KINETICS OF ALKALINE LEACHING PROCESS OF TITANIUM(IV) FROM ILMENITE

Snizhana Pysarenko[1,2], Oleksandr Kaminskyi[2], Olena Chyhyrynets[1], Roman Denysiuk[2],
Olena Anichkina[2], Volodymyr Chernenko[1]

[1]*National Technical University of Ukraine*
"Igor Sikorsky Kyiv Polytechnic Institute"
Department of Physical Chemistry
37 Peremohy avenue, Kyiv, Ukraine, 03056
[2]*Zhytomyr Ivan Franko State University*
Department of Chemistry
40 Velyka Berdychivska str.
Zhytomyr, Ukraine, 10008
E-mail: snazhunka1107@gmail.com

ABSTRACT

The article deals with the kinetics process of alkaline leaching of ilmenite from the Irshan deposit; the prospects of obtaining potassium titanate in comparison with sodium titanate are presented. Using the methods of X-ray diffraction and electron microscopy, it has been studied that potassium and sodium titanates, obtained by the method of alkaline melting from ilmenite concentrate, correspond to the structures described in the reference literature. The degree of extraction depends on the time of interaction of ilmenite with sodium and potassium hydroxides, and the optimal kinetic conditions are determined. We have established that during alkaline leaching of titanium(IV) with potassium hydroxide, in the temperature range of 453 K - 533 K, the maximum degree of extraction is 86 % - 89 %. It is shown that the dependence "degree of transformation - time of isothermal interaction" is best described by the "compressed sphere" model. From the temperature dependences of the potassium titanate leaching process, the activation energy has been calculated, which is 22 kJ mol^{-1}, which may indicate a kinetic regime with a low activation energy, where the limiting stage is the chemical interaction between the melt components.

Keywords: ilmenite, alkaline leaching, sodium titanate, potassium titanate, chemical kinetics.

INTRODUCTION

The unique mineral and raw material base of Ukraine includes the presence of significant deposits of complex titanium ores. Among the most well-known and studied titanium deposits, which are being actively developed nowadays, the largest share is for ilmenite. A feature of Irshanskyi geological-industrial type of placer deposits of ilmenite ore has a high content TiO$_2$ compared to other types of similar deposits [1].

Various methods of ilmenite leaching are described in the scientific literature in order to obtain reactive forms of Ti(IV) with various functional purposes [2 - 5]. Nowadays several basic methods of ilmenite leaching are known, which are divided into acidic and alkaline depending on the leaching reagent. Chloride and sulfate methods of processing ilmenite concentrate are common among acid leaching methods [6]. An excess amount of the appropriate acid and long-term heating are required for the complete extraction of titanium from ilmenite by acid methods [7].

In the case of using the chloride method, the phase composition of the original mineral raw material is not important, though this technology requires slag smelting. The chloride technology of ilmenite concentrate processing involves lower economic costs for production due to a shorter technological scheme [8].

The advantages of the sulfate method of processing titanium-containing raw materials include the possibility of using ores with a low content of unchanged ilmenite. For altered (leucoxeninated) ilmenite, which is formed as a result of long-term weathering of the rock, that is, with

a high content TiO_2 (more than 70 %), the technology of acid processing of such ores is less effective [9]. Due to the formation of stable oxo salts of titanium the destruction of which occurs rather slowly even with a large excess of sulfuric acid. In order to increase the degree of Ti(IV) extraction from leucoxenized ilmenite, the authors suggest activating such raw materials with fluoride additives [6, 10 - 12].

The processes of alkaline extraction of titanium, which is an alternative and does not involve the use of fluoride activators, have become more and more widespread recently. The essence of the alkaline leaching method is that titanium - containing raw materials are subjected to heat treatment with potassium or sodium hydroxides. Although this method of titanium leaching does not belong to industrial methods, the high speed of the process of converting titanium into a soluble form of titanates and the level of efficiency in the use of raw materials indicate the prospects of treating titanium ores with alkalis [2 - 4, 13, 14].

