# CHAPTER I INTRODUCTION

# 1.1. Background

Entering the era of industrialization, required an industry that can provide a positive impact on the development of the industry in Indonesia. Industry titanium dioxide (TiO<sub>2</sub>) is one of it. Based on data from the Ministry of Industry, about 80-90% titanium dioxide is imported from outside. Titanium dioxide is used in the paint industry (50%), plastic, fiber, ceramics (15%) and the remainder is used as catalyst materials.

Industry mostly uses titanium dioxide as support material for strength similar to steel, but has a lighter weight than steel. Almost 90% of titanium is consumed in the world is a form of titanium dioxide (TiO<sub>2</sub>).

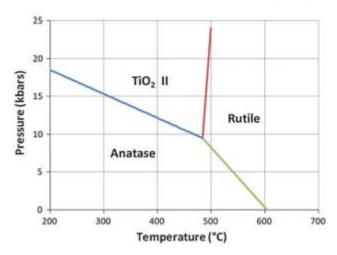


Figure. 1.1. Phase diagram of titanium dioxide

Titanium dioxide is composed of three types of structures, namely: rutile, anatase and brookite. rutile can be produced from a temperature of 600°C to a high temperature and pressure from low to high pressure. Anatase produced at a low temperature below 600°C and with pressure below 18 kbars. While, brookite produced at high pressure and high temperature (Hanaour, 2010).

Pigments are more often used in industry is rutile, because rutile TiO2 has several advantages.

Table 1.1. Comparison the characteristic of rutile and anatase (Subagia, 2013)

Comparison	Rutile	Anatase
Refractive index	2.76	2.52
Tinting strength	1750-1850	1250
Oil absorption	16-36	16-26

From Table 1.1 shows that rutile is better used as a pigment than anatase. Refractive index showed on comparison adhesion between particles, Value of tinting strength showed about the ability to change the color of other pigments, while oil absorption shows the ability to absorb oil. From the comparison above shows that rutile is better than the anatase.

Based on data from the Ministry of Energy and Resources, Bangka Belitung province is one of the largest ilmenite owners in Indonesia. Tetragonal rutile and anatase tetragonal very widely used in various industries.

Based on statistical data, it is estimated the needs of Titanium dioxide in Indonesia will increase. Therefore, to meet the needs in the country required a titanium dioxide industry, while industry titanium dioxide has not been established yet. By using ilmenite raw materials are derived directly from Bangka Belitung Province. These considerations that underlie our titanium dioxide factory set up in Indonesia.

# 1.2. Design of Capacity

In determining the design capacity based on several things, such as the minimum capacity of an existing plant and demand in the country. Determination of titanium dioxide plant capacity considerations are based on the following considerations:

# 1.2.1. Titanium Dioxide Consumption

Domestic needs of titanium dioxide of about 90% are imported from abroad. Titanium dioxide import developments in Indonesia can be seen in Table 1.2. below.

Table 1.2. Data of Titanium dioxide import in 2011-2014 (BPS, 2015)

Years	Consumption (tons)
2011	46706.11
2012	51581.24
2013	50381.63
2014	53456.76

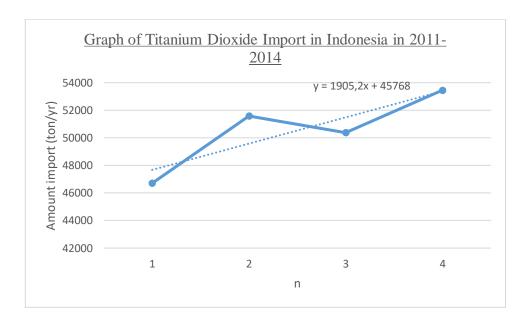


Figure 1.1. Graph of Titanium Dioxide Import in Indonesia in 2011-2014

Take the linear approach, will be obtained by the equation

$$y = 1905.2x + 45768 \tag{1-1}$$

Using equation 1-1 estimated in 2020 that Indonesia needs of titanium dioxide 57,199.20 tons.

# 1.2.2. Raw Materials Consumption

The raw material to produced titanium dioxide consists of ilmenite obtained from waste of PT. Timah Tbk. that's located on the Belitung Island. Rraw materials in Belitung Island reached 12,000 tons/ month and chlorine gas (Cl<sub>2</sub>) imported from China and coke as a reduction agent.

