Tio2 Purification From Ilmenite The Tin Industry By-Product For Pigment

S A Aviandharie1, N N Aidha1, B N Jati1, R Ermawati1, A A Cahyaningtyas1
1Badan Penelitian dan Pengembangan Industri, Jl Gatot Subroto Kav 52-53 Jakarta
Email : agathareginasilvie@gmail.com

Abstract. Ilmenite deposits, a by-product of the tin industry in Bangka, cause environmental problems. Ilmenite is very abundant and has great potential because it still contains 53.83% titanium oxide. One of TiO2 benefits is for pigment. TiO2 pigment in Indonesia still imported. TiO2 pigment can be applied to various industrial sectors such as paints, coatings, fillers, semiconductor materials. This research aims to extract TiO2 from ilmenite with purity level above 80%. The TiO2 extraction used repeated leaching methods with sulfuric acid. Then followed by the hydrolysis process with the addition of seed and calcined. TiO2 products were analyzed using X-ray fluorescence (XRF) and X-ray diffraction (XRD). The content of TiO2 obtained in this process is 83.36% and is in the form of rutile crystals. The purity and crystal formed of this TiO2 product suitable with the minimum standards of TiO2 pigments required by ASTM D 476 (2015). This research can be the alternative to solve environmental problems in the tin industry while increasing the economic value as TiO2 products that has great market potential in Indonesia since there is no TiO2 industry in Indonesia.

1. Introduction
Indonesia has abundant mineral resources, such as coal, copper, gold, natural gas, nickel, and tin. Indonesia is the second-largest tin producer in the world after China. Indonesia controls more than 30% of the world’s tin production annually [1]. Tin seeds contain the main minerals cassiterite (SnO2) and associated minerals such as [(Fe, Mn)(Ta, Nb)2O6], zircon (ZrSiO4), ilmenite (FeTiO3), rutile (TiO2), quartz (SiO2), pyrite (FeS2), xenotime (YPO4), and monazite (Ce, La, Y, Th)PO4 [2]. Ilmenite minerals as a by-product of tin mining can be used as an alternative source of raw material for the production of TiO2 [3]. Ilmenite contains 30% to 65% TiO2 [4]. More than half of the world’s titanium production is obtained from ilmenite and rutile [5].

Titanium dioxide (TiO2) is found in nature as ilmenite (FeTiO3) both as a rock or sand, rutile, anatase, and brookite, which although they have the same formula (TiO2) but have different crystalline structures [5]. Titanium dioxide (TiO2) is widely used in the paint industry, coatings, fillers, semiconductor materials such as optoelectronic tools, and sensors. The advantages of TiO2 include high stability, simple storage, and non-toxic[6]. About 95% of titanium production is the production of titanium dioxide as a pigment. TiO2 pigment has a high refractive index so that the potential to produce opacity or hiding power is much higher, making TiO2 pigment much better than other pigments. Every year more than 4.5 million tons of TiO2 are produced worldwide, and only about 4% - 5% is used to produce titanium metal [7].
The hydrometallurgical method for the production of TiO$_2$ from ilmenite has two processes using sulfate and chloride [8]. The chloride process used to high-grade ilmenite (90-95% TiO$_2$) and the sulfate process used to ilmenite (40%-60% TiO$_2$) [9]. The concentration of sulphuric acid is high (98%) [9] and 50% [10]. The high concentration of acid can cause air pollution. The high purity of TiO$_2$ content is obtained by the perfect separation of iron and TiO$_2$. Purification of TiO$_2$ from ilmenite, by-product of local zircon industry, using Becher method produces TiO$_2$ purity of 45.84% [3]. Purification of TiO$_2$ from ilmenite using sulfate process create rutile phase [10] [11]. Purification of TiO$_2$ from ilmenite, by-product of local tin industry, using the chloride process produces the anatase phase [11].

In this research, TiO$_2$ purification from ilmenite, a by-product local tin industry, for pigment with purity more than 80% (ASTM D476 Standard Classification for Dry Pigmentary Titanium Dioxide Products) using repeated low concentration sulfuric acid leaching method followed by the hydrolysis process with the addition of TiO$_2$ seed and calcination process. Low concentration sulfuric acid is used to minimize the health risk of researchers against exposure to acid vapor when working in a laboratory. This research can be the alternative to solve environmental problems in the tin industry while increasing the economic value as TiO$_2$ products that has great market potential in Indonesia since there is no TiO$_2$ industry in Indonesia.

