Upgrading of TiO_2 Separated From Ilmenite Mineral, Rosetta, Black Sands of Egypt

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ABSTRACT

The leaching of ilmenite paste (resulting from ilmenite treatment by KOH) using sulphuric or hydrochloric acids has been studied. Factors affecting the leaching of TiO_2 was investigated such as, acid concentrations (M), S/ L ratio, leaching time and temperature. Optimum results for sulphuric acid leaching of TiO_2 were 10M H_2SO_4 acid, S/ L ratio 1:10 and 180 min. of leaching time at 120º C. However, 6 M HCl acid, S/ L ratio of 1:6 and 120 min. of leaching time at 80º C were the best conditions for leaching of ilmenite paste.

After leaching factors were studied on ilmenite paste, the mixture was filtered then divided into two parts; the first part (filterate) and second part (residue formation Ti cake). The obtained products showed 95.55 % TiO_2 when using 6M HCl and 92.19% TiO_2 present when using 10M H_2SO_4.

Key words: Ilmenite / Leaching / HCl/ H_2SO_4.

INTRODUCTION

The Egyptian black sand deposits represent an important source for nuclear minerals as well as other industrial materials. They contain essential economic heavy minerals such as monazite, magnetite, garnet, ilmenite, rutile and zircon. These minerals contain a number of elements of great importance in the nuclear industry e.g. uranium, thorium, zirconium, hafnium, titanium, and rare earth elements. The latter minerals were separated through physical processing including electrostatic and magnetic techniques. These minerals have been used in a wide range of several technologies and nuclear industrial applications such as ceramic, catalysts, nuclear energy technologies, fluxing agents in blast furnace feeds and medical devices.

Titanium is relatively abundant in the earth's crust, which is usually found in igneous and metamorphic rocks as ilmenite ($FeTiO_3$), rutile (TiO_2) and titanomagnetite (Fe_2TiO_4–Fe_2O_4). A survey on the use of titanium in its various forms indicate that almost 95 % of its use is for the production of white colored TiO_2 pigment which has extensive application in paint, plastic and paper industries (1) .

The importance of titanium has been rapidly increased due to its excellent characteristics as an industrial material. It finds different useful applications in normal and nuclear industry. The two main mineral sources for the production of titanium and its oxides are ilmenite and rutile. These minerals contain a variety of other metallic impurities such as iron, chromium and vanadium. In Egypt, ilmenite occurs in two main deposits; namely, a massive-type interlayer with gabbroic rock in Eastern Desert and a placer type included in the black sand deposits at Mediterranean coast especially at Rosetta and Damietta. Ilmenite has become the major ore mineral of titanium which supplies about 91% of the worlds demand for titanium minerals (2).

The treatment of Abu Ghalaga massive ilmenite ore to prepare synthetic rutile by direct reductive leaching of ilmenite ore in HCl solution have been been studied (3) . The treatment of the coast ilmenite by HCl leaching under normal and reducing media has been able to prepare synthetic rutile (4). The dissolution of Rosetta ilmenite using sulphuric acid dissolution has been studied and realized up to 95% TiO_2 (5). The reductive hydrochloric acid leaching of Rosetta ilmenite using iron powder has proved to be quite successful for almost complete dissolution of both titanium and iron [6]. The chloride route is advantageous regarding both cost and waste management, however, it requires a high-grade titanium raw material; viz, natural or synthetic rutile or else titanium slag (> 90% TiO_2). The chloride process is less expensive to operate than the sulphate process at larger scales [7] .

The main purpose of this research is to develop leaching-selective extraction of TiO_2 from ilmenite which is separated from black sands collected from Rosetta beach sand and upgrading TiO_2 content as final products.

EXPERIMENTAL

Methods and Analysis

The hydrogen ion concentration for the solution was measured using Inolab digital pH-meter, level 1 (England) with an error of ±0.01 at ambient laboratory temperature. The major oxides SiO_2, Al_2O_3, TiO_2 and P_2O_5 were determined by spectrophotometer Metertech Inc model Sp-8001, (Germany) in the range 200-1100 nm and wavelength accuracy of ±1nm using standard method of analysis [8]. Sodium and potassium were determined by a Sherwood flame photometer model 410 (England), against series of chemical standard solutions. The final product of TiO_2 was characterized by Energy Dispersive X-ray (EDX) and Scanning Electron Microscope (SEM) model Joel JSM-5600 LV, Atomic Energy Authority, Cairo, Egypt.

