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SIMULTANEOUS RECOVERY OF TOTAL IRON AND TITANIUM FROM ILMENITE ORE BY HYDROMETALLURGICAL PROCESSING

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Abstract

Leaching and solvent extraction of total iron and titanium has been studied. A detailed investigation on quantitative leaching of the mineral and separation by solvent extraction were also carried out. The effect of some parameters such as acid concentrations and temperature has been investigated. Experimental results indicate that the dissolution rate is by diffusion control. With 2.0M HCl solution, about 85.4% of the ore was dissolved within 120 min. using solid: liquid ratio of 10g/L at optimal conditions. The calculated activation energy, reaction order and Arrhenius constant were 38.4 kJ/mol, 0.85 and $11.8 s^{-1}$, respectively. The mineralogical purity by X-ray diffraction (XRD) showed that apart from prominent Ilmenite, ($FeTiO_3$) peaks, the following compounds: $ZnSO_4$, SiO_2, $CaFeO_7$, $Fe_2(SO_4)_3$, $CaTiO_4$ and Mn_5O_8 were also present. The results of fundamental studies on solvent extraction of synthetic solutions of total titanium showed that extraction of metal ions increased with increasing extractant concentration. An extraction efficiency of 97% total titanium was obtained by 1.5 M TBP in kerosene from initial 10g/L ilmenite leach liquor at $25 \pm 2^{o}C$ in a single extraction stage. Iron was effectively eliminated using 3M ammoniacal solution at pH 3.5. The stripped titanium solution was recovered from TBP- organic phase by 0.1M HCl solution. A practicable hydrometallurgical flow chart summarizing the operational procedures for the extraction of total titanium from ilmenite ore is presented.

Key words: Ilmenite ore, Nigeria, Dissolution kinetics, Solvent extraction, Hydrochloric acid, Tributylphosphate (TBP)

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Introduction

Ilmenite ($FeTiO_3$) is an ore containing appreciable quantities of magnesium and manganese. Its full chemical formula can be expressed as (Fe, Mg, Mn, Ti)O_3. Ilmenite forms a solid solution with geikielite ($MgTiO_3$) and pyrophanite ($MnTiO_3$), which are magnesian and manganiferous end-members of the solid solution series [1]. 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 [2].

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 [3].

Titanium dioxide pigment can be produced from higher titanium feed stocks such as rutile and leucoxene via hydrochloric acid leaching. Raw ilmenite is refined by decreasing the iron content. Carbon (anthracite) is used to convert some of the iron oxide in the ilmenite to metallic iron. The products of this process are molten iron (pig iron) and a slag rich in titanium [4].

World ilmenite consumption rises approximately 5% per annum to 8% per annum, with demand growth most strongly centred in Asian economies. World demand in 2004 was 335,000 tonnes of TiO_2 units, representing about 2.4 million tonnes of ilmenite. Ilmenite is converted into titanium dioxide via the sulphate process. Sulphate process plants must utilise low-vanadium ilmenite, as vanadium is a penalty element. Ilmenite sand is also used as a sandblasting agent in the cleaning of die-casting [5].

Interestingly, the recovery of metals from aqueous chloride solutions has attracted much attention. This is due to the high efficiency of the chloride leaching processes which are now recognised as a logical choice for treating complex sulphide ore concentrates which cannot be easily or economically treated by other means. Among the separation methods allowing the recovery and purification of metals from chloride solutions, solvent extraction is highly attractive [6]. The recovery of titanium and iron from ilmenite is also of particular interest and various extractants such as Tributylphosphate and o-phenanthroline, respectively have been investigated [7].

A common ilmenite alteration mechanism can be explained as follows [8]:

$$\begin{array}{ccccccc} \text{Ilmenite} & \rightarrow & \text{Pseudorutile} & \rightarrow & \text{Rutile/ Anatase} & + & \text{Hematite} \\ (Fe^{2+}TiO_3) & & (Fe_2^{3+}Ti_3O_9) & & (TiO_2) & & (Fe_2O_3) \\ \text{Primitive hexagonal} & & & & \text{Tetragonal} & & \text{Hexagonal} \end{array}$$

Hence, the spectrophotometric determination of metals after extraction of metal complexes with organic solvents is widely used for trace determination of metal ions, but this method is applicable when the complex has a low partition coefficient in the aqueous: organic phase. Both the partition coefficient as well as the rate of formation of the complex increase with increase in temperature [9]. Therefore, the focus of this work is aimed at developing a hydrometallurgical route for the extraction and recovery of total iron and titanium from a Nigerian sourced ilmenite ore.

