UDC 669.662.791
DOI: 10.15587/1729-4061.2025.328308

IDENTIFYING THE CONDITIONS FOR PRODUCTION OF SYNTHETIC RUTILE BY LEACHING OF REDUCED SAMOTKAN ILMENITE WITH FERRIC SULFATE SOLUTIONS

Oleg Kozhura
Corresponding author
PhD*
E-mail: kozhuraoleg@gmail.com
Yevhen Tsybulia
PhD Student*
Alona Derimova
Assistant*
Viktoriia Yaroshenko*
*Department of Inorganic Substances and Ecology
Ukrainian State University of Science and Technologies
Nauky ave., 8, Dnipro, Ukraine, 49005

This study investigates the chemical beneficiation processes for Samotkan ilmenite concentrates, reagent regeneration, and the recycling of extracted iron compounds. The task addressed is to devise technology for obtaining synthetic rutile and converting by-product iron compounds into commercially valuable materials. Kinetic parameters of iron leaching from metallized ilmenite obtained by reducing Samotkan ilmenite concentrate with carbon at 1200 °C for 4 hours using ferric sulfate solutions were determined. Up to 8 % iron extraction, the kinetics followed the autocatalytic Prout–Tompkins model (kt=ln(a/(1–a)), with apparent activation energy Eapp=62.7 kJ/mol. At higher degrees of iron extraction, the process was consistent with the shrinking core model (kt=1–(1–a)1/3), with apparent activation energy Eapp=47.3 kJ/mol. The reaction order with respect to Fe^{3+} was found to be close to first order. Additional removal of impurities from the residue of oxidative leaching was achieved by treatment with 15 % H_2SO_4 solution at 60 °C and subsequent calcination at 800 °C, resulting in the production of synthetic rutile with a TiO_2 content of 92 %. It was established that the regeneration of oxidative leaching solutions could be carried out via catalytic oxidation of $FeSO_4$ solutions using oxygen. At pH 1.1–1.5 and 60 °C in the presence of NO, ferrous iron was quantitatively oxidized within 1–3 hours. Efficient mass transfer under high gas content in the gas-liquid mixture allows oxidation to proceed without elevated oxygen pressure or temperature. A portion of the ferric iron was recovered as high-purity crystalline $Fe_4(OH)_{10}SO_4$ precipitates, which, upon calcination at 750 °C, yielded 99.4 % Fe_2O_3, suitable for pigment production. The low reagent consumption and the conversion of iron into marketable products underscore the potential for industrial-scale implementation of this process

Keywords: Samotkan weathered ilmenite, synthetic rutile, ferric sulfate, hydroxysulphate, recycling, TiO_2

Received 07.02.2025
Received in revised form 28.03.2025
Accepted date 15.04.2025
Published date 30.04.2025

How to Cite: *Kozhura, O., Tsybulia, Y., Derimova, A., Yaroshenko, V. (2025). Identifying the conditions for production of synthetic rutile by leaching of reduced Samotkan ilmenite with ferric sulfate solutions. Eastern-European Journal of Enterprise Technologies, 2 (6 (134)), 14–23. https://doi.org/10.15587/1729-4061.2025.328308*

1. Introduction

The basic raw material for the production of titanium products is ilmenite concentrates from bedrock and placer deposits [1]. In the process of destruction of bedrock, the released grain of primary ilmenite ($FeTiO_3$) begins to weather, FeO from its composition is oxidized and washed out in the form of Fe_2O_3. Due to a strong decrease in the thermal effect of interaction with sulfuric acid, modified ilmenites, where the ratio $C_{Fe(II)}/C_{Fe(III)}$ has reached a value of 1:1, are not used in pigment production according to the sulfate scheme [2]. For the production of welding electrode coatings, obtaining pigment TiO_2 or titanium sponge using chlorine technology, it is necessary to remove impurities from ilmenite, primarily iron compounds. To this end, they are either remelted with coke using ore-thermal smelting methods at 1650–1750 °C to produce cast iron and slags with a high titanium content (TiO_2 81–85 %, FeO 5–8 %), or subjected to chemical beneficiation to obtain synthetic rutile (SR) (>90 % TiO_2). In 2023, the price of titanium slag was USD 1050/t; the average price of synthetic rutile from the largest producer, Iluka Resources, was USD 1332/t, while the average price of natural rutile was USD 1747/t [3]. Compared to natural (>96 % TiO_2), synthetic rutile is more porous, chlorinated faster and more efficiently with the formation of $TiCl_4$ [4], but it is cheaper due to the lower TiO_2 content (90—95 %) and higher impurity content.

The great advantage of ore-thermal smelting is the production of marketable iron and titanium products from low grades of ilmenite with minimal waste generation [5]. For TiO_2-rich ilmenites, the process of smelting titanium slags is quite inefficient, with an electricity consumption of more than 2.5 thousand kWh per ton of slag [6] due to the low iron content, the yield of pig iron is not significant, and the TiO_2 content in the slag compared to the concentrate increases by only 17–20 %.

Compared with the smelting of titanium slags, chemical beneficiation are characterized by lower energy costs, a higher TiO_2 content, and a lower content of impurities in SR [7]. At the same time, these processes face acute issues of high reagent consumption and their regeneration, as well as the removal of iron from the ilmenite composition not in the form of a valuable metal but in the form of low-value compounds and waste.

In Ukraine, only placer titanium deposits are currently being developed, and the main products of operating mining and processing enterprises are ilmenite concentrates of various degrees of alteration [8]. The most altered (highly leucoxenized) ilmenite concentrates (TiO_2 65–67 %, Fe_2O_3 26–28 %) are extracted from ores at the Samotkan and Vovchansk complex coastal-marine ilmenite-rutile-zirconium placers [9].

For highly altered ilmenites, it is more expedient to remove iron impurities by chemical enrichment; therefore, the issues of devising technological processes for obtaining synthetic rutile with low costs for the removal of iron oxide impurities, reagent regeneration, and recycling of iron-containing by-products are relevant.

2. Literature review and problem statement

To obtain synthetic rutile, numerous technological solutions have been proposed, which mainly combine pyrometallurgical preparation of the raw material and chemical extraction of impurities from it into aqueous solutions of leachants. In the industrially implemented Benelite process, ilmenite is reduced with heavy oil at <900 °C. The resulting FeO is leached with hydrochloric acid in autoclaves, obtaining SR with a TiO_2 content of up to 95 % [10, 11]. The use of relatively low temperatures at the preparatory stage reduces energy consumption and depreciation costs of furnace equipment. At the same time, due to the rather low chemical potentials of FeO, high-concentration hydrochloric acid is consumed for its leaching, and high interaction temperatures lead to significant energy consumption and increased requirements for corrosion resistance of equipment. The resulting waste of strongly acidic solutions of chlorides of leached metals is consumed only for the production of coagulants ($FeCl_3$ solutions), otherwise they are subjected to pyro hydrolysis for the regeneration of hydrochloric acid. High energy costs for water evaporation and thermal decomposition of $FeCl_2$ are critical for the production of SR by the Benelite process, so such enterprises are small and are set up in regions where there is a significant need for $FeCl_3$ solutions.

Improvements proposed in the Murso [12], Austpac [13], Altair [14] processes have increased the quality of the product of chemical beneficiation of ilmenites but the high costs of leaching FeO, recycling of $FeCl_2$ solutions, and regeneration of hydrochloric acid have not allowed these processes to go beyond pilot tests.

It is possible to reduce energy consumption at the stage of chemical enrichment, reduce the price and cost of reagents, and lower the requirements for corrosion resistance of equipment when reducing ilmenite iron oxides at 1100–1200 °C to iron. A larger carbon footprint and active wear of the furnace lining compensate for the high chemical potential of iron in reduced ilmenite (RI).

In the main industrial method for obtaining SR, the Becher process [15], reduced iron is extracted from 1–1.5 % NH_4Cl solutions by aeration with air at 60–70 °C for 9–16 h in the form of finely dispersed suspensions of iron (III) hydroxide. The method is characterized by low reagent consumption, moderate energy consumption, but requires the use of ilmenites with a high total content of titanium and iron oxides >93 % and is accompanied by the formation of up to 2 tons of waste per ton of SR. The possibility of burying waste in mining operations allows Australian producers to avoid the costs of their disposal but makes the development of the method dependent on the geological features of the region.

