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Intensification of Sulfuric Acid Leaching of Altered Ilmenite via Adding Fluoride Activator

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Abstract: A new method of altered ilmenite processing has been studied. In this method, sulfuric acid is used as the reaction medium of the process, and fluoride ions are activators of the dissolving process of the rutile part of the ore raw material. The regression model of the sulfate–fluoride leaching process was developed and analyzed by using the response surface method of 2³ matrix. The obtained model is adequate and well describes the studied process. The influence of Ti:F molar ratio, temperature, and sulfuric acid concentration on the leaching process are investigated in this work in order to optimize the studied process. It is experimentally proved that leaching at temperatures above 100 °C, at a molar ratio of Ti:F of more than 1:2, and the use of solutions of sulfuric acid with concentrations of more than 85 wt.% is not optimal because the extraction degree of titanium is reduced. The intensification of the process of sulfuric acid leaching by dividing the main stage of chemical dissolution of ilmenite into two stages was proposed. This method allows to leach up to 95.9% of titanium, which is 1.6–1.9 times higher in comparison with the classical technology of leaching altered ilmenite.

Keywords: sulfuric acid–fluoride leaching; altered ilmenite; rutile; response surface method; chemical kinetics



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1. Introduction

Titanium is one of the most common elements in the earth's crust, in terms of content it ranks ninth among 88 other elements. Titanium metal is one of the most common structural metals (titanium metal ranks fourth after aluminum, iron, and magnesium), and titanium dioxide pigment is used in paints, cosmetics, plastics, rubber, textiles, and in the food industry [1,2]. One of the raw materials of both titanium metal and titanium dioxide is ilmenite. However, most of the ilmenite is processed to produce TiO₂ pigment (about 90% of ilmenite FeTiO₃) [3,4].

Ilmenite can undergo leukoxenization. During this process, the oxidation of ferrous iron occurs, and, as a consequence, the molar ratio in the raw material changes to FeO/Fe₂O₃ < 1, while the “conventional ilmenite” has a molar ratio of FeO/Fe₂O₃ > 1. This geochemical process leads to the enrichment of ore with titanium in the form of rutile. Two types of ilmenite: low-altered (TiO₂ = 45–53%) and altered (TiO₂ = 53–65%) are known [5].

The most common industrial methods of processing titanium-bearing raw materials are hydrochloric [6–11] and sulfuric acid [12–23] leaching. The hydrochloride method is limited to the use of high-quality raw materials (concentrates must have an ilmenite content of 98–99%), because impurities can affect the stability of the process and the quality

of the target product. The sulfuric acid method is more commonly used in industry due to the possibility of processing ore with a lower content of ilmenite. However, this method allows the process of only low-altered ilmenite, and the degree of titanium extraction does not exceed 60% [24].

The existing technology of sulfuric acid decomposition of altered ilmenite is imperfect due to the impossibility of complete leaching of the ore. Therefore, the titanium extraction degree decreases, which significantly reduces the economic feasibility and overall efficiency of the production of TiO_2 pigment by the sulfuric acid method [24]. The reasons for the low titanium extraction degree using altered ilmenite can be explained by the presence of “rutile ballast”, which is dissolved very slowly (practically undissolved) in H_2SO_4 under industrial conditions of leaching. This “rutile ballast” accumulates in the sludge (it is generally thought of as an industrial waste) and it leads to large losses of titanium.

Today, the fluoride processing method of ilmenite and rutile is very actively developing [23–28]. This method is very promising and has a very strong basis for the development of this technology, because it is economical, has a low amount of waste, and has the ability to recycle the main components [29–37]. For example, the authors of [29,30,37] worked with titanium dioxide, which is found in industrial waste or in low-grade materials. They offered additional processing of this raw material. They also suggested using the residues of sulfate leaching into cement. Rodriguez et al. [33] show the leaching of titanium from lean ore by various leaching agents in an autoclave. The optimal process parameters were obtained to achieve 89% titanium recovery: leaching at 123 °C, 330 rpm, 80 min, and 1.8% *w/v* with a mixture of 15% HF and 10% H_2SO_4 . The works [31,32] describe the process of titanium dioxide treatment at high temperatures: 350–600 °C [31] and 700 °C [32]. In the course of these processes, gaseous reaction products were formed. In our opinion, it complicates the application of this technology in practice. The studies [33–37] describe the leaching of titanium-bearing raw materials by the hydrometallurgical method using hydrofluoric acid. The optimal parameters were established, which differ due to the use of raw materials with different chemical compositions. The most common fluorinating reagents are fluorine [38], HF [39,40], H_2SiF_6 [41,42], but ammonium fluoride and ammonium hydrobifluoride are now the most commonly used [43,44]. The use of such compounds in the ilmenite processing allows separating salts of titanium fluoride, iron fluoride, and ammonium fluoride directly during leaching. The process of initial processing of raw materials can be carried out at relatively low temperatures, which contributes to lower energy consumption [44,45]. However, the fluoride method also has significant disadvantages such as relatively high demand of leaching reagent and a large number of process stages. These disadvantages lead to an increase in product and technology costs compared to the method of leaching with sulfuric acid. Therefore, this method needs significant improvements.

In our opinion, the combination of the sulfuric acid method and the fluoride method will overcome the described shortcomings of both technologies. In previous works, as part of the idea of chemical activation of the process, we proved the positive effect of fluoride ions on the efficiency of altered ilmenite leaching with sulfuric acid, which was confirmed by calculations of the thermodynamic probability of reactions [46,47] and kinetic studies of the process [16]. It was found that the addition of sodium fluoride to the sample of altered ilmenite, for example in a mass ratio of 1:1, increased the titanium extraction degree by almost six times in one hour of leaching.

The aim of this work is to determine the optimal process parameters of sulfate acid–fluoride leaching: sulfuric acid concentration, molar ratio Ti:F, and process temperature.

2. Materials and Methods

2.1. Chemical Composition of Ilmenite Concentrate

Ilmenite concentrate from the Malyshevske deposit (Ukraine) and titanium dioxide (for optical glass melting) were utilized in the experiments. Grinding conditions and the particle size distribution of raw and ground material are described in our previous works [15,16,47].

Figures 1 and 2 show the studies of the chemical composition of ilmenite concentrate from the Malyshevske deposit (48°29'21" N, 34°5'27" E, Ukraine) using scanning electron microscopy (SEM) with energy-dispersive X-ray spectroscopy (EDXS). Element percentages are reported with bars, which present the average value from the obtained results for the studied sample (Table 1).