Experimental

Material

A ilmenite ore sourced from Oke-ode axis, Kwara State, Nigeria was used for this study. The elemental analysis of the ore was carried out by Inductively Coupled Plasma-Mass Spectrometry and the mineralogical purity was examined by X-ray diffraction (Philips Model PW 1800). The crushing of the ore was done using mortar and pestle and was sieved into three particle size fractions: 0.094□x□0.15, 0.15□x□0.25, 0.25□x□0.35mm. The size fraction: 0.094□x□0.15mm was used for all experiments in this study.

Reagents

All reagents used were analytical grades (BDH product) and doubly distilled water was used for the preparation of all aqueous solutions. The reagents used are: hydrochloric acid, sulphuric acid, hydrofluoric acid, distilled kerosene, O-phenanthroline and tributylphosphate. A mixture of Tributylphosphate, TBP, ($C_{12}H_{17}O_4P$) with 99% purity and distilled kerosene was used for the solvent extraction studies.

Leaching Procedure

Leaching experiments were carried out in a 250ml glass reactor equipped with a magnetic stirrer. For each leaching experiment, the solution mixture was freshly prepared by dissolving 10g/L of the ilmenite ore in 100 ml HCl solution at 55^{o}C. The fraction of the sample dissolved (α) with respect to the total (10g/L) was followed at various time intervals (10-120 minutes) and at various HCl concentrations (0.1M-4.0M). The concentration which gave the highest percentage of dissolution (2M) was used for the optimization of other parameters such as the system temperature. The activation energy was estimated from the Arrhenius plot [10, 11]. In all cases, the fraction of sample dissolved were calculated from the initial difference in weight of the amount dissolved or undissolved at various time intervals up to 120 minutes, after oven-dried at about 60^{o}C [12]. The residue at the optimal conditions was analysed [13] and was found to contained silica (α-SiO_2) [12].

Extraction Procedure

Liquid-liquid extraction experiments were carried out using leachate from the leaching of 10g/L ilmenite ore in 2M HCl solution at 80^{0}C. The leachate contains majorly of Fe: 116.2mg/L, Ti: 473.5 mg/L, Cu: 26.3mg/L. Other metal ions including Ag, Ca, Mn, Pb, Mg, and Sn were present in traces (their concentrations are less than 2 mg/L). The concentration of titanium and iron was determined spectrophotometrically using AQUAMATE Thermo-Electron Corporation UV-visible spectrometer coupled with EPSON LQ 2070 recorder. Batch experiments were carried out at (25±2^{o}C) by equilibrating equal volumes of 25 ml TBP solution and the leachate and shaking the mixture using GallenKamp Orbital Shaker (AMPS) for 30 minutes. After equilibration and phase separation, the concentration of titanium left in the aqueous phase was analysed. The concentration of the metal ion extracted into the organic phase was calculated by difference [14]. This was done after iron removal by 3M ammoniacal solution [10].

Preparation of Chromogenic reagents:

Preparation of Ascorbic Acid, Methylene-blue and Titanium standard Solutions:

Ascorbic acid: 0.02mol/L solution was prepared by dissolving 0.880g of ascorbic acid in water and diluting to 250ml with water. This solution was prepared daily [13]. Methylene solution (1.011x 10^{-4}mol/L) was prepared by dissolving 0.0360g of Methylene- blue in water and diluting to 1000ml. Also, Titanium standard was prepared by weighing 0.4085g of pure TiO_2 and dissolving it in 150ml of Hydrofluoric acid. 150ml of Hydrofluoric acid (HF) was measured into 500ml volumetric flask and diluted with distilled water to the mark.

