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Hydrometallurgical Treatment of Abu Ghalaga Ilmenite Ore

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Abstract

The present work aims to study the leaching of Abu Ghalaga ilmenite ore by hydrochloric acid and simultaneous reduction by iron powder method to dissolve its titanium and iron contents. Iron content in the produced liquor is separated by solvent extraction using TBP as a solvent. All parameters affecting the efficiency of the dissolution process were separately studied including the acid concentration, solid/liquid ratio which controls the ilmenite/acid molar ratio, temperature, time and grain size. The optimum conditions at which maximum leaching occur are 30% HCl acid with a solid/liquid ratio of 1/30 at 80°C for 4 h using ore ground to -350 mesh size.

At the same time, all parameters affecting on solvent extraction and stripping of iron content from the produced liquor were studied. Results show that, the best extraction is at solvent/solution 1/1 by shaking at 240 RPM for 45 minutes at 30 °C where as best striping of iron at H2O/solvent 2/1.

Keywords – Ilmenite ore, HCl Leaching, Solvent extraction of Titanium

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1. Introduction

A variety of titanium containing minerals occurs in nature where ilmenite ($FeO·TiO_2$ or $TiFeO_3$), rutile (TiO_2) and leucoxene ($Fe_2O_3·nTiO_2$) are the major ones. Ilmenite, containing 40–65%. Titanium dioxide reported to be about 91% of the world's demand for titanium minerals. In 2010, the world's ilmenite production reached about 5.8 million metric tons [1]. Titanium dioxide is used in the manufacture of paints, pigments, welding-rod coatings, ceramics, papers, painting inks, in heterogeneous catalysis as a photo catalyst, in solar cells for production of hydrogen and electric energy, as a gas sensor, as a corrosion- protective coatings, as an optical coating, in electric devices, and in other areas of chemical industry [2].

In Egypt, ilmenite occurs in two main deposits; namely, a massive-type interlayer with gabbroic rock at Abu Ghalga region in Eastern Desert and a placer type included in the black sands and deposits at the Mediterranean Beach especially at Rosetta and Damietta [3]. The ilmenite concentrate of both types is mineralogically different. According to [2] Abu Ghalaga is a massive ore composed of ilmenite, magnetite, hematite, rutile, goethite and anatase representing about 70%, while the balance is mainly silica. The Rosetta ilmenite concentrate is more complicated due to the presence of titano-magnetite. Hydrometallurgical processing of ilmenite ores with hydrochloric acid was studied by several researchers using i) direct leaching ii) leaching in the presence of oxidizing agent iii) leaching in the presence of reducing agent such as iron powder [3] and iv) leaching after pre-oxidation of the concentrate at high temperature [3-9]

The addition of $MgCl_2$ was reported to be very effective in the direct leaching of ilmenite ores with HCl [8-10]. Various flow sheets have been proposed to incorporate solvent extraction (SX) techniques to purify and concentrate the titanium in leach solutions [10].

Therefore, in the present work, we propose a process for the production of synthetic rutile based mainly on leaching of ilmenite ore with hydrochloric acid in presence of metallic iron as a reducing agent. The iron metal can be added as a pure powder. The iron and titanium contents in the ore will be continuously dissolved then separated by solvent extraction this trend is considered advantageous compared with the other mentioned processes. All parameters affecting the efficiency of the leaching process such as the acid concentration, solid/liquid, temperature, reaction time and ilmenite grain size have been studied and the optimum conditions at which maximum dissolution of titanium would be obtained. At the same time, all parameters affecting solvent extraction of iron content from titanium chloride in hydrochloric acid media using TPB as a solvent were studied.

2. Experimental

2.1 Materials

Ilmenite Ore: the ilmenite used in the present study is a natural placer mineral obtained from Abu Ghalaga region in the Eastern Desert in Egypt. Bulk chemical composition of the ilmenite ore in this study was determined using X–ray fluorescence analysis using Pnalytical Axios advanced XRF and is given in Table 1.

