



## New Development in Leaching of Ilmenite Ore and Titania Slag Mixture Using Sulfate Process

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### ABSTRACT

Egyptian ilmenite ore and titania slag mixture was characterized and technologically evaluated for the production of titanium dioxide by sulfuric acid process. The optimum conditions of this process were determined. About 94% of TiO<sub>2</sub> in the mixture was converted into titanyl sulfate in the leaching stage at 140 °C using 9.2 M H<sub>2</sub>SO<sub>4</sub>, solid/ liquid ratio 1:5 for 4 hours retention time and the ore grain size was 325 mesh.

### Introduction

Titanium dioxide is an important intermediate gradient in the manufacture of paints, pigments, welding rode coating, ceramics, papers, painting inks,.... etc. and other related industries which is widely used in cosmetics and food products because of its high index of refraction and non-toxic nature <sup>[1]</sup> and <sup>[2]</sup>. It is also used because of its photocatalytic activity <sup>[3]</sup>. The main titanium bearing of technical importance are rutile and ilmenite. As the reserves of rutile are rather limited, special attention has been paid to ilmenite deposits which occur extensively in various parts of the world. The titanium dioxide industry accounts for nearly 95% by weight of the world consumption of titanium bearing minerals, whilst the balance is used in making titanium metal, non titanium base alloys, carbides, fiber glass and chemicals.

In Egypt, abundance reserves of naturally accruing ilmenite ores are available and located at two main deposits. The first deposits estimated to be about 50 million tons are present at Abu Ghalaga mines of EL-Nasr phosphate company eastern desert. The second ilmenite ore occurs as an essential constituent of beach places, called black sands, which accumulate and become enriched along the shores of the Nile delta, particularly at Rosetta and Damietta.

White titanium dioxide pigment has been produced by two main processes; namely the sulfate and the chloride processes. Each of these two routes requires a different feedstock. In the sulfate process, the feedstock includes a finely ground ilmenite concentrate of minimum 44% TiO<sub>2</sub> or a sulfatable titanium slag of 78% TiO<sub>2</sub>.

Pyrometallurgical production of these feedstocks includes mainly ilmenite smelting and roasting. Smelting produces a high titanium slag and a low manganese iron by-product and this is mainly conducted in South Africa, Canada and Norway. On the other hand, ilmenite roasting to synthetic rutile (91–95% TiO<sub>2</sub>) involves two main variants; namely, the Becher Process (used in Australia) in which an ilmenite grade of 57–63% TiO<sub>2</sub> is reduced with coal and metallic iron is rusted away <sup>[4]</sup> and the Benelite Process <sup>[5]</sup> used in USA, India and Malaysia in which an acid leaching step follows the roasting process. Both can treat a wide range of ilmenite (50–63% TiO<sub>2</sub>).

In the chloride process, rutile (TiO<sub>2</sub>) is utilized as a raw material. However, shortage of natural rutile has encouraged research efforts to convert ilmenite into high titanium slag or synthetic rutile.

To realize this objective, several processes have been developed that depend upon pyrometallurgical and/or hydrometallurgical treatment of ilmenite deposits to eliminate most of the iron content and other possible impurities <sup>[6-11]</sup>. These processes include the partial reduction of iron at high temperature to Fe(II) state which is more amenable to acid leaching or its peroxidation followed by partial reduction to Fe(II) or else to metallic iron. Alternatively, ilmenite ore can be smelted in the presence of a carbonaceous reducing agent in an electric furnace where two saleable products are obtained; namely high quality pig iron and a titania rich slag containing typically 80-85% TiO<sub>2</sub>, <sup>[12]</sup>. In such a treatment, the composition of the titania slag product is chemically and mineralogical different from ilmenite.

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According to <sup>[10]</sup> titanium is present in ilmenite as Ti(IV) and about 20% of iron is present as Fe(III) and the rest as Fe(II). However, titanium in the titania slag occurs as Ti(III) and Ti(IV) and most of the associated iron is present as Fe(II). While Ti and Fe atoms in ilmenite are arranged in the form of hexagonal crystals.