Catalytic Determination of total Titanium

To a series of 10ml volumetric flask, 2.0ml of 1.011 X 10^{-4}mol/L of Methylene blue solution, 1ml of acetate buffer solution pH = 4, 1ml of standard titanium solution so that its final concentration would be in the range 3-25gml^{-1} in the final solution and enough distilled water to bring the solution to about 9ml were added. Then 1ml of 0.02mol/L ascorbic acid was added. The zero time was taken as the moment at which the last drop of ascorbic acid solution was added and the solution was thoroughly mixed. After 5min, a portion of the solution was transferred into a 1.0cm quartz cell and the absorbance was measured against distilled water at 666 nm (λ_{max}) [15].

Catalytic Determination of total Iron

A stock standard solution of iron (II) (1000µg/ml) was prepared by dissolving 7.01g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ and 2ml concentrated H_2SO_4 was then diluted to 10ml with distilled water. Solutions of 0.4-1.4ml standard Fe(II) (25µg/ml) were transferred into a 10ml volumetric flask, 2ml of acetate buffer pH 4 and 5ml of 5-nitro-6-amino-1,10-phenanthroline were added. The concentrations of Fe (II) used were 1.0, 1.5, 2.0, 2.5, 3.0, 3.5 and 4.0µg/ml in a 10ml volumetric flask. After shaking manually, the mixture was allowed to stand for 20 min at 25°C. The absorbance was measured against a blank solutions and a calibration curve was prepared [16].

Results and discussions:

Results of elemental studies by ICP-MS and mineralogical purity by XRD

The elemental analysis of ilmenite ore by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS) is summarized in Table 1.

Table 1. Elemental analysis of ilmenite ore by ICP-MS.

Element	Ti	Fe	Si	S	Cu	Ag	Ca	Mn	Pb	Mg	Cd	V	Sn
Comp. (%)	42.06	27.43	11.24	3.14	2.79	0.96	0.86	0.079	0.14	0.035	0.001	0.0021	0.002

**Oxygen(O) = 11.26%, obtained by difference. It is important to note that low vanadium concentration in this ore may suitably fit industrial applications in sulphate process plants [5].*

From Table 1, the major elements detected by ICP-MS are Ti, Fe, Si. S and Cu, while the minor element are Ag, Ca, Mn, Pb, and the elements such as V, Sn and Mg were recorded at trace level. The X-ray diffraction analysis lends the support of ICP-MS as the following compounds were detected (Table 2).

Table 2. Result of XRD analysis of Ilmenite ore.

Compound	Formula	JCPDS file no	Relative intensity(%)
Ilmenite	$FeTiO_3$	26-1354	49.53
Calcium iron oxide	$CaFe_4O_7$	39-1033	7.84
Iron sulphate	$Fe_2(SO_4)$	42-0225	13.21
Calcium titanium oxide	$CaTi_4O_9$	26-0333	5.85
Manganese oxide	Mn_5O_8	39-1218	4.93
Zinkosite	$ZnSO_4$	08-0491	3.04
α- quartz	α-SiO_2	46-1045	14.22

JCPDS = Joint Committee on Powder Diffraction Standard file number. Other compounds not detected by XRD = 1.38%.

Results of Leaching studies:

Effect of HCl concentration

The effect of hydrogen ion concentration as given by the total amount of hydrogen ion added as HCl on the rate of ilmenite ore dissolution has been examined. From the results shown in Fig. 1, it can be seen that increasing [H^+] ion increased the rate of reaction up to a concentration of 2.0M, above which there is no further significant increase in the reaction rate.

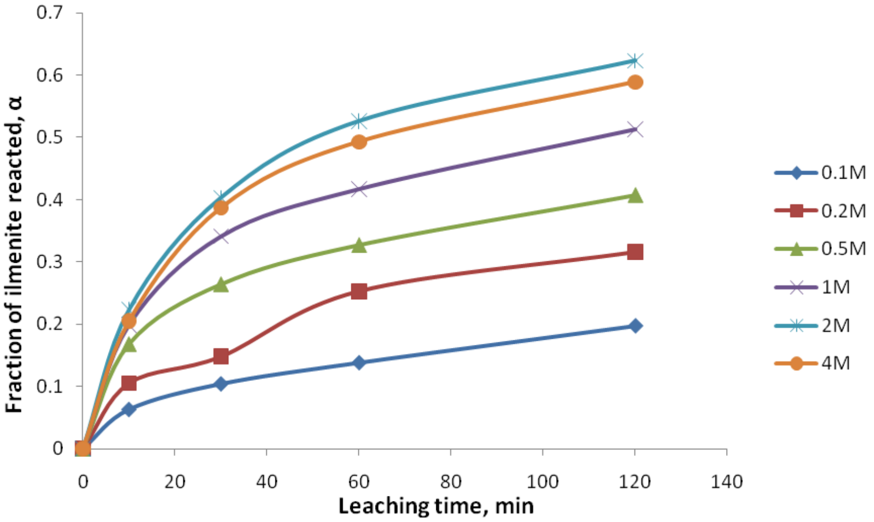

Fig. 1. Fraction of Ilmenite ore dissolved (α) versus time (min) at different HCl concentrations.