Table (1): Chemical Composition of Ilmenite Sample

Compo	Weight%	Compou	Weight%
TiO_2	30.523	Cr_2O_3	0.09
Fe_2O_3	55.37	MnO	0.24
SiO_2	7.14	Co_3O_4	0.107
MgO	1.53	NiO	0.093
Al_2O_3	2.73	CuO	0.087
Na_2O	0.40	ZnO	0.037
P_2O_5	0.147	SrO	0.015
SO_3	0.40	ZrO_2	0.074
K_2O	0.04	Nb_2O_5	0.013
CaO	0.87	Cl	0.052

One kilo of ilmenite ore from Abu Ghalaga region was thoroughly mixed and a representative sample of about 500 g was crushed and ground and used to conduct this work.

Leachant**:** Pure hydrochloric acid from Fisher Scientific was used. The acid concentration and density were 32% and 1.16 g/ml, respectively.

Reducing agent**:** Pure iron powder from Aldrich Co. was used. Organic solvent: The extractant tri-n-butyl phosphate from Xilong Chemical Co, Ltd was used without purification.

2.2. Procedure:

Acid leaching of ilmenite ore was carried out using a 250cm^3 glass reactor provided with mechanical agitator (K–EUROSTAR DIGITAL IKA-WERKE). The desired volume of hydrochloric acid of the required concentration was poured in the reactor and the required weight of ilmenite ore was added, the reactor was heated to the desired temperature using a thermostatically controlled glycerol/water (GFL-1083) bath and after a certain time a weighed amount of iron powder was added to the reaction medium. After the elapse of the reaction period, the slurry was filtered. Titanium was determined spectrophotometrically by hydrogen peroxide method at 410 nm (Jeffery et al., 1979) using lab spectrum USA spectrophotometer model: 1102 S.N 102100700. The interfering effect of iron can be removed by phosphoric acid. Iron determined by direct titration with EDTA using salicylic acid as indicator [2].

Solvent extraction experiments were performed in conical flasks by mechanically shaking, and then phase disengagement was conducted in separating funnels. After phase disengagement within 2 min., the concentrations of iron in both organic and aqueous phases were determined. Also, the concentration of Ti in aqueous phase was determined spectophotometry while the concentration in organic phase was obtained from mass balance. The loaded organic phase and stripping reagent (Distilled Water) were mixed in conical flasks by mechanically shaking, and then phase disengagement was conducted in separating funnels.

3. Results and Discussion

3.1. Dissolution (Leaching) Step:

3.1. 1. Effect of mesh size:

To study the effect of grain size upon ilmenite dissolution, six experiments were performed at different mesh size ranging from +100 meshe to -350 mesh using solid/liquid ratio 1/30, acid concentration 20% at 80 °C for 4 h and RPM 400 where 0.5 gm of iron powder was added after 25 minutes from the start of the reaction. The results showed in Fig.1 reveal that, the dissolution efficiency of ilmenite increased as the particle size decreased. This finding is in agreement with [11] which found that, particle size influences the rate of ilmenite dissolution. This may be due to increasing ore fineness, increase of specific surface area and changes and / or disorder in the crystalline structure [2]. The optimum size was found to be – 350 mesh at which 40.9% and 67.5 % of titanium and iron content, respectively, can be dissolved from ilmenite.

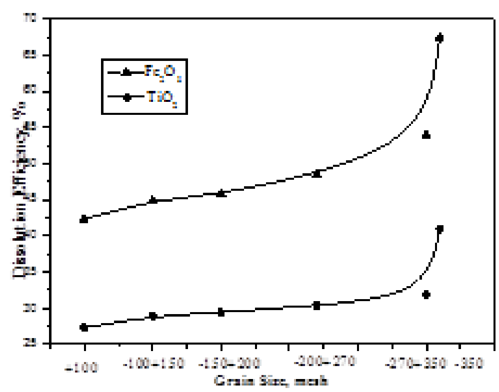

Fig (1): Effect of grain size of ilmenite on titanium and iron dissolution under reductive acid leaching conditions (20 %HCl, 80 °C, S/L ratio 1/30 and 4h

3.1. 2. Effect of solid / liquid ratio:

