

## **Preparation of titanium dioxide anatase pigment from Rosetta ilmenite concentrate via the sulfate route**

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### **ABSTRACT**

The sulfate route for the processing of Rosetta ilmenite concentrate for the preparation of pigment grade titanium dioxide is studied. The working concentrate is assaying 39.89%  $\text{TiO}_2$  while the FeO and  $\text{Fe}_2\text{O}_3$  assay 31.51 and 24.65% respectively. After optimizing the digestion factors, the obtained sulfate liquor was subjected to reduction followed by crystallization of copperas ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ). To this point, the process is in the black stage. The solution of the remaining titanium sulfate is then subjected to hydrolysis and the resultant solids are subjected to bleaching followed by calcinations to produce a product in which the  $\text{TiO}_2$  percent exceeds 98%. The obtained XRD pattern of the latter has shown its anatase structure. © 2015 Trade Science Inc. - INDIA

### **INTRODUCTION**

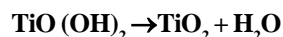
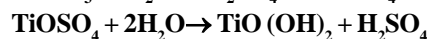
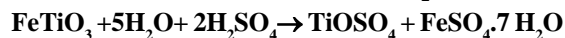
Titanium is relatively abundant in the earth's crust where its assay amounts to 0.44%. Its minerals are usually found in igneous and metamorphic rocks and are mainly represented by ilmenite ( $\text{FeO} \cdot \text{TiO}_2$ ), rutile ( $\text{TiO}_2$ ) and titanomagnetite ( $\text{Fe}_2\text{TiO}_4 \cdot \text{Fe}_2\text{O}_4$ ). Other minerals include anatase ( $\text{TiO}_2$ ) which is formed on joint planes and in veins in schists and gneisses as well as leucosene which is a weathered form of ilmenite and assays up to 85%  $\text{TiO}_2$ . Ilmenite supplies about 91% of the world's demand for titanium minerals and the world's ilmenite production reached 5.19 million metric tons in 2009<sup>[1,2]</sup>. World titanium sponge metal production reached 166,000 metric tons in 2008 (Gambogi, 2010). Titanium minerals are not only found in hard rock but also in beach sands, and their world reserves are attaining about 1300 million tons. Due to the highly extensive consumption of rutile, there is no doubt that ilmenite as the most important titanium resource will continue to dominate the titanium industry in the future. A survey on the use of titanium in its various forms indicates that almost 95% of its use is for the production of white col-

ored  $\text{TiO}_2$  pigment which has extensive application in paints, plastic, paper and rubber besides printing inks, cosmetics, soap and pharmaceutical industries.

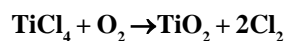
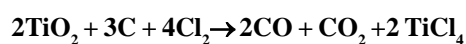
Two main processes are used to manufacture pigment grade  $\text{TiO}_2$  and titanium metal; namely the sulphate process and the chloride process. The two processes differ in both their chemistry and raw materials requirements<sup>[3]</sup>. Because the chloride process has some advantages over the traditional sulphate process in both cost and waste management, however, in the sulphate process low-grade titanium raw materials are acceptable. According to Harben (2002), the two routes can be summarized as follows. Thus, the sulfate route, fine grained ilmenite concentrate (minimum 44%  $\text{TiO}_2$ ) or sulfatable titanium slag (78%  $\text{TiO}_2$ ) is digested in sulfuric acid at 150-180 °C and the digested cake is dissolved in cold water followed by filtering the residual ferrous sulfate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ). The titanium sulfate in the filtrate is then heated with steam at 95-110 °C in the presence of  $\text{TiO}_2$  seed crystals to yield sulfuric acid (waste/regenerated acid) together with 93-96%  $\text{TiO}_2$  as an intermediate product. The latter is then washed, treated and calcined at 800-1000 °C to produce ana-

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tase or rutile titanium dioxide ( $\text{TiO}_2$ ).



