1 INTRODUCTION

1.1 Introduction

Ilmenite is an economically important and interesting mineral. Chemical formula is $FeTiO_3$. Ilmenite is an opaque mineral, black to brownish-red, with a metallic or submetallic luster, and belongs to class Oxide and Hydroxide, hematite group. Ilmenite is mined in Australia, Brazil, Russia, Canada, Sri Lanka, Norway, China, South Africa, Thailand, India, Malaysia, Sierra Leone, and the United States. In Thailand it was found in tin ore (cassiterite) deposit in Chiangrai, Chiangmai, Lamphun, Kanchanaburi, Ratchaburi, Suphun Buri, Phuket, Phangnga, and Ranong. Ilmenite is the chief source of titanium dioxide, TiO_2, which is used in paint pigment, welding-rod coating, and in the manufacture of the metal titanium.

Titanium dioxide is a white pigment that is used more and more in paint as lead paint has been discontinued due to health consideration. In fact, the largest percentage of world wide use titanium is for production of this white pigment. The pigment has great luster, good endurance, high opacity, and a pure white color. The pigment is also used to provide color for rubber, plastics, textile, ink, cosmetics, leather, ceramics, and paper. The two processes used in making titanium dioxide were the sulphate and chloride processes. In the sulphate process, titanium dioxide pigment has been produced by reacting ilmenite with concentrated sulfuric acid. However, this process is increasingly undesirable on environmental grounds due to the large volume of acidic wastes which it produces. In chloride process, rutile ore is chlorinated and the resulting titanium chloride vapors are oxidized to titanium dioxide. Chlorine is recycled within the system. Consequently the chloride process presents fewer environmental problems and has become the preferred method for titanium dioxide pigment production. Natural

rutile supplies are becoming scarce. Thus, there is an increasing need to convert the more plentiful ilmenite to synthetic rutile.

There are many processes used to upgrade ilmenite ore to synthetic rutile such as smelting with coal or coke, selective chlorination of ilmenite using hydrochloric acid or combination of chlorine and carbon monoxide at elevated temperatures and pressures, sulphidization of ilmenite using either H_2SO_4, H_2S, sodium sulphide with carbon or sulphur vapor at high temperature under pressure, and a solid state reduction of iron to metal in the presence of a catalyst and subsequent removal of the oxide as a slurry (Kothari, 1974). The processes to upgrade ilmenite ore depend on the basis of the physical and chemical properties, the relative proportions, compositions, and textures of the minerals. Nonetheless, the leaching of the ilmenite with hydrochloric acid in order to upgrade it to synthetic rutile continues to be of interest (Gergin, I., 1990). The advantage of hydrochloric acid leaching is that it has no effluent disposal problem and the acid may be recycled. So, in this research it is desirable to develop method to upgrade ilmenite ore by hydrochloric acid leaching and analyses for the composition of the initial ore and the residue after leaching were carried out using X-ray Fluorescence (XRF) spectrometer. Ilmenite ore itself is only partially soluble in acid and the residue is the insoluble part of the ore. Since atomic absorption can only analyze samples in solution form, the analysis of the insoluble residue is thus beyond the atomic absorption capacity. This problem, however, can be handled quite readily by XRF spectrometer (Wongnawa, *et al.*, 1997).

1.2 Review of Literature

Ilmenite is a titanate of ferrous iron ($Fe^{+2}Ti^{+4}O_3$) rather than a double oxide of ferric iron and titanium ($Fe_2^{+3}Ti^{+3}O_3$). The formula of ilmenite may be more fully expressed as (Fe, Mg, Mn)TiO_3 with only a limited amount of Mg and Mn (Deer, *et*

al., 1979: 412-414). It is named for its place of discovery at Ilmen Lake in the Ilmen Mountains, Miask in the southern portion of the Ural Mountains of Russia. Ilmenite forms as a primary mineral in mafic igneous rocks and is concentrated into layers by a process called magmatic segregation. It crystallizes out of a magma relatively early before most of the other minerals. As a result, the heavier crystals of ilmenite fall to the bottom of the magma chamber and collect in layers. It is these layers that constitute a rich ore body for titanium miner. Ilmenite also occurs in pegmatites and some metamorphic rocks as well as in the sedimentary rocks that are formed from the weathering and erosion of them. Ilmenite crystallizes in the hexagonal system but it is so rarely in good megascopic crystals within rocks that its form is not important. It typically occurs as embedded grains and masses or as plates that are irregular or hexagonal in outline. It is brittle and has no cleavage. Fracture is conchoidal. The color is iron black, and in rare instances, with a faint reddish or brownish tinge. The luster is submetallic and the streak is black to brownish red. Ilmenite is opaque. It has a hardness of 5.5 to 6 and a specific gravity of 4.7 (Dietrich and Skinner, 1977: 72-73).

Ilmenite, hematite, and corundum all have similar structures and belong to a more or less informal group called the Hematite Group with a general formular A_2O_3. The structure is composed of alternating layers of cations and oxygens. The cations occupy sites in the layers in the bottom layer. Not all of the sites available for these cations are occupied as only two out of three are filled. Ilmenite lends it name to a group of similar, simple, trigonal, titanium oxides called the Ilmenite Group, a subgroup of the Hematite Group of mineral. The general formular for the group is $ATiO_3$, where the A can be iron, magnesium, zinc, and manganese. The Ilmenite Group members differ from the other members of the Hematite Group in that the structure is more ordered with the titaniums and A ions occupying alternating layers between the oxygen layers (Figure1). The oxygen layers are hexagonally packed. Each metal ion is bonded to three oxygens in the oxygen layer above and three oxygens in the layer below.