Experimental conditions: [HCl] = 0.1-4.0M; Temperature = 55^0C; Solid: liquid ratio: 10g/L; Stirring speed: 360rpm.

Effect of Temperature

The effect of temperature on the dissolution rate of 10g/L ilmenite ore was investigated in 2.0M HCl solution between 28^{0}C and 80^{o}C temperature ranges. The results obtained are shown in Fig 2. The rate of dissolution increases with temperature. The investigation was limited to 80^{o}C in order to avoid significant loss of HCl vapour at higher temperatures [2].

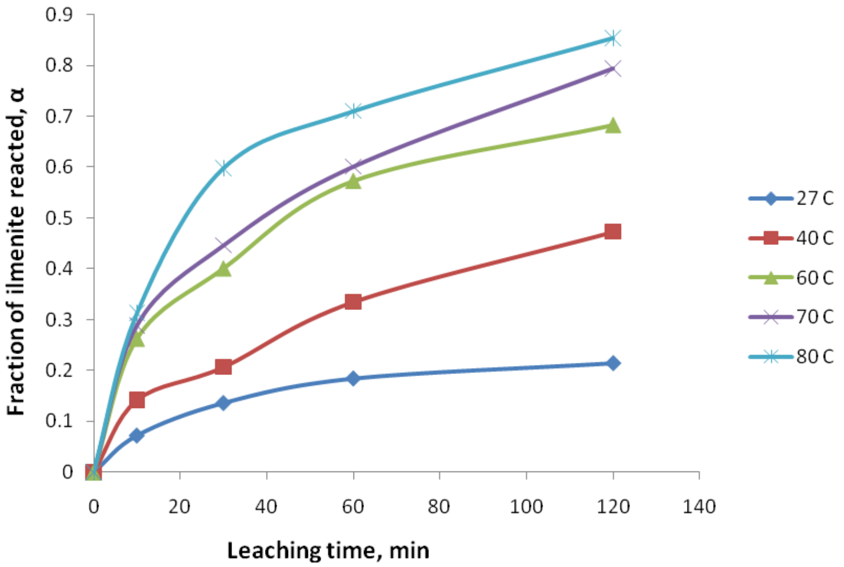

Fig 2. Fraction of Ilmenite ore dissolved (α) versus contact time (min) at different temperatures.

Experimental conditions: [HCl] = 4.0M; Temperature = 28^{o}C – 80^{o}C; Solid: liquid ratio = 0.5g/L; Stirring speed = 360rpm.

Shrinking core model fitting

The dissolution rates of ilmenite ore under study was analysed using the shrinking core models based on the assumption that the material is a homogenous spherical solid phase [2, 12,17- 19]. The two most commonly used shrinking core models are:

$$1- (1-\alpha)^{1/3} = K_1 t \qquad (1)$$

$$1 - 2/3\alpha - (1-\alpha)^{2/3} = K_2 t \qquad (2)$$

Where α is the fraction of ilmenite ore reacted; t is the contact time (min) and K_1, K_2, are the respective reaction rate constants for the model equations (1-2), respectively. Equation (1) is applicable to a chemical reaction controlled process at the interface. Equation (2) is a diffusion controlled process through the product layer. In this present study, all data in Figs. 1 and 2 have been analyzed and were found to perfectly fit the diffusion controlled reaction and of the form: $1 - 2/3\alpha - (1-\alpha)^{1/3} = Kt$.

Hence, the experimental data in Fig. 1 has been analyzed and then linearized using equation (2). The apparent rate constants, K, obtained from the slopes of the straight lines were used in construction of the plot in Fig. 3 to obtain the reaction order of 0.85 ≈ 1. This value showed that the reaction order for the dissolution process was assumed to be first order mechanism with respect to HCl concentrations (≤2M).

