

Extraction of Ultrafine Titania from Black Sands Broaden on the Mediterranean Sea Coast in Egypt by Molten Alkalies

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Abstract: The work in this article was devoted to investigate the different reaction variables affecting the extraction of titania from ilmenite fraction separated from black sands broaden along the beach of Mediterranean Sea coast, North Egypt, by means of interaction with fused KOH as well as NaOH. The complete extraction of titania was found to be achieved in case of heating one mole of TiO_2 (in ilmenite) with 3 moles of fused KOH at 350°C for 1 h, whereas this achievement could be verified, only, when one mole of titania, (in ilmenite) reacted with 4 moles of fused NaOH at 350°C for 1h. The reaction products were identified in order to suggest the processes which lead to preparation of pure titania and exploitation of produced iron oxide as well as excess reagent in producing commercially useful inorganic compounds. The products in case of reaction with fused KOH namely are, K_2TiO_3 , KFeO_2 , K_3FeO_4 , $\text{K}_3\text{Ti}_8\text{O}_{17}$, Fe_3O_4 , FeTiO_3 , $\text{KAl}_6\text{O}_{9.5}$, TiO_2 , SiO_2 and KAlO_2 , whereas in case of using fused NaOH they are namely, Na_2TiO_3 , NaTiO_2 , Fe_3O_4 , NaFe_2O_3 , Na_5AlO_4 , NaFeO_2 , $\text{Na}_4\text{Ti}_3\text{O}_8$, FeTiO_3 . The reaction processes which governed the formation of these compounds were discussed thoroughly where the chemical equations which clarified these processes were presented. Depending on the results of investigation, a method was proposed for preparation of pure titanium dioxide as well as iron oxide in addition to the desire salt produced from neutralization of excess alkali. The proposed method is promising and economic since the price of chemicals and acids used in preparation of titania comprise not more than 60% of price of titania and resulted byproduct salt (eg. Na_2SO_4).

Key words: black sands, fused NaOH, Fused KOH, Titanium dioxide.

INTRODUCTION

The present article is considered as an extension of the previous one which devoted to extraction of titania from ilmenite fraction separated from black sands using hydrochloric and sulfuric acids (M.F.R. Fouda, *et al*). The results obtained in the previous article clarified that the complete extraction of titania from ilmenite fraction was achieved, only, in case of reaction with excess amounts of attacking acids. The molar ratio between titania and sulfuric acid was found to be amounted to 1:378 at 110°C , whereas it was amounted to 1:208 at 100°C in case of hydrochloric acid. The disadvantage of using the large excess amount of the acids was partially eliminated via conversion of the excess amount of the acid to the corresponding valuable salts which find wide applications in several industrial purposes such as sulfates or chlorides of sodium or potassium.

The present article was devoted to investigation of a different approach other than acid one for extraction of titania from ilmenite. The proposed approach is based on the fact which stated that titanate anions is considered as a hard anion and possesses a high tendency towards hard cation. Although some investigations were carried out on the extraction of titania from ilmenite (Hirano, 1976; Amer, 1997; Kim and Choi, 1982; Liu, *et al* 2006), the characterization of reaction products was not studied in detail as far as known to the author. So that the present investigation focused on the characterization of reaction products and determination of iron and titanium in these products, in order to determine the optimum reaction conditions that lead to the highest percentage of extraction of titania from ilmenite.

MATERIALS AND METHODS

The chemicals used in the present investigation were of analytical grade supplied from Merck company (Darmstadt, Germany).

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Ilmenite Concentrate Fraction:

The ilmenite concentrate separated from Egyptian black sands accumulated at Rosetta beach was obtained from the group of the black sands project in Nuclear Materials Authority (NMA) in Egypt. The quantity of ilmenite fraction (20 Kg) used throughout the investigation was ground to 75 μ m, followed by sampling according the usual manner followed in that respect (A.S.T.M., 1969)

The chemical analysis of the ilmenite fraction separated from Egyptian black sand presented in table 1.

