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TOPAZ CONCENTRATE DESILICONIZATION WITH AMMONIUM BIFLUORIDE

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Fluoridizing agent for the process of topaz concentrate desiliconization has been selected, topaz thermodynamic potentials have been appraised, thermodynamic probabilities of fluorination reaction of topaz concentrate main constituents have been calculated. The results of studying the concentrate desiliconization process with ammonium bifluoride by the methods of thermogravimetry, RFA, microphotography are presented.

The perspective of modern ceramic industry is the development of competitive product both on the basis of traditional raw material resources and involving new raw materials unused before. Development of technology of light mullite refractory obtaining from natural topaz concentrate allows meeting a demand on domestic market and decreasing significantly expenses for mullite goods production. Mullite represents aluminum silicate of the composition $3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$, stable at temperature up to 1700 °C, possessing a number of unique physicochemical properties and being one of the main crystal phases in many ceramic materials [1]. It is traditionally obtained by the method of solid-phase reactions (sintering aluminum and silicon oxides in stoichiometric ratio) as well as burning native minerals. Main natural raw material for mullite obtaining is kaolin and topaz [2].

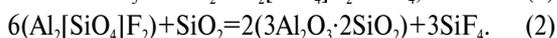
Topaz is the mineral of island silicate subclass $\text{Al}_2[\text{SiO}_4](\text{F},\text{OH})_2$. The uniqueness of topaz is in the fact that it is the only native mineral which turns into mullite without intermediate phases when burning at 1100...1200 °C. Topaz refers to precious stones of the III class; this is the reason why mullite production from it is economically unpractical. However, there are ores containing topaz which can not be applied in jewelry industry it is so-called commercial topaz. The unique deposit of commercial topaz «Kopna» which is on the territory of Kemerovo region near settlement Ursk was explored in Siberia. On the basis of the deposit the ore-dressing and processing enterprise «Urskoe» is developed. Quartz is a dominant ore generating mineral of this deposit with the content from 60

to 92 %. Topaz forms from 7 to 38 % of ore; close relation with quartz is typical for it. After ore enriching topaz concentrate contains up to 50 % of excess silicon oxide which should be removed before mullite obtaining. Besides, in topaz constituent of ore there is up to 12 % of F which is segregated at burning in the form of SiF_4 [3]. Thus, there is a necessity of developing such technology which could allow removing excess quartz from topaz concentrate without touching topaz constituent. So it was necessary to chose desiliconizing agent to research the technique of desiliconization of topaz concentrate as well as mullitization processes of desiliconized topaz residual.

1. Selection of fluoridating agent

One of the efficient methods of silicon oxide removing (desiliconization operation) from ores is fluoride method. Main fluoridating agents in modern industry are elemental fluorine and fluorohydrogen as well as ammonium fluorides. Thermodynamic calculations carried out in the paper [4] showed that all three fluoridating agents may be used for desiliconization of topaz concentrate. However, there is a number of problems limiting F_2 and HF application for these purposes. In particular, using elemental fluoride requires development of fluoride additional production that increases expenses for ultimate goods production. Application of HF as well as F_2 results in emission of toxic gas SiF_4 which requires special conditions of working and utilization. Therefore, it is technologically more profitable to use ammonium bifluoride for desiliconization.

To estimate fluoridation probability of topaz directly with ammonium bifluoride it is necessary to know its thermodynamic potentials. They are not given in reference literature. Let us choose two equations of reaction with fluoride-topaz for their searching: reaction of its formation from aluminum fluoride and silicon oxide and decomposition reaction with mullite formation:



Temperature of the beginning of the reaction (1) is 970 K, reaction (2) is 1373...1473 K [5]. As thermodynamic potentials for the rest participants of the reaction are known Gibbs energy of topaz formation may be searched by the corollary from Hess law supposing that the given temperatures are equilibrium temperatures that is $\Delta G_f \approx 0$. Then

$$\begin{aligned} \Delta G^0(\text{Al}_2[\text{SiO}_4]\text{F}_2) &= \\ &= 2\Delta G^0(\text{AlF}_3) + 2\Delta G^0(\text{SiO}_2) - \Delta G^0(\text{SiF}_4) \\ \Delta G^0(\text{Al}_2[\text{SiO}_4]\text{F}_2) &= \\ &= 1/3\Delta G^0(3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2) + 1/2\Delta G^0(\text{SiF}_4) - 1/6\Delta G^0(\text{SiO}_2) \end{aligned}$$

Substituting reference data, we find that

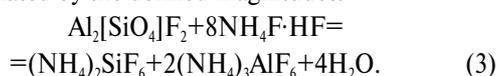
- by the reaction (1) at $T=970$ K,
 $\Delta G^0(\text{Al}_2[\text{SiO}_4]\text{F}_2) = -3119,6$ kJ/mole,
- by the reaction (2) at $T=1373$ K,
 $\Delta G^0(\text{Al}_2[\text{SiO}_4]\text{F}_2) = -3224,599$ kJ/mole,
- by the reaction (2) at $T=1473$ K,
 $\Delta G^0(\text{Al}_2[\text{SiO}_4]\text{F}_2) = -3246,53$ kJ/mole.

It is obvious that magnitudes obtained in such a way are of the same order and differ in less than 4 %. To calculate ΔH^0 of topaz it is necessary to know its entropy. Comparing known entropies of other silica-alumina compounds such as mullite, kaolin, andaluzite etc., it may be noticed that their entropy is in the range of 50...250 J/mole·K [6]. As topaz is a solid substance and refers to silica-alumina compounds it might be supposed that its entropy does not also exceed 250 J/mole·K. The results of calculations in determining topaz thermodynamic parameters are given in Table 1.

Table 1. Results of calculation of topaz thermodynamic parameters for reactions (1) and (2)

$S, \text{J/mole}\cdot\text{K}$	$\Delta H_1, \text{kJ/mole at } 970 \text{ K}$	$\Delta H_2, \text{kJ/mole at } 1373 \text{ K}$	$\Delta H_2, \text{kJ/mole at } 1473 \text{ K}$
50	-3071	-3155	-3172
100	-3022	-3087	-3099
150	-2974	-3018	-3025
200	-2925	-2950	-2951
250	-2877	-2881	-2878

Average values amount to $\Delta H_f^0 = -3024,5$ kJ/mole, $S_f = 150$ J/mole·K. Thermodynamics of fluorination reaction of topaz directly with ammonium bifluoride may be calculated by the defined magnitudes.

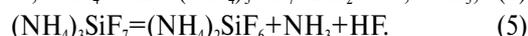
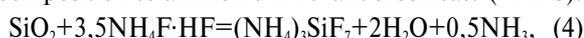


For the given process $\Delta H^0 = -556,9$ kJ/mole, $\Delta G^0 = -484,7$ kJ/mole that is this reaction is exothermic and is probable thermodynamically.

Thus, ammonium bifluoride (ABF) may be used for desilicization of topaz concentrate: main components of initial concentrate (SiO_2 , topaz) may interact with $\text{NH}_4\text{F}\cdot\text{HF}$ forming ammonium fluorometallate.

2. Desilicization of topaz concentrate

Desilicization of topaz concentrate was studied by thermogravimetric analysis and kinetic investigations. Thermogravimetric analysis was carried out at the device Derivatograf Q-1500D, heating rate amounted to 10 °C/min, batch mass was 20...40 mg. As it is known quartz interaction with ammonium bifluoride results in formation of ammonium hexafluorosilicate. In some papers, in particular in [7] it was supposed that this interaction occurs in two stages originally with formation of ammonium hepta-fluoride-silicate and its further decomposition to ammonium hexafluorosilicate (AHFS):



Interaction of original components starts already in ordinary conditions at intensive continuous grinding, however the peak of the beginning of reaction presents at 381 K at thermogravigram of fresh mixture (Fig. 1).