Ilmenite is common as an accessory mineral in many igneous and metamorphic rocks and may also occur as veins and disseminated deposits, sometimes of large extent, in association with gabbros, notrites, anorthosites, etc. Primary ore deposits of ilmenite are found in Norway, the USSR, Finland, Canada, and the USA. Secondary ore deposits are more important raw materials in view of their easier processing (sands). They are found in South Africa, Australia, India, Brazil, Malaysia, and Egypt (Deer, *et al.*, 1979: 412-414).

Ilmenite is the major source of titanium. It is used principally in the manufacture of titanium dioxide for paint pigment, replacing older pigments, notably lead compounds. As the metal and in alloys, because of its high strength-to-weight ratio and high resistance to corrosion, titanium is used for aircraft and space vehicle construction in both frames and engines (Klein and Hurlbut, 1985: 303-304).
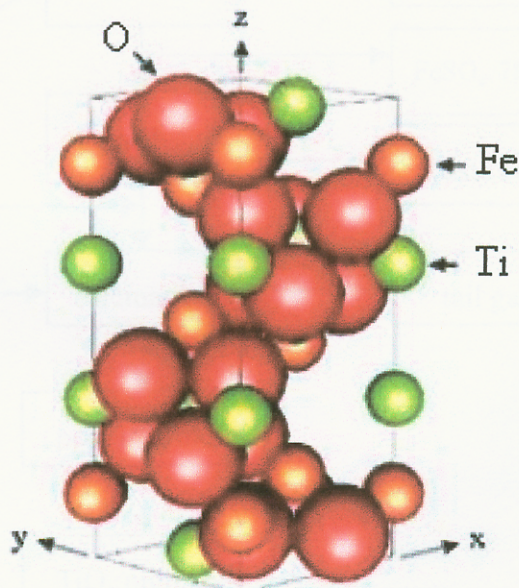

Figure 1 Crystal structure of ilmenite(Butler, et al.)

Titanium dioxide pigment (TiO_2) is a white powder with high opacity, brilliant whiteness, excellent covering power and resistance to color change. These properties have made it a valuable pigment and opacifier for a broad range of applications in

paints, plastic goods, inks, and paper. Generally, TiO_2 pigments are industrially produced by the older sulfate or newer chloride processes. The economics of the two processes are very much dependent upon the raw material available. The starting materials for TiO_2 production are ilmenite and titaniferous slag in the case of the sulfate process (Figure 2) and leucoxene, rutile, synthetic rutile, and in the future possibly also anatase for the chloride process (Figure 3) (Büchner, *et al.*, 1989: 523-525).
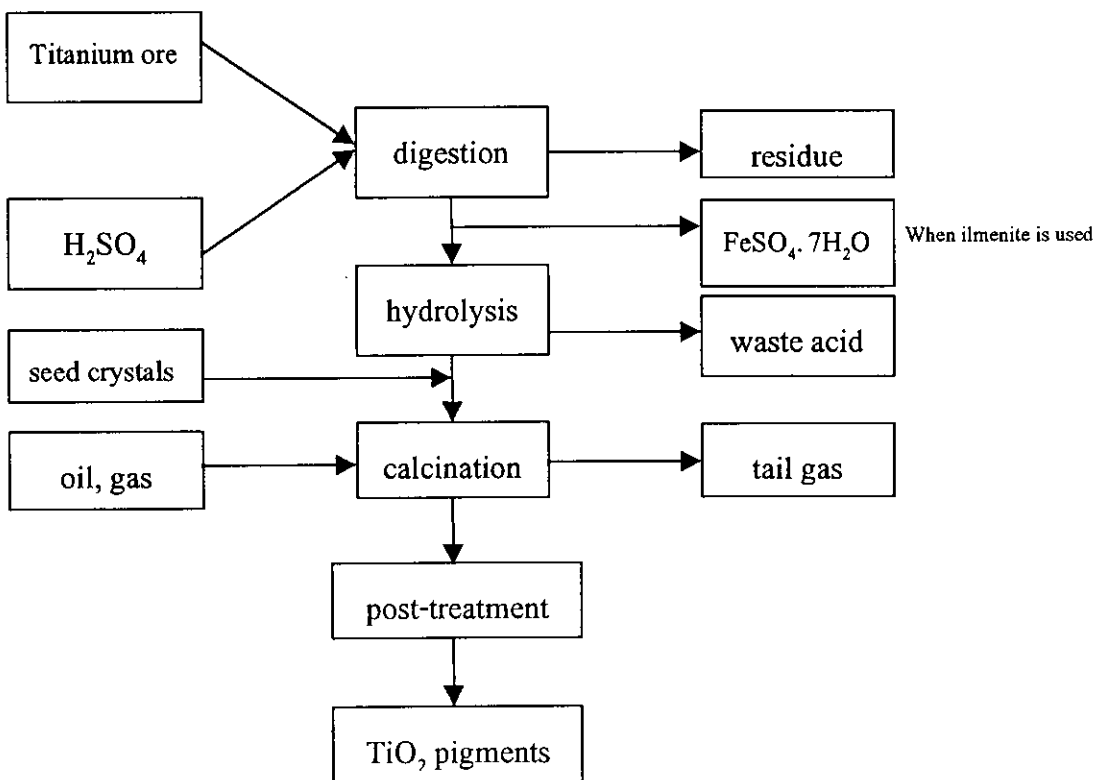

