

**LOSS OF SILICON FROM COPPER ENRICHMENT FACTORY WASTE USING  
AMMONIUM FLUORIDE**

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**Annotation:** *Waste storage sections and waste in the otvallar under JSC" olmalik KMK " are now considered reserves for the extraction of non-ferrous and rare metals. To date, the landfills contain a total of about 1,750,000 tons of waste, mainly generated by the flotation enrichment of copper. The content of copper in this waste is 0.17%. In addition to copper, the following metals are present: Au, Ag, Pb, Zn, s, Fe, SO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, etc. Therefore, the solution to the problem of waste recycling for the extraction of these raw materials has been very important in recent times.*

**Key words:** *waste, oxide compounds of iron, silicon dioxide in an amorphous state, sublimation cremation, ammonium fluoride, water solution of ammonia, ammonium hexaphthorsilicate, magnetic sorting, selective melting, silicified residue.*

Today, large quantities of minerals are mined underground and openly for the production of metals. One of the main directions of non-ferrous metallurgy is this copper industry. Emissions are also increasing as copper production increases. Therefore, the development of effective technologies for recycling waste and the extraction of valuable components from them and the improvement of existing technological schemes is one of the urgent tasks.

Currently, in most foreign countries, a policy of intensive involvement in the processing of man-made deposits and production waste, as well as saving mineral resources through the development of these waste processing technologies, is actively underway.

An example of this trend is the United States, where in 1993 the proportion of secondary raw materials in the production of non - ferrous metals was: copper - 55%, tungsten - 28%, nickel-25%. Similar work is being done in other countries, notably Canada, the Philippines, South Africa, Bulgaria, the United Kingdom, Spain, Russia and others.

Also in the USA in the 70s of the last century, two devices were launched for additional copper mining at the Arthur and Magna copper-molybdenum factories with a total capacity of 100 thousand tons per day, in which 97.2 thousand tons of waste per day were processed. The launch of these units made it possible to increase copper production from 234 thousand tons per year to 259 thousand tons.

96-97% of the ore crushed in Uzbekistan is considered waste and sent to waste storage areas. This waste is stored in 2 waste storage tanks. Landfill No. 1 was located 3.5 km from the copper enrichment factory on the Angren River Plain and started operation in 1961. There are emissions that have about 546.2 Million\ t useful components. Landfill No. 2 is located 13 km from the factory. It has operated since 1984. There are approximately 775.3 million tons of waste. Landfill No. 1 holds 6.7 mln/t per year, and landfill No. 2 holds 27.8 mln/t of enrichment residues. The storage of this waste is associated with large material costs and at the same time it is delivering some degree of harm to the environment.

During the factory's multi-year flotation enrichment process, a total of about 1,321.5 million tons of waste were accumulated in two landfills.

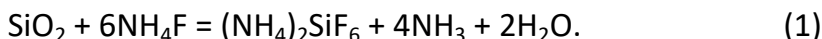
1. 546.2 thousand in the numbered landfill. tonne,

2. and in the numbered landfill, 775.3 thousand. There are tons of waste.

1. the number of landfills is 6.7 thousand per year. Tons, and landfill No. 2-27.8 thousand per year. The disposal of tons of waste continues.

To extract useful components from enrichment residues, it is necessary to extract silicon oxide and iron oxides from its composition.

For this purpose, a scheme was developed to de-silicify the enrichment residues considered abandoned waste using halogenoammonium salts ( $\text{NH}_4\text{F}$  or  $\text{NH}_4\text{F}\cdot\text{HF}$ ):



