# Isothermal and Kinetic Studies on Oxidation Roasting of Kahnooj Ilmenite Concentrate

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In this study, the effect of oxidation conditions, specifically reaction time, temperature and ilmenite particle size for Kahnooj ilmenite concentrate were investigated. Samples were oxidized in a muffle furnace by heating at temperatures of 700-1000°C for periods of 2-6 hours. In order to determine the oxidation reaction progress, changes in the weight of samples were measured before and after each experiment. XRD analysis and DTA were also used in order to phase characterization and determination of phase change temperature, respectively. Oxidation mechanism, phase transition, as well as oxidation kinetics of ilmenite concentrate were studied and the shrinking core model was applied to correlate the conversion data with time. Investigation of the oxidation behavior of Kahnooj ilmenite concentrate for pigment production has not been done before, which in this work it was conducted with a focus on the effect of the ilmenite concentrate particle size on oxidation degree and reaction rate.

## 1. Introduction

Titanium dioxide has been widely used in the production of paints, welding-rod coatings, ceramics, electronic devices and etc. Currently, the main source for production of titanium dioxide ($TiO_2$) is ilmenite ($FeO.TiO_2$). The chloride process and sulfate process are two routes that are currently exploited to produce titanium dioxide industrially. Some pretreatments like preheating, oxidative roasting and mechanical working of the ilmenite are performed to improve the properties of the raw material before the main. The goal of the oxidation process is to make the ore composition uniform. Titanium ores contain a mixture of many oxides that will cause different rates of reduction and sometimes less iron dissolution. The preoxidation process collapses the dense structure of the ore and produces some pores in the particles, which then accelerate the reduction process (Zhang et al., 2002; Xiao et al., 2014). Preoxidation enhances the reduction rate and produces lattice strain, which enhances leaching of the ore (Sarker et al., 2006; Bhat et al., 2015; Liu et al., 2016).

Studies demonstrated that during oxidation in high temperatures, some changes occur on the surface of the ilmenite particles, especially formation of hematite, which leads to dissolution of the iron selective (Vasquez et al., 2008). The reducing medium enhances dissolution of iron oxides in HCl (Lu et al., 1988). Thus, it is suggested to promote the leaching of the ilmenite in HCl by the addition of the iron powder to the solution as a reductant (Mahmoud et al., 2004). In oxidation roasting process, conversion of $Fe^{2+}$ to $Fe^{3+}$ ions results in the formation of more ferric oleate on the surface of the ilmenite particles as a hydrophobic layer which improves ilmenite floatability (Mehdilo et al., 2016). During the oxidation of the ilmenite concentrate, iron migrates towards the surface of the particles which is desired in the iron removal step. The formation of the pseudobrookite also occurs at 900°C which is favorable to upgrade ilmenite concentrate to rutile by breaking the crystalline structure of the particles (Ping, 2011). The preoxidation of the ilmenite reduces the activation energy of the subsequence carbothermic reduction process by increasing the specific surface area of the particles (Gou et al., 2015). However, these effects may be different from one raw material to another, as for some of them, the preoxidation step does not have any advantage in the titanium pigment production (Janssen et al., 2011). The present work aims to study the oxidation roasting of the ilmenite concentrate, which is produced by Kahnooj Titanium Company in the south of Iran. The effects of different parameters on the oxidation of ilmenite concentrate have been studied and the oxidation mechanism has been discussed.

## 2. Experimental

The ilmenite used in this work was acquired from Kahnooj Titanium Company in Southern Iran, which chemical composition of the produced concentrate is given in Table 1.

