TECHNOLOGY OF HIGH-PURITY SILICON DIOXIDE PRODUCTION

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ABSTRACT

The possibility of SiO_2 5N production by staged purification of ammonium hexafluosilicate $(NH_4)_2SiF_6$ is discussed. High-purity silicon dioxide can be obtained with fluoridation of quartz concentrate by solid NH_4F at 100 °C, with further sublimation of the product at 320 °C, its dissolution, ammonia hydrolysis, filtration and drying of $SiO_2 \cdot nH_2O$. This is accompanied by regeneration of the processing reagent - NH_4F.

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INTRODUCTION

Production of high-purity silica-5N (SiO_2 content over 99.999%) is an important and urgent task of the modern chemical industry. This material is used in the manufacture of optical glass, optical fibers for internet cables, silicon for solar power and electronics.

Quartz concentrate is raw material for the production of silicon dioxide. The existing technologies of synthetic silicon dioxide were introduced in the mid-twentieth century. These methods are energy-consuming, multi-step and do not meet stringent environmental requirements. In fact, as some conventional technologies became obsolete; it became necessary to develop new methods for the production of synthetic silica. We believe that the fluoride technology of processing of quartz materials by ammonium fluoride is the most promising direction.

In industry, silicon dioxide marked "Silica White" is obtained by liquid-phase method. The method consists of the precipitation of amorphous silica from sodium silicate solutions with acids. The resulting product is filtered, washed and dried. Depending on the deposition conditions and nature of the coagulant the "Silica White" is acidic, neutral or alkaline. The dry product is subjected to grinding. The degree of dispersion and porosity of the particles of Silica White depends on the nature of decomposition agent (a substance that decomposes the silicate) and coagulant, conditions of sedimentation, filtration and drying. During the drying process the silica particles are sintered into aggregates of a few millimeters.

Silica marked "Aerosil" is produced by hydrolysis of $SiCl_4$ with water vapor at 1,000 – 1,100 °C. This forms hydrated and very pure product with high dispersion and low porosity. However, this method has considerable energy consumption, high cost of raw materials and the formation of a large quantity of HCl. Implementation of a new method for producing high-purity silica is carried out in the Tomsk Polytechnic University. Fluoride technology is used as the basis of the method.

Ammonium fluoride is selected as a fluorinating reagent, which is a waste byproduct of fluoride industries such as aluminum and plastics plants. Ammonium fluoride under normal conditions is non-aggressive, solid, and crystalline substance. The molten ammonium fluoride is a strong fluorinating reagent. Instead of ammonium fluoride, it is possible to use ammonium hydrogen difluoride NH_4HF_2. The melting point of NH_4HF_2 is 126 °C. The enthalpy of melting is 19.1 kJ/mol. NH_4HF_2 characterized by the presence of a large thermal effect of premelting (0.435 kJ/mol). Boiling point of NH_4HF_2 is 239.5 ° C. The expansion of the liquid NH_4HF_2 proceeds with an activation energy of 63 kJ/mol and the enthalpy of decomposition is 216 kJ/mol. Vapors of NH_4HF_2 mainly consist of HF and NH_3.NH_4HF_2 is readily soluble in water and in anhydrous HF hydrofluoric acid.

The advantages of NH_4F and NH_4HF_2 are vigorous interaction with the molten silicon oxide, and forming a solid $(NH_4)_2SiF_6$. Upon heating, $(NH_4)_2SiF_6$ sublimes without decomposition, and desublimes when cooled - this property is used to clean impurities from the quartz concentrate.

At first the quartz concentrate is added with fluoride (NH_4F), or ammonium hydrogen difluoride ($NH_4F \cdot HF$) while mixture is heated.

Ammonium fluoride reacts with silica according to the following reaction:

$$SiO_2 + 6NH_4F = (NH_4)_2SiF_6 + 2H_2O + 4NH_3 \quad (1)$$

Ammonium hydrogen difluoride reacts with silicon oxide by the following reaction:

$$SiO_2 + 3NH_4F \cdot HF = (NH_4)_2SiF_6 + 2H_2O + NH_3 \quad (2)$$

The resulting $(NH_4)_2SiF_6$ when heated turns into a gaseous state. Gaseous $(NH_4)_2SiF_6$ is condensed and treated with ammonia water which accompanies with regeneration of the fluorinating agent. This process is described by the following reaction:

$$(NH_4)_2SiF_6 + 4NH_4OH = SiO_2 + 6NH_4F + 2H_2O \quad (3)$$

Then the hydrated silica is separated by the filtration from the solution of ammonium fluoride. The separated solution of ammonium fluoride is evaporated and crystallized in the form of technical ammonium fluoride with composition of 25% NH_4F, 75% $NH_4F \cdot HF$. Silicon dioxide in finely divided form is obtained by drying and calcining of the precipitate.