Preparation of Titanium Paste

The ilmenite sample was separated from black sands which collected from Rosetta coast in Egypt. This ilmenite was treated with concentrated potassium hydroxide solution (70%) to form ilmenite paste as follows [9] :

$$3\ FeTiO_3 + 4\ KOH \rightarrow K_4Ti_3O_8 + 3\ FeO + 2\ H_2O. \qquad (1)$$

Based on this equation, 100g ilmenite with -200 mesh size was treated with 500 ml of 70% KOH solution with a ratio (1:5). This treatment was carried out on a hot plate at 120ºC for 3 hours. The slurry was filtered and washed with distilled water. This ilmenite paste was subject to leaching investigations using sulphuric or HCl as leaching agents. The chemical analysis of ilmenite sample was determined as shown in (Table 1).

Table (1): Chemical analysis of the ilmenite sample separated from black sands.

Sample / Oxides (%)	Ilmenite
TiO_2	46.38
FeO	25.13
Fe_2O_3	20.0
SiO_2	1.312
Al_2O_3	0.07
P_2O_5	0.004
MgO	0.2
CaO	0.28
V_2O_5 *	0.178
Cr_2O_3*	0.29
MnO *	1.15

**After El-Hazek et al., 2007* [6]

RESULTS AND DISCUSSION

Leaching Procedure

Two series of leaching procedures were investigated to obtain the optimum leaching conditions of titanium ions from titanium paste resulting from treating titanium powder with KOH.

1-Leaching by H_2SO_4

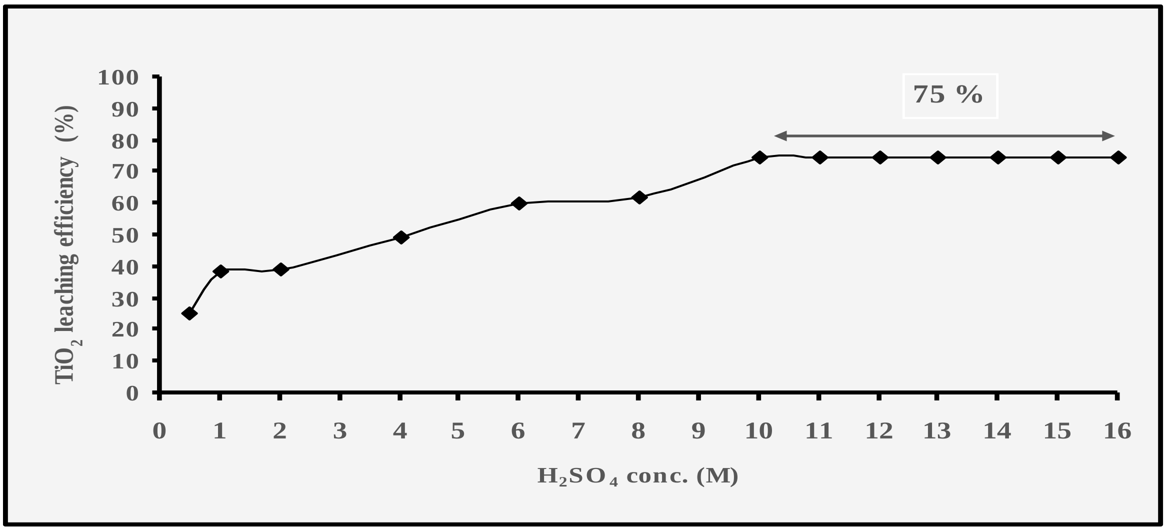
The reaction of ilmenite paste with sulphuric acid has been described by different authors(5,6,10-19):

$K_4Ti_3O_8$ +FeO + 6 H_2SO_4→ 3 $TiOSO_4$ +$FeSO_4$ +2 K_2SO_4 +6 H_2O. (2)

The main parameters that influence this reaction was studied e.g. H_2SO_4 concentration (M), ilmenite paste: 10M H_2SO_4 (S/L ratio), temperature and leaching time.

1.1-Effect of H_2SO_4 Concentration (M)

Different sulphuric acid concentrations ranged from 0.5 to 16 M have been applied during the conditions experiments run to study the leaching of titanium from its ilmenite paste. It was found that, the leaching (%) of TiO_2 increases with increasing H_2SO_4 concentrations and reaches its maximum leaching efficiency at 10 M H_2SO_4 acid which dissolved about 75% TiO_2, then the leaching efficiency became up to 16 M H_2SO_4 acid (Fig. 1).

