ash consists of bed material and dense ash. The fly ash consists of collected fine fractions of ilmenite lost during the separation process in the cyclone (Gyllén, A., 2019). According to industrial partner (Eon representative, personal communication, 12 May 2021), the lost ilmenite fraction in the cyclone is assumed to be in the range of 0-20%.

During the OCAC process the activated ilmenite forms a Ti-rich core surrounded by an Fe-rich outer layer. Ilmenite interacts also with fuel ash compounds. The ilmenite interaction with potassium and calcium originating from fuel ash results in migration of potassium to the particle core (Corcoran et al., 2018, p. 8849), and the formation of a Ca layers surrounding the segregated iron layer (Hildor, F.,2017). The formed around ilmenite particle Ca-rich layer increases in thickness with time as a result of the exposure to biomass ash, thereby enclosing the segregated Fe layer. This shows that the segregated Fe migrates through the Ca-rich ash layer to the surface where it reacts with oxygen and forms a Fe-rich layer in the outer surface leaving Ti in the core of the particle. This migration demonstrates that it becomes more difficult to oxidize ilmenite after several circulations' cycles, and this is also depending on the type of ilmenite applied in the process (Gyllén, A., 2019).

The OCAC process has a different impact on the sand and rock ilmenite which is expresses in different types of structural degradation. Cavities and cracks are formed as the mineral is weakened during the OCAC process, during the Fe migration. Sand ilmenite during the OCAC process is broken to small pieces and cavities bound by ash-layer are formed between the fines. The rock ilmenite during the process forms a distinct split of the cavity and the ash layer that is formed around the particle. The rock ilmenite is less resistant to mechanical stress at first, which resistance is changed over time. For sand ilmenite it is the other way around, with time sand ilmenite develops weak resistance to mechanical stress (Corcoran et al., 2018). This shows that rock ilmenite can operate longer in the OCAC process than the sand ilmenite due to better stress-tolerable structure, this implies that rock ilmenite is more suitable for the OCAC process. However, it should be noted that the overall ilmenite has its advantage in oxygen carrying capability compared to other existing bed material.

Comparing quartz sand and ilmenite as a bed material in the OCAC process one can see a reduction in formed CO emissions which is due to bed material substitution to ilmenite which is an OC (Rydén et al., 2018, p. 2657). Ilmenite also leads to a 19% smaller steam-to-fuel ratio compared to quartz sand in the OCAC process. This means that ilmenite requires less additional fuel in the combustion process and compared to quartz sand ilmenite is a more sustainable bed material Berdugo Vilches et al., 2016).

After the ilmenite has been exposed to the OCAC process, ilmenite residues show an increasing value of high magnetic susceptibility which is due to Fe migration to the surface layer during the OCAC process (Gyllén et al., 2020). To ensure an optimized waste stream handling after the OCAC process, the bed material can be sorted in magnetic separator to separate the ilmenite with remanent oxygen carrying capabilities and iron-rich fractions from the deactivated ilmenite, which contains Ti-rich fractions (Gyllén, A., 2019). The separated ilmenite with remanent oxygen carrying capabilities can be reused up to eight times per batch according to information from industry partner. When ash surrounding the ilmenite thickens and the Fe cannot longer migrate to the surface to react with oxygen and be separated, the ilmenite is considered as deactivated (Gyllén et al., 2020). The magnetic separation is a sufficient optimization method to minizine ilmenite waste streams to reduce landfill and allows the ilmenite rate in the OCAC process to be reduced from 3 kg/MWh to 1 kg/MWh (Lind, F., 2017). According to the industry partner (Eon representative, personal communication, 12 May 2021), up to 90% of the separated ilmenite is activated after one cycle and the rest 10% is deactivated. Currently the deactivated ilmenite is sent to landfill.

The deactivated ilmenite fraction from the magnetic separator contains high Ti-rich fractions, that can potentially be applied for feed stock in titanium dioxide production instead of depositing it at landfill (Gyllén, A., 2019).

2.4 LCA

Live-cycle assessment/analysis (LCA) is a method that is widely used in order to determine and understand what impact processes, activities, and products have on the environment through emission and waste. (Rebitzer et al., 2004, p. 719). The method was created when awareness of the impact on the environment from consumption increased. The impact on the environment can be of different such as water use, toxic waste, land use, noise, and more. The parameters indicate how sustainable a process, or a product can be. LCA allows users of the method to compare different processes and products.Processes in LCA are defined by the flow of material and energy in the form of exchanges, i.e., total input and output from the process system to a defined environment. The output can often be in form of types of emissions, solid waste amounts, and products. Within LCA the system process is made up of multiple subprocess with individual inputs and outputs. The processes can represent product use, recycling, waste management, product distribution, material acquisition and/or process in manufacturing context. To decide the impact of the process, data is needed for the input and output of the process. LCA is very data driven to assess environmental impact (Muralikrishna and Manickam, 2017). There are two general types of data that are important to know in order to perform LCA. The first type is called foreground data. This represents data that is specific and needed to obtain a model for the system, typically data that defines a specialized product system. Background data is the data for the transport, energy, material, and systems for waste management. Budget and mass balance can be carried out in LCA once the data is gathered. The results from the mass balance in LCA are used to compare similar system processes that uses/produces the same material or products in order to have an estimate of how big of an impact they have on the environment.

In the method section the LCA will be simplified and will not follow any conventional guideline for LCA to better suit the thesis. This is due to the lack of data in OCAC and simplifying the content in chloride and sulphate process.

3 Method

In this chapter, the overall method of the thesis will be explained. It will summarise how, and questionnaires are done. The method chapter will also explain the simplified life cycle analysis and the data used and obtained from it. Finally, the chapter will explain how information gathering is done and how we chose the data relevant for the report.

3.1 Questionnaire and interview

The information gathered from the companies was mainly from a self-designed questionnaire that was sent via, email to selected companies involved in ilmenite handling but also through annual reports that the companies have (usually published on their websites). We sent out around 20 emails to leading companies in ilmenite production and titanium dioxide companies. However, only three companies answered as seen in the appendix. The questions are structured so that different companies receive the same questionnaires, and we use their results for estimations and comparisons. Some of the gathered information is from leading researchers in the field of OCAC and fluidized beds, where the involved researchers were referring to their own articles, and the information was acquired via email. For the research part, we sent email to Bo Leckner and Fredrik Lind. Bo Leckner is a leading researcher in the field of fluidized beds and Fredrik Lind is the patent holder of OCAC and one of the lead researchers in Improbed, the company that is commercializing the OCAC concept. An interview over teams was conducted with Fredrik Lind.

3.2 Simplified life-cycle analysis

LCA, as discussed in the theory section is very data-driven method. Due to the limitations of specific the information needed regarding how waste is handled, emissions and energy usage for ilmenite, the LCA will be simplified. The simplified LCA follows the flow of ilmenite and thus does not expand on how wastes or emissions are being further processed. The method only focuses on how much waste or emission are being emitted from the different processes and emission from the transportation of ilmenite. The result from the LCA are presented in two parts- the first part being a high-level overview that looks at emissions from transportation and the second - a low-level overview that looks at the processes individually.

Chemical reactions calculation of the sulphate process and chloride process are used to define the material waste during both processes. It should be noted, however, that ilmenite/slag are not pure and hold a lot of impurities that need further treatment which the calculations does not consider. The waste/emission from these impurities during the treatment are not considered either. Another reason to simplify is that the ilmenite rock is largely consisting of $FeTiO_3$ and thus most of the waste and energy usage will be used on handling those elements. Thus, the simplified LCA and flow chart will focus on $FeTiO_3$ and Fe_2TiO_5 for the combined flow. Pseudobrookite (Fe_2TiO_5) is the structure that forms after ilmenite has been activated and achieved the highest level of oxidation (Gyllén, A. (2019)). The energy usage of the chloride and sulphate process will be derived from the data from Reck and Richards (Reck and Richards, 1997). There is currently a lack of data on the energy usage of the OCAC process in proportion to the amount of ilmenite used which is the reason why the OCAC process is not be considered. The result from the LCA are discussed separately in the results either in high-level such as transportation or low-level such material waste and energy usages. This is so that the answers for the thesis questions is clearer if presented separately.

3.3 Retrieval and application of data and information

The gathered information is from various database sources, mainly those available through Chalmers library and Google Scholar. In the process of finding reliable sources with relevant information, all the non-trustable articles, sources and databases have been avoided for quality purposes. Snowballing which is the method of finding sources through a relevant source is also used to make it easier to find further sources.

3.4 Calculations

3.4.1 Flow chart mass

Calculation for the mass in the flow chart were done by using the chemical reactions involved in the chloride and sulphate processes. It was done by assuming that the process was producing 1kg TiO_2 and by using the molar ratios from each reaction. By using the molar stoichiometric calculations, we were able to determine the mass ilmenite needed to produce for 1kg of TiO_2 . The calculation was then done backwards to calculate the mass of the input.

3.4.2 Graph for losses

Losses in combined flow was performed in python to loop the calculation for 1-20% of losses in OCAC and how it would affect the amount of deactivated ilmenite. The calculations assumed that the mass was constant, that magnetic separation was done in 8 cycles and that 10% of the separated ilmenite is deactivated. The equation used is $f(x) = x \times 4.0694 \times 0.1 \times 8$ where x is $x = 1 - loss$ and loss ranges from 0.8 to 0.99. The graph was then generated by python using the values from the calculations.

3.4.3 Bed boiler ilmenite capacity

Bed boilers ilmenite capacity are calculated by using the MWth capacity of fluidized bed boilers, (Leckner, B. 2011) (Leckner, B. 2017) and multiplied with the amount of ilmenite needed per MWth. Bed boiler capacity is multiplied by 3 kg/MWth or 1kg/MWth if we assume the bed boilers are using magnetic separator (Lind, F., 2017).

3.4.4 Emissions from transport of ilmenite

The carbon dioxide emissions from TiO_2 feedstock distribution were calculated by using a CO_2 calculator for transport and logistics obtained from carboncare.org. The required information for calculating the CO_2 emissions was achieved from previous chapter information, sources for production and consumption and gained data in results. The detailed calculation was also complemented with the help of Google Maps for appreciating distances.

3.5 Mapmaking

The maps were generated by using excel and the website Mapchart. Excel generates maps using data and the different gradients of a colour to indicate the value of the data, where notable examples of maps are presented on Figure 1 and 4. The maps that are generated by mapchart are the maps that are coloured in order to describe a location and uses arrows to indicate distribution. The maps using mapchart are manually edited where an example is Figure 23.

