Titanium Dioxide Production by Hydrochloric Acid Leaching Of Roasting Ilmenite Sand

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Abstract- Ilmenite ore (FeO.TiO₂) is source of titanium dioxide (TiO₂) production. Titanium dioxide occurs in polymorphic forms as rutile, and anatase phase. In Indonesia, ilmenite sand was found in Bangka island. Modification of a commercial process capable to produce TiO₂ high grade from ilmenite. In this research, production of TiO₂ from ilmenite had been conducted and resulted the excellent procedure through roasting and leaching process. Result of hydrochloric acid leaching of roasted ilmenite deposited gradually in order to obtain TiO₂. Fine crystalline anatase phase TiO₂ was generated through hydrolysis and condensation route via titanium isopropoxide complexes formation. Further hydrolysis process in 2-propanol-water of 9:1 v/v solvent ratio produce the anatase TiO₂.

Index Terms- roasted ilmenite, hydrochloric acid leaching, titanium dioxide

I. INTRODUCTION

Titanium dioxide (TiO₂) is the most important white pigment used in the coatings industry. It is widely used because it efficiently scatters visible light, thereby imparting whiteness, brightness and opacity when incorporated into a coating. Titanium dioxide occurs in polymorphic forms as rutile, anatase and brookite. Titanium dioxide is commercially available in two crystal structures, anatase and rutile. Rutile TiO₂ pigments are preferred because they scatter light more efficiently, are more stable and are more durable than anatase pigments [4]. Rutile TiO₂ pigments impart greater durability than anatase.

The black sands of ilmenite are found along the Bangka Island, Indonesia. Ilmenite, separated from black sands, which is the mineral of choice in the present article, is used economically for production of titanium dioxide. The last compound is used in many fields of application such as catalysts [2], cosmetics [10], solar batteries [12] and ceramic materials [14]. The extraction of titania from ilmenite (ore or mineral) was the subject of numerous studies [6, 8, 3, 11, 13]. Most of these studies were concerned with the extraction of titania from ilmenite by H₂SO₄ and HCl, whereas few ones were directed to extraction of titania by interaction with alkaline reagents [9, 1, 7]. Sulfate process and chloride process produces TiO₂ intermediates and ferrous sulfate. In the finishing process, through the stages of surface modification, filtration, washing and drying, we’ll get packing TiO₂.

The growing inability of the world’s natural rutile resources, now principally derived from Australia to meet the raw materials of the ‘cloride’ pigment manufacturers is one of the reasons for studying the upgrading of ilmenite into synthetic rutile [15]. The reactivity of ilmenite towards hydrochloric acid depends on the nature of the mineral. It is commonly recognised in altered igneous rocks as leucoxene and unaltered form as rutile. Generally, the unaltered ilmenite is more readily leached by hydrochloric acid than the altered ilmenite [16].

A common ilmenite alteration mechanism can be explained as follows [17]:

\[
\text{Ilmenite} \rightarrow \text{Pseudorutile} \rightarrow \text{Rutile / Anatase} \rightarrow \text{Hematite}
\]

(Fe²⁺TiO₃) \rightarrow (Fe³⁺Ti₃O₈) \rightarrow (TiO₂) \rightarrow (Fe₂O₃)

Primitive hexagonal \rightarrow Tetragonal \rightarrow Hexagonal

Transformation phase rate of ilmenite to pseudorutile, then to rutile - anatase and hematite phases is influenced by the processing conditions and the ratio of iron: titania in the ilmenite source.

II. EXPERIMENT AND METHOD

A. Materials.

Ilmenite sand (FeO.TiO₂) was obtained from Laboratory of Metallurgy Research Centre for Metallurgy – Indonesian Institute of Sciences (LIPI), while 2-propanol, iron powder, hydrochloric acid and sulfuric acid using a Merck product. Whereas sodium sulfide is a local product.

B. Modified chloride process
Ilmenite was pre-oxidized in air for periods of 6 hours and at temperatures of 500, 600, 700, 800, and 900 °C with added sodium sulfide at a certain ratio. The results are dissolved in hydrochloric acid at various concentrations and heated at temperature of 100-105 °C. Amount of metallic iron powder were added also in those mixture. The process produces dissolved ilmenite and sediment. Dissolved ilmenite may contain metal cations such as Fe(III), Fe(II) and Ti(IV). The filtrate of dissolves roasted ilmenite was added 2-propanol for further separation by precipitation. Finally, the resulting solids were TiO$_2$ (anatase, rutile), while a large of Fe ions still retained in solution phase.

C. Techniques and Measurements:

1) X-ray Diffraction Patterns (XRD):
X-ray diffractograms of ilmenite ore, different reaction products and titania were obtained by means of a chart recording Bruker D8 advance x-ray diffractometer using copper (K$_\alpha$) target

2) X-ray Fluorescence Spectra (XRF):
Quantitative oxide compound was measured with S2 Ranger XRF from Bruker.