The authors studied ilmenite concentrate (in %: TiO_2 - 44.7; FeO - 15.8; Fe_2O_3 - 29.3 and impurities) manufactured by Kahnooj Titanium Complex, Kerman (Iran) [2]. An 85 % solution of potassium hydroxide has been used for the complete extraction of titanium from ilmenite by acid methods. Leaching has been carried out at a temperature of 493 K, atmospheric pressure and the presence of air oxygen.

The interaction of ilmenite from the deposit on the island of Bangka (Indonesia), which has the following basic chemical composition TiO_2 - 38.3 %; Fe_2O_3 - 49.44 % and impurities with a concentrated solution of alkali (KOH) has been carried out in an autoclave under elevated pressure and a temperature of 473 K [14].

Ilmenite samples (%: TiO_2 - 46.38; FeO - 25.13; Fe_2O_3 - 20.0 and impurities), separated from the black sands of the Rosetta coast (Egypt) have been subjected to alkaline leaching with solutions of potassium and sodium hydroxides (70 %) in two stages [3]. At the first stage, hydrothermal treatment of ilmenite has been carried out with the appropriate alkali solution at a temperature of 393 K, and the obtained ilmenite paste is subjected to acid leaching during the second stage. The obtained product is used as a U(VI) sorbent.

The authors during processing ilmenite of the Rosetta coast (Egypt) used a fusion reaction with crystalline alkalis at different molar ratios of components

in the temperature range of 623 K - 723 K in order to obtain titanates of different chemical composition [13].

The authors investigated the influence of temperature and the molar ratio of components on the course of the process of alkaline leaching of titanium from ilmenite concentrates of various deposits in works [2 - 4, 13]. It is stated that, depending on the external conditions, it is possible to obtain Ti(IV) compounds of different chemical composition. Thus, at a temperature of 623 K during one hour of fusion of the original ilmenite with potassium hydroxide, it is possible to obtain K_4TiO_4 and K_2TiO_3, an increase in the interaction time leads to the formation of $K_3Ti_8O_{17}$. The possibility of formation of various titanium salts is confirmed by thermodynamic calculations of the authors [3, 4].

It should be noted that in previous studies by the authors it has been experimentally determined that the K_2TiO_3 optimum conditions for the formation of alkaline leaching are a temperature of 453 K and a molar ratio of components $FeTiO_3$: KOH (1 : 2) [1, 15]. It is found that increasing the heating temperature of the ilmenite melt with alkali in such a molar ratio does not significantly increase the yield of the product, and increasing the amount of alkali at a given fusion temperature leads to its accumulation in the form of an inactive reagent.

Since the ilmenite of the Irshansk deposit has the following chemical composition: TiO_2 - 79.21 %; FeO - 20.02 %; V_2O_5 - 0.45 % and impurities that distinguish it from ilmenites of other deposits, there is a need to study the kinetic dependences of the alkaline extraction of Ti(IV) from such an ore, which is the purpose of this article.

EXPERIMENTAL

The Ilmenite concentrate of the Irshansk GZK is used as the research object in this paper. The mineral composition of ilmenite is determined by scanning electron microscopy with X-ray spectral elemental microanalysis on an electron microscope "JSM - 6490 LV" with energy dispersive (EDS) and wave dispersive (WDS) spectrometers "Energy Plus" ("Oxford Instruments"), which corresponds to the ratio of the main components indicated above.

The phase composition of the original ilmenite ore, products of alkaline melting with potassium and sodium hydroxides, is investigated by X-ray diffraction using a

DRON-3M diffractometer (copper radiation, Kα line, λ = 0.1540 nm).

Electron microscopic studies of purified titanates have been carried out on a Selmi scanning electron microscope at a resolution of 50 - 200 μm.

The peroxide method of quantitative determination of titanium in solution using a spectrophotometer UV-1200 is used to study the degree of extraction of Ti(IV) during leaching from ilmenite [1].