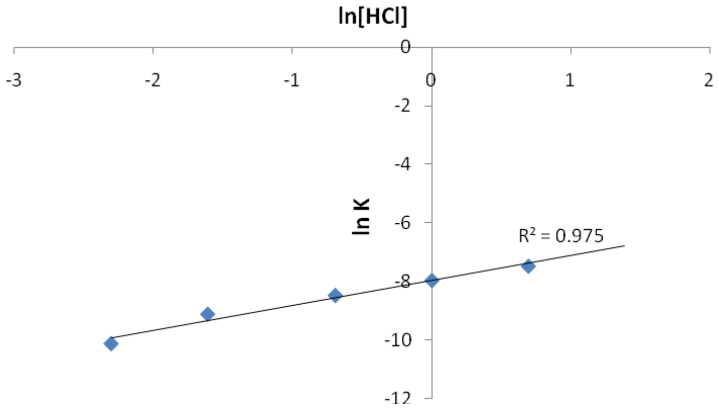

Fig. 3. ln K versus ln [HCl]. Experimental conditions: Same as in Fig. 1.

The apparent rate constant, K, was also defined for the experimental data for various temperatures in Fig. 2 (following the same data fitting procedure as applicable to Fig. 1) to obtain the Arrhenius relation given in Fig. 4.

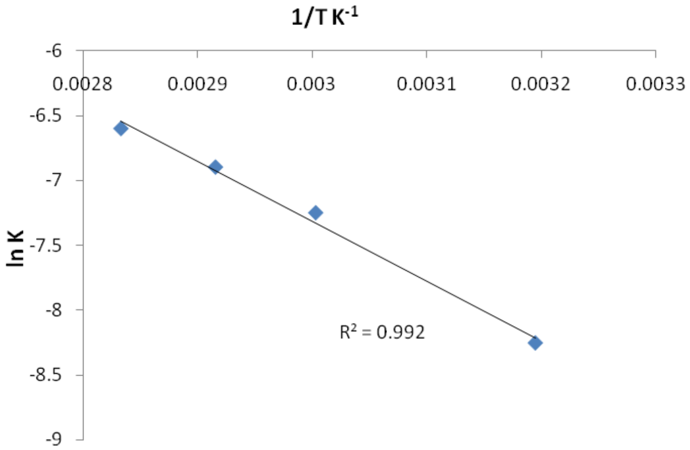

Fig. 4. A plot of ln K versus 1/T (K^{-1}). Experimental conditions: Same as in Fig. 2.

From this relation in Fig. 4, activation energy of 38.4 kJ/mol was calculated for the dissolution process. This value suggests that the rate of dissolution is diffusion controlled. Some studies on ilmenite by HCl leaching have also recorded extremely high values of activation energies of 48.9 and 53.7kJ/mol, respectively for titanium and iron [2, 21] through diffusion controlled dissolution. Also, the re-plot of the data of Fig. 4 from the origin [22] gave Arrhenius constant of 11.8s^{-1} for the dissolution process.

Results of Solvent extraction studies:

Calibration Working Curve for Total Titanium Standard

The reaction between Methylene blue and ascorbic acid is very slow, but when trace amount of Titanium (IV) are present, the rate of reaction is increased. Therefore, it was on the basis for which the quantitative determination of total Titanium is based. However, a linear correlation was obtained between absorbance and total Fe concentration over the range of 0.1-4 g/mL; the regression equation for the straight line was $A = 0.249C+0.0014$, where A is the absorbance at 520 nm and C is the concentration of total iron (g/mL) and ($r = 0.9999$). The detection limit is 0.1µg/mL. The standard and relative standard deviation of the slope and intercept are 0.001-0.016 and 0.57%-2 %, respectively [16].

Total iron removal from ilmenite pregnant leach liquor

The ilmenite leachate at 80^{0}C whose composition had been stated in Extraction procedure section was used for this investigation. The total iron in the leachate was eliminated first by 3M ammoniacal solution at pH 3.5 [10]. At this pH, the total iron was successfully precipitated and the fade brown colloidal suspension obtained was filtered to obtain a clear and colourless solution. This solution contained mainly total titanium ions. The result of this investigation is summarized in Table 3.