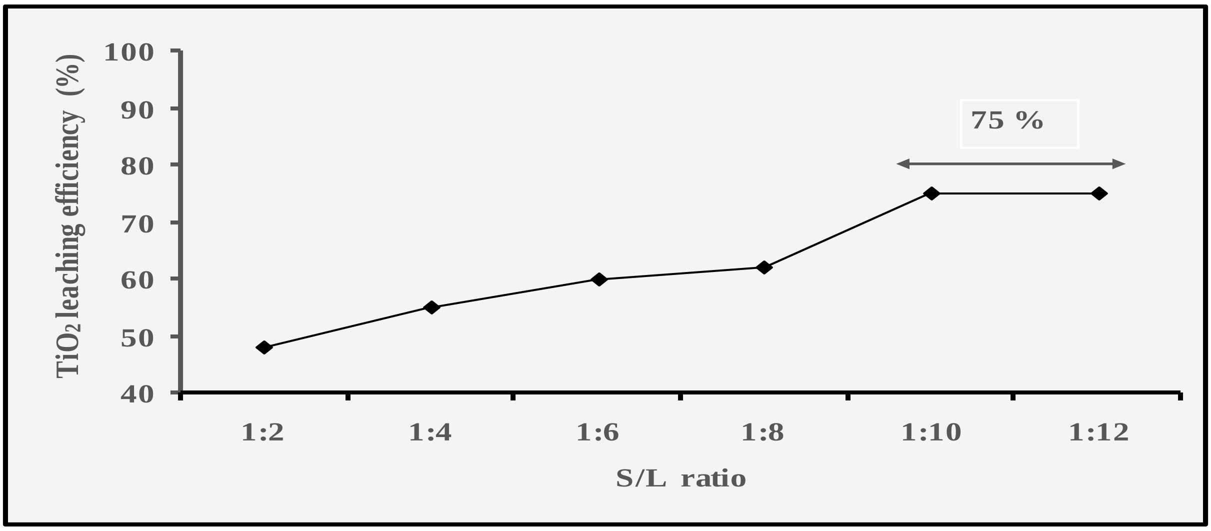


Leaching conditions
Temperature: 90º C and leaching time 2h. , S / L ratio: 1/10

Fig. (1): Effect of H_2SO_4 concentration on TiO_2 leaching (%).

1.2- Effect of S/L Ratio

The effect of ilmenite paste: 10 M H_2SO_4 (S/L ratio) on the leaching of TiO_2 was studied, in the ratios varying from 1:2 to 1:12 ratio. The other parameter was fixed at 10 M H_2SO_4. From the obtained results, it is clear that the dissolution effecting TiO_2 increased up to 1/10 S/L ratio. Nearly 75% TiO_2 was leached then kept constant till 1:12 ratio (Fig. 2).

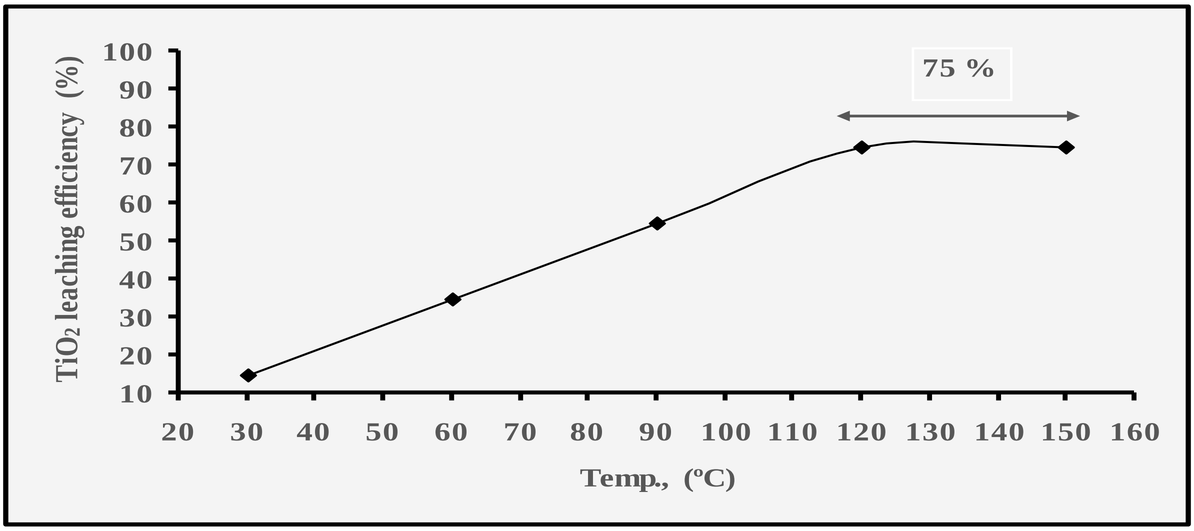


Leaching conditions
10M H_2SO_4 acid, temperature: 90º C and leaching time 2h.