Table 1: Chemical analysis of the ilmenite fraction (separated from black sands in Egypt)

Constitute	Content(Wt %)	Constituent	Content(Wt %)	Constituent	Content(Wt %)
SiO ₂	03.21	TiO ₂	39.57	Al ₂ O ₃	1.35
Fe ₂ O ₃ (tot)	51.66	MnO	01.43	MgO	1.07
CaO	00.45	Na ₂ O	00.25	K ₂ O	0.05
P ₂ O ₅	00.07	SO ₃	00.03	Cr ₂ O ₃	0.53
ZrO ₂	00.15	Cl	00.08	L.O.I	0.20

Techniques and Measurements:**I- X-ray Diffraction Patterns (XRD):**

X-ray diffractograms of ilmenite ore, different reaction products and titania were obtained by means of a chart recording Broker D₈ advance x-ray diffractometer using copper (K α) target with a secondly monochromator. The instrument properly calibrated and adjusted with respect to the x-ray source, as the patterns were run at a scanning rate of 8° in 2 θ /min at 40kv and 40mA.

II- X-ray Fluorescence Spectra (XRF):

The investigated sample was crushed then ground in a Herzog mill to obtain rich fine powder. The last one was mixed with 1.6g of binding wax in a small mill, on a speed rate equal 380 rpm for one minute. The sample was then put in an aluminum cup, after that it was pressed in an automatic pressed machine under 130 KN. The yielded disk specimen was measured by using AXIOS, WD-XRF Sequential Spectrometer (P Analytical, 2005), The Axios is a sequential instrument with a single goniometer based measuring channel, covering the complete measuring range. The instrument is microprocessed and controlled from an external computer, running an analytical software package (Super Q 4).

III- Electronic Absorption Spectra of Solutions:

The electronic absorption spectra of titanium solutions were measured in the matched 1cm fused silica cells with an automatic Shimadzu 240 graph spectrometer.

Reaction Mixtures:

The different reaction mixtures were prepared by mixing, grinding and homogenizing mixtures of ilmenite fraction and sodium- or potassium hydroxide. This process was followed by sieving below 200 mesh (particle size 75 μ m). The molar ratios between titanium dioxide (in ilmenite) and alkali hydroxide amounted to 1:4, 1:8 and 1:16.

RESULTS AND DISCUSSION

In order to define the proper conditions for extraction of titanium from ilmenite using molten sodium and potassium hydroxide, it is favorable to characterize the reaction products before conducting the experiments which aim to prepare a pure titanium dioxide compound.

Characterization of Reaction Products Resulted from Interaction of Ilmenite with Molten Potassium Hydroxide:

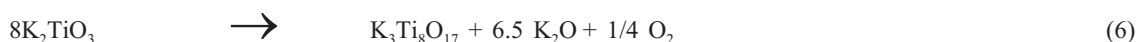
The characterization of products resulted from interaction between ilmenite fraction and molten potassium hydroxide by means of XRD clarified that the reaction products composed essentially of numerous compounds as we can see from Figs. 1 and 2. These compounds namely are: K₂TiO₃, KFeO₂, K₃FeO₄, K₃Ti₈O₁₇, Fe₃O₄, FeTiO₃, Al₆KO_{9,5}, TiO₂, SiO₂, K₃FeO₂ and KAlO₂.

The values of the observed "d" spacing of the previous compounds coincide with those published in JCPDS-ICDD cards having the numbers: 18-1045, 83-2153, 79-1010, 72-1699, 01-1111, 71-1140, 79-1474, 02-1196, 88-2483 and 02-0897.

The different chemical reactions which may be taken place between 350 and 450°C and lead to formation of the previous titanium compound can be represented by the following suggested equations,



The formation of $\text{K}_3\text{Ti}_8\text{O}_{17}$ may be ascribed to the thermal dissociation of K_2TiO_3 by prolonged heating, which leads to volatilization of some portions of alkali from the reaction mixture, hence transformation of the later titanium compound to the polytitanate compound ($\text{K}_3\text{Ti}_8\text{O}_{17}$), according to the following eqn.



