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O.V. Kozhura, E.O. Tsybulya, I.L. Kovalenko

LEACHING OF REDUCED ILMENITE CONCENTRATE FROM THE SAMOTKAN DEPOSIT USING SULFURIC ACID SOLUTIONS

Ukrainian State University of Science and Technologies, Dnipro, Ukraine

A strongly altered ilmenite concentrate from the Samotkan deposit was reduced with coal at 1200^{0}C for 4 hours, yielding a product in which 90% of iron was reduced to the metallic state. Iron was leached from the reduced ilmenite using 6–22% sulfuric acid solutions at temperatures of 20–70^{0}C for three hours. It was found that the leaching of metallic iron by acidic solutions proceeds rapidly in the initial period, following a first-order reaction mechanism with an apparent activation energy of 40.2–42.6 kJ/mol, indicating kinetic control of the process. The reaction order with respect to hydrogen was determined to be 0.36–0.42. After approximately 57% of iron was extracted, the leaching mechanism changed, causing a sharp slowdown in the process. Laboratory modeling of a two-stage countercurrent process was conducted to produce synthetic rutile by leaching the reduced ilmenite with titanium white waste acid. By metering the feed of reduced ilmenite, the rapid iron dissolution stage can be utilized to regulate the acidity of the waste to a level of 3–5 g/L H_2SO_4. The required level of impurity removal was achieved by exposing the partially leached reduced ilmenite to an excess of the initial 22% titanium white waste acid for 3 hours at 70^{0}C. Calcination of the solid residue at 800^{0}C yielded synthetic rutile containing 92% TiO_2 and 2.6% FeO. After the crystallization of iron sulfate, the residual slightly acidic solution, containing iron(II), aluminum, magnesium, and titanium(III) sulfates, was found to contain about 22–24 mg/L of scandium.

Keywords: ilmenite, kinetic control, acid leaching, titanium white waste acid, synthetic rutile, diffusion control.

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Introduction

In 2020–2024, about 450–640 thousand tons of rutile concentrates (TiO_2 content of greater than 95%) and 7.6–8.8 million tons of ilmenite concentrates (TiO_2 content of 37–67%) were mined and produced worldwide. Rutile concentrates are scarce and highly liquid, mainly consumed by producers of welding electrode coatings. The production of titanium pigments, titanium sponge, ferroalloys, etc. is based on ilmenite concentrates [1].

According to the National Minerals Information Center (USA), Ukraine's proven titanium reserves are currently estimated at 8.4 million tons in terms of TiO_2: 5.9 million tons in ilmenite concentrates and 2.5 million tons in rutile concentrates. Of the 40 deposits of various genesis discovered, about 15 are well explored, and 8 deposits are currently being commercially developed [2].

Ilmenite ($FeTiO_3$) grains from different deposits differ in the degree of weathering (leukoxinization) and content of MnO, MgO, V_2O_5, and Al_2O_3 impurities. During the leucoxenization of ilmenite, iron(II) oxide is oxidized and gradually weathered, and the TiO_2 content increases. The ratio of

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FeO/Fe_2O_3 oxides, contained not in the concentrate but in ilmenite grains, is a characteristic indicator of the degree of its alteration [3]. In addition to 90–98% ilmenite, concentrates produced by mining and processing plants contain impurity minerals, due to which they additionally differ in the content of their components, such as P_2O_5, Cr_2O_3, SiO_2, etc.

Among the deposits currently under development, the least leukoxenized are the ilmenites of the Byrzulove continental eluvial-deluvial deposit, from which LLC VKF Velta extracts TiO_2-rich, weakly altered ilmenites (FeO/Fe_2O_3~2) (Table). Irshansk continental alluvial-deluvial deposits are exhausted to a greater extent. Of these, the United Mining and Chemical Company, in addition to weakly altered concentrates for the sulfuric acid production of pigment TiO_2 (FeO/Fe_2O_3=1–1.8), additionally produces rich ilmenite concentrates with a FeO/Fe_2O_3 ratio of 0.1–1 with a TiO_2 content of 60–65% for the pyrometallurgy of titanium products [4]. The most strongly altered (FeO/Fe_2O_3<0.01, TiO_2 65–68%) ilmenites are represented by complex coastal-sea ilmenite-rutile-zircon deposits of the Vovchansk and Samotkan deposits.