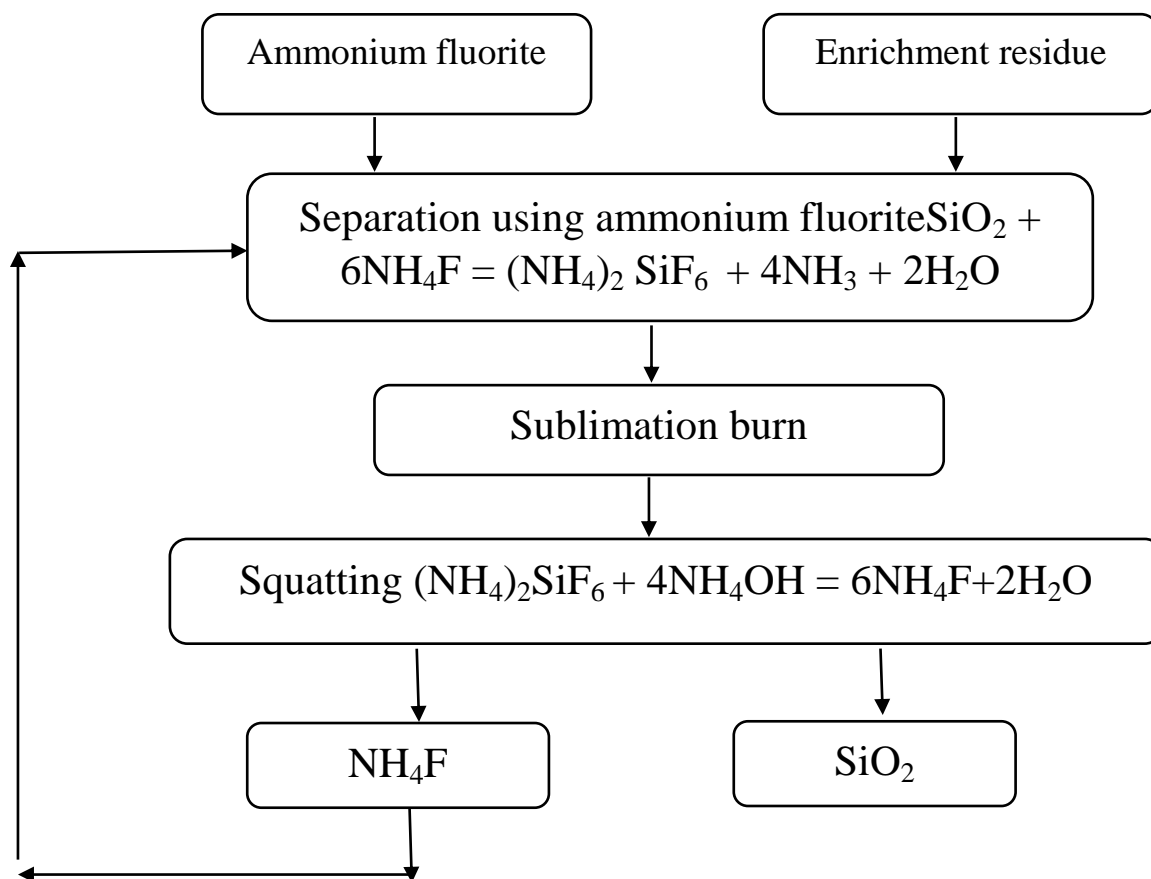
The hexafluorosilicate ammonium salt, which is formed by a chemical reaction, is very convenient from a technological point of view in terms of its physicochemical properties. Under normal conditions, the solid is sublimated, and at 320°C, it passes into the gas phase.

The advantage of using fluoride ammonium as a кремнилатыng reagent is that it can be regenerated.

At 70°C, the solubility of hexafluorosilicate ammonium in ammonia water reaches 370 g/L. As a result of interaction with ammonia (2), it is hydrolyzed according to the reaction, and silicon oxide falls into the sediment in the amorphous state:

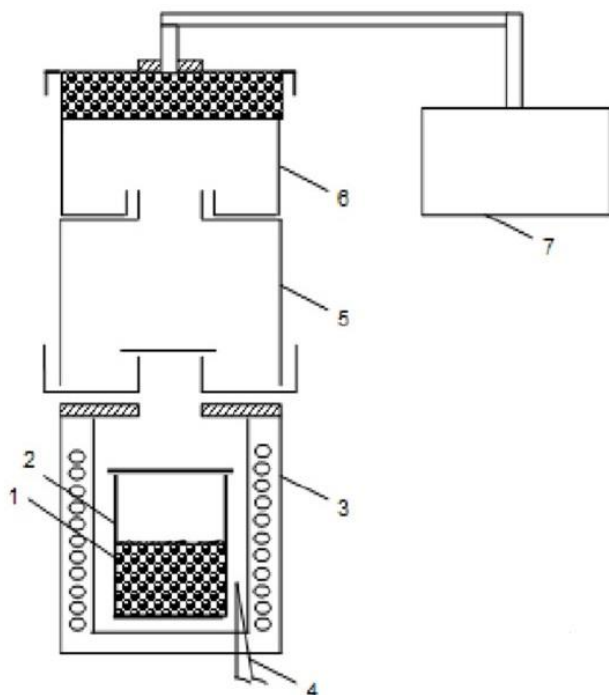


The restoration of ammonium fluoride gives continuity to the process of de-silicification and the possibility of extracting the Quartz organizers in the waste to obtain the "white powder" ("belaya saja") variety of silicon oxide in a fine dispersion state.



