

## Decomposition of Ilmenite in Hydrochloric Acid to Obtain High Grade Titanium Dioxide

SAYEKTI WAHYUNINGSIH<sup>1,\*</sup>, EDI PRAMONO<sup>1</sup>, FLORENTINUS FIRDIYONO<sup>2</sup>, EKO SULISTIYONO<sup>2</sup>,  
SENTOT BUDI RAHARDJO<sup>1</sup>, HARI HIDAYATTULLAH<sup>1</sup> and FAUCHI A. ANATOLIA<sup>1</sup>

<sup>1</sup>Inorganic Material Research Group, Department of Chemistry, Faculty of Mathematics and Natural Science, Universitas Sebelas Maret Surakarta, Indonesia

<sup>2</sup>Metalurgy Extraction Laboratory, The Central of Metalurgy Research LIPI, Serpong, Indonesia

\*Corresponding author: E-mail: w.sayekti@yahoo.com

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Ilmenite is an economically important and interesting mineral. It is found as a by-product of tin mining in Bangka Indonesia. This mineral can be used as the source of making titanium metal, titanium dioxide (TiO<sub>2</sub>) pigment and material for dye sensitized solar cell. The aim of this research is to investigate the possibility of using Bangka ilmenite mineral to obtain TiO<sub>2</sub> pigments solar cell grade. The main feature of the process is the use of Fe<sup>0</sup> as reducing agent to reduce iron value in ilmenite to acid leaching form. In order to obtain high grade TiO<sub>2</sub>, ilmenite was oxidized and leached with a hydrochloric acid solution at several conditions. Oxidation was performed at temperatures of 400, 500, 600, 700, 800, 900, 100 and 1100 °C without and with Na<sub>2</sub>S addition. Several parameters of leaching such as iron particles addition and hydrochloric acid concentration were evaluated. Ilmenite without oxidation was also leached for comparison. Original ilmenite and solid products of both oxidation and leaching were characterized by X-ray diffraction and X-ray fluorescence, whereas solutions obtained after leaching were analyzed by atomic absorption and UV-VIS spectrophotometry for iron and titanium determination, respectively. It was established that pre-oxidation contributes with iron dissolution due to the iron diffusion that occur during that process. However for iron dissolution is crucial the presence of iron particles as they reduce the ferric iron obtained after oxidation. The temperature of oxidation has an effect on type, proportion and distribution of phases. Pseudobrookite and randomly distributed rutile are obtained at higher temperatures and they showed great crystallinity and grade of product, nevertheless the presence of pseudobrookite promotes titanium dissolution.

**Key Words:** Ilmenite, Pre-oxidation, Leaching, Pseudobrookite, TiO<sub>2</sub>.

### INTRODUCTION

Titanium dioxide has been widely used as pigment for the manufacture of paints and paper. Recently, the importance of this particular oxide has increased exponentially, due to its good semiconducting behaviour and photosensitivity, which made it adequate as solar cell material. Today, the main source for synthetic TiO<sub>2</sub> production is ilmenite (FeTiO<sub>3</sub>), which can be found worldwide, principally in Australia, Egypt, USA, China, Venezuela and also in Indonesia. In Indonesia, ilmenite can be found in Bangka, as a by-product of tin mining. Usually, ilmenite is treated *via* hydrochloric acid leaching<sup>1</sup> or dry chlorination for the removal of iron<sup>2</sup>. Many researchers have developed to improve TiO<sub>2</sub> extraction from ilmenite. Chun *et al.*<sup>3</sup>, for instance, proposed mechanical activation of ilmenite to increase dissolution rate and reduce the amounts of solution needed. Other authors<sup>4,5</sup> have suggested the use of a heat treatment followed by hydrochloric acid leaching. That heat treatment involves mainly carbothermic reduction to reduce iron

for easy removal by leaching. A stage of oxidation prior to reduction has also been proposed, because several authors have reported an increment of reduction rates<sup>6</sup>.