*Table 1: The chemical analysis of Kahnooj ilmenite concentrate*

| Component | Weight, % | Component | Weight, % | Component | Weight, % | Component | Weight, % |
|---|---|---|---|---|---|---|---|
| $SiO_2$ | 3.65 | $TiO_2$ | 44.74 | FeO | 35.50 | V (ppm) | 925 |
| $Al_2O_3$ | 0.97 | CaO | 1.10 | MnO | 0.80 | Cr (ppm) | 67 |
| $Fe_2O_3$ | 11.80 | MgO | 1.31 | $P_2O_5$ | 0.10 | | |

The ilmenite concentrate powder was subjected to sieve analysis by a vibratory sieve shaker. In order to identify the phases, the X-ray diffraction analysis (XRD) was done using a JOEL JDX-8030 instrument with Cu Kα radiation at 30kV and 20 mA.

Sieve analysis of the used ilmenite concentrate (based on U.S. Standard sieve analysis) and the particle size distribution curve of the material is shown in Figure 1. According to the results, the average particle size of ilmenite concentrate is approximately 290µm and 90% by weight of the sample is bigger than 0.149 mm size.
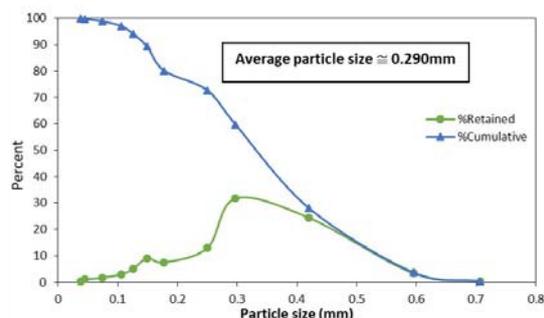


*Figure 1: Sieve analysis curves for used ilmenite concentrate*

The ilmenite concentrate powder was put in the oven at 105°C for 1 hour to ensure completely removing the moisture. The 5 gram samples were heated at temperatures from 700 to 1000°C for 2-6 hours. A digital scale measured the weight of each sample before and after roasting. XRD and DTA analysis were carried out for some of the particle sizes in order to show phase transitions occurring under every experimental condition. Since during roasting of ilmenite, $Fe^{2+}$ gets oxidized to $Fe^{3+}$, the amount of oxygen in the powder increases. Hence the samples' mass increases as the roasting continues.

## 3. Results and discussion

### 3.1 Weight changes

To calculate the ilmenite oxidation conversion, each sample weight was recorded before and after being in the oven. The results shown in Figure 2 indicate an increase in the weight of almost all samples after heat treatment. This increase is due to diffusion of the oxygen into the structure which leads to oxidation of $Fe^{2+}$ to $Fe^{3+}$ (Fu et al., 2010; Samanta et al., 2014). Figure 2 shows that the reaction rate increases with temperature and time. At low temperatures, a decrease in the size of the powder particles has a direct effect on the reaction rate. But at high temperatures, this effect gradually decreases, so that at 1000°C (Figure 2c) there is not much difference between the curves. The occurrence of sintering is a possible reason for this behavior, which can diminish diffusion of oxygen into the particles. However, unlike the temperature, sintering does not have much effect on diffusion of oxygen into the particles. The oxidation rate is very slow at a temperature of 700°C initially, and then increases with more than 4 hours soaking time. At 850°C, isothermal oxidation reaction curves show an increase in weight of samples with time and particle size of powder until 0.125mm and then the curves drop off because of agglomeration of particles. Up to approximately 80% degree of oxidation was achieved in the first two hours of the process at 1000°C due to the high specific surface area and high diffusion rate. The maximum oxidation was achieved for the particle size of 0.177mm at 1000°C in 6 hours (more than 90%). At high temperatures, the influence of temperature on the reaction rate is more significant than time and particle size. The oxidation temperature severely affects the rate of morphological changes, i.e., the evolution rate increases with increasing the oxidation temperature (Zhang et al., 2013).
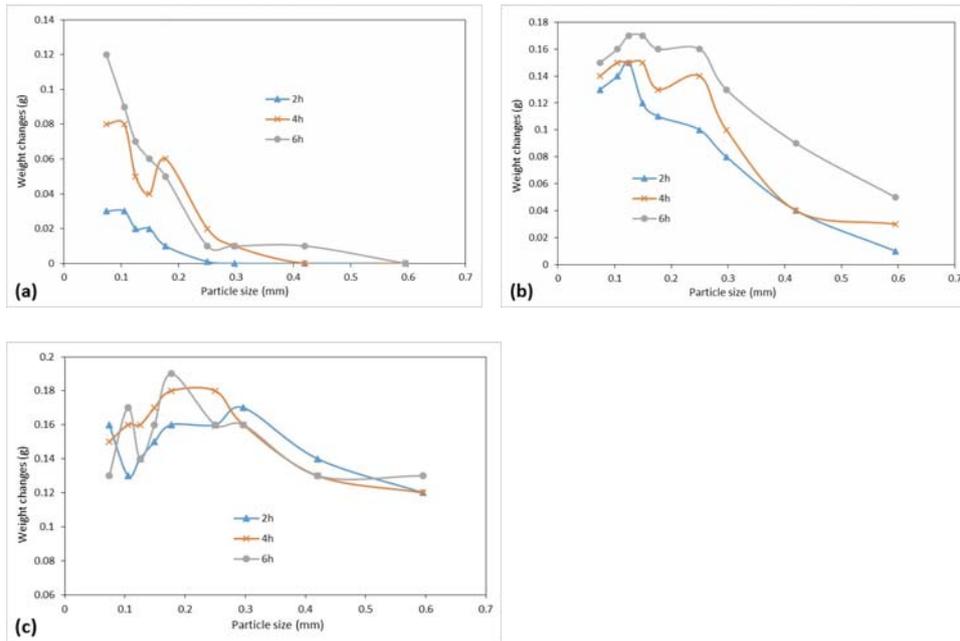
*Figure 2: Changes in the weight of 5.00 grams of ilmenite powder after various heating periods at a) 700°C, b) 850°C and c) 1000°C.*

