Chapter

Ammonium Fluorides in Mineral Processing

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Abstract

The possibility of using ammonium fluoride as a new reagent for processing mineral raw materials is considered. Ammonium fluorides are the most convenient and technological fluorinating agents for the decomposition of the silicon component of ores. Advantages the use of ammonium fluoride (or hydrodifluoride) as a desiliconizing agent, the possibility of its complete regeneration. The processes of deep processing of silicon, zirconium, titanium, and beryllium minerals are considered. The excellence of using ammonium fluoride in the processing of mineral raw materials have been proven. The physicochemical laws of the processes are considered, technological schemes are proposed. The material will be useful in the further introduction of fluoride technologies at enterprises for the processing of quartz, zircon, ilmenite, and phenakite.

Keywords: mineral raw materials, ammonium fluoride, beryllium, zirconium, titanium dioxide, silicon dioxide

1. Introduction

Hydrometallurgy of non-ferrous and rare metals with a high energy intensity of the release of microcomponents from mineral raw materials and a significant negative situation on the biosphere. These factors lead to the need to create fundamentally new technologies in which the amount of waste is minimized. In an ideal chemical technology, any waste should become a commercial product, and the reagents should undergo complete regeneration and return to production.

Currently, one valuable component is usually extracted from complex ores, the rest go into slag. The amount of waste in modern chemical plants is boggles the imagination.

The basis of mineral and technogenic raw materials is usually silicon oxide and iron oxides. The opening of the silica component is chemically difficult, and the removal of a large amount of the cheap iron component can make the entire processing of the material unprofitable. Silicate minerals interfere with the hydrometallurgical interaction of the recovered commercial component with the reagent. Pyrometallurgical technologies are energy consuming.

One of the promising technologies is the fluoroammonium technology for processing mineral raw materials.

This article is devoted to the technology of complex processing of natural mineral and technogenic raw materials using ammonium fluorides.

The difference in the properties of ammonium fluorometallates is the physico-chemical basis of the decomposition of mineral raw materials using ammonium fluorides. Metal fluorides notably differ in their in boiling point. Some are volatile and evaporate or sublimate when heated, separating from the main mass. Other fluorides are soluble and can be leached out of the fluorinated mass. Some undergo pyrohydrolysis or have different precipitation pH. After fluorination in a molten ammonium fluoride, a mixture of fluorides and ammonium fluorometallates is obtained.

By varying the differences in the physicochemical properties of ammonium fluorides and fluorometallates, it is possible to select modes for the complete separation of the mineral mixture into individual components.

Ammonium fluoride NH_4F under normal conditions is a non-aggressive, solid, and crystalline substance. Molten ammonium fluoride is an energetic fluorinating agent. Instead of ammonium fluoride, it is possible to use ammonium bifluoride NH_4HF_2. The melting point of NH_4F is 126°C, the boiling point of NH_4HF_2 is 239°C. NH_4HF_2 vapors are mainly composed of HF and NH_3. NH_4HF_2 is highly soluble in water, anhydrous HF, and hydrofluoric acid.

The interaction of most oxides with elemental fluorine, hydrogen fluoride, and hydrofluoric acid has been studied in sufficient detail [1]. The fluorination of mineral raw materials with ammonium fluorides requires further study. Silicon oxide is removed from the system in the form of volatile ammonium hexafluorosilicate at temperatures above 320°C.

Fluorination of metal oxides with fluoride and ammonium hydrodifluoride has been studied to a lesser extent. And the reactions of some fairly common oxides (Sn, Cu, Mn, and Ca), in order to create technological processes, have practically not been studied. The desiliconization cycle makes it possible to project similar processes of fluorination and regeneration of ammonium fluoride onto other oxides.

Regeneration is carried out due to the fact that oxides react well with molten ammonium fluorides at elevated temperatures, but do not react with ammonium fluoride solution in an alkaline medium.

2. Methodology

Thermal analysis was performed using thermogravimetric analysis (DTA)—is the starting characterization test for any thermal analysis. This characterization test gives an understanding of the thermal stability of a sample by giving a weight loss/gain signal as the sample is heated at a known rate in time and exposure to a given atmosphere. Hydrofluorination of oxides in a molten ammonium fluoride was carried out using a TGA/DSC/DTA analyzer SDT Q600 with software processing of data from TA Universal V4.2E instruments. Sample weight: up to 200 mg. Thermocouples: Pt/Pt-Rh. Crucibles: platinum, volume 110 µl. The temperatures of the onset of the reaction, the formation, and decomposition of complex fluoroammonium salts were investigated by the DTA-methods [2].

Thermal analysis of the interaction of oxides with ammonium hydrodifluoride made it possible to determine the temperature ranges in which complex fluoroammonium complexes are formed and their thermal destruction to individual oxides occurs. SiO_2, Al_2O_3, Fe_2O_3, and TiO_2 form complex fluoroammonium

compounds with ammonium fluorides—ammonium hexafluorometallates. NiO form ammonium tetrafluorometalate. CaO, CuO, and KOH—fluorinated to simple fluorides. Thermogravimetric analysis revealed the regularities of oxide fluorination, which are necessary for solving technological problems. The kinetic experiment made it possible to determine the activation energy and the reaction rate constant.

