Optimal conditions for carrying out desiliconization process are: process temperature 423...473 K, process time 30...40 min.

4. For fluorination of topaz concentrate the excess of ammonium bifluoride of 15...30 % is required. At such quantity all excess quartz is managed to be removed from concentrate and obtain needle-shaped mullite with the length of crystals about 100 mkm and thickness of 1 mkm as a result of topaz residual mullitization.

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Utilization of fluorine-containing gases was always an actual problem in modern industry. Traditional techniques of their utilization have a number of disadvantages the main of which is the formation and accumulation of solid wastes which could not be further recycled [1].

In the developed technique of obtaining mullite from topaz concentrate it is desiliconized with ammonium bifluoride:

\[
\text{SiO}_2 + 3\text{NH}_4\text{F} + \text{HF} \rightarrow (\text{NH}_4)\text{SiF}_6 + 2\text{H}_2\text{O} + \text{NH}_3
\]

Quartz excess quantity contained in concentrate is removed in the form of gaseous ammonium hexafluorosilicate (AHFS) at temperatures higher than 592 K. Along with AHFS there are water vapors, ammonia and a number of fluorine-containing gases in gas phase. To define gas phase composition extracting at fluoridation of topaz concentrate the equilibrium composition of gas phase was calculated by bundled software «TERRA» intended for computing thermodynamic parameters and equilibrium in different systems. The software is conjugated with data base of thermodynamic properties of individual substances and complex of subprograms for thermodynamic simulation [2]. The computation was carried out per 1 kg of quartz in temperature range of 273...623 K and at pressure 0,1 MPa. The results of computations are presented graphically in Fig. 1.

![Equilibrium composition of gas phase](image)

Really, water, ammonia and ammonium hexafluorosilicate should be the main components of gas phase.
Increasing temperature water content in gas phase rises and achieves maximum at 373 K. AHFS is formed as a result of reaction (1) originally in condensed state and only at temperatures higher than 573 K, owing to sublimation, its content in gas phase becomes practically constant. Ammonia amount in the system rises at temperature increase and has maximum at 473 K then its content decreases. Presence of silicon tetrafluoride in the system does not exceed $10^{-6}$ mole therefore its concentrations are not presented on the graph. Hydrofluoride occurs in the system in quantities of 0,1 mole only at temperature 473 K, however, its content is insignificant.

To confirm these results the investigations in topaz concentrate fluoridation with gas phase analysis at the device mass-spectrometer ME-1201 were carried out. The results of these investigations are given in Table 1.

The main components of gas phase extracting at interaction of topaz concentrate with ammonium bifluoride at 573 K are ammonia, water and ammonium hexafluorosilicate. Content of silicon tetrafluoride with higher concentration than it is theoretically calculated in the system and absence of hydrofluoride is probably explained by interaction of the extracted HF with quartz. Experimentally determined contents of gas phase components differ from theoretically calculated ones. It is probably connected with desublimation of ammonium hexafluorosilicate in nonheated gas flues of devices-analyzer. Though, the presence of such components as ammonia, water and AHFS was managed to be determined in gas phase.

### Table 1. Gas phase composition at 573 K

<table>
<thead>
<tr>
<th>Component</th>
<th>Volume content, rev. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH$_3$</td>
<td>33,0033</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>33,0033</td>
</tr>
<tr>
<td>(NH$_4$)$_2$SiF$_6$</td>
<td>33,9924</td>
</tr>
<tr>
<td>SiF$_4$</td>
<td>9,9 $10^{-4}$</td>
</tr>
<tr>
<td>Total</td>
<td>100,0</td>
</tr>
</tbody>
</table>

### Fig. 2. Basic diagram of utilization of fluorine-containing gases

Thus, the main fluorine-containing gases which should be utilized are silicon tetrafluoride and ammonium hexafluorosilicate. The utilizations techniques of SiF$_4$ are studied and introduced into industry [1]. Some ways of AHFS utilization are described in scientific literature [3, 4], however, they did not find practical application by a number of reasons.

In this connection, in the given paper the utilization techniques of gas mixture (NH$_3$, H$_2$O, (NH$_4$)$_2$SiF$_6$, SiF$_4$) obtained in the process of topaz concentrate desiliconization were studied. Basic diagram of these gases utilization given in Fig. 2 includes:

- desublimation of (NH$_4$)$_2$SiF$_6$;
- dissolution of (NH$_4$)$_2$SiF$_6$ in ammonia water obtaining silicon dioxide and ammonium fluoride;
- absorption of SiF$_4$ by solution NH$_4$OH and ammonium fluoride return to the fluoridation stage of topaz concentrate.

### Studying the process of sublimation-desublimation of (NH$_4$)$_2$SiF$_6$

The investigations were carried out at the device, Fig. 3, according to the following technique: batch of (NH$_4$)$_2$SiF$_6$ with mass of 10 g was placed in sublimator, the device was pressurized and put into furnace, preliminary heated up to a certain temperature, and kept for a specified time. After extraction from the furnace a cup with residual product was weighted, degree of sublimation was determined by the mass of residual. Desublimate is also extracted from cooled part of the reactor and weighted. The degree of desublimation was determined by the mass of desublimate. The results are graphically presented in Fig. 4.
Investigations of desublimation process show that the whole evaporated product is condensed in refrigerated zone of the device.

