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**FLUORIDE PRODUCTION FROM PHOSPHATE RAW MATERIAL
TREATMENT IN RUSSIA**

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Introduction

Russia is the largest producer of non-organic fluoride compounds, the application of which in modern conditions is an integral part of technical progress in various areas of industry and technology. Inorganic fluorides are used in the production of metallic aluminium, rare and radioactive elements, and fluoro-organic substances possessing valuable anti-corrosive and thermochemical properties. Non-organic fluorides play a significant role in the production of ferrous and non-ferrous metals, construction materials, glass, antiseptic treatment of woodware in electronics, rock beneficiation, for decomposition of zirconium concentrates, medicine and other numerous fields of application.

Fluorspar and to a lesser degree, fluorine of phosphate rocks are mainly used as raw materials in the production of non-organic fluorides in Russia. Acid grade fluorspar concentrate is used for hydrogen fluoride and hydro-fluoric acid production. The former in turn supplies fluorides for heavy metals: tantalum, niobium, uranium, and molybdenum, refrigerate fluoro-organic polymers, pure non-organic fluorides, elemental fluorine, EP hydrofluoric acid. Technical pure hydrofluoric acid is used for cryolite and aluminium fluoride production.

In the Russian Federation, the fluoride recovered in the Kola and Kovdor apatite concentrates treatment process as 18-22% fluorosilicic acid solution is utilized in the manufacture of aluminium fluoride and also silica fluorides of sodium, potassium and ammonium.

In general, despite the low fluoride concentration in the phosphate rock materials (Kola apatite - 3%, Kovdor apatite - 1%), but taking into account the gigantic scale of phosphate rock materials treatment for mineral fertilizers production, fluorine present is of significant practical interest.

The estimated recoverable reserves of fluorine in phosphate rocks of the Russian Federation exceed the fluorine reserves in fluorspar by two to three times.

At present, the main volume of fluorine salts is obtained by the treatment of apatite concentrate from Kola (production in 1998 - more than 8 million t).

On the basis of actual state of operating plants producing mineral fertilizers, the Research Institute for Fertilizers considers it possible to attain the following fluorine yields from Kola apatite concentrate: dehydrated wet-process phosphoric acid (evaporation stage) 48-50 kg F/t P₂O₅; semihydrated -30-35 kg F/t P₂O₅; nitric decomposition of Kola concentrate (precipitation of Na₂SiF₆) - 45 kg F/t P₂O₅.

In the fertilizer production, fluorine-containing gases are trapped with water in the gas-cleaning systems. To trap fluorine compounds, various facilities are applied, the main absorption is performed in the hollow spray-jet

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scrubbers, foam absorbers. Meanwhile, it should be noted here, that a great deal of experience is accumulated in Russia on the development and operation of various systems of absorption [1].

Al₃ and cryolite production

In 1998, Russia produced approximately 3 million tonnes of primary aluminium and used 75 Kt of AlF₃ and 60 Kt of cryolite. The capacity of workshops AlF₃ is defined by the volumes of fluosilicic acid treated of required quality. Data for capacity and production of AlF₃ are as follows:

<u>1998 AlF₃ Production (Kt)</u>	<u>Capacity</u>	<u>Production</u>
AO "Voscresenscie mineral fertilizers"	14	10
AO "AMKO"	15	14,6
AO "Polevskoy cryolite factory"*	27	12,1**
AO "Jogno-Ural cryolite factory"*	26	17,1**
Nevinnomusskoe PO "Azot"	3,5	-
Total	85,5	

* from fluorspar

** 6 months 1998 year

The production is realized by two principal processes:

1. Crystallization from the solution of the reaction between aluminium hydroxide and fluorosilicic acid. The tri-hydrate of aluminium fluoride is subjected to drying and calcining with the formation of ready product.
2. Crystallization from supersaturated solution of aluminium fluoride, ammonium fluoroaluminate with the subsequent calcining. As a result, aluminium fluoride is formed and ammonium fluoride recycled to the stage of ammonium fluoroaluminate crystallization.