Oxidative leaching of iron with RI acidified solutions of ferric salts with regeneration of the leachant during oxidation of ferric salts with air is proposed in the Summit process [16]. Compared with the Becher process, an order of magnitude higher leaching rate is achieved while reducing its costs. However, the low rate of oxidation of ferric solutions with air during regeneration of the leachant and the low quality of the precipitates of by-products of ferric hydroxide salts have become an obstacle to the development of this process. To increase the value of the by-product of the Summit process, methods have been devised for obtaining a range of valuable iron oxide pigments from spent weakly acidic solutions of $FeCl_2$ [17]. Methods for regeneration of $FeCl_3$ solutions were also analyzed and the conclusion about the prospects of catalytic oxidation of iron (II) solutions with air or oxygen was confirmed. The studies performed showed that activated carbon and $CuCl_2$ are ineffective catalysts for the oxidation of iron (II) with oxygen at concentrations >0.1 M. Therefore, the issue of regeneration of leaching solutions for the Summit process remained unresolved.

Oxygen oxidation of iron (II) salt solutions at pH less than 2 occurs slowly. Its acceleration is achieved by carrying out oxidation under autoclave conditions at elevated oxygen pressure and high temperatures. The oxidation process can also be accelerated by introducing catalysts based on bound nitrogen compounds in oxidation states 2–4 into the solution, which showed higher catalytic activity than copper salts and activated carbon. In [18], the catalytic action of nitrites was investigated and the reaction mechanism of catalytic oxidation of $FeSO_4$ solutions in 1 M sulfuric acid with oxygen was proposed. To confirm the mathematical models, the oxidation process was simulated at elevated oxygen pressure (4 atm) at 25 °C. For quantitative oxidation of 0.1 mol/l of Fe^{2+} salt solution, 4.5 mmol of nitrite must be introduced into it, which during oxidation is converted to nitrate ion. Autoclave oxidation of $FeSO_4$ with oxygen in an acidic medium in the presence of sodium nitrite and nitric acid at 120 °C was also investigated in [19]. Nitric acid has practically no effect on the interaction of oxygen with Fe^{2+} ions, whereas sodium nitrite catalyzes this interaction. For the quantitative oxidation of 0.2 mol/l $FeSO_4$ within an hour, the nitrite consumption was 3.89 mmol/l. Oxygen oxidation of acidic solutions of iron (II) salts catalyzed by bound nitrogen compounds can be used in the regeneration of solutions of iron (III) salts. However, the data presented relate to oxygen oxidation only of strongly acidic solutions of iron (II) salts. Instead, it is desirable to combine the regeneration of the oxidant during chemical beneficiation of RI with hydrolytic precipitation of leached iron from weakly acidic solutions. This is possible during the catalytic oxidation of weakly acidic iron (II) solutions with oxygen, which has remained unnoticed by researchers.

Due to the high content of TiO_2 and the low content of impurity minerals, it is advisable to subject the ilmenite concentrates from the Samotkan deposit to chemical beneficiation in SR after carbothermic reduction to iron. The extraction of iron from RI with ferric (III) solutions should be carried out efficiently and at low costs. To devise a complete, competitive technological solution, it is necessary to solve the problem of regeneration of the leachant and recycling of by-products of ferric iron by catalytic oxidation with oxygen of weakly acidic solutions of ferric (II) salts.

3. The aim and objectives of the study

The purpose of our study is to determine the conditions for carrying out the processes of chemical beneficiation of ilmenites from the Samotkan deposit to synthetic rutile, regeneration of reagents and recycling of iron into products for which there is a demand. This could create opportunities not only to export fossil raw materials but also to process them into products with higher added value.

To achieve the set goal, it is necessary to solve the following tasks:

– to carry out carbothermic reduction of iron compounds from the Samotkan ilmenite concentrate to metallic iron;

– to establish the kinetic parameters of iron leaching from metallized ilmenite with solutions of ferric(III) sulfate;

– to carry out additional acid extraction of impurities from the intermediate beneficiation product and obtain synthetic rutile with a high TiO_2 content;

– to investigate the processes of regeneration of leaching solutions and recycling of iron-containing compounds extracted during leaching.

4. The study materials and methods

The object of our study was the processes of chemical beneficiation of Samotkan ilmenite concentrates, regeneration of reagents, and recycling of extracted iron compounds.

The principal hypothesis of the study is to determine the possibility of simultaneously solving the tasks of reagent regeneration and recycling of extracted iron compounds using catalytic oxidation with oxygen of weakly acidic solutions of iron (II) salts in the presence of nitrogen compounds (II–IV).

In aqueous solutions of iron salts, coalescence of gas bubbles is sharply reduced compared to water. According to the assumption adopted, the creation of a stable gas-liquid suspension with a high gas content in the entire volume of the reactor should allow the oxidation of a weakly acidic solution of $FeSO_4$ with oxygen in the presence of NO without the use of elevated pressure and temperature.

The significant difference in the conditions of carbothermic reduction of laboratory samples from the process conditions in industrial furnaces imposes restrictions on the extension of the conclusions of laboratory studies to industrial conditions.

To protect the product of carbothermal reduction from oxidation, the crucible with the material was purged with argon. In previous work [20], ilmenite reduction was carried out without the use of a protective inert gas, and, possibly due to the action of atmospheric oxygen, the composition of the upper RI layer differed from the main part of the material. A 200 g sample was dried at 120 °C for 2 h and the averaged Samotkan ilmenite concentrate (Fig. 1) (chemical composition, %: TiO_2 – 66.3, Fe_2O_3 – 26.7, MnO – 0.25; fractional composition, μm: −160+150 (10 %); −150+106 (54 %); −106+75 (35 %); −75+63 (1 %)) in a corundum crucible (Ø 60 mm, height 125 mm) were thoroughly mixed with 50 g of activated carbon (BAU-A fraction – 250 μm). The mixture was covered with a ~30 mm layer of activated carbon (fraction −5+3 mm) and covered with a ground corundum lid. Two corundum tubes were inserted into the holes of the lid: a tube 500 mm long was used to supply argon to the crucible, $Ø^{out}$=5 mm and $Ø^{int}$=2 mm, and gaseous products of the interaction were removed with a tube 30 mm long, $Ø^{out}$=5 mm and $Ø^{int}$=0.7 mm. The crucible with the prepared charge was placed in a mine laboratory electric furnace SSHOL-1.1,6/12–MOZ (Ukraine), the argon supply tube was passed through the hole in the furnace lid, and it was connected to the argon supply line. By passing argon at a rate of ~120 ml/min, the mixture was isolated from the oxidizing effect of air, the crucible with the charge was heated to predefined temperature (1050 to 1200 °C), kept for 4 h, the heating was turned off and cooled to room temperature without stopping the argon supply.

The reduced ilmenite was sieved through a 0.160 μm sieve and separated from excess coal by flotation in water. For this purpose, the product of reduction calcination was mixed with 1 l of distilled water in a 1 l measuring cylinder, after settling the concentrate (density ≥4 g/cm^3) for 2 min, ~800 ml of the mixture of water and coal suspended in it (density<0.9 g/cm^3) was decanted. The volume of the mixture was brought to 1 l with distilled water, and the separation was repeated 7–8 times. The resulting metallized ilmenite was filtered and dried at 120 °C for 1 h. The dark brown ilmenite concentrate turns into a black reduction product, while the particle size distribution of the material does not change.

Fig. 1. Grains of Samotkan ilmenite concentrate. Carl Zeiss Jena NU-Microscope

The content of metallic iron in reduced ilmenite was determined by oxidimetric titration of the solution formed by leaching a 0.5 g sample of reduced ilmenite in 100 ml of 1 M $FeCl_3$ solution in 2 M KCl solution at 50 °C for 5 h.