**Studying the interaction of (NH₄)₂SiF₆ with NH₄OH**

In spite of the fact that AHFS is a marketable product used in sleeper industry and in glass etching it is not of great demand on the market. Therefore, besides sublimation it is suggested to be utilized by absorption in ammonia water

\[
(NH_4)_2SiF_6 + 4NH_4OH = SiO_2 + 6NH_4F + 2H_2O \quad (2)
\]

Formed as a result of SiO₂ called in other words «carbon white» is widely used as a reinforcing filler of polymer materials in tire, rubber, chemical industry as well as in building industry for obtaining high-quality concrete.

For ascertaining equilibrium composition and yields of interaction products of ammonium hexafluorosilicate and ammonia water for reaction (2) in temperature range of 298...373 K and pressure \( P = 0.1 \text{ MPa} \) thermodynamic calculation of equilibrium composition per 1 kg of initial AHFS was carried out. As calculations showed concentration of main reaction products (SiO₂, NH₄F and H₂O) in the given temperature range are constant.

HF content in the system rises at temperature increase; however, its concentration is very low in comparison with the rest products of the reaction.

Investigations in AHFS interaction with ammonia solution showed that the conversion degree of \((NH_4)_2SiF_6\) into SiO₂ achieves 95 % already at ammonia concentration of 5 % and process duration of 120 s. Increasing ammonia concentration the rate of the process rises and at concentration of NH₄OH 20 % and higher reaction proceeds practically instantly and ammonium hexafluorosilicate is completely transformed into silicon dioxide for several seconds.

Interaction kinetics of ammonium hexafluorosilicate and ammonium hydroxide was studied by the following technique: batch of solid ammonium hexafluorosilicate was dissolved in the excess of ammonium hydroxide with concentration of 3 % during the preset time and at preset temperature, constantly stirring. Then concentrated hydrochloric acid was added into the system for neutralization of residual ammonium. The laid-down sediment consisting of silicon oxide and undissolved AHFS, was filtered and dried to constant mass after which concentrated hydrofluoric acid was added to the sediment for removing silicon oxide. The degree of AHFS conversion was determined by the difference of sediment masses before and after removing SiO₂. The results of investigation are represented by a diagram in Fig. 5.

Mathematical treatment of the obtained data was carried out by the model equations. Experimental data are described in the most proper way with correlation coefficient of 0.95...0.98 by the equation of reducing sphere (Fig. 6). On the basis of calculations the value of activation energy \( E_a \) was obtained and kinetic equation of the process was driven.

\[
E_a = 0.92 \text{ kJ/mole,} \\
1 - (1 - \alpha)^{1/3} = 0.003414 \cdot e^{-920/(RT \cdot \tau)}.
\]

The obtained equation describes authentically (with correlation coefficients 0.95...0.97) the kinetics of the given process in the temperature range of 293...323 K at \( \alpha = 0...0.75 \). Activation energy amounts to 0.92 kJ/mole, that indicates the fact that it proceeds in diffusive response area.

The pilot sets of silicon dioxide obtained by the given technique were analyzed by spectral analysis according to the method of OST 95 555-2002 for presence of impurities. The results of investigations are given in Table 3.
The investigations showed that silicon oxide obtained by the given reaction differs in chemical purity: content of SiO<sub>2</sub> amounts to 99.9%. Specific surface of the obtained samples was determined by the method of BET [5] for argon thermal desorption with inner standard. The investigations were carried out in the Institute of solid body and mechanochemistry of RAS SD. Sample of SiO<sub>2</sub> was warmed up in gas current Ar + He at 393 K during 0.5h before measuring. According to the obtained data specific surface of silicon dioxide achieves 92 m<sup>2</sup>/g that corresponds to the grade «carbon white».

**Regeneration of fluoridizing agent**

Ammonium fluoride obtained as a result of ammoniac hydrolysis may be returned to the stage of fluoridation of quartz-containing ores. Ammonia and water contained in gas phase are used for obtaining ammonia water by the methods existing in modern industry [1]. Thus, the suggested scheme allows avoiding the formation of unreclaimable wastes of fluoride production as well as regenerating fluoridizing agent with its further reuse in the process.

**Conclusions**

1. The method of utilization AHFS by sublimation–desublimation and dissolution in ammonia water were studied. The basic diagram of utilization of fluoride-containing gases of fluoride-ammonium technology of topaz concentrate recycling was suggested.
2. Equilibrium composition of gas phase at fluoridation process of topaz concentrate the main constituents of which are ammonia, water and ammonium hexafluorosilicate was determined by thermodynamic calculation and experimentally at 573 K.
3. The process of sublimation–desublimation of ammonium hexafluorosilicate was studied. It was shown that the rate of sublimation process amounts to 7 g/m<sup>2</sup>.s at temperature 823...873 K in this case the desublimation degree of AHFS achieved 98...99%.
4. The process of ammonia hydrolysis of ammonia hexafluorosilicate was studied. It was stated that (NH<sub>4</sub>)<sub>2</sub>SiF<sub>6</sub> is completely converted in silicon dioxide at ammonia concentration 5% and process duration of 120 s. Activation energy amounted to 0.92 kJ that indicates the diffusive area of the given process.
5. Silicon dioxide obtained by ammonia hydrolysis of AHFS has specific surface of 92 m<sup>2</sup>/g and purity of 99.9 wt. % that corresponds to the grade «carbon white».

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