In the aluminium fluoride manufacture by the first process, due to the impossibility of complete return of liquor solutions into the process, the liquor solutions can be:

- used in cryolite production;
- partially used for HF, SiF₄ absorption.

The flow sheet of aluminium fluoride production process by the first method and subsequent treatment of the liquor solution into cryolite is presented in Figure 1.

The interaction of fluorosilicic acid and aluminium hydroxide is complete within 10 minutes. Prior the aluminium hydroxide introduction, the acid is heated by steam up to 90°C. The reaction mass is filtered at the belt vacuum-filter that washes the silica-gel sediment with water with a temperature of 60-80°C. Aluminium tri-hydrate fluoride is crystallized within 3 hours in the presence of a seed crystal. At the beginning of crystallization, the solution is heated with steam up to 95°C. Aluminium tri-hydrate fluoride suspension is separated from the liquor solution at drum or belt vacuum-filters prior delivering materials with 50-55% humidity to the dehydration stage. The aluminium fluoride paste calcination is conducted in drum dryers equipped special heat-exchanges, with counter current movement of heat-carrier and material, resulting in a high quality product manufacture (Table 1). This technology is registered by patents in the Russian Federation [2, 3, 4, 5].

Table 1 - Comparative Data on Aluminium Fluoride Quality

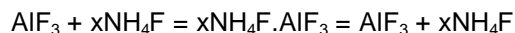
Indices, % by weight	Country, Company						
	Russia*	Switzerland Alusuisse*	Austria Chemie-Linz*	Japan Morita**	Japan, China Acita Chem**	Italy Montedison**	France Aluminium Pechiney**
Loss on Ignition	1,5-2,5	0,5	0,5	0,27	1,68	0,1	1,5
AlF ₃	93-96	96	96	92,6	91,5	88-90	78-82
Al ₂ O ₃	3-5	3	3	6	no data	no data	7-10
SiO ₂ + Fe ₂ O ₃	0,2-0,3	0,2 ± 0,07	0,2 ± 0,07	0,1 ± 0,01	0,2	0,4	0,5-0,8
SiO ₄ ²⁻	< 0,01	0,05	0,05	0,02	no data	no data	1,5
P ₂ O ₅	< 0,05	0,02	0,02	0,02	0,01	no data	0,03-0,05

* from fluorosilicic acid

**from fluorspar

The aluminium fluoride production process through ammonium fluoroaluminate precipitation state is shown in Figure 2.

This technology involves fluorosilicic acid decomposition by aluminium hydroxide, silica-gel separation, ammonium fluoroaluminate precipitation, ammonium fluoroaluminate centrifuging and its thermal decomposition [6].



The gaseous products of ammonium fluoroaluminate thermal dissociation are trapped in the absorption system and returned to the double salt precipitation. The comparative data for aluminium fluoride quality produced in Russia and by companies of Austria, Japan, Italy, Switzerland and France are presented in Table 1. It should be mentioned, however, that with the exclusion of Chemi-linz products, all the above-mentioned companies manufacture their product by the aluminium hydroxide hydrofluorination process.

The coefficient of fluorine used is in the average way, % (from the amount introduced with the raw materials):

- with silica dioxide	5-10
- effluents	9-10
- dusting	2-5
- pyrohydrolysis (under dehydration)	2-6
- mechanical loss	1,5-3

Sodium, potassium and ammonium silica fluorides production

At present, the technology for silica fluorides production involves fluorosilicic acid neutralization with ammonia or sodium and potassium carbonate solution up to $hY = 33,5$ with the subsequent drying of the solution or suspension obtained in the fluidized bed unit with an inert layer at the temperatures 120-140°C. The process scheme is presented in Figure 3.

Silica fluorides meet the following requirements (Table 2).