4 Results, Analysis and Discussion

The structure of the result, analysis and discussion is done in various levels starting at low-level, and then at high-level overview. At the low-level overview, the result will explain improvements on current flow and processes of ilmenite. The second part of the results will explain the potential improvement of the overall ilmenite flow on a global scale. The improvements will mostly be in regard to impact and sustainability.

4.1 Low-level overview - processes

Figure 11: Material flow of the chloride processes with the goal to produce 1kg TiO_2. Energy usage such as heat of individual subprocesses are not taking into account due to lack of data. The process uses 1.905 kg ilmenite for pre-treatment. The resulting slag calculated to be around 1.111kg is then used for feed stock for the TiO_2 production. It is under assumption that the treated slag is 90% pure.

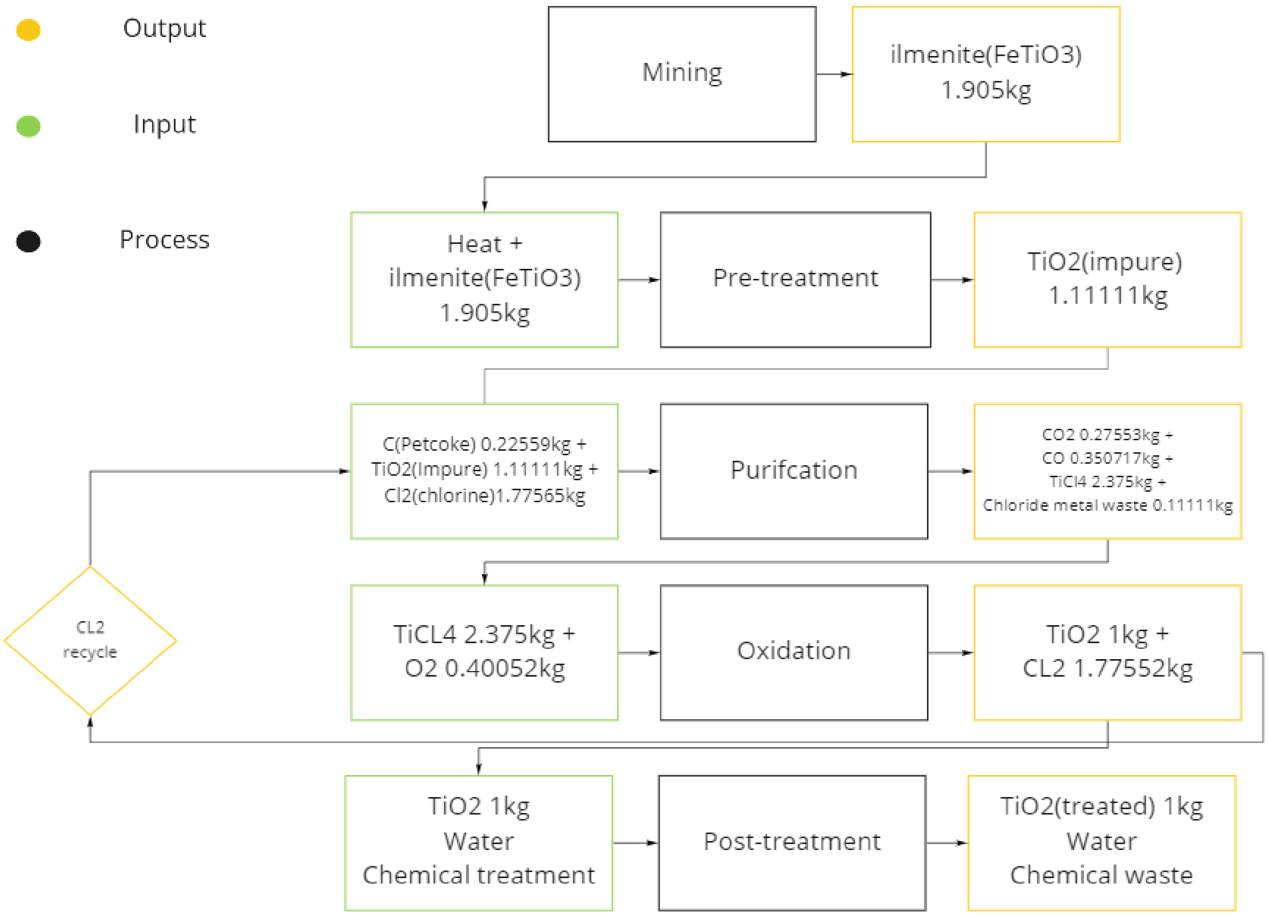


Figure 12: Material flow of the sulphate processes with the goal to produce 1kg TiO_2. Energy usage such as heat of individual subprocesses are not taking into account due to lack of data The resulting ilmenite needed for the processes was calculated to be around 1.86kg but this does not take impurities in account due to simplification. The chemical coating waste is not taking in account for and the n in the TiO_2. n× H_2O is assumed to be 1.

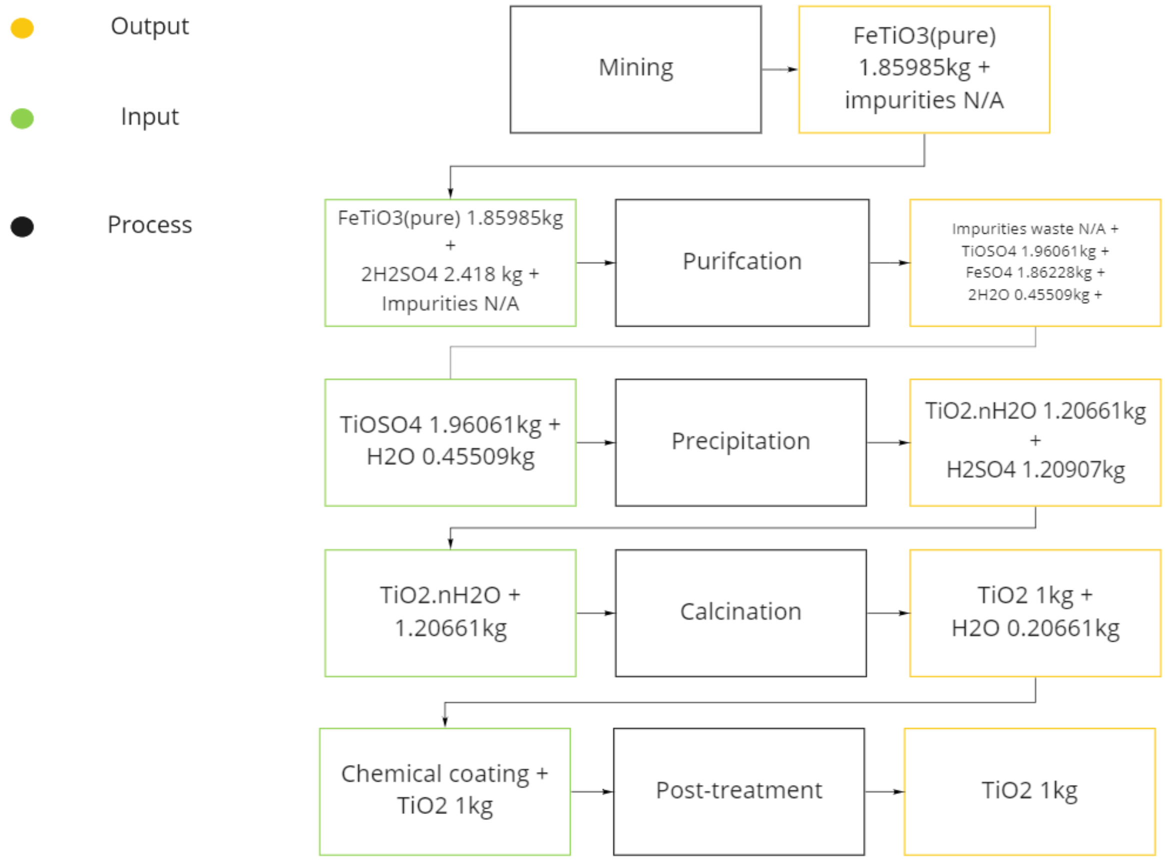
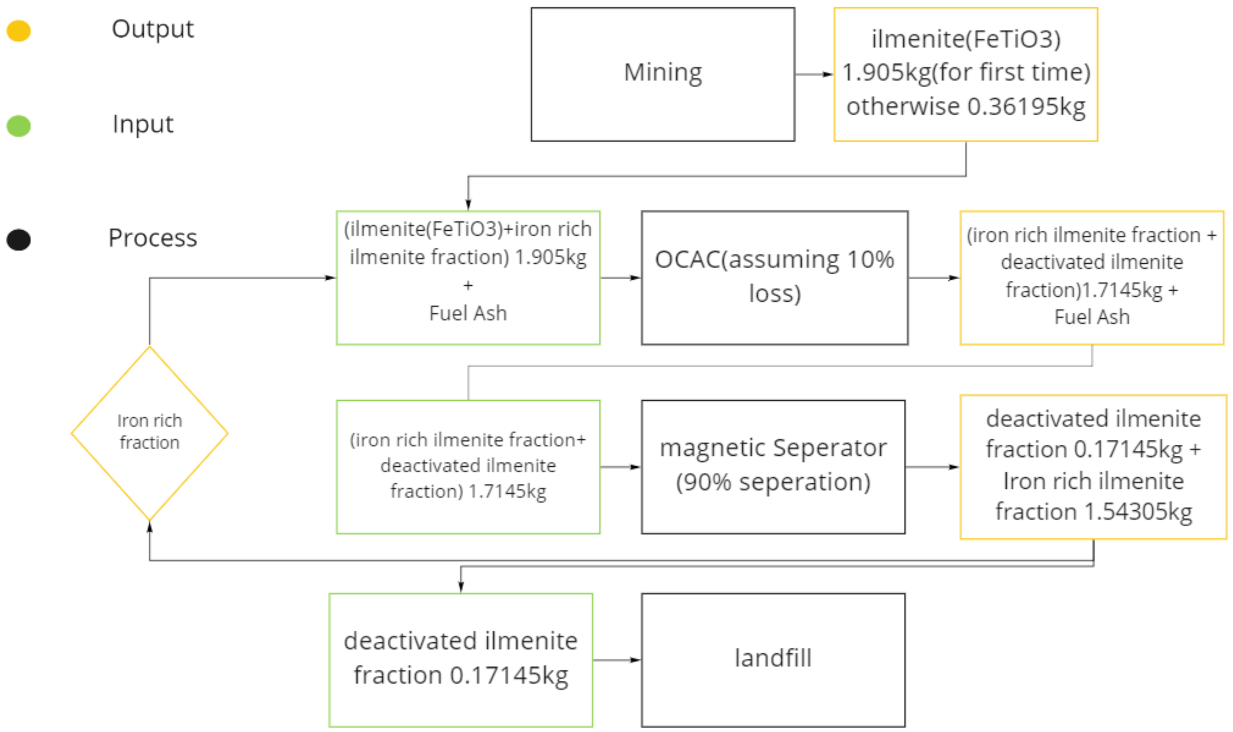


Figure 13: Flow chart of OCAC process with magnetic separator at 96% efficiency and 10% loss during the OCAC. It assumed that it goes for 8 cycles and that the mass is constant for all cycles. The mass is assumed to be the same that chloride method consumes.