Table 1. The elemental composition of ilmenite concentrate from the Malyshevske deposit.

Element	Ti	Fe	Mg	Mn	Cr	P	V	Al	Si	Ca	O
ω , wt.%	41.0	19.9	0.540	0.190	0.100	0.080	0.120	0.420	0.370	0.040	37.2

It was found that the molar ratio of Ti:Fe exceeded the stoichiometric ratio by 2.4 times. This fact allows us to conclude that the ilmenite of the Malyshevske deposit is significantly altered.

The chemical composition of the ilmenite concentrate was determined at the mining and processing plant and was presented in the certificate (TYU14-10-005-98) for the studied samples of the concentrate. Additionally, the titanium content in this concentrate was determined additionally by us with the traditional gravimetric method. The obtained data is presented in a Table 2 ($n = 3, p = 0.95$).

Table 2. The chemical composition of ilmenite concentrate from the Malyshevske deposit.

Oxide	TiO ₂	SiO ₂	Cr ₂ O ₃	Al ₂ O ₃	Moisture
ω , wt.%	68.5 ± 1.2	0.71 ± 0.24	0.14 ± 0.07	0,35 ± 0.11	0.15 ± 0.08

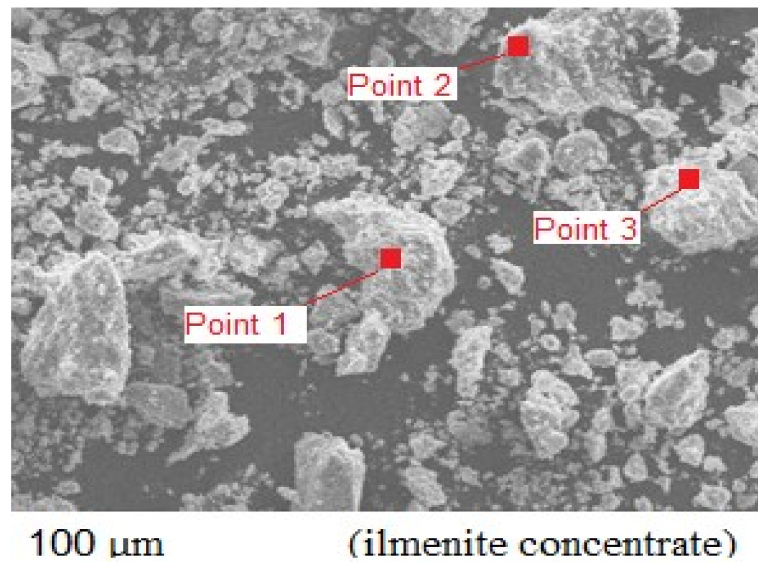


Figure 1. SEM of the ilmenite concentrate sample.

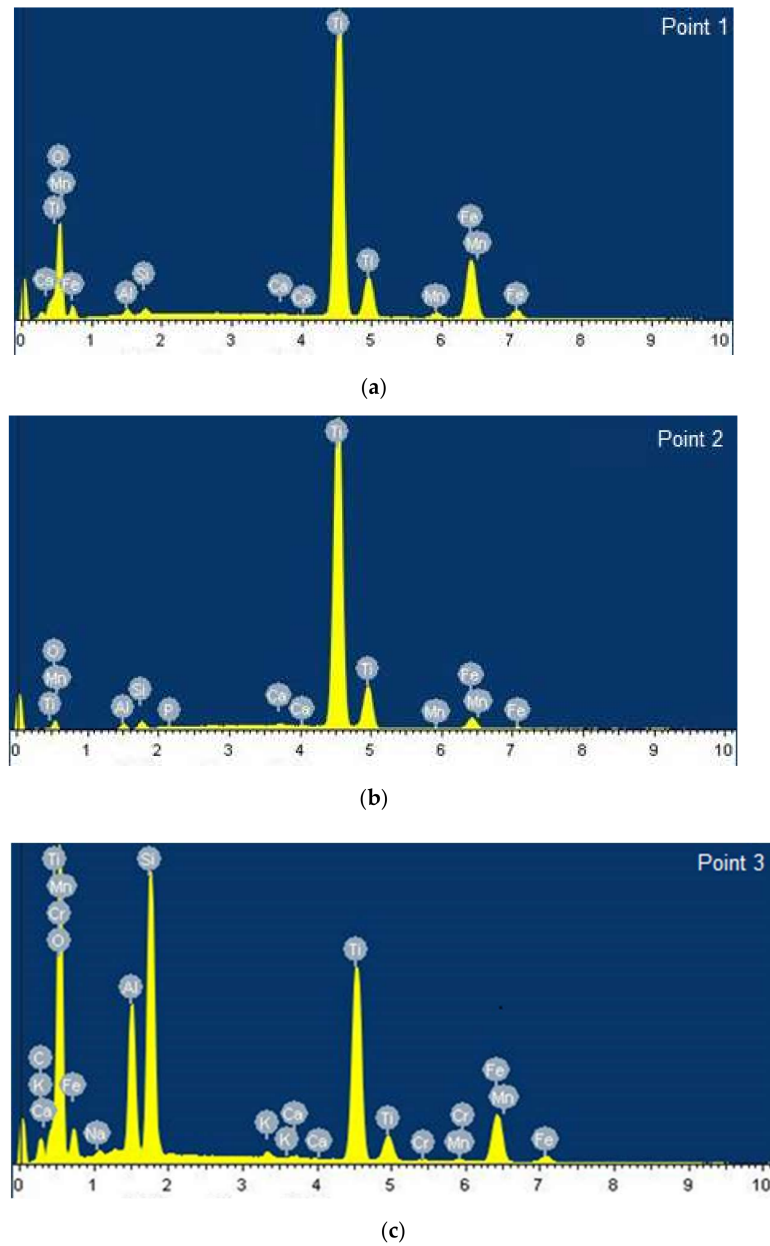


Figure 2. EDXS spectrum of the ilmenite concentrate sample with the maximum value on the scale: (a)–12389 imp; (b)–14022 imp; (c)–10965 imp.

2.2. Experimental Methods and Procedures

The equipment to perform the microscopy investigations and software for analyzing the diffraction patterns were described previously [13].

The titanium content in ilmenite concentrate was determined by the traditional gravimetric method with the following procedure: a weighed portion of the ilmenite concentrate was dissolved at heating in sulfuric acid with the addition of hydrofluoric acid until complete dissolution; then the reduction of Fe^{3+} to Fe^{2+} was carried out by adding metallic iron; the precipitation of metatitanic acid was carried out at $\text{pH} = 2\text{--}3$, which was adjusted by adding a solution of NH_4OH ; the precipitate was filtered off and washed to remove FeSO_4 , excess acid, and sulfates of other metals on an ashless filter and dried; then calcined in a muffle furnace at a temperature of $900\text{ }^\circ\text{C}$ in order to get rutile titanium dioxide.

