

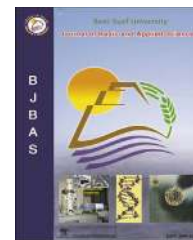
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## Full Length Article

# Synthesis of high purity rutile nanoparticles from medium-grade Egyptian natural ilmenite

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## ABSTRACT

The Egyptian magmatic ilmenite is classified as a medium-grade ore. The present work is an attempt to produce a high-quality TiO<sub>2</sub> that can be used in several industries from this medium-grade raw material using the mechanical activation, carbothermic reduction, hydrochloric acid leaching and calcination. A mixture from the ilmenite (FeTiO<sub>3</sub>) and activated carbon was milled for 30 h. This mixture was annealed at 1200 °C for one hour and the product was leached by hydrochloric acid and calcined at 600 °C for two hours. The role of the ball milling was to grind the raw ilmenite to obtain the nano size, and the carbothermic reduction was to reduce all the Fe-Ti phases to a mixture from Fe metal and TiO<sub>2</sub>. Leaching procedure was carried out to remove all the Fe metal and obtain a high-grade TiO<sub>2</sub>. After leaching and calcination of the milled and annealed mixture of FeTiO<sub>3</sub>/C under the optimal conditions, TiO<sub>2</sub> nanoparticles with a size of 10–100 nm and purity more than 95% were obtained. The qualifications of the synthesized high purity rutile nanoparticles from the Egyptian natural ilmenite match the conditions of many industrial applications.

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## 1. Introduction

The mineral ilmenite (nominally FeTiO<sub>3</sub>) is a huge resource of rutile (TiO<sub>2</sub>), which can be used directly as pigment or for the manufacture of welding-rod coatings, ceramics, papers, and in other areas of chemical industry (Diebold, 2003; Mahmoud et al., 2004). White titanium dioxide pigments have been produced by two processes, namely the sulfate process, and the dry

chlorination process (Mahmoud et al., 2004). In the sulfate process the ilmenite ores are reacted with concentrated sulfuric acid; it is well known and widely applied, but it is lengthy and costly, and the by-product ferrous sulfate is less marketable (Abdel-Aal et al., 2000; Afifi, 1994), while in the chlorination process the ilmenite ores are chlorinated to form titanium tetrachloride, which then re-oxidized to form pigments; it presently enjoys more favorable economics and generates less waste materials (Mackey, 1994). In recent years many researchers' efforts have been

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directed to produce the synthetic rutile ( $\text{TiO}_2$ ) from the natural ilmenite using the chlorination processes (Mahmoud et al., 2004; Tao et al., 2012) due to the shortage in the natural rutile.

There are several processes for the production of synthetic rutile from ilmenite, most of which fall into one of the following categories:

- A. Reduction of the iron content of the ilmenite to the metallic iron followed either by corrosion with oxygen and ammonium chloride (Becher, 1963; Farrow and Ritchie, 1987) or by leaching with sulfuric and hydrochloric acid at elevated temperatures (Natziger and Elger, 1987).
- B. Pre-oxidation and reduction of ilmenite followed by hydrochloric acid leaching, Becher process (Sinha, 1972, 1979).
- C. Processing of the natural ilmenite by roasting and magnetic separation followed by hydrochloric acid leaching, ERMS process (Walpole, 1997).
- D. The reductive leaching for the natural ilmenite using the hydrochloric acid as a leaching reagent and the iron metal as a reductive reagent (Mahmoud et al., 2004).
- E. Reduction of the mechanically activated natural ilmenite to metallic iron followed by acid leaching and calcination (Tao et al., 2012).

The last process which includes mechanical activation followed by acid leaching and calcination is the most favorable for the author as it provides high-quality synthetic rutile nanoparticles that have wide industrial applications. Mechanical activation has a very important role in increasing the efficiency of carbothermic reduction and accelerating dissolution process due to several reasons, such as extension of crystal defects and lattice distortions, decreasing the particle size, and increasing the specific surface area (Chen et al., 1997 and Wei et al., 2009). The reduction is employed to reduce the ilmenite completely or partially into iron metal and  $\text{TiO}_2$ . Acid leaching has an important role in the leaching of the metallic iron from the reduction products; the hydrochloric acid is preferred in leaching as it has some advantages, such as fast leaching, excellent impurity removal and acid regeneration technology (Demopoulos et al., 2008), which can efficiently remove residual iron and other impurities from ilmenite to form synthetic rutile (Mahmoud et al., 2004). Calcination processes have been employed to obtain a highly crystalline product and to remove any carbon impurities from the reduction processes. Only a few works have been carried out on the Egyptian magmatic ilmenite ore to produce the synthetic rutile for the chlorination processes (e.g. Mahmoud et al., 2004). Mechanical activation, carbothermic reduction, hydrochloric acid leaching and calcination methods were applied for the first time on the Egyptian ilmenite ore to obtain high-quality synthetic rutile nanoparticles that can be directly used in industry.