The flow charts for the sulphate and chloride process as seen in figures 11 and 12 were made with the purpose to determine the material flows of ilmenite for both processes. The flow chart is used to illustrate and determine the process input and outputs. The calculations in the material flow does not take the impurities within the ilmenite mineral into account and only took in account for Fe, Ti, and O. The calculations in the material flow taking the impurities in account will most likely result in higher amounts of Cl_2 or H_2SO_4 needed to separate the other elements such as Mg, Si, Al etc. The increase in chemicals needed for treatment of impurities will result in increased waste, which is especially sound for sulphate process since unlike the chloride method, in its present form, it lacks a way to re-use the H_2SO_4 in the same way as Cl_2 is recycled in chloride process. The sulphate process however lacks a necessity of a pre-treatment process like the chloride processes has and thus will result in lower energy usage. Sulphate process does not require a specific purity of the ilmenite such as are the titania slag/synthetic rutile for the chloride process and can instead use the mined ore directly. This suggests that the sulphate process can extract TiO_2 from an impure mineral but also from other ilmenite waste streams, such as for example the deactivated ilmenite/ash mix that is generated from OCAC process that is seen in

Figure 13. The result indicates that it is possible to combine the two processes if using the sulphate process without further modifications to the existing flows.

4.1.1 Combined flow

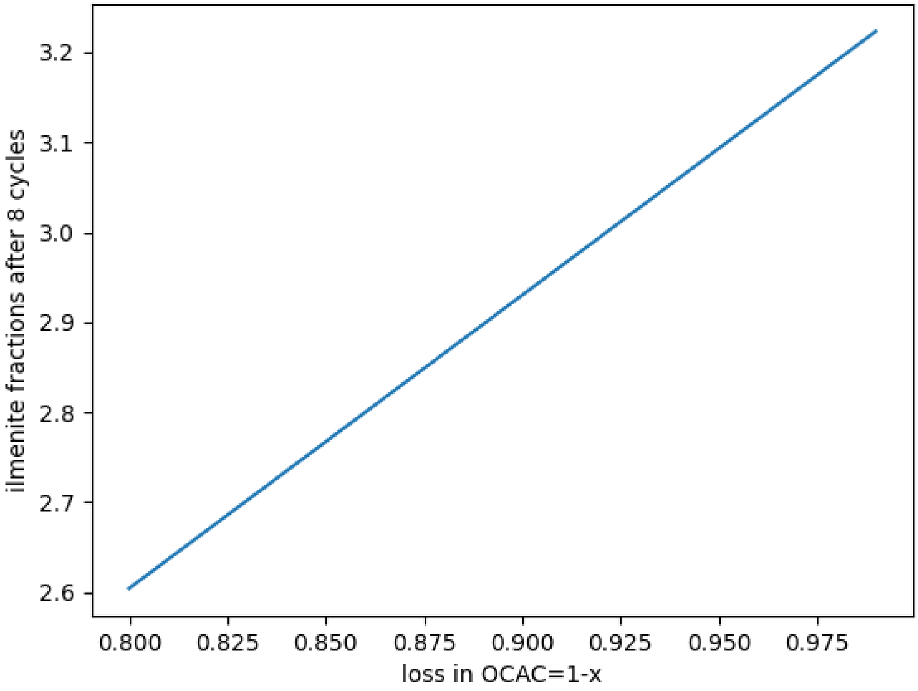
Figure 14: A common ilmenite flow for combined OCAC and sulphate process for 1kg TiO_2 production. The deactivated ilmenite is assumed to be fed directly as a feed stock in the sulphate process. The flow chart uses the assumption that the OCAC process creates 10% loss and has 96% efficiency in the magnetic separator which overall represents a conservative estimation. The mass of the iron rich fragment combined with ilmenite is assumed to be constant at 4.0694kg. Due to being activated and oxidized the deactivated ilmenite is assumed to be at the highest state of oxidation namely pseudobrookite (Fe_2TiO_5).

Due to the feedstock being $\mathrm{Fe_2TiO_5}$ in Figure 14 the amount of $\mathrm{H_2SO_4}$ had to be increased to accommodate for the increase in iron in the mineral. This results in more waste in form of $\mathrm{Fe_2}(SO_4)_3$ than the singular flow of the sulphate process as seen in Figure 12. The presented flow only takes in account the elements of the mineral in its purest form and does not consider for impurities in the ash layer or impurities present in the mineral. The implication for such calculation that even more waste is expected to be generated. Due to the high waste generated by combination of the sulphate and the ilmenite containing ash, it could be more beneficial to use the chloride method in the long-term. The chloride process however is limited by the fact that it requires titania slag/synthetic rutile to function and thus the deactivated ilmenite must undergo pre-treatment. Due to the higher degree of impurities from the ash layer, the deactivated ilmenite might need further pre-treatment than the conventional mineral. The changed structure could also potentially facilitate the pre-treatment of the ilmenite due to the natural separation obtained between the iron and titanium oxides - shell of Fe-oxides around the mineral and Ti-oxides being in the core. This potentially could result in an effective pre-treatment due to the Fe being in a location that implies easier extraction. The implication from the present model and calculations is that there are too many unknown variables on how to pre-treat the material for chloride process to be suitable for processing deactivated ilmenite. This results in the sulphate method being the only current viable option for processing deactivated ilmenite. Further research regarding the pre-treatments that is suitable for deactivated ilmenite should be done before implementation of chloride process.

4.1.2 Losses during OCAC in combined flow

The material losses in the model shown in Figure 15 only represents a assumed loss and the loss can vary which will be presented in Figure 16.

Figure 15: Graph presenting 1-20% loss during the OCAC process in the combined flow and how it affects deactivated ilmenite after 8 cycles in magnetic separation.



The loss is linear and there is a 0.63kg disparity between 1% and 20% loss, that means that if the example of 10% loss is taken into taken into consideration, around 0.3kg of the ilmenite used as bed material in the OCAC would become waste that can be included in the production of TiO_2. The implication is that further research on effectivization of the cyclone in the OCAC process is beneficial in order to avoid material losses.

4.1.3 Waste and energy usage for 1kg TiO_2 production

Figure 16: Wastes and energy usages from OCAC, chloride, sulphate processes and the combined flow. Due to lack of information regarding energy usages for material handling in OCAC this is not considered, and it is assumed that the combined flow shares energy usage with sulphate process.

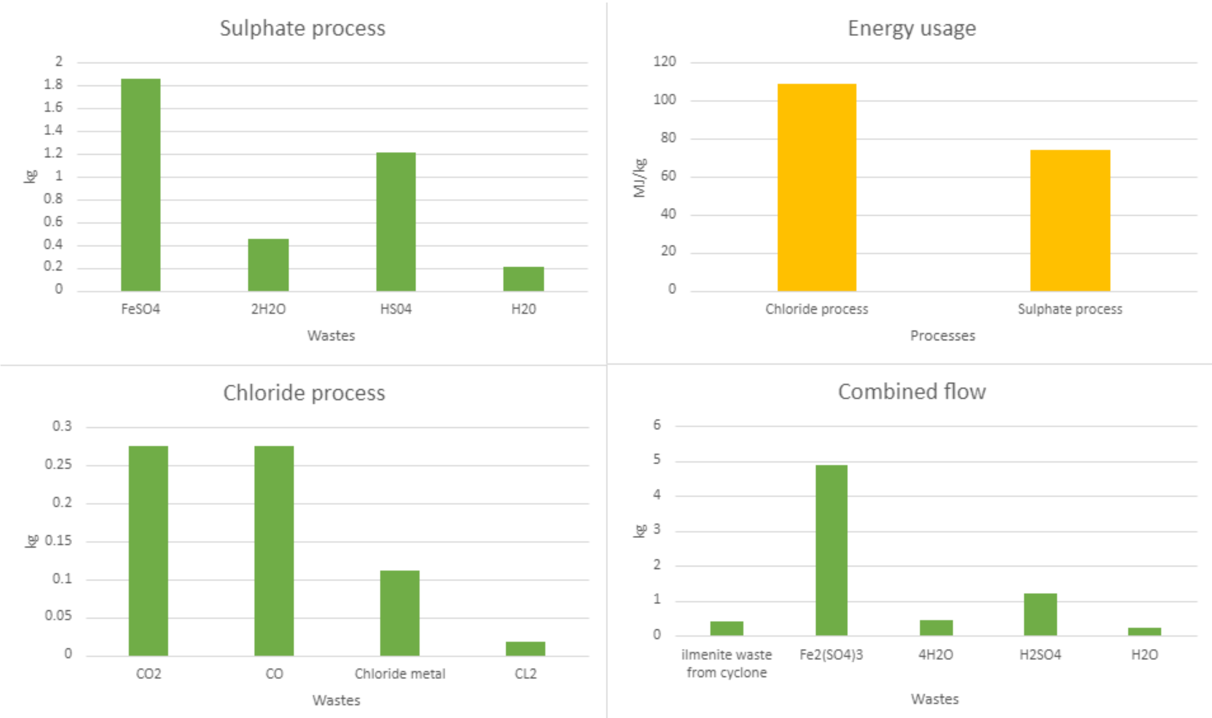


Figure 16 shows the waste generated by 1kg TiO_2 production and the combined flows total at around 6.8kg, the majority being $Fe_2(SO_4)_3$. Looking at the singular flow processes, the material waste for chloride method is around 2.7kg and this is not taking in account the pre-treatment of the waste material from OCAC, and the sulphate process is around 3.7kg. It can also assume that OCAC uses 1.9kg ilmenite that could otherwise have gone to produce 1kg TiO_2 for the singular processes. If the losses to OCAC are considered, it will result in around 4.6kg waste for chloride process or around 5.4 kg if pre-treatment waste is considered and around 5.6kg for sulphate. This results in combined flow generating greater amount of waste in mass than the singular processes. Generally, increase in the waste flow is seen as detrimental for the environment. However, difference between type and content of waste should be made. The value of the waste in form of Ti-rich ash from using ilmenite in OCAC is more detrimental to sustainability as Ti being considered a scarce resource. If the ilmenite flows currently and, in the future, used in the OCAC processes eventually get landfilled, this will result in further overuse of a scarce resource which then can become even more scarce. This implies that from a sustainability point of view it is more beneficial to generate more waste in form of $\mathrm{Fe}_2(SO_4)_3$ from combined flow in order to prevent landfilling of Ti-streams. Further research should be done on if $\mathrm{Fe}_2(SO_4)_3$ and equivalent in the chloride process can be processed and recycled. This will result in the combined flow becoming even more sustainable from material usage context. As for energy consumption of the processes we can assume the combined flow uses the same amount of energy as the sulphate method which is 74 MJ/kg, and the chloride process uses 109 MJ/kg. It can even be argued that the combined flow will consume less energy in total due to the purpose of fluidized bed boiler being to generate heat and energy. Further research should be done on energy usage on OCAC and energy gain from OCAC due to ilmenite used as bed material to determine if this argument is true.