Fig. (2): Effect of S/L ratio on TiO_2 leaching (%)

1.3- Effect of Temperature

Different temperatures ranged from 30º to 150º C have been applied during the experiments run to study the leaching of TiO_2 from its ilmenite paste. It was noticed that, the TiO_2 increased with increasing the temperature and reach its maximum at 120º C which dissolves 75% TiO_2 then the leaching efficiency became up to150º C (Fig. 3).

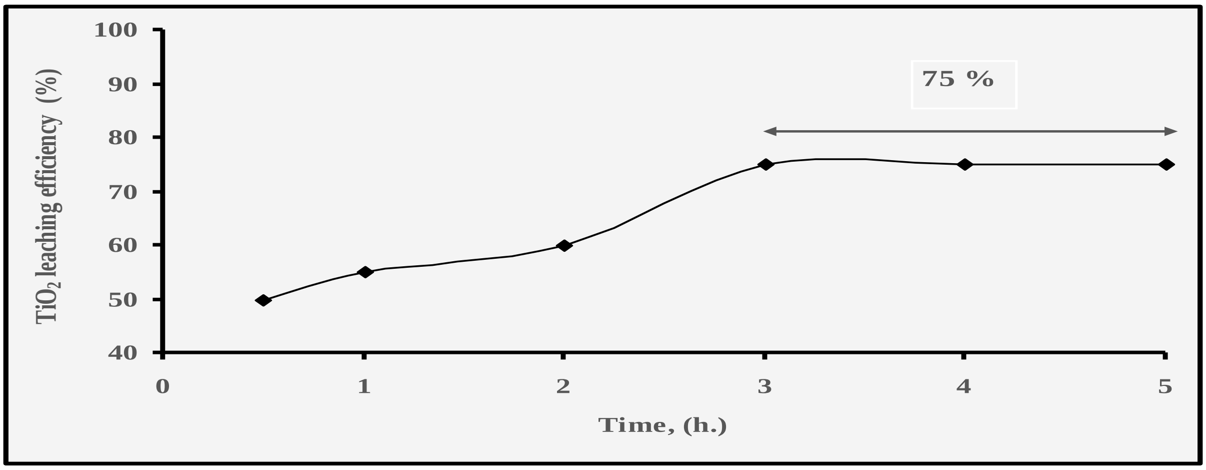


Leaching conditions
10M H_2SO_4 acid, S /L ratio: 1/10 and leaching time 2h.

Fig. (3): Effect of temperature (ºC) on TiO_2 leaching (%)

1.4- Effect of Leaching Time

The effect of leaching was studied in the time range from 0.5 to 5 hours while fixing the other parameters at their optimized values. Figure (4) shows that the leaching efficiency of TiO_2 increases with time tell it reaches about 75% in 3 hours, after which it keeps constant at that value up to a leaching time of 5 hours. (Fig. 4).



Leaching conditions
10M H_2SO_4 acid, S / L ratio: 1/10 and temperature 120° C.

Fig. (4): Effect of leaching time (h.) on TiO_2 leaching (%)

2-Leaching by HCl

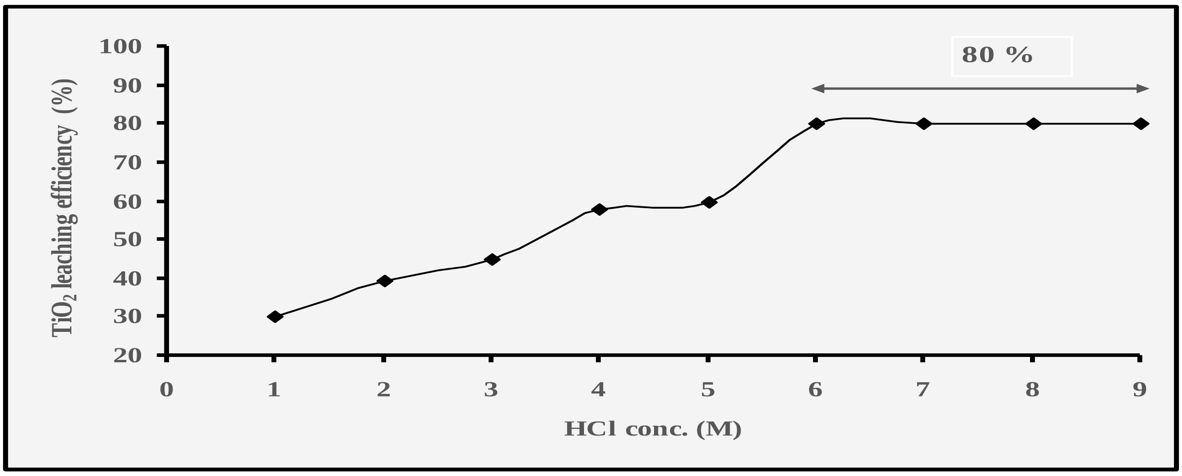
The leaching of ilmenite paste using HCl was investigated by different authors [20-23]:

$K_4Ti_3O_8$ +FeO + 12HCl $\longrightarrow$ 3$TiOCl_2$ + $FeCl_2$ + 4 KCl +6 H_2O (3).