On the other hand, in the chloride route, natural rutile (94 – 98%  $\text{TiO}_2$ ) or synthetic rutile (92-95%  $\text{TiO}_2$ ), anatase (90-95%  $\text{TiO}_2$ ), leucosene (> 86%  $\text{TiO}_2$ ) chlorinatable titanium slag (80 – 90%  $\text{TiO}_2$ ) together with oil coke and chlorine are treated in fluid bed reactors at 925 - 1000 to give raw  $\text{TiCl}_4$  (tickle) mixed with a reducing agent and distilled. Combustion of the purified tickle with pure oxygen at 985 would result in anatase or rutile titanium dioxide.



As a matter of fact two main grades (crystal phases) of  $\text{TiO}_2$  pigment could be produced; viz rutile or anatase. Rutile has a more closely packed crystal structure making it denser than anatase, with its higher refractive index (2.8 with an optimum particle size in organic binder of 0.19 $\mu\text{m}$ ) and chemical stability (outdoor paints, plastics, printing ink, cosmetics). On the other hand, anatase has a bluer tone (refractive index 2.55 with an optimum particle size in organic binder of 0.24 $\mu\text{m}$ ) and is less abrasive (indoor paints, paper, textiles rubber, soap and pharmaceutical)

Rutile  $\text{TiO}_2$  has a relative scattering power of up to 800 whereas anatase  $\text{TiO}_2$  its 600, both of which compare favorably with zinc sulfide ( $\text{ZnS}$ ) at 360 and barite at 25. As a pigment, titanium dioxide is indeed the premier white pigment with a high R.I. of 2.55 – 2.80 (provide good pacifying strength or hiding power) and reflectivity (generates brightness and whiteness or lightening power); inertness and chemical stability (being essentially insoluble in acids, bases, and other solvents including air pollutants); resistance to UV degradation (color retention); tinting strength; nontoxicity; thermal stability over a wide range of temperature; and a favorable price / effect ratio (paper, paint, plastics, rubber, ceramic, textiles and cosmetics).

According to Harjane and Call (1984), the titanium dioxide is generally prepared commercially by hydrolytic precipitation from solution of titanium sulfate or vapor phase oxidation of titanium tetrachloride. Normally, hydrolysis from sulfate solutions yields the ana-

tase form and hydrolysis from chloride solutions (sulfate-free) yields the rutile form. These normal products can be reversed in either case by special techniques such as e.g. seeding with nuclei of the other form or by addition of chemical additives.

In recent years, hydrometallurgical processes have been developed where direct hydrochloric acid leaching and solvent extraction are used to produce pigment grade  $\text{TiO}_2$  of a purity exceeding 99.5% and titanium metal through conventional fused electrolysis<sup>[6-12]</sup>. Improved sulphate processes have also been developed and become more and more important due to its low energy requirement compared to the conventional thermo and electro chemical processes.

The present work is concerned with the direct preparation of anatase grade  $\text{TiO}_2$  pigment from Rosetta ilmenite concentrate using the sulphate process. In this process, the ore containing titanium is dissolved in sulfuric acid, yielding a solution of titanium, iron and other metal sulfates. Then, through a series of steps including chemical reduction, purification, precipitation, washing and calcination, pigmentary-size intermediate  $\text{TiO}_2$  is produced. The crystal structure, anatase or rutile, is controlled by proper nucleation conditions besides those of calcination. To realize this purpose, the provided Rosetta ilmenite concentrate was first subjected to digestion using concentrated sulphuric acid under different conditions in order to determine their optimum values. Before hydrolyzing the titanyl sulfate solution, proper separation of ferrous sulfate (Copperas) was undertaken.

## EXPERIMENTAL

### Material

A technological sample of Rosetta beach ilmenite concentrate was kindly provided by the Black Sands Project of the Nuclear Materials Authority (NMA). In TABLE 1 the chemical composition of this concentrate is shown<sup>[14]</sup>.