4.2 High-level overview – ilmenite globally

The map shown in Figure 18 was created to illustrate the global capacity for bed boilers if all of them were using ilmenite as bed material. This assumption was done by using the bed boilers global capacity in MWh and multiplying it with 3kg/MWh, which is the amount of ilmenite needed for bed boilers.

Figure 17: Yearly capacity of most bed boilers in the world. This map was created under the assumption that all bed boilers use ilmenite as bed material. The map does not take in account for magnetic separator for re-use of ilmenite in bed boilers and thus has three times the increased capacity for ilmenite yearly than if it would not.

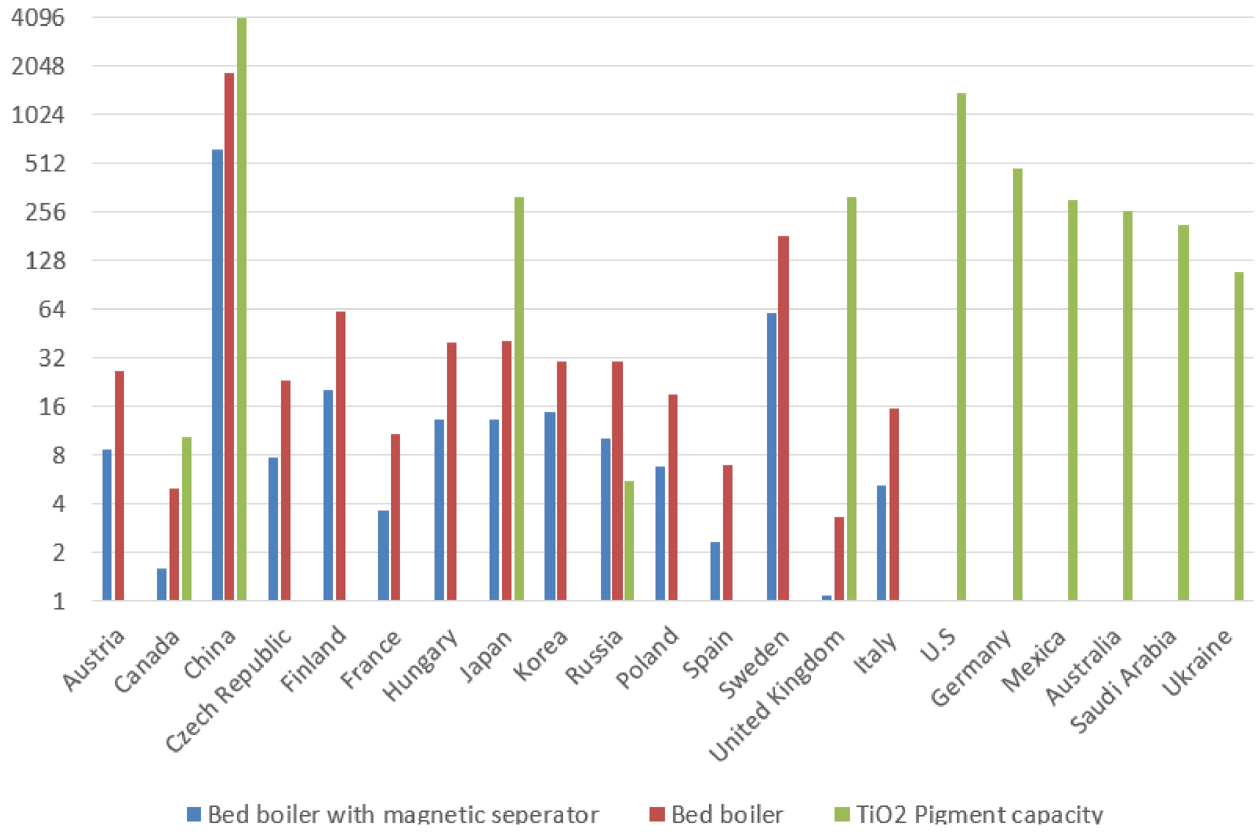
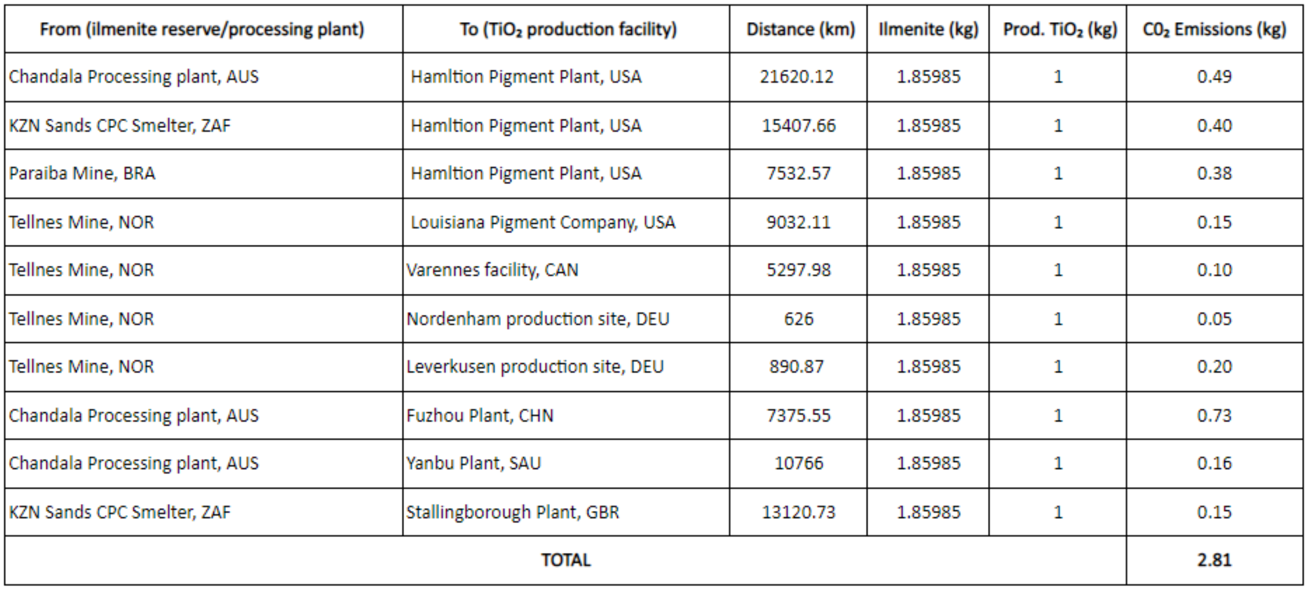


Figure 18: Annual ilmenite capacity in global production in three perspectives for each country: the annual consumed ilmenite if all the bed boilers used ilmenite as a bed material with and without magnetic separator, and the annual consumption of ilmenite as feedstock for TiO_2 production. The unit used in the diagram is 10^3 ton.

4.2.1 Annual TiO_2 pigment capacity and feedstock distribution

As seen in Figure 18 China has the leading annual capacity in global titanium dioxide (TiO_2) production, followed by United States and then by Germany. China is not only leading in global TiO_2 production but also in ilmenite mine production and reserves, and most of the ilmenite used in TiO_2 production is domestically produced in China. Compared to China most of the ilmenite used in TiO_2 production in the United States is mainly produced in South African, Australian and Norwegian mines. The Norwegian mines have the largest ilmenite reserve in Europe and provides ilmenite to several countries for TiO_2 production like Germany the largest annual capacity in TiO_2 production in Europe, United States, Belgium, and Canada.

According to the shown data, shipment of ilmenite to TiO_2 production facilities is necessary for some countries, due to ilmenite reserve`s not being located near a TiO_2 production facility. One such country, that is dependent on import, as mentioned previously, is U.S, which is dependent on the ilmenite reserves in Australia, South Africa and Brazil.



From (ilmenite reserve/processing plant)	To (TiO_2 production facility)	Distance (km)	Ilmenite (kg)	Prod. TiO_2 (kg)	CO_2 Emissions (kg)
Chandala Processing plant, AUS	Hamltion Pigment Plant, USA	21620.12	1.85985	1	0.49
KZN Sands CPC Smelter, ZAF	Hamltion Pigment Plant, USA	15407.66	1.85985	1	0.40
Paraiba Mine, BRA	Hamltion Pigment Plant, USA	7532.57	1.85985	1	0.38
Tellnes Mine, NOR	Louisiana Pigment Company, USA	9032.11	1.85985	1	0.15
Tellnes Mine, NOR	Varennes facility, CAN	5297.98	1.85985	1	0.10
Tellnes Mine, NOR	Nordenham production site, DEU	626	1.85985	1	0.05
Tellnes Mine, NOR	Leverkusen production site, DEU	890.87	1.85985	1	0.20
Chandala Processing plant, AUS	Fuzhou Plant, CHN	7375.55	1.85985	1	0.73
Chandala Processing plant, AUS	Yanbu Plant, SAU	10766	1.85985	1	0.16
KZN Sands CPC Smelter, ZAF	Stallingborough Plant, GBR	13120.73	1.85985	1	0.15
TOTAL					**2.81**

Table 3: Carbon dioxide emissions from ilmenite distribution, together with required ilmenite to produce 1 kg of TiO_2 pigment as assumed from the previous chapter of flow calculations. The only transport medium considered for calculation of transport emission is shipment with boats and trucks, where trucks emit 3x10^-4 kg/km CO_2 and boats emit 5x10^-6 kg/km CO_2. The calculated emissions take in account international transportation from mine to production facility and not emissions connected to domestic transportation (CO2 Calculator of Greenhouse Effects for Transport and Logistics, 2021).