The main parameters that influence the rate of this reaction was studied e.g. HCl acid (M), ilmenite paste: 6M HCl (S/L ratio), temperature and leaching time.

2.1-Effect of HCl Concentration (M)

Different concentrations of hydrochloric acid ranged from 1 to 9M were carried out during the experiments to study the leaching of TiO_2 from its ilmenite paste. It was found that, TiO_2 leaching efficiency increased with increasing of HCl concentrations (M) and reached its maximum leaching (%) at 6M, which dissolved 80 % TiO_2. Further increase up to 9M HCl solution did not affect the leaching % of titanium ions, (Fig.5).

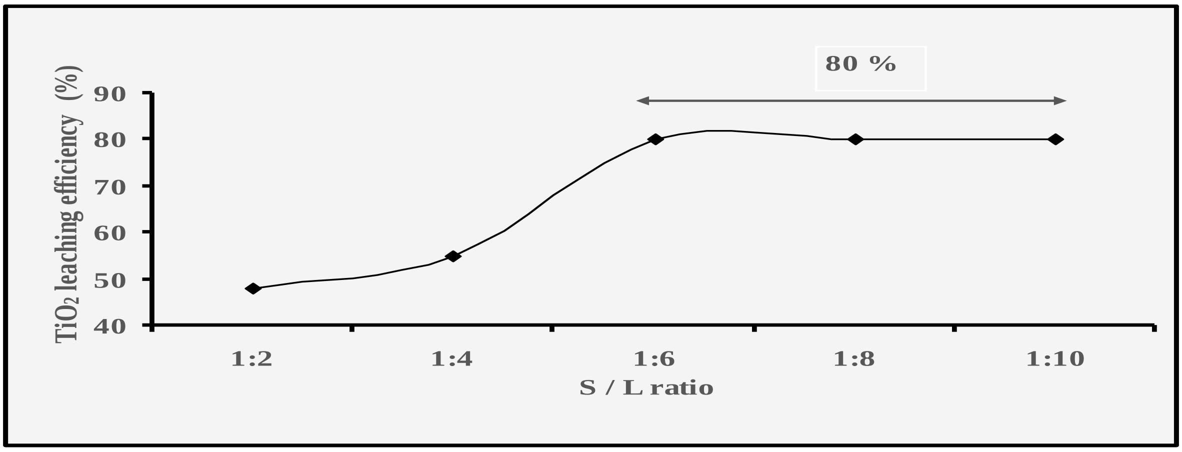


Leaching conditions
Temperature 80°C , leaching time 2h. and S / L ratio: 1/9.

Fig. (5): Effect of HCl concentration (M) on TiO_2 leaching (%)

2.2- Effect of S: L Ratio

The effect of ilmenite paste: 6M HCl (S/L ratio) on the leaching of TiO_2 was studied from 1:2 to 1:10 ratio with fixing the other parameter at 6M HCl. From the obtained results, it was clear that the dissolution of TiO_2 increased up to S/L ratio 1:6. It dissolved about 80 % TiO_2 from the ilmenite paste then was kept constant till 1:10 ratio (Fig. 6).