The formation of pentavalent iron compound, K_3FeO_4 , may be ascribed to the oxidation of trivalent iron with the peroxide anion formed from fusion of KOH, according to the following eqn.(Goff and Kent Murinans, 1971; Audette, *et al* 1972; Sharples and Flood, 1971)



Factors Affecting the Percentage of Extraction of Titania from Ilmenite Fraction:

The present section is devoted to investigate the process of extraction of titania from the ilmenite fraction by reaction with fused KOH via formation of soluble titanium compounds taking into consideration the variables which affect the values of extraction, (e.g. time and temperature of reaction as well as the molar ratio between reactants).

Effect of Time of Reaction on the Percentage of Extraction of Titania:

By inspection of the results illustrated in Figs. 3-5 one can say, generally, that the value of percentage of extraction of titania from ilmenite by interaction with fused KOH increased gradually by increasing the reaction time until it reached a maximum limit followed by a pronounced decrease in such value of extraction by a further increase in time. This decrease may be due to that the elongation of time of reaction leads to an evaporation of a significant portion of potassium hydroxide from the reaction mixture, hence a decrease in the molar ratio between alkali and titania in ilmenite fraction. Such created reaction condition may lead to formation of a relatively less soluble poly-titanates e.g. $\text{K}_3\text{Ti}_8\text{O}_{17}$, which were formed as a result of thermal instability of K_4TiO_4 and K_2TiO_3 at higher temperatures (eqns.3 and 4). This hypothesis was confirmed by the presence of the $\text{K}_3\text{Ti}_8\text{O}_{17}$ phase (Fig. 1) in the reaction products resulted from the interaction between sand beach ilmenite fraction and molten KOH with a molar ratio equals 1:2 at 350°C for 5 h.

Effect of molar ratio between molten KOH and TiO_2 in beach sand ilmenite on the percentage of extraction of titania:

Generally speaking the values of extraction of titanium from the ilmenite beach sand by reaction with fused KOH was found to be increased by increasing the molar ratio between the reactants(Figs.3-5). This increase may be ascribed to the increase in the extent of formation of relatively high soluble ortho- and metatitanates, i.e. K_4TiO_4 and K_2TiO_3 (Fig. 2). This finding may also indicate that the last two compounds are stable in highly alkaline medium. In that context one can say that the last two compounds have molar ratios between K_2O and TiO_2 higher than that characteristic for less soluble polytitanate compound, $\text{K}_3\text{Ti}_8\text{O}_{17}$.

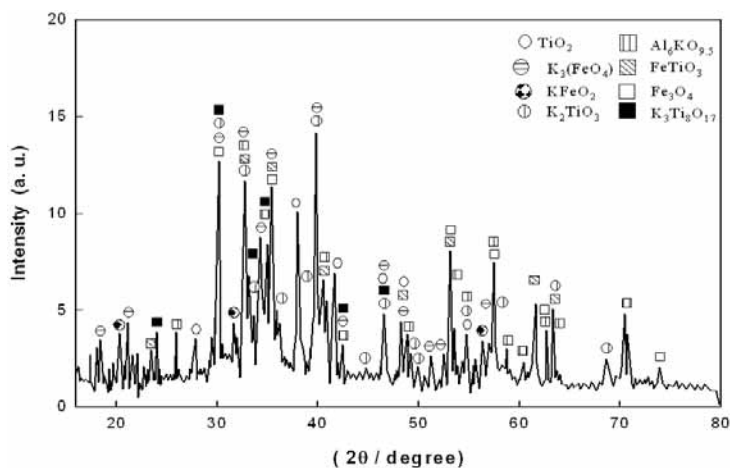


Fig. 1: X-ray diffraction patterns of Egyptian ilmenite fraction diffused with potassium hydroxide at 350°C with molar ratio 1:2.