### 3.2 X-Ray diffraction pattern

Oxidation conditions for these samples are given in Figure 2. Phase composition of the samples were characterized by XRD and are shown in Figure 2. It is obvious that the $FeTiO_3$ is a major phase. In order to study the oxidation behavior of the Kahnooj ilmenite concentrate, five samples were chosen.

*Table 2: Oxidized Samples that were selected for the XRD analysis*

| Sample | Particle size(mm) | Temperature (°C) | Time (h) |
|---|---|---|---|
| a (raw material) | ≈290 | - | - |
| b | 0.595 | 700 | 6 |
| c | 0.177 | 1000 | 6 |
| d | 0.125 | 850 | 6 |
| e | 0.105 | 1000 | 2 |
| f | 0.074 | 700 | 6 |
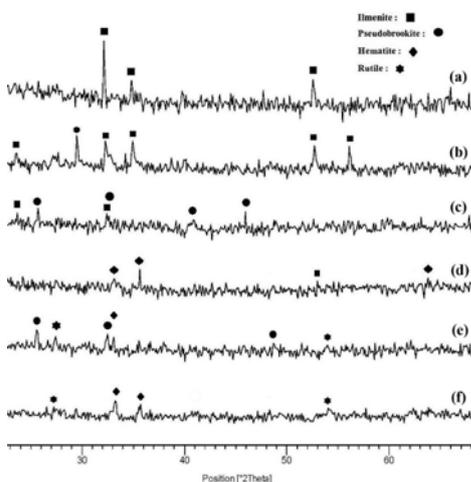


*Figure 3: X-Ray diffraction patterns of the samples. a) Before,b-f) after oxidation based on the Table 3.*

Since the ore has many impurities which have different thermal expansion coefficients in comparison with ilmenite, the thermal expansion coefficient of the sample material is affected by these impurities. This causes a strain in the crystallites of the particles. If the crystallite is strained, then the "d-spacing" will change and a compressive stress in the particle would make the d-spacing smaller. From Figure 3, it can be seen that corresponding peaks for some phases (especially ilmenite) are shifted slightly to the left, due to the mentioned strain. Such strain could be described as the homogeneous strain affecting all crystallites the same amount. Another point which is obvious from Figure 3, is peak broadening in the XRD patterns for oxidized samples which is named as "strain broadening". Heterogeneous strain can broaden the powder diffraction peak(Williamson et al., 1953; Smith, 1999). Crystal lattice distortion (micro-strain) is induced due to dislocations and concentration gradients in effect of non-uniform temperature distribution on the particles surface. As mentioned above, powder particles are exposed to both homogeneous and heterogeneous stains.