2. Materials and Experimental

2.1. Materials
Materials used in this research were Ilmenite, a by-product of the tin industry, from Bangka, H$_2$SO$_4$ (p.a), NH$_4$OH (p.a), TiO$_2$ (Degussa P25), distilled water. Material characterization before and after the leaching process is done using X-ray Fluorescence (XRF) (Thermo Scientific ARL 9900) and X-Ray Diffraction (XRD) (PANalytical Expert PRO seri PW3040/XO).

2.2. Experimental
The TiO$_2$ extraction from ilmenite was conducted by using repeated leaching methods with 25% sulphuric acid as a solvent at 80 °C for 5 hours. The filtrate is neutralized by ammonium solution (NH$_4$OH) 30%. After that, the filtrate was hydrolyzed at 80°C for 4 hours with the addition of various TiO$_2$ seed (0%, 0.25%, 0.50%, or 0.75%). The solid phase of the hydrolysis product is continued by the calcination process at temperature 300°C. Then an X-ray fluorescence (XRF) analysis of the product is carried out to determine the purity of the TiO$_2$ product.

3. Result and Discussion
The ilmenite by product of the Bangka tin processing industry has a high grade ilmenite (purity up to 85.87%). Ilmenite takes the form of powder and black in color. The composition of the compound in ilmenite based XRF analysis results showed two main compound namely TiO$_2$ and Fe$_2$O$_3$ (Table 1).

| Compound | TiO$_2$ | Fe$_2$O$_3$ | SnO$_2$ | ZrO$_2$ | SiO$_2$ | MnO | La$_2$O$_3$ | Al$_2$O$_3$ | Nd$_2$O$_3$ | Others |
|----------|---------|-------------|---------|---------|---------|-----|-------------|-------------|-------------|--------|
| Content (%) | 52.48 | 26.60 | 3.52 | 3.44 | 3.11 | 2.23 | 1.49 | 1.26 | 1.04 | 4.83 |

The leaching method used in this study uses 25% sulfuric acid as a solvent. Sulfuric acid was chosen as a solvent instead of hydrochloric acid because the raw material ilmenite used had a TiO$_2$ content of only 52.48% unsuitable for using hydrochloric acid which had to use ilmenite with a TiO$_2$ content
more than 85% [8]. The concentration of sulfuric acid used is also not too high to reduce the health risk of researchers against exposure to acid vapor when working in a laboratory.

In the leaching process, ilmenite is dissolved in sulfuric acid which will form a titanium sulfate solution. Subsequently the titanium sulfate solution was purified by hydrolysis to produce TiO$_2$. The use of sulfuric acid can break the bonds of FeTiO$_3$ to form FeSO$_4$. Its chemical reaction is as follows:

\[
\text{FeTiO}_3 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{FeSO}_4 + \text{TiOSO}_4 + 2 \text{H}_2\text{O} \tag{1}
\]

In the first leaching process, TiO$_2$ in the residue is still high and has decreased in the second leaching process. So it can be concluded that the leaching process must be repeated up to three times to obtain the optimal process so the final TiO$_2$ produced will be purer. The composition of the oxide compound in the solid residue after the leaching process can be seen in table 2.

| Table 2. The composition of the compound in the solid residue after the leaching process |
|---|---|---|---|
| Compound | First Leaching | Compound | Second Leaching |
| TiO$_2$ | 51.613 | TiO$_2$ | 43.462 |
| SO$_3$ | 17.868 | Fe$_2$O$_3$ | 23.905 |
| SiO$_2$ | 6.541 | SO$_3$ | 12.872 |
| Fe$_2$O$_3$ | 4.058 | SiO$_2$ | 7.768 |
| NbO | 1.077 | SnO$_2$ | 5.556 |
| SnO$_2$ | 0.877 | MnO | 2.289 |
| MnO | 0.431 | CeO$_3$ | 1.317 |

Insoluble ilmenite impurities are separated by sludge pouring. The remaining solution is neutralized to separate Fe from the solution and then filtered. The remaining solution is hydrolyzed by adding TiO$_2$ seed to get the rutile form of tetrahedral TiO$_2$.