As seen in table 3 the shipment of ilmenite to prominent TiO_2 production facilities emit 2.81 kg carbon dioxide to produce 12 kg TiO_2 worldwide, and the overall emission rate is 0.281 kg ￼ per 1kg produced ￼ in global distribution. This assumption is based on the mass from the sulphate process in Figure 12. It should be noted that the rate of emissions in global ￼ feedstock distribution can be only compared if all the bed boilers used ilmenite as bed material, a hypothesis that will be further analysed in the next chapters.

4.2.2 Annual ilmenite capacity in bed boilers

As seen in Figure 18 China has the leading annual ilmenite capacity if all the fluidized bed boilers used ilmenite as a bed material, followed by Sweden and then by Finland. As mentioned, China has the ilmenite resources to provide ilmenite as a bed material for bed boilers, but this does not apply for Sweden and Finland. These latter mentioned countries do not have the resources to provide ilmenite as a bed material, so shipment from countries with high mine production is necessary. Figure 18 also demonstrate a reduced annual ilmenite usage capacity when ilmenite is used as bed material in all the bed boilers, compared to all fresh ilmenite directly delivered as a feedstock to TiO_2 production. An additional reduction in annual ilmenite capacity is made when the ilmenite is used as bed material in all the bed boilers with magnetic separation, as only a third of the required ilmenite is needed per MWh.

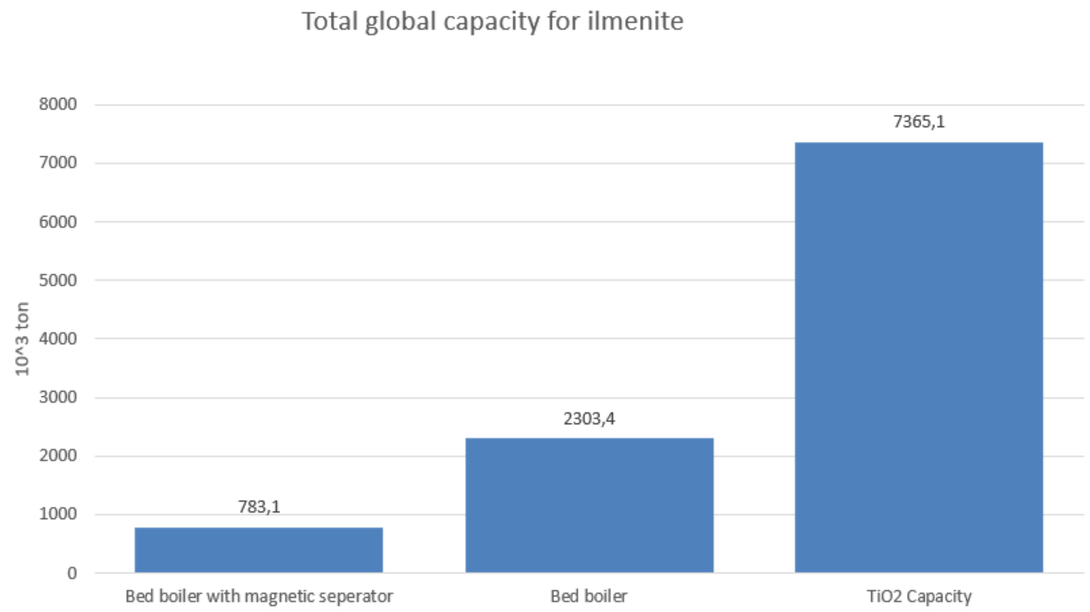


Figure 19: Total global capacity for ilmenite under assumption that all bed boilers use ilmenite as bed material. This diagram demonstrates the total annual ilmenite production capacity in three perspectives: the total annual consumption of ilmenite if all the bed boilers used ilmenite as a bed material with and without magnetic separator, and the total annual consumption of ilmenite as feedstock for TiO_2 production.

Note. The information for the diagram is gathered from Figure 18.

Figure 20 shows the capacity of ilmenite in bed boilers and TiO_2 production which can be used to see the proportion of the material needed for heat and power that overlaps with the material needed for ￼ production. With the overlap we can analyse what is the share of the material from fluidized bed boilers that will contribute to the TiO_2 production in a combined flow case. In case of a combined flow, the current installed fluidized bed boilers plants would only stand for 31% of the total ilmenite in TiO_2 production, where bed boilers with magnetic separation would stand for 11% of the total TiO_2 production and the rest would be from fresh ilmenite resources. This proportion of ilmenite use would be possible if every country with bed boilers is assumed to have enough ilmenite resource for all the existing bed boilers. Potential new routes in ilmenite distribution from prominent ilmenite reserves to prominent TiO_2 production and bed boiler facilities could make this possible. Combined flow for ilmenite use will result in an increase in the driving force to exchange ilmenite in existing fluidized bed boiler. This will be further discussed in the next chapter.

4.2.3 Potential ilmenite distribution to TiO_2 production and bed boiler facilities

In order to have ilmenite as a bed material for all the existing and future fluidized bed boilers, there is a need new for potential routes of ilmenite distribution. Figure 22 has only introduced potential ilmenite distribution to prominent countries with bed boiler production facilities, TiO_2 production facilities and ilmenite reserves/processing plants.