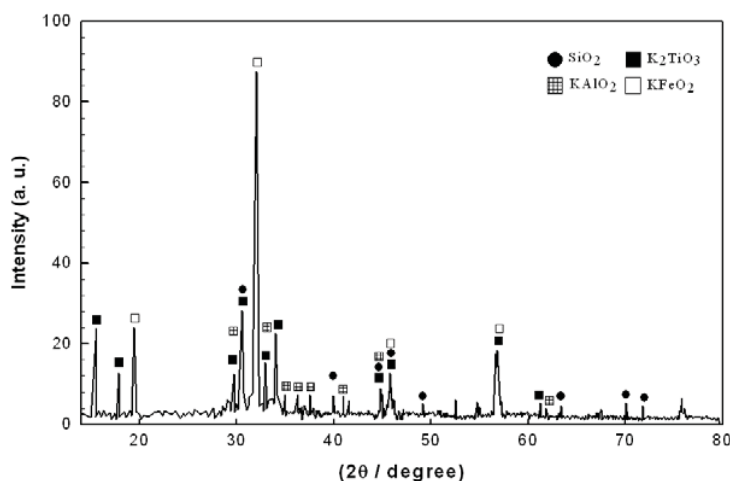


Fig. 2: X-ray diffraction patterns of Egyptian ilmenite fraction diffused with potassium hydroxide at 450°C with molar ratio 1:2.

Effect of Temperature of Reaction on the Percentage of Extraction of Titania:

By inspection of the results illustrated in Figs. 3-5 it can be seen that the increase in the temperature of reaction from 350-450°C leads to an increase in the value of extraction of titanium from beach sand ilmenite with molten KOH and a decrease in the period of time needed for achievement of this maximum value.

The percentage of extraction of titania was found to be reached 100% in case of interaction between titanium dioxide in ilmenite fraction and molten KOH with molar ratios 1:4 and 1:6 at 350, 400 and 450°C after 1h. This finding may be attributed to that the relatively high content of alkali in the reaction mixture leads to formation of acid soluble K_4TiO_4 , and $KTiO_3$. By increasing the time of reaction under these experimental conditions, the percentage of extraction was found to tend to decrease in its value. This phenomenon may be ascribed to the thermal transformation of ortho- and metatitanate to polytitanates (e.g. $K_3Ti_8O_{17}$), which expected to be less soluble in acids than meta- and orthotitanate. This transformation may be enhanced by the prolonged heating from one side and the decrease in the alkali content in the mixture of reaction mixture from the other side, as it was mentioned before.

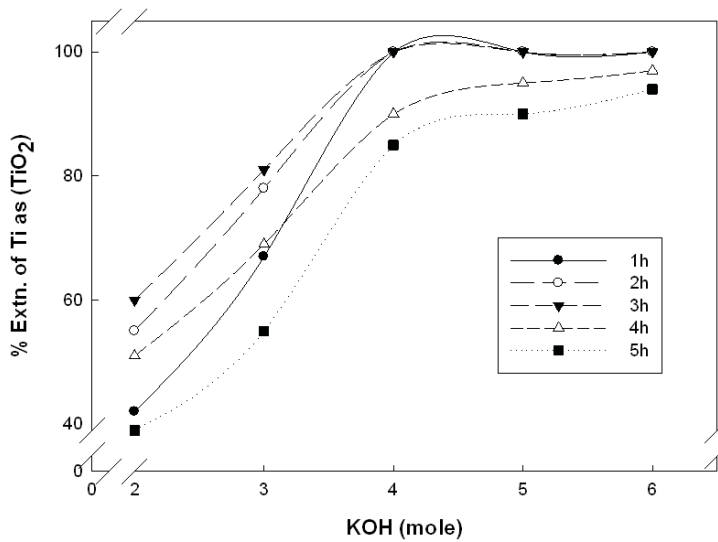


Fig. 3: Variation of the percentage of extraction of titania resulted from reaction of one mole of TiO₂ in the ilmenite fraction with different moles of KOH at 350°C.