3) Electronic Absorption Spectra of Solutions:
The electronic absorption spectra of titanium solutions and iron solutions were measured in the matched 1cm fused silica cells with an automatic Perkin Elmer Lambda 25 UV Vis Spectrophotometer.

III. RESULT AND DISCUSSION

Now it is the time to articulate the research work with ideas gathered in above steps by adopting any of below suitable approaches:

A. Row Materials Preparation

The Bangka ilmenite contain 35 to 45 % TiO$_2$ and are regarded as a huge resource to the production of Titania slag and pig iron, while the rutile (TiO$_2$) usually was produced from the commercial grade which contain more percent of TiO$_2$, which can be used directly as pigment or for the manufacture of titanium. However, extraction of the iron from the ilmenite has been, and it’s still, an expensive undertaking. Ilmenite (FeO.TiO$_2$) and rutile (TiO$_2$) are the two dominant resources minerals of titanium. In the conventional process, a large fraction of ilmenite is being rejected undissolved and the co-dissolved other transition metal ions may be co-precipitated with titanium, which may seriously discolor the white pigment color of titanium dioxide. In our laboratory, a few processes have also been tested for the recovery of titanium dioxide.

The previous studies [11] 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 pre-oxidized ilmenite with HCl solution. In the addition of sodium sulfide affects to pre-oxidation process. The treatment also affects the dissolution of pre-oxidized ilmenite.

Ilmenite used in this work was acquired from Bangka in Indonesia. 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$_3$ (Fig. 1).
While the XRF data of original ilmenite ore from Bangka shown in Table 1 below

Table 1. Chemical composition of Ilmenite from Bangka Indonesia by XRF (%)

<table>
<thead>
<tr>
<th>Content</th>
<th>TiO₂</th>
<th>Fe₂O₃</th>
<th>Cr₂O₃</th>
<th>MnO</th>
<th>MgO</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level</td>
<td>34,01</td>
<td>53,36</td>
<td>0,09</td>
<td>1,07</td>
<td>1,73</td>
<td>2,39</td>
<td>1,39</td>
</tr>
</tbody>
</table>

B. High Temperature Oxidation

Oxidation products at temperatures of 400, 500°C, 600°C, 700°C, 800°C, 900°C calcinated by Na₂S addition were characterized by X-ray diffraction (XRD) (Fig. 2). Pre-oxidation processes really improve the formation of pseudobrokite phase (Fe₂TiO₅), as intermediate product to form TiO₂. This result is very different from the results of previous studies [13] which indicates the formation of a dominant pseudobrokite. Annealing result at 900°C to 1100°C of raw ilmenite, a matrix of Fe₂TiO₅ with TiO₂ and Fe₂O₃ distributed randomly are the only detectable products [13].

![Figure 2. XRD pattern of roasting ilmenite with Na₂S addition annealed at various temperature of (a) 500 °C (b) 600 °C (c) 700 °C (d) 800 °C (e) 900 °C. I= ilmenite, H= hematite, R= TiO₂rutile, A= TiO₂anatase, N= Na₂SO₄.](image)

Table 2. Chemical composition of roasting ilmenite with Na₂S addition by XRF

<table>
<thead>
<tr>
<th>Content</th>
<th>SO₃</th>
<th>Fe₂O₃</th>
<th>Na₂O</th>
<th>TiO₂</th>
<th>SiO₂</th>
<th>MgO</th>
<th>SnO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Level</td>
<td>(%)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Level</td>
<td>39,20</td>
<td>21,06</td>
<td>19,64</td>
<td>11,75</td>
<td>1,44</td>
<td>1,06</td>
<td>0,75</td>
</tr>
</tbody>
</table>

Chemical composition of roasting ilmenite with Na₂S addition was conducted with XRF shown in Table 2. Increasing the Na₂O and SO₃ content are influenced on Na₂S addition in roasting process. 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. Once the iron cations arrive to the surface of the particle, they are oxidized, and a hematite eggshell is formed. The oxidation processes occur during roasting process follow the reaction:
\[2\text{FeTiO}_3 + \frac{1}{2} \text{O}_2 \rightleftharpoons \text{Fe}_2\text{O}_3 + 2\text{TiO}_2\]  

(1)

It is not clear to be understood that \(\text{Na}_2\text{S}\) have violently conversion the solid composition after roasting process. \(\text{Na}_2\text{S}\) definitely act as a reductant of hematite as well as titanium dioxide in the ilmenite structure. The formation of molten (fused mass) at roasting ilmenite with \(\text{Na}_2\text{S}\) addition is likely to reduce the rate of \(\text{O}_2\) diffusion to the entire layer (innermost) to resist the pseudobrookite formation. Ilmenite decomposition may occur by salt complexes formation mechanism [18]. The presence of \(\text{Na}^+\) ions and \(\text{S}_2^-\) of \(\text{Na}_2\text{S}\) initiated complexation reactions to form salt complexes according to the following reaction:

\[5\text{TiO}_2(s) + 2\text{Na}_2\text{S}(s) + 4\text{O}_2(g) \rightleftharpoons \text{Na}_4\text{Ti}_5\text{O}_{12(s)} + 2\text{SO}_3(g)\]  

(2)

\[3\text{Fe}_2\text{O}_3(s) + 3\text{Na}_2\text{S}(s) + 2\text{O}_2(g) \rightleftharpoons 5\text{NaFeO}_2(s) + \text{NaFeS}_2(s) + \text{SO}_3(g)\]  

(3)

Salt complexes formation is expected to be more easily dissolved in HCl.