Picture 1. Scheme of silicification of enrichment residues

The mining and Metallurgical Industry carried out research on the de-silicification of man-made products in the halogenoammonium method in a device made up of furnace, gas-catcher and ammonia-absorbing devices that directly convert a solid into gas, created anew and without analogues in practice.



Picture 2. scheme of an experimental device for extracting Silicon from enrichment residues: 1-sample, 2-container made of metal, 3-oven, 4-thermoapparate, 5,6-Gas-Holding Device, 7-ammonia-absorbing device.

Initially a sample of 30 gr was taken from the landfill site to make a shixta (85% of the total sample size – 0.074 mm class). The amount of silicon dioxide in the sample was mixed with the addition of ammonium fluoride in a stoichiometric ratio and given to the device shown in (NH<sub>4</sub>) for launch at 2Sif6 sight.



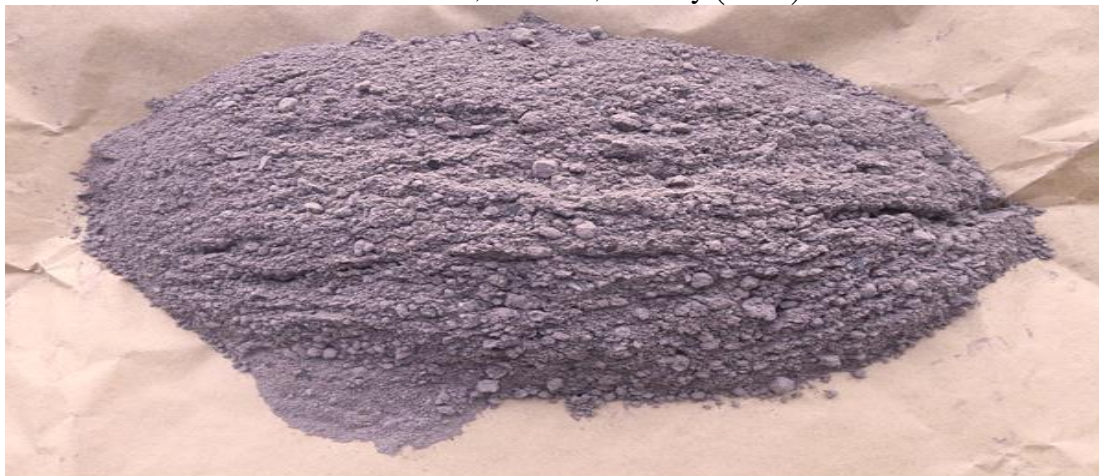
Picture 3. The copper enrichment factory is an early example in an abandoned landfill.



Picture 4. Pure hexaphthorsilicatoammonium (AGFS)



Picture 5. The finished product is silicon dioxide (white burnt residue) in an amorphous state.



Picture 6. After the separation of silicon dioxide, the residue (burnt residue )

At the beginning of the process, the oven is launched and the temperature rises to 170-190°C for 1 hour, after which the temperature is again increased to 350-390°C and held for 1 hour at this temperature.

A thermopar was used to measure temperature. The hardware contains systems of retaining capacitors. The condenser is primarily designed to capture and collect  $(\text{NH}_4)_2\text{SiF}_6$ , and (Schedule 1 # 2 sample) is surrounded by a barrier that prevents it from becoming a silicified product, while the condenser is equipped with a filter made of fluoroplast struts serving to collect dust. The capacitor temperature is at 250-350°C while the capacitor is held from 220°C to room temperature. The results of extracting AGFS from a 30 gr sample are shown in Table 1.

Table 1

The results of the separation of hexaphorsilicate ammonium.

Designation	1	2	3	4
$(\text{NH}_4)_2\text{SiF}_6$ , g	48	47	47	48
Residual, g	14,5	14	14,5	14

As seen in Table 1, the AGFS separation results are close to the value given in the theoretical data.