It is calculated that the thermodynamically optimal temperature for hydrofluorination of multicomponent silicate mixtures is 500 ± 20 K. At a lower temperature, chemical reactions slow down. Increasing the temperature is not advisable, because decomposition of ammonium bifluoride into gaseous ammonia and hydrogen fluoride.

Based on DTA, the decomposition temperatures of fluoride compounds Al, Fe, Ni, Mn, Ca, and Cu, formed as a result of hydrofluorination in the melt of ammonium bifluoride, were found. The formation temperature of aluminum fluoride is 355°C, calcium fluoride 240°C, manganese fluoride 215°C, iron fluoride 365°C, nickel fluoride 295°C, and copper fluoride 260°C [3–5].

The kinetics of chemical reactions was investigated using the method of weighing the reacting mixture in the course of a chemical reaction. Weight loss occurs due to the formation of gaseous ammonia and water. The processing of experimental data was carried out according to the well-known methods of formal heterogeneous kinetics [6].

The possibility of separating multicomponent oxide silicate mixtures into individual oxides using only ammonium fluoride as an opening reagent has been experimentally proved.

Below are some specific examples of the application of ammonium fluoride technologies for the processing of mineral raw materials.

3. Results and discussion

3.1 Silicon dioxide processing

High-purity silicon dioxide (SiO_2 content over 99.999%) is used in the production of optical glasses, optical fiber for Internet networks, silicon for solar energy, and electronics. The market for silicon dioxide is constantly growing and the demand for high-purity grades of silicon dioxide is especially high.

The raw material for the production of silicon dioxide is SiO_2-mineral and concentrate or quartz sand. The existing technologies for the production of synthetic silicon oxide are energy-consuming, multi-stage, and do not meet modern environmental requirements. We consider that the most promising direction is the fluoride technology for processing quartz raw materials using ammonium fluoride.

The advantages of NH_4F and NH_4HF_2 are the vigorous (energetic) interaction of the melt with silicon oxide, thus forming solid $(NH_4)_2SiF_6$ [7]. When heated, $(NH_4)_2SiF_6$ sublimes without decomposition, and when cooled, it desublimes. Multiple sublimation-desublimation is used for deep purification of quartz concentrate from impurities [8].

Ammonium fluoride reacts with the original mineral quartz sand according to the reaction:

$$SiO_2 + 6NH_4F \rightarrow (NH_4)_2SiF_6 + 2H_2O + 4NH_3 \qquad (1)$$
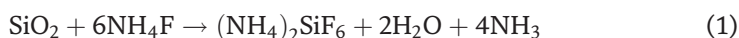
Ammonium bifluoride reacts with silicon oxide according to the reaction:

$$SiO_2 + 3NH_4HF_2 \rightarrow (NH_4)_2SiF_6 + 2H_2O + NH_3 \tag{2}$$
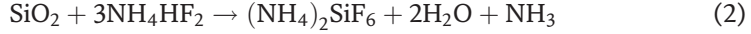
The $(NH_4)_2SiF_6$ formed as a result of the reaction turns into a gaseous state when heated. Gaseous $(NH_4)_2SiF_6$ is condensed and treated with ammonia water with associated regeneration of the fluorinating agent. This process is described by the reaction:

$$(NH_4)_2SiF_6 + 4NH_4OH \rightarrow SiO_2 + 6NH_4F + 2H_2O \tag{3}$$
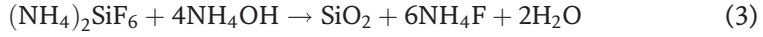
Next, the precipitate of hydrated silicon oxide is separated by filtration from the ammonium fluoride solution. The separated solution of ammonium fluoride is evaporated and crystallized in the form of technical ammonium fluoride of the composition 25% NH_4F and 75% NH_4HF_2. As a result of drying and calcining the precipitate, silicon oxide is obtained in a finely dispersed form.

The process is clearly displayed so-called fluoroammonium cycle (**Figure 1**).

Quartz sand with a known impurity content was used as a raw material (**Table 1**).

When the raw material interacts with NH_4HF_2, the compounds of impurity elements form the following fluorides:
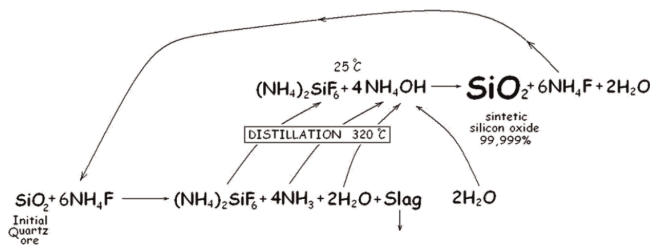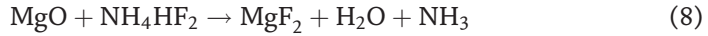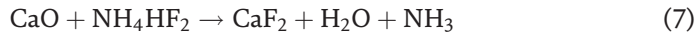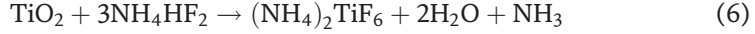
$$Al_2O_3 + 6NH_4HF_2 \rightarrow 2(NH_4)_3AlF_6 + 3H_2O \tag{4}$$

$$Fe_2O_3 + 6NH_4HF_2 \rightarrow 2(NH_4)_3FeF_6 + 3H_2O \tag{5}$$

$$TiO_2 + 3NH_4HF_2 \rightarrow (NH_4)_2TiF_6 + 2H_2O + NH_3 \tag{6}$$

$$CaO + NH_4HF_2 \rightarrow CaF_2 + H_2O + NH_3 \tag{7}$$

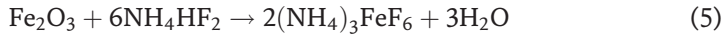$$MgO + NH_4HF_2 \rightarrow MgF_2 + H_2O + NH_3 \tag{8}$$
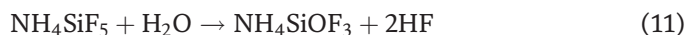