Experiments on the sulfuric acid leaching with the participation of fluoride ions were carried out in the high-pressure reactor RVD-2-700 with a Teflon coating without stirring.

The molar module of Ti:F was varied in the range of (1:1)–(1:4). The concentration of H₂SO₄ was varied from 30 to 96 wt.%, and the reaction temperature was also varied in the range of 70 to 100 °C. One-factor experiments to study the effect of temperature, acid concentration, and the molar ratio of Ti:F were carried out in Teflon tubes (PTFE). The titanium content in the filtrate was also determined spectrophotometrically. The titanium content in the solution was determined photometrically in the form of a peroxide complex at a wavelength of 410 nm using an SF-46 spectrophotometer. The presence of iron was masked with phosphoric acid.

The extraction degree of titanium was calculated as the ratio of the amount of titanium that passed into solution after the leaching process to its content in the sample of rutile or ilmenite before the leaching process.

All the reagents used for the leaching and chemical analysis were of analytical grade (“Reachem” supplier).

The regression model of the sulfate acid–fluoride leaching process was developed and analyzed by using the response surface method of 2³ (matrix of three factors each at two levels). The molar ratio of components Ti:F, a concentration of sulfuric acid, and process temperature were chosen as independent variables. The titanium extraction degree (%) was taken as the response of the designated experiment. The software Statgraphics Centurion XVI (Version 16.2.04) was used in this study to plot response surfaces and analyze the experimental data.

3. Results and Discussion

3.1. Influence of Input Parameters of Sulfate Acid–Fluoride Leaching Process

3.1.1. Experimental Design

Before using the Design of Experiments (DOE) tool, pilot experiments were performed to determine the approximate range of each independent variable. Further experiments were used for the basis of this study to find the optimal and technologically expedient parameters of the leaching process. The experimental ranges and levels of independent variables and experimental results are shown in Table 3.

Table 3. Experimental range and levels of the independent variables for Design of Experiments (DOE) matrix.

Definition	Parameters	Coded Levels		
	Independent Variable	−1	0	+1
x ₁	The molar ratio of components Ti:F	(1:1)	(1:1.5)	(1:2)
x ₂	The concentration of sulfuric acid, wt.%	85	90	95
x ₃	The process temperature, °C	70	85	100

As shown in Table 3, the actual levels of the process parameters are Ti:F molar ratio of components of (1:1)–(1:2), the concentration of sulfuric acid at 85–95 wt.%, and process temperature at 70–100 °C. The actual levels and ranges of the process parameters are denoted in coded values as −1 (minimum), 0 (center), +1 (maximum). The total number of runs was eight to form a matrix design 2ⁿ, where $n = 3$ (n is the number of factors). The experiments were randomly run to minimize errors between variables and eliminate biases during trials. An empirical model of the sulfate–fluoride leaching process was developed.

3.1.2. Response Surface Methodology and Analysis

In the present study, the relationship between response (titanium extraction degree) and three independent factors (the molar ratio of components Ti:F, the concentration of sulfuric acid, and the process temperature) was studied. Table 4 provides the performed experiments and results for each experimental run.

Table 4. DOE matrix and experimental results for the responses.

Experimental Number	x ₁	x ₂	x ₃	x ₁ x ₂	x ₁ x ₃	x ₂ x ₃	\bar{y} , %
1	–	–	–	+	+	+	7.20
2	+	–	–	–	+	–	9.70
3	–	+	–	–	–	+	4.10
4	+	+	–	+	–	–	5.50
5	–	–	+	+	+	–	17.50
6	+	–	+	–	–	+	30.10
7	–	+	+	–	–	–	8.50
8	+	+	+	+	+	+	11.50

A regression model of the sulfate–fluoride leaching process was developed:

$$y = 11.7625 + 2.4375 \cdot x_1 - 4.3625 \cdot x_2 + 5.1375 \cdot x_3 - 1.3375 \cdot x_1 \cdot x_2 + 1.4625 \cdot x_1 \cdot x_3 - 2.5375 \cdot x_2 \cdot x_3 \quad (1)$$

The analysis of variance (ANOVA) for the titanium sulfate–fluoride leaching has been presented in Table 5.

Table 5. ANOVA for the titanium sulfate–fluoride leaching process.

Source	Sum of Squares	Df	Mean Square	F-Ratio	p-Value	Remarks
A:x ₁	47.5313	1	47.5313	47.53	0.0000	Significant
B:x ₂	152.251	1	152.251	152.25	0.0000	
C:x ₃	211.151	1	211.151	211.15	0.0000	
AB	14.3112	1	14.3112	14.31	0.0002	
AC	17.1113	1	17.1113	17.11	0.0000	
BC	51.5113	1	51.5113	51.51	0.0000	
Total error	9.03125	1	9.03125	9.03	0.0027	
External sigma			1.0			
Total (corr.)	502.899	7				
The R-Squared Results						
R-squared					98.2042%	
R-squared (adjusted for d.f.)					87.4291%	
Standard Error of Est					3.0052	
Mean Absolute Error					1.0625	

The correlation coefficient value (R^2) estimates the excellence of the model established by the software. As the R^2 value gets closer to 100%, the model is said to be better and gives predicted values closer to the actual. There was an excellent correlation between the experimental data and the predicted data as the R^2 value is 98.20%, which was found to be closed to 100%. In addition, the closeness value of adjusted R^2 (87.43%) is highly acceptable. Therefore, the obtained model is adequate and can be used to describe the studied process.

All variables, including the molar ratio of components Ti:F (A), concentration of sulfuric acid (B), and process temperature (C), as well as interactions AB, BC, and AC, were significant based on the p -value less than 0.05 as is shown in Table 5 and Figure 3 (bars going beyond the vertical line of significance).