## 2. Methodology

### 2.1. Ore materials characterization

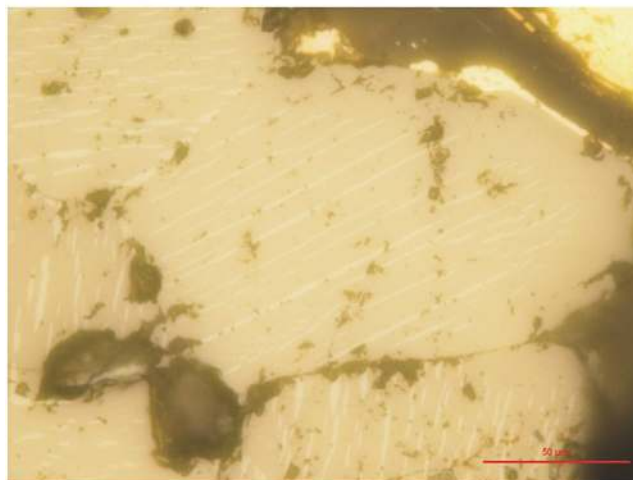
The magmatic Fe-Ti oxides deposits of Egypt are present in the South Eastern Desert. Among these deposits, there are

considerable reserves of ilmenite ore in Abu Ghalaga region. The estimations of the reserves of ilmenite ore in Abu Ghalaga area are variable, ranging from 3 million tons (Holman, 1956), through 10 million tons (Moharram, 1959) to 50 million tons (Mahmoud et al., 2004).

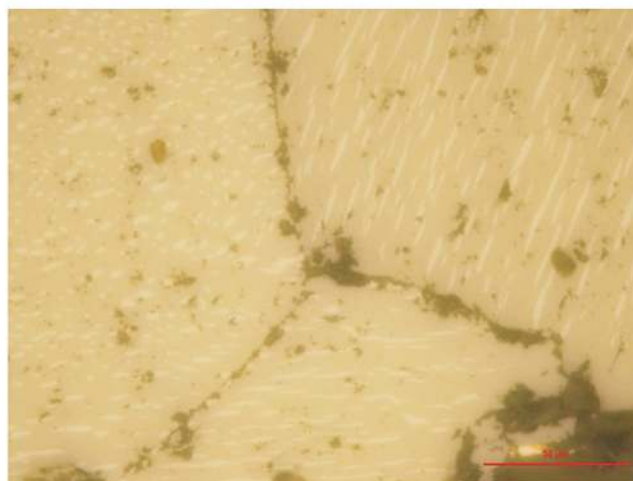
The Abu Ghalaga ilmenite ores can be classified into black (fresh) ore and red (oxidized) ore but our experiments were carried out on the black ore because this ore represents the major reserves in Abu Ghalaga ilmenite open-pit mine.

Phase identification for the ilmenite ore was carried out using the reflected-light microscope and X-ray diffraction. Under the reflected-light microscope, it can be seen that ilmenite grains enclose exsolution bodies of hematite. It also reveals that minute hematite lamellae are segregated within the ilmenite host (Fig. 1a). Small grains of hematite are exsolved and segregated at the borders of ilmenite grains (Fig. 1b). The XRD showed two mineral phases present; these are ilmenite and hematite (Fig. 2). Thus, the ore is mainly formed from ferri-ilmenite together with small quantities of titanohematite.

a



b



**Fig. 1 – Reflected light Microscopic photographs for Abu Ghalaga ilmenite ore showing (a) Minute hematite lamellae segregated within the ilmenite host, and (b) Small grains of hematite are exsolved and segregated at the borders of ilmenite grains.**