The content of Fe^{2+} and Fe^{3+} in solutions and solid materials was determined by oxidimetric titrations. Samples of concentrates of 0.1–1 g were previously decomposed with a mixture of 30 % sulfuric and 40 % hydrofluoric acids in a mass ratio of 2:1. All leaching, decomposition, and titration operations were carried out in a protective gas atmosphere (Ar).

After determining the concentration of Fe^{2+} in the leaching solutions, the amount of metallic iron consumed for the reduction of $Fe_2(SO_4)_3$ was calculated. The degree of iron extraction $\alpha(Fe)$ was determined in relation to this amount to the initial content of total iron in the sample.

Studies on the kinetics of leaching of metalized ilmenite with $Fe_2(SO_4)_3$ solutions, the processes of extracting impurities from the product of oxidative leaching with H_2SO_4 solutions, and the study on the processes of regeneration of $Fe_2(SO_4)_3$ solutions by oxidation of $FeSO_4$ solutions with oxygen were carried out in the installation shown in Fig. 2. 300 ml of the studied solutions of a given composition were introduced into a cylindrical reactor (1) $Ø^{int}$ 65 mm, height 120 mm, volume 360 ml. The leaching processes of metalized ilmenite and its oxidative leaching product were studied at a stirrer rotation speed of 600 rpm.

To analyze the change in the concentration of iron (II), the filtrates of the oxidative leaching solutions were sampled continuously at a given speed by a dosing pump (9). An adjustment was made for the time required for the solution to pass through the sampling lines at different pump speeds. Samples of about 1 ml were initially taken every 30 seconds, after the leaching slowed down, the sampling time was gradually increased to 300–500 seconds. Analysis of the selected samples revealed the composition of the solution at the middle of the range of sampling times for each sample.

The intermediate product obtained during oxidative leaching was subjected to leaching with sulfuric acid solutions with a concentration of 5–25 % at 40–80 °C for 3 hours at a solid:liquid ratio=1:5.

The predefined temperature of the solutions was set and controlled with an accuracy of ±0.05 °C.

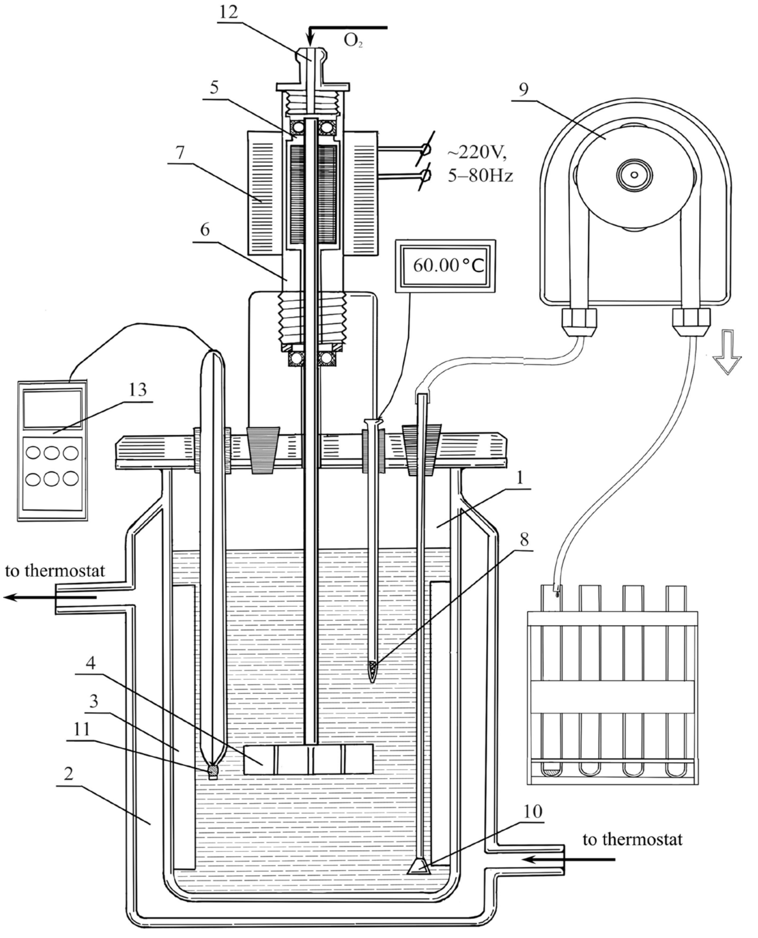

Fig. 2. Installation for leaching iron from reduced ilmenite and oxidation of $FeSO_4$ solutions with oxygen: 1 — glass cylindrical reactor; 2 — heat exchange jacket; 3 — reflective membranes; 4 — turbine mixer; 5 — magnetic rotor; 6 — protective sleeve; 7 — motor stator; 8 — thermal resistance; 9 — dosing pump; 10 — Schott filter; 11 — combined platinum electrode; 12 — oxygen supply pipe; 13 — potentiometer

Intensive mass transfer for the oxidation of a weakly acidic (pH 1.5) $FeSO_4$ solution was provided by mechanical gas dispersion with an 8-blade turbine mixer (blade height 8 mm, length 18 mm) at a shaft rotation speed of 3000 rpm. This ensured the creation of a stable gas-liquid suspension in a reactor equipped with four reflective membranes with a height of h=7 mm, which filled the entire volume of the reactor and had a high 16.7 % (vol.) gas content. When studying the oxidation processes of $FeSO_4$, the free volume of reactor (1) was purged with oxygen, branch pipe (12) was connected to a gas holder of a volume meter filled with (99.8 %) oxygen. A predefined volume of nitrogen (II) oxide was introduced under the $FeSO_4$ solution layer, and stirring was turned on. The rate of oxidation of Fe^{2+} ions was controlled indirectly, by the volume of absorbed oxygen.

The phase composition of the obtained products was determined on a DRON-2 X-ray diffractometer (JSC Bourevestnik, Russia) using Co-K_a radiation.

5. Results investigating the processes of chemical beneficiation of ilmenite

5. 1. Carbothermal reduction of Samotkan ilmenite concentrate

The completeness of the reduction of the samples was controlled by the fraction of ferrum reduced to metallic iron. An increase in the reduction temperature from 1050 to 1200 °C leads to a sharp increase in the fraction of metallic iron in the reduction product from 60 to 90 % (Table 1).

Table 1

Change in metallization of Samotkan ilmenite concentrate depending on the temperature of carbon reduction

Temperature, °C	Fe_{mtl}/Fe_{gen}, %
1050	57.9
1100	64.7
1150	87.3
1200	90.2

In this case, the change in the metallization of the sample when the temperature increases from 1150 °C to 1200 °C was small and did not exceed 4 %. According to the data on chemical analysis, within 4 h at 1100–1200 °C, the iron (III) of the initial ilmenite concentrate is completely reduced by carbon. In the X-ray diffraction pattern of the reduction product at 1200 °C, the reflexes of Fe_2O_3 and pseudo rutile characteristic of Samotkan ilmenite disappear (Fig. 3). The composition of the ilmenite concentrate reduced at 1200 °C for 4 h is TiO_2 – 72.1 %, $Fe_{gen.}$ – 20.2 %. In the diffraction pattern of the reduced product, the reflexes of rutile are preserved, and intense reflexes of iron (α-Fe) and pseudo brookite appear.

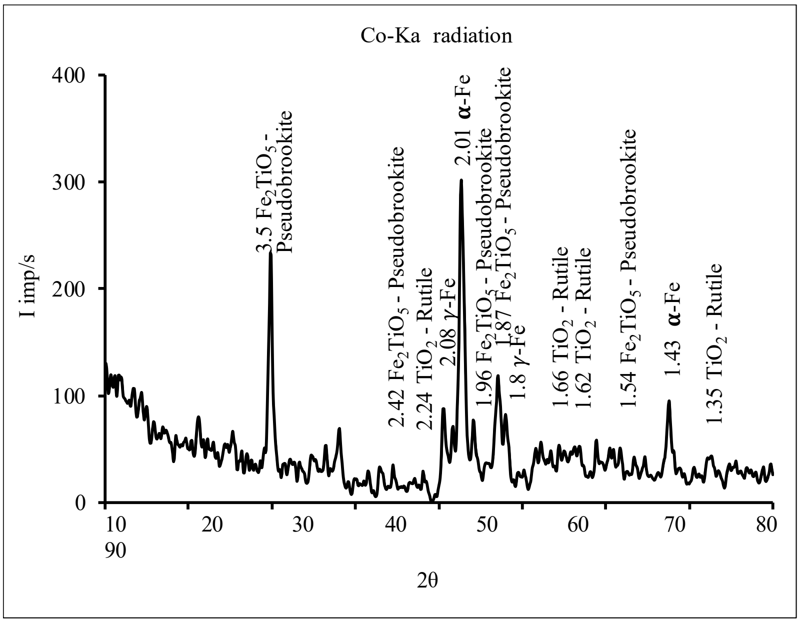

Fig. 3. X-ray diffraction pattern of carbon-reduced Samotkan ilmenite concentrate at 1200 °C for 4 h

During the reduction process, the granulometric composition of the initial concentrate does not change; the metal phase formed is distributed in the grain structure of the initial mineral [21, 22].