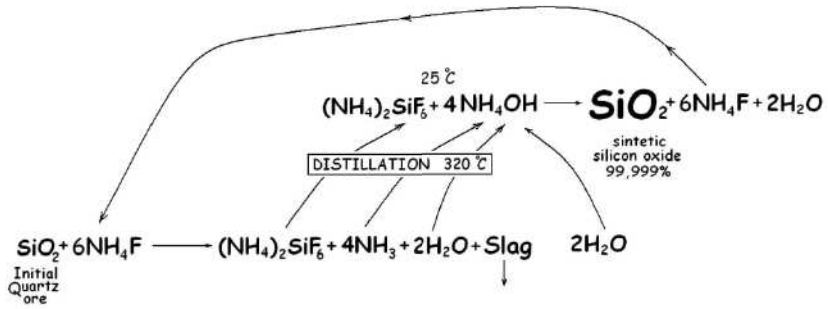


Figure 1 – Schematic diagram of ammonium fluoride treatment of silicon dioxide

The production process of high-purity synthetic silicon dioxide is easy to organize in industrial scale. The technology uses standard chemical apparatus.

Raw materials (quartz sand) and reagent (ammonium fluoride), mixed in the auger and fed into a rotary kiln. Heating in the furnace causes a reaction of quartz with ammonium fluoride and formation of solid $(NH4)_2SiF_6$ and gaseous water and ammonia at a temperature of 200 – 220 °C. The primary $(NH_4)_2SiF_6$ is quite dirty. It contains unreacted silica and products of fluorination of the impurities contained in the raw quartz sand. The gaseous phase containing the ammonia and water vapor are entered the stage of absorption for the production of ammonia. The solid phase (the primary $(NH_4)_2SiF_6$) enters the stage of sublimation purification in the next stage. Evaporation of the gas $(NH_4)_2SiF_6$ takes place in the sublimation furnace at a temperature of 320 – 350 °C. The impurities are retained in the solid form. Thus there is a purification of the product from impurities. The design of the sublimation furnace is important. It is necessary to achieve high process productivity, but prevent the ingress of impurities into the gas phase. The impurities can get into the gas phase due to the high velocity of gas flow or as a result of intensive mixing of the reacting masses and the formation of dust.

We propose to use the furnace with a fixed reacting layer, to prevent the ingress of dust and impurities in evaporated $(NH_4)_2SiF_6$. Gaseous $(NH_4)_2SiF_6$ from the sublimation furnace feds into the cold condenser. The cooling and condensation of solid $(NH4)_2SiF_6$ takes place in condenser. The sublimation and desublimation operations can achieve high purity $(NH_4)_2SiF_6$. The content of impurities can be reduced to 1 ppm. High-purity $(NH_4)_2SiF_6$ is dissolved in water. Ammonia water is added to the solution and the deposition of silicon oxide occurs. Regeneration of ammonium fluoride occurs due to the reaction of $(NH_4)_2SiF_6$ with ammonia water. The resulting precipitate of silica is filtered for the separation of ammonium fluoride solution. Silicon oxide is calcined in a furnace to remove moisture. A solution of ammonium fluoride is evaporated and crystallized. Regenerated ammonium fluoride re-enters to the decomposition stage of raw quartz sand. A simplified version of the apparatus circuit manufacturing process is shown in Figure 2.