Working with 20% HCl at 80 °C for 4 h and -350 mesh ilmenite ore the effect of solid / liquid ratio was studied in the range of solid to liquid ratio from 1/10 to 1/30. The obtained results are plotted in Fig. 2. The results indicate that, the dissolution of titanium is strongly dependent on the ratio of ilmenite to acid. At low ilmenite /acid 1/10 which equivalent to 20 g ilmenite dissolved in 200 ml HCl there is low dissolution of both titanium and iron, by increasing ilmenite /acid ratio up to 1/30 which equivalent to 6.6 gm ilmenite to 200 ml HCl dissolution of both titanium and iron increase reaching to 40.9% and 67.5% for titanium and iron, respectively ,due to decreasing the pulp density of the solution and increasing the available free acid leading to an increase in titanium and iron dissolution and less hydrolysis of titanium [2]. Therefore, the optimum ilmenite to acid ratio is 1/30 g/ml.

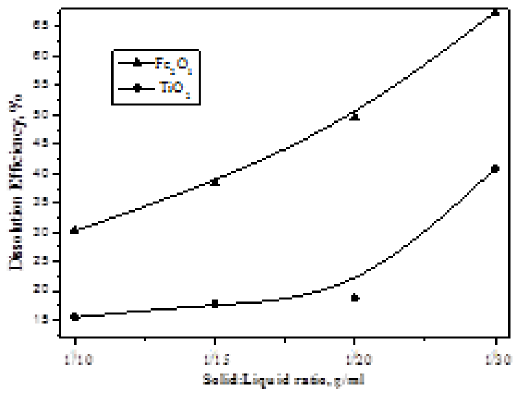

Fig (2): Effect of solid / liquid ratio on titanium and iron dissolution under reductive acid leaching conditions (20% HCl, 80 °C, 4 h &-350 mesh).

3.1.3. Effect of dissolution time:

To study the effect of dissolution time upon ilmenite dissolution, six experiments were performed at different time periods ranging from 30 minutes to 5 h by using solid/liquid ratio 1/30, acid concentration 20%, at 80 °C, RPM 400, -350 mesh size and adding 0.5gm of iron after 25 minutes. The results in Fig. 3 show that, the dissolution efficiency of titanium increased as the time increased until 4 h, then, there is no pronounced change after 4 h while that of iron has increased. Extending the leaching time above 4 h has a slight adverse effect upon the dissolution of titanium this may be due to hydrolysis effect [2]. Therefore 4 h would represent an optimum time for maximum titanium dissolution.

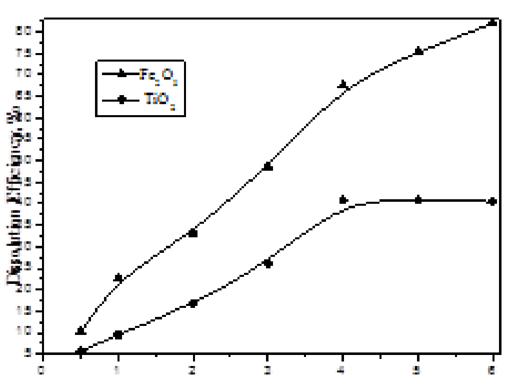

Fig (3): Effect of Time on titanium and iron dissolution under reductive acid leaching conditions (20% HCl, S/L 1/30, 80 °C& -350 mesh)

3.1. 4. Effect of temperature

Several dissolution experiments were performed at different temperatures ranging from 40°C to 90°C by using 20% HCl, solid /liquid 1/30, and -350 mesh for 4 h dissolution time. The results in Fig.4 show that, the extent of ilmenite dissolution increases significantly with temperature, at 40°C only 1.04% titanium and 22.5% iron dissolve respectively this is due to the low reactivity of ilmenite at this low temperature. As temperature increases dissolution of both titanium and iron increase reaching to 40.9% titanium and 67.5% iron at 80°C but, increasing the temperature up to 90°C decreases titanium dissolution. Titanium dissolution decreases may be due to polymerization and hydrolysis. [2, 11] therefore, temperature plays an important role in the hydrolysis of dissolved Titanium and 80°C would be considered as the optimum temperature.