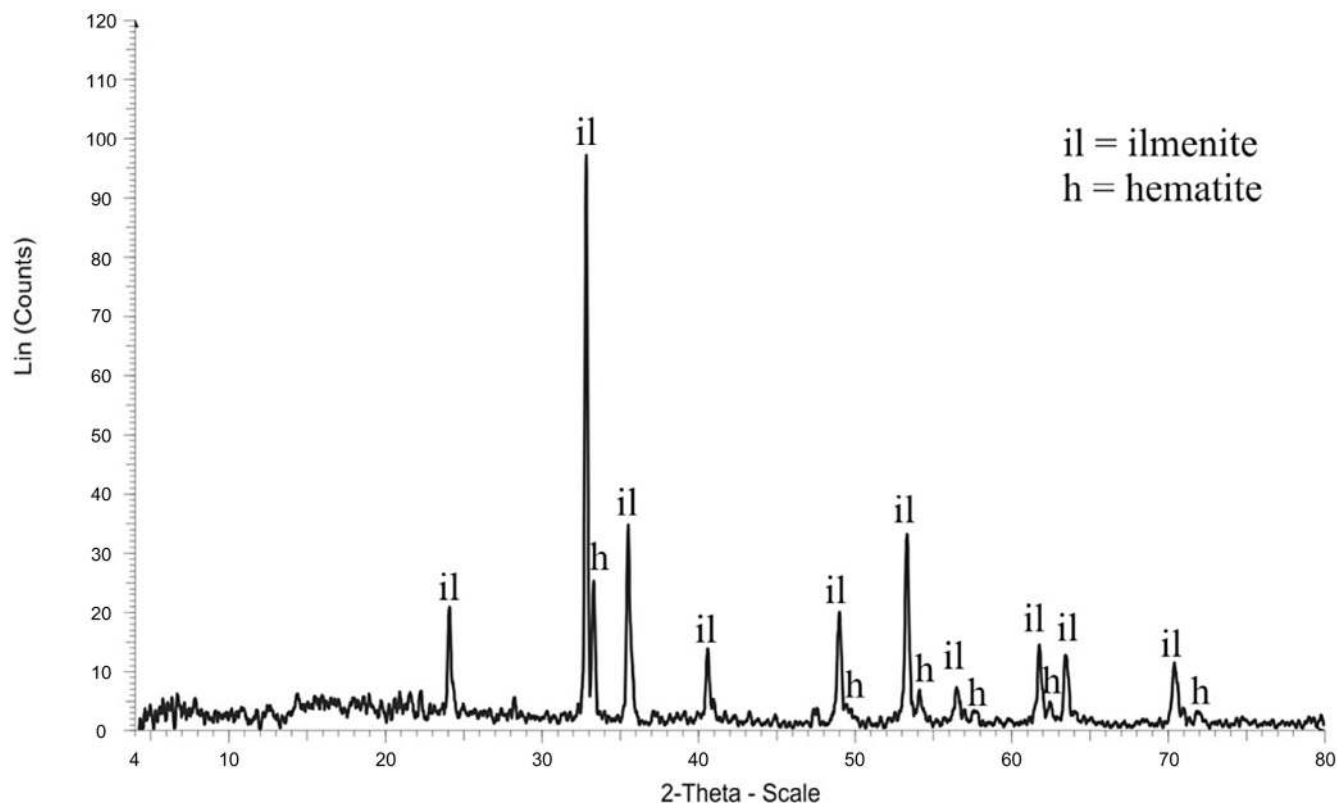


Fig. 2 – XRD pattern for the Abu Ghalaga ilmenite raw material.

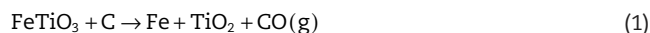
For the geochemical investigations, a weighted representative composite sample from the black ilmenite ore has been prepared by mixing several samples from the stored crushed ore at the Abu Ghalaga ilmenite mine. The geochemical analysis of Abu Ghalaga ilmenite was carried out in Acme Analytical Labs in Canada. The ilmenite ore composite sample was prepared by the code R200-250 that includes crushing of 1 Kg to 80% passing 10 meshes, split 250 g and pulverize to 85% passing 200 meshes. Analyses were carried out with the code 4AB1 that includes the packages 4A02 + 4B02. Group 4A02 includes analyses of 11 major oxides and several minor elements by ICP-Emission Spectrometry (ICP-ES) following a lithium borate fusion and dilutes acid digestion of a 0.2 g sample pulp. This group includes also loss on ignition (LOI) by sintering at 1000 °C and Leco analysis for total carbon and sulfur.