Figure 2 TiO_2 pigment manufactured by the sulfate process
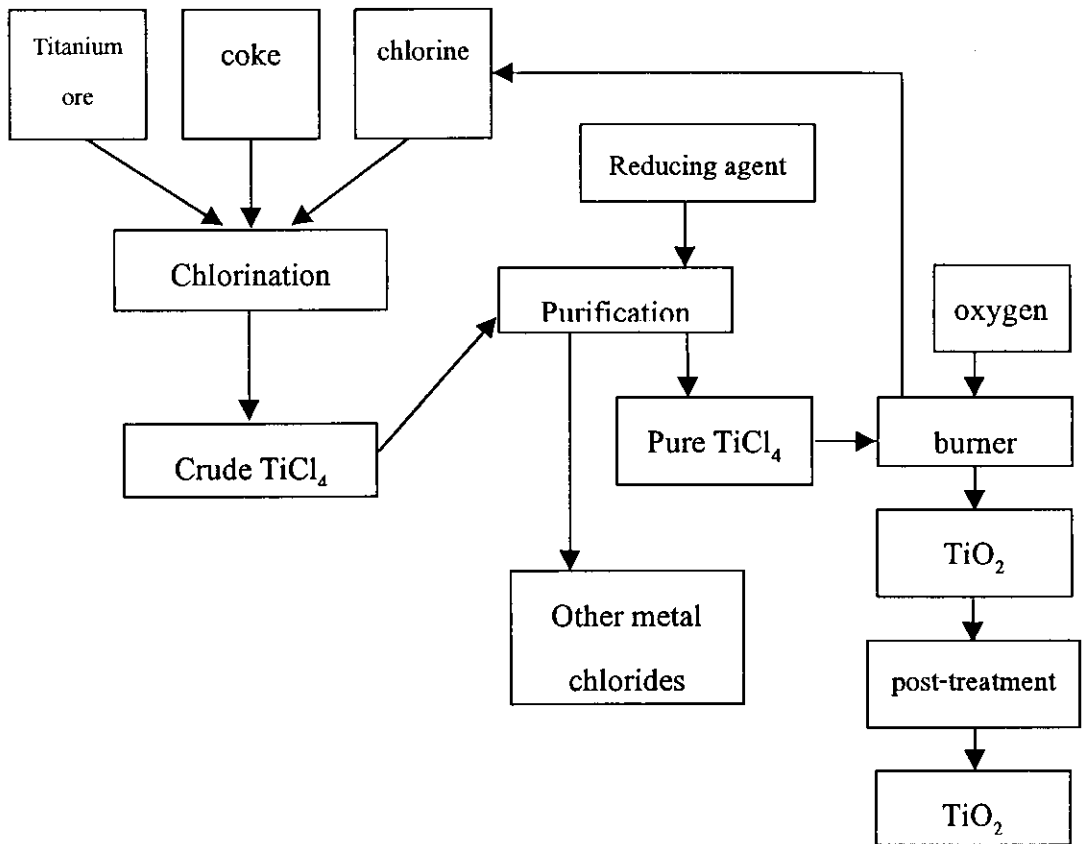
(Büchner, *et al.*,1989 : 526).

Figure 3 TiO_2 pigment manufactured by the chloride process
(Büchner, *et al.*,1989 : 528).

The sulfate process was the first commercial scale technology used to convert ilmenite to TiO_2. The process started from digestion the finely ground raw materials in an exothermic reaction with concentrated sulfuric acid, the digested cake dissolved in cold water and the residue separated off. To prevent their precipitation during the subsequent hydrolysis the Fe(III) ions are reduced to Fe(II) by adding a Ti(III) solution or scrap-iron. Upon evaporation of the solution, the large quantities of iron(II) sulfate heptahydrate are produced when ilmenite is used, and crystallize out. The titanium oxysulfate is then hydrolyzed to titanium oxyhydrate by heating the clarified solution with steam at 95-110°C. TiO_2 seed crystals are added or formed before hydrolysis to ensure yields of 93-96 % TiO_2 and to obtain a hydrolysis product which yields the

optimum particle size of ca. 0.2 μm upon firing. Diluted sulfuric acid remains as "waste acid". The hydrolysis product is washed, treated with a Ti(III) solution to remove adsorbed heavy metal ions (Fe, Cr, Mn, V) and calcined at temperature between 800-1,000°C. Anatase or rutile pigments can be produced in the calcination process depending upon the choice of additives, which determine the characteristics of the product. TiO_2 obtained in this way usually has the structure of anatase since the sulfate ions stabilize this modification (Hadjiivanov, et al., 1996) which cannot be removed during the process of washing. The transformation temperature must take place at high temperature (about 1,000°C) to obtain rutile TiO_2 (Yang, et al., 2002). The disadvantages of this process include a necessarily high input of energy, expensive and complicated equipment, long processing times, and undesirably large volumes of acidic liquid wastes, containing iron sulfate (Duyvesteyn, 2002).

The newer chloride process offers tighter product control, less labors intensive, avoids the iron sulfate waste problem and, at larger scales, is cheaper to operate. Currently about 60 % of 4 million tones of pigment produced world-wide is produced by this process. This process required the natural or synthetic rutile ore with a TiO_2 content of ca. 96 %. The chloride process started from the reaction of chlorine with synthetic rutile to form raw titanium tetrachloride which is then mixed with reducing agent to convert impurities such as vanadium oxychloride, iron chloride to lower oxidation state compounds. It is then distilled yielding titanium tetrachloride in almost any required purity. Finally, it is combusted with pure oxygen to TiO_2 and chlorine, which is reused in the chlorination (Figure3).

In recent years the prices for natural rutile have increased due to the scarcity of exploitable deposits. To provide a cheap raw material for the removal of iron from ilmenite ore have been developed. A number of different processes have been developed to upgrade ilmenite to synthetic rutile, the most widely used commercially being the Becher process. The Becher process involves the following main stages.