5. 2. Studying the kinetics in leaching reduced ilmenite

For leaching of metalized ilmenite, weakly acidic solutions of ferrum(III) sulfate were used. The completeness and rate of iron extraction over time (Fig. 4) with an increase in the concentration of Fe(III) to (1 mol/l) in the leaching solution consistently increases (from 62 to 83 %). The selected ratio of solid:liquid – 1:20 provided a 1.5–3-fold excess of leachant in each experiment. Despite the developed surface of the finely dispersed metallic iron in ilmenite and its low potential (–0.441 V), at the beginning of the interaction, 300–400 seconds, the dissolution of iron occurs very slowly. Subsequently, the leaching accelerates sharply, and a sigmoidal section characteristic of autocatalytic processes appears on the kinetic curve. Within 2–3 hours, the leaching of iron from the reduced ilmenite is complete, and more than 83 % of the initial iron content in the original ilmenite is removed.

These dependences were analyzed for compliance with the equations of diffusion-kinetic models of the kinetics of heterogeneous reactions. The ability of the model to linearize the experimental data in a wide range of iron removals was taken as a compliance criterion. For the first section (from 0 to 600–1200 s) of the kinetic curves in the range of iron removals of 1–8 %, the most linear regions corresponded to the Prout Tompkins model $\ln(\alpha/(1-\alpha))=K\cdot\tau$ shown in Fig. 5.

The Prout-Tompkins rate law describes the process of accelerated interaction, chain formation, and branching, which terminates when the starting compound is exhausted.

The Prout Tompkins model is usually used to analyze the initial part of the kinetic curve, where the acceleration of the interaction occurs. An equation of this form was used by Prout and Tompkins in their study of the decomposition of potassium permanganate [23]. Analysis of the second part (from 1000–2300 to 6000–7000 s) or above 8 % iron recovery revealed that the kinetic data obtained (Fig. 6) fit the shrinking sphere model (R3) $kt=1-(1-a)^{1/3}$ [24].

To determine the order of the reaction of the first and second stages of iron dissolution by the concentration of Fe^{3+} ions, the time to achieve 3 % and 30 % iron extraction from the reduced ilmenite was determined and curves were constructed in the coordinates $\lg(\alpha/\tau)$ – $\lg C(Fe^{3+})$: Fig. 7. The angles of inclination of the trend lines of the obtained curves 1.236 and 1.296 indicate a reaction order close to the first for Fe^{3+} ions.

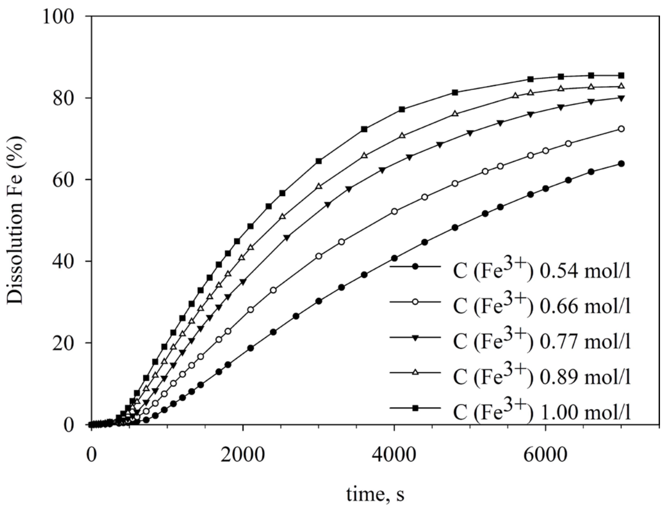

Fig. 4. Change in iron extraction over time with increasing Fe^{3+} concentration in leaching solutions: *t*=25 °C, pH 1.0, S:L=1:20

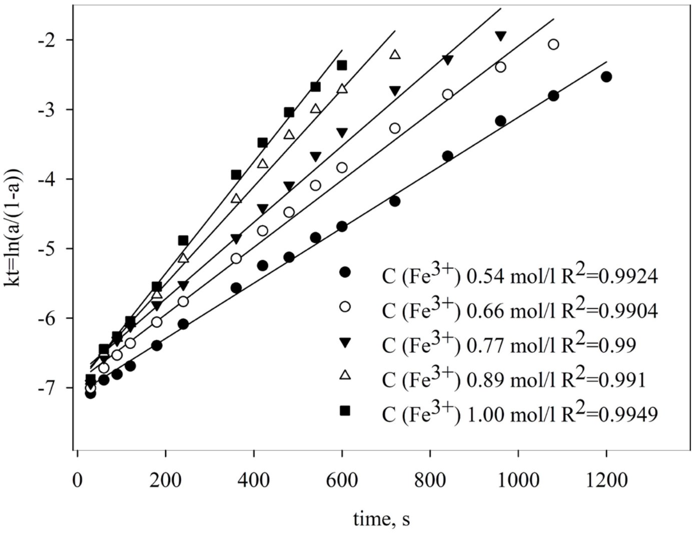

Fig. 5. Dependence of parameter of the kinetic equation of the Prout Tompkins model on the iron leaching time

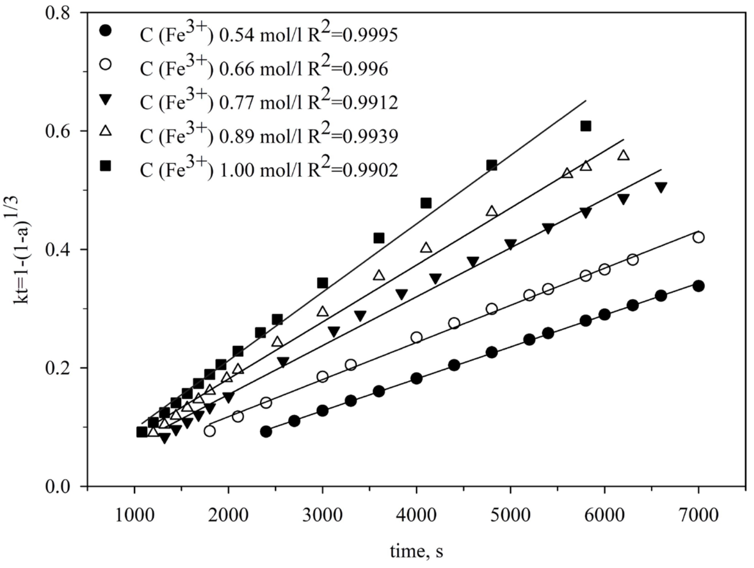

Fig. 6. Dependence of parameter of the kinetic equation of the shrinking sphere model (R3) on the iron leaching time

The effect of temperature on iron extraction over time is shown in Fig. 8. These dependences were used to determine the apparent activation energy of individual stages of the process using a differential approach.

The kinetic curves were used to determine the time to achieve constant iron extraction of 3 and 30 % for each temperature. Presented in the coordinates of the Arrhenius equation, these data represent two linear relationships, each with a coefficient of determination R^2 close to unity (Fig. 9).

The slope of the obtained lines was used to determine the apparent activation energy of both stages of the iron dissolution process in ferric sulfate solutions.