The results of the geochemical analysis for the representative composite sample of ilmenite ore are given in Table 1. This sample contains 40.91% TiO<sub>2</sub> and 51.90% total iron. Consequently, the Abu Ghalaga ilmenite is considered as medium-grade ore since it contains a relatively small amount of titanium. The analyzed composite ore sample also contains 1.97% SiO<sub>2</sub>, 0.05% P<sub>2</sub>O<sub>5</sub>, 0.25% MnO and 3.38% MgO, and relatively high concentration of minor elements such as Cr (Table 1). Most of the

impurities in the investigated ilmenite ore sample are expected to be removed by carbothermic reduction and acid leaching.

## 2.2. Experimental procedures

The experimental work was carried out on a representative ilmenite ore bulk sample ground to a mean particle size of 90 μm. Carbon black powder (190 μm) with a high purity (>99%) was used as the reducing agent. Ilmenite and carbon were mixed at the stoichiometric ratio of 4:1 to provide sufficient carbon for full reduction of ilmenite to TiO<sub>2</sub> and Fe according to the following reaction:



This mixture was milled in a vertical planetary ball mill with an agate cell containing silicon nitride balls of 20 mm diameter. The weight ratio of ball to powder (BPR) of 10:1 and rotational speed of 180 r/min were maintained all throughout. The powder mixture was milled for 30 h.

A portion of the milled sample was reduced at 1200 °C for 1 h. Reduction reaction was performed in an argon atmosphere control tube furnace (Fig. 3) to prevent the sample from

Table 1 – Chemical composition of Abu Ghalaga ilmenite ore.

Oxide	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MnO	Cr <sub>2</sub> O <sub>3</sub>
Wt%	1.97	40.91	1.10	51.90	3.38	0.33	0.07	<0.01	0.05	0.25	0.071

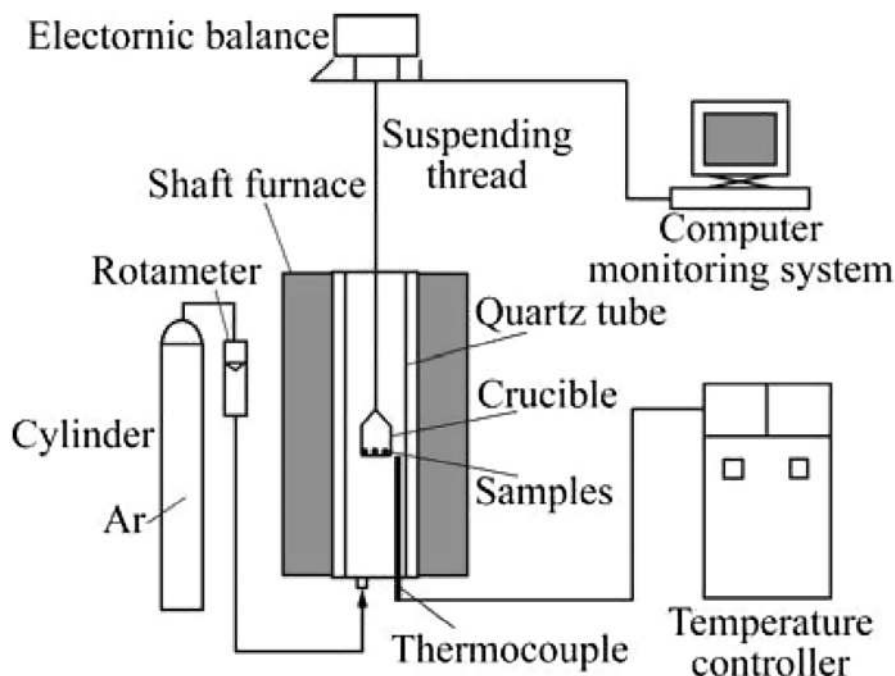


Fig. 3 – Schematic diagram for the reduction system (after Wang et al., 2008).

oxidation and undesired reactions. To decrease the oxygen impurity in argon gas, argon was passed through purification system that contains heated copper turning in a tube furnace at 500 °C and pyrogallol tower, and then dried over blue silica gel to remove moisture.