1. Reduction, in a rotary kiln, of the iron oxides contained in the ilmenite feed largely to metallic iron, at temperatures in the range 900 - 1200°C, using coal as the heat source and the reductant. The principal product is known as reduced ilmenite (RI).

2. Cooling, in an oxygen-free environment, the solids discharging from the reduction kiln.

3. Dry physical separation of the reduced ilmenite and surplus char.

4. Aqueous oxidation (known as aeration) of the reduced ilmenite to covert the metallic iron to iron oxide particles discrete from the TiO_2- rich mineral particles.

5. Wet physical separation to remove the iron oxides from the TiO_2- rich mineral. Hereinafter the product of this step is referred to as "aerated product".

6. An optional leaching stage to remove a portion of the residual iron and some manganese and magnesium.

7. Washing, dewatering and drying of the synthetic rutile product (Aral *et al.*, 1998).

Many researches studied the process for upgrading ilmenite ore to synthetic rutile such as:

Aral, *et al.*, (1998) discloses a process for facilitating removal of one or more impurities from titaniferous material containing the impurities in a form which is highly soluble in acid. The material is in turn leached with a sulfuric acid solution and with a hydrochloric solution in either order, and wherein the hydrochloric acid leach is augmented by addition of an effective amount of an added chloride salt, pre-treatment of the titaniferous material with a solution of an effective amount of a carbonate salt, and or pre-treatment of the titaniferous material with a solution of an effective amount of a hydroxide, whereby to enhance the susceptibility of the impurities to removal.

Welham (1996) reported that the changing surprisingly little of the Becher process by ball milling ilmenite and coal together prior to thermal processing leads to a decrease in both temperature and time of reaction compared with powders milled separately then mixed, and studied the effect of milling time and annealing conditions on the extent of reduction and leach ability of products. The reduced ilmenite were obtained from milling ilmenite with coal for 2, 10, 50, and 200 hours at room temperature under vacuum in a vertical 316S stainless steel ball mill using five 1" diameter 420C stainless steel balls confined in the vertical plane. The motion of the balls was controlled by the positioning of a magnet to give a reproducible action. Approximately 50 mg of milled powder was heated in Shimadzu TGA-50 thermogravimetric analyzer at $20^{\circ}C$ min^{-1} under dried, flowing argon to $1100^{\circ}C$ then held for 15 minutes. The data was normalized to 100 % mass at $200^{\circ}C$ to account for any moisture variation within the sample. Subsequent sample were isothermally annealed under an argon atmosphere to determine the effect of annealing parameters. Annealed sample were then subjected to an agitated in 10 % hydrochloric acid for 24 hours to estimate the leach ability of element iron. The resulting solution was analyzed for iron and titanium by spectrophotometry. All products were analyzed by X-ray diffraction (XRD) to give a profile of the reaction. The traces were normalized to give the same maximum peak intensity to account for variations of intensity due to dilution with non-crystalline material. The stoichiometry of the system was examined by increasing the fraction of coal within the system from 3.9 wt % to 35.5 wt %, thus giving a range of conditions from insufficient coal for reduction to TiO_2 to a three fold excess of carbon. All samples were milled under vacuum for 50 hours, annealed and then leached. The results indicated that the intimate mixing of coal and ilmenite is greatly enhanced by milling them together leading to a decrease in both time and temperature required for the reduction of ilmenite. Increasing the milling time decreased the reduction temperature of both ilmenite and rutile with the law of

diminishing return applying. The leaching step is much faster than conventional processing, primarily due to the much finer particle size. No elemental iron could be detected by X-ray diffraction after leaching. Leaching indicated that reduction of rutile was detrimental to iron removal and led to increased dissolution. This was attributed to the formation of mixed iron-titanium oxide phases by reaction between element iron and TiO_2.

Fukushima (1976) disclosed a process for producing artificial rutile of high TiO_2 grade produced by chlorine treatment of titaniferous ore such as ilmenite which comprising a combination of a pretreatment step in which the ore was oxidized by roasting at a temperature below the sintering temperature thereof thereby to activate the ore, a chloridization step in which the pretreated ore was subjected to a chlorine treatment in a fluidized bed chloridization furnace there by to chloridize and remove selectively iron oxides within the ore without the formation of $TiCl_4$, and after treatment step which comprised subjecting the ore to magnetic separation with a magnetic field of at least 20,000 gauses and further treatments thereafter, as necessary, such as a wet table treatment and electrostatic separation at from 5,000 to 30,000 volts.

Jayasekera, *et al.*, (1995) studied the leaching of iron from reduced ilmenite at elevated temperatures and pressures at fundamental level by electrochemical techniques and at a practical level by pressure leaching trials. The pressure leaching experiments were carried out using 300 g of reduced ilmenite at a pulp density of 14 % in 0.2 M NH_4Cl solutions. Throughout the leach, at the required gas partial pressure and temperature, a gas bleeds of 1 l min^{-1} was maintained. All tests were carried out at an impeller speed of 400 rpm. Solid samples taken at regular intervals were washed and decanted to separate the synthetic rutile product from iron oxides and metallic Fe content were analyzed by SATMAGAN. The type of iron oxide was determined by X-

ray powder diffraction. Electrochemical study showed that the rate of oxidation of iron increased with temperature, and that the rate of oxygen reduction increased with increasing temperature and pressure. Reasonable agreement was obtained between independent electrochemical methods of determining the rate of the leaching reaction of iron by oxygen. These results also indicated an increase in leaching rate with temperature and pressure. A pressure leach would speed up the rate of the iron removal during the aeration step of the Becher process. Preliminary pressure leaching trials indicated that the rate of reaction was indeed significantly increased at elevated temperatures and pressures.