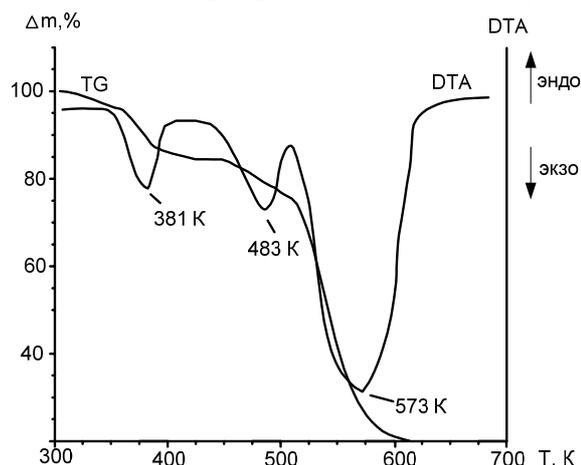


Fig. 1. Thermogravigram of SiO_2 interaction with $\text{NH}_4\text{F}\cdot\text{HF}$. DTA is the differential-thermal analysis, TG - is the change of mass m of the sample

Change of batch mass amounts to 14, 5 % at the given stage that practically coincides with theoretically calculated one 14, 9 % and corresponds to ammonia and water extraction by the reaction (4). Then ammonium hepta-fluoride-silicate is decomposed to ammonium hexafluorosilicate by reaction (5) which is indicated by the peak with maximum at 483 K. Calculations by reaction equation show that theoretical change of batch mass at the given stage should amount to 14, 3 %, however, practical mass loss amounted to 9 %; it means that about 63 % of ammonium hepta-fluoride-silicate was decomposed to ammonium hexafluorosilicate at the given stage. Peak with maximum at 573 K probably corresponds to AFHS sublimation which finishes by complete mixture evaporation at 600 K. This indicates that silicon dioxide reacted completely with ammonium bifluoride and therefore that part of $(\text{NH}_4)_3\text{SiF}_7$ which was

not decomposed at the previous stage, was decomposed and evaporated.

Topaz concentrate interaction with ammonium bifluoride was studied at stoichiometric and excess quantity of fluoridating agent. As the researches showed there are peaks of quartz interaction with NH_4FHF meeting the formation and decomposition of $(\text{NH}_4)_3\text{SiF}_7$ with further sublimation of ammonium hexafluorosilicate at stoichiometric quantity of ABF at thermogravigram (Fig. 2).

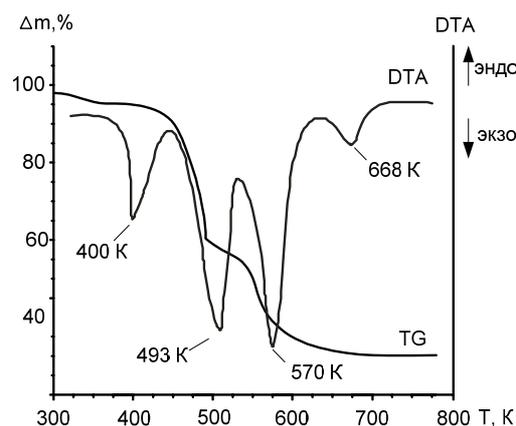
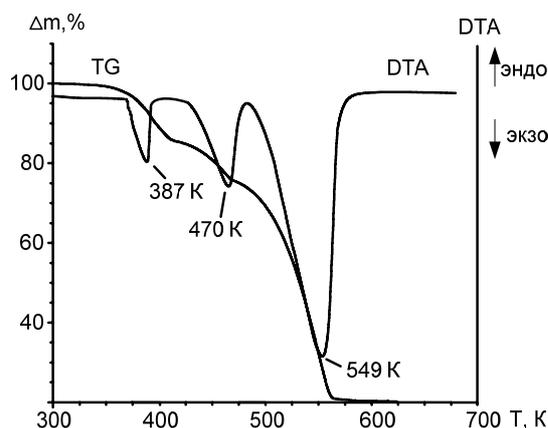


Fig. 2. Thermogravigram of topaz concentrate interaction with ABF: a) with stoichiometric quantity; b) with excess quantity

At considerable excess (100 %) of fluoridating agent topaz constituent is damaged that is indicated by the peak at thermogravigram at 668 K (Fig. 3). Hypothetically it meets decomposition of fluoroaluminate ammonium compounds which were formed as a result of topaz damage by the reaction (3) however there was no possibility to identify them.