Presence of  $\text{Fe}_2\text{O}_3$  is due to partial oxidation of the  $\text{FeO}$  in the ilmenite mineral the ferric state besides possible solid solution. On the other hand, it is interesting to refer to the presence of 0.42%  $\text{Cr}_2\text{O}_3$  and 0.21% of  $\text{V}_2\text{O}_5$  which might be present as minor chromite and

**TABLE 1 : Chemical composition of the working Rosetta ilmenite concentrate**

Oxides	Wt. %
TiO <sub>2</sub>	39.89
FeO	31.51
Fe <sub>2</sub> O <sub>3</sub>	24.65
MnO	1.35
Al <sub>2</sub> O <sub>3</sub>	0.88
MgO	0.61
CaO	0.12
SiO <sub>2</sub>	0.30
Total	99.31

vanadiferous titanomagnetite respectively.

## Experimental procedures

### (a) Ilmenite digestion

Several dissolution experiments of the provided ilmenite concentrate sample was performed under different conditions in a manner to determine their optimum conditions. Thus the effects of sulfuric acid / ilmenite ratio, digestion temperature and time have been studied. In these experiments the ore size used ranged from (-100 to +150 mesh). After digestion, the leaching ilmenite values were dissolved by water during 1hr followed by adding 35 kg/ton iron powder to reduce the leached ferric iron to the ferrous state. These steps were then followed by filtration and washing for separation of iron, the prepared solution was subjected to evaporation in a manner to crystallize FeSO<sub>4</sub>.7H<sub>2</sub>O by proper cooling down -5C.

### (b) TiO<sub>2</sub> hydrolysis

An aqueous solution of titanyl sulphate after separation of ferrous sulfate and containing the equivalent of 250 grams TiO<sub>2</sub> per liter and an acid to titanium weight ratio of 1.8 was hydrolysed by water addition in proportion of 20 parts water per 100 parts of titanyl sulfate solution at 90 over a period of 15 minutes. The obtained slurry was then maintained at a temperature of 100 for about 3hr where in order to attain complete hydrolysis.

## Analytical procedures

### (a) Ti control analysis

For titanium control analysis, a suitable sample vol-

**TABLE 2 : Effect of sulfuric acid / ilmenite weight ratio upon the efficiency of Rosetta ilmenite breakdown**

H <sub>2</sub> SO <sub>4</sub> /Ilmenite Wt. Ratio	Breakdown efficiency, %
1/1	35
1.5/1	40
2/1	47
2.5/1	55
3/1	57