### 3.3 Oxidation mechanism of ilmenite

The products of oxidation are different in each condition. Temperature and particle size are two important factors in the oxidation of ilmenite. It can be seen from the XRD patterns that despite the low temperature for the particle size of 0.074, ilmenite has been completely oxidized to rutile and hematite; while at the same temperature but particle size of 0.595, most of the ilmenite remains unreacted and there is a small amount of pseudobrookite in the product. At 1000°C, there is an obvious difference between the particle size of 0.177 and 0.105 in products which can represent the effect of particle size on the oxidation conversion(Wei et al., 2013). The oxidation rate of particle sizes of 0.105 and 0.125 are practically the same. Hence it can represent the effect of temperature on the oxidation conversion. The oxidation reactions for temperatures higher than 700°C(Wei et al., 2013; Mehdilo et al., 2014) could thus be written accordingly as follows:

$$4FeTiO_3(s) + O_2(g) \rightarrow 4TiO_2(s) + 2Fe_2O_3(s) \tag{1}$$

Another possible reaction is the production of $Fe_2O_3.2TiO_2$ as an intermediate phase:

$$2FeTiO_3(s) + 0.5O_2(g) \rightarrow Fe_2O_3.2TiO_2(s) \tag{2}$$

Decomposition of $Fe_2O_3.2TiO_2$ with the formation of hematite and rutile is in subsequent reaction:

$$Fe_2O_3.2TiO_2(s) \rightarrow Fe_2O_3(s) + 2TiO_2(s) \tag{3}$$

Formation of pseudobrookite ($Fe_2O_3.TiO_2$) is the result of these 3 reactions at temperatures higher than 850°C:

$$Fe_2O_3.2TiO_2(s) \rightarrow Fe_2O_3.TiO_2(s) + TiO_2(s) \tag{4}$$

$$Fe_2O_3(s) + TiO_2(s) \rightarrow Fe_2O_3.TiO_2(s) \tag{5}$$

$$2FeTiO_3(s) + 0.5O_2(g) \rightarrow Fe_2TiO_5(s) + TiO_2(s) \tag{6}$$
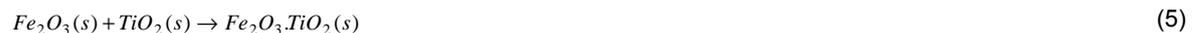
## 4. Oxidation kinetics

### 4.1 Kinetic Model

Equations 1, 2 and 6 are related to the oxidation of ilmenite in which $FeTiO_3$ and $O_2$ react stoichiometrically at a ratio of 1:0.25. It means that the stoichiometric oxygen amount absorbed by the ilmenite is 5.27 wt.% of the initial mass of pure ilmenite. Table 1 shows that the purity of the ilmenite in Kahnooj ilmenite concentrate is approximately 75%, which is related to the weight percent of FeO and $TiO_2$. Accordingly, when 3.95% increase in the initial mass of the concentrate occurs, the oxidation of ilmenite content has been performed completely. It can be seen from Figure 2 that the oxidation percentage increases by decreasing the particle size for all test temperatures. This relationship is more significant for higher temperatures. However, for small particle sizes and high temperatures, particles are exposed to sintering and agglomeration. Therefore, the temperature of 1000°C has been adequate for the complete oxidation of ilmenite concentrate in particle sizes 0.149-0.250 and for periods of 4-6 hours. The results of the experiments were compared to well-known kinetic models. As indicated by (Ishida et al., 1968, 1971 a; b), the shrinking core model is the best describing model for the majority of reacting gas–solid -systems. Therefore, this model has been selected for the oxidation of ilmenite. According to the shrinking core model, if the reaction at the interface of the product layer and particle core (unreacted solid) is controlling the rate of the reaction, the kinetic model can be expressed as equation 7 (Spencer et al., 1929), while if the diffusion of oxygen through the solid is the rate-controlling step, the kinetic model can be expressed as equation 8 (Mozammel et al., 2013).