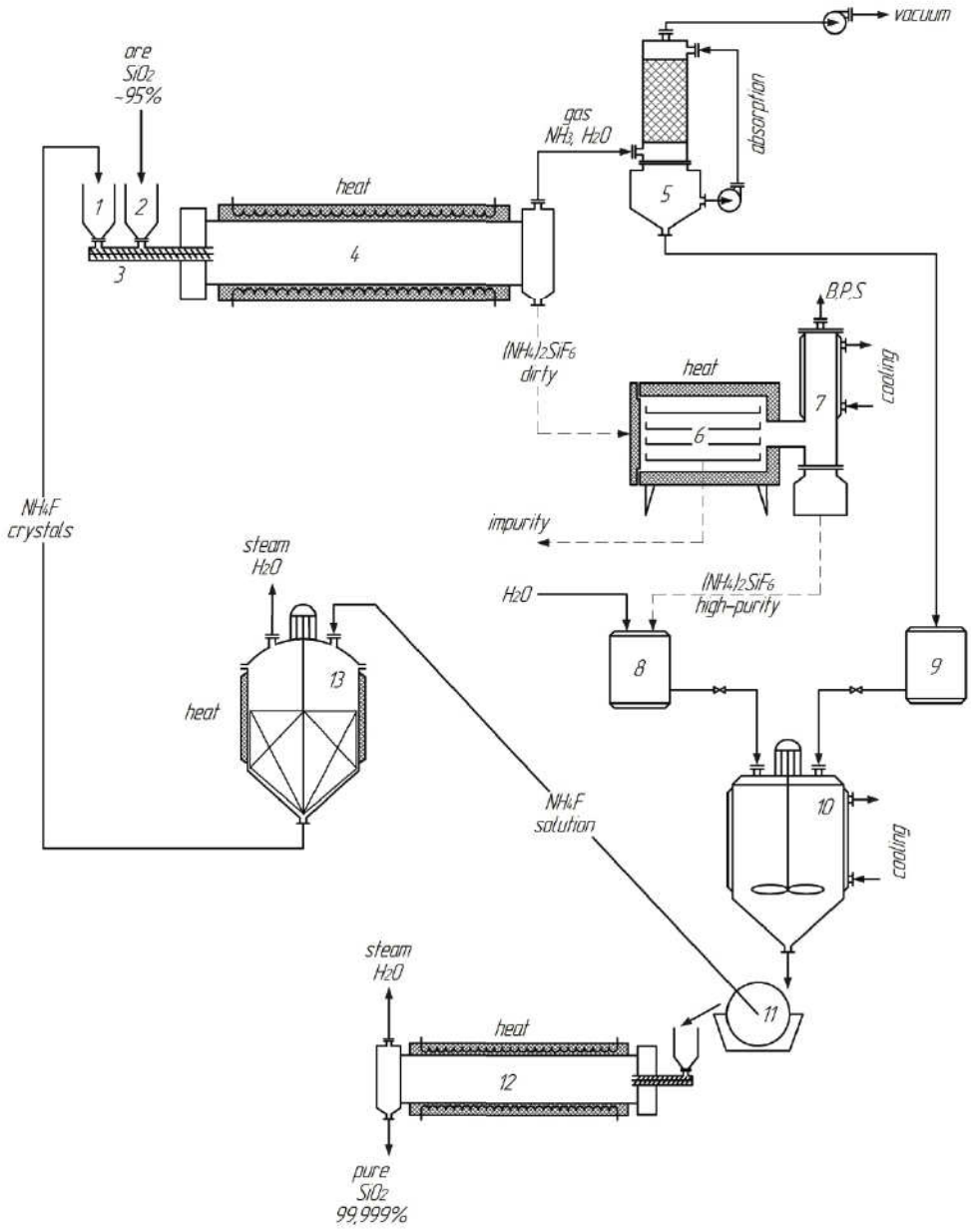


Figure 2 – The apparatus technological scheme

1 – Storage bin (Silo) of ammonium fluoride, 2 – Storage bin (Silo) of raw materials, 3 – Screw mixer, 4 – Rotary kiln, 5 – ammonia absorber , 6 – Sublimation furnace, 7 – Condenser, 8 – Tank for dissolving $(NH_4)_2SiF_6$, 9 – Ammonia storage tank water, 10 – Reactor for deposition of SiO_2, 11 – Vacuum filter, 12 – Furnace for drying SiO_2.

It is impossible in one article to describe in detail all of the production technology of silicon oxide, so here we present only some basic aspects of the proposed process.

FLUORINATION OF QUARTZ RAW MATERIALS

Table 1 – The composition of raw materials (quartz sand)

Material	elemental composition, wt.%							
	Si	Al	Ti	Na	Mg	K	Ca	Fe
Quartz sand	97,5	0,28	0,11	0,059	0,063	0,1	0,84	0,96

Impurities participate in the following reaction to produce different fluorides during dissolution of raw material with NH_4HF_2:

$$Al_2O_3 + 6NH_4HF_2 = 2(NH_4)_3\,AlF_6 + 3H_2O \quad (4)$$

$$Fe_2O_3 + 6NH_4HF_2 = 2(NH_4)_3\,FeF_6 + 3H_2O \quad (5)$$

$$TiO_2 + 3NH_4HF_2 = (NH_4)_2\,TiF_6 + 2H_2O + NH_3 \quad (6)$$

$$CaO + NH_4HF_2 = CaF_2 + H_2O + NH_3 \quad (7)$$

$$MgO + NH_4HF_2 = MgF_2 + H_2O + NH_3 \quad (8)$$

The main problem that we faced in the implementation of the technology was formation of silica gel in the product. The gel is very difficult to filter and t was not possible to obtain high-quality synthetic silica. The reason for the formation of silica gel was the incorrect organization of fluorination process in the rotary kiln.

Along with the main reaction (1 and 2) in a drum rotary kiln the following reactions occur:

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

$$SiO_2 + 4NH_4HF_2 = (NH_4)_3SiF_6F + 2H_2O + NH_3 + HF \quad (10)$$

$$NH_4SiF_5 + H_2O = NH_4SiOF_3 + 2HF \quad (11)$$

It is known that the reaction 9 can only occur at temperatures above 180 ºC so, in our case the reaction 9 does not proceed at fluoridation. This reaction proceeds in the following apparatus for the sublimation purification of $(NH4)_2SiF_6$ from impurities. This suggests that the formation of silica gel by dissolving and subsequent precipitation of $(NH_4)_2SiF_6$ 25% with solution of ammonia is due to presence of NH_4SiOF_3 in the product.

$$NH_4SiOF_3 + H_2O = SiO_2(gel) + NH_4F + 2HF \quad (12)$$

In preliminary experiments, we used a rotary kiln in which the gas and solid phase are moved in one direction (Figure 3). Fluoridation is carried out in rotary kiln drum with a drum diameter of 325 mm and a length of 2,500 mm. Sixty (60) kg of metal balls with 30 mm in diameter were loaded into the kiln for intensive mixing of reagents. The angle of inclination of the kiln was 1°. The temperature in kiln was 130 °C. Lowering the temperature leads to the condensation of water vapor and ammonia at the end of the kiln and the emergence of the reverse reaction 3.