The annual design capacity of domestic mining and processing plants (MPP) for ilmenite concentrates is as follows: Irshansk – 400 thousand tons, Mezhyrichensk – 180 thousand tons, Valky Ilmenite – 65 thousand tons, Birzuliv – 270 thousand tons, Demuryne – 50 thousand tons and Vilnohirsk Mining and Metallurgical Plant – 200 thousand tons. In 2021, the operating MPPs remained at no more than half capacity and sold 430 thousand tons of ilmenite concentrates, of which only 20% were sold to the domestic market [11]. In-house processing is limited by low profitability and the high environmental impact of available technical solutions.

Promising technological processes need to address the following issues: high consumption of reagents in the extraction of iron compounds, limited demand for iron-containing products, and high costs for reagent recovery and waste recycling.

The sulfuric acid process for producing pigment TiO_2 from weakly altered ilmenite concentrates of Irshansk MPP, implemented at PJSC Sumykhimprom, involves generation of approximately 7 m^3 of titanium white waste acid (TWWA) per 1 ton of pigment TiO_2. Recycling TWWA for phosphate fertilizer production requires its concentration by evaporation, which accounts for up to a third of the cost of pigment production. Meanwhile, this multi-ton industrial waste can be directly used as an affordable reagent for the extraction of iron compounds in the chemical beneficiation of ilmenite concentrates (37–68% TiO_2) to synthetic rutile (90–96% TiO_2). The processes of producing synthetic rutile from ilmenite are currently considered the most promising for deepening the in-house processing of ilmenite concentrates in the near future.

In the production of synthetic rutile, impurities of iron compounds in ilmenite are commonly pre-activated by reduction. In most cases, altered ilmenite concentrates of deposits are reduced at $1100-1200^0$C to thinly embedded metallic iron in rutile granules. The metallic iron is leached by one method or the other to produce synthetic rutile.

This paper focuses on the Samotkan ilmenite concentrate as the object of study of synthetic rutile production processes. Its advantage is the lowest iron content and, accordingly, a lower yield of iron-containing by-products and a high content of titanium dioxide (Table).

The purpose of the study is to determine the kinetic parameters of the sulfuric acid leaching of

Chemical composition of ilmenite concentrates from deposits being developed by Ukrainian MPPs and the Stremihorodsk indigenous deposit

Component	Content, %									
	Stremiho-rodsk indigenous	Byrzulove	Mezhyrichensk	Irshansk weakly altered	Irshansk alluvial	Valky-Gatskiv alluvial	Vovchansk	Samotkan		
	ref. [3]	ref. [5]	ref. [6]	ref. [3]	ref. [3]	ref. [7]	ref. [8]	ref. [3]	ref. [9]	ref. [10]
TiO_2	49–51	52.8–55.2	54–62	52–54	64.13	57.4–66.8	62.8	66.24	68.4	67.1
FeO	41–44	25.6–32.7	12–25	28–30	1.78	2.5–17.5	–	0.24	0.12	–
Fe_2O_3	2.2–6.4	12.7–16.9	12–24	15–16	27.75	22.2–29.3	25.2–27.5	25.17	26.6	28.4
MgO	0.15–0.3	0.22–1.2	0.13–1	0.6–0.7	0.23	0.56–0.95	0.3	0.16–0.18	0.9	0.9
MnO	0.12–0.27	0.48–0.86	0.4–0.5	0.72	0.33	0.23–0.9	0.94	0.65	0.14	0.25
V_2O_5	0.2	0.18–0.21	0.2–0.3	0.2–0.25	0.2	0.11–0.33	0.27	0.2	0.21	0.21
Al_2O_3	0.15–0.87	0.3–0.78	0.5–1.7	0.75	1.8	0.6–0.77	0.42	1.38	0.8	0.8
CaO	0.17	–	0.14–0.51	0.8–0.99	0.14	0.06–0.5	0.05	0.003	–	0.056
SiO_2	3.5	0.45–0.51	0.9–2.0	0.6–2	3.03	0.81–1.1	0.2	1.28	–	0.79
Cr_2O_3	0.01–0.06	0.01–0.03	0.02–0.03	0.02–0.05	0.066	0.04–0.05	0.74	0.28	0.15	0.14
P_2O_5	0.02–0.08	0.06–0.08	0.05–0.1	0.02–0.1	0.29	0.13–0.27	–	0.13–0.14	0.18	0.19

iron from previously reduced ilmenite concentrates of the Samotkan deposit and the possibility of utilizing titanium white waste acid from the production of pigment titanium dioxide in the processes of synthetic rutile production.