$$1-(1-X)^{0.33}=kt \tag{7}$$

$$1+2(1-X)-3(1-X)^{0.67}=kt \tag{8}$$

Where $X$ is the fraction of ilmenite which has been oxidized, $t$ is time and $k$ is rate constant. If both the chemical reaction and diffusion control the rate for oxidation of ilmenite, the kinetic model will be of the following equations (El-Tawil et al., 1993):

$$3k_1[1-(1-X)^{0.33}]+1.5k_2[1-0.67X-(1-X)^{0.67}]=t \tag{9}$$

According to previous studies, the rate of oxidation of the ilmenite is controlled by the intraparticle diffusion at applied temperatures (Sun et al., 1993). Nonetheless, the chemical mechanism and mixed control mechanism were checked by equations 7 and 9, respectively, and a good fit was not observed. As a result, the diffusion-controlled rate model (equation 8) was fitted to the isothermal weight gain data. Results show that experimental data for most of the particle sizes are in agreement with this equation, especially with particle sizes smaller than 0.177. As a result, the shrinking core is the best kinetic model for oxidation of ilmenite for particle sizes smaller than 0.177. Moreover, this model has a good applicability for the temperature 850°C in almost all particle sizes. Although the shrinking core model cannot represent the best applicability for the oxidation of ilmenite, it is applicable for this reaction, especially at temperature approximately 850°C.

### 4.2 Evaluation of Activation Energies

Activation energy can be evaluated by using the Arrhenius equation:

$$k = A.\exp(-E_a/RT) \tag{10}$$

Where $k$ is the rate constant, $A$ is the frequency factor, $E_a$ is the activationenergy (J mole$^{-1}$), $R$ is the gas constant (8.314 J mole$^{-1}$ K$^{-1}$) and $T$ is the absolute temperature (K). The calculated activation energy for each particle size is shown in Table 3. The influence of the particle size on oxidation was indicated in previous sections. Oxidation of the coarser particles is slower than fine particles, which is due to less total surface area, fewer leakage points and developed product layer (Rao et al., 1975). It can be seen from Table, the activation energy of oxidation increases with increasing the particle size of the powder. This result has a good agreement with the previous results about the effect of particle size on oxidation of the ilmenite.

*Table 3: The activation energy of the reaction for each particle size of the ilmenite concentrate*

|  | Particle size | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
|  | 0.595 | 0.420 | 0.297 | 0.250 | 0.177 | 0.149 | 0.125 | 0.105 | 0.074 |
| Activation Energy (kJ mole$^{-1}$) | 112.7 | 114.1 | 104.5 | 99.6 | 61.7 | 49.3 | 35.1 | 30.3 | 1.03 |

## 5. Conclusions

The investigation of oxidation of Kahnooj ilmenite concentrate has not been done before and in this work, it has performed with a focus on the effect of ilmenite concentrate particle size on the degree of oxidation and the rate of the reaction. The oxidation percentage of ilmenite increases by the decrease of particle size for all test temperatures. This relationship is more significant for higher temperatures. However, for small particle sizes and high temperatures, particles are exposed to sintering and agglomeration. The temperature of 1000°C has been adequate for the complete oxidation of Kahnooj ilmenite concentrate in particle sizes 0.149-0.250 for periods of 4-6 hours. The shrinking core model, is the best kinetic model for oxidation of ilmenite, especially for particle sizes smaller than 0.177. Although the shrinking core model cannot represent the best applicability for the oxidation of ilmenite, especially at temperatures approximately 850°C. Evaluation for activation energy of oxidation shows that it increases with increase in particle size of the powder.

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