Table 2 - The technical indices of sodium, potassium, ammonium silica fluorides

Indices, %	Sodium silica fluoride*	Potassium silica fluoride*	Ammonium silica fluoride
Na ₂ SiF ₆	98	-	-
K ₂ SiF ₆	-	98	-
(NH ₄) ₂ SiF ₆	-	-	92
H ₂ SiF ₆	0,2	0,2	0,4
As	0,003	-	-
Pb	0,05	-	-
Humidity	0,5	0,5	1,0
Water insoluble residue	-	-	6

*highest grade

Raw materials and energy consumption rate coefficients per tonne of different silica fluorides are as follows:

	Indices						
	NH ₃ , (100%) t	H ₂ SiF ₆ , (100% F), t	Na ₂ CO ₃ , (100%), t	K ₂ CO ₃ (100%), t	Electro-energy kW/h	Fuel, kg	Steam, Gkal
Na ₂ SiF ₆	- -	0,61 - 0,82	0,62 - 0,85	-	290 - 250	125 - 359	0,06 - 0,08
K ₂ SiF ₆		0,51 - 0,52	-	0,93 - 0,94	490 - 760	363 - 390	0,025 - 0,027
(NH ₄) ₂ SiF ₆	0,194-0,20	0,7-0,71	-	-	430 - 432	463 - 508	0,0245-0,0252

Other methods of utilization fluoride in treatment phosphate rocks

The treatment of fluoride off-gases to obtain ammonium difluoride has been performed in the Russian Federation. The authors have developed a process for ammonium difluoride production, which involves decomposition of ammonium silica fluoride solution or fluorosilicic acid by ammonium water at pH = 8,5-9 with the production of ammonium fluoride and its evaporating up to the formation of ammonium difluoride-fluoride melt at the temperatures of 100-150°C with the subsequent crystallization during cooling with water shafts.

Raw materials and energy resources consumption rates in the ammonium difluoride-fluoride production (per tonne of product) are as follows:

NH ₃	0,75 t
Electro-energy	130-145 kW/h
Steam	5,7-6,2 Gkal

The product has the following quality indices shown in Table 3.

Table 3 - Technical Characteristics of Difluoride-fluoride

Indices, %	Grade A	Grade B
Fluorine content	60	60
HF content	26	24
(NH ₄) ₂ SiF ₆ content calculated as SiO ₂	1,2	1,0
H ₂ O	7,0	7,0
Non-volatile residue	0,2	no norm
Chlorine content	0,005	no norm

The content of ammonium difluoride in the product is 68-74%.

The improvement in ammonium difluoride technology has been carried out with the development of NH₄HF₂ crystallization process from solutions system NH₄F-HF-(NH₄)₂SiF₆-H₂O.

Two types of crystallization for ammonium difluoride manufacture are developed and tested: isohydric and vacuum.

The melt containing no more than 50% of ammonium difluoride is diluted with steam condensate to 35-37% of ammonium difluoride and is subjected to crystallization at the temperatures of 17-23°C. The suspension obtained is separated at the centrifuges of continuous duty. The product is by no means inferior in quality to ammonium difluoride produced from hydrogen fluoride (Table 4).

Table 4 - Ammonium Difluoride Quality Produced by Crystallization Route

Indices	Mass fraction, %	
	Grade A	Grade B
NH ₄ HF ₂	96	94
NH ₄ F	3	4
(NH ₄) ₂ SiF ₆	0,5	0,8
H ₂ O	5	5
Non-volatile residue	0,1	no norm
Cl	0,005	no norm

Hydrogen fluoride and hydrofluoric acid

The technology of ammonium difluoride-fluoride production and its subsequent sulphuric acid decomposition is based on dihydrous hydrogen fluoride technology production from fluorosilicic acid [7]. Ammonium difluoride-fluoride melt is mixed with sulphur acid mono-hydrate leading to the formation of solution with a mole ratio NH₃.H₂SO₄ = 1,0 + 0,1. Upon heating the solution in the electrofurnace of bath type to thermal decomposition, gaseous hydrogen fluoride and ammonium disulphate melt are obtained. The melt is dissolved in the steam condensate and is used in wet-process phosphoric acid production. The gaseous hydrogen fluoride at the furnace outlet is subjected to rectified purging from highly boiled admixtures (water and sulphuric acid with the formation of 95-98% raw acid).

The raw acid is converted into dihydrous hydrogen fluoride by the classical scheme of rectification in 2 steps.