The degree of extraction (X, %) of titanium from altered ilmenite is determined by the formula:

$$X = \frac{m(Ti(IV))_e}{m(Ti(IV))_o} \cdot 100\%$$

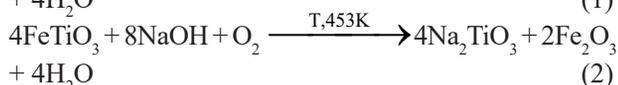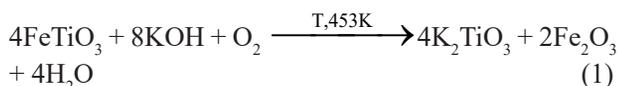where: $m(Ti(IV))_e$ - mass of extracted titanium, mg; $m(Ti(IV))_o$ - mass of titanium in the original melt, mg.

To conduct kinetic studies, mixtures of the original ilmenite and the corresponding alkali have been prepared in a molar ratio of 1:2. The reaction mixture has been heated in a glycerine bath at a temperature of 453 K for a period of 30 - 210 minutes. To construct temperature dependences, similar mixtures have been heated for 60 minutes in the temperature range of 453 K - 533 K.

Cleaned-up samples of potassium and sodium titanates are obtained by precipitation of saturated aqueous solutions of the corresponding melts with ethyl alcohol and examined using X-ray diffraction.

RESULTS AND DISCUSSION

The processes of alkaline extraction of titanium(IV) from ilmenite using KOH and NaOH are described by the reactions:

$$4FeTiO_3 + 8KOH + O_2 \xrightarrow{T,453K} 4K_2TiO_3 + 2Fe_2O_3 + 4H_2O \quad (1)$$

$$4FeTiO_3 + 8NaOH + O_2 \xrightarrow{T,453K} 4Na_2TiO_3 + 2Fe_2O_3 + 4H_2O \quad (2)$$

Gibbs energies are calculated using the Tiomkin - Schwartzman method under standard conditions. It has been stated that the formation of potassium titanate ($\Delta G_{298}^0 = -840.76$ kJ mol^{-1}) is more energetically beneficial than the formation of sodium titanate ($\Delta G_{298}^0 = -418.94$ kJ mol^{-1}) [15]. This is probably due to the fact that the formation of an orthorhombic structure K_2TiO_3 is less energy-consuming than a monoclinic structure Na_2TiO_3 [16, 17]. Fig. 1 shows diffractograms K_2TiO_3 (a) and Na_2TiO_3 (b)

As it is seen from Fig. 1, an intense reflex, which are in the range of 29 - 34° angles 2θ, indicate that as a result of the leaching process is formed K_2TiO_3 [16]. On the diffractogram (Fig. 1(b)), a series of intense peaks in the range of 29 - 42° angles 2θ indicates the formation of a phase Na_2TiO_3 [17].

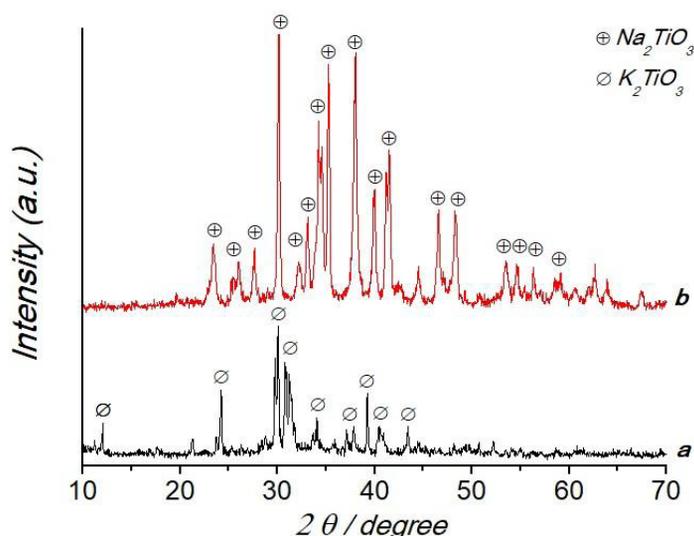The morphology of the particles of synthetic