Due to these differences and the complex nature of titania slag, the above processes developed for beneficiating ilmenite concentrates are not applicable in some cases for titania slag. Other processes have thus been developed for its beneficiation including chlorination or fluxing of the associated impurities, sulfatisation and oxidation-reduction roasting or else salt roasting. The first process of chlorination has been suggested by <sup>[13-16]</sup> for treating of titania slag containing at least an alkaline earth impurity. In this procedure, the slag is treated with HCl gas at high temperature in the absence of oxygen to prevent oxidation of Ti(III). Iron and alkaline earth chlorides are formed and subsequently water or HCl acid leached. Alternatively, <sup>[17]</sup> have proposed upgrading the slag through heating in presence of a glass forming fluxing agent, such as P<sub>2</sub>O<sub>5</sub> or the oxides of Na, K or Si, which results in the formation of a crystalline rutile phase and a glassy phase containing most of the impurities which would be removed by treatment with a mineral acid. In titania slag sulfatisation, <sup>[18]</sup> propose mixing of the slag with an alkaline salt e.g Na<sub>2</sub>CO<sub>3</sub> before reaction with either SO<sub>3</sub> or with mixtures of SO<sub>2</sub> and O<sub>2</sub> at 700°C to 1100°C. Alternatively, sulfidisation in presence of a mixture of H<sub>2</sub>S + N<sub>2</sub> and S<sub>2</sub>+C at 1100°C was proposed by <sup>[19]</sup>, followed by water or HCl acid leaching of the iron sulfides at room temperature.

Both **Van Dyk, et al.** <sup>[10]</sup> and **Borowiec, et al.** <sup>[20]</sup> have indicated that slag can be directly upgraded by oxidation reduction thermal treatment before acid leaching. **Borowiec, et al.** <sup>[20]</sup> described a process that is now commercially employed for upgrading Sorel slag (78.3-84.84 TiO<sub>2</sub>%). It involves thermal treatment where oxidation is accomplished at temperature (1000°C-1050°C) for 1-1.5 h, and the succeeding reduction step is performed at 800°C for 1 h using smelter gas. In the oxidation step, Fe(II) and Ti(III) are converted to Fe(III) and Ti(IV) which help in decomposing the glassy phase. In the subsequent reduction step Fe(III) is reduced back to Fe(II) and a MgO rich ilmenite-geikielite solid solution is formed which is more amenable to leaching than the original phases. However, proper pre-treatment of the slag is required involving fine sizing of the titania to allow iron reactions at the exposed surfaces during oxidation and reduction. The treated slag is then leached at 145-155°C in a two stages procedure using 20% HCl for 6 h or in one stage procedure for 8 h under pressure. The assay of the beneficiated slag after washing and calcinations attains 95% TiO<sub>2</sub>.

In the present work, the target was to realize the dissolution of the Rosetta beach ilmenite concentrate and Titania rich slag as reductant in dilute sulfuric acid

to prevent the hardness of the pulp in the reactor and enhance the extraction and determine the optimum conditions at which maximum dissolution of titanium would be obtained. The aim was to dissolve titanium as a pre-requisite for its separation by hydrolysis to obtain titanium dioxide. For this purpose, several series of dissolution experiments were performed in which the slag/ilmenite ratio, acid concentration and solid/liquid ratio were varied. The effects of temperature and reaction time have also been studied.

## Materials and Methods

### Characteristics of Rosetta ilmenite concentrate and titania slag

The sample obtained from Rosetta beach ilmenite concentrate was kindly provided by the Black Sands project of the Nuclear Materials Authority (NMA). The sample was separated from the tabling of bulk Rosetta black sand concentrate as a moderately magnetic fraction using a cross-belt magnetic separator (model Dinges 3EBK). Three fractions were obtained, namely, a highly magnetic fraction (mainly magnetite), a moderately magnetic fraction (mainly ilmenite), and a non-magnetic fraction (garnet, colored silicates, rutile, monazite and zircon mineral grains). Mineralogically, the obtained ilmenite concentrate is moderately contaminated with trace amounts of magnetic zircon, rutile or leucosene, chromite and chrome-spinel. This sample has been chemically analyzed in the present work for both the major and minor oxides as shown in (Table 1).