Figure 1.
*Schematic diagram of fluoroammonium purification of silicon dioxide.*

Elements,%							
SiO$_2$	AI	Ti	Na	Mg	K	Ca	Fe
97.5	0.28	0.11	0.06	0.06	0.1	0.84	0.96

Table 1.
Composition of raw materials (quartz sand).

Side reactions of the formation of nonstoichiometric silicon fluorides:

$$5(NH_4)_2SiF_6 + SiO_2 \rightarrow 6NH_4SiF_5 + 4NH_3 + 2H_2O \qquad (9)$$

$$SiO_2 + 4NH_4HF_2 \rightarrow (NH_4)_2SiF_6 + 2H_2O + NH_3 + HF \qquad (10)$$

$$NH_4SiF_5 + H_2O \rightarrow NH_4SiOF_3 + 2HF \qquad (11)$$
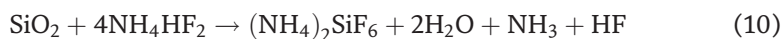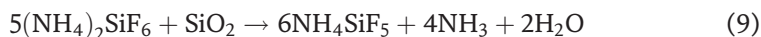
It is known that reaction (9) can occur only at temperatures above 180°C. There-fore, upon fluorination, in our case, reaction (9) does not proceed. This reaction takes place in the next apparatus with sublimation purification of $(NH_4)_2SiF_6$ from impurities. Upon dissolution and subsequent precipitation of $(NH_4)_2SiF_6$ with a 25% ammonia solution, an undesirable hard-to-filter silica gel is formed due to the presence of NH_4SiOF_3.

$$NH_4SiOF_3 + H_2O \rightarrow SiO_2(gel) + NH_4F + 2HF \qquad (12)$$
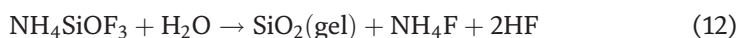
In the sublimator $(NH_4)_2SiF_6$ evaporates and decomposes according to the reaction:

$$(NH_4)_2SiF_6 \rightarrow 2NH_3 + 2HF + SiF_4 \qquad (13)$$
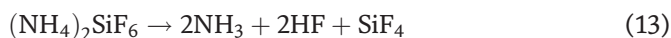
In the desublimator NH_3, HF, and SiF_4 are cooled to form $(NH_4)_2SiF_6$

$$2NH_3 + 2HF + SiF_4 \rightarrow (NH_4)_2SiF_6 \qquad (14)$$
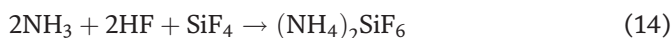
Experimentally, we noticed that the temperature of the desublimation process strongly affects the quality of the resulting desublimate, in particular, the ratio of the amount of ammonium fluoride and $(NH_4)_2SiF_6$, as well as the amount of impurities in condensed $(NH_4)_2SiF_6$. A series of experiments was carried out to determine the effect of temperature.

The freeze-drying process consists of two stages:

1. from 110 to 280°C—side reactions. Capturing NH_4HF_2, NH_4F, NH_4SiF_5, and NH_4SiOF_3. Removal of excess NH_3.

2. from 280 to 380°C—sublimation and capture of $(NH_4)_2SiF_6$.

To determine the thermal properties of the compounds formed as a result of hydrofluorination in the ammonium fluoride melt, and the temperatures of their decomposition, DTA were carried out (**Figure 2**).

The initial temperature of weight loss is equal to 100°C, the change in weight stops at a temperature of 252°C, 16% of the total weight of the sample remains not flown away. This residue is fluoride of silica sand impurities. The DTA graph shows two exothermic peaks with maximums at 152 and 243°C.

The second peak characterizes the sublimation of $(NH_4)_2SiF_6$ and NH_4HF_2. Using TA instruments Universal V4.2E, the enthalpies of these processes were calculated in the first case ΔH = 214 J/g, in the second case ΔH = 1547 J/g. Heat of the sublimation process: Q = −1761 J/g.