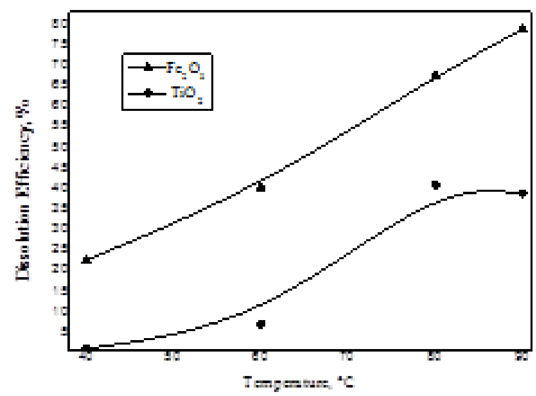

Fig (4): Effect of temperature on titanium and iron dissolution from ilmenite (20% HCl, 4h, S/L 1/30 & -350 Mesh).

3.1. 5. Effect of acid concentration

Several dissolution experiments were performed at different temperatures ranging from 40°C to 90°C by dissolution experiments were performed using concentrations varying from 10% to 32%. The other dissolution parameters were fixed at S/L ratio=1/30 gm/ml; temperature 80 °C; 4 h dissolution time and ilmenite grain size-350mesh. The obtained results are plotted in Fig.5 from the obtained results; it is clearly evident that, the dissolution efficiency of TiO_2 and total iron is strongly dependent on the acid concentration. At 32% HCl about 92.5% of titanium and 98.2% of iron are dissolved; but at 20% HCl, iron dissolution is much higher than that of TiO_2. The low dissolution of TiO_2 in 20% HCl is most probably due to hydrolysis and precipitation of TiO_2 would be inhibited at high acidity [2]. Therefore, 32% acid concentration is the optimum acid concentration for ilmenite dissolution.

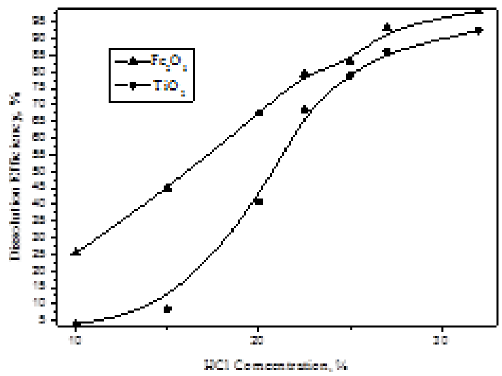

Fig (5): Effect of acid concentration on titanium and iron dissolution under reductive acid leaching conditions (80 °C, 4 h, 1/30 gm/ml & -350 mesh).

Accordingly, it can be concluded that, leaching of Abu Ghalaga ilmenite using iron powder has proved quite successful for almost dissolution of both titanium and iron. The optimum conditions involve working with HCl concentration of 32%, solid/liquid ratio of1/30 gm/ml at 80 °C for 4 h, using ore grounded to -350 mesh sizes. At these conditions 92.5% and 98.2% of titanium and iron are dissolved respectively.

3.2. Solvent Extraction Process:

Based on the previous study, 2 liters of leached chloride liquor that contains total iron (Fe) approximately 14 g/l as chloride and 9.3 g/l TiO_2 as chloride were prepared under the predetermined optimum dissolution conditions and used for solvent extraction process.

Solvent extraction study will involve two steps namely, extraction and stripping and in the following part the factors that affect these two steps will be studied.