Table 3. Total iron removal by 3M ammoniacal solution at pH 3.5.

Metal ion	Concentration before total iron removal (mg/L)	Concentration after total iron removal (mg/L)	pH before iron removal	pH before iron removal
Total titanium	473.5	472.1	3.5	2.4
Total iron	116.2	4.4	3.5	2.4
Total copper	26.3	< 2.0	3.5	2.4

Other metal ions including Pb, V, Sn and Cd occur in traces. Their concentrations are ≤ 2 mg/L.

The result from Table 3 showed that total iron extraction efficiency was 97.6%

Effect of extractant concentration on total titanium extraction

The result of the extractant concentration on total titanium extraction from ilmenite leachate by TBP in kerosene is presented in Fig. 5.

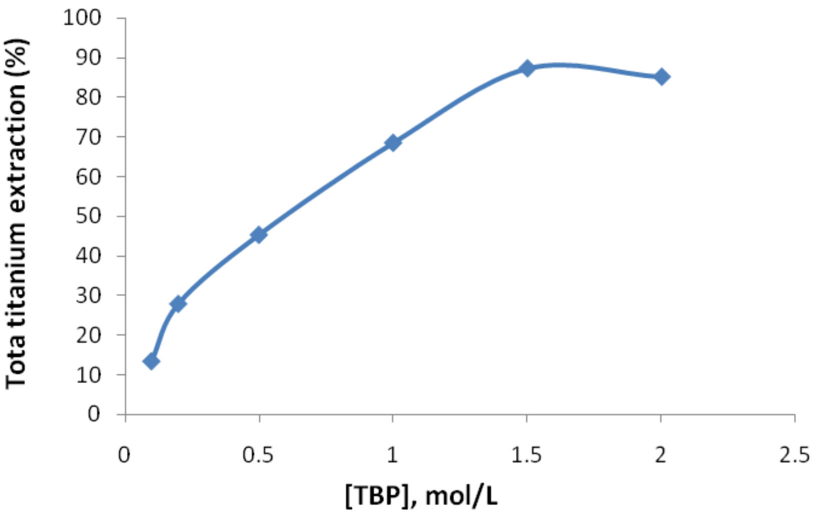

Fig. 5. Effect of extractant concentration on total Titanium extraction.

From Fig. 5, it is evident that an increase in the extractant concentration (0.1 – 1.5 TBP in kerosene) leads to a better extraction, evidently because the ratio of [TBP]/[total Ti] increases. Therefore, it is important to note that increase in the initial TBP concentration in the organic phase considerably improves the extraction which reaches 87.35 % at [TBP] = 1.5 mol/L.

Solvent extraction of total Titanium by TBP in kerosene

The clear solution containing total Titanium after iron removal was contacted with 1.5M TBP in kerosene for 30 minutes. The result of the extraction process is summarized in Table 4.

Table 4. Result of solvent extraction of total Titanium from ilmenite leachate by TBP in kerosene after total Iron removal.

Initial total titanium concentration before extraction(mg/L)	Quantity of total titanium extracted into organic phase (mg/L)	Quantity of total titanium left unextracted in aqueous phase (mg/L)	% total Titanium extracted
472.1	456.5	15.6	96.6

The result from Table 4 showed that the extraction efficiency by TBP in kerosene was ≈ 97 % at a single stage extraction.

Stripping of total titanium from the TBP extracts by 0.1M HCl.

The result of the stripping of total Titanium from TBP organic phase by 0.1 M HCl is presented in Table 5.

Table 5. Stripping of total Titanium from TBP organic phase by 0.1 HCl.

Initial total titanium concentration before stripping (mg/L)	Quantity of total titanium stripped by 0.1M HCl (mg/L)	% total Titanium stripped
456.5	432.7	94.8

The result of the stripping investigation showed that about 94.8% of total titanium was stripped from the TBP organic phase by 0.1 M HCl. The use of hydrochloric acid for the recovery of metal ions including Titanium is preferred due to the ease of possible electrowinning [14, 23]. Therefore, the hydrometallurgical flow chart describing the Ilmenite ore processing leading to the extraction of total Titanium is presented in Fig. 6.