**Table 1:** Chemical compositions of East Rosetta ilmenite concentrate

Oxides	Wt.%
TiO <sub>2</sub>	43.95
FeO	27.90
Fe <sub>2</sub> O <sub>3</sub>	22.01
MnO	1.17
V <sub>2</sub> O <sub>5</sub>	0.175
Cr <sub>2</sub> O <sub>3</sub>	0.27
MgO	0.70
Al <sub>2</sub> O <sub>3</sub>	1.00
CaO	0.51
SiO <sub>2</sub>	0.74
P <sub>2</sub> O <sub>5</sub>	0.28

A titania slag sample was prepared from Rosetta ilmenite by its carbothermal reduction in an electric arc furnace and was kindly provided from the Nuclear Materials Authority (NMA) titanium project. The obtained titania slag blocks were crushed and sized and a representative sample of about 50 kg was obtained. A sample ground to -325 mesh was then subjected to chemicals and atomic absorption spectroscopic analysis as shown in (Table 2).

**Table 2:** Chemical compositions of the titania slag

Oxides	Wt.%
TiO <sub>2</sub>	71.94
Fe <sup>t</sup>	12.59
MnO	1.58
V <sub>2</sub> O <sub>5</sub>	0.56
Cr <sub>2</sub> O <sub>3</sub>	0.41
MgO	0.59
Al <sub>2</sub> O <sub>3</sub>	1.90
CaO	0.79
SiO <sub>2</sub>	8.91
P <sub>2</sub> O <sub>5</sub>	0.06

## Methods

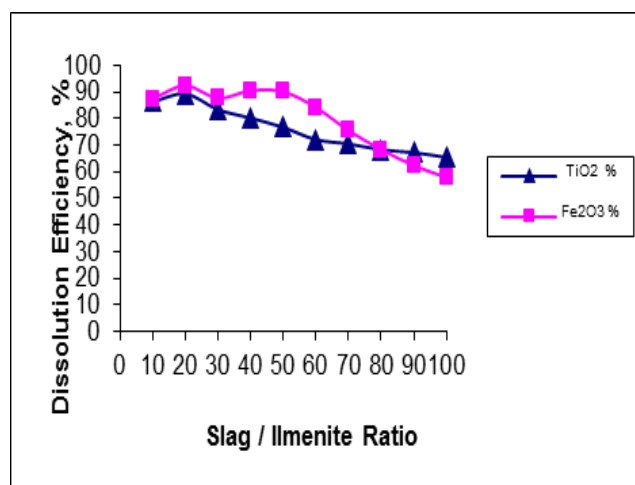
The dissolution experiments were performed in 500 ml conical flasks fitted with a reflux condenser. After adding the required amounts of the ilmenite concentrate and slag sample and sulfuric acid solution, the obtained slurry was agitated at various temperatures at 350 rpm. At the end of each dissolution experiment, the slurry was filtered, washed with distilled water and the filtrate was analyzed for iron and titanium to calculate their dissolution efficiencies. The ilmenite concentrate and slag were analyzed by firstly fusion with potassium pyro-sulfate. Titanium and total iron analyses of feed, products and filtrates were determined using colorimetric and titrimetric analytical methods respectively. Total iron was titrimetrically determined against EDTA using sulfosalicylic acid while the ferrous content was analyzed titrimetrically against standard potassium dichromate. The spectrophotometric determination of titanium content was performed at 430 nm using tiron as complexing agent (Unicam UV2-100). Both calcium and magnesium were titrimetrically determined against EDTA using murexide and Eriochrome Black T indicators. The molybdate reagent in the presence of tartaric acid has been used for determination of the silica content. Analysis of the trace elements present (Cr, V and Mn) was performed by means of an atomic absorption (Unicam 969 Model) at 357.9, 318.4 and 279.5 nm, respectively.