Materials and methods

A Samotkan ilmenite concentrate consists of black, well rolled grains with the following fractional composition (μm): −160+150 (10%); −150+106 (54%); −106+75 (35%); and −75+63 (1%). In dried and averaged samples of the studied concentrate, the content of TiO_2, Fe_2O_3 and MnO is 66.3%, 26.7% and 0.25%, respectively. A moistened mixture of 200 g of ilmenite concentrate and 50 g of BAU-A charcoal (−250 μm) was thoroughly mixed and placed in a tall corundum crucible, covered with an approximately 30 mm layer of BAU-A charcoal (−3+1 mm), filled with quartz wool, and the crucible was closed with a lapped corundum lid equipped with a gas vent tube. The prepared sample was dried in a muffle furnace for 12 h at 120^0C, then heated to 1200^0C for 4 h, removed from the furnace and cooled to room temperature. The excess coal was separated by flotation in water, after which the precipitate of reduced ilmenite was dried at 120^0C for 2 hours.

The leaching of the reduced ilmenite samples with model H_2SO_4 solutions was carried out in a 130-mL cylindrical reactor equipped with a heat exchange jacket. The top-drive turbine stirrer (600 rpm) had a mechanical shaft seal that ensured the tightness of the reaction volume. A 2,000 g sample of the reduced ilmenite was placed in a glass test tube, the metallized material was fixed on the outside with a neodymium magnet magnetic field, and the inverted test tube was connected to one of the reactor inlets. 80 mL of H_2SO_4 solution of a given composition was added to the reactor, the stirrer was turned on, the desired solution temperature was set to $\pm 0.05^0$C, the reactor was sealed, and the magnet was removed. The sample of the reduced ilmenite was dropped into a sulfuric acid solution, and the hydrogen that started releasing was taken through a gas vent tube to a volumeter, which determined the gas volume with an accuracy of ±0.1 mL. The rate of dissolution of metallic iron was controlled indirectly by the volume of hydrogen released. The volumetric measurement of the degree of iron extraction was verified by redox titration of Fe^{2+} in the final leach solution. The concentration of scandium was verified by the atomic absorption spectral method.

The phase composition of the samples of the original and reduced ilmenite, as well as of the obtained synthetic rutile, was determined by X-ray phase analysis of the samples under Cu-Kα radiation using a DRON-2 diffractometer.

Results and discussion

Figures 1 and 2 show X-ray diffraction patterns of the initial ilmenite concentrate and the product of its reduction by coal.

Within 4 hours at 1200^0C, the trivalent ferric iron of the initial ilmenite concentrate is completely reduced by excess coal. Chemical analysis shows that 90% of the iron is reduced to metal, the rest is reduced to FeO. The composition of the reduced ilmenite is as follows: TiO_2 71.9% and Fe 20.1%. The diffraction pattern of the reduced ilmenite (Fig. 3), when compared with that of the original mineral (Fig. 2), shows the preservation of rutile reflexes, the disappearance of pseudorutile $Fe_2Ti_3O_9$ and α-Fe_2O_3 reflexes characteristic of the original strongly altered ilmenite, and the appearance of intense α-Fe reflexes and weak ilmenite reflexes.

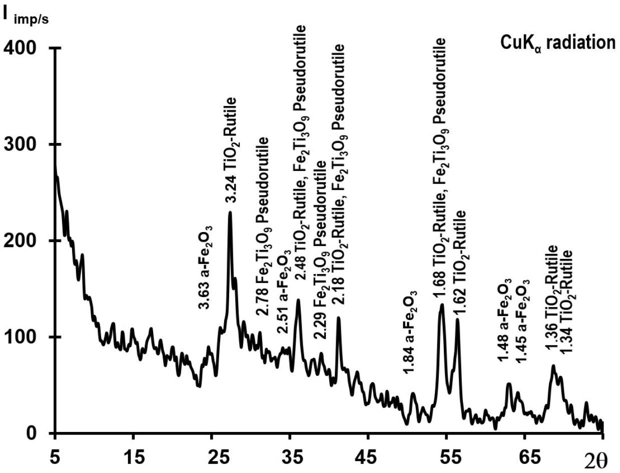

Fig. 1. X-ray diffraction pattern of ilmenite concentrate from the Samotkan deposit