The feedstock (quartz sand) and the reagent (ammonium fluoride) are mixed in the mixer screw and fed to the rotary drum kiln. In the furnace, a chemical reaction of interaction between quartz and ammonium fluoride takes place. The formation of
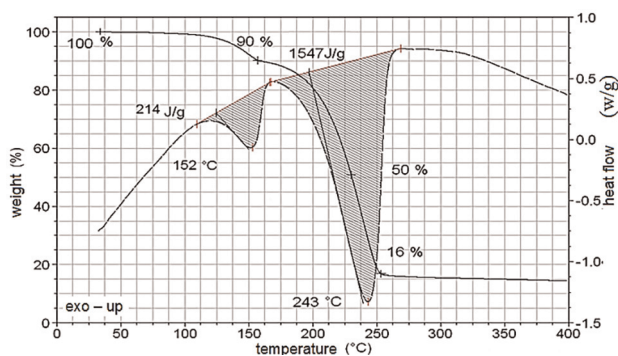
Figure 2.
Thermogravimetric and differential thermal analyzes of the decomposition of a fluorinated product. Heating rate 10°C/min.

solid primary $(NH_4)_2SiF_6$, gaseous water and ammonia is observed at a temperature of 200–220°C. The formed $(NH_4)_2SiF_6$ is heavily contaminated. It contains unreacted quartz and impurity fluoridation products. Impurities of Al, Fe, Ca, and many other substances are always contained in the original quartz sand. The gaseous phase containing ammonia and water vapor enters the absorption stage to produce ammonia water.

The solid phase [primary $(NH_4)_2SiF_6$] goes to the stage of sublimation purification in the next furnace. In a sublimation oven at a temperature of 320–350°C, gaseous $(NH_4)_2SiF_6$ evaporates. Impurities remain solid. Thus, the product is purified from impurities. The design of the sublimation oven is important. It is necessary to ensure high productivity of the process, but to prevent the ingress of impurities into the gas phase. Impurities can enter the gas phase due to the high velocity of the gas flow or due to intensive mixing of the reaction mass and the formation of dust. We suggest using a fixed bed furnace to prevent dust and impurities from entering the vaporized $(NH_4)_2SiF_6$. Gaseous $(NH_4)_2SiF_6$ from the sublimation furnace enters the condenser, where the gas is cooled and solid $(NH_4)_2SiF_6$ condenses. Sublimation and desublimation operations allow for high purity $(NH_4)_2SiF_6$. The impurity content can be reduced to 1 ppm. High purity $(NH_4)_2SiF_6$ dissolves in water.

Ammonia water is added to the solution and silicon oxide is precipitated. Regeneration of ammonium fluoride occurs as a result of the reaction of interaction of $(NH_4)_2SiF_6$ with ammonia water. The obtained silica precipitate is filtered to separate the ammonium fluoride solution. Silicon oxide is calcined in an oven to remove moisture. The ammonium fluoride solution is evaporated and crystallized. The regenerated ammonium fluoride again enters the stage of decomposition of a new portion of quartz sand. The hardware diagram of the experimental section consists of a number of standard and specially designed chemical devices (**Figure 3**).

As a result of studying the process of obtaining high-purity silicon oxide, the optimal conditions for the process of sublimation purification of $(NH_4)_2SiF_6$ were determined. In the temperature range from 110 to 280°C NH_4HF_2, NH_4F, NH_4SiF_5, and NH_4SiOF_3 are evaporated and excess NH_3 is removed. At temperatures from 280 to 380°C—sublimation and capture of $(NH_4)_2SiF_6$. It has been determined that at a desublimation temperature of 110–120°C it is possible to obtain the purest product with the highest content of $(NH_4)_2SiF_6$. The studies carried out made it possible to launch a pilot production of high-purity synthetic silicon oxide with a basic substance SiO_2 content of 99.999%.
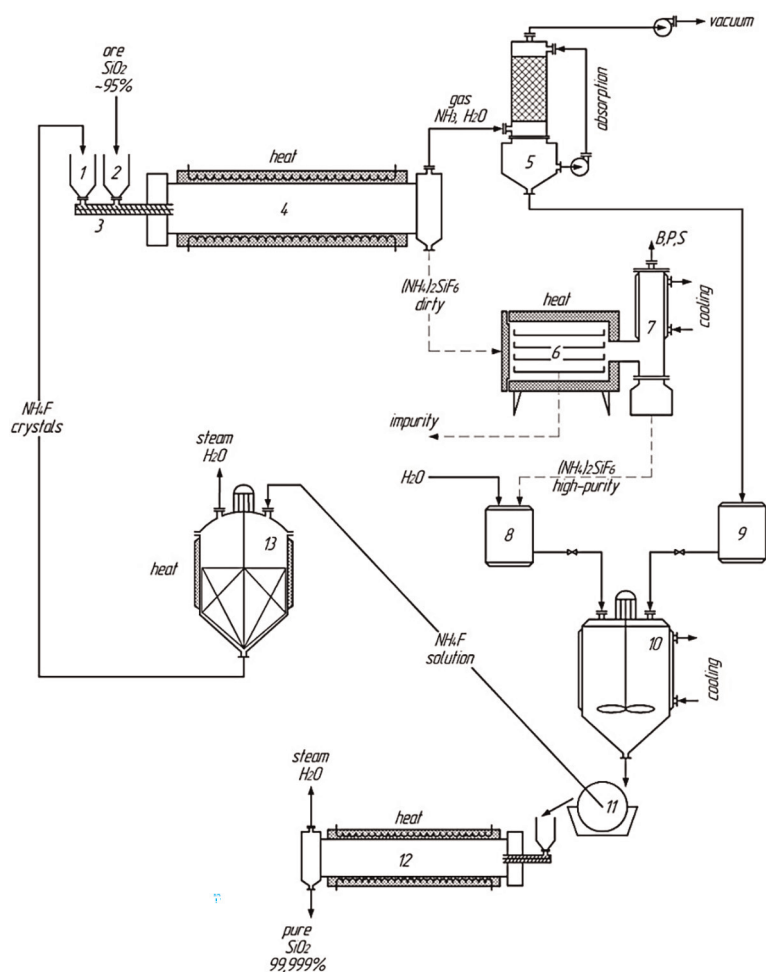
Figure 3.
Hardware diagram of fluoroammonium production of silicon dioxide. (1) Bunker for loading ammonium fluoride, (2) bunker for loading raw materials, (3) mixer screw, (4) drum rotary kiln, (5) ammonia absorber, (6) sublimation furnace, (7) condenser, (8) dissolution tank $(NH_4)_2SiF_6$, (9) tank for storing ammonia water, (10) reactor for precipitation of SiO_2, (11) vacuum filter, and (12) oven for drying SiO_2.