**TABLE 3 : Effect of digestion temperature upon the efficiency of Rosetta ilmenite breakdown**

Temperature C <sup>0</sup>	Breakdown efficiency, %
150	55
200	85
250	90
300	95

**TABLE 4 : Effect of digestion time upon the efficiency of Rosetta ilmenite breakdown**

Digestion time, hr	Breakdown efficiency, %
1	30
2	62
3	90
4	95
5	98

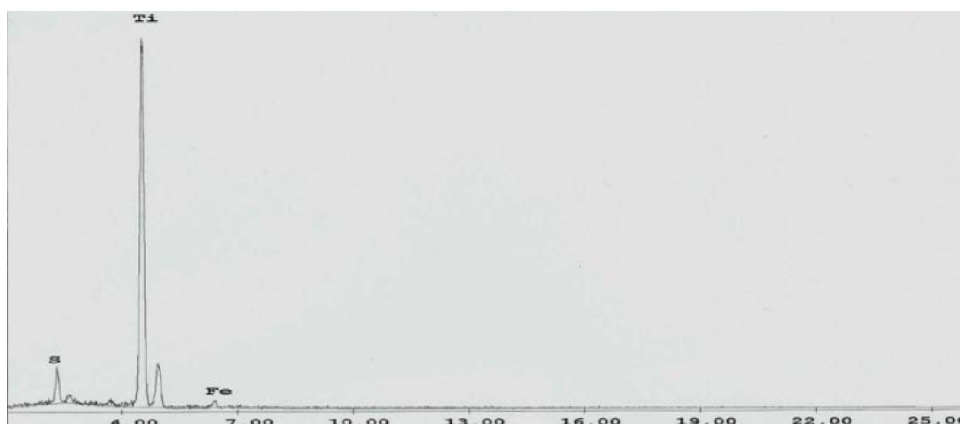
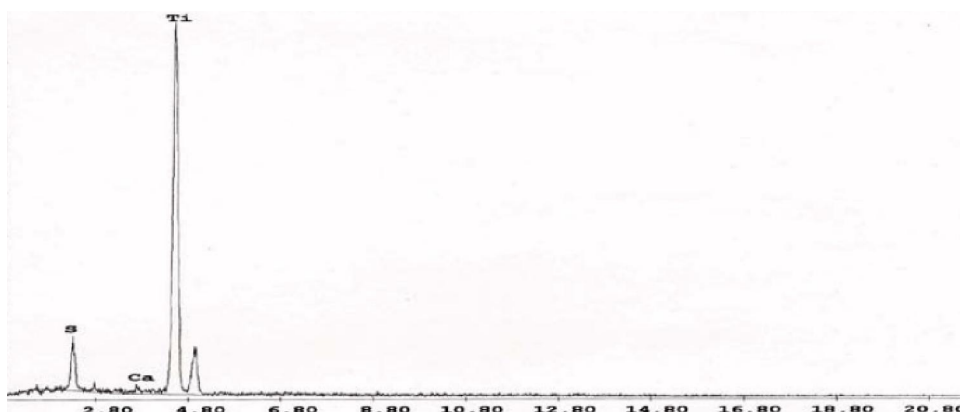
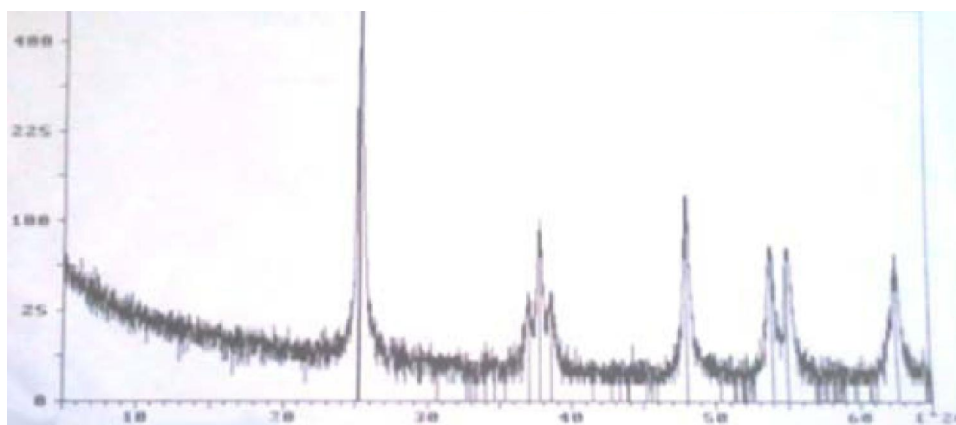
ume, assaying not more than 2µg Ti/ml, was mixed with 5 ml of 2% tiron solution, 5 ml of 0.05 M EDTA solution, 10 ml of the buffer solution (pH 4.5) and 50 mg of sodium dithionite. Each mixture was shaken well, completed up to a suitable volume and measured at  $\lambda_{\max} = 430$  nm within 15 min<sup>[15]</sup>.

### (b) Product analysis

A semi-quantitative of ESEM analysis was used for identifying the purity of the final product. The final product pigment anatase was subjected to X-ray diffraction analysis to determine its pattern and crystal structure. Also for this purpose a Philips PW-3710 with generator PW-1830, Cu target tube and Ni filter at KV and 30 mA. Instrument of the Nuclear Material Authority was used.

## RESULTS AND DISCUSSION

### Optimization of the sulfate route breakdown factors

Figure 1 : Hydrate of  $\text{TiO}_2$  before bleachingFigure 2 : Hydrate of  $\text{TiO}_2$  after bleachingFigure 3 : XRD of  $\text{TiO}_2$  pigment product