AGFS is isolated after the condenser silicon dioxide is lost. The density of a solution with ammonia of 10-12% is measured using an areometer. Hexafluorosilicate ammonium is placed in a flask with a rounded bottom and an aqueous solution of 10% ammonia is poured over it, 20% more than the stoichiometric amount. The resulting mixture is mixed at room temperature for 1 hour, after which the precipitate is separated from the filtrate and dried at 3 stages of washing (rinsing) and 110°C. After drying, a high-dispersion product (sample No. 3 Table 1) is taken. It is observed that the solution color obtained from the washing of hexafluorosilicate ammonium is blue, like the color of the copper solution. It should also be taken into account that after sublimation of silicon dioxide, a product is formed in the form of a reddish-brown film on the top when the starch is heated. The obtained sample analysis is carried out at the Central Analytical Laboratory (Olmalik KMK) JSC. The results of the analysis are given in 2 tables.

Table 2

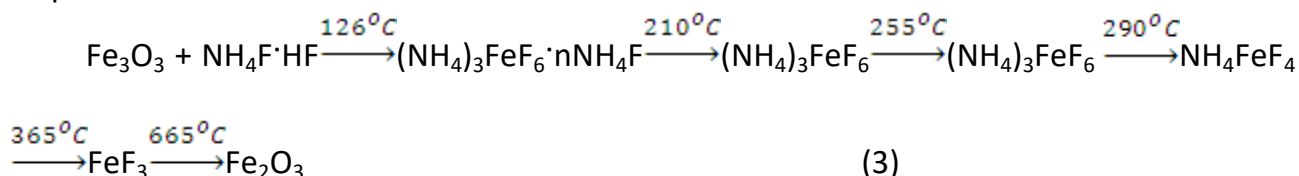
The composition of the residual cuticle:

Sample No	Cu, %	Zn, %	Fe, %	SiO <sub>2</sub> , %	Au, g/t	Ag, g/t
1	0,11	0,02 6	8,69	67,3 1	0,6	3,0
2				5,14		
3				99,9		
4	0,33	,079	26,5	0,21	1,83	9,1

Table 2 shows that after the loss of silicon dioxide from the process, the amount of valuable components increased. We can see that the amount of copper increased by 4 times the initial amount after the separation of silicon dioxide, zinc – 2 times, and Iron-3 times, compared to the amount contained in the initial ore. From the initial sample, a separation of Silicon by 99.7% was achieved, obtaining a white powder with a fine dispersion content that contained silicon dioxide in an amorphous state of 99.9%. In addition, after the extraction of silicon dioxide, an increase in the amount of Rare Metals was also observed in the cake. This figure was in gold – 5 times, and in silver-1.3 times.

Silicon oxide was obtained as a result of the interaction of components contained in man-made waste with fluoride ammonium.

On the basis of thermodynamic analysis, the temperature dependence and sequence of the course of chemical reactions were obtained:

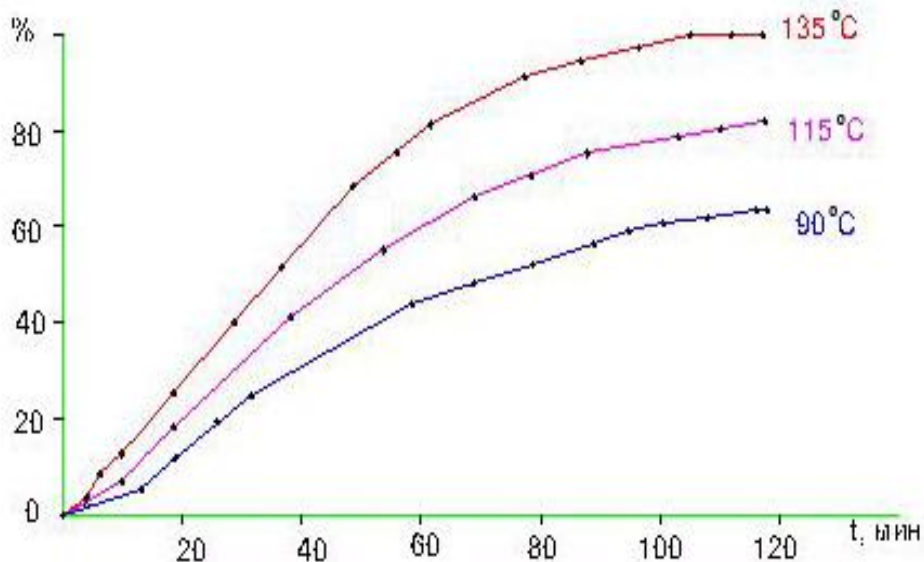


Picture 6 shows the dependence of the change in the degree of decay of silicate compounds during fluorination on the heating time at different temperatures.