To leach Fe from the reduced sample, a preheated HCl solution (100 mL, 4 mol/L) and 4 g of reduced sample were added in a 250 mL glass reactor. A magnetic stirring bar with a length of 14 mm was used in leaching processes, and the stirring speed was 800 r/min throughout all the experiments. The leaching experiments were carried out isothermally at 90 °C for 4 h. At the end of the leaching experiments, the sample was filtered and washed, and then the residual solid was calcined at 600 °C for two hours in air to remove residual carbon from the product.

The product of the acid leaching processes was reduced by hydrogen under the same conditions as the carbothermic reduction to reduce any iron titanium compounds still present to obtain high purity rutile. The product of this reduction was leached with HCl using the same previous concentration and ratio for 4 h and calcined at 600 °C for 2 h in air.

### 2.3. Products characterization

The structure and morphology of the synthesized rutile (SR) nanoparticles were characterized by XRD (PW 1170 Phillips). Scanning Electron Microscope Model Jeol 6510 JSM, LA equipped with an energy-dispersive X-ray analyzer (EDX) was used for describing the mineral grain surfaces; the relative element contents of the products were determined with the energy-dispersive X-ray spectrometry (EDS). The SEM unit is housed in the analytical labs of the Faculty of Science, Beni-Suef University.

## 3. Results and discussion

### 3.1. Characterization of the produced rutile nanoparticles

Ilmenite particles are transformed to titanium rich phases with spherical morphology as indicated by SEM image (Fig. 4). The light particles are iron that can be removed by the HCl acid leaching process. The XRD pattern of the SR revealed that rutile is the most common phase in the sample (Fig. 5). The SR contains more than 95 TiO<sub>2</sub>% (Table 2).

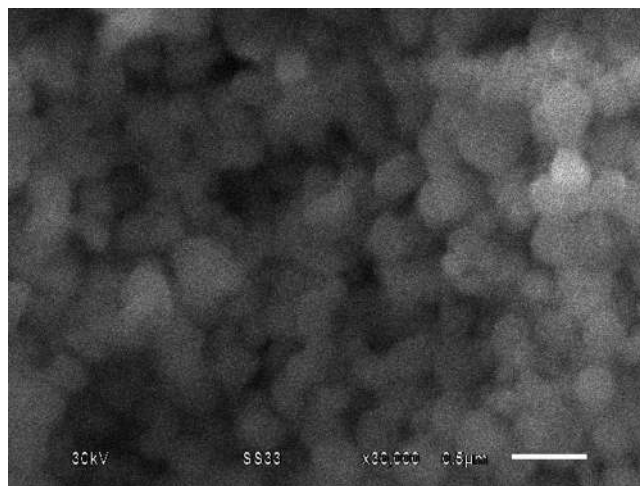


Fig. 4 – SEM image for the produced rutile shows transformation of ilmenite to titanium rich phases with spherical morphology. The light spherical nanoparticles are iron.