3.2. 1. Solvent extraction step:

3.2. 1.1. Effect of solvent /solution ratio:

To study the effect of solvent/solution ratio upon extraction of Fe four experiments were performed at different ratio of solvent to the chloride solution ranging from 0.5/1 to 2/1 under constant of other extraction conditions (Time 30 minutes, Temp 30° C, RPM 170). The results in Fig. 6 show that, increasing solvent /solution ratio from 0.5/1 to 1/1 increases extraction of iron in Organic phase from 85.9 %to 93.8 %. By contrast, the extraction of iron merely increased from 93.8% to 95.8% as phase ratio (solvent/solution) varied from 1:1 to 2:1. The distribution coefficient reached maximum value at solvent /solution ratio amounts to 1:1. Higher phase ratio (solvent/solution) means an increase in extracting consumption and large equipment volume. Based on the comprehensive consideration of extraction efficiency and operation cost, the phase ratio (solvent /solution) suitable for iron extraction in this system was determined as 1:1 which is in agree with [12] results.

At this ratio about 95 % of TiO_2 content remains in the aqueous phase (raffinate phase) with only about 6% of its iron content.

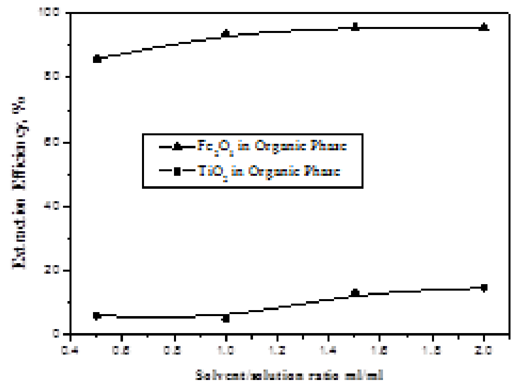

Fig (6): Effect of solvent to solution ratio on extraction of iron and titanium by TBP in organic phase

3.2. 1.2. Effect of agitation speed, RPM:

To study the effect of agitation speed, RPM, upon extraction of Fe four experiments were performed at different RPM values from 60 RPM to 240 RPM under constant of other extraction conditions (Time 30 minutes, Temp 30 C, solvent/solution 1/1). The results in Fig. 7 shows that extraction efficiency of Fe in organic increases from 62.7% to 97.5% with increasing agitation speed from 60 RPM to 240 RPM. So that, the optimum agitation speed for maximum extraction of Fe in organic phase is at 240 RPM at which only 2.5% of iron content remains in the aqueous phase (raffinate phase) with 95% of its titanium content.

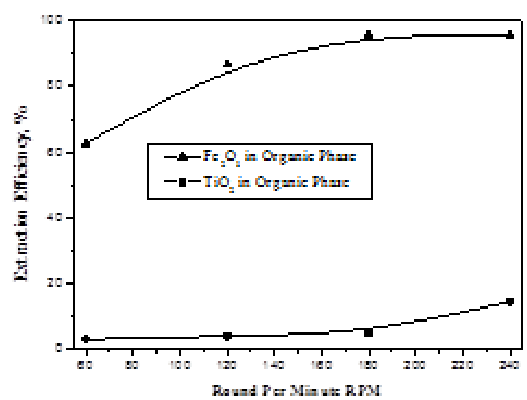

Fig (7): Effect of RPM on extraction of iron and titanium by TBP in organic phase.

3.2. 1.3. Effect of temperature:

To determine the effect of temperature upon extraction of Fe four experiments were performed at different temperature ranging from 30°C to 60°C under constant of other extraction conditions (Time 30 minutes, RPM 240, solvent /solution 1/1).

The results in Fig. 8 shows that, as temperature increases the extraction efficiency of Fe in Organic phase increases slowly from 97.5% to 99.6%, indicating that the extraction of iron was endothermic. Higher temperature will cause more volatilization and more TiO_2 extraction reaching 25% at 60 °C; meanwhile, the iron extraction was not significantly increased with temperature. Therefore, room temperature of 30° C was chosen as operation temperature for iron extraction at which 97.5 % of iron content with only 6 % of its TiO_2 content are extracted with TPB solvent.

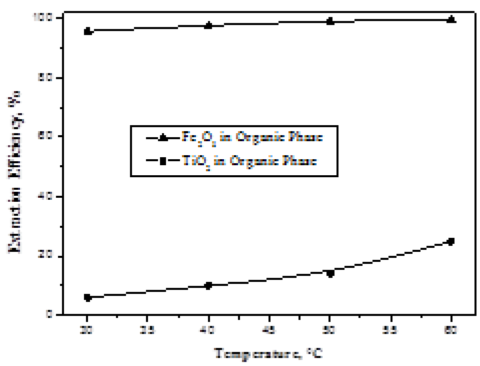

Fig (8): Effect of Temperature on extraction of iron and titanium by TBP in organic phase.