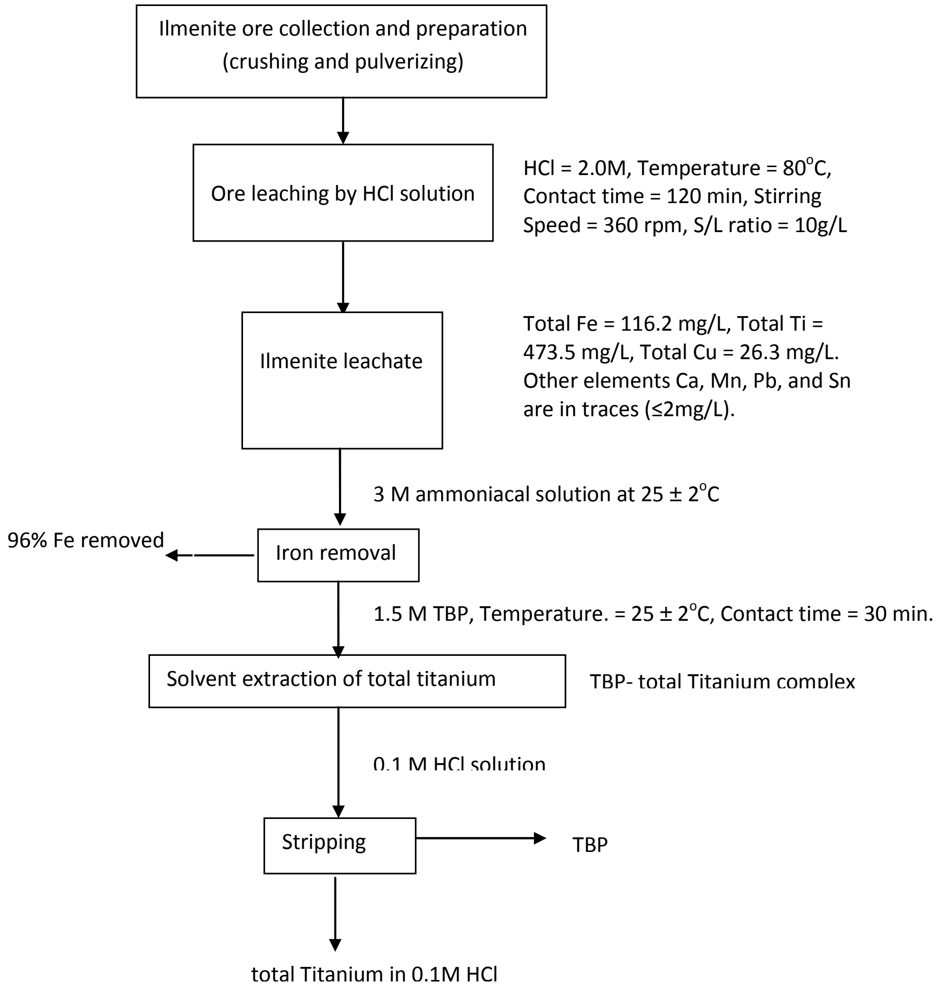

Fig. 6. Hydrometallurgical flow chart for ilmenite ore processing.

Conclusions

The following conclusions can be drawn from this study:

1. Both system temperature and concentration of hydrochloric acid have significant influence on the rate of dissolution of ilmenite ore.
2. With 2.0M HCl solution, and a temperature of 80°C using solid: liquid ratio of 10g/L, about 85.4% of ilmenite ore was dissolved within 120 min. The activation energy of 38.4 kJ/mol has been calculated for the process, while the order of reaction is 0.85 with respect to H^+ ion concentration ($\leq$2mol/L). Arrhenius constant of 11.8s^{-1} was also determined for the dissolution process.
3. The dissolution results indicated that the shrinking core model for spherical particles is applicable. The surface diffusion controlled process has been established to be the rate-controlling step for the dissolution process.
4. About 97.6% of total iron was precipitated by 3M ammoniacal solution at pH 4.
5. 1.5M TBP in kerosene was successfully used to extract about 97% total Titanium from initial 10g/L of ilmenite leach liquor at 25 ± 2°C and stirring time of 30min at a single stage extraction.
6. About 94.8 % of total titanium was recovered by stripping with 0.1 M HCl solution.

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