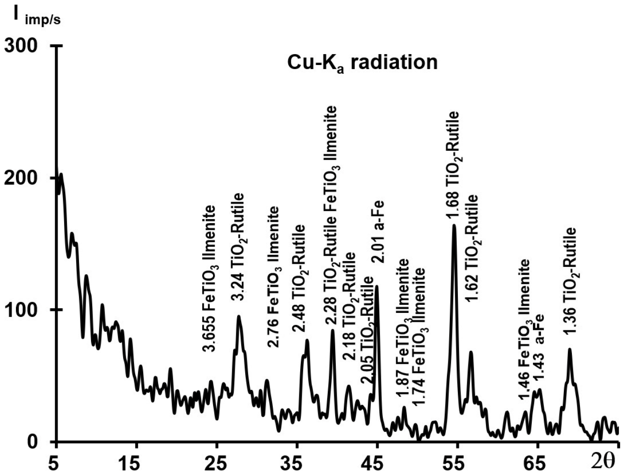

Fig. 2. X-ray diffraction pattern of Samotkan ilmenite concentrate reduced by coal at 1200^0C for 4 h

Figure 3 shows the time dependence of the degree of metallic iron extraction at different temperatures for the leaching of reduced ilmenite in 5 N sulfuric acid solutions. The degree of Fe extraction is the ratio of the weight of Fe that has passed into solution to its total initial weight in the sample of the reduced concentrate. The concentration of sulfuric acid in the model solution was chosen in accordance with the concentration of TWWA, which is 21–23% or approximately 5 Eq/L [3].

The extraction of iron from the coal-reduced Samotkan ilmenite concentrate, using 5 N sulfuric acid solution, proceeds as follows: ~57% of iron is extracted rapidly for 3 to 25 minutes depending on the process temperature, after which the leaching slows down sharply; at 70^{0}C, the degree of extraction reaches 92% and stops increasing after 2.5 hours of leaching.

The two mechanisms of iron extraction by hydrochloric acid from reduced ilmenite concentrates from Bangladeshi deposit were previously reported [12]. Ilmenite, annealed at 950^{0}C to oxidize all the iron and destroy the crystal structure of the primary mineral, was reduced with coal at 1050^{0}C. At 30–70^{0}C, 46–49% of iron was leached from this material using 5–15% hydrochloric acid solutions for 10–20 minutes under kinetic control, after which another 40% of the iron was extracted by long-term leaching under diffusion control of the process. In concentrates that were not subjected to oxidation before reduction, the process control was initially diffusion-based. It was concluded [12] that the particles of the reduced ilmenite have a surface layer and a core that differ in the metal availability for leaching.

Due to the high degree of leukoxenization, the Samotkan concentrates contain virtually no primary ilmenite and ferrous iron. After reduction, their properties may be closer to those of the pre-oxidized reduced Bangladeshi ilmenites. However, despite certain similarities, the kinetic curves of these materials differed. The metal leached at this stage was taken to be 100%, the degree of leaching was recalculated relative to this amount of iron α'(Fe)=(Fe)/0.57, and the kinetic dependences were plotted (Fig. 4).

The obtained kinetic dependences were analyzed for compliance with the 21 equations of diffusion-kinetic models of formal and informal kinetics of heterogeneous reactions [13]. The ability of models to linearize the experimental data over the widest possible range of leaching rates was taken as the criterion for the model's fit. The data analysis shows that the largest linear regions were observed for the first-order kinetic model of the reaction F1[1] ($-\ln(1-\alpha)$ vs. Kτ) shown in Fig. 5.

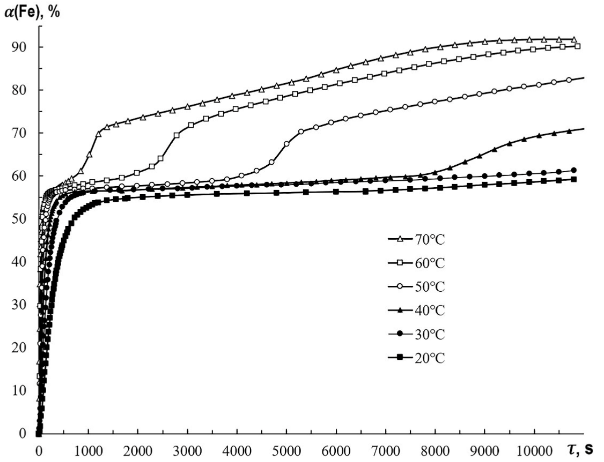

Fig. 3. The degree of iron leaching from the reduced Samotkan ilmenite concentrate at different temperatures. C^0(H$_2$SO$_4$)=5 Eq/L