The consumption rate per tonne of HF are:

NH ₄ HF ₂	~ 2,1 t
100% H ₂ SO ₄	~ 3,4 t
Electro-energy	~ 1500 kW/h

Figure 1

The principal scheme for the treatment of fluorosilicic acid with the formation of aluminium fluoride and cryolite.

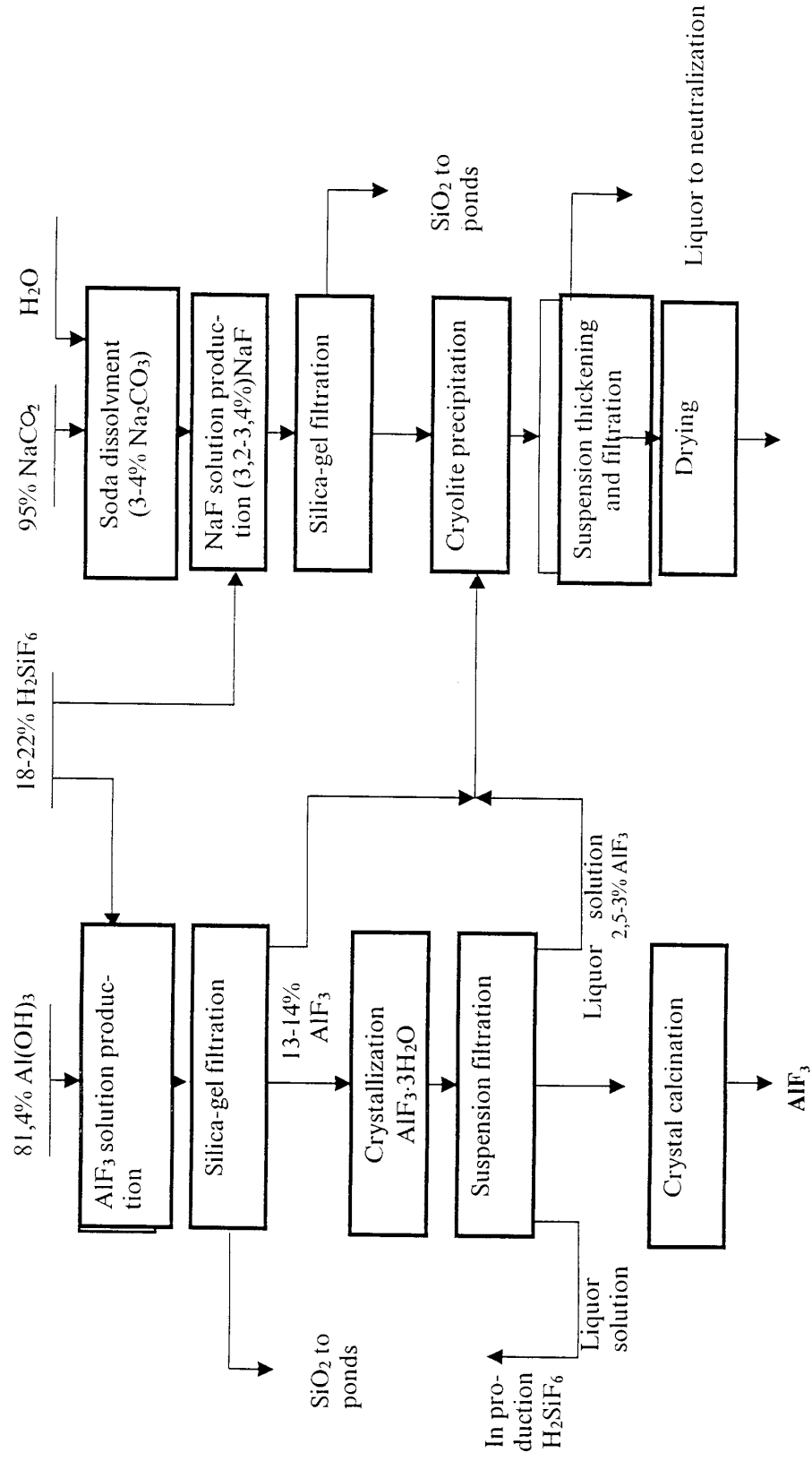


Figure 2

The Principal Scheme of Aluminium Fluoride Production Through Fluor-aluminate of Ammonia