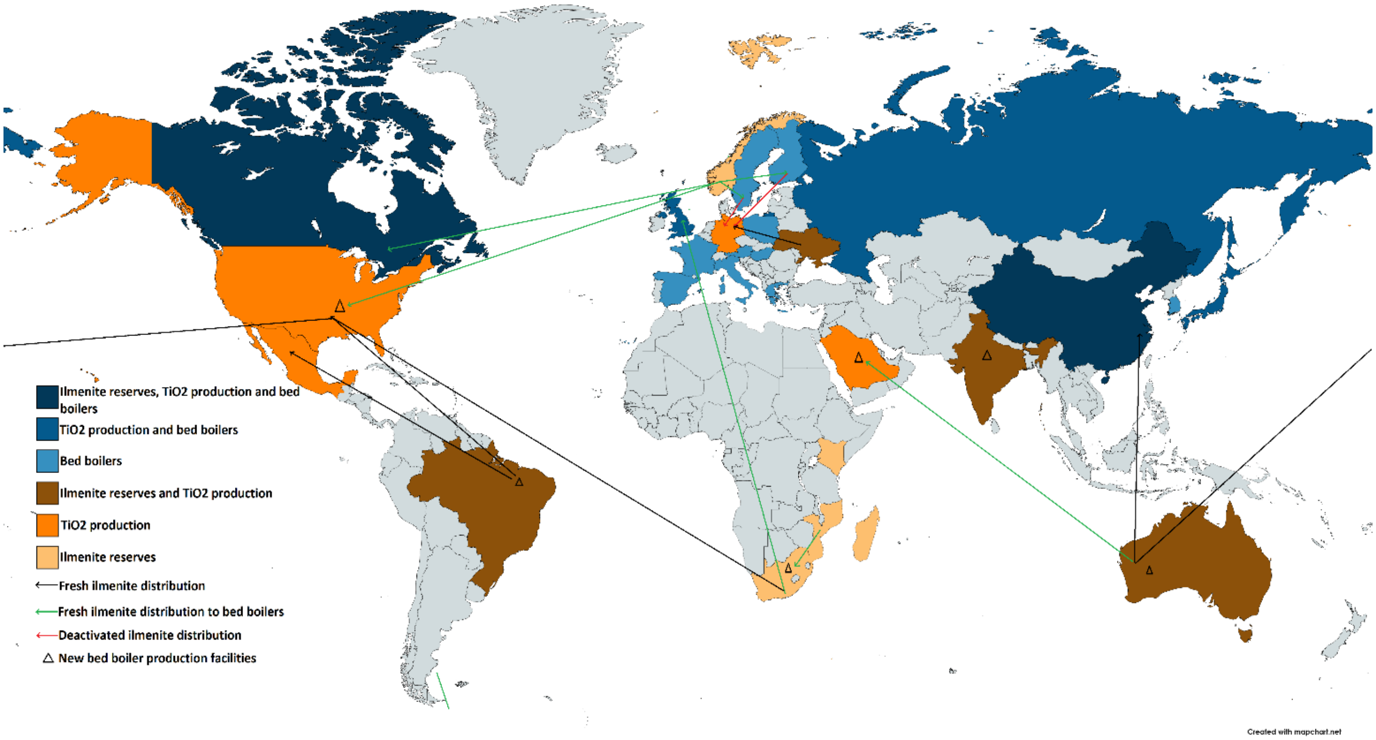


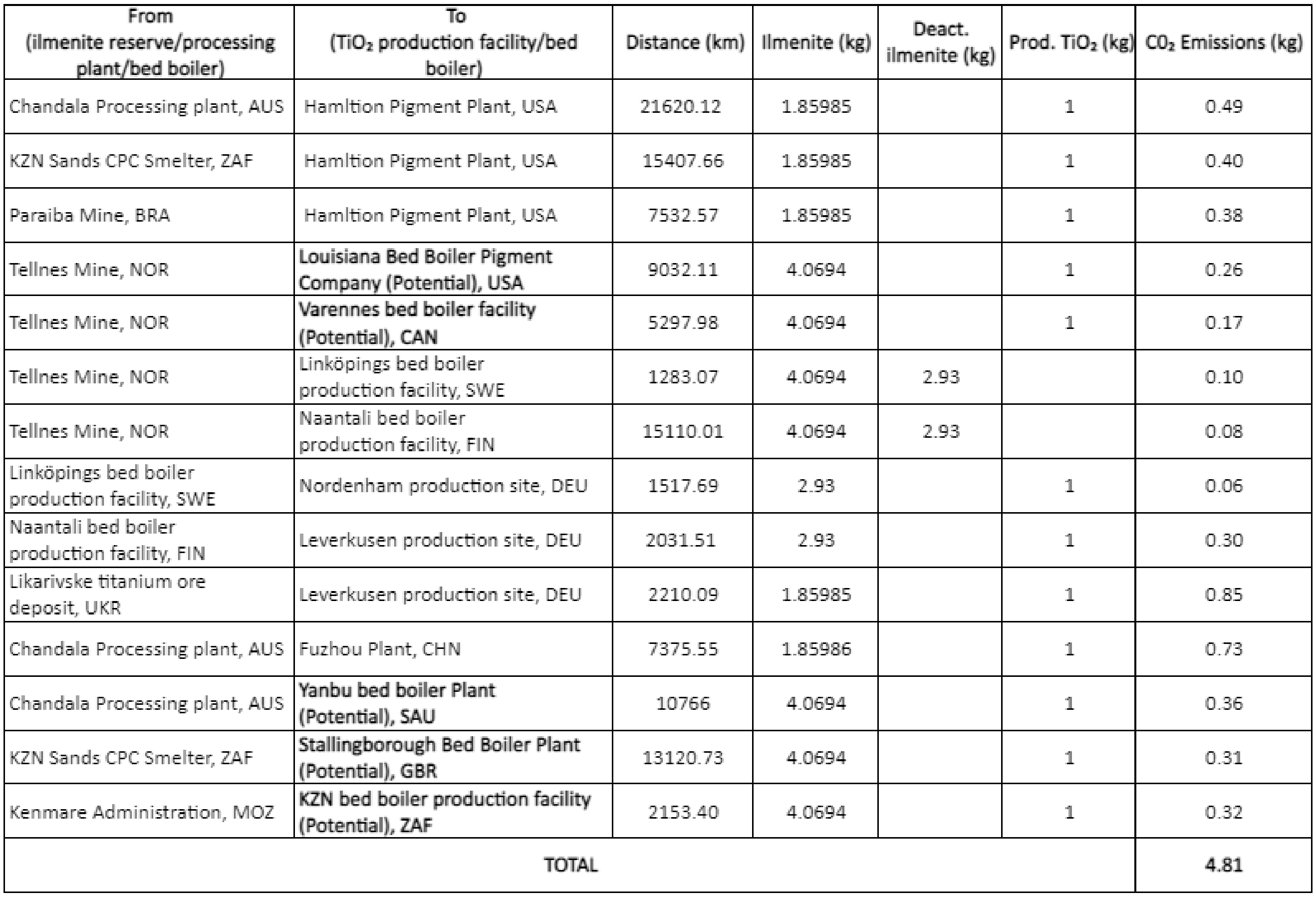
Figure 20: Map chart showing the potential distribution of ilmenite to assure a combined flow of ilmenite from reserves/processing plants to TiO_2 production and bed boiler production facilities. This chart also shows the deactivated ilmenite distribution from bed boilers to TiO_2 production facilities and potential new bed boiler production facilities for some counties.

Note. The information for the map chart is gathered from Figure 1,4,5 and 9.

The map chart in Figure 20 illustrates several new routes of ilmenite distribution, for instance the recent ilmenite distribution route to bed boilers in Sweden and Finland. The reasoning behind this new route is that these countries do not have the resources to provide ilmenite as a bed material, so shipment from countries with high mine production is necessary. The closest country with high ilmenite production is Norway. To avoid large amount of carbon dioxide emission Norwegian ilmenite from Tellnes is chosen as a bed material resource for bed boilers in Sweden and Finland. After the ilmenite has been processed in Swedish and Finnish bed boilers, the produced deactivated ilmenite containing Ti-rich fractions can be distributed as feedstock resource to nearest prominent TiO_2 production facilities, which is Germany. The two-remaining routes from Tellnes ilmenite is to new potential bed boiler production facility in Louisiana, USA and Varennes, Canada. Compared to the map chart of ilmenite distribution without accounting for the use in fluidized bed boilers in Figure 5, the distributed ilmenite from Tellnes mines is delivered as feedstock to TiO_2 production facility in Louisiana and Varennes and not as bed material to bed boilers. The accounted scenario will cause a larger amount of ilmenite distributed to those facilities and increase the carbon dioxide emissions, due to the fact that ilmenite from fluidized bed boiler facilities require more fresh ore to produce 1kg of TiO_2. The rest of the production facilities in United States will continue use ordinary TiO_2 production facility. The largest production facility Hamilton maintains exporting regular amount of ilmenite from Brazil, South Africa and Australia to produce TiO_2, due to a small amount of existing fluidized bed boilers. China, on the other hand, has the largest fluidized bed boiler capacity in the world and potentially would produce the highest amount of TiO_2 from fluidized bed boiler units where most of the ilmenite is from external sources and Australia. Changed ilmenite distribution routes can also be established for potential bed boiler production capacity in United Kingdom and Saudi Arabia as seen in Figure 20. The current production facility in Saudi Arabia and United Kingdom is replaced with bed boiler production facility but the main vendor for resources remains unchanged, with larger amount of ilmenite distributed.

All the mentioned potential bed boiler production facilities have a combined single flow, where the produced deactivated ilmenite from bed boilers during the OCAC process goes directly from the magnetic separator to TiO_2 production. Except the bed boiler production facility in Linköping, Sweden and Naantali, Finland, ilmenite is used to produce deactivated ilmenite for distribution.

Countries with external ilmenite distribution like India, Brazil, Australia and partly South Africa, can also potentially establish new bed boiler production facilities. Unfortunately, the emission calculations data for Figure 20 have been not complete and thereby these distribution routes have not been presented.



From (ilmenite reserve/processing plant/bed boiler)	To (TiO_2 production facility/bed boiler)	Distance (km)	Ilmenite (kg)	Deact. ilmenite (kg)	Prod. TiO_2 (kg)	CO_2 Emissions (kg)
Chandala Processing plant, AUS	Hamltion Pigment Plant, USA	21620.12	1.85985		1	0.49
KZN Sands CPC Smelter, ZAF	Hamltion Pigment Plant, USA	15407.66	1.85985		1	0.40
Paraiba Mine, BRA	Hamltion Pigment Plant, USA	7532.57	1.85985		1	0.38
Tellnes Mine, NOR	**Louisiana Bed Boiler Pigment Company (Potential), USA**	9032.11	4.0694		1	0.26
Tellnes Mine, NOR	**Varennes bed boiler facility (Potential), CAN**	5297.98	4.0694		1	0.17
Tellnes Mine, NOR	Linköpings bed boiler production facility, SWE	1283.07	4.0694	2.93		0.10
Tellnes Mine, NOR	Naantali bed boiler production facility, FIN	15110.01	4.0694	2.93		0.08
Linköpings bed boiler production facility, SWE	Nordenham production site, DEU	1517.69	2.93		1	0.06
Naantali bed boiler production facility, FIN	Leverkusen production site, DEU	2031.51	2.93		1	0.30
Likarivske titanium ore deposit, UKR	Leverkusen production site, DEU	2210.09	1.85985		1	0.85
Chandala Processing plant, AUS	Fuzhou Plant, CHN	7375.55	1.85986		1	0.73
Chandala Processing plant, AUS	**Yanbu bed boiler Plant (Potential), SAU**	10766	4.0694		1	0.36
KZN Sands CPC Smelter, ZAF	**Stallingborough Bed Boiler Plant (Potential), GBR**	13120.73	4.0694		1	0.31
Kenmare Administration, MOZ	**KZN bed boiler production facility (Potential), ZAF**	2153.40	4.0694		1	0.32
TOTAL						**4.81**

Table 4: Potential carbon dioxide emissions from ilmenite distribution, and the required ilmenite amounts to produce 1 kg of TiO_2 pigment. The ilmenite required in form of to produce deactivated ilmenite from fluidized bed boilers to later produce 1 kg of TiO_2 pigment. This information is based on the previous chapter of flow calculations. Just like in Figure 20 the assumption is that it is international transportation emissions and emissions from boats and land vehicle (CO2 Calculator of Greenhouse Effects for Transport and Logistics, 2021)

The schedule in table 4 demonstrate the total emission of distributed ilmenite and deactivated ilmenite in the potential distribution map chart. The total emission is calculated to be around 4.81 kg carbon dioxide to produce 12 kg of TiO_2 worldwide, this is equal to 0.4 kg CO_2 per 1kg produced TiO_2 in global distribution. These numbers can be compared to the total emission of ilmenite distribution without fluidized bed boiler production units, which is 0.281 kg CO_2 per 1kg produced TiO_2. So, based on the presented numbers, the total emission for production of 1kg TiO_2 with potential bed boiler production facilities would increase by 42.3 %. This is due to ilmenite distribution to potential bed boiler production facilities require a higher volume of ilmenite and this would obviously increase the total emission.

When analysing the total emission of global ilmenite distribution, most of generated carbon dioxide emission are emitted during transportation with land vehicles. So, recommendations for reduction of carbon dioxide emissions for future implementations, would be to build most of the new fluidized bed boiler production facilities near ports. This will result in reduction of emissions, due to the fact that water transportation emits smaller amount of carbon dioxide. So, for example if comparing the route with almost same distance from Naantali bed boiler production facility to Leverkusen production with the route with the largest emissions from Likarviske titanium ore deposit to the same production facility. This shows that distribution from Naantali which is through water transportation emit a smaller amount of carbon dioxide compared to land dominated distribution from Likarviske. So, if a proportion of the Leverkusen production site is located near a port, the emission would reduce. This is also true for other production facilities that require distribution through land.

5 Future outlook and conclusions

The aim of the thesis is to identify the impact ilmenite use as it is today and expected future change have on sustainability and circular economy and find potential solutions for improvements. Based on the data gathered through research and analysis it can be concluded some of the multiple factors that impact ilmenite use have been identified. The factors include the emissions emitted from the processes itself and how the transportation of ilmenite between facilities can impact the environment. The results have been narrowed down to indicate that in overall combining the flows of ilmenite for TiO_2 production and OCAC is beneficial for sustainability. This is because titan is a scarce resource and the waste generated is not significantly more than the waste generated by having separate flows. The thesis shows clearly how much waste is generated by processing $FeTiO_3$ and Fe_2TiO_5, but it raises the question on how much waste is generated by the impurities in the minerals and the impurities introduced by the different processes and how this will affect the total waste. Further research should be done on how impurities affect the total emission by the processes and if the results still suggest that the waste flows should be combined.

The expectation for the combined flow was that it would generate less waste in form of material and emission. However, the results shows that it emits more in the processes due to the higher mass of the deactivated ilmenite necessary to produce 1 kg TiO_2 through the combined flow.

The methodology for calculating the wastes is limited by factors such as not taking impurities into consideration, only taking sea and land transportation in account and assumed loss percentage for ilmenite during the OCAC process.