Further, the fluorination product was processed according to the schemtic shown in Figure 2. The resulting silica after deposition (in the device 10 Figure 2) contained 5 to 10% of the gel, which did not allow effective filtration.

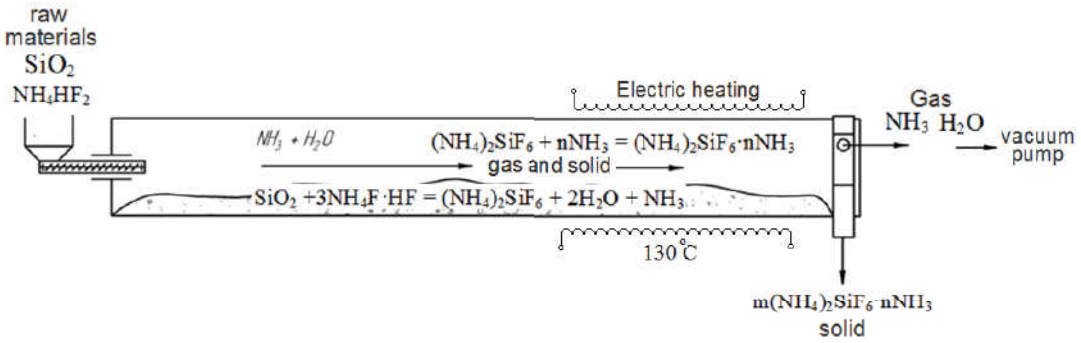


Figure 3 – Schematic representation of the processes in co-current kiln

Incorrect design of the furnace was the cause of the gel formation. The following reaction occurs by addition of ammonia to $(NH_4)_2SiF_6$:

$$(NH_4)_2SiF_6 + nNH_3 = (NH_4)_2SiF_6 \cdot nNH_3 \quad (13)$$

Ammonia is not removed by the sublimation purification. The dissolution is probably the following:

$$m(NH_4)_2SiF_6 \cdot nNH_3 + H_2O = m(NH_4)_2SiF_6 + nNH_3 + 2xH_2O$$
$$= xSiO_{2(gel)} + 6NH_4F + 2H_2O + n\text{-}4xNH_3 + m\text{-}x(NH_4)_2SiF_6 \quad (14)$$

The resulting gel complicates the filtering.

After many attempts to avoid the formation of $m(NH_4)_2SiF_6 \cdot nNH_3$, we came to a conclusion about the necessity of separation gaseous and solid reaction products at the moment of formation. Drum rotary kiln has been upgraded to separate the reaction products. The generation of gaseous ammonia and water occur on the different sides of the kiln (Figure 4).

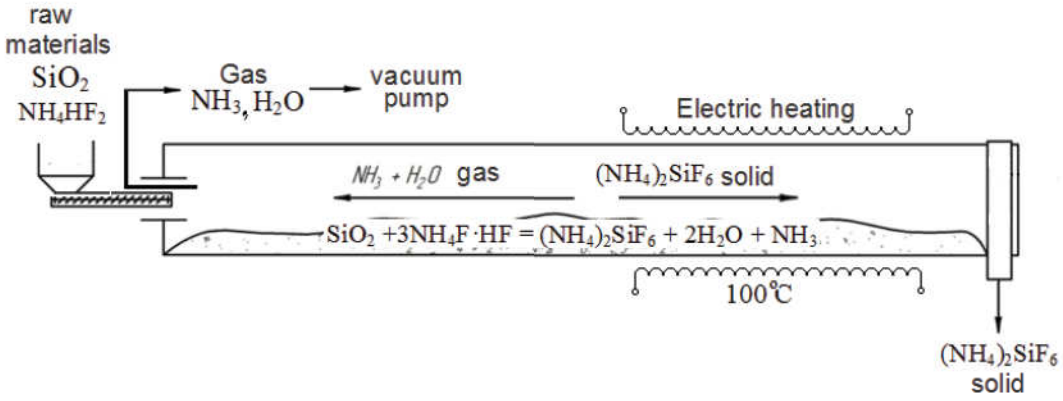


Figure 4 – Schematic representation of the processes in countercurrent furnace

In the counter-current furnace, the gaseous products are immediately separated from the $(NH_4)_2SiF_6$ and leave the reaction zone. This allows avoiding the process of absorption of ammonia molecules in the $(NH_4)_2SiF_6$. Immediately after the organization of the process according to the scheme shown in Figure 4, we were able to get the silicon dioxide with minimal content of gel. The gel content in the sediment of silica decreased to 0.5% after optimizing the parameters. This allowed filtering silica without any problems.

An important factor that improves the technical and economic indices of fluorination process was an opportunity to reduce the temperature of fluorination from 130 °C to 100 °C.

Thus we were able to optimize the fluorination of the quartz sand and recommend this as the most successful variant of the process organization and the construction of drum rotary kiln.