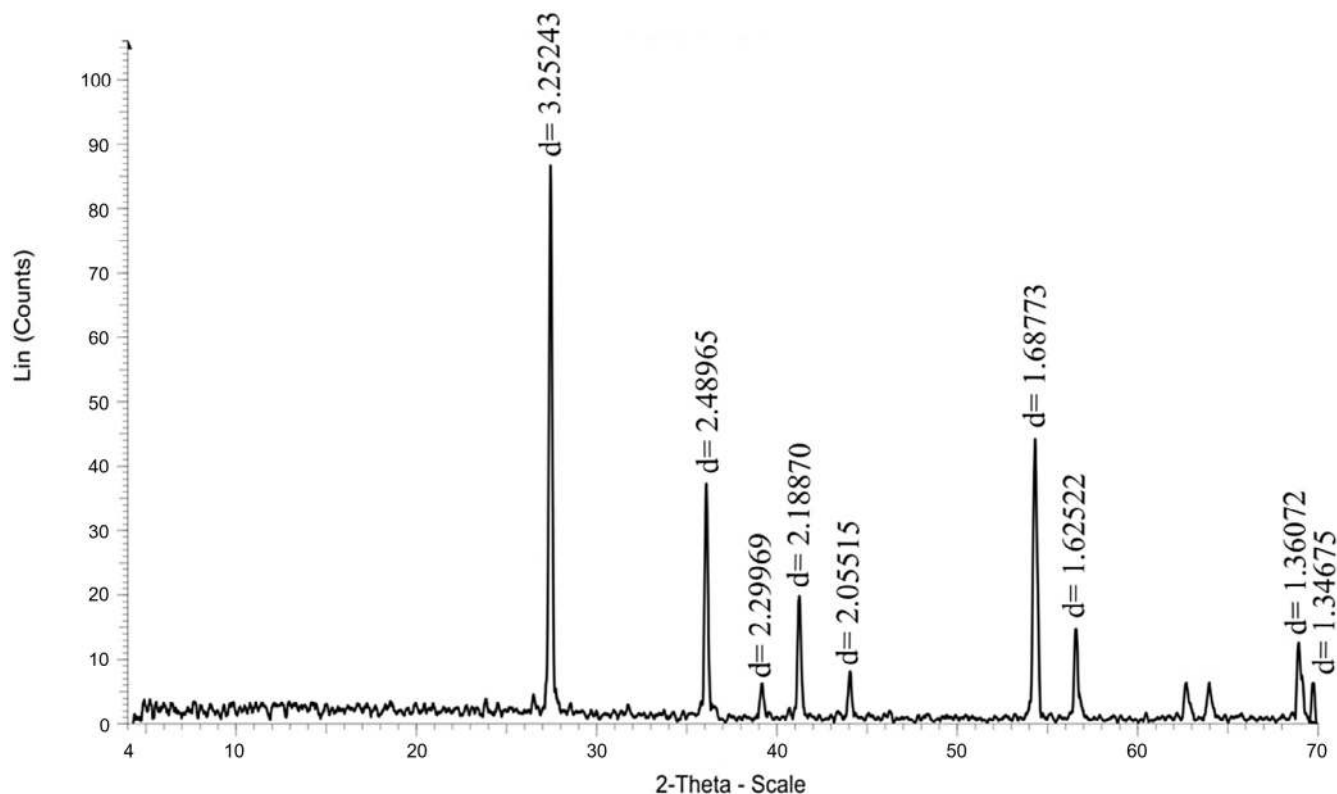


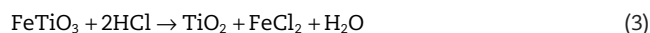
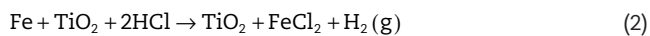
Fig. 5 – XRD pattern for the produced rutile.

The SR impurities are mainly light elements such as Si, Al, and Mg (Table 2). SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and MgO are related to silicate minerals, while some of Al<sub>2</sub>O<sub>3</sub> and MgO are confined to ilmenite lattice.

The XRD pattern (Fig. 5) of the final product shows the presence of the rutile phase with a particle size in the range of 10–100 nm. The diffraction peak of the produced rutile is strong and very sharp, reflecting a high degree of crystallinity. The purity of the rutile (>95%) produced from Abu Ghalaga ilmenite in the present work is higher than that of the rutile (90%) produced from the same ore by other processes (e.g. Mahmoud et al., 2004).

### 3.2. Role of the reduction by hydrogen in the preparation of TiO<sub>2</sub>

The carbothermic reduction products were iron metal and rutile; the other titanium containing phases are unreduced ilmenite and anatase (Fig. 6). Leaching of the products with HCl and calcinations were applied to obtain high purity TiO<sub>2</sub> according to the following reactions:



The XRD pattern for the acid leaching and calcinations products (Fig. 7) shows the presence of rutile and Fe-Ti oxides phases. In order to obtain a high purity rutile that can be used directly in industry, it was necessary to reduce all the remaining Fe-Ti oxides phases to iron metal and TiO<sub>2</sub>, so the reduction by hydrogen was required to reduce all the remaining Fe-Ti oxides phases according to the following reaction:



The reduction by hydrogen products were re-leached with HCl and calcined, and the final product was the high purity rutile.

### 3.3. Qualifications of the produced synthetic rutile for industrial applications

The chemical compositions of ilmenite and the obtained TiO<sub>2</sub> nanoparticles, analyzed by EDS, are shown in Table 2. The synthetic rutile nanoparticles contain 95.92 TiO<sub>2</sub> and only 0.42 iron as Fe<sub>2</sub>O<sub>3</sub>. The coloring metals (MnO and Cr<sub>2</sub>O<sub>3</sub>) are not detected

Table 2 – Chemical composition of studied natural ilmenite and synthesized rutile.