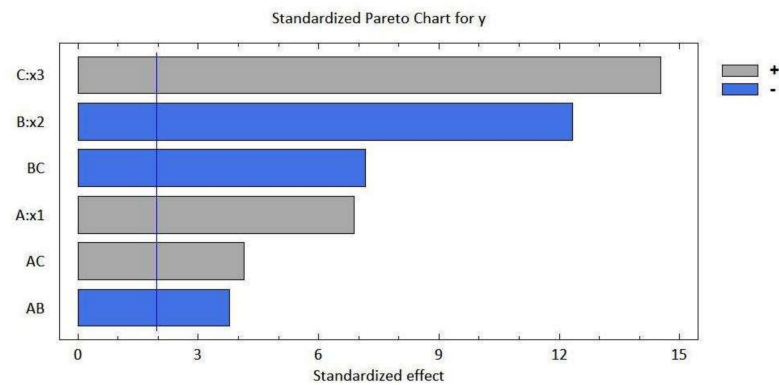


Figure 3. Analysis of the influence and significance of three independent factors and their interactions.

As shown in Figure 3, the process temperature (C) has the largest effect on the leaching process among the other parameters. The acid concentration (B) also has fairly significant effects on the studied process. Therefore, it is obvious that the synergistic interaction of the BC variables also has a significant effect. The molar ratio of the components (C) also has a big influence on the process.

Most of the data was found to lie along a straight line as observed in the normal probability plot of residuals shown in Figure 4a. This indicates that the selected model terms are only significant factors and the errors are normally distributed. A well-fitted regression that scattered along a straight line could be seen in the predicted (software calculated) versus observed (experimental) values plot shown in Figure 4b. This confirmed that the model is very well designated and adequate.

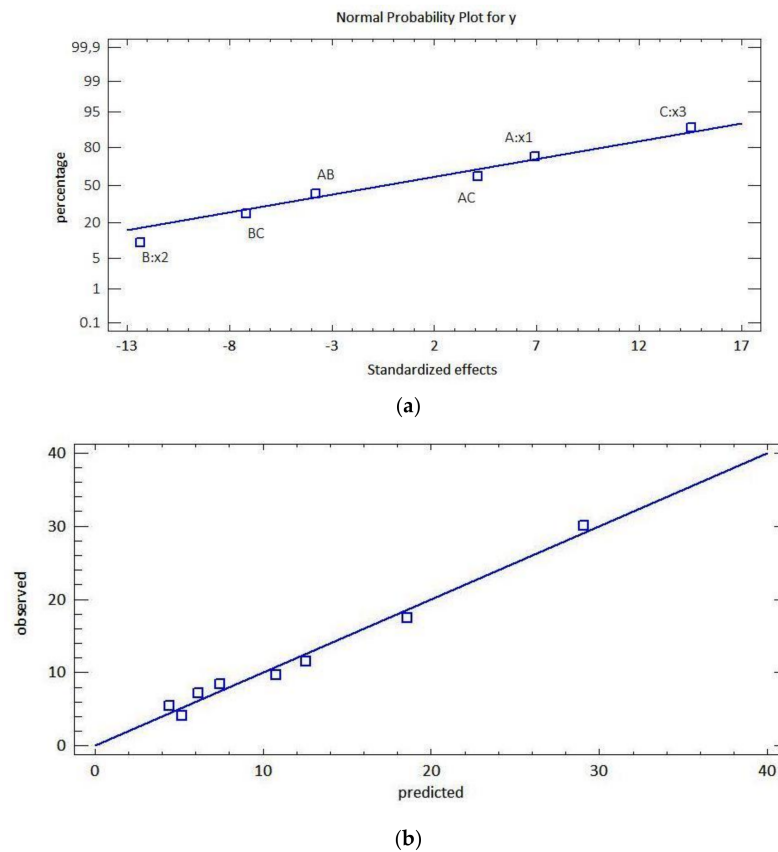


Figure 4. Normal plot of residuals (a) and predicted vs. actual plot (b).

The two-dimensional representation of the sulfate acid–fluoride leaching process for the selected parameters is shown by the contour plot presented in Figure 5a–c. The titanium degree leaching values indicated in the plot of each contour increases (5b) or decreases (5a, 5c) almost linearly from the first to the last contour depending on chosen parameters for the data representation. The influence of chosen parameters on the studied process in the form of a 3D surface plot has been presented in Figure 5d. The plot shows the changes of extraction degree depend on the simultaneous influence of three factors with their various combinations.

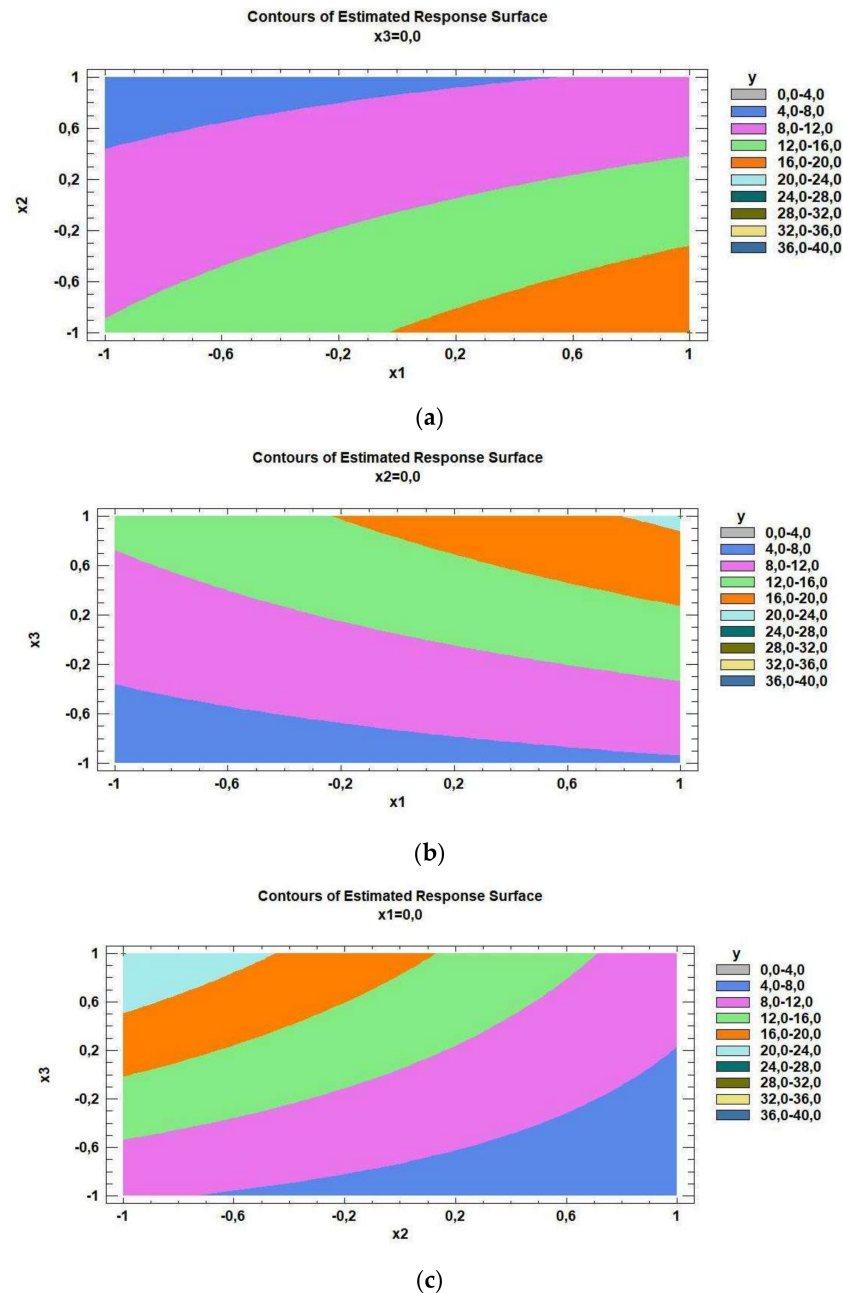
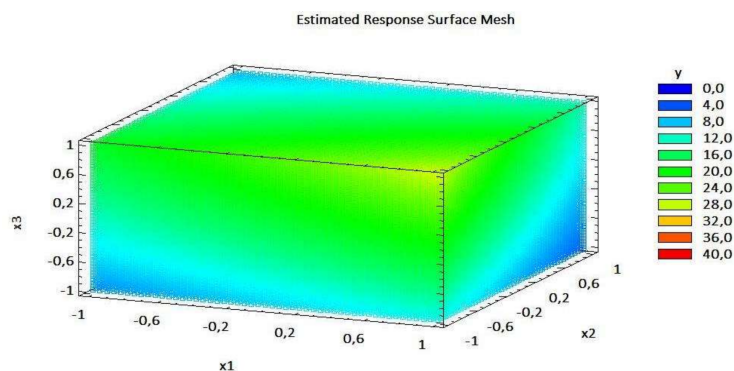