Previous studies<sup>7</sup> demonstrated important changes that occur on the surface of ilmenite during high temperature oxidation, particularly the formation of hematite. This condition propitiates selective iron extraction because it is concentrated on surface. Thus, in this work it is proposed to leach preoxidized ilmenite with HCl solution. Owing to the fact that ferric iron obtained after oxidation could be difficult to dissolve, in this process it will be used iron particles, following the suggestion of Mahmoud *et al.*<sup>8</sup>. They found that iron dissolved in HCl solution could act as reducing agent improving the dissolution. For the reasons exposed, this work presents a study of the surface modifications generated by oxidation, on the dissolution of iron from ilmenite in hydrochloric acid both with and without Fe<sup>0</sup> addition by reduction process, in order to obtain optimum conditions for high grade TiO<sub>2</sub> production.

## EXPERIMENTAL

**Raw material preparation:** Ilmenite used in this work was obtained from Bangka in Indonesia. It was concentrated by magnetic separation using optimized operation parameters previously established. The initial characterization of original Ilmenite involved X-ray diffraction of powders and X-ray fluorescence.

**High temperature oxidation:** Oxidation were performed in a furnace Thermolyne 4800. Samples were placed inside the furnace once the temperature was reached with the help of an porcelain crucible. In all cases the process was developed in open air for periods of 6 h and at temperatures of 400, 500, 600, 700, 800, 900, 1000 and 1100 °C. Oxidation products were characterized by XRD.

**Leaching:** Leaching was carried out with hydrochloric acid at various concentrations. In all cases 2 g of ilmenite were mixed with 100 mL of acid solution. Also, amount of metallic iron powder were added to the reactor, 20 min later of the beginning of the test. The tests were performed, using hot plates with magnetic agitation with temperature 95-105 °C. The products were separated by filtration. Solids were washed with 0.1 M HCl and introduced in an oven at 60 °C, calcined at 400 °C for 2 h. The later residu was determinate by XRD. Liquids were analyzed by UV-VIS spectrophotometry and atomic absorption spectrophotometry (AAS) in order to determine iron and titanium dissolved. Amount of Fe<sup>0</sup> was added to promote Fe<sup>3+</sup>.

## RESULTS AND DISCUSSION

**Raw material preparation:** Ilmenite used in this work was acquired from Bangka in Indonesia. It was concentrated by magnetic separation using optimized operation parameters previously established. The initial characterization of original Ilmenite involved X-ray diffraction (XRD) of powders and X-ray fluorescence (XRF). XRD patterns revealed that the principal crystalline phase corresponds to FeTiO<sub>3</sub>, without and with magnetization (Fig. 1(a-b)).

The XRF data of original ilmenite from Bangka shown in Table-1.

**High temperature oxidation:** Oxidation products at 400, 500, 600, 700, 800, 900, 1000 and 1100 °C calcination were characterized by X-ray diffraction (XRD) (Fig. 2). Pre-oxidation process really improve the formation of pseudobrookite phase (Fe<sub>2</sub>TiO<sub>5</sub>), as intermediate product to form TiO<sub>2</sub>. Pseudobrookite and randomly distributed rutile are obtained at higher temperatures and they showed great crystallinity and grade of product, nevertheless the presence of pseudobrookite promotes titanium dissolution.

It is evident that at 400-800 °C, the products of oxidation still contain ilmenite, hematite and rutile (Fig. 2). At higher temperatures, however, a new phase: pseudobrookite is formed as a result of the following reaction:

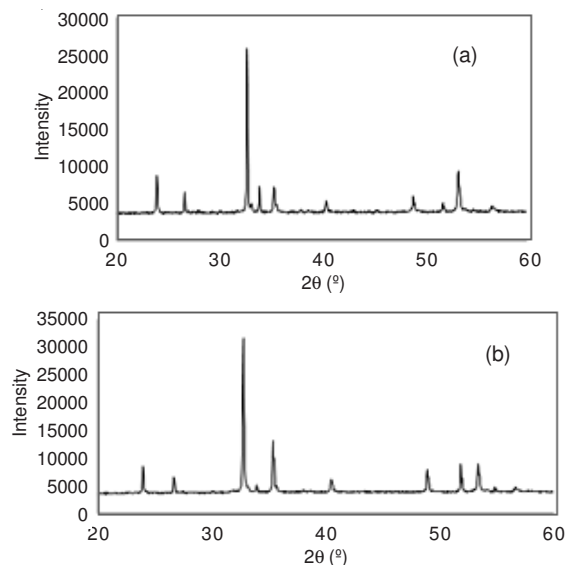


Fig. 1. XRD patterns of FeTiO<sub>3</sub>, (a) without magnetization and (b) with magnetization