Thus, as a result of studying the fluoridation process of man-made products at different temperatures, the degree of formation of silicon oxide was determined.

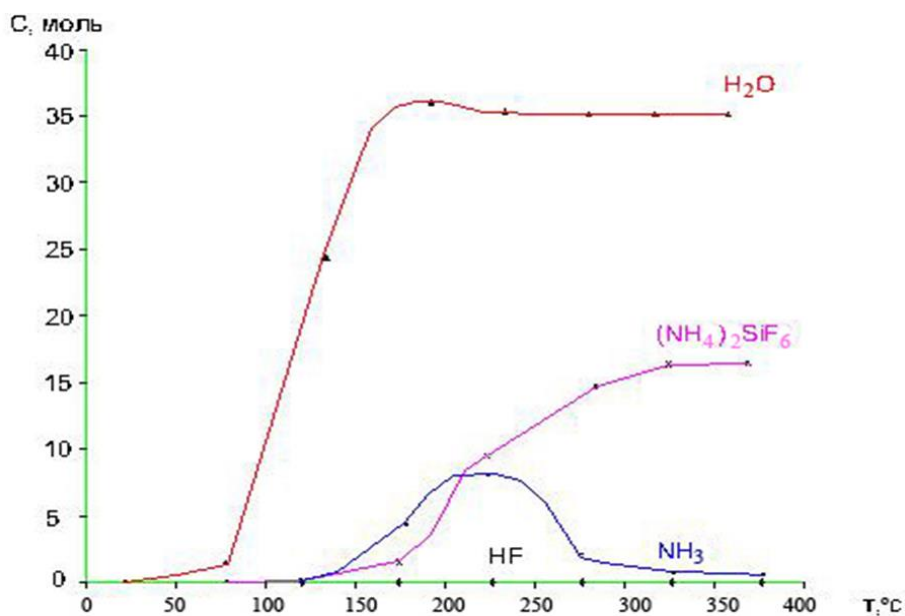
The processing of quartz raw materials with ammonium fluoride, a low-temperature process of up to 4000c was applied. Ammonium fluoride was used to purify silicon oxide using fluorides.

The technology, developed for the purpose of processing enrichment residues, is characterized by environmental friendliness, energy efficiency, simplicity in addition to the economic efficiency of extracting additional useful components, and a complete regeneration of fluorinating reagents.



Picture 6. The dependence of the change in the degree of decay of silicate compounds during fluorination on the heating time at different temperatures

The composition of the gas phase equilibrium state of the silicon oxide fluorination reaction is shown in Picture 7.



Picture 7. Composition of silicon oxide fluorination reaction in gas phase equilibrium state

The study of the possibility of silicification of enrichment residues was carried out in the following sequence method:

the sample obtained was mixed stoichiometrically with ammonium biftoride, depending on the amount of Silicon two oxides;

the mixture was loaded into the oven and the mouth of the oven was tightly sealed;

the process is 100°C, 150°C, 200°C, at temperatures of 250°C and 10, 20, 40, 60 min. carried in continuity;