OPTIMIZATION OF THE SUBLIMATION PROCESS

In sublimatore, $(NH_4)_2SiF_6$ evaporates and decomposes in thegas phase by the following reaction:

$$(NH_4)_2SiF_6 = 2NH_3 + 2HF + SiF_4 \quad (15)$$

In desublimers NH_3, HF, SiF_4 are cooled and form $(NH_4)_2SiF_6$.

$$2NH_3 + 2HF + SiF_4 = (NH_4)_2SiF_6 \quad (16)$$

It was experimentally observed that the temperature of the desublimation process is strongly influenced by the quality of the desublimate, in particular on the ratio of fluoride and ammonium $(NH4)_2SiF_6$, as well as the amount of impurities in the condensed $(NH_4)_2SiF_6$. To determine the influence of temperature a series of tests were carried out.

The purpose of the experiments was to determine the dependence of the quality of the desublimate asa function of the temperature of the desublimer. Fluorinated product was loaded into the sublimation furnace. It contained excess of NH_4NF_2, $(NH_4)_2SiF_6$, SiO_2 and fluorinated impurities.

The following reactions can occur at temperatures 110 °C to 280 °C:

$$SiO_2 + 3NH_4HF_2 = (NH_4)_2SiF_6 + 2H_2O + NH_3 \quad (17)$$

$$NH_4HF_2 = NH_3 + 2HF \quad (18)$$

$$(NH_4)_2SiF_6 + nNH_3 = nNH_3 \cdot (NH_4)_2SiF_6 \quad (19)$$

$$nNH_3 \cdot (NH_4)_2SiF_6 = (NH_4)_2SiF_6 + nNH_3 \quad (20)$$

$$5(NH_4)_2SiF_6 + SiO_2 = 6NH_4SiF_5 + 4NH_3 + 2H_2O \quad (21)$$

$$NH_4SiF_5 + H_2O = NH_4SiOF_3 + 2HF \quad (22)$$

The following reactions can occur at temperatures from 280 °C to 380 °C:

$$(NH_4)_2SiF_6 = 2NH_3 + 2HF + SiF_4 \quad (23)$$

$$(NH_4)_2SiF_6 + nNH_3 = nNH_3 \cdot (NH_4)_2SiF_6 \quad (24)$$

The process of sublimation purification consists of 2 stages:

1) from 110 °C to 280 °C - side reactions occur. Capture NH_4HF_2, NH_4F, NH_4SiF_5, NH_4SiOF_3 and removal of excess NH_3.
2) from 280 °C to 380 °C - sublimation and the capture of $(NH4)_2SiF_6$.

To determine the thermal properties of compounds that formed as a result of hydrofluorination in the melt of ammonium fluoride, and decomposition temperature thermogravimetric and differential thermal analysis tests were carried out Figure 5.

Thermal studies were performed on the combined TGA / DSC / DTA analyzer SDTQ600 with data enhancement software – TA instruments UniversalV4.2E. Derivatografic studies were conducted in an argon atmosphere with a heating rate of 10 °/min.

The initial temperature of mass loss was equal to 100 °C, the change in mass was terminated at a temperature of 252 °C, the residue was 16% of the total sample weight. This residue represents the fluoride impurities of quartz sand and corrosion of equipment.

On the DTA curve there are two exothermic peaks with maxima at 152 °C and 243 °C.

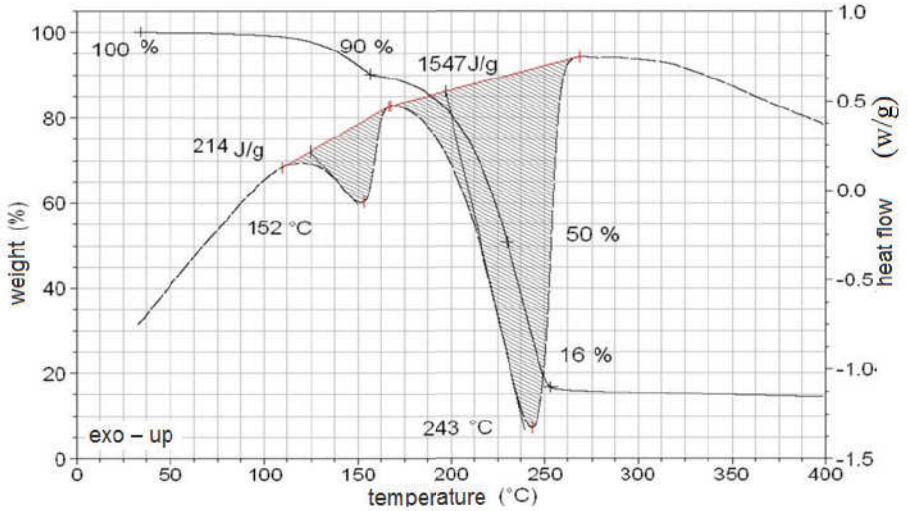


Figure 5 – Thermogravimetric and differential thermal analyzes of the decomposition of fluorinated product obtained in the rotary kiln, heating rate 10 °C/min

The second peak characterizes the sublimation of $(NH_4)_2SiF_6$ and NH_4F*HF. The calculated enthalpy of these processes for the first case is $\Delta N = 214$ J/g, and for the second case is $\Delta N = 1547$ J/g (by means of TAinstrumentsUniversalV4.2E).