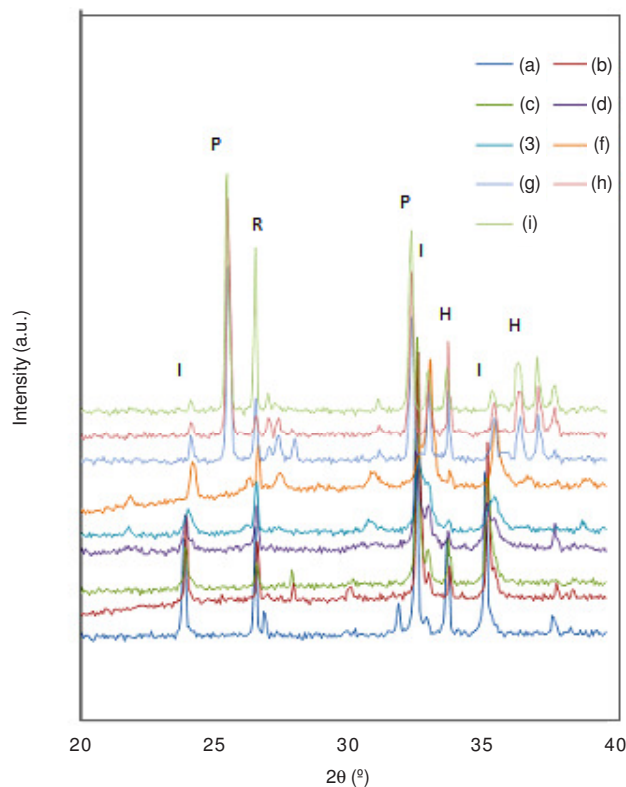


Fig. 2. XRD Patterns of preoxidation treatment of Ilmenite of the various temperature (a) 150 (b) 400 (c) 500 (d) 600 (e) 700 (f) 800 (g) 900 (h) 1000 (i) 1100. I = ilmenite A = anatase, P = pseudobrookite, H = hematite

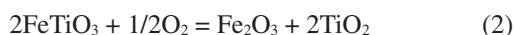
The proportion and distribution of pseudobrookite changes with temperature as observed in Fig. 2 for ilmenite preoxidized at 900, 1000 and 1100 °C, respectively. It is clear that at lower temperature pseudobrookite is localized between

TABLE-1  
CHEMICAL COMPOSITION OF IMENITE FROM BANGKA INDONESIA BY XRF (%)

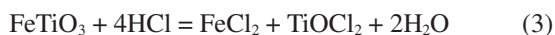
Content	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>	MnO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>
Level	34.01	53.36	0.09	1.07	1.73	2.39	1.39

Fe<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> whereas at 900-1100 °C, a matrix of Fe<sub>2</sub>TiO<sub>5</sub> with TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> distributed randomly are the only detectable products.

**Leaching:** Leaching of pre-oxidation product was carried out with hydrochloric acid at variation concentration. Pre-oxidation of ilmenite produce surface modifications as a result of diffusional processes that take place at high temperature on air. In this particular case, iron moves faster than titanium and they tend to migrate towards the high oxygen potential region<sup>9,10</sup>. Once the iron cations arrive to the surface of the particle, they are oxidized and a hematite eggshell is formed. The oxidation process is given by<sup>6</sup>:



In the case of original ilmenite, the main iron cations are in the ferrous form, which are easier to dissolve, they have to migrate to the surface to be leached. In addition, it has been reported that dissolution of ilmenite follows the reaction specified by<sup>8</sup>:



It is clear that HCl not only promotes iron removal but also could dissolves titanium. Fig. 3 illustrates titanium extraction from the samples. This reveals the high removal of titanium from non preoxidized samples (Fig. 3(a)). The addition of Fe<sup>0</sup> to the pre-oxidation ilmenite with ratio of ilmenite : Fe<sup>0</sup> = 2:1 show progressive separation.