Ismail, *et al.*, (1983) upgraded ilmenite ore following the oxidation-reduction-leaching process. Oxidation of ilmenite ore was carried out in a temperature-controlled furnace. Formation of fine pores on the ilmenite particles. The presence of microcracks and pores in the ilmenite particles facilitates the reduction of ilmenite to rutile. Therefore this prior oxidation step is required. The major products formed by oxidation of ilmenite at temperature greater than $900^{\circ}C$ were ferric pseudobrookite and rutile. Oxidized ilmenite is then reduced in a closed vessel with sawdust as the reductant. The experiments carried out showed that the sawdust reduced the iron values in ilmenite to acid-leachable form. The first stage of reduction is conversion of Fe^{3+} to Fe^{2+} in the form ilmenite. The second stage of reduction is conversion of Fe^{2+} to metallic iron. Hence the ilmenite concentration progressively decreased and reduced rutile. The optimum temperature for the reduction was found to be $1100^{\circ}C$. This reduced product was leached with 15-20 % HCl and the leached product was then calcined at $1000^{\circ}C$ to get synthetic rutile having 90-95 % TiO_2.

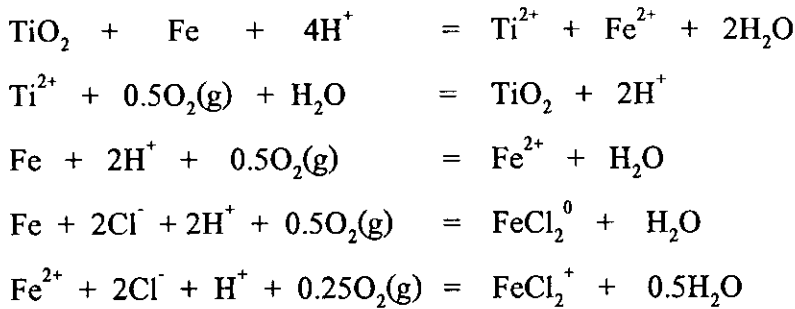Biswas, *et al.*, (1996) studied the processing of ilmenite through salt (NaCl, $NaNO_3$, and Na_2SO_4)-water vapor roasting, followed by hydrochloric acid leaching.

The roasted ilmenite was prepared by drying and grinding a specified amount of ilmenite and the salt at a given ratio and placed in a ceramic, which was placed inside a steel pipe (2.52 cm I.D.). The pipe was inserted horizontally into an electric tube furnace and connected to a nitrogen gas cylinder through a water-bubbling device, which was immersed up to its neck in a thermostatic water bath. For leaching, 50 mL of the leaching agent (2 M HCl) was placed in a conical flask (500 mL) fitted with a reflux condenser, heated by a hot plate to its boiling point and then a definite amount of roasted mass (S/L = 0.02 kg/L) was added. The solid mass was agitated magnetically. At intervals, duplicate aliquots (0.5 mL) of solution were removed, diluted and analyzed colorimetrically, one for titanium content and the other for iron content after oxidizing with nitric acid. The roasted mass giving the best dissolution was characterized by X-ray diffraction. The results indicated that the optimum condition for roasting are $800^{\circ}C$ ($885^{\circ}C$ for Na_2SO_4), 90 min (75 min for NaCl), ilmenite to salt (wt.) ratio were 1.70 for $NaNO_3$, 2.00 for Na_2SO_4 and 0.67 for NaCl, N_2 flow rate 84 mL/cm^2 min, and water vapor pressure 0.042 bar. For the optimum leaching ore, with a solid to liquid phase ratio (S/L) of 0.02 kg/L, a HCl concentration of 6 M (2 M for Na_2SO_4), a temperature of ~ $110^{\circ}C$, and a pulp agitation speed of ~ 360 min^{-1} were required. Under the above conditions 72.5 %, 44.50 %, and 86.5 % titanium and 96.0%, 55.9 %, and 71.0 % iron were dissolved from ilmenite for NaCl, Na_2SO_4, and $NaNO_3$ system, respectively. X-ray diffraction patterns suggested the formation of new phase, such as $NaFeTiO_4$, during roasting with $NaNO_3$ and Na_2SO_4. The leaching characteristics of the roasted product obtained from the Na_2SO_4 roasting were not usual in the sense that the dissolution percentages decreased extensively as the leachant concentration was increased above 2 M. Sodium nitrate roasting gave the greatest extent of titanium dissolution from the ilmenite roasted product with the shortest leaching time of 90 min. Titanium and iron could be recovered with an overall titanium yield of over 80 %.

Biswas, *et al.*, (1992) reported that a very good quality titanium dioxide could be prepared from the hydrofluoric acid leach solution of ilmenite by leaching ilmenite (0.05 kg) with 1 L HF (5.5 M) at its boiling point (110°C) under reflux in a 2 L flat-bottomed flask for 5 hours. The recovery of titanium dioxide from hydrofluoric acid leached solution of ilmenite was obtained by the following steps: (1) precipitating out the Ti and Fe compounds from fluoride leach solution using sodium hydroxide solution, (2) oxidizing Fe(II) to Fe(III) using HNO_3 acid, (3) dissolving the solid mass in 7.5 M HCl, (4) extracting most of the Fe(III) by two-stage methylisobuthylketone (MIBK) extraction, (5) adjusting the pH of the aqueous phase to zero in order to extract titanium with di-2-ethylhexylphoric acid (D2EHPA) and left siliceous materials in the aqueous phase, (6) stripping the organic phase with 0.5 M Na_2CO_3 solution to get a quantitative precipitation of metatitanic acid, and (7) filtration of the aqueous suspension of metatitanic acid, oven-drying and finally ignition at 1000°C. The overall recovery yield of TiO_2 from the leach solution was greater than 92.5 % (wt.).