At the stage of autocatalytic acceleration of the interaction, the apparent activation energy was 62.7 kJ/mol. For the part of the leaching process, the kinetics of which are consistent with the shrinking sphere model, the apparent activation energy was 47.3 kJ/mol.

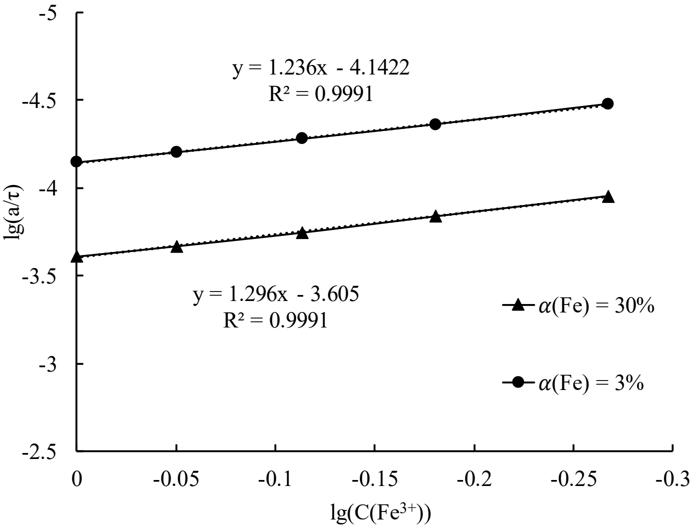

Fig. 7. Graphical determination of the order of reaction of iron with the Fe^{3+} ion

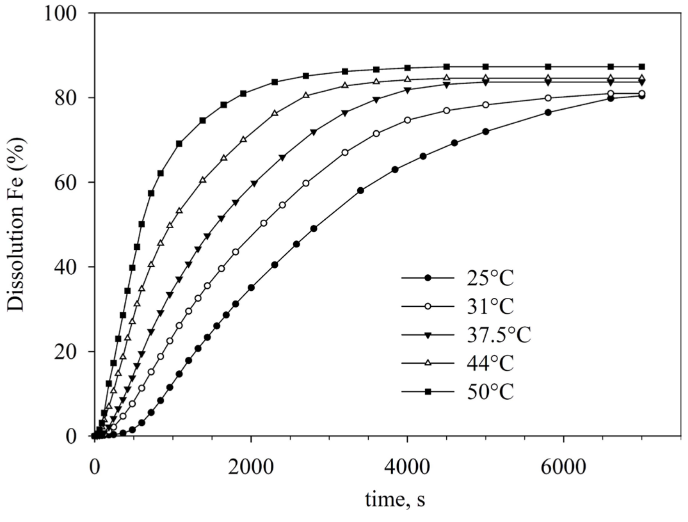

Fig. 8. Change in iron extraction over time with temperature change in leaching solutions: $C(Fe^{3+})$=0.77M, pH° – 1.0, S:L=1:20

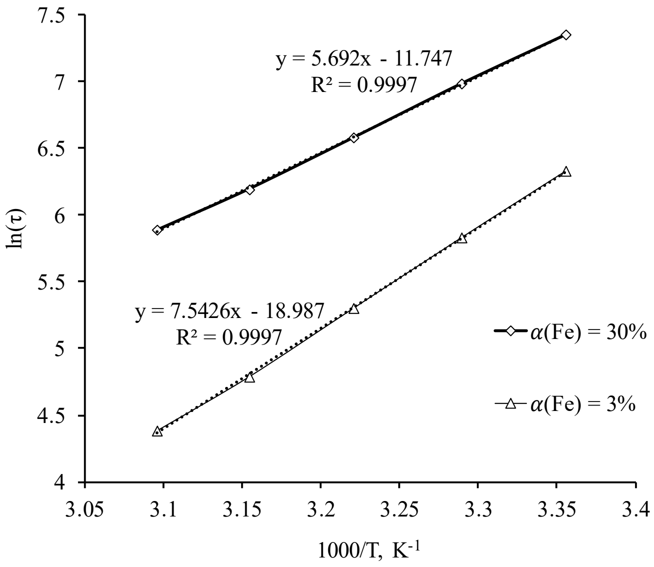

Fig. 9. Data on the time to reach a constant degree of iron leaching from reduced ilmenite in the coordinates of the Arrhenius equation

5. 3. Acid extraction of impurities

Oxidative leaching with weakly acidic solutions practically does not remove ferric oxide impurities and part of iron from RI. The intermediate product obtained by oxidative leaching at 50 °C in 1M $FeCl_3$ solution for 2 h was subjected to leaching with sulfuric acid solutions (Tables 2, 3). The resulting suspensions were filtered, washed, and the precipitates were calcined at 800 °C for 2 h.

Table 2

The content of iron and TiO_2 in synthetic rutile after leaching of impurities with 15 % H_2SO_4 solutions of different temperatures

Temperature, °C	$C(Fe_{gen})$, %	$C(TiO_2)$, %
40 °C	3.8	87.1
50 °C	2.8	89.6
60 °C	1.7	91.9
70 °C	1.6	92.1
80 °C	1.5	92.2

A decrease in the content of total iron and an increase in the content of TiO_2 during acid leaching is observed with an increase in temperature from 40 to 60 °C and a concentration of sulfuric acid from 5 to 15 %.

Table 3

The content of iron and TiO_2 in synthetic rutile after leaching of impurities with sulfuric acid solutions of various concentrations at 65 °C

$C(H_2SO_4)$, %	$C(Fe_{gen})$, %	$C(TiO_2)$, %
5 %	3.6	87.5
10 %	2.4	89.9
15 %	1.7	92.0
20 %	1.6	92.0
25 %	1.5	92.2

Further increase of leaching temperature to 80 °C and acid concentration to 25 % has little effect on the composition of the leach residue. The X-ray diffraction pattern of the acid leach residue calcined at 800 °C (65 °C, 15 % H_2SO_4) is shown in Fig. 10.

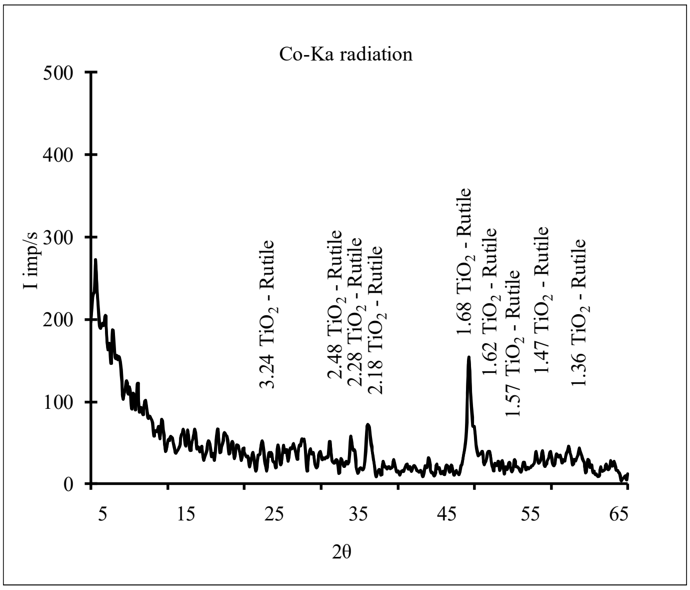

Fig. 10. X-ray diffraction pattern of a synthetic rutile sample

The obtained material mainly contains rutile reflexes; intense pseudo brookite and α-Fe reflexes are not recorded.

5. 4. Regeneration of ferric(III) sulfate solutions

The oxidation of weakly acidic (initial pH 1.5) ferric(II) sulfate solutions with oxygen was studied in a gas-liquid reactor at moderate temperatures of 20–70 °C without the use of elevated oxygen pressure. At a $FeSO_4$ concentration of 0.5 mol/L and a selected range of catalyst concentrations, under conditions of intensive mass transfer, the oxidation process of ferric(II) at 60 °C is completed within 30–90 min (Fig. 11).