3.2. 1.3. Effect of time:

To study the effect of time upon extraction of Fe four experiments were performed at different time ranging from 15 minutes to 1 h under constant of other extraction conditions (temp 30 °C, RPM 240, solvent /solution 1/1). The results in Fig. 9 shows that, as time increases the amount of Fe extracted in organic phase increases until 45 minutes then amount of Fe extracted decreases. So that, the optimum time is 45 minutes at which the maximum amount of extracted Fe in the organic phase is 99.9% with about 7% of its TiO_2 content. Whereas, about 0.1 % of iron content and 93 % of TiO_2 contents are remain in the raffinate phase.

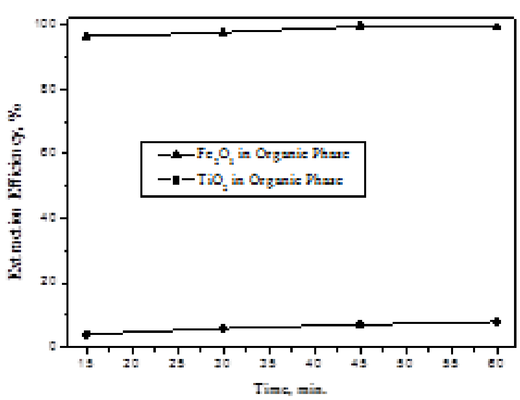

Fig 9: Effect of Time on extraction of iron and titanium by TBP in organic phase.

It can be concluded that, about 99.9% of iron content only with about 7% of titanium in the Leachant liquor (solution) can be extracted with TBP at solvent/solution 1/1, time 45 minute, RPM 240 and at temp 30° C leaving about 93% of titanium content with only less than 0.1 % of iron content in the solution (rffinate phase).This solution can be hydrolysed to obtain pure TiO_2 and the organic phase will be directed to stripping step to strip its iron content from TPB solvent to be recycled in the extraction process.

3.2. 2. Stripping of iron from solvent

Fe can be stripped from the organic solvent using water under certain conditions [12]. The factors effect on stripping of Fe from the organic solvent will be studied.

3.2. 2.1. Water/solvent (organic phase) ratio:

To study the effect of water /solvent ratio upon stripping of Fe from loaded solvent six experiments were performed at different ratio of water to the organic phase ranging from 0.5/1 to 3/1 under constant of other stripping conditions (Time 45 minutes, temp 30° C, RPM 240).

The results in Fig. 10 show that, as the ratio of water to solvent increases the amount of Fe stripped in the aqueous phase increases sharply until 2/1 then slightly increases so the optimum ratio is 2/1 water/solvent at which 85.2 % of iron content with only 22.7% of titanium content stripped in the solution leaving the rest of contents in the solvent phase (organic phase).

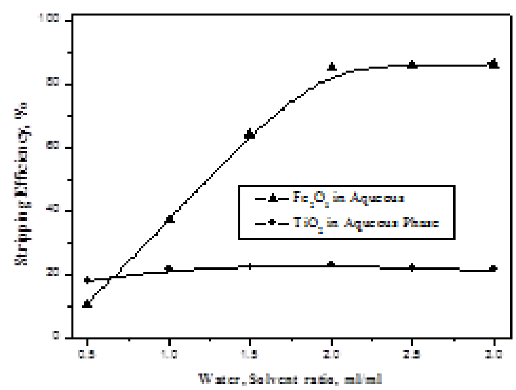

Fig (10): Effect of water solvent ratio on stripping of iron and titanium in aqueous phase.