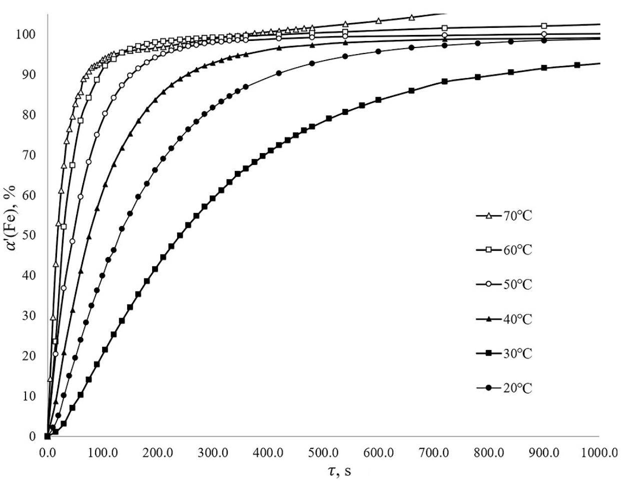

Fig. 4. The degree of leaching of the ferrous iron fraction available for rapid extraction from the reduced ilmenite concentrate as a function of time at different temperatures. C^0(H$_2$SO$_4$)=5 Eq/L

The rate of iron extraction from the reduced Samotkan ilmenite at the first stage of leaching is consistent with the first-order reaction model to a value of α'(Fe)=0.90–0.95 with a determination coefficient in the range of R^2=0.9913–0.9992. As the values of α'(Fe) approach one, the model curves begin to deviate from linearity. The slope of the linear sections of the isothermal curves represents the leaching reaction rate constants at the first stage of the process. These values were used to determine the apparent activation energy according to the integral approach. To do this, a graph of the dependence of the natural logarithm of the reaction rate constants on the inverse

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[1] The designation «F1» is taken form ref. [13].

temperature was plotted in the coordinates of the Arrhenius equation (Fig. 6). The slope of this curve is equal to $\mathrm{tg}\beta = -E_{app}^{act}/R$, where E_{app}^{act} is the apparent activation energy and R is the universal gas constant. The obtained value of the apparent activation energy of 40.4 kJ/mol corresponds to the kinetic control of the first stage of iron leaching.

The time required to achieve a constant degree of transformation α'(Fe) at each temperature was determined using the differential approach for calculating the apparent activation energy from the kinetic curves of Fig. 4. Presenting these data in the coordinates of the Arrhenius equation (Fig. 7) allows determining the apparent activation energy and tracing its change with the degree of iron leaching. With an increase in the degree of metal extraction α'(Fe) from 0.5 to 0.9 and the exhaustion of iron available for leaching, the apparent activation energy decreases from 42.6 kJ/mol to 40.2 kJ/mol, which may indicate a change in the mechanism of interaction, with the transition of the process to intradiffusion control.

To determine the reaction order of the initial stage of iron leaching with respect to the concentration of hydrogen ions, the dependence of the degree of iron extraction over time at different concentrations of sulfuric acid was obtained (Fig. 8). These kinetic curves were used to determine the time to achieve a given degree of iron extraction at different concentrations of sulfuric acid and to plot curves in the coordinates lg(α/τ) vs. lg[H^+] at different degrees of iron extraction α(Fe) (Fig. 9). The slopes of the trend lines of the obtained curves (0.36–0.42) represent the order of the leaching reaction with respect to the hydrogen ion at different degrees of conversion. These values show that the rate of iron leaching at the first stage is weakly dependent on the acidity of the solution, and reduced ilmenite is a promising material for utilizing titanium white waste acid in iron (II) sulfate solutions with low residual acidity.

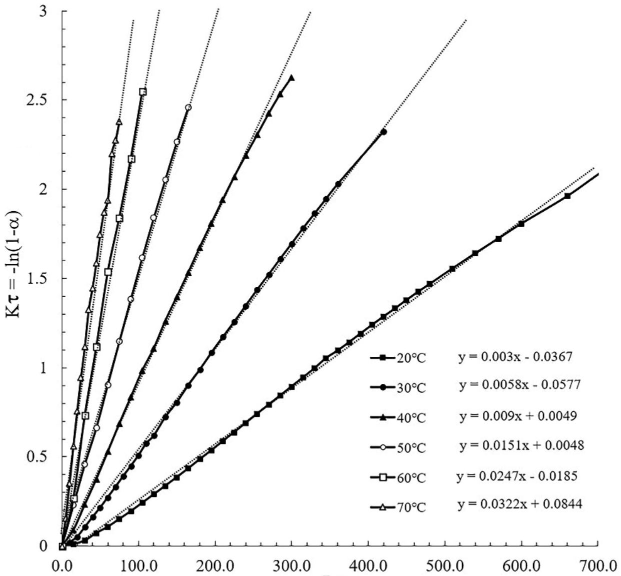

Fig. 5. Dependence of the parameter of the kinetic equation of the first-order reaction model F1 on the time of iron leaching