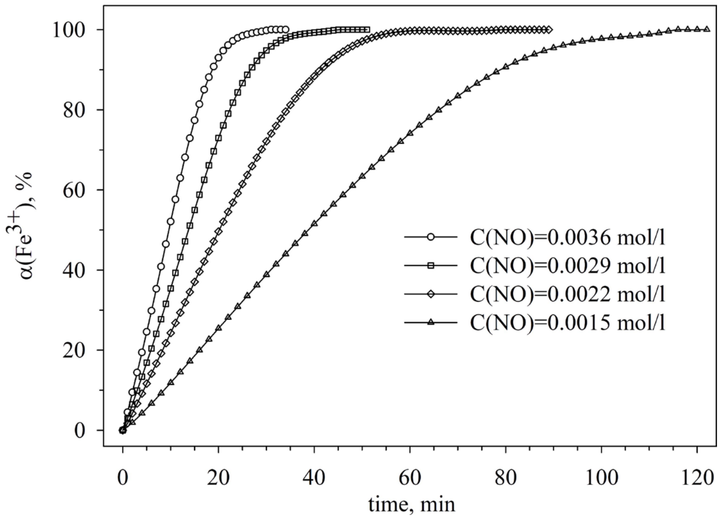

Fig. 11. Change in the proportion of iron(III) compounds during the oxidation of iron(II) sulfate with oxygen as a function of catalyst concentration over time: $C(FeSO_4)$=0.5M, t=60 °C, pH° – 1.5

The oxidation reaction consists of numerous reversible and irreversible reactions in the liquid, gas phase, and at the interface [25]:

$$\left[Fe(NO)\right]^{2+}_{(aq)} \rightleftarrows Fe^{2+}_{(aq)} + NO_{(g)}\uparrow, \quad (1)$$

$$2NO_{(g)}+O_{2(g)} \rightleftarrows 2NO_{2(g)}, \quad (2)$$

$$NO_{2(g)} + 3Fe^{2+}_{(aq)} \rightarrow 2Fe^{3+}_{(aq)} + \left[Fe(NO)\right]^{2+}_{(aq)}, \quad (3)$$

$$N_2O_{3(g)}+H_2O_{(g)} \rightleftarrows 2HNO_{2(aq)}, \quad (4)$$

$$HNO_{2(aq)} + 2Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + \left[Fe(NO)\right]^{2+}_{(aq)}, \quad (5)$$

$$4NO_{(g)}+O_{2(g)} \rightleftarrows 2N_2O_{3(g)}, \quad (6)$$

$$N_2O_{3(g)} + 4Fe^{2+}_{(aq)} \rightarrow Fe^{3+}_{(aq)} + 2\left[Fe(NO)\right]^{2+}_{(aq)}. \quad (7)$$

Modeling of oxygen oxidation of iron(II) in solution shows that, while maintaining a sufficient concentration of the $[Fe(NO)]^{2+}$ complex, the rate of the overall interaction is limited by reactions (2) and (6). Due to the intensive mass transfer and interaction of oxygen and nitrogen oxides mostly in the gas phase with rapid reactions of reduction of NO_2, N_2O_3, and HNO_2 by Fe^{2+} ions to NO, the process occurs at a speed acceptable for the technological process (1–3 h) and low catalyst consumption.

Additionally, hydrolysis products precipitate in the solution. The suspension obtained in the oxidation process is easily stratified and filtered. When washing the precipitates, peptization of the material does not occur, the humidity of the washed precipitates is 47–51 %. An optical photograph of the sample at 500-fold magnification (Fig. 12) shows that it is composed of finely crystalline material.

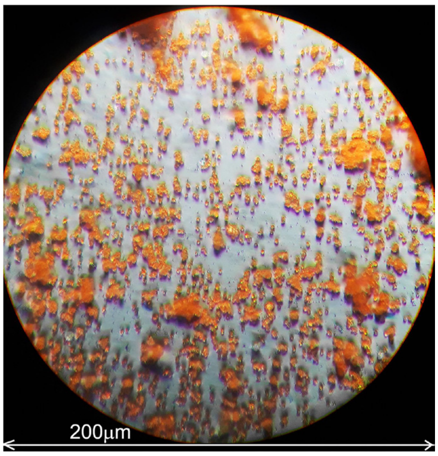

Fig. 12. Precipitate $Fe_4(OH)_{10}SO_4$ Carl Zeiss Jena NU-2 Microscope

The X-ray diffraction pattern of the thoroughly washed and dried at room temperature precipitate (Fig. 13) shows that it contains the $Fe_4(OH)_{10}SO_4$.

Whereas at the beginning of oxidation the acidity of $FeSO_4$ solutions was set at pH≤1.5, then in the oxidation process, in addition to iron(III) ions, only impurities of titanium(IV), which is more susceptible to hydrolysis, are transferred to the precipitate. Oxidation of $FeSO_4$ solutions containing impurities Cr^{3+}, Al^{3+}, Mn^{2+} at an initial pH of 2–4 leads to co-precipitation of impurities.

The X-ray diffraction pattern of the dried and calcined material at 750 °C for 3 hours (Fig. 14) corresponds to α-Fe_2O_3. The resulting red material, according to X-ray fluorescence analysis, contains 99.4 % Fe_2O_3 and could be a valuable raw material for the production of iron oxide pigments.

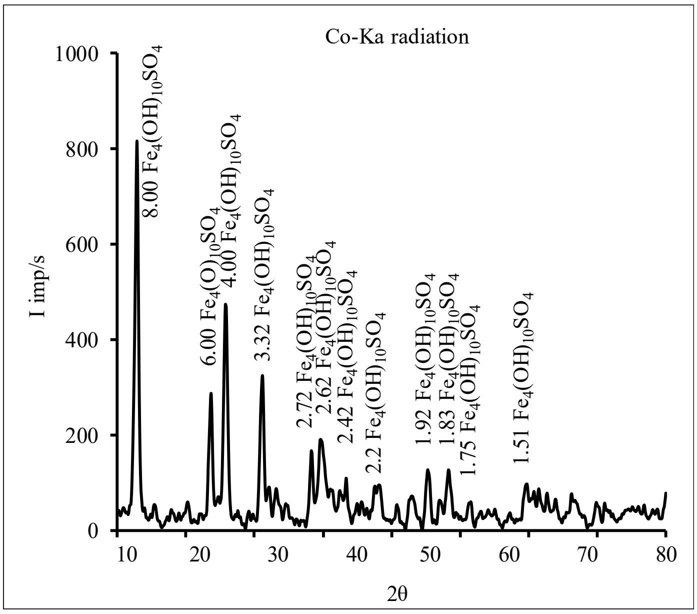

Fig. 13. X-ray diffraction pattern of the precipitate formed from solutions of oxidation of iron(II) sulfate

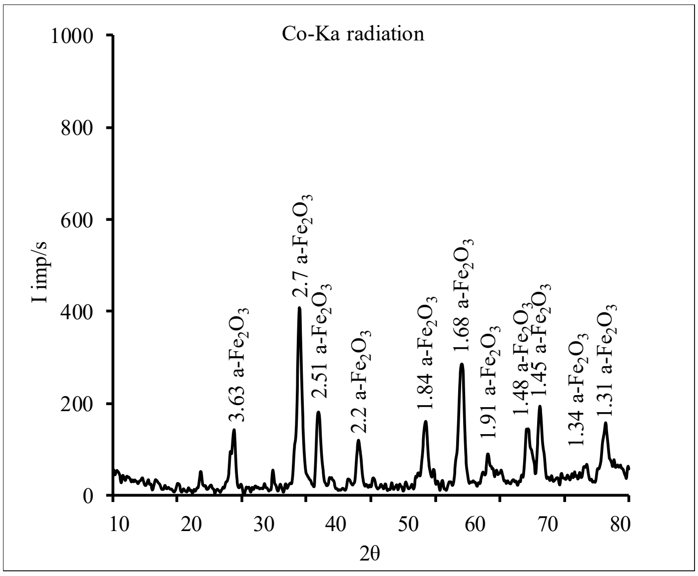

Fig. 14. X-ray diffraction pattern of the product of calcination $Fe_4(SO_4)(OH)_{10}$ at 750 °C for 3 h

The resulting filtrates are transparent, their initial acidity increases from pH 1.5 to pH 1.1, they contain 0.35–0.36 mol/l Fe(III) and do not contain Fe(II). About a third of the Fe(III) ions, depending on the initial acidity of the $FeSO_4$ solutions, are precipitated as a result of hydrolysis. That is, the amount of iron that enters the solution and the leaching stage and is removed at the regeneration stage are proportional.