### (a) Effect of acid/ilmenite mass ratio

To study the effect of sulfuric acid / ilmenite mass ratio on the breakdown of Rosetta ilmenite concentrate, several experiments were performed using ratios varying from 1:1, to 3:1 ratio at 150 for a curing time of 3hrs. The grain size of the working ilmenite concentrate was fixed in all experiments to range from (-100 to +150 mesh) in closed system. The results for the breakdown

efficiency of ilmenite was determined by  $\text{TiO}_2$  analysis in the obtained solution after its proper dissolution in water and filtration. From these data TABLE 2, it is clearly evident that the dissolution efficiency has ranged from 35 to 57% by increasing the acid / ilmenite ratio from 1/1 to 3/1 respectively. These relatively low efficiencies are most probably due to the relatively low digestion temperature. Therefore, the work was then oriented towards increasing the digestion temperature

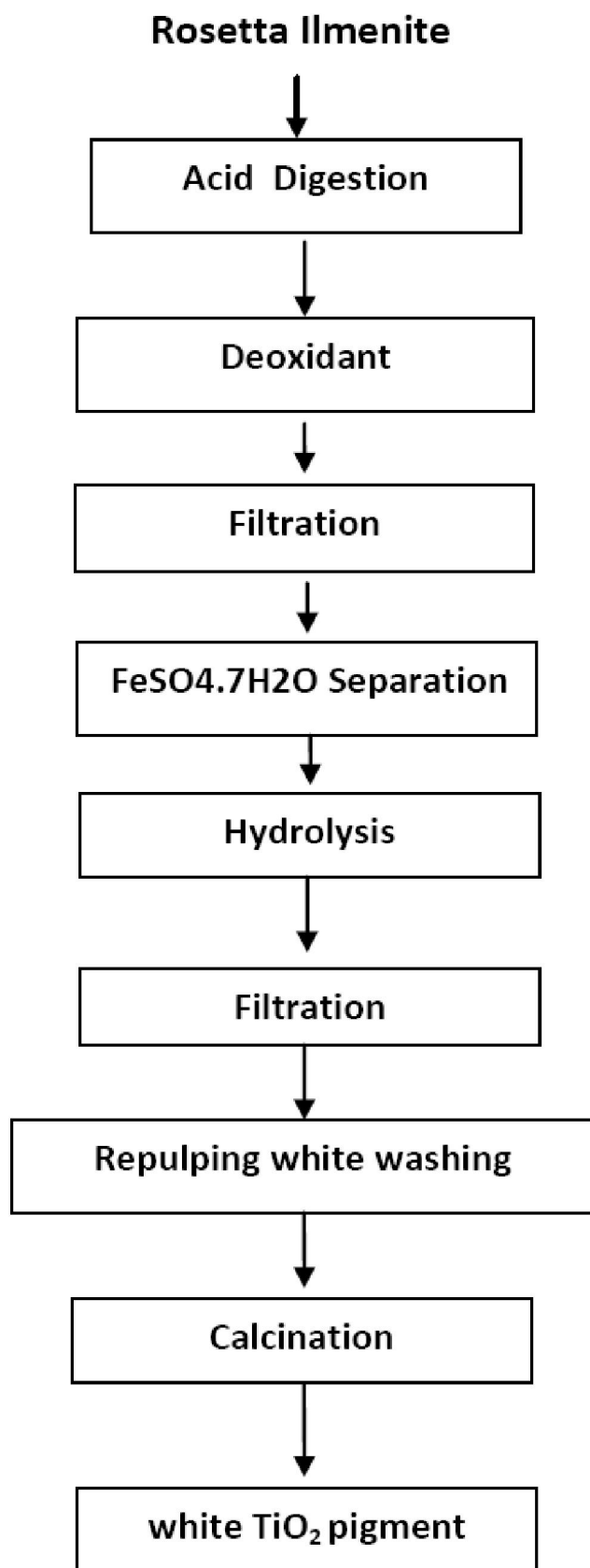


Figure 4 : Flow sheet for treatment of ilmenite by sulfate process to form white titanium anatase pigment

for improving the breakdown efficiency.

### (b) Effect of digestion temperature

Another series of digestion experiments upon Rosetta ilmenite concentrate was performed at various temperature was ranging from 150 to 300 using an acid amount/ ilmenite weight ratio of 2.5/1 for a digestion time 3h. In these experiments, the ore size was fixed in the range from -100 to +150 mesh and the digestion time was fixed at 3hr. The obtained results shown in TABLE 3 were found to range from 55 up to 95% where the digestion temperature was raised from 150 to 300 respectively. However, to avoid excessive energy consumption, 250 was chosen as the optimum digestion temperature which resulted in 90% dissolution efficiency and to investigate the effect of the digestion time.