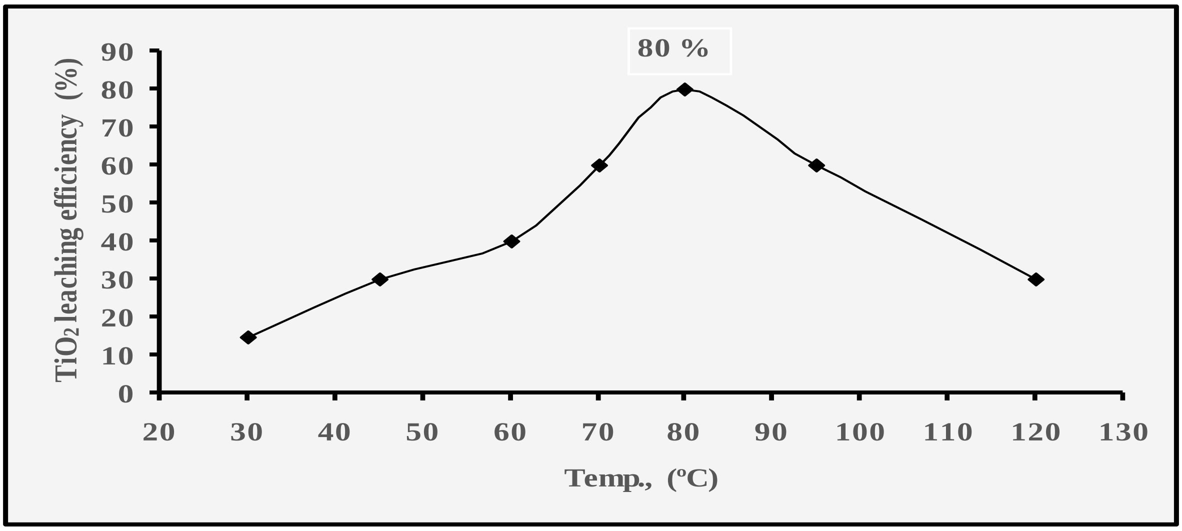


Leaching conditions
6M HCl acid, temperature 80° C and leaching time 2h.

Fig. (6): Effect of S/L ratio on TiO_2 leaching (%)

2.3- Effect of Temperature

Different temperatures ranged from 30º to 120º C had been applied during the experiments run to study the leaching of TiO_2 from its ilmenite paste. It was noticed that, the TiO_2 leaching efficiency increased and reached its maximum leaching (%) at 80º C, which dissolved 80 % TiO_2 from the ilmenite paste then the leaching (%) decreased with increasing the temperatures (Fig. 7).

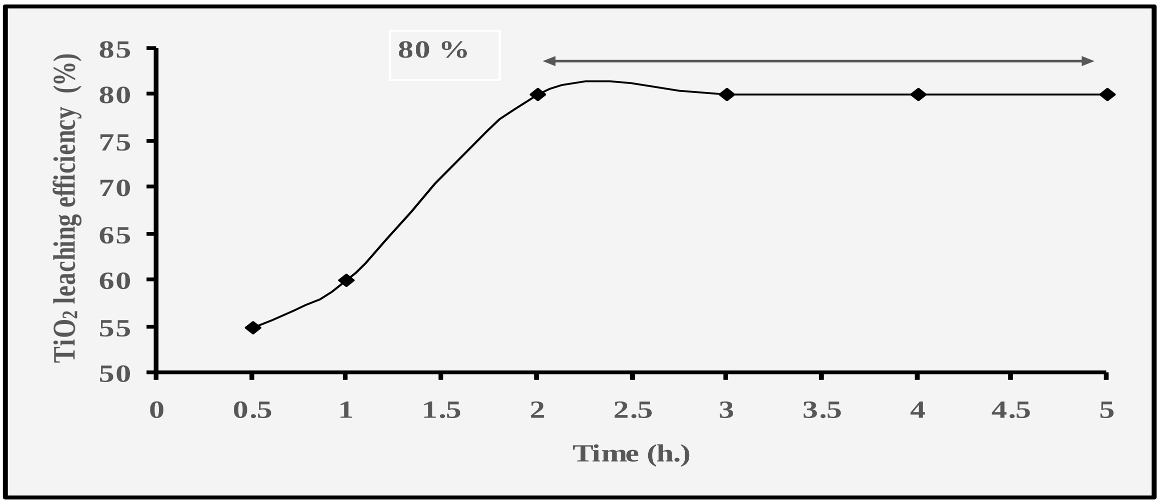


Leaching conditions
6M HCl acid, S / L ratio: 1/6 and leaching time 2h.

Fig. (7): Effect of temperature (ºC) on TiO_2 leaching (%)

2.4- Effect of Leaching Time

The effect of leaching time was studied from 0.5, 1, 2 till 5 hours and fixing the other parameters .The obtained results proved that, the leaching efficiency % of TiO_2 attained its maximum (%) at 2 hours (Fig. 8).



Leaching conditions
6M HCl acid, S / L ratio: 1/6 and temperature 80°C.

Fig. (8): Effect of leaching time (h) on TiO_2 leaching (%)

Comparison Between H_2SO_4 and HCl Acid as Leaching Factors

The leaching of TiO_2 from ilmenite paste was studied using two leaching acids H_2SO_4 or HCl. The main parameters affecting the leaching efficiency of TiO_2 which include acid concentration (M), leaching time, temperature and ilmenite paste to acid ratio (S/L ratio) are given in (Table 2).