Thus, at deficiency and stoichiometric ratio of topaz concentrate and ammonium bifluoride quartz constituent is fluoridated in the first place. Topaz constituent is damaged only at significant excess of fluoridating agent.

Kinetics of desiliconization process was studied by the following technique: batches of topaz concentrate with mass 5 g were burdened with a little excess of NH_4FHF and stirred accurately. The obtained samples were placed into porcelain crucibles. Crucibles were heated in the furnace up to the specified temperature and

kept for a certain time and then reaction vessel was filled up with water. As a result, formed ammonium hexafluorosilicate and nonreacted ammonium bifluoride were dissolved. Then the sample underwent filtration and washing after which dry residual was calcined in muffle furnace. After cooling down the sample was weighed and the degree of α transformation was calculated. The results are given in Figure 3.

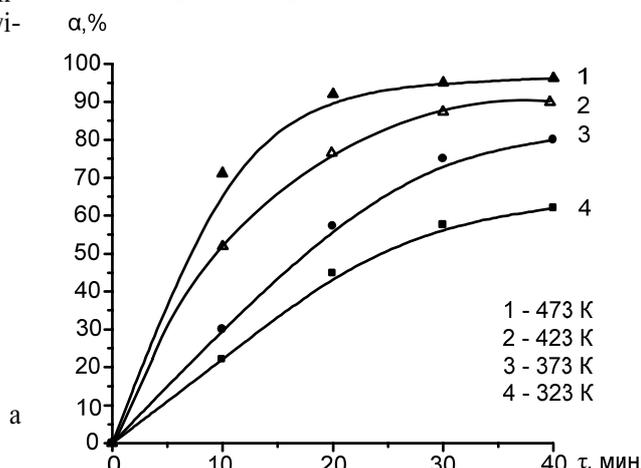


Fig. 3. Kinetic curves of topaz concentrate desiliconization

The investigations show that the reaction degree achieves 95 % at temperature 473 K and process time $\tau=30$ min mathematical treatment of experimental data was carried out at different model levels (Kazeev-Erofeev, Yander, reduced surface etc.). Experimental data are treated the most reasonably with correlation coefficient of 0,95...0,98 by the equation of reduced sphere $1-(1-\alpha)^{1/3}=k\tau$ (Fig. 4).

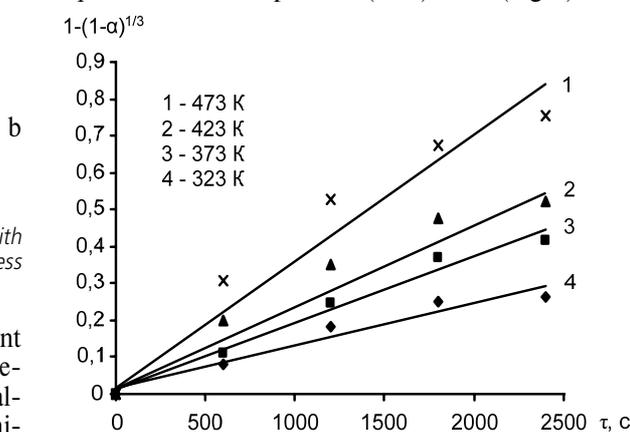


Fig. 4. Experimental data treatment by the equation of reduced sphere

Further mathematical treatment allowed determining activation energy and withdrawing dependence of reaction degree on the temperature and time of the process:

$$E_A=9,2 \text{ kJ/mole,}$$

$$\alpha=1-[1-0,00362 \cdot e^{(-9200/RT)} \cdot \tau]^3.$$

The results of theoretical calculations of α by the given equation coordinate rather well with experimental data for temperatures 323, 373, 423 K (correlation coefficients amount to 0,94...0,97), so the obtained equation may be used for determining the degree of topaz

concentrate fluorination at specified time and temperature of the process.