C. Leaching

Leaching of roasted ilmenite products were carried out by hydrochloric acid solution at various concentrations. 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 [8]:

\[\text{FeTiO}_3 + 4 \text{HCl} \rightleftharpoons \text{FeCl}_2 + \text{TiOCl}_2 + 2\text{H}_2\text{O}\]  

(4)

whereas if the reaction was initiated by salt complexes, the reactions had better through following reaction:

\[\text{Na}_4\text{Ti}_5\text{O}_{12(s)} + \text{NaFeO}_2(s) + \text{NaFeS}_2(s) + 18\text{HCl}_{(aq)} \rightarrow 6\text{NaCl}_{(aq)} + 5\text{TiOCl}_2_{(aq)} + \text{FeCl}_2_{(aq)} + 7\text{H}_2\text{O}_{(aq)} + 2\text{H}_2\text{S}_{(aq)}\]  

(5)

It’s clear that HCl not only promotes iron removal but also could dissolve titanium. Fig. 3 illustrates titanium extraction from the samples. This reveals the high removal of titanium from roasting ilmenite samples (Fig. 3(a)). The addition of \(\text{Fe}_0\) to the pre-oxidation ilmenite with ratio of Ilmenite : \(\text{Fe}_0\) = 5:1 show progressive separation (Fig. 3(b)).
Addition of Fe\(^0\) showed increased dissolution of Fe and Ti, respectively, but addition a large amount of Fe is not necessary to avoid dissociation reaction. Maximum solubility of roasting ilmenite were gained at leaching process under 6-8 M HCl condition, whereas ratio of ilmenite : Fe\(^0\) = 5:1.

Furthermore the TiOCl\(_2\) production from dissolution roasted ilmenite will further react through complexation reactions, hydrolysis, and condensation. Finally we will get anatase TiO\(_2\) nanoparticles in last step.

\[
\begin{align*}
4 \text{TiOCl}_2 + \text{HOiPr} & \rightarrow \text{TiO(OiPr)\()_2\} + 2\text{HCl} \quad (6) \\
\text{TiO(OiPr)\()_2\} + \text{HOiPr} & \rightarrow \text{Tit(OiPr)\()_2\)(OH)\()_2\} + 2\text{HCl} \quad (7) \\
\text{Ti(OiPr)\()_2\)(OH)\()_2\} + \text{H}_2\text{O} & \rightarrow \text{Ti(OH)\()_4\} + 2\text{HOiPr} \quad (8)
\end{align*}
\]

Precipitation of leaching product solution was carried out with 2-propanol – water addition at various volume ratio. Fig. 4 is the XRD pattern of TiO\(_2\)-presipitated result. We found that the addition at a ratio of 2-propanol: water = 9: 1(v/v) was obtained pure anatase TiO\(_2\) nanoparticle products. XRD Pattern TiO\(_2\) obtained (Fig. 4) is in accordance with
the JCPDS standard anatase TiO$_2$ (No. 78-2486). TiO$_2$ gained after further hydrolysis in 2-propanol-water solvent at certain solvent volume ratio. The addition of 2-propanol drastically greatly enhances the formation of titanium isopropoxide complexes were subsequently hydrolyzed and condensed to produce TiO$_2$. The iron will be further separated by the addition of 2-propanol solvent. Optimum conditions occur in the ratio of 2-propanol: water = 9:1 (v/v), that is the excellent conditions for separating iron and titanium.

Figure 4. XRD pattern of TiO$_2$ precipitation results with 2-propanol-water solvent at a ratio of 2-propanol: water = 9:1 (v/v).

IV. CONCLUSION
Roasting ilmenite with Na$_2$S addition could improve the TiO$_2$ separation in solid phases. Na$_2$S addition in the preoxidation process decreases pseudobrookit formation. This study indicates that leaching of roasting ilmenite with Na$_2$S addition could improve the dissolution both titanium and iron, respectively. The iron, which is successfully removed, is in fact metallic iron, which can precipitate by the disproportionation reaction, which is triggered by slight oxidation. Precipitation leaching product was facilitated the solvent condition of 2-propanol-water mixture gain the high crystalline anatase TiO$_2$.

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