Table (2): Main parameters of ilmenite paste leached by H_2SO_4 or HCl acid.

Parameters	H_2SO_4 acid	HCl acid
Acid concentration (M)	10M	6M
Time of leaching	180 min. (3h.)	120 min. (2h.)
Temperature	120º C	80 ºC
Ilmenite / acid (M) ratio	1:10	1:6

After applying the studied leaching factors on ilmenite paste, the mixture was filtered then divided into two main parts; first part (filterate) and the second part (residue forming TiO_2 cake).

The optimized conditions of the two leaching acids were applied on a proper sample of ilmenite mineral. The chemical analysis of the leachate was 76 % TiO_2 using 10M H_2SO_4. However, 80 % TiO_2 released using 6M HCl acid (Table 3).

Table (3): Chemical analysis of leach liquor of ilmenite paste.

Oxides (%) \ Sample	10M H_2SO_4 acid	6M HCl acid
TiO_2	76	80
Fe_2O_3 ^{T}	21	17
Al_2O_3	0.3	0.3
CaO+ MgO	0.7	0.7

The filterate solution was concentrated by boiling its volume to 1/10. The precipitate was dried then calcinated at 1000º C for 3 hours. The final product of titanium cake showed that, 95.55 % TiO_2 obtained by leaching with 6M HCl. While, 92.19 % TiO_2 formed by leaching with 10M H_2SO_4 (Table 4).

Table (4): Chemical analysis of associated elements of titanium cakes.

Oxides (%) \ Sample	Product I leached by 10M H_2SO_4 acid	Product II leached by 6M HCl acid
TiO_2	92.19	95.55
Fe_2O_3 ^{T}	1.59	0.799
Al_2O_3	1.27	0.97
SiO_2	0.75	0.55

Proposed Flow Sheet Diagram

A flow diagram based on 10M H_2SO_4 or 6M HCl acid leaching was proposed and tested (Fig.9). In this case, 100g ilmenite separated from black sand of Rosetta area, with particle size of -200 mesh size was taken and digested with 500 ml of 70% KOH solution with ratio 1:5 (wt/v) for three hours at 120ºC. The obtained paste washed with water till neutrality. The ilmenite paste was analyzed then leached by 10M H_2SO_4 or 6M HCl acid. The solution was filtered and divided into two parts mainly; filterate and residue. The residue leached by 6M HCl or 10M H_2SO_4, the solution concentrated by boiling its volume to 1/10, the precipitate was calcinated at 1000º C , the product show that 95.55 % TiO_2 when using 6M HCl and 92.19% TiO_2 present when using 10 M H_2SO_4 (Fig. 9). The final product was confirmed by EDX and SEM (Figs. 10 and 11).

CONCLUSION

The ilmenite sample was treated by 70% KOH solution to form ilmenite paste. The ilmenite paste leached by 6M HCl or 10M H_2SO_4 then filtrated to form filtrate and residue. Optimum results for sulphuric acid leaching of TiO_2 were 10M H_2SO_4 acid, S/ L ratio 1:10 and 180 min. of leaching time at 120º C. However, 6M HCl acid, ilmenite paste/ HCl acid ratio of 1:6 and 120 min. of leaching time at 80º C were the best conditions for leaching of ilmenite paste.

After leaching factors were studied on ilmenite paste, the mixture was filtered then divided into two parts; first part (filterate) and second part (residue formation Ti cake). The product shows that 95.55 % TiO_2 when using 6 M HCl and 92.19% TiO_2 present when using 10 M H_2SO_4. These steps were used for upgrading of TiO_2.

