The use of beryllium fluoride in nuclear power is studied: in melt with lithium fluoride as coolant and solvent for uranium, plutonium and thorium salts in high-temperature molten-salt nuclear reactors (ZhSR, MSR) as well as for making fluoroberyllate glass for regulating low neutron fluxes and welding special purpose articles. The existing methods of obtaining beryllium fluoride are described. A new method is proposed for obtaining high-purity fused beryllium fluoride from beryllium wastes by evaporating a saturated solution with fluorine-to-beryllium molar ratio 2.06–2.18.

A great deal of value is now attached to increasing beryllium production, mainly, in connection with the increased demand for the latest technologies, specifically, in the nuclear industry (reactor building), aviation, controllable projectiles, space technology, electronics and others. Beryllium is included in the first group of strategic materials, whose reserves are continually increasing. It has a special place in nuclear power, being an integral part of research reactors and new fuel compositions. Undoubtedly, the sphere of applications of beryllium and its compounds is expanding.

Beryllium is produced on a commercial scale by multistage processing of beryllium-containing concentrates with successive extraction of intermediate products (beryllium hydroxide, ammonium fluoroberyllate and beryllium fluoride) and reduction of beryllium fluoride by magnesium metal.

Beryllium fluoride has a definite niche in nuclear power. It is used for making fluoroberyllate glass for regulation of low neutron fluxes, as a protective-degassing flux in the reduction melting of beryllium and in welding special-purpose articles.

Beryllium fluoride in melt with lithium fluoride is used as coolant and solvent for uranium, plutonium and thorium salts in high-temperature molten-salt reactors. The coolant is a molten-salt mixture at high temperature and low pressure, which decreases mechanical stresses and increases reactor safety. The nuclear fuel is liquid and itself is the coolant, which simplifies the design of the reactor, smoothes fuel burnup and makes it possible to replace the fuel without stopping the reactor. One form of nuclear fuel is a melt based on $^{232}$Th and $^{233}$U fluorides.

Fluorine compounds make it possible to develop a new-generation molten-salt nuclear reactor where there are no fuel elements and uranium and thorium fluorides dissolved in the beryllium and lithium fluoride melt serve as coolant and energy source. A range of melt compositions (Li, Na, Be/F, Li, and Be/F) with satisfactory melting temperature, the requisite solubility of actinide trifluorides in the working temperature range of ZhSR-S and similar thermophysical properties and good compatibility with the structural materials has been found and recommended for practical applications [1]. The main advantage of such a reactor is the simplicity of spent-fuel regeneration: uranium can be extracted by fluorination to UF$_6$ in salt melt. It is also important that the nuclear fuel for such a reactor can be prepared quite simply: there is no need to fabricate pellets, fuel-element cladding, cassettes and fuel assemblies. In addition, proliferation of a component of nuclear weapons (plutonium) can be prevented and the volume of wastes can be reduced many-fold. Nuclear power becomes more profitable because,
first and foremost, there is no yearly loading-unloading of expensive fuel elements, the costs of storing and reprocessing spent fuel and decommissioning of reactors are lower [2].

Beryllium fluoride is a necessary component of the salt composition for nuclear reactors. It is obtained on an industrial scale by decomposition of ammonium fluoroberyllate crystals at 900–950°C (reaction 1):

\[(\text{NH}_4)_2\text{BeF}_4 \rightarrow \text{BeF}_2 + 2\text{NH}_4\text{F}.\]  (1)

This method makes it possible to obtain glassy beryllium fluoride with the requisite quality and density ~2 g/cm³, but the process is not perfect [3]. The decomposition of the crystals proceeds violently and is accompanied by intense release of aerosols of fluorine compounds of beryllium, emissions of melt and inflammation of ammonia. This hinders the operation of gas-purification systems and creates additional dangerous factors for maintenance personnel working on the decomposition furnace. In addition, the beryllium fluoride obtained is contaminated with impurities, which lowers the quality of metallic beryllium and precludes its use in thermonuclear reactors.

In Russia, the possible sources for obtaining metallic beryllium and its compounds are secondary beryllium as well as process wastes accumulated and newly formed in the production of beryllium-containing materials [4]. This made it necessary to modify the conventional technology of obtaining beryllium compounds, specifically, beryllium fluoride.

There are many alternative methods of obtaining beryllium fluoride. But, they have not found application in industry for various reasons: low process indices, inadequate quality of beryllium fluoride or complexity of equipment layout.

Beryllium fluoride systems, similarly to silicates, form glasses easily [5]. X-Ray structural studies of beryllium fluoride showed that BeF₂ has a chaotic three-dimensional reticular structure where the beryllium atoms are surrounded tetrahedrally by fluorine atoms and the fluorine atoms by two beryllium atoms. This structure is similar to that of glassy silica and germanium dioxide.

Beryllium fluoride has a modification similar to β-quartz that is stable at room temperature (corresponding to the low-temperature modification of quartz SiO₂). At 220°C, this form transforms into a modification similar to α-quartz, which transforms into the tridymite form when heated slowly at 420–450°C [5]. At 680°C, this phase spontaneously transforms into the α-cristobalite modification of beryllium fluoride, corresponding to the cristobalite form of silicon dioxide. The transitions between these three modifications of beryllium fluoride occur very slowly, precisely as between different forms of silicon dioxide.

The properties of fused fluoride can serve as an illustration of the similarity of beryllium fluoride and silicon dioxide. It has a high viscosity and low electric conductivity. These properties also attest to the fact that liquid beryllium fluoride possesses nonionic reticular structure similar to that of fused silicon dioxide. In fluoride systems, it is sometimes more difficult to induce crystallization than to determine the precise conditions for obtaining a product in the glassy state [6]. For this reason, beryllium fluoride crystallizes with difficulty and in practice high-purity BeF₂ is obtained in a glassy form.

Attempts have been made to obtain beryllium fluoride from fluoride solutions by evaporation. In this case, because of swelling the product obtained has low density (from 0.1 to 0.9 g/cm³) and high content of beryllium oxyfluoride (to 10%), making its subsequent use for its intended purpose impossible. Many researchers have noted that the true nature of water solutions of beryllium fluoride is complex – the ions BeF⁺, BeF₅⁻, and BeF₄²⁻ are found in them. The relative concentration of the ions depends on the ratio F/Be and pH [6].

The problem of obtaining beryllium fluoride from solutions consists in the fact that beryllium fluoride partially hydrolyzes in water solutions (reaction 2):

\[\text{BeF}_2 + \text{H}_2\text{O} = \text{BeOHF} + \text{HF}.\]  (2)

In the process of evaporation of solutions, hydrogen fluoride is removed, the equilibrium of the reaction shifts rightward and oxyfluoride remains in the beryllium fluoride powder formed. For this reason, it is impossible to obtain high-quality glassy beryllium fluoride by simply evaporating a solution. Likewise, attempts to evaporate solutions with excess hydrofluoric acid, so as to shift the equilibrium to leftward, have been unsuccessful.

The development of new-generation reactors is predicated on the use of pure and highly pure materials, including fluoride salts. High impurity content makes these materials less effective [7]. The main impurities in beryllium fluoride