# 1.2.3. Minimum Capacity

The minimum capacity of the plant can be seen from the capacity of factories that have existing. List of titanium dioxide plant in the world and its capacity.

<u>Table 1.3. List of Titanium Dioxide Companies in the World and Its</u>
<u>Production Capacity</u>

Company	Production Capacity (tons/ year)	Location	Source
Kronos Worldwide	40,000	Cranbury,	http://kronostio2.com/en/componen
Inc.		New Jersey	t/content/category/17-
			manufacturing-facilities
Nanjing Titanium	80,000	Jiangsu,	www.nthcl.com/ecompany.html
Dioxide Chemical		China	
Co., Ltd.			
Zhejiang Ningbo	100,000	Shanghai,	http://xinfu-
Xinfu Titanium		China	tio2.com/en/aboutus.html
Dioxide Co., Ltd.			
Shandong Dongja	160,000	China	www.dongjianggroup.com/about.as
Group, Henan			px
Billions Chemicals			
Co., Ltd.			
CNNC Hua Yuan	200,000	Shanghai,	www.sinotio2.com/node/37
Titanium Dioxide		China	
Co., Ltd			
Tronox Inc.	225,000	Mississippi,	http://www.tronox.com/electrolytic
		USA	s-and-specialty-
			chemicals/operations/hamilton-
			mississippi-u-s/
The National	500,000	Ashtabula,	http://www.cristal.com/news-
Titanium Dioxide		USA	room/news/Pages/Cristal-Global-
Company, Ltd.			announces-a-groundbreaking-TiO2-
("Cristal")			industry-partnership-with-
			Outotec.aspx

From the results of the review of existing plant capacity and absorption in the domestic market. we decided to make a titanium dioxide plant with a capacity of 50,000 tons / year. This plant will start operating in 2020.

# 1.3. Plant Location

The plant will be built in East Belitung. Factors affecting of the location of the plant on the island of Belitung, namely:

#### 1.3.1. Raw Materials

Raw materials of plant titanium dioxide (TiO<sub>2</sub>) is obtained from the rock ilmenite mining around the island of Belitung and chlorine gas imported from China.

# 1.3.2. Marketing

To reduce transportation costs and the problem of product sales, then marketing factors need to be taken into account in the selection of the plant site. Titanium dioxide is a finished product and is often used as an additive for ceramics, paints, and cosmetics industry. This product is planned to be distributed for domestic needs, the location of the plant is located close to the port to reduce transportation costs of products from the factory to the ship. On the Belitung Island, there is Manggar Port are being traffic import-export trade on the Belitung Island.

# **1.3.3.** Utility

Utility requirements that need covering electricity, water and fuel. The demand for electricity can be obtained from the Steam Turbine Generator. Water requirements can be obtained from the river near the plant that is Manggar river.

#### 1.3.4. Labor

Based on the number of productive workers who have not been channeled, since it was for labor can be obtained easily from the surrounding community. Based on statistical data, amounted to 60.71% of Belitung community included in the working age population and the remaining 39.29% is not a resident of the labor force (school, taking care of the household and others.

# 1.3.5. Transportation and Telecommnication

Transport is one of the factors to consider in selecting the location of the plant, because with good transport will help the process of factory work in distribution and communication. In this case the transportation will be easy because of the location to the harbor and trans-Sumatra road, so the distribution of the product will be easy.

#### 1.4. Literature Review

#### 1.4.1. Production Process Description

There are two processes of Titanium Dioxide manufacturer, namely:

# a) Chloride Process

The chloride process begins with the conversion of high-grade ilmenite into titanium tetrachloride. This step occurs in a fluidized bed chlorinator in the presence of chlorine gas at a temperature of approximately 900°C. Coke also is added as a reductant. The volatile TiCl<sub>4</sub>, including FeCl<sub>3</sub>, CO, N<sub>2</sub>, Cl<sub>2</sub>, exit the chlorinator as overhead vapor. And residue of impurities, the unreacted coke and ore solids are removed from the gas stream and from the bottom of the chlorinator. The gaseous product stream is purified to separate the titanium tetrachloride from other metal chloride impurities using condensation. Vent gases from the chlorinator are scrubbed in the Caustic Scrubber to absorb Cl<sub>2</sub> content taken in the gas stream. The purified TiCl<sub>4</sub> is then oxidized to TiO<sub>2</sub>, driving off chlorine gas, which is recycled to the chlorinator. The pure TiO<sub>2</sub> is slurred and sent to finishing process (U.S. Evironmental Protection Agency, 2001).