Oxide	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MnO	Cr <sub>2</sub> O <sub>3</sub>
Raw ilmenite	1.97	40.91	1.10	51.91	3.38	0.33	0.07	<0.01	0.05	0.25	0.071
Synthetic rutile	3.2	95.92	0.10	0.42	0.35	–	–	–	–	–	–

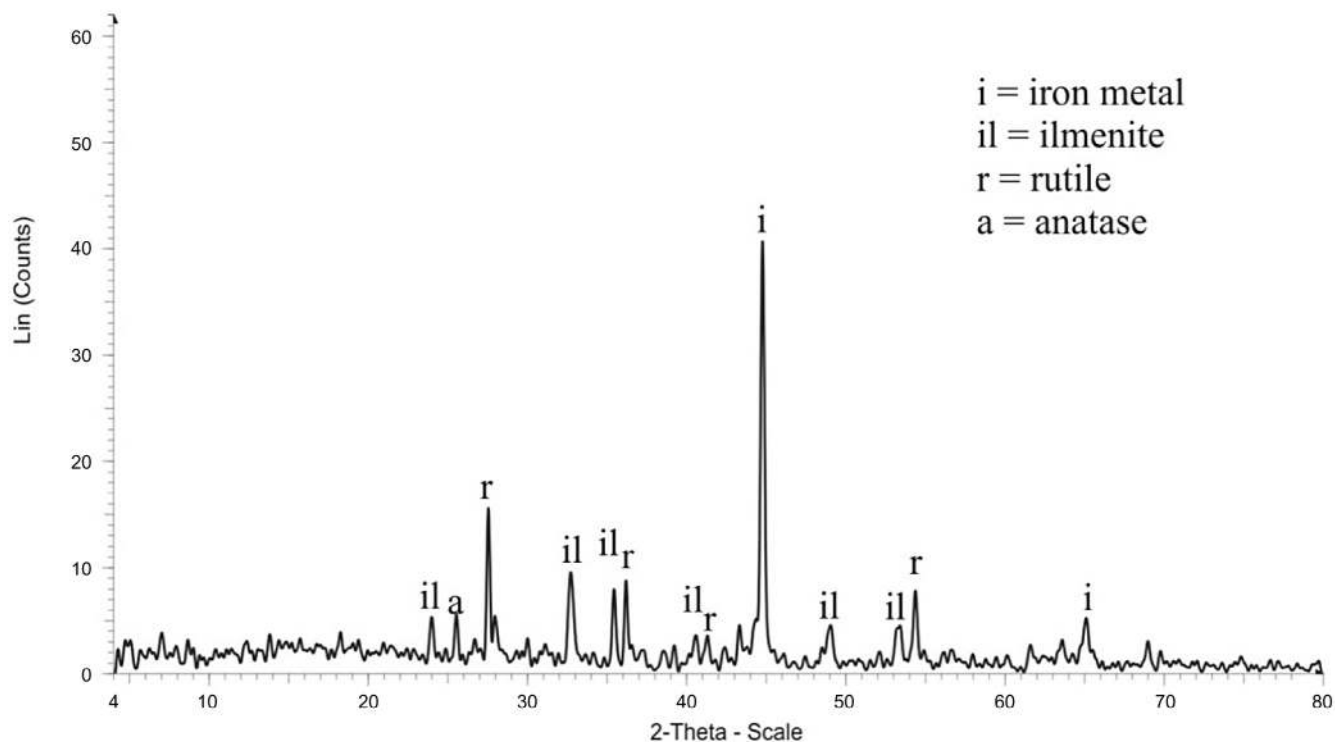


Fig. 6 – XRD pattern for the carbothermic reduction products.