Ogasawara, *et al.*, (2000) investigated the hydrochloric acid leaching of a pre-reduced ilmenitic concentrate, with the purpose of obtaining synthetic rutile. The hydrochloric acid leaching was carried out after pre-reduction of the ilmenitic concentrate to the metallic iron plus TiO_2 mixture. Prior to pre-reduction, the ilmenitic concentrate was submitted to an oxidative calcination in air (0.181 standard dm^3 min^{-1} flow rate) keeping at a temperature of 820°C for 2 hours, then ilmenite ore was subjected to a standard 2.25 dm^3 min^{-1} flow rate of pure hydrogen in order to prevent re-oxidation. Both pre-oxidation and later reductions were carried out in a horizontal tube furnace. The hydrochloric acid leaching tests were performed in a programmable Parr 4562 model agitated titanium autoclave. A mass of 10 g of the ilmenitic concentrate was placed in the Teflon liner containing 200 mL of the hydrochloric acid solution, providing a solid:liquid ratio of 1:20. The autoclave was closed and put in the

mantle furnace. The autoclave was closed and put in the mantle furnace. The presence of the metallic iron in the pre-reduced material required the supply of an oxidizing agent, which consisted of air bubbling for 20 min prior to the start of the autoclave heating, then, with the valves of the autoclave closed, the heating program was put into operation. After the end of the leaching, the autoclave was cooled down out of the furnace and then the leaching mixture was filtered with the help of a vacuum pump. Electrochemical potential and pH of the resultant leach liquor were determined. The solid residue was washed in distilled water, dried in an oven and weighed. The filtrate and residue sample were subjected to chemical analysis. X-ray diffraction analysis was used to determine the phases present in both starting material and the final residue of the leaching tests. Under the condition tested, the best results were obtained by leaching the pre-reduced ilmenitic concentrate with a 4 M hydrochloric acid concentration at $100^{O}C$, 97.5 % extraction of iron 47.5 wt. % Ti in the solid residue (equivalent to 79.2 wt. % TiO_2). Oxidation prior to reduction does not significantly alter the leaching results (percent of iron extraction and percent titanium content of the solid residue), during hydrochloric acid leaching of ilmenitic concentrate. In the leaching of the pre-reduced ilmenitic concentrate, the increase of the hydrochloric acid concentration from 2 to 4 M increases iron extraction by 3.035 % mean difference and titanium content of the solid residue by 4.38 wt % mean difference. X-ray diffraction pattern of the ilmenitic concentrate in its pre-oxidized state shows the peaks of Fe_2TiO_5 (psudo-brookite), Fe_2O_3, TiO_2, SiO_2, and V_2O_5. The reduced ilmenitic concentrate resulting from a sample previously submitted to oxidation shows only peaks for TiO_2 and α-Fe and the leach residue generated in the autoclave leaching of the pre-oxidized/reduced ilmenitic concentrate at $150^{O}C$ using 2 M hydrochloric acid shows only the peaks of the TiO_2 (corresponding to synthetic rutile). The important reactions taking place in the course of the hydrochloric acid leaching of a pre-reduced ilmenite would be as follows.

$$TiO_2 + Fe + 4H^+ = Ti^{2+} + Fe^{2+} + 2H_2O$$

$$Ti^{2+} + 0.5O_2(g) + H_2O = TiO_2 + 2H^+$$

$$Fe + 2H^+ + 0.5O_2(g) = Fe^{2+} + H_2O$$

$$Fe + 2Cl^- + 2H^+ + 0.5O_2(g) = FeCl_2^0 + H_2O$$

$$Fe^{2+} + 2Cl^- + H^+ + 0.25O_2(g) = FeCl_2^+ + 0.5H_2O$$

Lanyon, *et al.*, (1999) studied the hydrochloric leach processes for upgrading ilmenite to synthetic rutile are being considered for use with the Australian ilmenite concentrates that cannot be treated by the commonly used Becher process. These acid leach processes consist of a pre-leach thermal treatment, a hydrochloric acid leach that extracts iron from the concentrate, and a regeneration step that forms hydrochloric acid from the ferrous chloride produced in the leach. The leach process carried out in a glass fluid bed reactor (Figure 4). The reactor was made of Pyrex glass and was joined by a glass flange to a Pyrex lid. Before the fluidizing liquor entered the reaction zone, it was dispersed by passing it through first, a glass disk drilled with an array of 1 mm holes, and secondly, a 10 mm layer of loosely packed 2 mm zirconia balls. The fluidization liquor was circulated through the bed at ~11 mm/s by a peristaltic pump. The acid leach processes differ in their thermal pre-treatments, but common to them all is a leach at temperatures near the boiling point of the acid. The present investigation of the acid leach step, applied to a western Australian ilmenite concentrate, clarifies factors that affect the rate of extraction of iron. The four controlled variables studied were the concentrations of ethanol, hydrochloric acid, and ferrous chloride in the leach liquor, and the quantity of oxygen injected into the liquor. The results show that the hydrochloric acid leach of roast-and-reduced ilmenite occurs in two sequential steps.