6. Discussion of results based on investigating the processes of obtaining synthetic rutile

Above 1020 °C, the reduction of iron oxides by carbon occurs through carbon gasification: $C+CO_2 \rightleftarrows 2CO$ and interaction with carbon (II) oxide [26]. In the temperature range of 1000–1200 °C, the reduction of impurities of mixed iron oxides (III) occurs, first to FeO, then to iron. At 1200 °C for 4 h, the iron oxides from Samotkan ilmenite concentrates are reduced by 90 % to iron, which is distributed in a finely dispersed form in the composition of the initial granules but remains available for leaching (Table 1). Manganese impurities in ilmenite are not reduced even under the conditions of ore-thermal smelting of titanium slags above 1650 °C. Together with magnesium, they bind part of FeO in the reduction-resistant pseudo brookite phase (Fig. 3), so complete reduction of ferric oxides to metal does not occur. To reduce the influence of manganese on the reduction of iron in ilmenite, sulfur is added to the Becher process reduction furnace, which binds manganese to sulfides [27]. Due to the relatively low content of manganese compounds in the Samotkan concentrates (0.25 %), the addition of sulfur-containing compounds for its binding was not used. At the same time, the achieved degree of metallization in 90 % of the reduced Samotkan ilmenite is higher compared to concentrates from other deposits, which is probably due to the low content of manganese impurities in it and the developed surface of the activated carbon used as a reducing agent.

When using weakly acidic solutions of ferric (III) sulfate, the bulk of iron from RI is leached in the form of highly soluble $FeSO_4$ in 2–3 h (Fig. 4, 8), with low energy consumption in simple equipment. Compared with the Becher process, where aeration of RI can take up to 22 h [28], reducing the leaching time allows reducing the volumes of processed suspensions and significantly reducing the number of reactors and energy consumption. The process is not accompanied by the formation of significant amounts of hydrogen and does not impose high requirements on the corrosion resistance of the equipment.

Oxidative leaching with weakly acidic solutions of ferric (III) sulfate does not allow obtaining synthetic rutile with a high content of TiO_2. Increasing the content of TiO_2 in synthetic rutile allows additional removal of impurities by acid leaching (Tables 2, 3). The removal of not only iron, but also part of FeO is evidenced by the disappearance of intense pseudo brookite reflexes in the X-ray diffraction patterns of synthetic rutile (Fig. 10). In [29], such phases were not decomposed during acid leaching of aeration products of reduced ilmenite, a possible explanation for this is the high manganese content (1.62 % MnO) in ilmenite (Ha Tinh, Vietnam) and the low magnesium content (0.01 % MgO).

It was found that the regeneration of leaching solutions by catalytic oxygen oxidation of weakly acidic $FeSO_4$ solutions in the presence of NO occurs rapidly (Fig. 11). Quantitative oxidation of 0.5M iron can be carried out within 0.5–1.5 h with the introduction of only 1.5–3.6 mmol/l NO as a catalyst. The proposed solution for the regeneration of oxidative leaching solutions by catalytic oxidation with oxygen has high efficiency and can be the basis for creating a complete, competitive technological solution for the chemical beneficiation of ilmenite concentrates into synthetic rutile.

One of the main tasks of chemical beneficiation of ilmenite is to obtain by-products of iron, not in the form of production waste, but in the form of a product for which there is consumer demand. In most cases, these issues are not resolved, iron-containing products are either sent to landfill or spend significant resources on their processing for the purpose of regenerating the leachant [30].

The proposed method for regenerating the leachant simultaneously allows the removal of by-products of iron from production solutions. Leached iron is precipitated in the form of an individual compact product $Fe_4(SO_4)(OH)_{10}$ (Fig. 12, 13) for which consumer demand is possible.

It should be noted that the introduction of some cations (Mg^{2+}, Ni^{2+}, Cu^{2+}) can completely suppress the formation of $Fe_4(SO_4)(OH)_{10}$ particles in the solution [31]. When using a cycle of oxidative leaching of metallized ilmenite with iron (III) sulfate and regeneration of the leachant by catalytic oxidation of iron (II) sulfate solutions with oxygen, impurity ions will accumulate in them. This may disrupt the conditions for the formation of a compact crystalline precipitate of iron (III) hydroxysulphate or affect its quality. Pilot studies of the process are necessary to identify such phenomena.

The waste of the proposed scheme for chemical beneficiation of ilmenite will be part of the recycled oxidative leaching solutions. To dispose of such waste, their neutralization with lime is currently widely practiced obtaining relatively safe waste red gypsum. Also, similar to the Summit process, the low acidity of spent $FeSO_4$ solutions after oxidative leaching allows them to be utilized to obtain a range of iron oxide pigments.

As in the Becher process, a significant limitation of the proposed RI chemical beneficiation scheme is the need to direct high-quality ilmenites with a low content of foreign minerals and a total content of titanium and ferric oxides of at least 92–93 % to obtain synthetic rutile.

Our study addresses the issue of developing technological foundations for processes for chemical beneficiation of reduced ilmenite to synthetic rutile with low costs for reagent regeneration (8.5–9.5 kg of oxygen and up to 15 kW of electricity per 1 kmol of Fe^{3+}) and obtaining iron-containing materials as a by-product for which consumer demand is possible. Nevertheless, to clarify the prospects for the industrial implementation of such a process scheme, a thorough analysis of costs is required, in particular for the process of pyrometallurgical reduction of ilmenite concentrate.

The difference in the conditions of pyrometallurgical reduction of laboratory samples with activated carbon from industrial conditions in rotary kilns may significantly limit the extension of the conclusions of laboratory studies to industrial conditions of the reduction process and oxidative leaching. Further studies are needed aimed at using industrially available reducing agents and reducing the reduction temperature while maintaining a high degree of RI metallization.

After the completion of the laboratory stage, there is now a need for a detailed program of research into hydrometallurgical processes on an enlarged laboratory and pilot scale.

7. Conclusions

1. Reduction of ilmenite concentrates from the Samotkan deposit with carbon at 1200 °C for 4 h leads to the reduction of 90 % of ferric oxides into metallic iron. This value exceeds the degree of metallization of reduced ilmenites from other deposits under such conditions and can be explained by the low content of manganese and magnesium impurities in the Samotkan ilmenite.

2. Oxidative leaching of reduced ilmenite concentrate with weakly acidic solutions of $Fe_2(SO_4)_3$ to a degree of iron extraction of 7–8 % occurs according to the autocatalytic model by Prout Tompkins $kt=\ln(a/(1-a))$ with an apparent activation energy E_{app}=62.7 kJ/mol. At higher iron extractions, the process transitions to a model of a contracting sphere $kt=1-(1-a)^{1/3}$, with an imaginary activation energy E_{app}=47.3 kJ/mol. The reaction order for Fe^{3+} of the first and second leaching stages was 1.24 and 1.30, respectively.

3. Additional leaching of the oxidative leaching product at 65 °C in 15 % H_2SO_4 for 3 h reduces the iron content to 1.5–1.6 %. After calcination at 800 °C for 1 h, synthetic rutile with a TiO_2 content of 92 % was obtained.

4. The use of nitrogen (II) oxide as a catalyst for the oxygen oxidation of weakly acidic $FeSO_4$ solutions can be used in the regeneration of spent oxidative leaching solutions. Intensive mass transfer at a high gas content in the gas-liquid mixture allows catalytic oxidation without the use of elevated pressure and temperature. At pH 1.1—1.5 and 60 °C in the presence of 1.5–3.6 mmol/l NO, a 0.5M solution of $FeSO_4$ was quantitatively oxidized for 0.5—1.5 h. Precipitation of a portion of the iron into a high-purity crystalline $Fe_4(SO_4)(OH)_{10}$ precipitate can be used to recycle leached iron into products for which there is a demand. Calcination of the $Fe_4(SO_4)(OH)_{10}$ precipitate at 750 °C yielded 99.4 % Fe_2O_3, suitable for pigment production.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

Funding

The study was conducted without financial support.