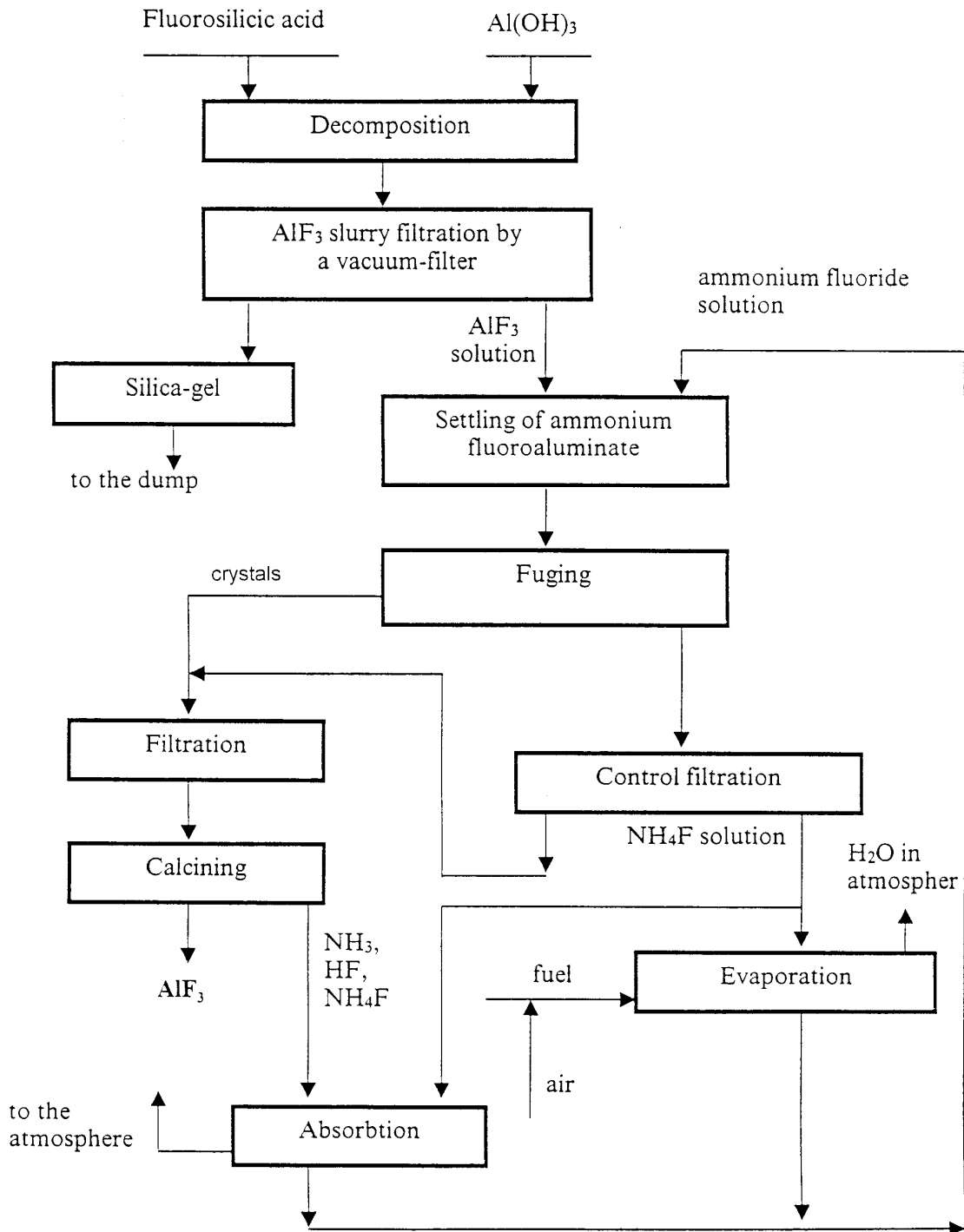


Figure 3

The Scheme of Silica Fluorides Production in Fluidized Lay