Hydrolysis reaction as follows:

\[
\text{TiOSO}_4 + 2 \text{H}_2\text{O} \rightarrow \text{TiO}_2\cdot\text{H}_2\text{O} + \text{H}_2\text{SO}_4 \tag{2}
\]

After hydrolysis, the hydrated titanium oxide was incubated at 300 °C with the following reaction:

\[
\text{TiO}_2\cdot\text{H}_2\text{O} \rightarrow \text{TiO}_2 + \text{H}_2\text{O} \tag{3}
\]

TiO$_2$ products after being analyzed by X-ray fluorescence (XRF) with the variations of TiO$_2$ seeds can be seen at table 3, 4, 5, and 6.

| Table 3. The composition of the compound in the product using 0% seeds |
|---|---|
| Compound | Content (%) |
| TiO$_2$ | 31.327 |
| SO$_3$ | 58.165 |
| SiO$_2$ | 9.413 |
| K2O | 0.279 |
| Fe$_2$O$_3$ | 0.618 |
| CaO | 0.093 |
| MnO | 0.031 |
If no seeds were added at all, only 31.327% of the TiO$_2$ formed (table 3).

| Compound | Content (%) |
|----------|-------------|
| TiO$_2$  | 54.469      |
| Fe$_2$O$_3$ | 33.636    |
| Cr2O3    | 6.267       |
| SiO$_2$  | 3.609       |
| MnO      | 1.414       |
| ZrO$_2$  | 0.158       |
| CaO      | 0.139       |

The addition of TiO$_2$ seed will trigger the titania synthesis reaction during the hydrolysis process. Addition of 0.25% seed will increase TiO$_2$ to 54.469% (table 4) or increase by 42.48%.

| Compound | Content (%) |
|----------|-------------|
| TiO$_2$  | 83.636      |
| Al$_2$O$_3$ | 10.77     |
| SiO$_2$  | 5.367       |
| CaO      | 0.153       |
| NbO      | 0.027       |
| CuO      | 0.020       |
| ZrO$_2$  | 0.018       |

If the seeds are added 0.50%, it will increase the TiO$_2$ to 83.636% (table 5) or increase by 62.54%.

| Compound | Content (%) |
|----------|-------------|
| TiO$_2$  | 60.221      |
| Fe$_2$O$_3$ | 22.412    |
| SnO$_2$  | 6.986       |
| SiO$_2$  | 4.095       |
| MnO      | 4.095       |
| ZrO$_2$  | 1.632       |
| CeO$_2$  | 0.702       |

Conversely, if the seeds were added too much by 0.75%, the TiO$_2$ formed only rose to 60.221% (table 6) or the increase in TiO$_2$ was only 47.98%. This happens because the addition of too much seed will actually interfere with the synthesis process of titania. The best product with the highest TiO$_2$ 83.636% is obtained with the optimal seed addition of 0.50% (table 5). Crystal type of TiO$_2$ (0.50% seed) was characterized using X-ray Diffraction (figure 1).
Based on the results of the XRD analysis, the obtained TiO$_2$ crystal form is rutile and the products contained 83.636% TiO$_2$. Standard Classification for Dry Pigmentary Titanium Dioxide Products types 3 and 4 [12] requires that the minimum purity of TiO$_2$ is 80% and the crystal form of TiO$_2$ is rutile so this research meets the specified requirements.

Compared with similar research, where is the refining of TiO$_2$ from Bangka ilmenite through a different process with the HCl leaching process by the addition of iron powder during leaching. Then proceed with the hydrolysis and condensation process using 2-propanol and H$_2$O solvents. They produced anatase TiO$_2$ with a purity of only 32.72% [13] while this research is able to produce TiO$_2$ with higher purity and the right shape of TiO$_2$ crystals to be applied in the pigment industry.