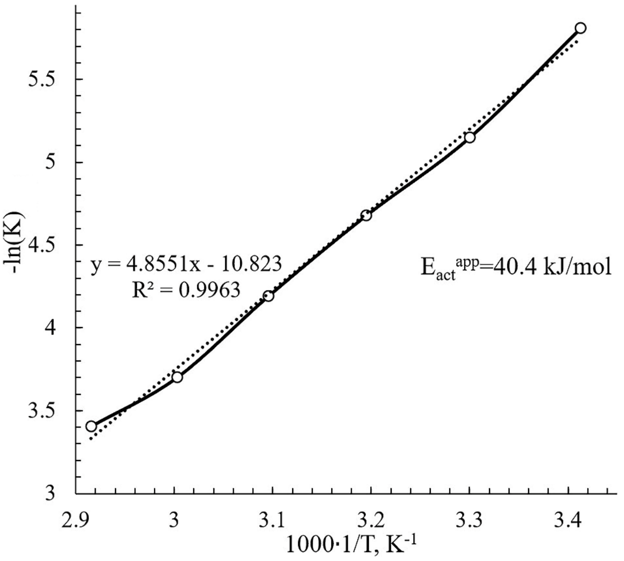

Fig. 6. Arrhenius curve of iron leaching from reduced ilmenite concentrate, according to the kinetic data of the F1 model, Kτ=−ln(1−α'(Fe))

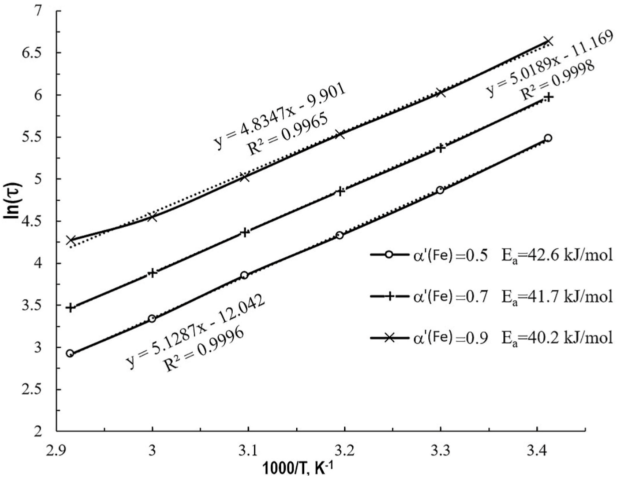

Fig. 7. Arrhenius curves of iron leaching from reduced ilmenite concentrate, by the time of reaching a constant degree of conversion

The results of kinetic studies allowed proposing a two-stage leaching scheme for the recovered Samotkan ilmenite concentrate with the production of synthetic rutile and utilization of TWWA. In the first stage, the reduced ilmenite, from which about half of the iron content was partially removed by pre-leaching, was leached for 3 h at 75°C with a double excess of a fresh portion of titanium white waste acid of the following composition: H_2SO_4 22%, $FeSO_4$ 8%, and $TiOSO_4$ 1%. The resulting precipitate was filtered, washed with water, and calcined at 800^0C for 1 hour. According to the chemical analysis, the content TiO_2, FeO and MnO in the samples was 92%, 2.6% and 0.32%, respectively. In the X-ray diffraction pattern of the obtained synthetic rutile (Fig. 10), the main reflexes are related to the rutile form of titanium dioxide, and several weak reflexes are attributed to the impurity of ilmenite, probably represented by a mixture of complex oxides of iron, manganese and titanium. The mother liquor was cooled to $+15^0$C to crystallize and separate the $FeSO_4{\cdot}7H_2O$ precipitate. In the second stage, the calculated amount of reduced ilmenite was dosed with stirring into the partially neutralized TWWA filtrate heated to approximately 60^0C. The process was terminated when the desired residual acid concentration was reached (3–5 g/L, ~1 hour). After separation of the suspension by filtration, the partially leached precipitate was transferred to the stage of interaction with a fresh portion of titanium white waste acid.