Fig. 1. Diffractograms of purified samples K_2TiO_3(a) and Na_2TiO_3 (b).

potassium and sodium titanates has been researched using the SEM method (Fig. 2). It has been determined that the size of the particles K_2TiO_3 is up to 30 μm (Fig. 2(a), (b)), and Na_2TiO_3 has a particle size of up to 25 μm (Fig. 2(c), (d)). Sodium titanate particles are more prone to aggregate formation than potassium titanate. Fig. 2(a) and 2(b) show individual potassium titanate crystallites, which have a shape close to orthorhombic, and monoclinic crystals of sodium titanate in Fig. 2(c) and 2(d) are visible, which are also confirmed by the X-ray diffraction method.

Kinetic curves have been constructed in order to study the kinetic characteristics of the processes of leaching of ilmenite with potassium and sodium hydroxides

Fig. 3 shows the dependence of the degree of titanium(IV) extraction on the contact time of ilmenite with alkalis (KOH, NaOH) at a temperature of 453 K. It has been found out that in the first 30 minutes of interaction of the starting substances, the degree of extraction in both cases reaches almost 50 %. The maximum degree of titanium extraction according to equation (1) is 86.13 %, while according to equation (2) this value reaches 68.49 %.

Heating the melts for more than 3 hours at this temperature the yield of the soluble form of Ti(IV) does not increase, which is possibly due to the presence of impurities in the initial concentrate and the formation of ferrum (III) oxide, which prevents the further penetration of alkali to the reaction centers of ilmenite.

Taking into account the almost two-fold higher degree of titanium(IV) extraction during the treatment of ilmenite with potassium hydroxide, further kinetic calculations and studies have been carried out specifically for this process.

As we can see from Fig. 4, the degree of extraction of titanium(IV) increases with increasing temperature. At this molar ratio of components, the temperature does not significantly affect the yield of titanium(IV) even during a five-hour interaction. Thus, in the temperature range of 453 K - 533 K, the maximum degree of extraction is 86 % - 89 %.

The reaction constants at different temperatures have been calculated in order to determine the reaction mechanism (1) and to calculate the activation energy according to the Arrhenius equation. In the process of analyzing the experimental results, various kinetic equations have been used to describe heterogeneous
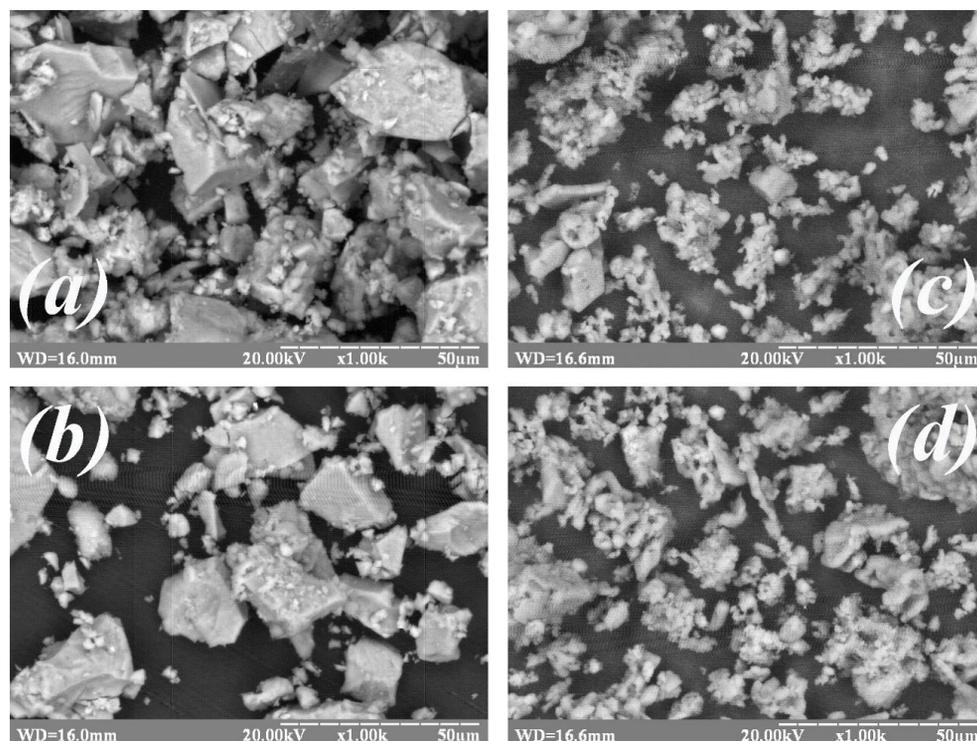