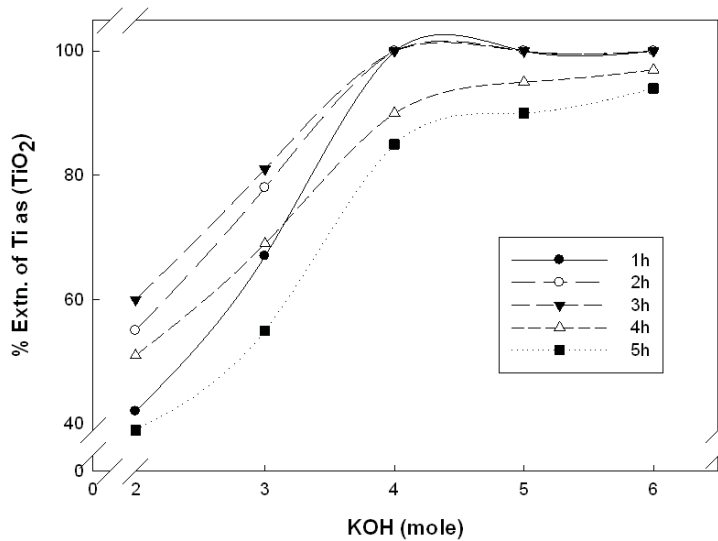


Fig. 4: Variation of the percentage of extraction of titania resulted from reaction of one mole of TiO₂ in the ilmenite fraction with different moles of KOH at 400°C.

Characterization of Reaction Products Resulted from Interaction of Ilmenite Fraction with Molten Sodium Hydroxide:

The chemical reaction between Egyptian beach sand ilmenite and molten NaOH with different molar ratios leads to formation of a large number of sodium compounds (Figs. 6-7). These compounds were found to be less crystalline than the corresponding potassium ones. The resulted sodium compounds namely are: Na₂TiO₃, NaTiO₂, NaFe₂O₃, NaFeO₂, Na₄Ti₃O₈, FeTiO₃, Fe₃O₄, Na₃AlO₄, NaAlO₂, SiO₂, and Ti₂O₃ and Ti₄O₇. The values of the observed “d” spacing (Å) of the previous compounds coincide with those published in the corresponding JCPDS-ICDD cards having the numbers: 37-0345, 16-0251,32-1100,20-1115,38-0730,75-1210,89-0691,37-0208,42-0034,33-1200,88-2483,71-1054 and 77-1392. The different chemical reactions carried out between 350 and 450°C led to formation of the previous compounds, according to the following equations,

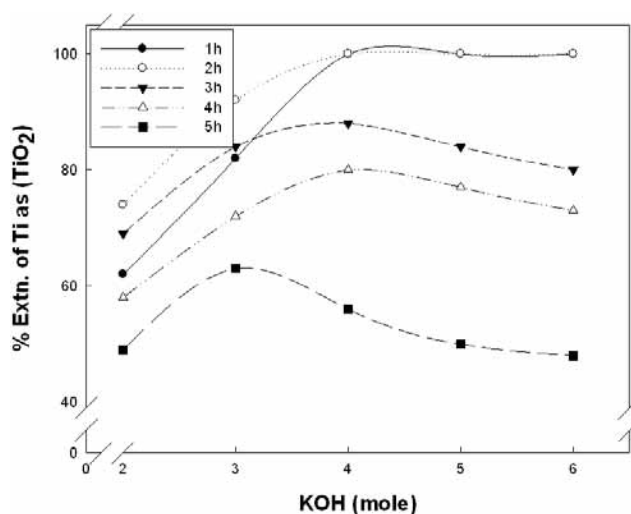
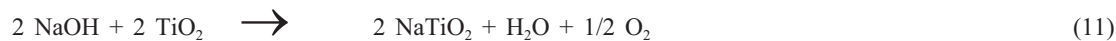
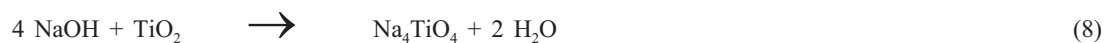


Fig. 5: Variation of the percentage of extraction of titania resulted from reaction of one mole of TiO_2 in the ilmenite fraction with different moles of KOH at 450°C .