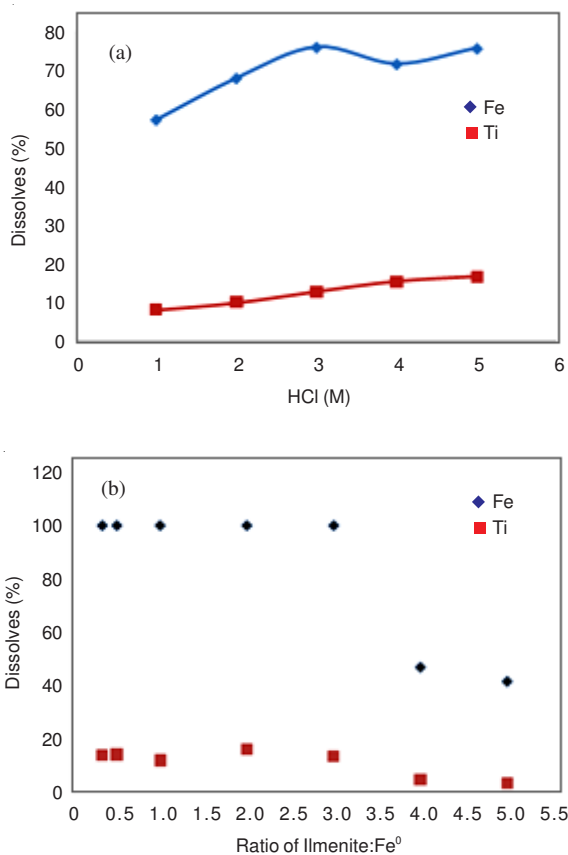


Fig. 3. Influence of (a) HCl using in leaching process and (b) Ilmenite to Fe<sup>0</sup> ratio

Leaching residual solid material called slag titania is material containing pseudobrookite, rutile and anatase, as

shown in Fig. 4. Addition of Fe<sup>0</sup> (ilmenite: Fe<sup>0</sup> = 2:1) showed increased dissolution pseudobrookite to gain the anatase and rutile TiO<sub>2</sub> phase and hematite (Fe<sub>2</sub>O<sub>3</sub>), indicated by the decrease in intensity at 26.5 and by the increase in intensity at 25.3, 27. 3, 34.7 and 32.2 (Fig. 5). Finally, the addition of Na<sub>2</sub>S in preoxidation process with ilmenite to Na<sub>2</sub>S ratio = 2:1 discourage the pseudobrookite phase formation and route of decomposition looks through the different mechanism pathway. Fig. 6 shows the results of the optimum separation of hematite gain TiO<sub>2</sub> content in the solid phase very high.