4. Conclusion
One leaching process was not enough to get minimum purity of TiO$_2$ pigment requirement (> 80% TiO$_2$). The residues of first and second leaching still had high TiO$_2$ which can be purified by repeating the leaching process. The best result of TiO$_2$ products was the one that used 0.50% seed TiO$_2$ during hydrolysis. The products contained 83.636% TiO$_2$ and the crystal type was rutile. Both the purity and the crystal type of this TiO$_2$ product have met the minimum requirement of Standard Classification for Dry Pigmentary Titanium Dioxide Products type 3 and 4 [12]. This research can be a solution to the environmental problems in the tin industry and also increasing the economic value as TiO$_2$ products that has great market potential in Indonesia since there is no TiO$_2$ industry in Indonesia.
5. Acknowledgement
Our gratitude goes to the Center for Chemical and Packaging program that has funded this research and also to PT Timah, Tbk who have supported by giving the ilmenite as a raw material in this research.

References
[1] Z. Salim and E. Munadi, *Info Komoditi Timah*. 2016.
[2] A. Suhandyanto, E. Sulistiyono, and F. Firdiyono, “Pelarutan Terak Timah Bangka Menggunakan Larutan NaOH,” *Maj. Metal.*, vol. V, no. 29.3, p. 7, 2014.
[3] M. T. Mohar, D. Fatmawati, and S. B. Sasonoko, “Pembuatan Pigment Titanium Dioxide (TiO2) Dari Ilmenite (FETIO3) Sisa Pengolahan Pasir Zircon Dengan Proses Becher,” *J. Teknol. Kim. dan Ind.*, vol. 2, no. 4, pp. 110–116, 2013.
[4] S. Wahyuningsih, P. P. Sari, and A. H. Ramelan, “Recovery TiO2 by leaching process of carbothermic reduced Kalimantan ilmenite,” *AIP Conf. Proc.*, vol. 1964, 2018.
[5] M. Contreras, J. Gazquez, and J. P. Bolivar, “Isolation and Characterization of the Mineral Phases in Ilmenite Ore: Optimization of the TiO2 Pigment Process Abstract,” *J. Waste Recycl.*, vol. 2, pp. 1–9, 2017.
[6] H. Poernomo, D. Biyantoro, and M. V. Purwani, “Kajian Konsep Teknologi Pengolahan Pasir Zirkon Lokal yang Mengandung Monasit, Senotim dan Ilmenit,” *Eksplorium*, vol. 37, no. 2, p. 73, 2016.
[7] M. J. Gázquez, J. P. Bolivar, R. Garcia-tenorio, and F. Vaca, “A Review of the Production Cycle of Titanium Dioxide Pigment,” *Mater. Sci. Appl.*, vol. 5, no. May, pp. 441–458, 2014.
[8] W. Zhang, Z. Zhu, and C. Y. Cheng, “Hydrometallurgy: A literature review of titanium metallurgical processes,” *Hydrometallurgy*, vol. 108, no. 3–4, pp. 177–188, 2011.
[9] M. J. Gázquez, M. Contreras, M. Romero, D. De Fisicaaplicada, U. De Huelva, and C. De, “Recycling wastes coming from the pigment TiO2 industry.”
[10] W. Phoohinkong *et al.*, “Characterization and X-Ray Absorption Spectroscopy of Ilmenite Nanoparticles Derived from Natural Ilmenite Ore via Acid-Assisted Mechanical Ball-Milling Process *,” *Adv. Nat. Sci. Nanosci. Nanotechnol.*, vol. 8, pp. 1–8, 2017.
[11] S. Wahyuningsih *et al.*, “The Effects of Leaching Process to the TiO2 Synthesis from Bangka Ilmenite,” in *IOP Conference Series: Materials Science and Engineering*, 2018, pp. 1–6.
[12] ASTM D 476: 2015 Standard Classification for Dry Pigmentary Titanium Dioxide Products
[13] S. Wahyuningsih, H. Hidayatullah, E. Pramono, S.B. Rahardjo, A.H. Ramelan, F. Firdiyono, E. Sulistiyono. “Optimizing of TiO2 Separation from Bangka Ilmenite by Leaching Process Using HCl” *ALCHEMY jurnal penelitian kimia*, vol. 10, no. 1, pp.54-68, 2014.