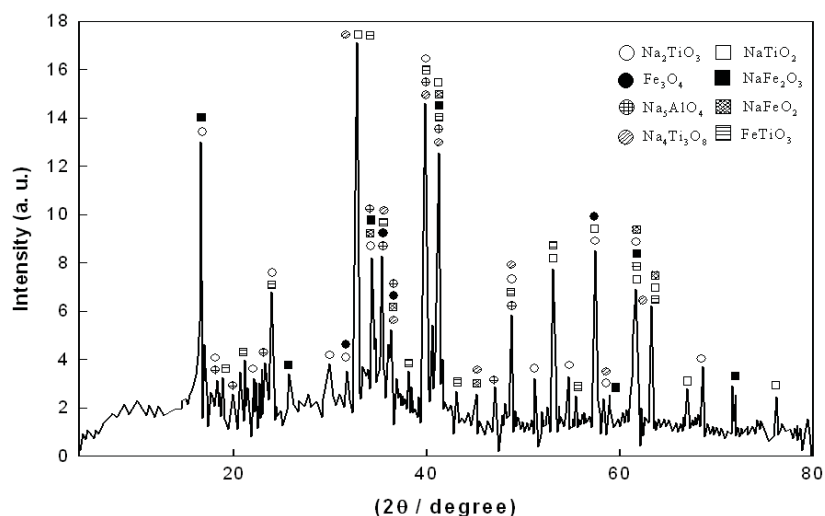


Fig. 6: X-ray diffraction patterns of Egyptian ilmenite fraction diffused with sodium hydroxide heated at 350°C for 5 h with a molar ratio equals 1:2.

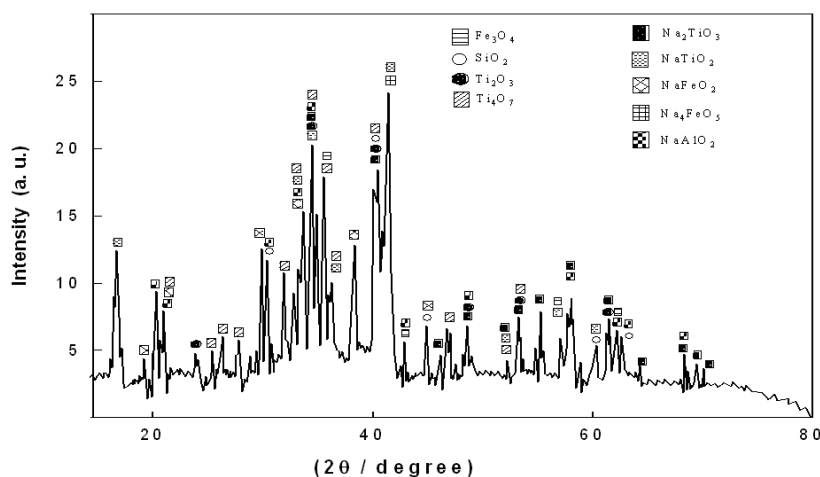


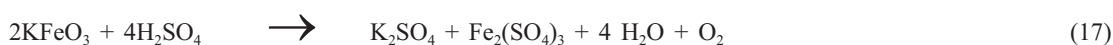
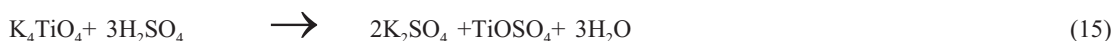
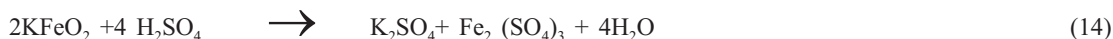
Fig. 7: X-ray diffraction patterns of Egyptian ilmenite fraction diffused with sodium hydroxide heated at 450°C for 3 h with a molar ratio equals 1:4.

Extraction of Titania from the Reaction Products Produced from Interaction of Ilmenite Fraction with Molten Sodium Hydroxide:

By inspection of results illustrated in Figs. 8-10, it can be seen that the trends of variation, of the percentages of extraction of titania from beach sand ilmenite with the variation of molar ratio between reactants, as well as time and temperature of reaction are similar to a great extent that noticed in case of extraction of titania using fused KOH. On the other hand it was found that the percentages of extraction of titania from the ilmenite fraction by interaction with fused NaOH are lower in their values in comparison with that found in case of fused KOH. This phenomenon may be attributed to that the meta- and orthotitanates of potassium persisted the transformation to the corresponding less soluble polytitanates and titanium oxides (Ti₂O₃, Ti₄O₇) more than the corresponding sodium ones. The reverse order was observed in case of reaction of the two fused alkalis with cassiterite ore (Sn,Fe)O₂, which indicated that Ti⁴⁺ behaved as a harder acid than Sn⁴⁺. The appearance of titanium oxides (Ti₂O₃, Ti₄O₇) which are sparingly soluble in acids may be ascribed to the thermal instability and thermal dissociation of titanates of sodium compared to that of potassium.