The calculation of high-level overview shows that most of the emissions are generated by land vehicles. Thus, the recommendation is that ilmenite, especially deactivated ilmenite and ilmenite used as bed material should primarily be transported through sea. This is due to the higher mass of deactivated ilmenite needed to produce 1kg TiO_2 compared to conventional mean use of fresh ore. This will result in lower emission compared to current singular flow. This could be done by building facilities for bed boilers and TiO_2 productions near harbours. This however raises the question at what distance does land travel becomes unfeasible for combined flow compared to singular flow from a sustainability context. More research is therefore needed when looking for at what distance traveling with land vehicle makes it unsustainable to do a combined flow in comparison to singular flow.

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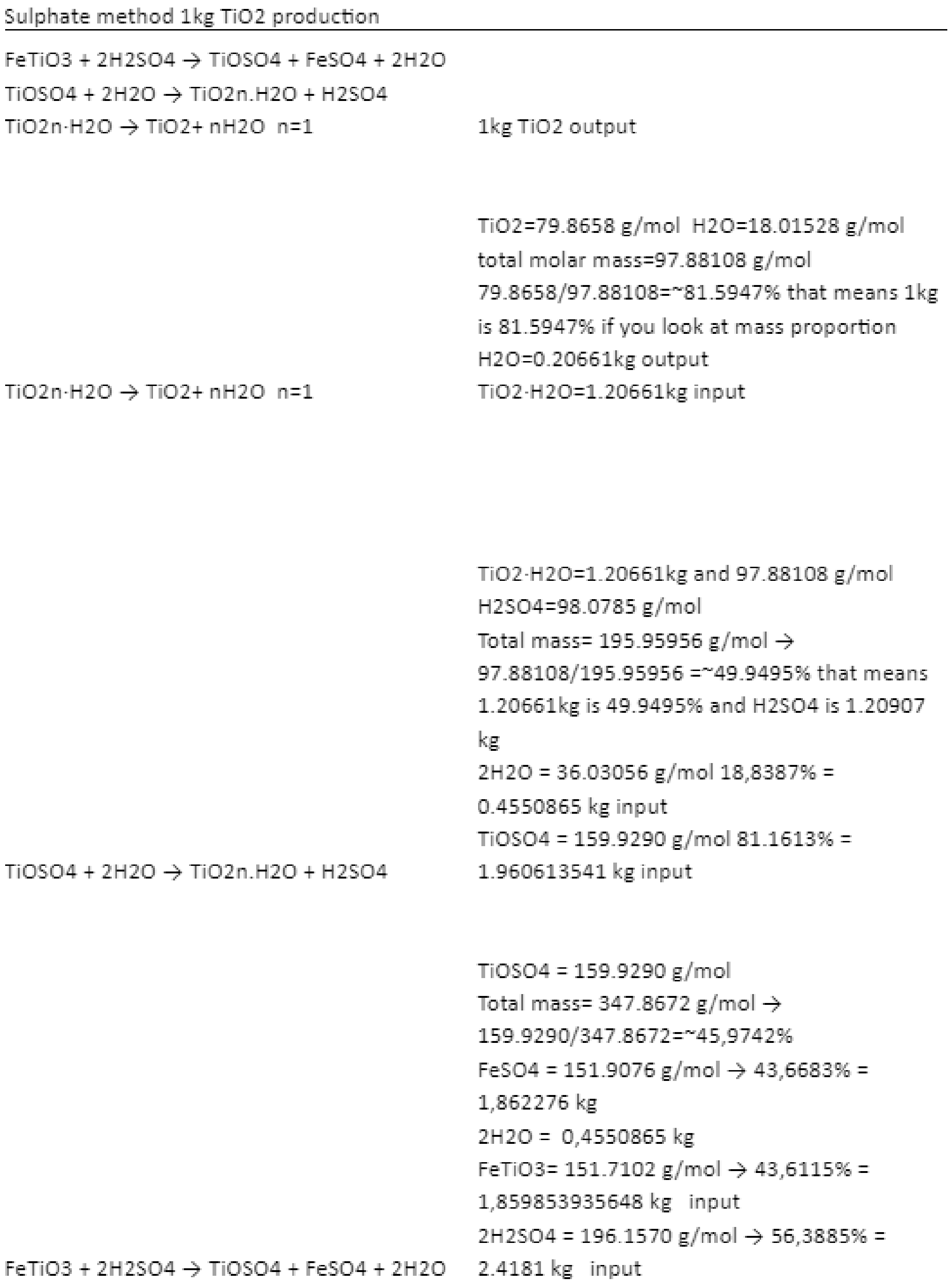
Appendix

Appendix A - calculation sulphate



Sulphate method 1kg TiO2 production

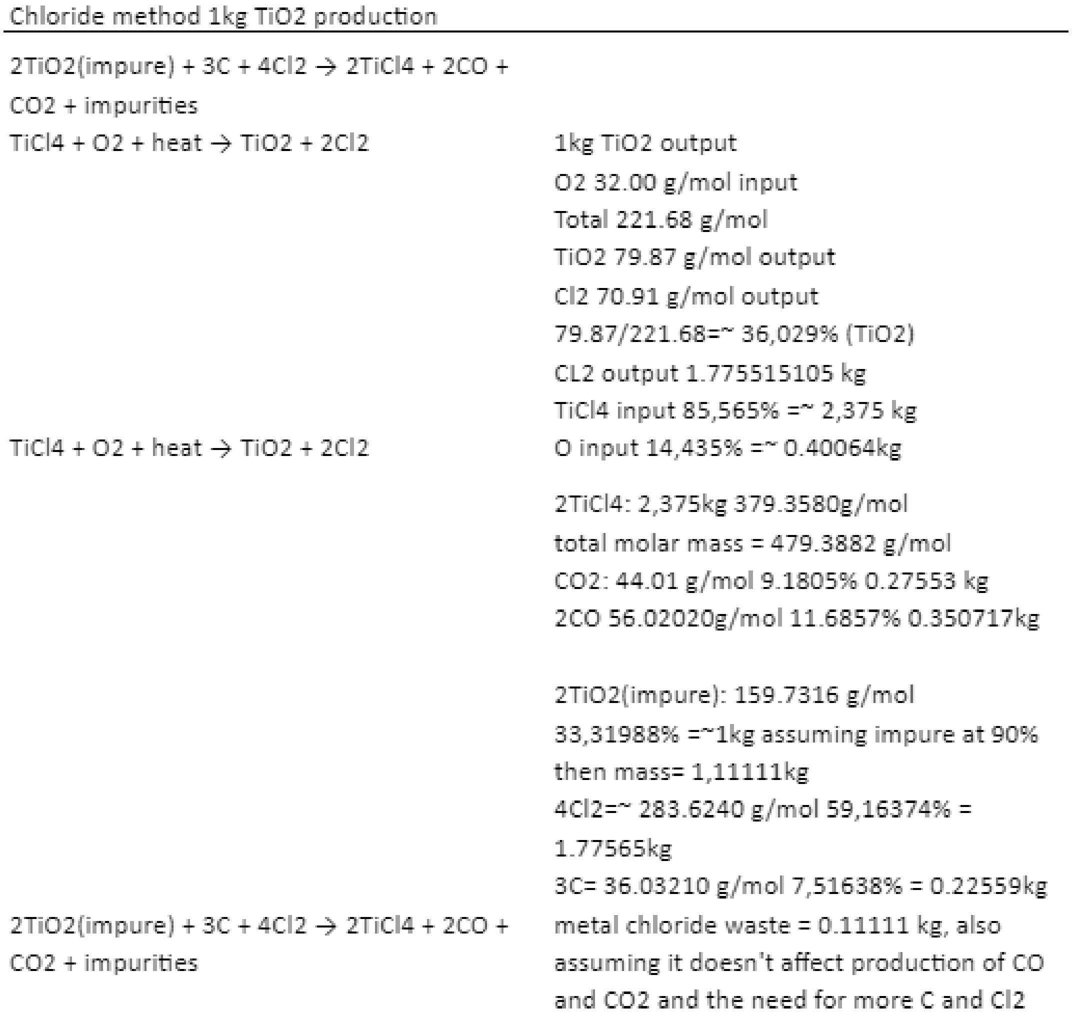
FeTiO3 + 2H2SO4 → TiOSO4 + FeSO4 + 2H2O
TiOSO4 + 2H2O → TiO2n.H2O + H2SO4
TiO2n·H2O → TiO2+ nH2O n=1 — 1kg TiO2 output

TiO2=79.8658 g/mol H2O=18.01528 g/mol
total molar mass=97.88108 g/mol
79.8658/97.88108=~81.5947% that means 1kg is 81.5947% if you look at mass proportion
H2O=0.20661kg output
TiO2n·H2O → TiO2+ nH2O n=1 — TiO2·H2O=1.20661kg input

TiO2·H2O=1.20661kg and 97.88108 g/mol
H2SO4=98.0785 g/mol
Total mass= 195.95956 g/mol →
97.88108/195.95956 =~49.9495% that means 1.20661kg is 49.9495% and H2SO4 is 1.20907 kg
2H2O = 36.03056 g/mol 18,8387% = 0.4550865 kg input
TiOSO4 = 159.9290 g/mol 81.1613% =
TiOSO4 + 2H2O → TiO2n.H2O + H2SO4 — 1.960613541 kg input

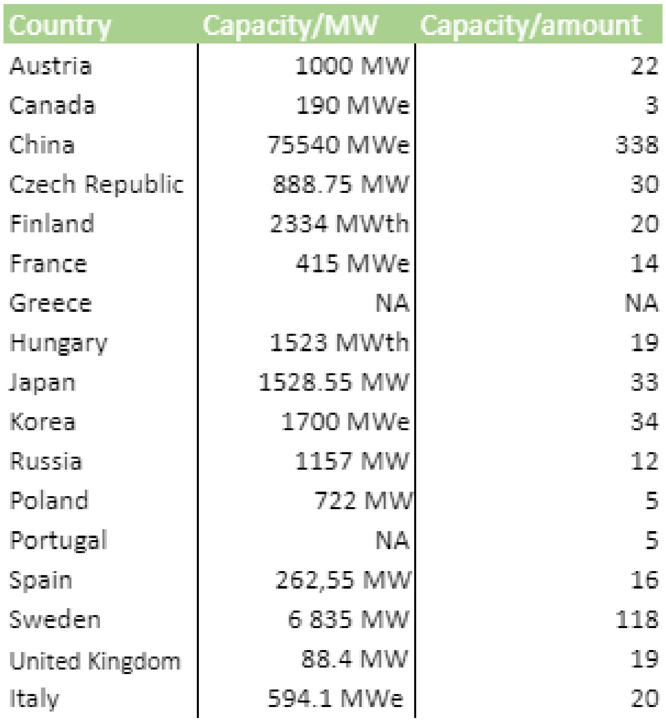
TiOSO4 = 159.9290 g/mol
Total mass= 347.8672 g/mol →
159.9290/347.8672=~45,9742%
FeSO4 = 151.9076 g/mol → 43,6683% = 1,862276 kg
2H2O = 0,4550865 kg
FeTiO3= 151.7102 g/mol → 43,6115% = 1,859853935648 kg input
2H2SO4 = 196.1570 g/mol → 56,3885% =
FeTiO3 + 2H2SO4 → TiOSO4 + FeSO4 + 2H2O — 2.4181 kg input