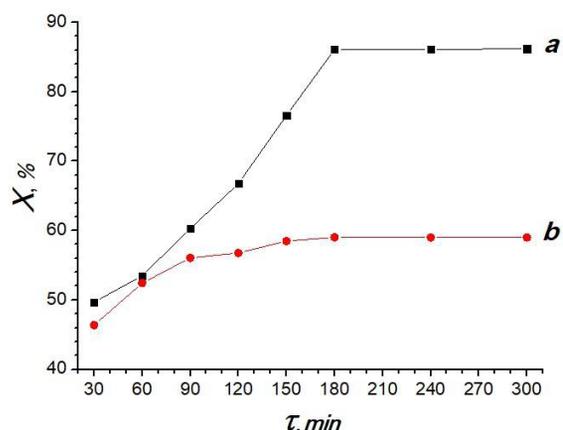Fig. 2. SEM images for K_2TiO_3 (a, b) and Na_2TiO_3 (c, d).

Fig. 3. Dependence of the degree of extraction (X, %) on the time of heating the melts with the molar ratio of the components ilmenite: alkali (1:2) KOH (a) and NaOH (b) at T = 453 K.
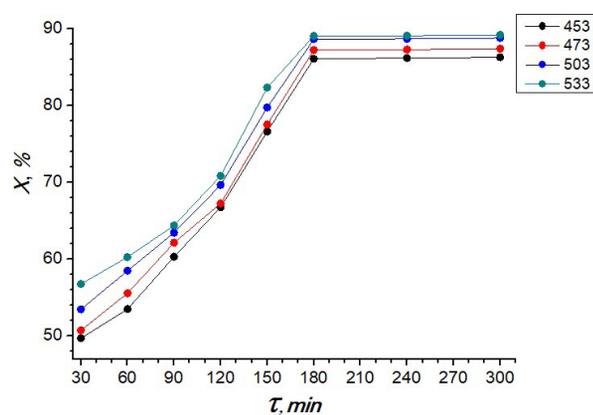

Fig. 4. Dependence of the degree of extraction (X, %) of titanium(IV) on time at different leaching temperatures.
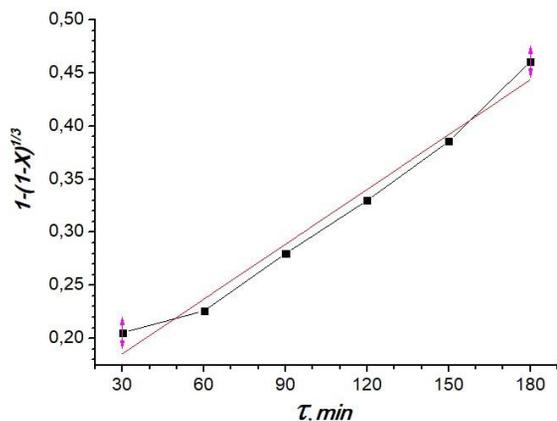