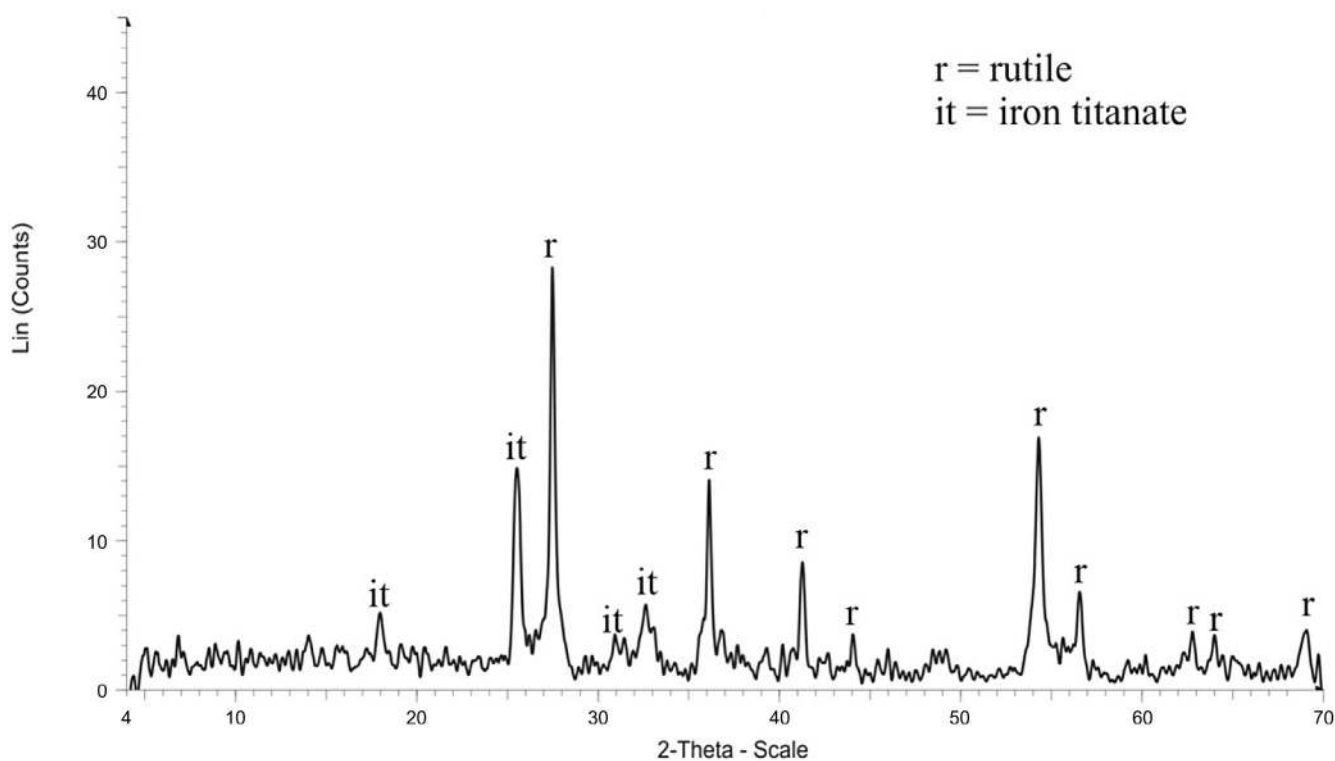


Fig. 7 – XRD pattern for the leaching products after carbothermic reduction for 4 h.

in the produced rutile, rendering it perfectly suitable for production of white pigments by chlorination. The sum of MgO, CaO and Al<sub>2</sub>O<sub>3</sub> (the chlorine consuming components) is about 0.45, which is acceptable for the chlorination process. It is

significant that the acid leaching removes most of the coloring and other deleterious elements from the ilmenite feed, which are subsequently fixed in the waste. The product also contains 3.2% SiO<sub>2</sub>, which can be minimized by further

purification. Silica is not a major problem in the chloride process; it chlorinates but oxidizes to form a white powder.

#### 4. Conclusion

In summary and based on the above results, it can be concluded that a high purity synthetic rutile can be prepared from the medium-grade Abu Ghalaga natural ilmenite by mechanical activation followed by reduction, leaching with HCl and calcination. This combined method produces a higher purity rutile than the other previously used methods.

Carbothermic reduction required high temperatures to reduce all the ilmenite to  $TiO_2$  and Fe metal. Reduction by hydrogen reduced all the remaining Fe-Ti oxides phases into Fe metal and  $TiO_2$ .

The synthesized rutile nanoparticles range in size from 10 to 100 nm and contain about 95.92%  $TiO_2$  and only 0.8% iron as  $Fe_2O_3$  with the absence of coloring metals. Consequently, the qualifications of the rutile synthesized from the Abu Ghalaga ilmenite ore in the present work guarantee its successful usage in production of white pigments and other industrial applications.

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