Preparation of Ultrafine Titania, Iron Oxide and Potassium (Or Sodium) Sulfate:

In order to prepare ultrafine titania from beach sand ilmenite via interaction of the last one with fused KOH or NaOH, it is desirable to select the proper reaction conditions that leads to complete extraction of titania from ilmenite. So that the extraction process were done using the reaction mixture which composed of ilmenite and fused KOH with a molar ratio equals 1:4 and heated at 350°C for 1h. The reaction products were dissolved in an excess amount of 9 M H₂SO₄ solution higher than that required for neutralization of the excess amount of alkali in order to prevent the hydrolysis of titanates from one side and conversion of the different reaction products to the corresponding sulfates from other side. The acid reactions lead to conversion of KFeO₂, K₄TiO₄ and excess amount of KOH to Fe₂(SO₄)₃, TiOSO₄ and K₂SO₄. The last products may be produced according to the following representative equations:



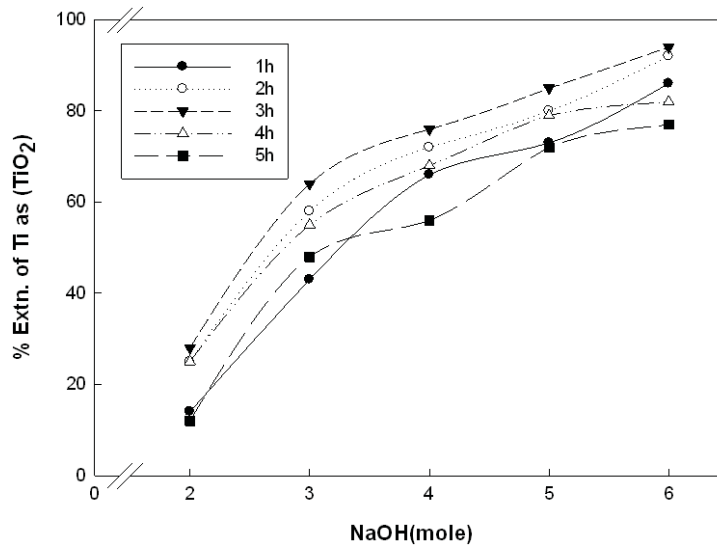


Fig. 8: Variation of the percentage of extraction of titania resulted from reaction of one mole of TiO₂ in ilmenite fraction with different moles of NaOH at 350°C

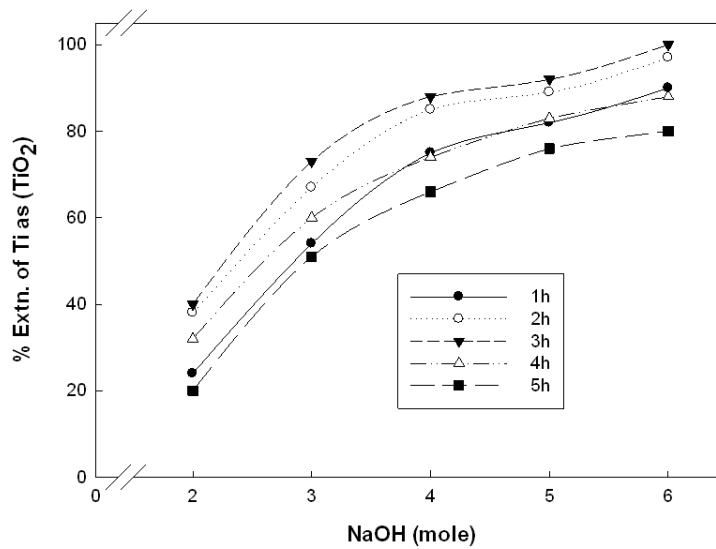


Fig. 9: Variation of the percentage of extraction of titania resulted from reaction of one mole of TiO₂ in the ilmenite fraction with different moles of NaOH at 400°C

The solution may also contain minor amounts of zirconyl sulfate and potassium chromate species. The chromate may be formed as a result of oxidation of trivalent chromium with fused alkali. The residue was composed of insoluble materials such as SiO₂. The resulted solution was then filtered to remove the insoluble residue.