## Results and discussion

### Effect of slag/ilmenite ratio

To study the effect of slag/ilmenite ratio several dissolution experiments were performed using slag percent varying from 10% to 100%. The other dissolution parameters were fixed at acid concentration 10M; S/L ratio=1/4; temperature 140°C; 3 h reaction time and ilmenite grain size-325 mesh. The obtained results are plotted in **Fig. 1**. The results indicate that the dissolution of titanium is dependent on the increase in the slag percent up to 20% which suitable to make reduction for ilmenite and the excess of slag percent will decrease titanium dissolution due to the large amount of

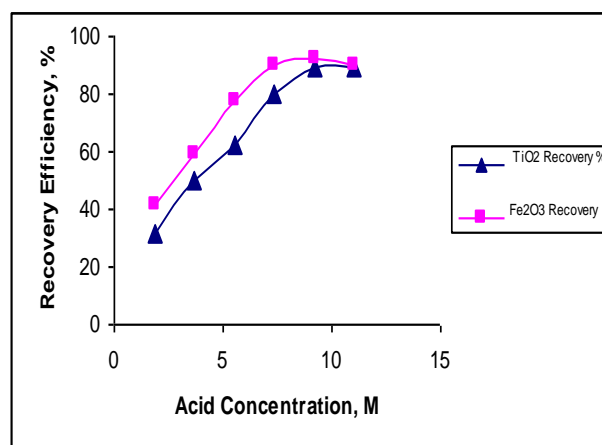
slag that needs hard conditions as high concentrated acid and high temperature.



**Fig 1:** Effect of slag/ilmenite ratio on titanium and iron dissolution from ilmenite and slag mixing (10 M H<sub>2</sub>SO<sub>4</sub>, 3 h, S/L 1/4, 140°C).

### Effect of acid concentration

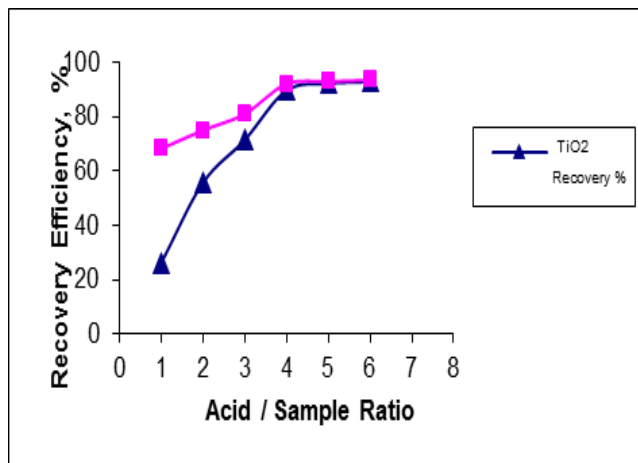
In the present work, several dissolution experiments were performed using sulfuric acid concentrations varying from 1.84 M to 11.03 M. The other dissolution parameters were fixed at slag 20%; S/L ratio=1/4; temperature 140°C; 3 h reaction time and ilmenite grain size-325 mesh. The obtained results are plotted in **Fig. 2**. From the obtained results, it is clearly evident that the dissolution efficiency of TiO<sub>2</sub> and total iron is strongly dependent on the acid concentration. In 9.2 M H<sub>2</sub>SO<sub>4</sub> about 89% of titanium and 92% of iron are dissolved. It is found that increasing the sulfuric acid concentration leads to decreasing the recovery extent of TiO<sub>2</sub> and total Fe; this may be explained by the fact that high concentration of sulfuric acid enhances its oxidizing effect which forms a passive layer of Fe<sub>3</sub>O<sub>4</sub> which prevents deeper acid attack. This oxidizing effect is more pronounced due to the smaller particle size.



**Fig 2:** Effect of acid concentration on titanium and iron dissolution from ilmenite and slag mixing (slag 20%, 140°C, 3 h, S/L ratio 1/4).

### Effect of liquid/Solid ratio

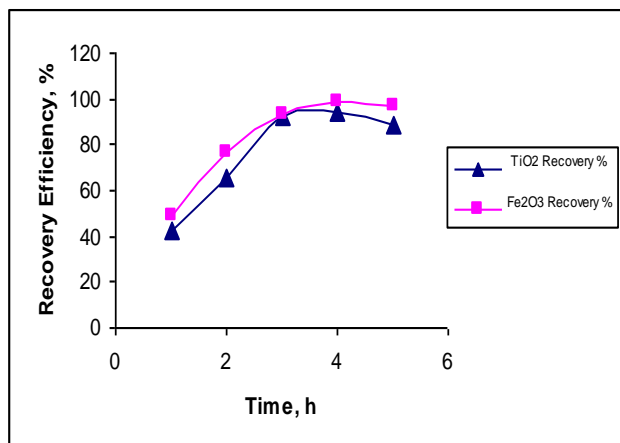
Working with 9.2 M  $H_2SO_4$ , the effect of pulp density was studied in the range of solid to liquid ratio of 1/1 to 1/6. The obtained results are plotted in **Fig. 3**. In the curve the recovery percent of  $TiO_2$  and total iron Fe increase with increasing the amount of sulfuric acid until reach 1:5 sample / acid ratio. Any further increase of sulfuric acid has no significant effect on increasing  $TiO_2$  and total Fe recovery extents.