Figure 5. Cont.



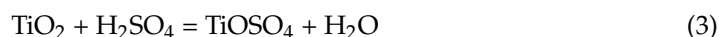
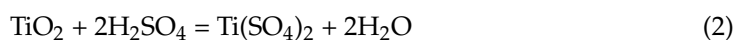
(d)

Figure 5. Contour (a–c) and 3D (d) plots.

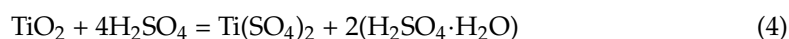
Thus, it can be noted that the technologically optimal parameters of the sulfate acid–fluoride leaching process are the following parameters [+1; −1; +1]: molar modulus of Ti:F = 1:2, sulfate acid concentration = 85 wt.%, and process temperature = 100 °C.

3.2. Optimization of the Molar Ratio Value of Ti:F in the Reaction Mixture

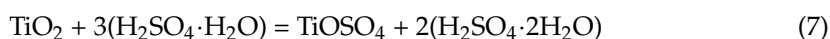
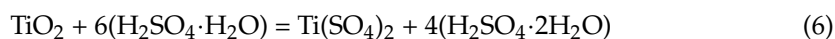
The dissolution of titanium dioxide in sulfuric acid with the formation of two products, $\text{Ti}(\text{SO}_4)_2$ and TiOSO_4 , was considered at the first stage of thermodynamic modeling in our previous works [46,47]. It is generally accepted to consider such reactions in the most simplified form, as the reactions which are accompanied by the release of water:



Obviously, water cannot be considered as a pure phase in concentrated solutions of sulfuric acid, i.e., in the standard state, due to the formation of relatively strong hydrates $\text{H}_2\text{SO}_4 \cdot n\text{H}_2\text{O}$. Therefore, reactions (2) and (3) were rewritten taking into account the formation of sulfuric acid hydrate:



Similarly, it is possible to write the equations for the dissolution of titanium dioxide in 85% sulfuric acid (the molar ratio of $\text{H}_2\text{SO}_4/\text{H}_2\text{O} = 1$). The number of moles of sulfuric acid in such equations should generally depend on the degree of conversion of titanium dioxide and excess sulfuric acid. We considered one of the possible options which involve two acid hydrates with $n = 1$ and 2:



To obtain the optimal ratio of Ti:F, experiments were performed by varying the molar ratio of Ti:F from 1:1 to 1:4 (Figure 6). The other two parameters were constant in the value determined by response surface methodology: the concentration of sulfuric acid was 85 wt.% and the temperature of the sulfate acid–fluoride leaching was 100 °C.

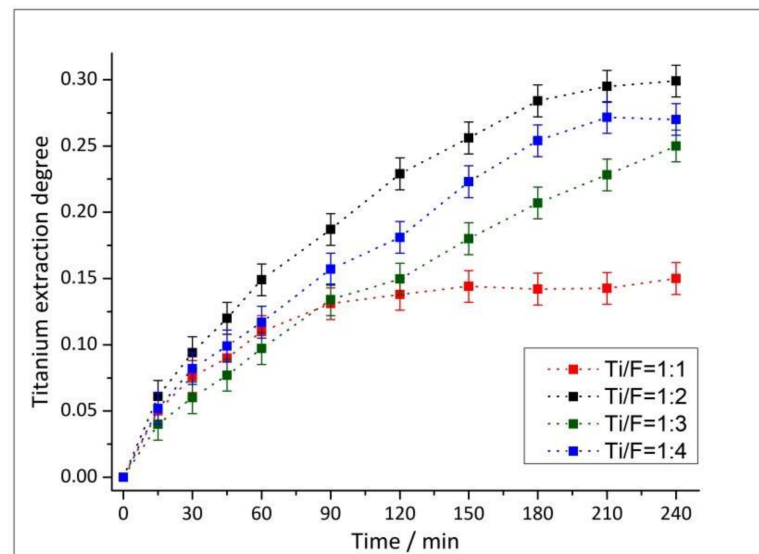


Figure 6. The dependence of the titanium extraction degree from rutile on time and the molar ratio of Ti:F, when varying the molar ratio of Ti:F from (1:1) to (1:4); the concentration of sulfuric acid was 85 wt.%; the temperature of the sulfate acid–fluoride leaching was 100 °C; the solid:liquid mass ratio was 1:2.