# b) Sulfate Process

The sulfate process starts with dried and milled slag TiO<sub>2</sub> being dissolved in sulfuric acid and water in a digester. This produces a titanyl sulfate liquor. From the digester the titanyl sulfate liquor goes to a clarification tank where the undissolved ore and solids are allowed to settle. The titanium liquor then is concentrated and hydrolyzed to titanium dioxide hydrate. The titanium dioxide hydrate precipitates from the ferrous sulfate and sulfuric acid is separated through filtration. After filtration the hydrated titanium dioxide slurry is sent to a calciner, where the titanium dioxide crystals grow to their final crystalline size

and residual water and  $H_2SO_4$  are removed. The dried titanium dioxide is sent to pigments finishing. This finishing phase involves any required milling and or chemical treatment, such as surface coating with silica or alumina (U.S. Evironmental Protection Agency, 2001).

Table 1.4. Comparison of Titanium Dioxide Manufacture Process

Aspect	Sulphate Process		Chloride Process		
Operating Conditions	Reactor 1 $P = 3.5 \text{ atm}$ $T = 473.15 \text{ K}$		Reactor 1 $P = 1 \text{ atm}$ $T = 1173.15 \text{ K}$	Reactor 2 $P = 1$ atm $T = 1273.15$ K	
Waste	FeSO <sub>4</sub> formed in can cause problems	*****		No form of waste in large quantities	
Product Quality	Produce titanium dioxide anastase type of low quality		Produce titanum dioxide rutile type of high quality. Rutile is the most stable oxide titania		

Based on the above considerations, titanium dioxide plant will use the chloride process for titanium dioxide which would be produced in the form of rutile that to be used as a pigment in the paint, ceramics, fiber industry an others.

# 1.4.2. Uses of Titanium Dioxide

Titanium dioxide is used as a white pigment (in paints, plastics, rubber, paper), industrial ceramics, fiber, cosmetics, and also used as catalysts and photocatalysts.

# 1.4.3. Physical and Chemical Properties of Raw Materials and Products

# a) Raw Materials

1. Ilmenite

Chemical composition (Subagja, 2013):

-  $TiO_2$  : 38.30%

-  $Fe_2O_3$  : 49.44%

- Impurities : 12.26%, which consist of:

•  $SiO_2$  : 1.76%

•  $Al_2O_3$  : 1.78%

• MnO : 2.00%

• MgO : 1.44%

• CaO : 0.08%

•  $K_2O$  : 0.03%

•  $P_2O_5$  : 0.17%

•  $Cr_2O_3$  : 2.66%

•  $SnO_2$  : 1.16%

#### 2. Titanium Dioxide

Physical Properties (Perry, 1997):

Formula : TiO<sub>2</sub>

- Formula weight, g/mol : 79.90

- Specific gravity : 4.26

- Melting point at 1 atm, °C : 1640

- Boiling point at 1 atm, °C : 3000

- Formation heat, kcal/ mol : -225.0

- Gibbs energy, kcal/ mol : -221.9

# Chemical properties (Kirk and Othmer, 1981):

- Not flammable

- Not corrosive

- Insoluble in water

# 3. Iron (III) Oxide

Physical Properties (Perry, 1997):

- Formula : Fe<sub>2</sub>O<sub>3</sub>

- Formula weight, g/mole : 159.70

- Specific gravity : 5.12

- Melting point at 1 atm, °C : 1560

- Boiling point at 1 atm, °C : 3600 - Formation heat, kcal/mole : -198.5

- Gibbs energy, kcal/mole : -179.1

# Chemical properties (Kirk and Othmer, 1981):

- Solution in acid
- Insoluble in water and organic solvents

# 2. Chlorine

Physical Properties (Perry, 1997):