Consequently, the heat of sublimation:

$$Q = -1761 \text{ J/g}$$

The heat required for sublimation:

$$Q_{sub} = Q \cdot m(\text{F-product}) = -5681743 \text{ J}$$

The experiment was conducted at the experimental site (Figure 2) in the sublimation furnace 6 and condenser 7. The internal surfaces of the apparatus were made of aluminum. The aluminum surface is covered with a thin layer of aluminum fluoride, thus avoiding contamination of the product. The walls of the condenser 7 were cooled by water. The wall temperature could be changed depending on the rate of water flow.

Scheme of the experiment (Figure 6) with sublimation furnace and the condenser is shown below.

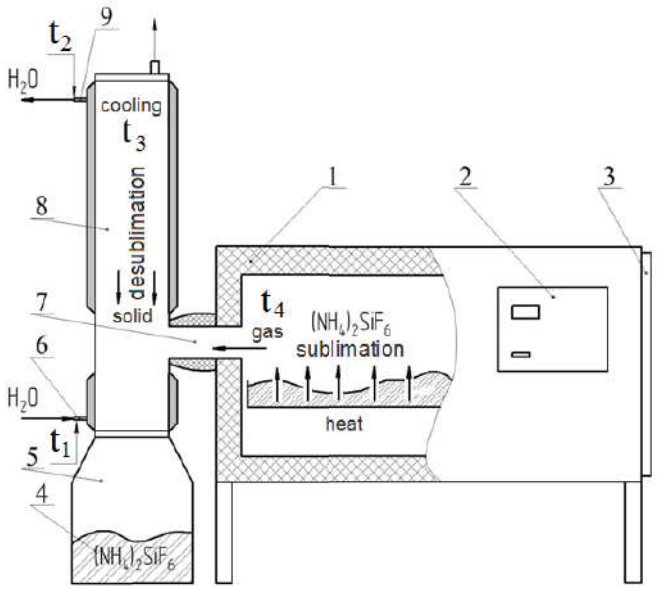


Figure 6 – The scheme of sublimation furnace and condenser

1) Sublimation furnace, 2) Remote control, 3) Door of the furnace, 4) $(NH_4)_2SiF_6$ separated from impurities, 5) Collection tank of $(NH_4)_2SiF_6$, 6) Input cooling water, 7) Branchpipe of sublimer and desublimer, 8) Water cooled condenser cooled by water, 9) Output of cooling water. T1 - temperature of inlet cooling water, T2 - temperature of outlet cooling water, T3 - the temperature inside the desublimer, T4 - the temperature inside the sublimation furnace, T1 - temperature of water coming from the municipal water supply. The main parameter is T3 - the temperature in the volume of desublimer. This option is controlled by varying the water consumption. Parameter (T2-T1) - shows the amount of heat consumed by desublimation.

The experimental results are presented in Figure 7. The area of desublimer is 0.740 m^2. Water flow rate to maintain the temperature of sublimation from is about 1 to 2 L/hr. The experiment was carried out for 9 hours. The temperatures recorded every 30 minutes. Registration of temperature (T1 and T2) occurs at the beginning of the change in temperature T3.

The heating was carried out smoothly. Heating was stopped for 30 minutes and maintained at temperatures of 100, 200 and 300ºC. Slight heating was required to provide more or less uniform heating of the fluorinated product. Heat loss to cooling water was around 2,260 (J/mol/h) in the working mode for 3 hours.

The product begins to desublimate at a temperature of 220 ºC and after 2 hours of heating. It was found that in the temperature range 220 – 280 ºC the product was mostly represented by NH_4F (Figure 8).

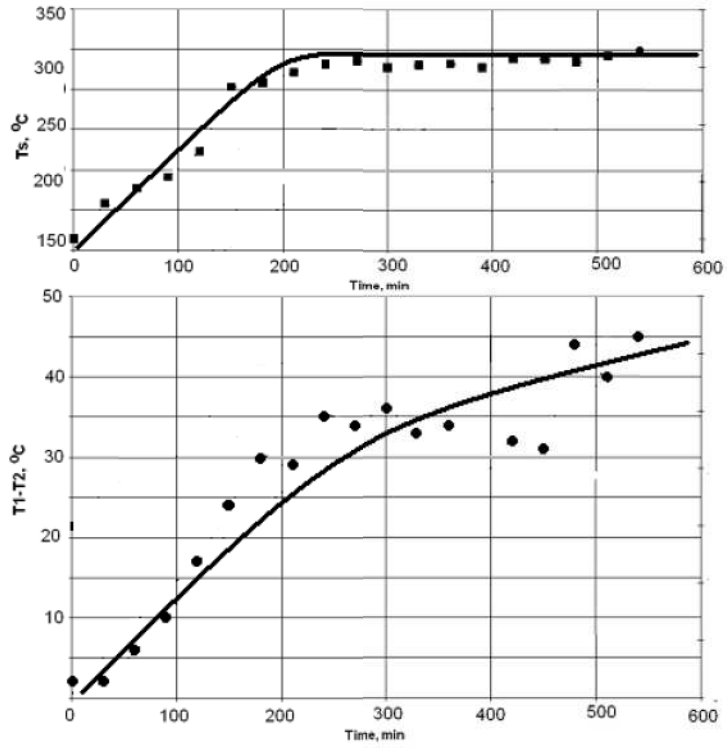


Figure 7 – A plot of heat transfer (T2-T1) from time and temperature inside the furnace, depending on the sublimation time (T4)