Appendix B - calculation chloride



Chloride method 1kg TiO2 production	
2TiO2(impure) + 3C + 4Cl2 → 2TiCl4 + 2CO + CO2 + impurities	
TiCl4 + O2 + heat → TiO2 + 2Cl2	1kg TiO2 output
	O2 32.00 g/mol input
	Total 221.68 g/mol
	TiO2 79.87 g/mol output
	Cl2 70.91 g/mol output
	79.87/221.68=~ 36,029% (TiO2)
	CL2 output 1.775515105 kg
	TiCl4 input 85,565% =~ 2,375 kg
TiCl4 + O2 + heat → TiO2 + 2Cl2	O input 14,435% =~ 0.40064kg
	2TiCl4: 2,375kg 379.3580g/mol
	total molar mass = 479.3882 g/mol
	CO2: 44.01 g/mol 9.1805% 0.27553 kg
	2CO 56.02020g/mol 11.6857% 0.350717kg
	2TiO2(impure): 159.7316 g/mol
	33,31988% =~1kg assuming impure at 90% then mass= 1,11111kg
	4Cl2=~ 283.6240 g/mol 59,16374% = 1.77565kg
	3C= 36.03210 g/mol 7,51638% = 0.22559kg
2TiO2(impure) + 3C + 4Cl2 → 2TiCl4 + 2CO + CO2 + impurities	metal chloride waste = 0.11111 kg, also assuming it doesn't affect production of CO and CO2 and the need for more C and Cl2

Appendix C - bed boiler capacity

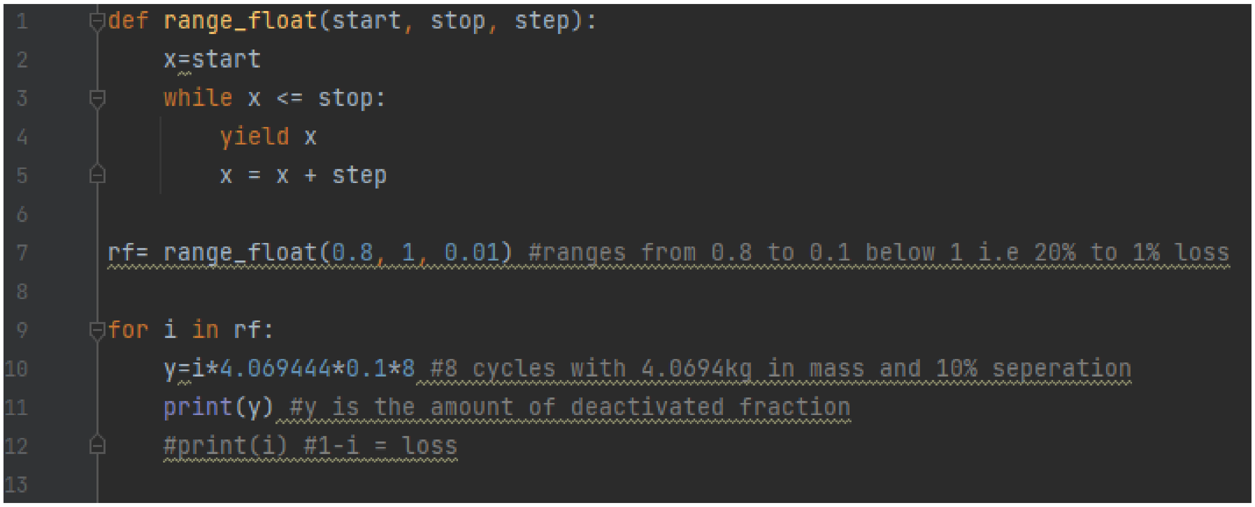


Country	Capacity/MW	Capacity/amount
Austria	1000 MW	22
Canada	190 MWe	3
China	75540 MWe	338
Czech Republic	888.75 MW	30
Finland	2334 MWth	20
France	415 MWe	14
Greece	NA	NA
Hungary	1523 MWth	19
Japan	1528.55 MW	33
Korea	1700 MWe	34
Russia	1157 MW	12
Poland	722 MW	5
Portugal	NA	5
Spain	262,55 MW	16
Sweden	6 835 MW	118
United Kingdom	88.4 MW	19
Italy	594.1 MWe	20

Appendix D – questionnaire

Questions	Tronox ltd.	Chemours	Iluka
Where do you find ilmenite today and how much do you estimate the volume to be?	https://pubs.usgs.gov/periodicals/mcs2021/mcs2021-titanium-minerals.pdf	Below is publicly-available information from the USGS you can find online. There are other ilmenite reserves not listed that Chemours is aware of, such as in Greenland and Paraguay. It comes down to project economics whether a mine site is opened. There are hundreds of years of ilmenite supply available on our planet at current consumption rates. Remember that Ti is the ninth most abundant element in the earth's crust	You will be able to source all required information on our website: https://www.Iluka.com.au
What use has ilmenite currently and how does it's distribution look like both geographical distribution and with different industries?	https://www.usgs.gov/ centers/nmic/titanium-statistics-and-information	Wikipedia has a lot of good information: https://en.wikipedia.org/wiki/IlmeniteIlmenite is mostly used (exclusively?) in the manufacture of titanium dioxide, either by the chloride-route or sulfate-route or even HCl extraction technologies. I do not know of any other industrial use. Ilmenite is typically upgraded (beneficiated) through a slagging process that produces an iron product and the Ti-rich slag product. There is also a acid-leaching beneficiation process that some folks use to make a synthetic rutile. The slag and synthetic rutile are used as feedstocks for TiO2 manufacturing. Only Chemours has the technology to use higher-grade ilmenites, and even leucoxenes, as feedstocks to their chloride-route TiO2 process.	See above
How much of the ilmenite that processes becomes a product and how much becomes waste fraction?	When ilmenite is processed through the sulfate process to produce TiO2 pigment, ~7% is lost. This is landfilled or in some cases recycled.	I'm not sure I understand the question. Is this question associated with the processing of the ilmenite into TiO2, or slag, or synthetic rutile? Or is the question associated with separating efficiencies of the ilmenite mineral from heavy mineral concentrate at ore processing plant where the ziron, rutile, leucoxene, ilmenite, etc. minerals are separated? If the question is associated with conversion of the Ti content into the intermediate, TiCl4 from chloride-route or titanyl sulfate from sulfate-route, then the general answer is likely in the range of 90 to 98%. It depends on the processability and impurity levels of the feedstock and on the capability of the equipment.	-||-
What do you do with the wastes that doesn't become a product?	See above	This would be a long and windy explanation which I do not have time to address. The short answer is, it depends. The disposition is typically specific to locale. If possible, the metal chloride, which is mainly FeCl2 and FeCl3 in the case of chloride-route technology, can be neutralized and landfilled; or deep well injected; or treated and sold as a wastewater treatment brine; or converted into a creted co-product and sold into construction of roadways and such. For sulfate, the waste can be landfilled; or converted into a fertilizer and sold; or converted into a product for addition to cement manufacturing; etc. All producers are working hard to generate value from these streams and also reduce their environmental footprint. Some sulfate producers, particularly in China, are harvesting scandium from their waste metal stream.	-||-
What happens with the waste from the products that were made using ilmenite?	TiO2 pigment is used in paints, plastics and papers. It cannot be recycled	Again, it really depends. See above. Very site-specific.	-||-

Appendix E – loss loop



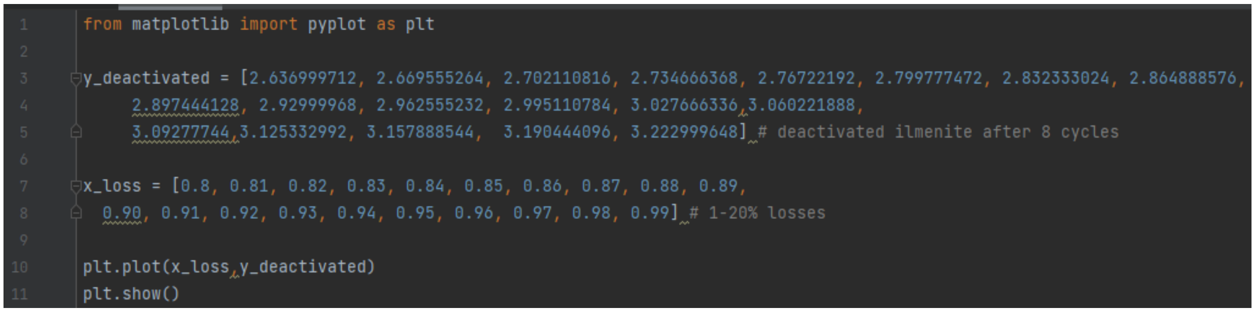
```python
def range_float(start, stop, step):
    x=start
    while x <= stop:
        yield x
        x = x + step

rf= range_float(0.8, 1, 0.01) #ranges from 0.8 to 0.1 below 1 i.e 20% to 1% loss

for i in rf:
    y=i*4.069444*0.1*8 #8 cycles with 4.0694kg in mass and 10% seperation
    print(y) #y is the amount of deactivated fraction
    #print(i) #1-i = loss

```

Appendix F – loss plot



```python
from matplotlib import pyplot as plt

y_deactivated = [2.636999712, 2.669555264, 2.702110816, 2.734666368, 2.76722192, 2.799777472, 2.832333024, 2.864888576,
     2.897444128, 2.92999968, 2.962555232, 2.995110784, 3.027666336,3.060221888,
     3.09277744,3.125332992, 3.157888544,  3.190444096, 3.222999648] # deactivated ilmenite after 8 cycles

x_loss = [0.8, 0.81, 0.82, 0.83, 0.84, 0.85, 0.86, 0.87, 0.88, 0.89,
  0.90, 0.91, 0.92, 0.93, 0.94, 0.95, 0.96, 0.97, 0.98, 0.99] # 1-20% losses

plt.plot(x_loss,y_deactivated)
plt.show()
```