### (c) Effect of digestion time

A third series of breakdown experiments was performed to investigate the effect of digestion time upon the breakdown efficiency of Rosetta ilmenite concentrate. The applied digestion time was varied from only 1hr. to 5hr. In these experiments, the acid / ilmenite weight ratio was fixed at 2.5 / and the applied digestion temperature was fixed at 250 . The obtained digestion efficiency of  $\text{TiO}_2$  TABLE 4 was found to range from only 30 to 98 % respectively. The results indicated that the magnitude of curing time of ilmenite breakdown in increasing the leaching efficiency of  $\text{TiO}_2$  is quite relevant.

### Characteristic of the $\text{TiO}_2$ product

For preparation of the  $\text{TiO}_2$  product, a 500g sample portion of Rosetta ilmenite concentrate was properly treated as previously mentioned. From the analysis of the reduced prepared solution shown in TABLE 5, it is clear that it assays 140g/l  $\text{TiO}_2$  and 365g/l  $\text{FeSO}_4$

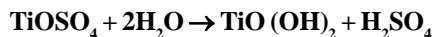
Chemical Composition of the reduced Sulfate Solu-

Constituents	Grams per liter
$\text{TiO}_2$	140
$\text{FeSO}_4$	360
$\text{H}_2\text{SO}_4$	340
$\text{H}_2\text{SO}_4/\text{TiO}_2$	2.42
$\text{FeSO}_4/\text{TiO}_2$	2.57
Specific gravity	1.6

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tion of Rosetta Ilmenite Concentrate

This solution was then subjected to evaporation, ferrous sulfate crystallization. The titanyl sulfate solution left behind was then properly hydrolyzed according to the, following equation:



The precipitated titanium hydroxide was analyzed before and after its bleaching using ESEM technique (Figures 1 and 2). It is found that in (Figure 1) the percent of iron assay 3.64% causes problems in color and quality where the high quality of the titanium pigment must contains not more than 50 ppm of iron so the bleaching technique using Zn powder to eliminate any co-precipitated iron followed by filtration and calcinations of the product to  $\text{TiO}_2$  at 920 for 3hrs. The obtained  $\text{TiO}_2$  pigment product after analysis have an assay exceeding 98% was then subjected to XRD analysis where its anatase structure is confirmed.

### CONCLUSION

The optimum factors of the sulfate route processing of Rosetta ilmenite concentrate was found to involve an acid/ ilmenite weight ratio of 2.5/1 at 250 for 5hr. The obtained titanyl sulfate solution was subjected to ferric reduction followed by concentration through evaporation followed by copperas crystallization by proper. After filtration of the latter, the titanyl sulfate solution was subjected to hydrolysis by water addition in the volumetric ratio of 20 parts / 100 parts at 95 for 3hr. Elimination of the co-hydrolyzed iron was achieved by proper bleaching process using zinc powder. Chemical analysis of the pigment product after calcinations at 925 has resulted in the pigment grade  $\text{TiO}_2$  of an assay exceeding 98%. The crystal structure of the obtained pigment was determined through XRD analysis where its anatase structure has been revealed. A method for producing a high-quality titanium dioxide pigment having the crystal structure of anatase Compared to the thermo-chemical and electro-chemical processes, direct hydrometallurgical leach processes are advantageous in processing abundant ilmenite ores, low energy consumption and produce sufficiently high quality of anatase pigment  $\text{TiO}_2$  products for a wide range of application and major demand the main drawbacks of the conventional sulphate processes are the high consump-

tion of  $\text{H}_2\text{SO}_4$  and the production of large amount of sulphate wastes and high cost for the treatment. This work has developed several improved sulphate processes involving leaching strategies, bleaching step to reduce chromophores into their soluble forms and recycling acid or reusing in treatment of  $\text{CaCO}_3$  to  $\text{CaSO}_4$  in cement industry.

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