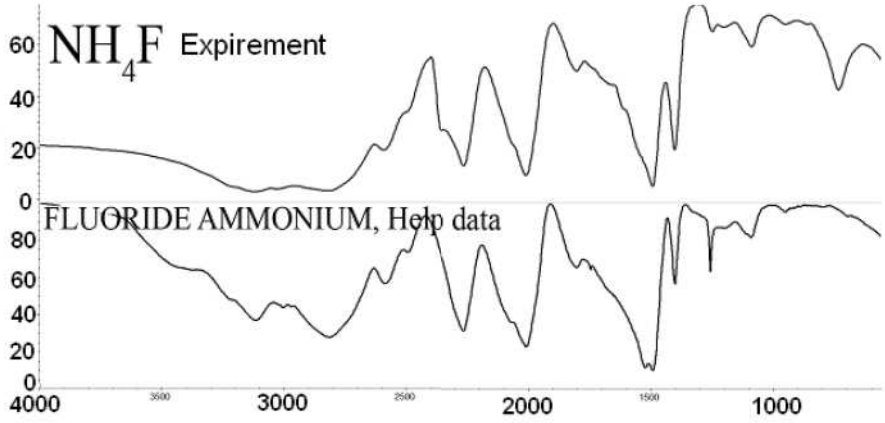
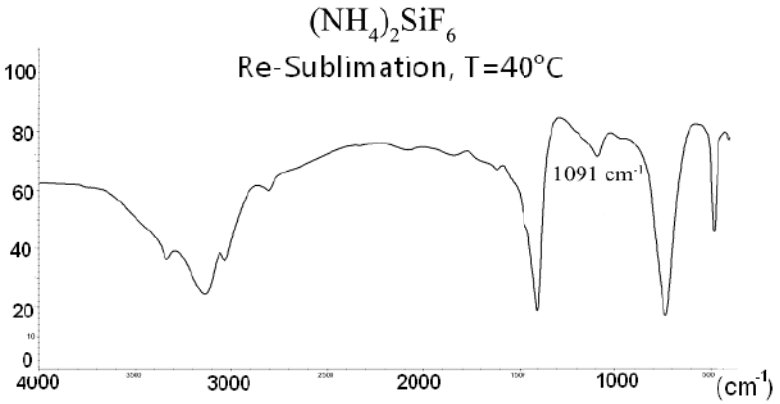


Figure 8 – IR spectra of the NH4F obtained in desublimer and NH4F spectra taken from a database of software Nicolet 6700 Termo (program Omnicver. 7.3), the coincidence is 83.56%

Change in the quality of the product occured at a temperature higher than 280 °C. The solid (condensate) in the capacitor was only a $(NH_4)_2SiF_6$. This was proved by InfraRed - spectra.

The first experiment was conducted at a temperature in the condenser T3 = 40 °C. The walls of the condenser was cold, the rate of sublimation was high. The product was identified as $(NH_4)_2SiF_6$ (Figure 9). Impurities were also determined.

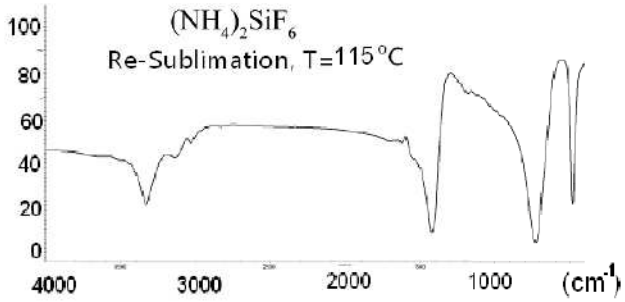


Impurity, %	
B	0,001648404
Na	0,000338372
Mg	0,000115157
Al	0,002347135
P	0,006879662
Ca	0,003013888
Sc	0,001671009
Ti	0,000287365
Fe	0,001365208
Cu	0,000301414
Zn	0,000044897
As	0,004202701
Sb	0,000483475
Impurity	0,02269
Cleanliness	99,977

Figure 9 – IR spectrum of the $(NH_4)_2SiF_6$ obtained in desublimer at a temperature 40 – 50 °C

In Figure 9 shows the IR spectrum of $(NH_4)_2SiF_6$ obtained in desublimer at a temperature 40 – 50 °C. There is a bandwidth which characterizes the relation of Si-O-Si (1.091 cm^{-1}). Perhaps the product has a small amount of $(NH_4)_2SiOF_4$. The presence of this substance leads to the formation of the gel.