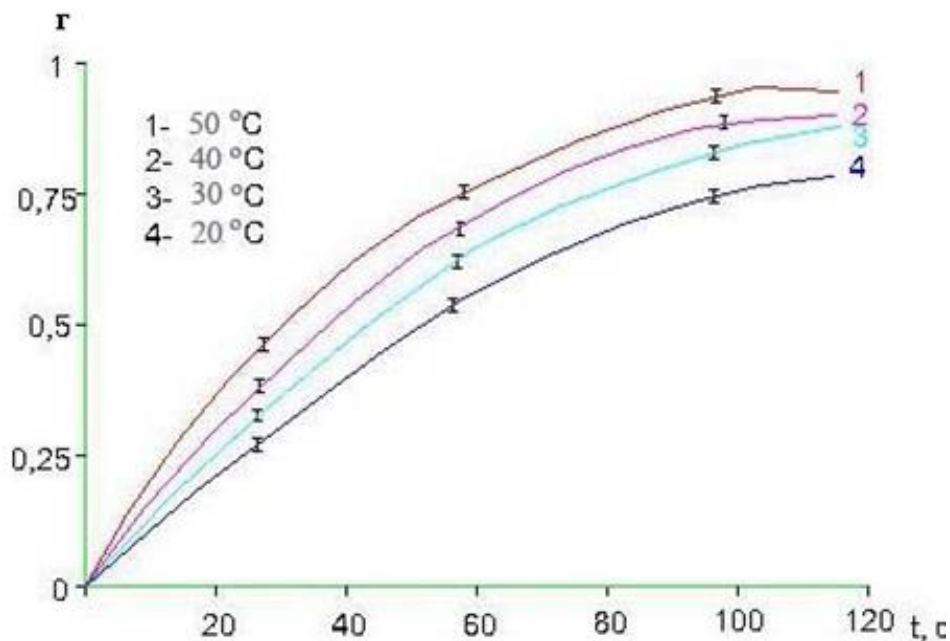
after the process, the resulting product was taken to another container and mixed with distilled water;

with the help of filtration, the pulp was separated into solid and liquid phases;

cake farfor, a filter-top product, was placed in a container and mixed with ammonia water in order to separate the ammonium biftoride;

the liquid is filtered into a well, and the cake is placed in a drying oven (oven temperature should not exceed 600);

the dried mass is cooled and pulled by the moment, and according to the ratio of weights, the degree of exposure is determined.



Picture 8. Kinetics of exposure of  $(\text{NH}_4)_2\text{SiF}_6$  to a solution of 10% li  $(\text{NH}_4)\text{OH}$

The cake was found to melt in a solution of 10% li  $(\text{NH}_4)\text{OH}$ , and melting results in  $\text{NH}_4\text{F}\cdot\text{HF}$ .

The interaction kinetics of the process is shown in Picture 4. The degree of exposure of ammonium hexafluorosilicate and ammonium hydroxide according to the change in the weight of the sample is determined by measuring the cooled mass.

A technical mixture consisting of 25% ammonium fluoride and 75% ammonium biftoride was used to break down the enrichment residues of the Mining-Metallurgical Industry. The extraction of iron was carried out in a magnetic separator. According to the results of the research carried out, a technological scheme for the processing of man-made products was created, which included fluoridation, sublimation of AGFS, extraction of ammonium water, extraction of silicon oxide in the amorphous state, regeneration and reuse of fluoride ammonium.

The advantage of using ammonium fluoride as a silicifying reagent is that it can be regenerated.

This makes it possible to carry out the process of silicification without interruption and extract the so-called "white powder" variety of silicon oxide with a small dispersion from Quartz-containing waste.



Table 3 lists the amount of silicon oxide and other additives in the sample after silicification, and tables 4 and 5 show the material balance of obtaining silicon oxide and ammonium biftoride.

Table 3.

The amount of silicon oxide and other additives after silicification

Sample No	Cu, %	Zn, %	Fe, %	SiO <sub>2</sub>	Au, g/t	Ag, g/t
1	0,11	0,02	8,6	67,31	0,6	3,0
2				5,1		
3				99,9		
4	0,33	,079	26,5	0,21	1,8	9,1

Table 4

Material balance of obtaining silicon oxide

Name	Introduction, kg	Name	Output, kg
10 % NH <sub>4</sub> ON	964,6	N <sub>2</sub> O	857,1
(NH <sub>4</sub> ) <sub>2</sub> SiF <sub>6</sub>	184	NH <sub>4</sub> F	228,2
		SiO <sub>2</sub>	62,2
Total:	1148,6	Total:	1147,32

Table 5

Material balance of ammonium biftoride intake

Name	Introduction, kg	Name	Output, kg
NH <sub>4</sub> F	228,2	NH <sub>4</sub> F*HF*H <sub>2</sub> O	231,28
H <sub>2</sub> O	850,9	H <sub>2</sub> O	795,4
		NH <sub>3</sub>	52,42
Total:	1079,1	Total:	1079,1

The resulting ammonium biftoride was used to fluoridate the next batch.

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