Lid

Liquor Out

Reactor
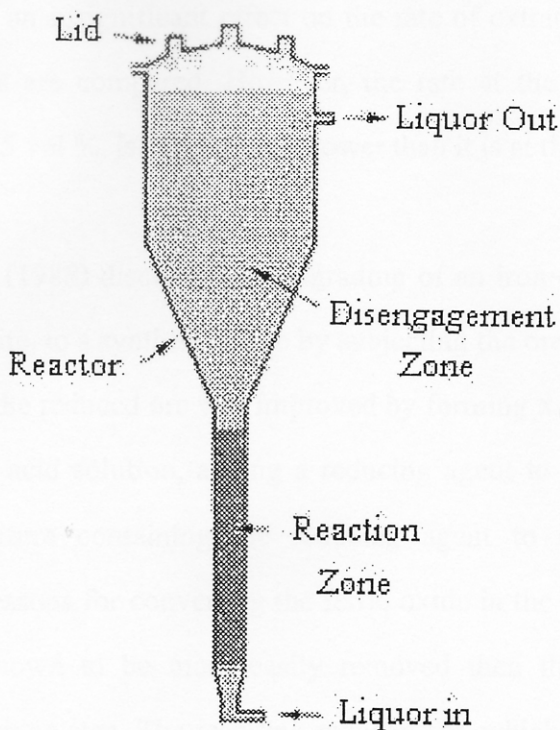
Disengagement Zone

Reaction Zone

Liquor in

Figure 4 Sketch of the fluid bed reactor used in the hydrochloric acid leached

processes by Lanyon, et al., (1999).

In the first step, ilmenite is decomposed to rutile and iron is rapidly leached, and in the

second, iron is slowly extracted from rutile. The iron concentration at the end of the

first stage is between 0.42 and 0.65 % mass Fe_2O_3. The extraction of iron during the

second stage is controlled by its diffusion, first to the surface of the crystallites and

second from the surface of these crystallites, of which the grains are comprised, to the

surface grains. This initially rapid rate of iron extraction is altered by process of liquor

conditions. Thus, it is reduced by ethanol addition, and increased in more concentrated

acid. For any acid concentration, the rate of iron extraction is increased by increasing

the concentration of ferrous chloride, up to a limiting concentration. Beyond this limit,

further increase in concentration lower the rate of extraction. The limiting ferrous

chloride concentration is a function of the acid concentration. Injection of oxygen into

the leach liquor has an insignificant effect on the rate of extraction of iron when the high and low levels are compared. However, the rate at the intermediate level of oxygen addition, 10.5 vol %, is substantially lower than it is at the other levels.

Baldwin, *et al.*, (1988) disclosed the upgrading of an iron-containing titaniferous ore, known as ilmenite, to a synthetic rutile by subjecting the ore to reduction followed by acid leaching of the reduced ore was improved by forming a mixture of the ore and an aqueous sulfuric acid solution, adding a reducing agent to this mixture and then subjecting this mixture containing the reducing agent to reduction at elevated temperatures. The reasons for converting the ferric oxide in the ore to ferrous oxide is that the latter is known to be more easily removed then the ferric oxide in the subsequent acid leaching step. The resulting reduced ore, which is characterized by an increase in the ferrous iron content thereof and an increase in its specific surface area, exhibits an enhanced response to subsequent acid leaching to provide a synthetic rutile of improved purity.

Balderson, *et al.*, (1999) disclosed a method for producing synthetic rutile which regenerates hydrochloric acid from the ferrous chloride and other metal chlorides resulting from the process. Method of leaching which, following the ilmenite ore first oxidized and then reduced in two or three fluidized bed stages, the reduced sample then proceeds to a multiple stages leaching process taking place in fluidized leaching columns using hot hydrochloric acid, and involving one or two evaporation steps. Finally, the product is subjected to filtration, calcinations and magnetic separation. This process results, the remaining residue contains a high titanium dioxide content about 95 % titanium dioxide.

Hollott, *et al.*, (1995) disclosed a process for production of synthetic rutile from a titaniferous ore or concentrate. The process involves three basic steps which are reduction, removal of iron by leaching or aeration and removal of other impurities by leaching in a solution of a strong mineral acid such as hydrochloric acid or sulphuric acid. The conditions of reduction are controlled to promote the formation of metallic iron, a major rutile phase and minor impurity bearing phase. The minor impurity phase may be a metatitanate, an anosovite or a psudobrookite. However, formation of a metatinatate is normally preferred. Suitable reductants include carbonaceous materials or hydrogen bearing gases such as natural gas or synthetic gas. The process is capable of removing more than 80 % of each of the contained iron magnesium and magnesium remaining as oxides after reduction. Substantial proportions of contained aluminium can also are removed.

Duyvesteyn, *et al.*, (2002) disclosed a hydrometallurgical process for producing pigment grade TiO_2 from titaniferous mineral ores, and in particular from ilmenite ore. The ore is leached with a hydrochloric acid, preferably a recycled solution at high hydrochloric acid concentration, to form a leachate containing titanium and iron chloride and residue. The leachate may be filtered to separate the leachate from residue. The leachate is cooled to a temperature sufficient to form crystals of $FeCl_2$, which are separated from the leachate. The leachate may be subjected to a reduction step to reduced Fe^{3+} to Fe^{2+}, before crystallizing. The leachate is subjected to a first solvent extraction to form a pregnant strip solution containing titanium and ferric irons and a raffinate containing ferrous ions. This strip solution is subjected to a second solvent extraction to form a second strip solution containing ferric ions and raffinate containing titanium ions. The first strip solution may be subjected to an oxidization step before the second solvent extraction. The second raffinate containing titanium ions is hydrolyzed. The hydrolysis can be by water addition or spray hydrolysis. Iron

chloride is converted to iron oxide and hydrochloric acid. All product streams containing chlorides are recycled, producing gaseous hydrochloric acid that is used for regenerating the leaching solution.