The following experiments were carried out with a gradual increase of temperature. The most interesting results were obtained at a temperature T3 = 110 – 120 °C (Figure 10).



Impurity, %	
B	0,000110000
Na	0,000370146
Mg	0,000024514
Al	0,000049944
P	0,000610000
Ca	0,004016562
Sc	0,000403904
Ti	0,000028171
Fe	0,000062067
Cu	0,000121225
Zn	0,000052026
As	0,000010000
Sb	0,000012649
Impurity	0,0058
Cleanliness	99,994

Figure 10 – IR spectrum of the $(NH_4)_2SiF_6$ obtained in desublimer at a temperature 110 – 120 °C

IR spectrum is a typical spectrum of $(NH_4)_2SiF_6$ at a temperature in desublimer of 115 °C. After 8 hours the temperature in the condenser began to increase. Loss of product to the receiving container was almost negligible. This indicates the end of the process of sublimation. At this moment begin to evaporate the decomposition products are not volatile at a temperature of 300 – 310 °C fluoro-ammoniates.

The following conclusions were made as a result of studying the process of sublimation – desublimation:

1. It was determined that the desublimation temperature greatly affects the quality of the product. With strong cooling occurring due to rapid precipitation of condensed particles. This may be accompanied by enrichment of the solid phase of the impurities.

2. The temperature in the condenser is T3 = 110 – 120 °C. $(NH_4)_2SiF_6$ is condensed well. Impurities do not condense. Desublimation allows clearing the product from boron and phosphorus in 10 times, and some of the other impurities in the 100 and more than once time and get rid of the gel.
3. A further increase in temperature in the condenser greatly reduces the rate of desublimation.

ENERGY BALANCE

Analysis of reactions 1 and 3 from the viewpoint of thermodynamics, it can be assumed that they are going with the same absorption (1) and heat generation (3).

Table 2 – Direct fluorination reaction of quartz in the drum rotary kiln

$SiO_2 + 6NH_4F = (NH_4)_2SiF_6 + 4NH_3 + 2H_2O$				
T, K	298	400	600	800
ΔH^0_t (kJ/mol)	386,6	386,7	387,1	387,5
ΔH^0_t (kJ/g$(NH_4)_2SiF_6$)	2,172	2,172	2,174	2,177
ΔG^0_t (kJ/mol·K)	100,6	2,8	-189	-381
	Substances do not react		Substances react	

Table 3 – The reverse hydrolysis reaction and treatment with ammonia and water

$(NH_4)_2SiF_6 + 4NH_3 + 2H_2O = SiO_2 + 6NH_4F$				
T, K	298	400	600	800
ΔH^0_t (kJ/mol)	386,6	386,7	387,1	387,5
ΔG^0_t(kJ/mol·K)	-100,6	-2,8	189	381
	Substances react		Substances do not react	

$\Delta G^0_t = \Delta H^0_t - T \cdot \Delta S^0_t$ - Gibbs energy - shows the direction of the process. The process can take place only in the forward direction with a negative value of Gibbs energy.

All the energy is consumed for the process of fluoridation, and then released during the hydrolysis.

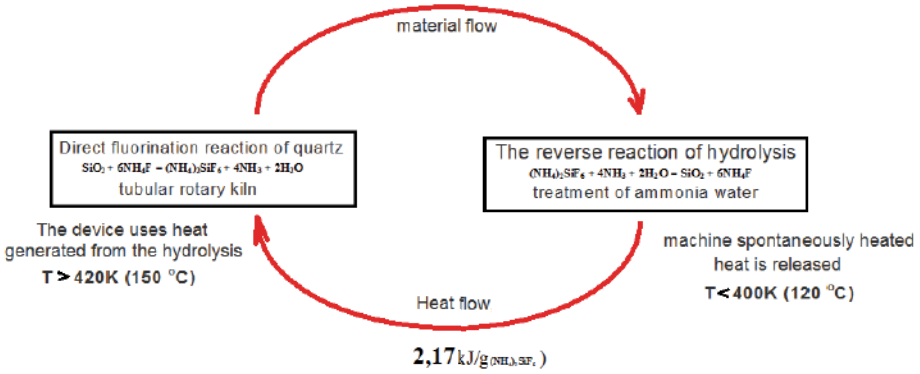


Figure 11 – Scheme of the energy flows of fluorination reactions and regeneration of ammonium fluoride

Observed of energy conservation; the energy on heating in the first unit, is released during the hydrolysis. If it was possible to make machines without heat loss, it was possible to carry out this process without external energy.

CONCLUSION

A number of useful conclusions could be withdrawn from the study of the process of obtaining high-purity silica in the pilot plant. Operation of fluoridation of quartz sand in a drum rotating furnace was optimized. The most optimal design of the furnace and the distribution of flows were determined. Optimal conditions for purification of dye-sublimation process $(NH_4)_2SiF_6$ were determined. Temperature at which it is possible to obtain the most pure product with the highest content of the $(NH_4)_2SiF_6$ was found.

The research allowed start of pilot production of high-purity synthetic silicon dioxide with the content of the base material SiO_2 with a purity of 99.999%.