3.2 Zircon processing

A method for the autoclave decomposition of zircon with ammonium fluorides with the aim of producing zirconium oxide has been proposed and investigated.

It is known that zircon $(ZrSiO_4)$ is one of the most chemically strong compounds. The molten ammonium fluoride at atmospheric pressure weakly interacts with zircon according to the reactions [9, 10]:

$$ZrSiO_4 + 13NH_4F \rightarrow (NH_4)_3ZrF_7 + (NH_4)_2SiF_6 + 8NH_3 + 4H_2O \qquad (15)$$

$$2ZrSiO_4 + 13NH_4F \cdot HF \rightarrow 2(NH_4)_3ZrF_7 + 2(NH_4)_2SiF_6 + 3NH_3 + 8H_2O \qquad (16)$$
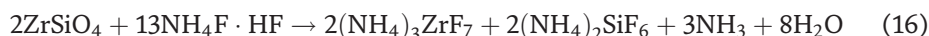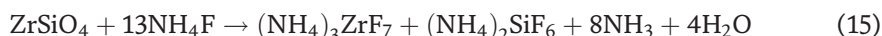
Our studies have shown that fluorides react well with zircon at elevated pressures, that is, in an autoclave.

Having carried out a series of experiments on the decomposition of zircon with ammonium fluorides under various conditions, it was possible to find the optimal parameters that allow for a complete opening of the mineral and the conversion of zirconium into a soluble compound. It has been proven that the decomposition of zircon is faster when using ammonium bifluoride.

From the experimental data presented, it is possible to propose the optimal parameters of the process—the degree of response of more than 95% is achieved at a temperature of 300°C in 4 hours and at a temperature of 400°C in 1 hour.

The regeneration of ammonium fluoride provides a high economic attractiveness of the process and environmental safety. The resulting ammonium hexafluorosilicate sublimes at temperatures above 320°C and is removed from the mixture. As the temperature rises, $(NH_4)_2ZrF_6$ decomposes to zirconium tetrafluoride with the release of ammonia and hydrogen fluoride. The scheme of regeneration of ammonium fluoride and ammonium bifluoride is shown in **Figure 4**.

According to the proposed method, zircon, crushed to a particle size of 0.1 mm, is alloyed with ammonium bifluoride under isochoric conditions at a temperature of 300°C for 4 hours, while a pressure of up to 40 atm develops in the autoclave.

After decomposition, by the method of sublimation separation, zirconium tetra-fluoride is isolated and purified. From the obtained ZrF_4 with the help of ammonia, zirconyl hydroxide—$ZrO(OH)_2$ is isolated.

3.3 Titanium dioxide processing

Titanium dioxide is one of the twenty main products of the chemical industry and is used as a white pigment in paints and varnishes. The ammonium fluoride method makes it possible to isolate titanium tetrafluoride from ilmenite $FeTiO_3$ in one stage and convert it into the form of titanium dioxide [11]. The interaction of ilmenite with ammonium fluoride proceeds with the formation of ammonium hexafluorotitanate and ammonium pentafluoroferrate according to reaction (17).

$$FeTiO_3 + 11NH_4F \rightarrow (NH_4)_2TiF_6 + (NH_4)_3FeF_5 + 6NH_3 + 3H_2O \qquad (17)$$

This reaction begins at the melting temperature of ammonium fluoride—125°C, at a temperature of 280°C $(NH_4)_2TiF_6$ decomposes to TiF_4. At the same time, $(NH_4)_3FeF_5$ undergoes oxidation by atmospheric oxygen with simultaneous pyrohydrolysis according to reaction (18).
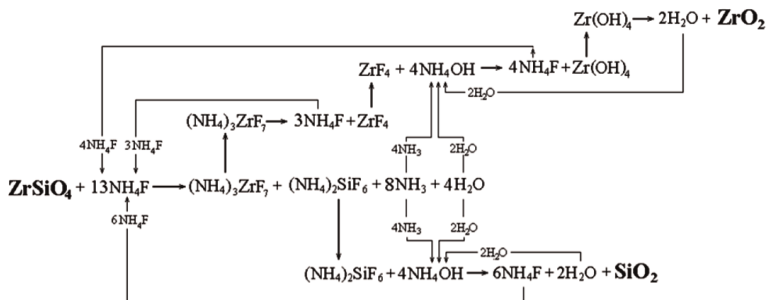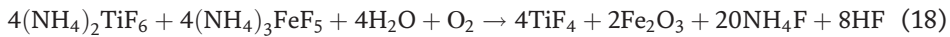

Figure 4.
Scheme of the decomposition of zircon into zirconium and silicon oxides.

$$4(NH_4)_2TiF_6 + 4(NH_4)_3FeF_5 + 4H_2O + O_2 \rightarrow 4TiF_4 + 2Fe_2O_3 + 20NH_4F + 8HF \quad (18)$$

Volatile titanium tetrafluoride, ammonia, water, ammonium fluoride at temperatures above 280°C are separated from iron(III) oxide. The kinetics of the fluorination of ilmenite with ammonium fluorides was studied experimentally.