The pH of the resulted filtrate was raised gradually, slowly and cautiously to a value not higher than 2 to precipitate nanosized titanium hydrous oxide. After filtration to separate the later compound, the pH of the filtrate was again raised with alkali to a pH value equals 3, while boiling for sufficient time to precipitate iron as hydroxide. The last compound was subjected for heating above 700°C for a sufficient time to change orange-red goethite species to red iron oxide which can be used in manufacturing of a red pigment. Some details concerned with the preparation of the red pigment will be published in the form of a patent. The pH

of the filtrate after separation of the previous oxides was raised to a pH equals 11 to separate the traces of Fe^{2+} , Mn^{2+} , Zn^{2+} , Al^{3+} and Mg^{2+} . After removal of the insoluble hydroxides of the previous cations by filtration, the pH of the filtrate was again decreased to neutrality by means of sulfuric acid to convert the excess amount of KOH (or NaOH) to the corresponding sulfate.

The resulting solution contained, essentially, high quantity of potassium sulfate was concentrated by evaporation followed by cooling at 2°C to separate crystalline hydrated K_2SO_4 which used as a fertilizer.

The same procedure can be followed with the reaction products of interaction between the beach sand ilmenite and molten NaOH. The byproduct compound in this case is beign Na_2SO_4 which used in various fields of applications.

Based on the foregoing discussions, one can say that the results of extraction of titanium from the concentrate of Egyptian beach sand ilmenite is considered promising, since the values of extraction, which amount to ca. 100%, can be achieved by reaction with molten KOH at a relatively moderate temperatures (350-450°C), and low values of molar ratios between reactants.

In addition, the high iron content in the beach sand ilmenite fraction may be considered as an additional advantague for the suggested process since it can be utilized in preparation of red iron oxide pigment which is considered as an environmentally save coloring compound.

The same procedure can also be performed, exactly, in case of using NaOH. The product which can be obtained in such case is TiO_2 , $Fe(OH)_3$, and Na_2SO_4 which used in a large scale in numerous industries.

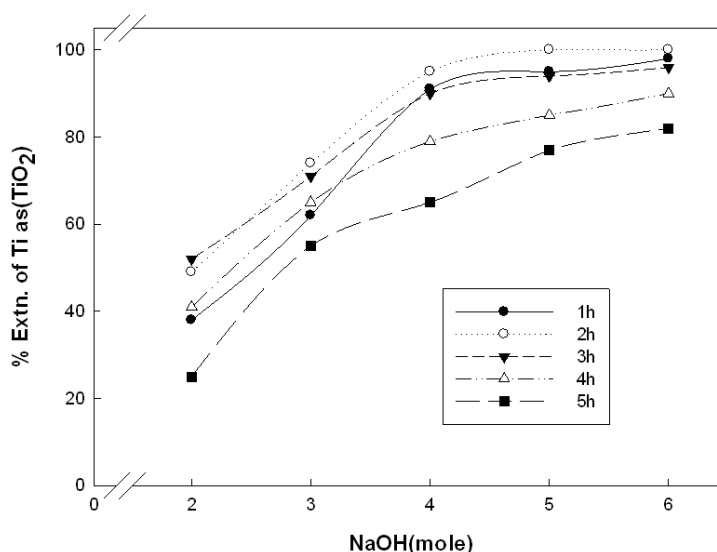


Fig. 10: Variation of the percentage of extraction of titania resulted from reaction of one mole of TiO_2 in the ilmenite fraction with different moles of NaOH at 450°C

Conclusions:

The complete extraction of titania from ilmenite fraction separated from beach black sands broaden along the Mediterranean Sea Coast, Egypt, these makes it possible to exploit these sands in production of titanium dioxide on an economic basis. The last conclusion was gained from the fact the price of yielded titania is higher, than the price of alkali used in its production.

The possibility of exploitation of high percentage of iron as a source of red iron oxide which used as an environmentally friendly pigment raise the economic value of the processes of production of titanium.

The production of sodium or potassium sulfate (or chloride) a byproduct is considered as an additional advantage of the economy to the process of production of titania.

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