An additional amount of $FeSO_4{\cdot}7H_2O$ was crystallized from the filtrate at $+15^0$C. The resulting slightly acidic 3–5 g/L H_2SO_4 filtrate contains 22–24 mg/L scandium in addition to sulfates of iron(II), magnesium, aluminum and titanium(III). Scandium can be extracted from the weakly acidic solution with an impregnated tributyl phosphate solid extractant, and the refinery can be separated or sent for disposal as solid waste after evaporation and neutralization. The scheme has been successfully tested at the laboratory level. Due to the growing demand for iron salts as a dechromator for cement mixtures and the expanding use of iron-containing reagents in wastewater treatment, regional markets are currently in need of additional quantities of iron sulfate.

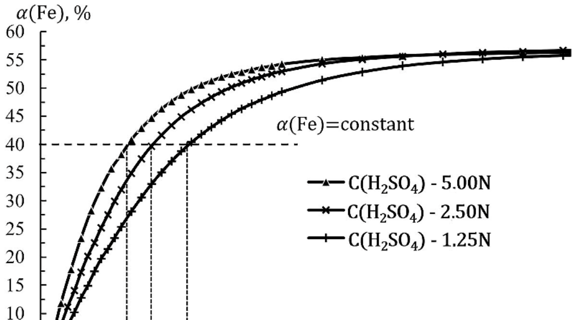

Fig. 8. Changes in the degree of iron leaching from reduced Samotkansky ilmenite over time at different concentration of sulfuric acid

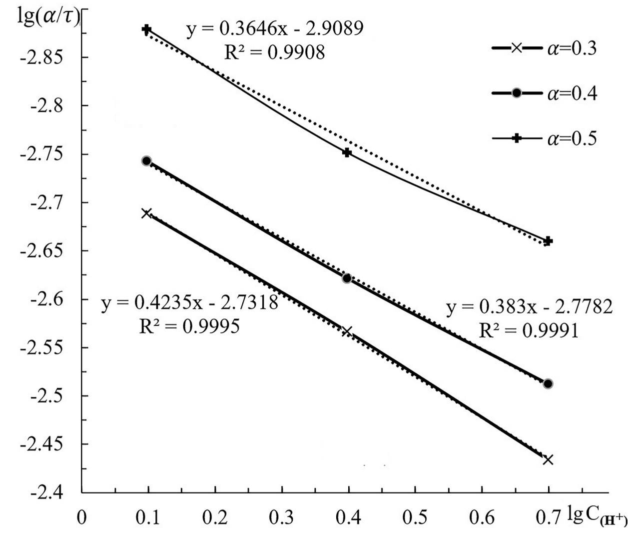

Fig. 9. Graphical determination of the reaction order of leaching of ferric iron by hydrogen ion

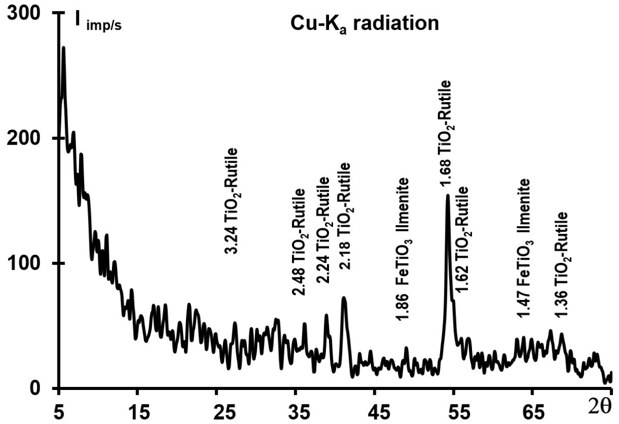

Fig. 10. X-ray diffraction pattern of synthetic rutile

Conclusions

The reduction of the ilmenite concentrate of the Samotkan deposit with coal at 1200^0C for 4 hours leads to the complete reduction of iron(III) compounds and the conversion of 90% of them to metallic iron. During leaching with sulfuric acid solutions, more than 50% of iron is removed from reduced ilmenite rapidly by a first-order reaction mechanism with apparent activation energy of 40.2–42.6 kJ/mol, which corresponds to the kinetic control of the process. The order of reaction with respect to hydrogen is 0.36–0.42. The transition of the process to diffusion control is accompanied by a sharp slowdown in leaching. The process of synthetic rutile production by leaching the reduced Samotkan ilmenite concentrate with titanium white waste acid was modeled in a laboratory experiment. Dividing the leaching of reduced ilmenite into separate stages with kinetic (60^{0}C, 1 hour) and diffusion control (75^{0}C, 3 hours) with countercurrent operation of the process allows obtaining synthetic rutile with a TiO_2 content of at least 92% and recycling titanium white waste acid into weakly acidic solutions of iron(II), aluminum, magnesium, titanium(III) sulfates and iron sulfate.