It was found that the highest titanium extraction degree was observed in experiments using the molar ratio of the reaction mixture Ti:F = 1:2. A larger excess of sodium fluoride (Ti:F = 1:3 and 1:4) leads to a decrease in the leaching rate. This regularity can be explained by the effect of blocking the surface of rutile with a relatively thick layer of NaF and Na₂SO₄ salts. This slows down the diffusion of ions and molecules involved in the chemical reaction. The low extraction degree using a molar ratio of the components of the mixture 1:1, in our opinion, is due to insufficient fluoride ions in solution to shift the equilibrium of the chemical reaction of rutile dissolution towards the formation of products. After 45 min of leaching, the kinetic curve reaches its maximum and the titanium extraction degree does not change further. In contrast to the experiment at Ti:F = 1:1, the kinetic curves do not reach their maximum even after 240 min in all other cases.

The effect of fluoride ions on the phase composition of the sludge remaining after sulfuric acid leaching of the altered ilmenite was studied by the X-ray diffraction method. A sample of sludge was obtained in the laboratory by treatment of crushed ilmenite with 85 wt.% solution of sulfuric acid. The process was carried out at 100 °C and a duration of one and a half hours. Then, the precipitate was separated from the solution: the first part was taken for analysis, and the second part was subjected to re-treatment with 85 wt.% sulfuric acid with the addition of hydrofluoric acid (Ti:F = 1:2), also at a temperature of 100 °C, however, with a process duration of half an hour to prevent the complete dissolution of the sample. Figure 7 shows the diffraction patterns of sludge samples before sulfuric acid–fluoride treatment and after it.

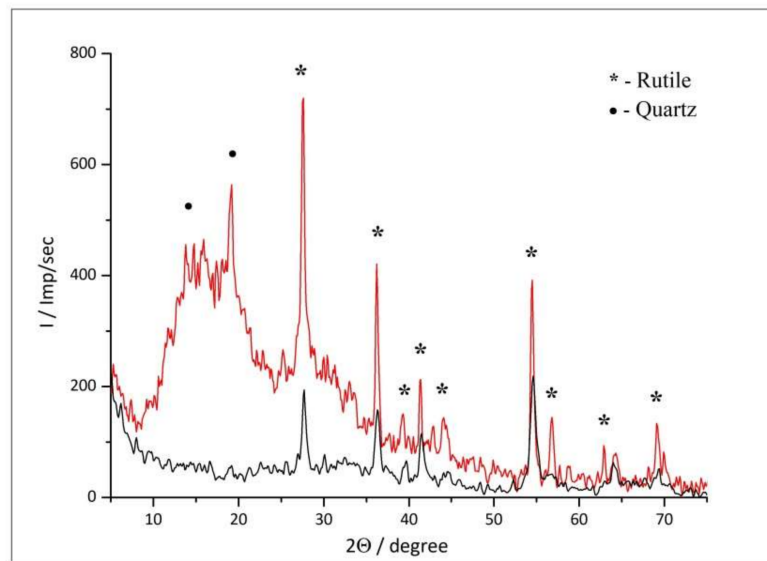


Figure 7. Diffraction pattern of a sludge sample processed with sulfuric acid but without the addition of sodium fluoride (red curve) and with the addition of sodium fluoride (black curve).

Analysis of diffraction patterns showed that in addition to rutile and pseudorutile residues, the sludge contains an admixture of sulfuric acid-insoluble silicon oxide in the amorphous and crystalline state (PCPDFWIN № 32-0993, 82-1563). It can be seen (Figure 7) on the presented diffractograms that the reflexes of the crystalline phases of SiO_2 in the range of $2\theta = 10\text{--}25^\circ$ disappear when adding fluoride ions to a solution of H_2SO_4 . It is well explained by the solubility of SiO_2 in hydrofluoric acid.

3.3. Optimization of the Process Temperature Value

The sulfuric acid–fluoride method was utilized for the study of the effect of temperature on the process of leaching of titanium under isothermal conditions at temperatures of $70\text{--}165^\circ\text{C}$, $\text{Ti:F} = 1:2$ and $C(\text{H}_2\text{SO}_4) = 85\text{ wt.}\%$. The results of ilmenite and rutile leaching by the sulfuric acid–fluoride method are presented in Figure 8.

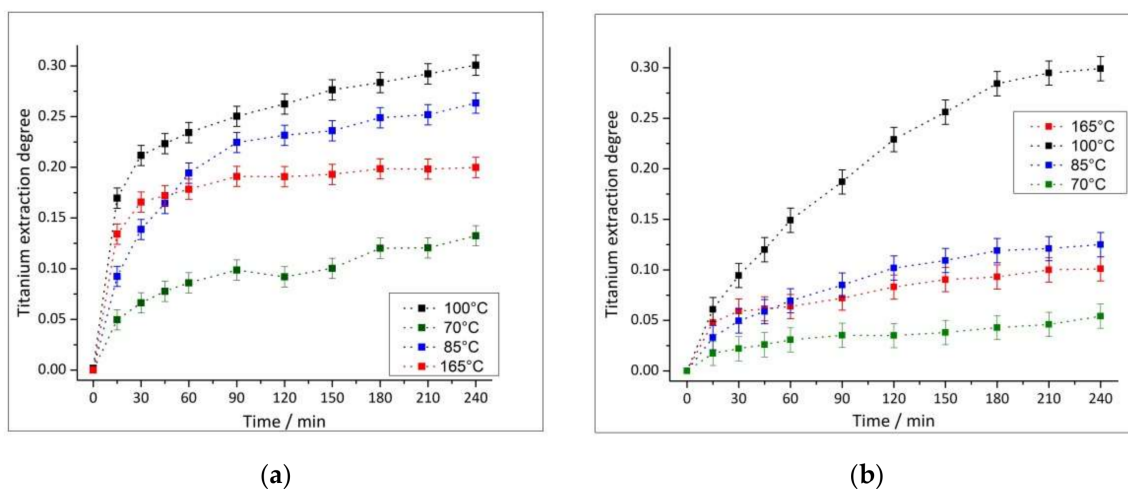


Figure 8. The dependence of the titanium extraction degree to ilmenite (a) and rutile (b) on time and temperature at $\text{Ti:F} = 1:2$ and $C(\text{H}_2\text{SO}_4) = 85\text{ wt.}\%$; the solid:liquid mass ratio is 1:2.

As can be seen in Figure 8, with increasing temperature, the highest titanium extraction degree into solution, both from ilmenite and rutile, is achieved during the process of sulfuric acid–fluoride leaching at 100 °C.

