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Titanium Dioxide Production by HydrochloricAcid Leaching Of Roasting Ilmenite Sand

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Abstract- Ilmenite ore (FeO.TiO_2) is source of titanium dioxide (TiO_2) production. Titanium dioxide occurs in polymorphic forms as rutile,and anatase phase. InIndonesia,ilmenite sand was found in Bangka island.Modification ofa commercialprocesscapable to produceTiO_2 high grade fromilmenite. In this research, the production of TiO_2 from ilminite had been conducted and resulted the excellent procedure through roasting and leaching process. Result ofthehydrochloric acidleachingofroastedilmenitedepositedgraduallyin order to obtainTiO_2.Fine crystallite anatasephase $TiO_2$was generatedthroughco-precipitation processes using hydrolysis and condensation route via titanium isopropoxide complexes formation. Further hydrolisis process in 2-propanol-water of 9:1 v/v solvent ratio produce the anatase TiO_2.

Index Terms- roasted ilmenite, hydrochloric acid leachingtitanium dioxide

I. Introduction

Titanium dioxide (TiO_2) 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 TiO_2 pigments are preferred because they scatter light more efficiently, are more stable and are more durable than anatase pigments [4]. Rutile TiO_2 pigments imparts 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 H_2SO_4 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 TiO_2 intermediates and ferrous sulfate. In the finishing process, through the stages of surface modification, filtration, washing and drying, we'll get packing TiO_2.

The growing inability of the world's natural rutile resources, now principally derived from Australia to meet the raw materials of the 'chloride' 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]:

Ilmenite →	Pseudorutile →	Rutile / Anatase →	Hematite
($Fe^{2+}TiO_3$)	($Fe_2^{3+}Ti_3O_9$)	(TiO_2)	(Fe_2O_3)
Primitive hexagonal		Tetragonal	Hexagonal

Transfomation 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.TiO_2) 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 ^{0}Cwith added sodium sulfide at a certain ratio. The results are dissolved in hydrochloric acid at various concentrations and heated at temperature of 100-105 ^{0}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 (Kα) 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 cantain 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 un-dissolved 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).

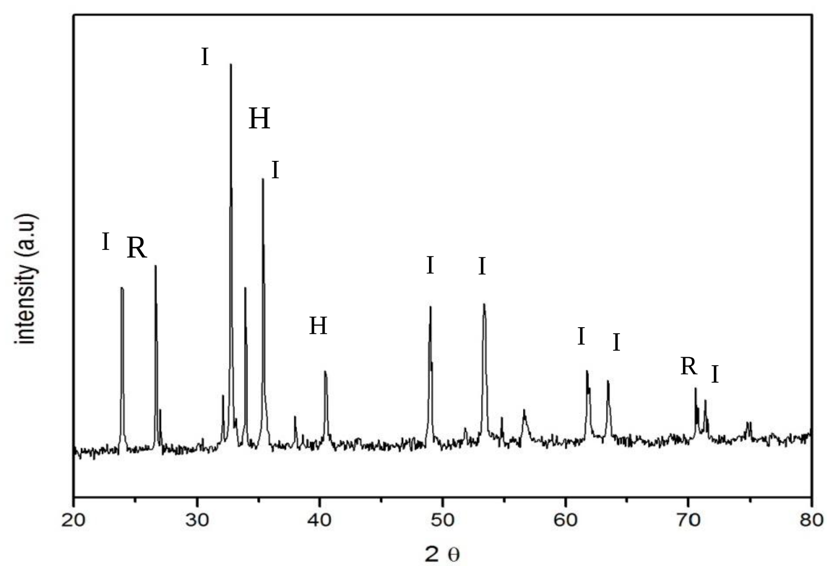


Figure 1. XRD patterns of ilmenite ore from Bangka

While the XRF data of original ilmenite ore from Bangka shown in Table 1 below

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

Content	TiO_2	Fe_2O_3	Cr_2O_3	MnO	MgO	SiO_2	Al_2O_3
Level	34,01	53,36	0,09	1,07	1,73	2,39	1,39

B. High Temperature Oxidation

Oxidation products at temperatures of 400, 500°C, 600°C, 700°C, 800°C, 900°C calcinated by Na_2S addition were characterized by X-ray diffraction (XRD) (Fig. 2). Pre-oxidation processes really improve the formation of pseudobrokite phase (Fe_2TiO_5), as intermediate product to form TiO_2. 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 Fe_2TiO_5 with $TiO_2$and Fe_2O_3distributed randomly are the only detectable products [13].