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ВИЛУГОВУВАННЯ ВІДНОВЛЕНОГО ІЛЬМЕНІТОВОГО КОНЦЕНТРАТУ САМОТКАНСЬКОГО РОДОВИЩА РОЗЧИНАМИ СУЛЬФАТНОЇ КИСЛОТИ

О.В. Кожура, Є.О. Цибуля, І.Л.Коваленко

Сильнозмінений ільменітовий концентрат Самотканського родовища при 1200^{0}C протягом 4 год відновлювали вугіллям до продукту у якому 90% заліза відновлено до металу. Залізо із відновленого ільменіту вилуговували 6–22% розчинами сульфатної кислоти протягом трьох годин при температурах 20–70^{0}C. Виявлено, що вилуговування металічного заліза кислими розчинами в початковий період відбувається швидко за механізмом реакції першого порядку $K\tau=-\ln(1-\alpha)$ з уявною енергією активації 40,2–42,6 кДж/моль, що відповідає кінетичному контролю процесу. Порядок реакції по водню склав 0,36–0,42. Після вилучення ~57% заліза механізм вилуговування змінюється, процес різко уповільнюється. Проведено лабораторне моделювання двостадійного протитечійного процесу одержання синтетичного рутилу при вилуговуванні відновленого ільменіту відходом гідролізної сульфатної кислоти. При дозованій подачі відновленого ільменіту стадія швидкого розчинення заліза може бути використана для керованого зниження кислотності відходу до рівня 3–5 г/л H_2SO_4. Необхідної глибини вилучення домішок досягнуто дією надлишку початкової 22% гідролізної кислоти на частково вилугуваний відновлений ільменіт протягом 3 год при 70^{0}C. Прожарюванням твердого залишку при 800^{0}C отримано синтетичний рутил, що містить 92% TiO_2 і 2,6% FeO. Після кристалізації залізного купоросу у залишку слабокислого розчину сульфатів заліза(II), алюмінію, магнію, титану(III) міститься 22–24 мг/л скандію.

Ключові слова: ільменіт, кінетичний контроль, кислотне вилуговування, гідролізна сульфатна кислота, синтетичний рутил, дифузійний контроль.

LEACHING OF REDUCED ILMENITE CONCENTRATE FROM THE SAMOTKAN DEPOSIT USING SULFURIC ACID SOLUTIONS

O.V. Kozhura [*]***, E.O. Tsybulya, I.L. Kovalenko***

Ukrainian State University of Science and Technologies, Dnipro, Ukraine

[*] **e-mail: kozhuraoleg@gmail.com**

A strongly altered ilmenite concentrate from the Samotkan deposit was reduced with coal at 1200^{0}C for 4 hours, yielding a product in which 90% of iron was reduced to the metallic state. Iron was leached from the reduced ilmenite using 6–22% sulfuric acid solutions at temperatures of 20–70^{0}C for three hours. It was found that the leaching of metallic iron by acidic solutions proceeds rapidly in the initial period, following a first-order reaction mechanism with an apparent activation energy of 40.2–42.6 kJ/mol, indicating kinetic control of the process. The reaction order with respect to hydrogen was determined to be 0.36–0.42. After approximately 57% of iron was extracted, the leaching mechanism changed, causing a sharp slowdown in the process. Laboratory modeling of a two-stage countercurrent process was conducted to produce synthetic rutile by leaching the reduced ilmenite with titanium white waste acid. By metering the feed of reduced ilmenite, the rapid iron dissolution stage can be utilized to regulate the acidity of the waste to a level of 3–5 g/L H_2SO_4. The required level of impurity removal was achieved by exposing the partially leached reduced ilmenite to an excess of the initial 22% titanium white waste acid for 3 hours at 70^{0}C. Calcination of the solid residue at 800^{0}C yielded synthetic rutile containing 92% TiO_2 and 2.6% FeO. After the crystallization of iron sulfate, the residual slightly acidic solution, containing iron(II), aluminum, magnesium, and titanium(III) sulfates, was found to contain about 22–24 mg/L of scandium.

Keywords: ilmenite; kinetic control; acid leaching; titanium white waste acid; synthetic rutile; diffusion control.

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