The sharp decrease in the extraction degree at 165 °C can be explained by the fact that in an acidic environment, fluoride ions are mainly bound to hydrogen fluoride molecules and, as a result, can evaporate rapidly from the reaction mixture. It is known that when HF solutions are heated, an azeotropic mixture with an HF concentration of 37.5% and a boiling point of 109 °C are formed. Therefore, raising the temperature above 100 °C sharply enhances the evaporation process of HF.

Additionally, it should be noted that all the curves in Figure 8 have the form of convex curves at the beginning of the leaching process, and then only the leaching curves at 165 °C reach saturation. This can be explained by slowing down and suspending the process of rutile dissolution due to the rapid loss of fluorine ions during chemical reactions at such high temperatures.

Thus, to maximize the processing speed, it is necessary to increase the temperature of the reaction mixture to 100 °C, but further heating leads to rapid loss of HF, which slows down and suspends the process of dissolving rutile.

3.4. Optimization of Sulfuric Acid Concentration Value

To determine the optimal concentration of sulfuric acid, the experiments were performed under isothermal conditions at a temperature of 100 °C, molar modulus Ti:F = 1:2, and with the varying of H₂SO₄ solutions concentration from 30 to 96%. The results of the kinetic studies are presented in Figure 9.

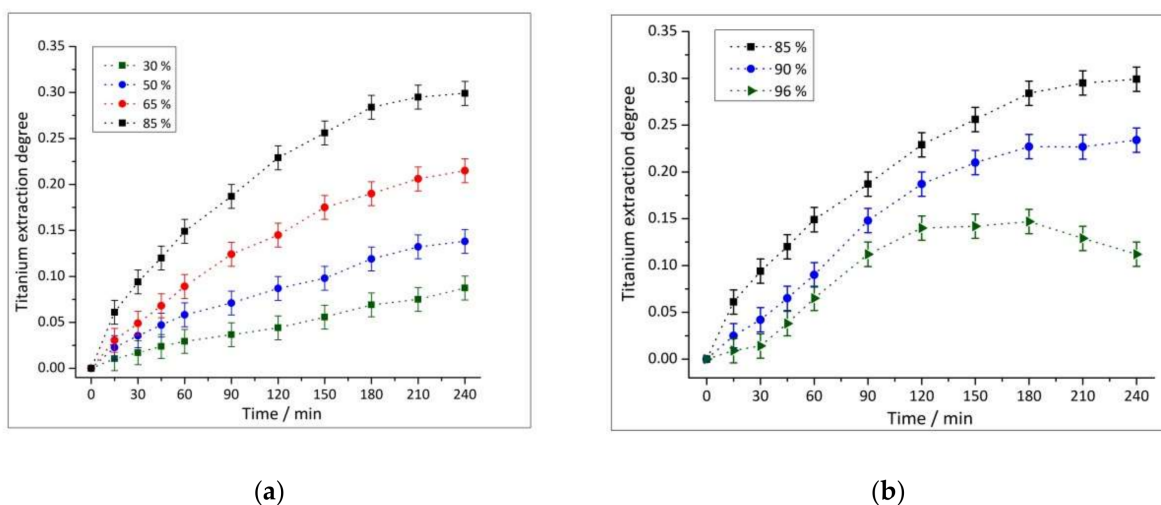


Figure 9. Dependence of the titanium extraction degree from rutile on the concentration of sulfuric acid 30–85 wt% (a) and 85–96 wt% (b) at a temperature of 100 °C; molar module of Ti:F = 1:2; the solid:liquid mass ratio is 1:2.

It was found that the dependences of the extraction degree on the time of rutile leaching in sulfuric acid solutions with concentrations of 30–85% have the form of convex curves (Figure 9a).

The dependences $X(t)$ are concave to the abscissa with 90 and 96 wt.% of acid solutions (Figure 9b, curves 1 and 2) compared to the data with 85 wt.% sulfuric acid. In this case, the rate of leaching of rutile is less.

Thus, the optimal concentration of sulfuric acid in the process of sulfuric acid–fluoride extraction is 85 wt.%.

3.5. Flow Sheet of the Leaching Process of Altered Ilmenite

Figure 10 presents a flow chart of the processing of altered ilmenite concentrate with an additional production site, for the process of the leaching sulfate–fluoride method.