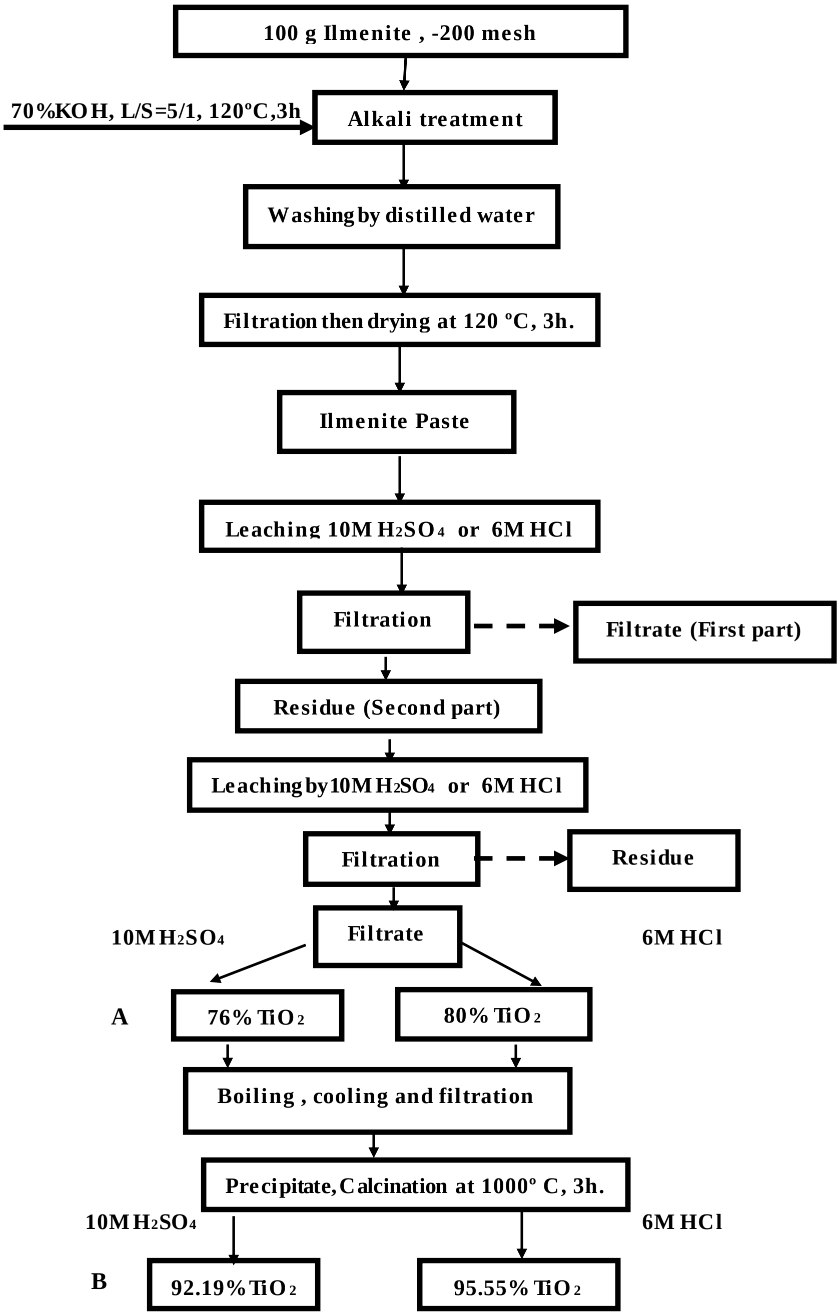


Fig. (9): Flow sheet summarizes upgrading of TiO_2 from ilmenite sample separated from black sands of Rosetta area leached by 10M H_2SO_4 or 6M HCl acid.

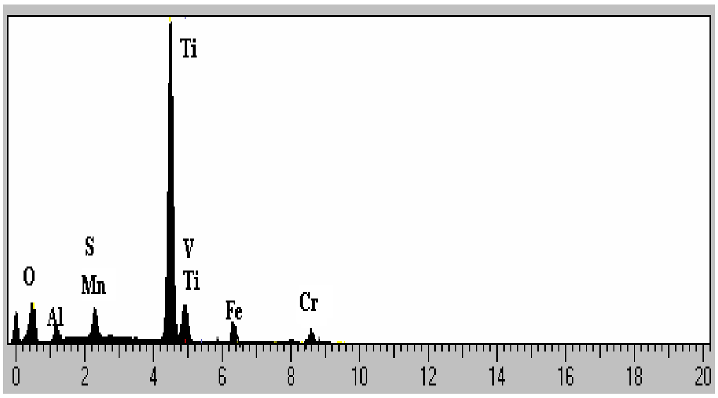


Fig. (10): EDX of titanium product separated from black sands , Rosetta coast, Egypt.

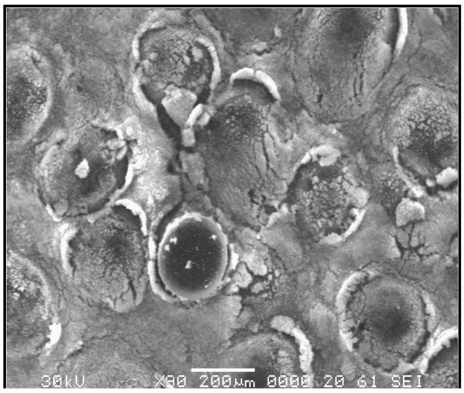


Fig. (11): SEM of titanium product separated from black sands , Rosetta coast, Egypt.

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