**Fig 3:** Effect of pulp density on the dissolution of titanium and iron dissolution from ilmenite and slag mixing (slag 20%, 140°C, 3 h, 9.2 M  $H_2SO_4$ ).

### Effect of time

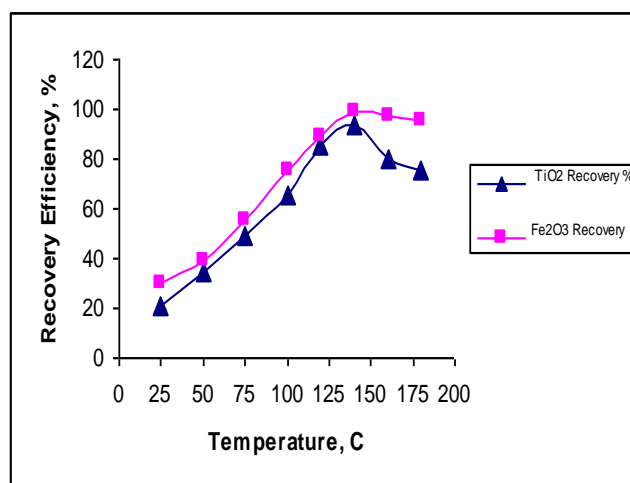
To study the effect of time upon ilmenite and slag dissolution, four experiments were performed at different time periods ranging from 1 to 5 h using -325 mesh size ore. The results in **Fig. 4** show that at 1 to 4 h, the dissolution efficiency of titanium increased from about 42.1 to about 94% while that of iron has increased from about 48.6 to about 98.9%. Extending the leaching time from 4 to 5 h however, has a slight adverse effect upon the dissolution of titanium and total iron due to hydrolysis effects. Therefore, 4 h would represent an optimum time for maximizing the leaching of both titanium and total iron.



**Fig 4:** Rate of dissolution of titanium and iron from ilmenite and slag mixing (slag 20%, 140 °C, 9.2 M  $H_2SO_4$ , S/L ratio 1/5).

### Effect of temperature

In the present work, several dissolution experiments were performed at temperatures ranging from room temperature to 180°C under optimum leaching conditions. The results in **Fig. 5** show that the extent of titanium and iron dissolution increases significantly with temperature. At room temperature, only 20.83% titanium and 29.75% total iron dissolve, respectively. The low titanium dissolution at room temperature is due to the low reactivity of ilmenite and slag. At 140 °C, about 94% titanium dissolves but increasing the temperature to 180 °C, seriously decreases affects titanium and total iron recovery, this due to the hydrolysis of titanyl sulfate  $TiOSO_4$  to give hydrated titanium dioxide  $TiO(OH)_2$  and give white precipitate. Therefore, temperature plays an important role in the hydrolysis of dissolved  $TiOSO_4$  and 140 °C would be considered as the optimum temperature for dissolution of about 94% of titanium and 98.9% of total iron.



**Fig 5:** Effect of temperature on titanium and iron dissolution from ilmenite and slag mixing (slag 20%, 140 °C, 9.2 M  $H_2SO_4$ , 4h, S/L ratio 1/5).

### Conclusions

To resolve the problem that the increasing of the pulp density in the leaching of titanium using concentrated sulfuric acid we can use titania slag as a reductive agent with ratio 20% which give high recovery for titanium dioxide 94% under optimum conditions 9.2 M sulfuric acid at a solid/liquid ratio of 1/5 at 140°C for 4 h and using an ore ground to -325 mesh size. By using these optimum conditions for leaching ilmenite only gives low titanium recovery 76.0% and iron 40.5%. On the other hand for leaching titania slag only with the same optimum conditions gives titanium recovery 69.7% and iron 59.7%.

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