In the temperature range 125–150°C, the activation energy of the process is 69 kJ/mol. The process takes place in the kinetic region of the reaction. The limiting stage of the process is the interaction of the reagents. The dependence of the degree of response on temperature and time is written by the Crank-Ginstling-Brounstein's equation:

$$\alpha = 1 - \left[1 - \sqrt{3,18 \cdot 10^4 \cdot e^{-\frac{68988}{R \cdot T}} \cdot \tau} \right]^3 \quad (19)$$

In the range 175–250°C, the activation energy of the process is 11 kJ/mol. The process takes place in the diffusion reaction region and is limited by the diffusion of the reaction products. In this interval, the degree of reaction can be determined by the Crank-Ginstling-Brounstein's equation:

$$\alpha = 1 - \left[1 - \sqrt{3, \cdot 10^{-3} \cdot e^{-\frac{11078}{R \cdot T}} \cdot \tau} \right]^3 \quad (20)$$

Ammonium hexafluorotitanate under the influence of temperature decomposes into gaseous titanium tetrafluoride, ammonia, hydrogen fluoride, and water. The gases are captured and interact when cooled according to reaction (21).

$$TiF_4 + 4NH_4OH \rightarrow Ti(OH)_4 + 4NH_4F \quad (21)$$
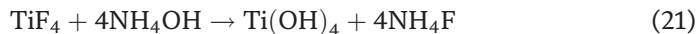
Ammonium fluoride is regenerated and titanium hydroxide is precipitated. **Figure 5** is a diagram showing the chemistry of the process and clearly depicting the return of ammonium fluoride to the cycle.

The only consumable reagent in the fluoroammonium processing of ilmenite is air oxygen, which is necessary for the oxidation of iron to the trivalent state. According to stoichiometry, 5.26 kg of oxygen is required for the oxidation of iron in 100 kg of ilmenite, which corresponds to 37 m^3 of air.

A schematic process flow diagram for producing titanium dioxide and iron oxide from ilmenite is shown in **Figure 6**.
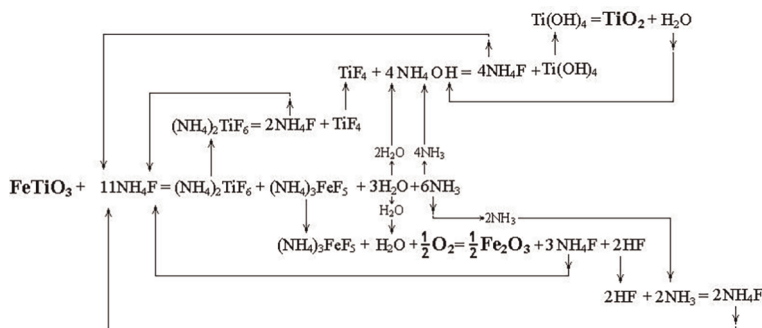

Figure 5.
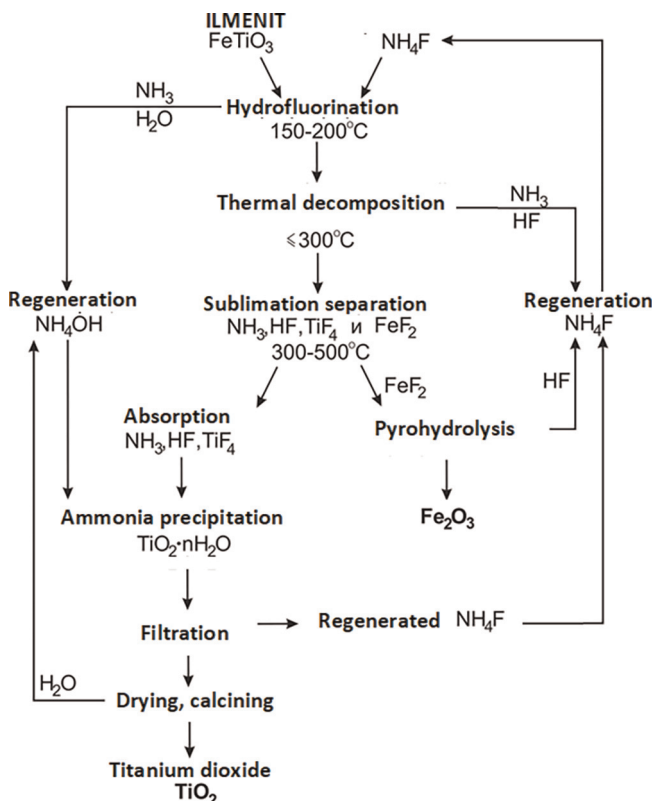*Scheme of decomposition of ilmenite to titanium dioxide and iron oxide.*

Figure 6.
Schematic diagram of fluoroammonium processing of ilmenite.