In the given below micrograph of topaz particles, Fig. 5, it is seen after desiliconization that there are interstices and honeycombs in them from which quartz particles had been removed.

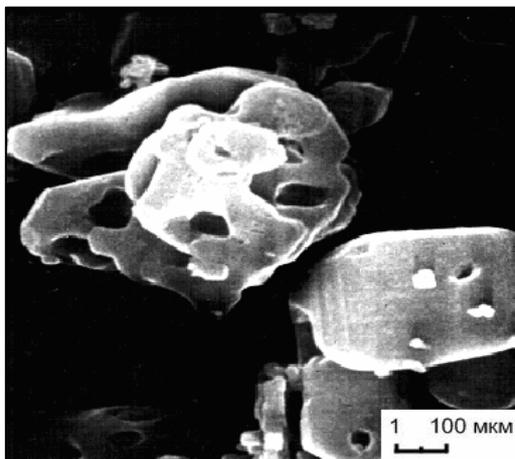


Fig. 5. Micrograph of particles after treating with ammonium bifluoride

Thus, the most optimal temperature condition of desiliconization process is 423...473 K for the time 30...40 min. Activation energy of the given process indicates diffusive character of the process therefore external action, for example, agents intensive stirring at fluorination is necessary for process acceleration.

2. Studying mullitization of desiliconized topaz concentrate

Mullitization was studied by the method of thermogravimetry, RPhA and microphotography. At thermogram of topaz concentrate interaction with ABF (Fig. 6) heating up to 1600 K there are peaks of interaction and removal of quartz in the form of $(\text{NH}_4)_2\text{SiF}_6$ as well as peak at 1436 K obviously meeting topaz decomposition forming mullite and extracting SiF_4 .

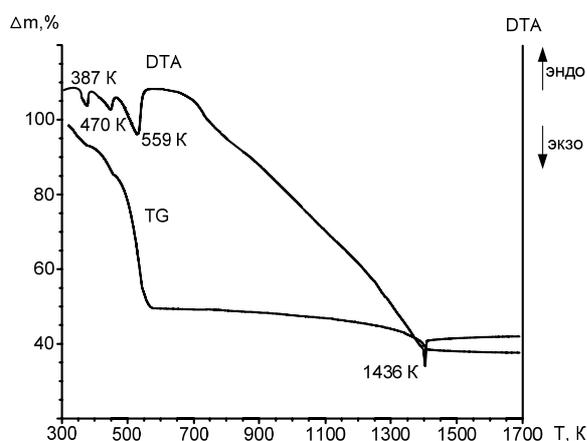


Fig. 6. Thermogravimetric analysis of the mixture of topaz concentrate with ammonium bifluoride

As it was indicated before quantity of fluorinating agent influences the fluorination of topaz concentrate. Ro-

entgen-phase analysis carried out at the device DRON (conditions of survey are $\text{Fe-K}\alpha$, $U=36$ kV, $I=19$ mA, $V_D=2^\circ/\text{min}$) showed that at deficiency of ammonium bifluoride the amount of mullite phase in the samples is insignificant and it is mainly presented by crystals of prismatic form. Increasing the amount of ammonium bifluoride mullite yield increases and needle-shaped crystals starts to appear and at excess of ABF 15...30 % the quantity of mullite in the sample achieves 95 % and it practically fully presented by crystals of needle-shaped habit.