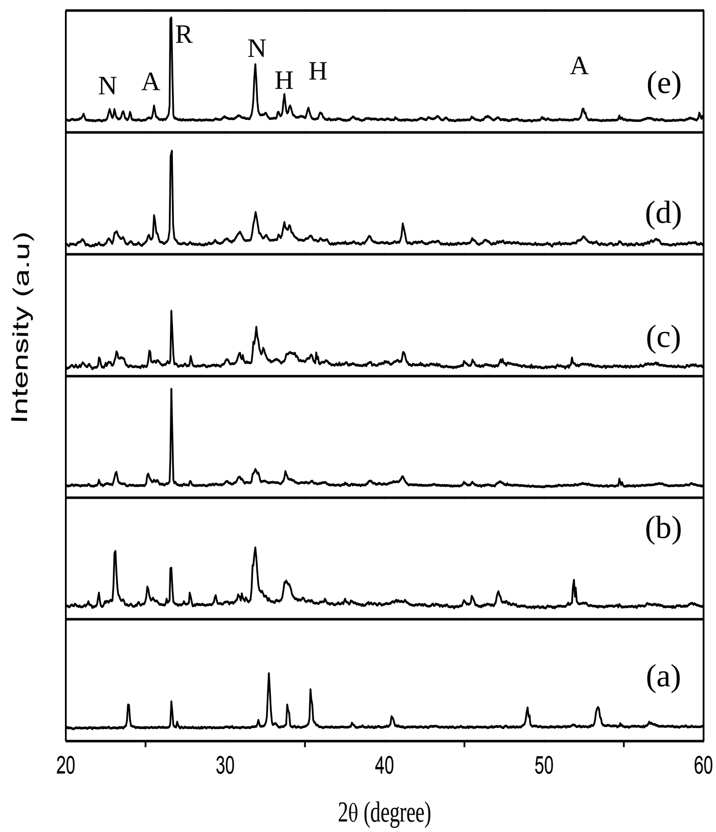


Figure 2. XRD pattern of roasting ilmenite with Na_2S addition annealed at various temperature of (a) 500 °C (b) 600 °C (c) 700 °C (d) 800 °C (e) 900 °C.. I= *ilmenite*, H= *hematite*, R= TiO_2*rutile*, A= TiO_2*anatase*, N= Na_2SO_4.

Table 2. Chemical composition of roasting ilmenite with Na_2S addition by XRF

Content	SO_3	Fe_2O_3	Na_2O	TiO_2	SiO_2	MgO	SnO_2
Level (%)	39,20	21,06	19,64	11,75	1,44	1,06	0,75

Chemical composition of roasting ilmenite with Na_2S addition was conducted with XRF shown in Table 2. Increasing the Na_2O and SO_3 content are influenced on Na_2S 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:

$$2FeTiO_3 + ½ O_2 \rightleftharpoons Fe_2O_3 + 2TiO_2 \quad (1)$$

It is not clear to be understood that Na_2S have violently conversion the solid composition after roasting process. Na_2S definitely act as a reductant of hematite as well as titanium dioxide in the ilmenite structure.
The formation ofmolten(fused mass) atroastingilmenitewithNa2Saddition is likely toreduce the rate ofO_2diffusion tothe entirelayer(innermost) toresistthe pseudobrookite formation. Ilmenite decomposition may occur by salt complexes formation mechanism [18]. The presence ofNa^+ionsandS_2^-ofNa_2Sinitiatedcomplexationreactionsto formsaltcomplexesaccordingto the following reaction:

$$5TiO_{2(s)} + 2Na_2S_{(s)} + 4O_{2(g)} \rightleftharpoons Na_4Ti_5O_{12(s)} + 2SO_{3(g)} (2)$$

$$3Fe_2O_{3(s)} + 3Na_2S_{(s)} + 2O_{2(g)} \rightleftharpoons 5NaFeO_{2(s)} + NaFeS_{2(s)} + SO_{3(g)} \quad (3)$$

Salt complexesformationis expected to bemore easilydissolvedin HCl.