- Formula : Cl<sub>2</sub>

- Formula weight, g/mol : 70.91

- Specific gravity : 2.49

- Melting point at 1 atm, °C : -101.6

- Boiling point at 1 atm, °C : -34.6

- Formation heat, kcal/mol : 0

- Gibbs energy, kcal/mol : 0

# Chemical properties (Kirk and Othmer, 1981):

- Not flammable
- Soluble in water
- Easy react with other compounds
- Toxic

# 3. Coke

Physical Properties (Perry, 1997):

- Formula : C

- Formula weight, g/mole : 12.01

- Specific gravity : 0.37-0.51

- Melting point at 1 atm,  $^{\circ}$ C : >3500

- Boiling point at 1 atm, °C : 4200

- Formation heat, kcal/mol : 0

- Gibbs energy, kcal/mol : 0

Chemical properties (Kirk and Othmer, 1981):

- React with oxygen and vapor
- Not corrosive

#### b) Products

1. Titanium Dioxide

Physical Properties (Perry, 1997):

- Formula : TiO<sub>2</sub>

- Formula weight, g/mole : 79.90

- Melting point at 1 atm, °C : 1855

- Boiling point at 1 atm, °C : 2500-3000

- Formation heat, kcal/mol : -225

- Gibbs energy, kcal/mol : -211.9

Chemical properties (Kirk and Othmer, 1981):

- Not easy to explode
- Insoluble in water
- Not corrosive

# 2. Iron (III) Chloride

Physical Properties (Perry, 1997):

- Formula : FeCl<sub>3</sub>

- Formula weight, g/mol : 162.22

- Specific gravity : 2.804

- Melting point at 1 atm, °C : 282

- Boiling point at 1 atm, °C : 315

- Formation heat (l), kcal/mole: -128.5

- Formation heat (g), kcal/mole: -129.5

- Gibbs energy (l), kcal/mole : -96.5

- Gibbs energy (g), kcal/mole : -97.8

Chemical properties (Kirk and Othmer, 1981):

- Corrosive
- Insoluble in water

#### 1.4.4. Process Review

Titanium dioxide is produced from the reaction between titanium dioxide ore contained in ilmenite with chlorine gas in the fluidized bed reactor at a temperature of about 900°C at atmospheric pressure with the addition of coke as a reducing agent. The reaction occurs as follows:

1. Coke Combustion Reaction

$$C + \frac{1}{2}O_2$$
  $\longrightarrow$   $CO$  (1-2)

2. Ilmenite Chlorination Reaction

$$TiO_2 + 2Cl_2 + CO$$
  $\longrightarrow$   $TiCl_4 + 2CO_2$  (1-3)

$$Fe_2O_3 + 3Cl_2 + 3CO \longrightarrow 2FeCl_3 + 3CO_2$$
 (1-4)

FeCl<sub>3</sub> formed from Fe<sub>2</sub>O<sub>3</sub> contained in ilmenite. Unreacted chloride non-volatile, residual coke and impurity ore ilmenite is removed from the gas stream through the bottom chlorinator. Out of chlorinator, the product temperature reaches 900°C. The stream of products in the form of gas is purified to separate the TiCl<sub>4</sub> from other gases through condensation, so that the product is entered into the cooler and cooled until the temperature reaches 170°C which FeCl<sub>3</sub> be condensed and then do the cooling again until the temperature reaches 40°C, and TiCl<sub>4</sub> already condensed. Flue gases such as CO, CO<sub>2</sub>, N<sub>2</sub>, and Cl<sub>2</sub> are supplied to the absorber for separation Cl<sub>2</sub> gas using caustic solution. Then the top products of the absorber will be channeled to the stack, where the CO is converted to CO<sub>2</sub>, which would then be discharged into the atmosphere. Pure TiCl<sub>4</sub> condensed incorporated into the oxidation reactor. Pure TiCl<sub>4</sub> is vaporized and oxidized in the oxidation

reactor at a temperature of 1000°C uses oxygen from the air to form titanium dioxide and chlorine gas. The reaction occurs as follows:

$$TiCl_4 + O_2 \qquad \longrightarrow \quad TiO_2 + 2Cl_2 \qquad (1-5)$$

Stream containing chlorine gas and  $TiCl_4$  is recycled toward chlorinator output. Pure  $TiO_2$  solids passed to the final stage, namely cooling and packaging to be marketed.