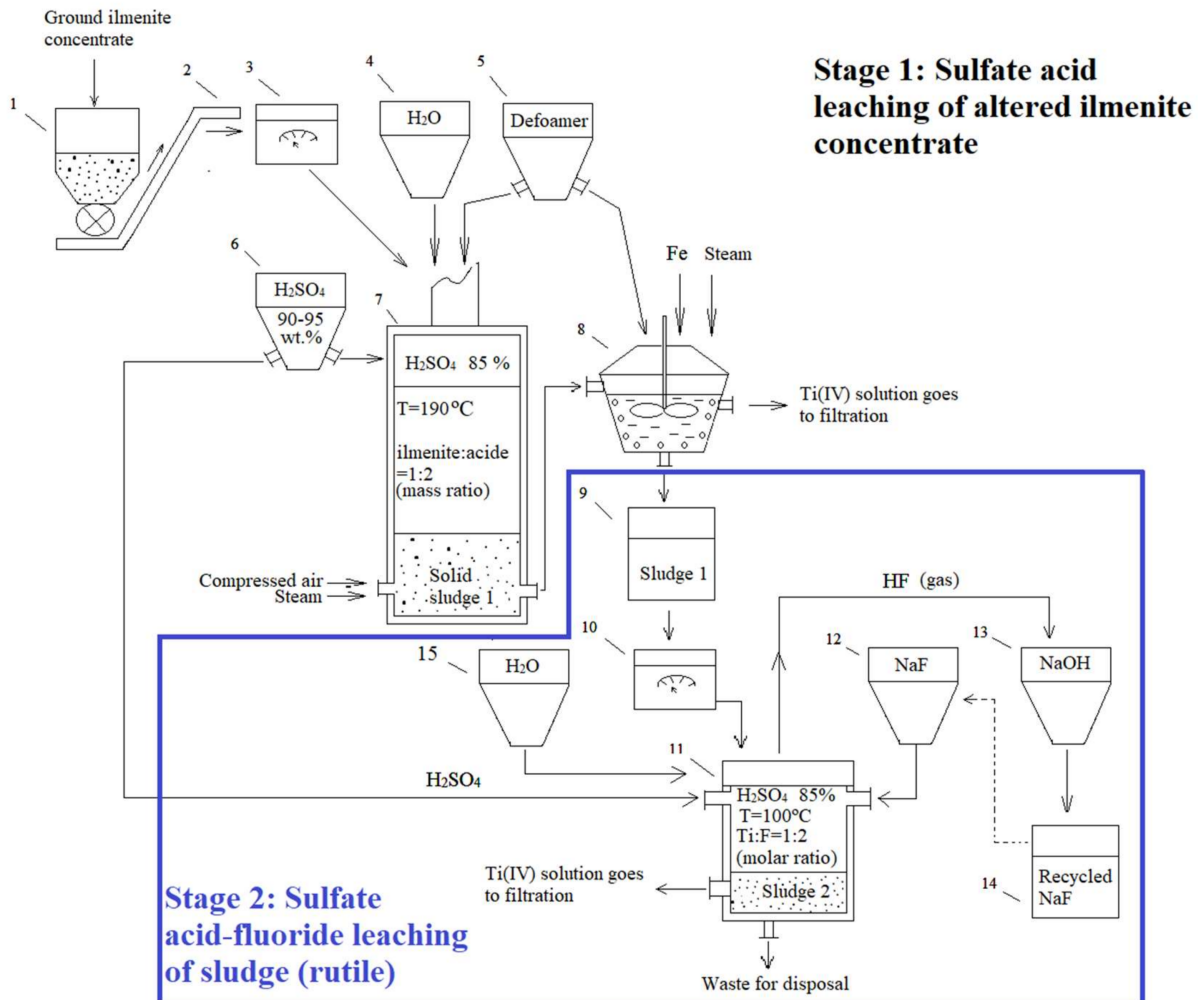


Figure 10. Flow sheet of the two-stage leaching process of altered ilmenite: where: 1—hopper for raw materials; 2—inclined redler; 3—hopper scales for raw materials; 4—the bunker batcher for water; 5—the bunker batcher for the defoamer; 6—hopper-dispenser for sulfuric acid; 7—main reactor of leaching ilmenite concentrate; 8—reactor for Fe reduction; 9—hopper for the sludge accumulation; 10—hopper scales for sludge; 11—sludge processing reactor; 12—the bunker batcher for NaF; 13—absorber with NaOH; 14—hopper for the accumulation of NaF (for possible recirculation of the reagent activator); 15—the bunker batcher with water.

Fluoride ions will be consumed in the leaching process not only for titanium but also for iron. In order to reduce the consumption of fluorinating agent, it is advisable to divide the leaching process into two stages:

- (1) sulfate acid leaching of ilmenite concentrates following the removal of iron compounds from reacting media;
- (2) sulfate acid–fluoride leaching of rutile-containing sludge (not dissolved in the previous stage), in the presence of sodium fluoride.

The first stage description is as follows. The ground ilmenite concentrate from the hopper (1) goes with inclined redler (2) through hopper scales (3) to the main leaching reactor (7). Acid from the hopper (6), water from the hopper (4) and defoamer from the hopper (5) go into the reactor before the solid component. The leaching process occurs with 85 wt.% H₂SO₄ at 190 °C and a mass ratio solid:liquid = 1:2. After the main reaction

of the chemical decomposition of the ilmenite concentrate, the solution is sent for filtration, having previously reduced the iron in the reactor (8). The remains of the undissolved solid fraction (sludge) go to the hopper for sludge accumulation (9). Additional heating and maintaining the temperature in the reactor is carried out by supplying steam.

The second stage description is the next, as follows. Concentrated sulfuric acid is fed in the reactor (11) from the hopper dispenser (6). After that, the solid components are loaded into the reactor: sludge from the hopper for the sludge accumulation (9), through the dispenser (10) and sodium fluoride from the hopper dispenser (12) at a molar ratio of solid components $Ti:F = 1:2$, the mass ratio of solid:liquid = 1:2. This method of loading the components (liquid–solid) promotes better mixing of the reaction mixture. After that, the reactor is fed water from the hopper (15), to dilute the sulfuric acid to the needed concentration (85 wt.%). This promotes the self-heating of the reaction mixture. The sulfate acid–fluoride leaching occurs at 100 °C. Additional heating and maintaining the temperature in the reactor is carried out by supplying steam. After the main reaction of the chemical decomposition of the sludge, the solution is sent for filtration. Next, we propose the absorption of gaseous waste and the recycling of NaF. The formed gaseous HF goes from the reactor (11) to the absorber (13), which contains NaOH. The resulting sodium fluoride is fed to the storage hopper (14), where NaF can flow through the dosing reactor (12) into the reactor (11); thus, the fluoride reagent can be recycled.

It is found that the proposed method of processing of altered ilmenite concentrates allows us to leach up to 95.9% of titanium, which is 1.6–1.9 times higher in comparison with the classical technology of leaching of altered ilmenite.

4. Conclusions

The regression model of the sulfate–fluoride leaching process was developed and analyzed by using the response surface method of 2^3 matrix of three factors each at two levels. The obtained model is adequate (R^2 value is 98.2042%) and well describes the studied process. The technologically optimal parameters of the sulfate–fluoride leaching process are the following parameters [+1; −1; +1]: a molar ratio of $Ti:F = 1:2$, sulfuric acid concentration = 85 wt.%, and the process temperature = 100 °C.

We have experimentally proven that the highest titanium extraction degree was obtained at the molar ratio of the reaction mixture $Ti:F = 1:2$. A larger excess or lack of sodium fluoride leads to a decrease in the leaching rate. The highest titanium extraction degree in the solution, both from ilmenite and rutile, was achieved during the process of sulfuric acid–fluoride leaching at 100 °C and using 85 wt.% of sulfuric acid.

Finally, in the study of the possibility to optimize the process, it was found that increasing and/or decreasing the process temperature, acid concentration, and molar modulus of $Ti:F$ is impractical because it reduces the degree of titanium extraction into solution.

The intensification of the process of sulfuric acid leaching by dividing the main stage of chemical dissolution of ilmenite into two stages is proposed:

1. Sulfuric acid leaching of the altered ilmenite concentrate is carried out under the following conditions: concentration of sulfuric acid = 85 wt.%, process temperature = 190 °C, the mass ratio of solid:liquid = 1:2.
2. Sulfate–fluoride leaching of rutilized sludge (raw materials that did not dissolve in the previous stage) is carried out under the following conditions: addition of sodium fluoride to the reaction mixture in a molar ratio of $Ti:F = 1:2$ and the mass ratio of solid:liquid = 1:2, process temperature = 100 °C, concentration of sulfuric acid = 85 wt.%.

The proposed method of processing of altered ilmenite concentrates allows us to leach up to 95.9% of titanium, which is 1.6–1.9 times higher compared to the classical technology of leaching of altered ilmenite.

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