Data availability

All data are available, either in numerical or graphical form, in the main text of the manuscript.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

References

1. Mineral commodity summaries 2024 (2024). US Geological Survey. https://doi.org/10.3133/mcs2024
2. Joy, M., Bhat, K. H. (2025). An overview of phase analysis and strategies on the development of acid soluble titania for sulphate process. Discover Chemistry, 2 (1). https://doi.org/10.1007/s44371-025-00110-5

3. Interim Report. For The Half-Year Ended 30 June 2024 (2024). Iluka Resources Limited. Available at: https://www.iluka.com/media/pannp5i3/2024-half-year-results-interim-report.pdf
4. Jung, E. J., Kim, J., Lee, Y. R. (2021). A comparative study on the chloride effectiveness of synthetic rutile and natural rutile manufactured from ilmenite ore. Scientific Reports, 11 (1). https://doi.org/10.1038/s41598-021-83485-6
5. Middlemas, S. C. (2014). Energy-conscious production of titania and titanium powders from slag. The University of Utah. Available at: https://core.ac.uk/download/276265554.pdf
6. Reck, E., Richards, M. (1997). Titanium dioxide – Manufacture, environment and life cycle analysis: The tioxide experience. Surface Coatings International, 80 (12), 568–572. https://doi.org/10.1007/bf02693848
7. Zhang, S., Liu, S., Ma, W., Dai, Y. (2018). Review of TiO2-Rich Materials Preparation for the Chlorination Process. Rare Metal Technology 2018, 225–234. https://doi.org/10.1007/978-3-319-72350-1_21
8. Ganzha, O., Kuzmanenko, H., Okholina, T., Remezova, O. (2022). Current State Of Mineral Base Of Titanium Deposits Of Ukraine. Visnyk of Taras Shevchenko National University of Kyiv. Geology, 4 (99), 60–66. https://doi.org/10.17721/1728-2713.99.08
9. Ganzha, O. A., Kovalchuk, M. S., Kroshko, Yu. V. (2024). Ore-Bearing Of The Vovchansk Zircon-Rutil-Ilmenite Deposit. Geochemistry and Ore Formation, 45, 30–43. https://doi.org/10.15407/gof.2024.45.030
10. Filippou, D., Hudon, G. (2009). Iron removal and recovery in the titanium dioxide feedstock and pigment industries. JOM, 61 (10), 36–42. https://doi.org/10.1007/s11837-009-0150-3
11. Thambiliyagodage, C., Wijesekera, R., Bakker, M. G. (2021). Leaching of ilmenite to produce titanium based materials: a review. Discover Materials, 1 (1). https://doi.org/10.1007/s43939-021-00020-0
12. Lakshmanan, V. I., Bhowmick, A., Halim, A.; Brown, J. (Ed.) (2014). Titanium Dioxide - Production, Properties and Applications. New York: Nova Science, 75–130.
13. Walpole, E. A., Winter, J. D. (2002). The Austpac ERMS and EARS Processes for the Manufacture of High-Grade Synthetic Rutile by the Hydrochloric Acid Leaching of Ilmenite. Chloride Metallurgy 2002 – International Conference on the Practice and Theory of Chloride/Metal Interaction. Available at: https://www.austpacresources.com/pdfs/techpub/EJW%20Paper%20Oct%202002.pdf
14. Verhulst, D., Sabachy, B., Spitler, T., Duyvesteyn, W. (2002). New development in the Altair hydrochloride TiO2 pigment process. Hydrometallurgy Fifth International Conference in Honor of Professor Ian Ritchie, 565–575.
15. Farrow, J. B., Ritchie, I. M., Mangano, P. (1987). The reaction between reduced ilmenite and oxygen in ammonium chloride solutions. Hydrometallurgy, 18 (1), 21–38. https://doi.org/10.1016/0304-386x(87)90014-4
16. Shiah, C. D. (1966). Pat. No. US3252787A. Process for prodúcing titanium dioxide concentrate and other useful products from ilmenite and similar ores. Available at: https://patents.google.com/patent/US3252787A/en
17. Ward, C. B. (1990). The production of synthetic rutile and by-product iron oxide pigments from ilmenite processing. Materials Science, 309–322.
18. Gok, O. (2011). Catalytic oxidation mechanism of oxy-nitrogen species (NOx) in FeSO4 electrolyte. Nitric Oxide, 25 (1), 47–53. https://doi.org/10.1016/j.niox.2011.05.003
19. Baldwin, S. A., Van Weert, G. (1996). On the catalysis of ferrous sulphate oxidation in autoclaves by nitrates and nitrites. Hydrometallurgy, 42 (2), 209–219. https://doi.org/10.1016/0304-386x(95)00092-u
20. Kozhura, O. V., Tsybulya, E. O., Kovalenko, I. L. (2025). Leaching of reduced ilmenite concentrate from the Samotkan deposit using sulfuric acid solutions. Voprosy Khimii i Khimicheskoi Tekhnologii, 2, 150–157. https://doi.org/10.32434/0321-4095-2025-159-2-150-157
21. Lv, W., Lv, X., Xiang, J., Hu, K., Zhao, S., Dang, J. et al. (2019). Effect of preoxidation on the reduction of ilmenite concentrate powder by hydrogen. International Journal of Hydrogen Energy, 44 (8), 4031–4040. https://doi.org/10.1016/j.ijhydene.2018.12.139
22. Sarker, M. K., Rashid, A. K. M. B., Kurny, A. S. W. (2006). Kinetics of leaching of oxidized and reduced ilmenite in dilute hydrochloric acid solutions. International Journal of Mineral Processing, 80 (2-4), 223–228. https://doi.org/10.1016/j.minpro.2006.04.005
23. House, J. E. (2007). Principles of chemical kinetics. Academic Press, 336.
24. Nikiforova, A., Kozhura, O., Pasenko, O. (2016). Leaching of vanadium by sulfur dioxide from spent catalysts for sulfuric acid production. Hydrometallurgy, 164, 31–37. https://doi.org/10.1016/j.hydromet.2016.05.004
25. Gok, O. (2012). Ferrous oxidation catalyzed by oxy-nitrogen species (NOX). Asian Journal of Chemistry, 24 (12), 5485–5489. Available at: https://asianpubs.org/index.php/ajchem/article/view/9911
26. El-Guindy, M. I., Davenport, W. G. (1970). Kinetics and mechanism of llmenite reduction with graphite. Metallurgical Transactions, 1 (6), 1729–1734. https://doi.org/10.1007/bf02642023
27. Rhamdhani, M. A., Ahmad, S., Pownceby, M. I., Bruckard, W. J., Harjanto, S. (2018). Selective sulphidation of impurities in weathered ilmenite. Part 1 – Applicability to different ilmenite deposits and simulated Becher kiln conditions. Minerals Engineering, 121, 55–65. https://doi.org/10.1016/j.mineng.2018.03.005
28. Xiang, J., Pei, G., Lv, W., Liu, S., Lv, X., Qiu, G. (2020). Preparation of synthetic rutile from reduced ilmenite through the aeration leaching process. Chemical Engineering and Processing - Process Intensification, 147, 107774. https://doi.org/10.1016/j.cep.2019.107774
29. Duong, B. N., Truong, T. N., Nguyen, T. T. (2020). The Upgrading of Ha Tinh Ilmenite to Synthetic Rutile by Becher Process. Materials Science Forum, 985, 115–123. https://doi.org/10.4028/www.scientific.net/msf.985.115
30. Abdelgalil, M. S., El-Barawy, K., Ge, Y., Xia, L. (2023). The Recovery of TiO2 from Ilmenite Ore by Ammonium Sulfate Roasting–Leaching Process. Processes, 11 (9), 2570. https://doi.org/10.3390/pr11092570
31. Matijević, E., Sapieszko, R. S., Melville, J. B. (1975). Ferric hydrous oxide sols I. Monodispersed basic iron(III) sulfate particles. Journal of Colloid and Interface Science, 50 (3), 567–581. https://doi.org/10.1016/0021-9797(75)90180-0