Ilmenite concentrate undergoes hydrofluorination in a molten ammonium fluoride at 150–200°C. In this case, fluoroammonium complexes of titanium and iron are formed, which decompose into iron difluoride and titanium tetrafluoride at temperatures above 300°C. After sublimation of titanium tetrafluoride, iron difluoride undergoes oxidative pyrohydrolysis with the formation of iron (III) oxide. Titanium tetrafluoride, separated from iron fluorides and impurities, is captured and precipitated by ammonia water to form hydrated titanium dioxide and ammonium fluoride solution.

After filtration, washing, drying and calcination of the resulting precipitate, titanium dioxide is obtained.

Based on the research carried out, a technological sequence of operations was developed. The modes of obtaining pigment TiO_2 and Fe_2O_3 from $FeTiO_3$ shown in **Table 2** were determined on a pilot batch of ilmenite concentrate.

A technique has been developed for processing ilmenite concentrate with ammonium fluoride to pigment titanium dioxide and iron (III) oxide. The optimal technological modes of fluoroammonium processing of ilmenite to TiO_2 (with the structure of rutile and anatase) and iron(III) oxide have been determined.

3.4 Beryllium processing

This chapter also describes the possibility of applying the fluorine-ammonium technology to the processing of beryllium ores—bertrandite $Be_4[Si_2O_7](OH)_2$ and phenakite Be_2SiO_4 and beryl BeO [12–14].

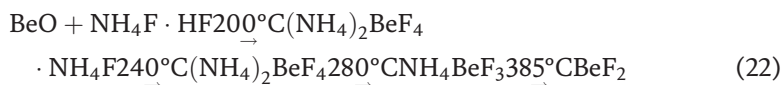| Stage (process)	Temperature, °C	Time, h	Product yield, %
Decomposition of ilmenite	150–200	1.5	95–99
Sublimation department TiF_4	400–500	1	95–98
TiF_4 capture	25	—	98.5
Sedimentation	25–35	0.5	99
Filtration	—	—	—
Anatase not less than 95%	500	2	—
Rutile not less than 95%	800	2	—
Pyrohydrolysis to Fe_2O_3	500	2	95
NH_4F regeneration (solution evaporation)	100–110		95

Table 2.
Modes of obtaining pigment titanium dioxide from ilmenite.

The thermodynamic probability of the reactions of interaction of the components of the beryllium concentrate with ammonium fluoride was calculated (**Table 3**).

The reaction of fluorination of phenakite with ammonium fluoride at temperatures above 500 K proceeds in the forward direction with the formation of ammonium tetrafluoroberyllate and ammonium hexafluorosilicate. The reaction of phenakite fluorination with ammonium hydroditoride begins already at a temperature of 127°C, with an increase in temperature, the reaction proceeds more fully with the formation of products.

The reaction begins to proceed at room temperature with the formation of the beryllium fluoroammonium complex $(NH_4)_2BeF_4 \cdot nNH_4F$ and with the release of gaseous ammonia and water. With further heating, the process of decomposition of the fluoroammonium complex of beryllium proceeds. At 200°C $(NH_4)_2BeF_4 \cdot NH_4F$ is formed, which, when heated to 240°C, decomposed to $(NH_4)_2BeF$. When the temperature rises to 280°C, $(NH_4)_2BeF_4$ decomposes to NH_4BeF_3, which, in turn, decomposes to BeF_4 at 385°C.

Based on the analysis of thermogravimetric studies, it is possible to propose the following chain of chemical transformations occurring during the interaction of beryllium oxide with fluoride and ammonium hydrodifluoride (20):

$$BeO + NH_4F \cdot HF \xrightarrow{200°C} (NH_4)_2BeF_4$$
$$\cdot NH_4F \xrightarrow{240°C} (NH_4)_2BeF_4 \xrightarrow{280°C} NH_4BeF_3 \xrightarrow{385°C} BeF_2 \qquad (22)$$

The decomposition kinetics of beryllium oxide is shown in **Figure 7**.

T, °C	25	127	227	327	427	527
$Be_2SiO_4 + 14NH_4F \rightarrow 2(NH_4)_2BeF_4 + (NH_4)_2SiF_6 + 8NH_3 + 4H_2O$						
ΔG, кДж/моль	20	−181	−384	−588	−793	−999
$Be_2SiO_4 + 7NH_4HF_2 \rightarrow 2(NH_4)_2BeF_4 + (NH_4)_2SiF_6 + NH_3 + 4H_2O$						
ΔG, kJ/mol	−224	−297	−353	−394	−424	−443

Table 3.
Thermodynamics of the process of phenakite fluorination with ammonium fluorides.

Figure 7.
Kinetics of interaction of beryllium oxide with ammonium fluoride. (1) 140°C, (2) 160°C, (3) 180°C, and (4) 200°C.

The kinetic equation for describing the rate of the process is found experimentally:

$$\alpha = 1 - \left(1 - 1,8 \cdot e^{-\frac{31000}{8,31 \cdot T}} \cdot \tau\right)^3 \tag{23}$$

The activation energy of the process was 31 kJ/mol, which indicates the occurrence of the reaction in the transition region between diffusion and kinetic. Kinetic studies have shown that in 20 minutes at a temperature of 200°C, the decomposition of beryllium oxide occurs by more than 95%.