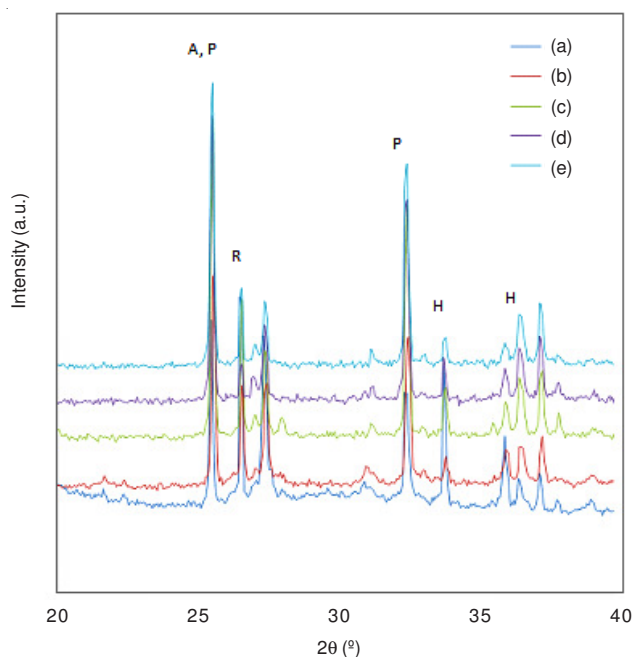


Fig. 4. XRD patterns of leaching of pre-oxidation ilmenite with Fe<sup>0</sup> addition (a) Ilmenite : Fe<sup>0</sup> = 1:1 (b) Ilmenite : Fe<sup>0</sup> = 2:1, (c) Ilmenite : Fe<sup>0</sup> = 3:1, (d) Ilmenite : Fe<sup>0</sup> = 4:1, (e) Ilmenite: Fe<sup>0</sup> = 5:1. A = Anatase, P = pseudobrookite, H = hematite, R = rutile, I = ilmenite

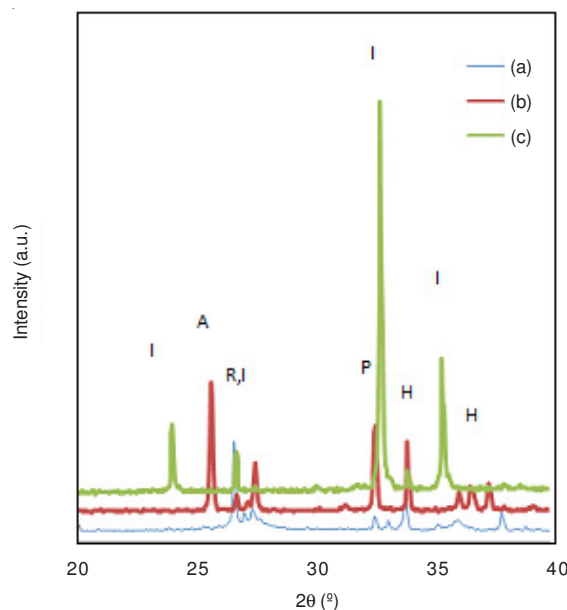


Fig. 5. XRD pattern of leaching residual solid materials (a) without pre-oxidation (b) with pre-oxidation and (c) ilmenite. A = Anatase, P = pseudobrookite, H = hematite, R = rutile, I = ilmenite. Pre-oxidation 900 °C

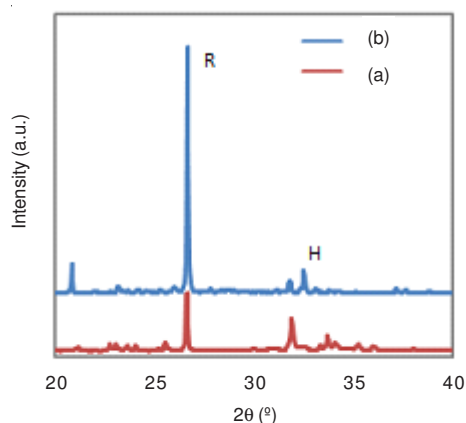


Fig. 6. XRD pattern of residual pre-oxidation with  $\text{Na}_2\text{S}$  addition materials (a) before leaching with HCl and (b) after leaching. H = Hematite, R = Rutile

### Conclusion

This study indicates that leaching of slag after heat treatment could improve the  $\text{TiO}_2$  separation. A titaniferous intermediate product produced by the process of heat treatment, which includes rutile and pseudobrookite phase.  $\text{Na}_2\text{S}$  addition in the preoxidation process decrease pseudobrookite formation. The iron, which is successfully removed is in fact metallic

iron, which can precipitate by the disproportionation reaction, which is triggered by slight oxidation. Advance acid treatment of the slag increased dissolution pseudobrookite to gain the anatase- rutile  $\text{TiO}_2$  phase and hematite ( $\text{Fe}_2\text{O}_3$ ).

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