Fig. 5. Kinetics of leaching of ilmenite with potassium hydroxide according to the "shrinking core" model (T = 453 K).
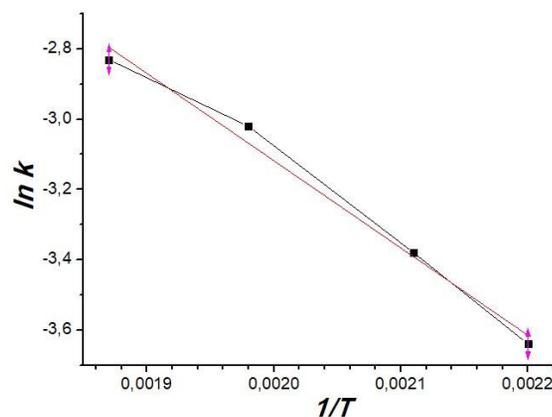

Fig. 6. Graph of dependence of the rate constant of the leaching process of potassium hydroxide with ilmenite on temperature.

processes: pseudo-first and pseudo-second orders, Yander, Ginstling-Brownstein, Zhuravlev-Lesokhin-Tempelman, Yerofeev -Abraham and "compressed sphere" [10, 18].

Statistical processing of the kinetic dependences "degree of transformation - time of isothermal interaction" according to Fisher's variance ratio at a significance level of 0.05 has showed that the hypothesis of linearity can be accepted for all equations, but the correlation coefficients when approximating the experimentally established dependences $X(\tau)$ differ significantly. The best results ($R^2 = 0.9728$) have been obtained while describing the speed of interaction of components according to the "compressed sphere" model: $k\tau = 1 - (1 - X)^{1/3}$ (Fig. 5).

A characteristic feature of solid -phase reactions, which reactions (1 - 2) belong to, is the localization of the reaction zone on the surface of the phase separation of the reactants. The "shrinking core" model indicates that at a certain point in time, active centers of interactions are formed on the surface of ilmenite crystals due to surface defects of the crystal lattice and microcracks. The solid-phase interaction is limited by the diffusion of alkali from the surface of the nucleus into the volume of ilmenite particles through the formed interaction products, which leads to the annihilation of the initial nuclei.

The activation energy of alkaline leaching has been calculated based on the temperature dependence of "lnk - 1/ T" (Fig. 6) and the Arrhenius equation, which is 22

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kJ mol^{-1} and indicates the kinetic mode of the process with low activation energy.

The conducted calculations will allow further development of the optimal technology for obtaining potassium titanate from ilmenite by the alkaline leaching method. The calculated activation energy of the kinetic mode of the process indicates that the determined conditions of the leaching process are practically optimal. At the same time, the overall speed of the process, the increase in the speed of the limiting stages of chemical interaction, and the energy costs for alkaline leaching of leucoxenized ilmenite are taken into account.

CONCLUSIONS

The technology of effective processing of ilmenite concentrate requires the use of necessary reagents, knowledge of kinetic laws of interaction and creation of optimal processing modes. The process of alkaline leaching of titanium(IV) from the ilmenite concentrate of the Irshansk deposit has been carried out using sodium and potassium hydroxide. At the same time, sodium titanate with a monoclinic structure and potassium titanate with an orthorhombic structure are formed, the crystal sizes of which are up to 30 μm.

It has been studied that the maximum extent of titanate extraction is achieved after 3 hours of thermal treatment of reagents at a temperature of 453 K, and the extraction of Ti(IV) from ilmenite with the participation of potassium hydroxide is almost twice as deep as compared to sodium hydroxide. It has been established that the kinetics of the dependence "degree of transformation - time of isothermal interaction" is best described by the "compressed sphere" model ($R^2 = 0.9728$).

The activation energy of the potassium titanate leaching process calculated from the temperature dependences (22 kJ mol^{-1}) indicates that the limitation of the process is provided by the kinetic stages with low activation energy.

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