Below is a diagram of a closed fluoroammonium cycle of decomposition of phenakite into silicon oxide and beryllium oxide with the regeneration of ammonium fluoride. The diagram in **Figure 8** clearly illustrates the closure of flows and the equality of material balance.

Thermodynamic and thermal analyzes of the considered system, which proved the theoretical and laboratory feasibility of the process, made it possible to proceed to the development of the process flow diagram (**Figure 9**).

The original fluorite-phenakite concentrate, containing 30% phenakite, was mixed with ammonium fluoride and heated to a temperature of 200°C. The interaction of phenakite with ammonium fluoride took place, with the formation of ammonium fluoroberrylate with ammonium hexafluorosilicate and the release of gaseous ammonia and water (24).

$$Be_2SiO_4 + 14NH_4F \rightarrow 2(NH_4)_2BeF_4 + (NH_4)_2SiF_6 + 8NH_3 + 4H_2O \tag{24}$$

Figure 8.
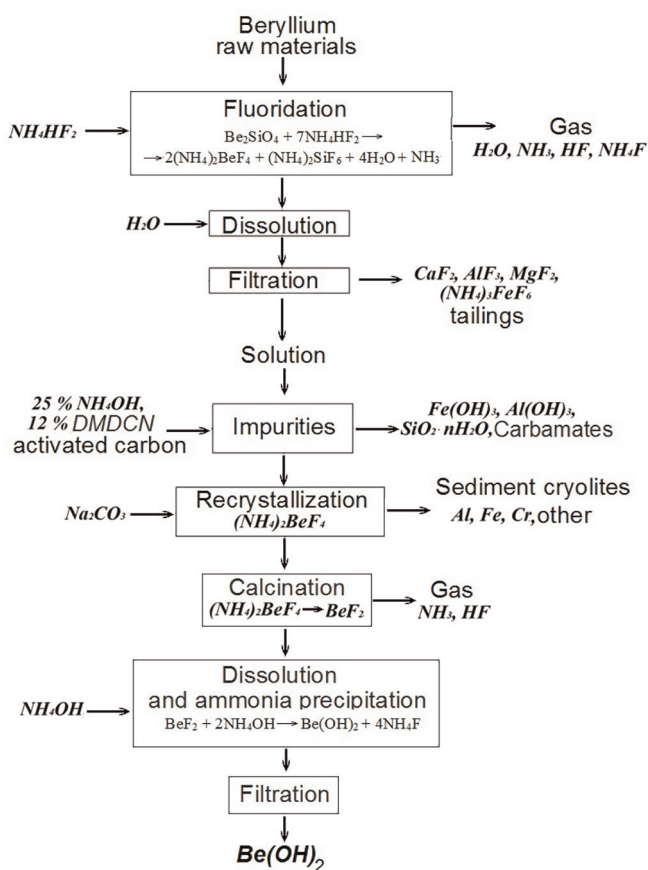*Scheme of the decomposition of phenakite to beryllium oxide and silicon oxide.*

Figure 9.
Scheme of processing beryllium phenakite concentrate.

Upon heating, silicon was sublimated in the form of gaseous ammonium hexafluorosilicate $(NH_4)_2SiF_6$. The solid fraction contains ammonium tetrafluoroberrylate and non-fluorinated fluoride. Leaching of ammonium tetrafluoroberrylate with water makes it possible to completely isolate it from the support rock, since the solubility of ammonium tetrafluoroberyllate reaches 32%, and calcium fluoride is practically insoluble. After separation of the ammonium tetrafluoroberyllate solution, it was purified from aluminum and iron impurities. Cleaning is carried out by the method of ammonia raising the pH of the solution to 8.5. At pH = 8.5, aluminum and iron hydroxides precipitate from the solution.

The separation of aluminum impurities by means of ammonia precipitation makes it possible to apply the fluoroammonium method also to the processing of beryl $(2BeO•Al_2O_3•6SiO_2)$. With a further increase in pH to pH = 12, a precipitate of beryllium hydroxide precipitates. The beryllium hydroxide separated by filtration, after calcination, transforms into the oxide form.

A technological scheme of fluorine-ammonium processing of fluorite-phenakite concentrate with the return of ammonium fluoride to the process and the release of beryllium oxide, silicon oxide and calcium fluoride is proposed [15].

4. Conclusion

The optimum conditions of natural quartz processing were determined. Sublimation purification of $(NH_4)_2SiF_6$ is carried out at temperatures from 280 to 380°C and desublimation at 110–120°C. Synthetic silicon oxide with basic substance SiO_2 content of 99.999% was obtained.

Technological scheme for fluoroammonium processing of zirconium and obtaining zirconium dioxide is developed. Zircon is completely decomposed by ammonium hydrodifluoride at temperature 400°C and pressure 40 atm in an autoclave.

The technological scheme of ilmenite concentrate processing by ammonium fluoride to pigmented titanium dioxide and iron oxide (III) is developed. The optimal technological modes of ilmenite fluorination at 150–200°C for 2 hours are determined.

The methods for fluoroammonium processing of fluorite-phenakite concentrate and production of beryllium oxide, silicon oxide, and calcium fluoride were proposed. Fluorination occurs at 200°C, purification from silicon at 300–350°C.

We experimentally proved the feasibility of fluoroammonium processing of quartz, zircon, ilmenite, and phenakite minerals. The next step of our research we can propose the adaptation of fluoroammonium technologies for implementation in production.

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