Girgin, *et al.*, (1991) investigated theoretically the effects of phenols on hydrochloric acid leaching of ilmenite with $HCl-CH_3OH$ and $HCl—C_2H_5OH$ solutions. In the experiments 2.50 g of ilmenite and 125 mL of leach solution were used. All experiments were performed in a 200 mL beaker at room temperature and under constant agitation with magnetic stirring. Aliquot of samples, 1 mL, were removed for analysis at varying intervals of time, the duration of leaching being kept 5 hours. All the leach solutions were analyzed for Fe and some for Mg and Ti by atomic absorption spectroscopy. It is found theoretically that the leaching rate is exponential to acid and phenol concentrations and any metal-phenol complex which can be decomposed by chloride ion should considerably increase the leaching rate by playing a role of active transport. Otherwise, phenols are expected to have a synergistic effect on the hydrochloric acid leaching of metal oxides.

Girgin (1990) studied the leaching of Tallness (Norway) ilmenite concentrate in $HCl-H_2O$, $HCl-CH_3OH-H_2O$, and $HCl-CH_3OH$ solutions. The leaching experiments were carried out at 3 M HCl concentration at temperature between $25^{\circ}C$ and $65^{\circ}C$. A 200 mL three-necked flask equipped with a reflux condenser, a thermometer, a sampling tube, and a thermocouple, was used as a reaction vessel. A sample weighed 2.50 g of ilmenite was added to 125 mL of leaching solution, the desired temperature was maintained within $\pm1^{\circ}C$ and the mixture was stirred continuously with a magnetic stirrer. Sample of 1 mL of solution was pipetted through a fine frit at 10 min intervals for the first hour and then at hourly intervals, the total time of leaching being five hours. Iron was determined for all time intervals, magnesium was determined for

hourly intervals and titanium was determined only for the final solutions. Iron, magnesium, and titanium were determined by atomic absorption spectroscopy and the chloride content of hydrogen chloride of saturated methanol solution was analyzed by microtitration using mercuric nitrate. The results of the leaching experiments show that the HCl-CH_3OH solution is a better solvent than the HCl-H_2O and HCl-CH_3OH-H_2O solutions for the dissolution of iron in ilmenite. This was attributed to stabilization of dissolved titanium ions in solution by the HCl-H_2O solution, at $65^{\circ}C$ and for a leaching time ≥ 4 hours, in the dissolution of magnesium which is the major impurity in ilmenite.

Wongnawa, et al., (1997) studied the determination of impurities in ilmenite ore and residue after leaching with HCl-ethylene glycol by energy dispersive X-ray fluorescence (EDXRF) spectrometry. The leaching experiments were carried out by leaching ilmenite ore, 3 g each, with 125 mL of a mixture of concentrated HCl-ethylene glycol (91 mL of concentrated HCl + 34 mL of ethylene glycol) at the boiling point of the leaching solution in 250 mL round bottom flask and a magnetic stirrer. The heating was furnished through a sand bath. The boiling point was 106-$109^{\circ}C$. The leaching times were in the range 70-130 hours. At the end of the leaching the residue was filtered and washed with water. The residues after leaching were analyzed by energy dispersive X-ray fluorescence (EDXRF) spectrometry. The results indicated that the leachant works well in removing Fe and Mn from the ore. Concentration of Fe and Mn dropped from 20.58 % and 1.57 % to < 0.78 % and < 0.11 %, respectively. The leachant was not capable of leaching out the other metals (i.e., Y, Zr, Nb, W and Sn)

Olanipekun (1999) studied the kinetics of the leaching of a Nigerian ilmenite ore by hydrochloric acid. The effect of (a)stirring speed ranging from 100 to 500 min^{-1}, (b)

particle size ranging from 20 to 74 μm, (c) acid concentration ranging from 7.2 to 9.6 M, and (d) temperature ranging from 70 to 90°C on titanium and iron dissolution are investigated. The experiment carried out by using a 200 mL three-necked round bottom flask equipped with a thermometer, a mechanical stirrer, and a reflux condenser as the batch reactor. The flask was heated by a thermostatically controlled isomantle to reach and maintain the desired temperature within ±1°C. For each run, 150 mL of HCl solution of predetermined molarity was charged into the reactor and heated to the required temperature. Thereafter, ilmenite (0.5 g) was added to the reactor and the contents were well agitated. Solution sample of 2 mL were withdrawn at appropriate times during a run and analyzed for titanium by colorimetry and for iron by atomic absorption spectrophotometry. The results indicated that the dissolutions rates of titanium and iron from ilmenite ore are significantly influenced by the temperature and concentration of the acid solutions. In all test, not more than 80 % of titanium and 85 % of iron dissolved. Apparently, this is due to the reactions conditions used which were not too vigorous. The actual amount of element leached depends on ilmenite mineralogy and reaction variables. The X-ray diffraction pattern indicated that during leaching a product layer consisting mainly of TiO_2, Ti_2O_3, SiO_2, and unleached $FeTiO_3$ are formed.

Chen and Huntoon (1977) disclosed the process for beneficiation of ilmenite ore. This process was applied to the hydrochloric acid leaching step of reduced ilmenite. A small amount of sulfate ion was added to the hydrochloric acid leach liquor used to beneficiate ilmenite ore whereby fines or slime formation in the mother liquor was minimized or reduced and the color of the solid beneficiated ilmenite product was lighter.

1.3 Objectives

1.3.1 To develop method for upgrading ilmenite ore by hydrochloric acid leaching.

1.3.2 To determine the impurities in ilmenite ore and residues after leaching with hydrochloric acid by X-ray fluorescence spectrometry.