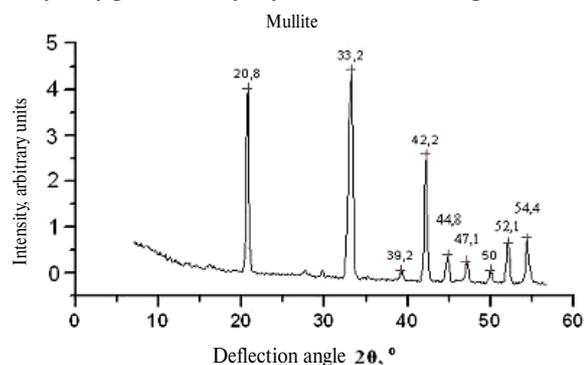


Fig. 7. Roentgenogram of mullite obtained at 30 % excess of $\text{NH}_4\text{F}\cdot\text{HF}$

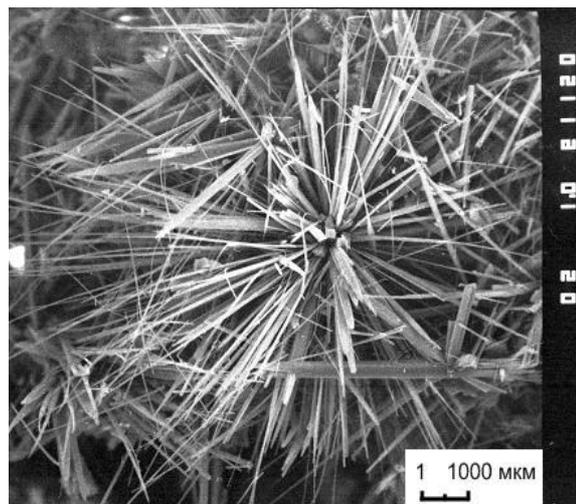


Fig. 8. Micrograph of mullite crystals at topaz concentrate treating with the excess of ammonium bifluoride of 30 wt. % from stoichiometric one

Conclusion

1. Fluorinating agent (ammonium bifluoride) was selected for the process of desiliconization of topaz concentrate.
2. Topaz thermodynamic potentials were estimated. It was shown that topaz can interact with ammonium bifluoride.
3. Desiliconization processes of topaz concentrate were studied. It was shown that at concentrate fluorination with stoichiometric quantity of $\text{NH}_4\text{F}\cdot\text{HF}$ first of all the interaction of quartz constituent occurs and topaz constituent starts reacting only at significant (100 %) excess of ammonium bifluoride.

Optimal conditions for carrying out desilicization 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

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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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STUDYING THE UTILIZATION TECHNIQUES OF AMMONIUM HEXAFLUOROSILICATE

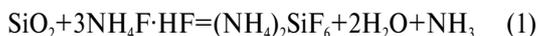
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The utilization techniques of ammonium hexafluorosilicate have been proposed and studied. Thermodynamic calculations of equilibrium gas phase compositions of topaz concentrate fluoridation reaction and reaction of $(\text{NH}_4)_2\text{SiF}_6$ absorption by ammonium hydroxide were given. Experimental investigations in studying gas phase composition were carried out. The sublimation process of ammonium hexafluorosilicate as well as the process of its dissolving in ammonia water with silicon dioxide obtaining was studied.

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 desilicized with ammonium bifluoride:



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.

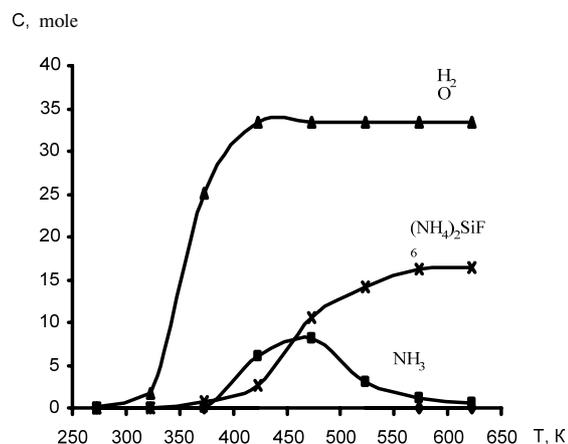


Fig. 1. Equilibrium composition of gas phase

Really, water, ammonia and ammonium hexafluorosilicate should be the main components of gas phase.