C. Leaching

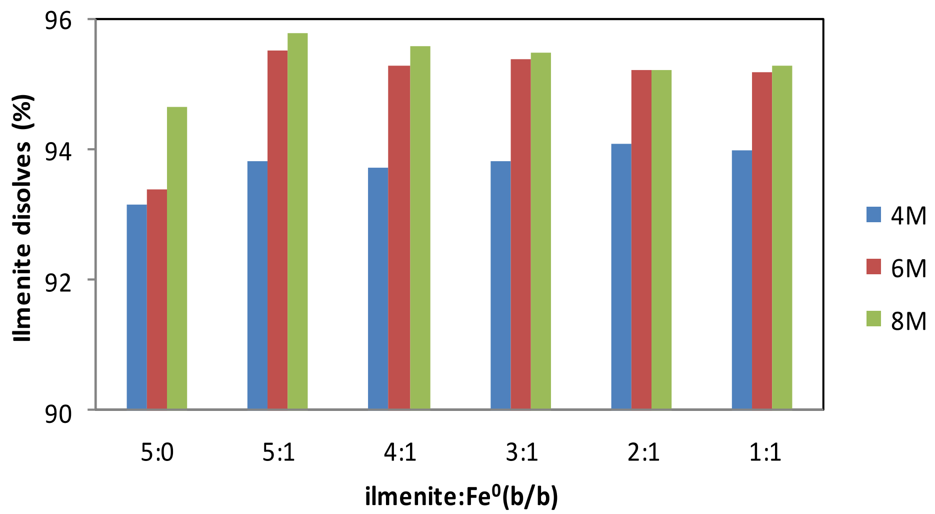
Leaching of roasted ilmenite products were carried out by hydrochloric acid solution at various concentrations. In the case of original ilmenite, the main iron cations are in the ferrous form, which are easier to dissolve, they have to migrate to the surface to be leached. In addition, it has been reported that dissolution of ilmenite follows the reaction specified by [8]:

$$FeTiO_3 + 4 HCl \rightleftharpoons FeCl_2 + TiOCl_2 + 2 H_2O \ (4).$$

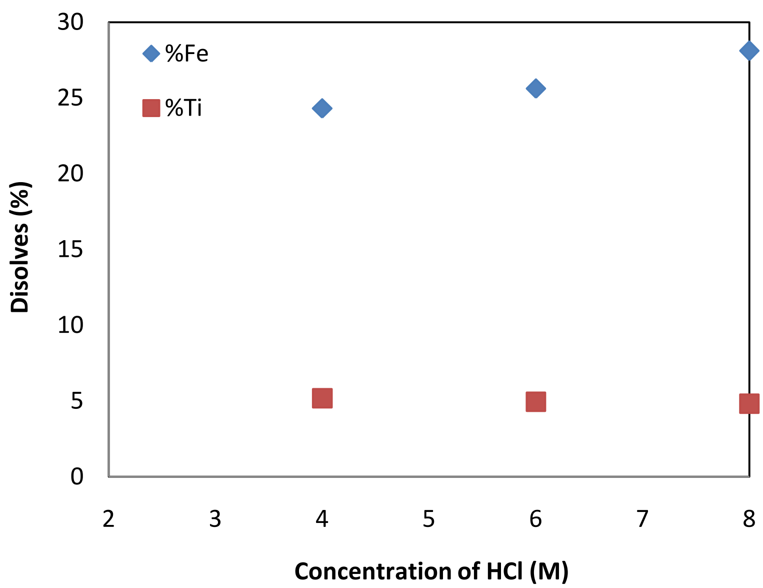
whereasif the reaction was initiatedby saltcomplexes, thereactions had better throughfollowing reaction:

$$Na_4Ti_5O_{12(s)} + NaFeO_{2(s)} + NaFeS_{2(s)} + 18HCl_{(aq)} \rightarrow 6NaCl_{(aq)} + 5TiOCl_{2(aq)} + FeCl_{2(aq)} + 7H_2O_{(aq)} + 2H_2S_{(aaq)} (5)$$

It's 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 roasting ilmenite samples (Fig. 3(a)). The addition of Fe^0 to the pre-oxidation ilmenite with ratio of Ilmenite : Fe^0 = 5:1 show progressive separation (Fig. 3(b)).