3.2. 2.2. Temperature:

To study the effect of temperature upon stripping of Fe from loaded solvent four experiments were performed at different temperature ranging from 30° C to 60° C under constant of other stripping conditions (Time 45 minutes, water/solvent ratio 2/1, RPM 240) The results in Fig. 11 show that as temperature increases from 30° C to 60° C the amount of Fe stripped in the aqueous phase decreases from 85.2 % to 3.8 %, i.e the temperature has adverse effect on the stripping of iron therefore, the optimum temperature is at 30°C at which Fe stripped in aqueous phase is 85% with 22.7% of the titanium content.

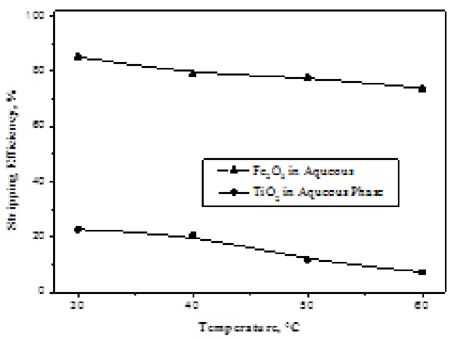

Fig (11): Effect of Temperature on stripping of iron and titanium in aqueous phase.

3.2. 2.3: Effect of Time of Stripping

To study the effect of time upon stripping of Fe from loaded solvent four experiments were performed at different time ranging from15 minute to 1 hour under constant of other stripping conditions (water/solvent ratio 2/1, temp. 30°C, RPM 240). The results in Fig 12 show that as time increases the amount of Fe stripped in the aqueous phase increases from 70.4% to 85.2% at 45 minutes then decrease to 77.5% after one hour. The optimum agitation time is 45 minutes at which the maximum amount of Fe (85.2%) is stripped in the aqueous phase with about 22.7% of its titanium content.

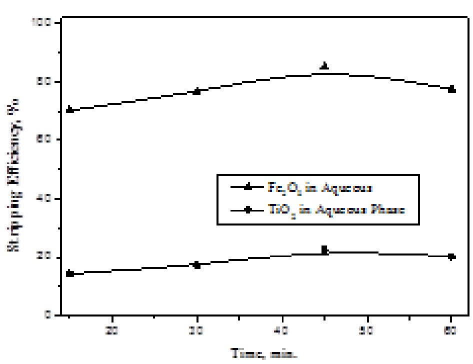

Fig (12): Effect of Time on stripping of iron and titanium in aqueous phase.

3.2. 2.4. Agitation speed, RPM:

To study the effect of agitation speed upon stripping of Fe from loaded solvent phase four experiments were performed at different RPM ranging from 60 RPM to 240 RPM under constant of other stripping conditions (water/solvent ratio 2/1, Temp. 30 °C, Time 45 minute). The result in Fig 13 show that, as RPM increases from 60 to 240 amounts of Fe stripped at aqueous phase increases from 58.4% to 85.2%. The optimum agitation speed is at RPM 240 at which Fe stripped is 85.2%.

Concluded that**,** about 85% of iron content in solvent phase (organic phase) can be stripped, with 22.7% of its titanium content. It can be from loaded TBP solvent phase by using water / solvent ratio 2/1, at 30°C and 240 RPM for 45 agitation time. This stripped solution can be utilized for iron pigments production.

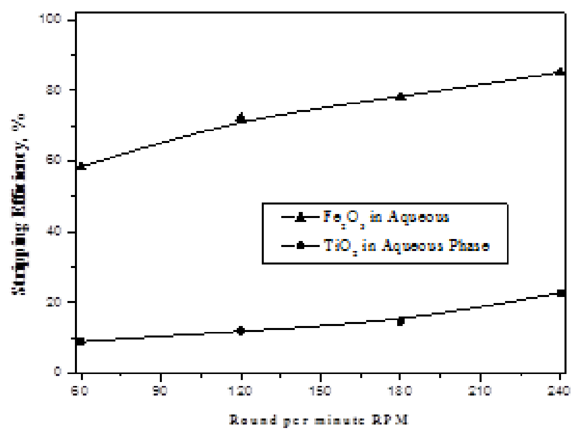

Fig (13): Effect of RPM on stripping of iron and titanium in aqueous phase.

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