(a)



(b)

Figure 3. Influence of dissolution (a) ilmenite to Fe^0 ratio and (b) HCl using in leaching process,

Addition ofFe^0showed increaseddissolutionof 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.

Furthermorethe $TiOCl_2$production from dissolution roasted ilmenitewillfurther reactthroughcomplexationreactions, hydrolysisandcondensation.FinallywewillgetanataseTiO$_2$nanoparticles in last step.

$$4\ TiOCl_2 + HOiPr \rightarrow TiO(OiPr)_2 + 2HCl \quad (6)$$

$$TiO(OiPr)_2 + HOiPr \rightarrow Ti(OiPr)_2(OH)_2 + 2HCl \quad (7)$$

$$Ti(OiPr)_2(OH)_2 + H_2O \rightarrow Ti(OH)_4 + 2\ HOiPr \quad (8)$$

Precipitation of leaching product solution was carry out with 2-propanol – water adition at various volume ratio. Fig. 4 is the XRD pattern of TiO_2presipitated result.Wefound thatthe addition at a ratio of2-propanol: water=9: 1(v/v) was obtainedpureanataseTiO_2nanoparticleproducts.XRDPatternTiO_2obtained(Fig. 4) is in accordancewith theJCPDSstandardanataseTiO_2(No.78-2486). TiO_2 gained after further hydrolysis in 2-propanol-water solvent at certain solvent volume ratio. The addition of2-propanol isdrasticallygreatly enhancethe formation oftitaniumisopropoxidecomplexes weresubsequentlyhydrolyzedandcondensedtoproduceTiO_2. Theiron will befurther separatedbythe addition of2-propanol solvent. Optimum conditionsoccur inthe ratio of2-propanol: water =9: 1 (v/v), that isthe excellent conditionsforseparatingironandtitanium.

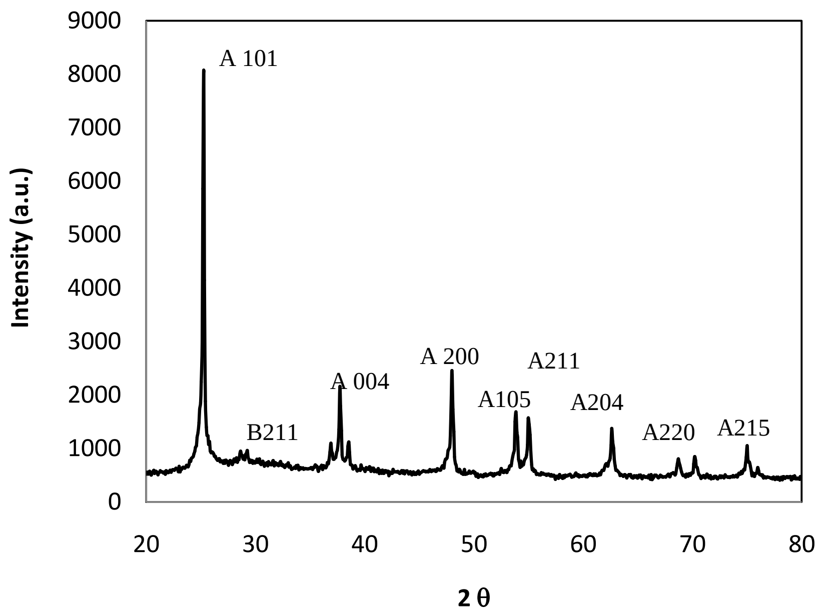


Figure 4. XRD pattern of TiO_2 precipitation resultswith 2-propanol-water solventat a ratio of2-propanol: water=9: 1(v/v).

IV. CONCLUSION

Roasting ilmenite with Na_2S addition could improve the TiO_2 separation in solid phases.Na_2S addition in the preoxidation process decrease pseudobrokite formation.This study indicates that leaching of roasting ilmenite with Na_2S 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 anataseTiO_2 .

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