

# Fluorine distribution during thermal treatment of sulfuric acid leaching products of complex beryllium raw materials at JSC UMP

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**Abstract.** X-ray diffraction, infrared spectroscopy, thermogravimetry and mass spectrometry were employed to study the behavior and distribution of fluorine in sulfuric acid treatment of the melt of beryl-bertrandite-phenakite-fluorite concentrates with alkali fluxes. It was established that fluorine in a solid phase is predominantly present in the form of sodium and calcium fluorosilicates and in a gaseous phase it is evolved in the form of silicon tetrafluoride and fluorosulfonic acid.

## 1. Introduction

Currently at JSC Ulba Metallurgical Plant the production of beryllium constitutes the processing of complex beryllium raw materials consisting of beryl concentrates  $\text{Be}_3\text{Al}_2[\text{Si}_6\text{O}_{18}]$  and collective concentrates of bertrandite  $\text{Be}_4[\text{Si}_2\text{O}_7](\text{OH})_2$ , phenakite  $\text{Be}_2[\text{SiO}_4]$  and fluorite  $\text{CaF}_2$ . Hydrometallurgical technology of their processing consists in preliminary melting with alkali fluxes ( $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$ ) at 1400 °C, water melt granulation and subsequent sulfuric acid (60%) leaching of the baked melt (hereinafter referred to as the melt). The resulting product is sulfate-silicate mass (SSM) which is subjected to aqueous leaching of soluble sulfates, including beryllium. After phase separation sulfate-silicate sludge (SSS) is sent for disposal, and sulfate solution is sent for alkaline precipitation of beryllium hydroxide. The presence of significant amounts of fluorine in the system leads to the formation of stable, highly soluble and hardly hydrolysable complex ions [1, 2]. In terms of hydrolysis resistance, complex ions can be arranged in a sequence:  $\text{BeF}_4^{2-} > \text{BeF}_3^- > \text{BeF}_2 > \text{BeF}^+$ . Therefore, to decompose complexes increasing pH up to 12 is required which causes conjoint precipitation of impurities and incomplete beryllium precipitation. For these reasons, fluorine removal before the precipitation stage of  $\text{Be}(\text{OH})_2$  is an urgent task.

In [3] the results of the research in thermal treatment of sulfate-silicate masses for fluorine removal are discussed. The nature of this process lies in leaching of the melt with 60% sulfuric acid and subsequent heating of sulfate-silicate masses up to 300 °C. Herein due to water evaporation the concentration of sulfuric acid occurs, i.e. leaching ends up with sulfatization with possible removal of fluorine in the form of HF and  $\text{SiF}_4$ . This method is rather attractive because it does not require any alteration of the existing technology.



It has been found that SSM calcination allows reducing fluorine content by 40-50% in solutions after the leaching of sulfates from SSM. However, fluorine behavior and the forms of its condition in these processes have not been established. Consequently, addressing these issues is the objective of the present paper.

## 2. Materials and methods

A representative sample of the crushed melt containing beryllium and fluorine, 2.90 and 2.85% by weight respectively was used for the present research. Complete elemental composition is given in [3].

The research methodology consisted in leaching crushed melt with 60% H<sub>2</sub>SO<sub>4</sub> at up to 140 °C followed by thermogram analysis up to 900 °C.

To determine the nature of element bonds in the initial melt and silicate-sulfate masses IR research on IR-Fourier spectrometer Nicolet 5700 in the range of 400-4000 cm<sup>-1</sup> wavenumbers was conducted. OMNIC database [4], as well as data from [5] were used to interpret spectra. Thermogravimetric research was carried out on synchronous thermal analyzer «SDT Q600». X-ray diffraction research was conducted on an automatic diffractometer Shimadzu XRD 6000 within scanning range of 10-70°. Mass spectrometer «PROLAB» by «Thermo» was involved for the analysis of gaseous products in the mass range of 1-150 a. m. u., simultaneously the identification of gaseous products was made with the help of mass spectra library NIST 08 [6].

## 3. Results and Discussion

### 3.1 Melt analysis

The preliminary research of the phase composition of the melt showed no diffraction signals, indicating that it is X-ray amorphous [3].

Infrared absorption spectrum showed that concentrate melting followed by water quenching leads to partial destruction of Si-O-Si bonds, as indicated by the shift of the maximum of Si-O bond in a silicon-oxygen tetrahedron towards low frequency range – 948.5 cm<sup>-1</sup>. The absorption bands in the 850-1150 cm<sup>-1</sup> and 600-850 cm<sup>-1</sup> regions indicate the violation of a distant order in the crystalline structure which is typical of amorphous solids. The break of Si-O-Me bonds and the formation of relatively simple silicates occur in a disordered structure. Also aluminates are formed, as evidenced by an intense absorption band at 463.4 cm<sup>-1</sup>, characteristic of the octahedrally coordinated aluminum. At 912.9 cm<sup>-1</sup>, 721.0 cm<sup>-1</sup>, 615.7 cm<sup>-1</sup> and ~ 520 cm<sup>-1</sup> oscillation frequencies of Al-OH appear in the tetrahedrally coordinated anion [Al(OH)<sub>4</sub>]<sup>-</sup> that proves the presence of aluminum in tetrahedral coordination.

A broad peak with a maximum at 3413.8 cm<sup>-1</sup> (valence vibrations of crystallization water in silicates) and 1625.2 cm<sup>-1</sup> (deformation vibrations of OH in H<sub>2</sub>O) indicate that water molecules are linked to the granulate crystal lattice. In the investigated melt spectrum fluorosilicate absorption bands are detected. At 753.3 cm<sup>-1</sup> the band corresponding to valence vibrations of SiF<sub>6</sub><sup>2-</sup> ion is present for calcium fluorosilicate and sodium fluorosilicate. Furthermore, in the 500 cm<sup>-1</sup> region sodium fluorosilicate spectrum reveals a set of bands at 482.4; 492.2; and 523.5 cm<sup>-1</sup> which is observed in the present spectrum. Calcium fluorosilicate spectrum is characterized by the presence of the absorption band at 571.2 cm<sup>-1</sup>.

Thus, X-ray and infrared investigations suggest that the melt is amorphous depolymerized partially hydrated aluminum silicate. The melt contains fluorine mostly in the form of sodium and calcium fluorosilicates.

### 3.2. Interaction of the melt with sulfuric acid solution

Melt samples were mixed with sulfuric acid solution and left at the temperature of 100-120 °C for 2 hours. Interaction of the melt with sulfuric acid solution may lead to the destruction of silicates and aluminates forming soluble sulfates, hydrosulfates and crystalline hydrates. Infrared spectroscopy,

thermal analysis and mass spectrometry were employed to determine the mechanism of the interaction of sulfuric acid solutions with the melt.

The comparison of absorption spectra of the melt and sulfate mass makes it possible to conclude that the interaction between the melt and H<sub>2</sub>SO<sub>4</sub> solution leads to the formation of hydrosulfates, absorption bands of which appear at 1321.4 cm<sup>-1</sup>, 1280.2 cm<sup>-1</sup>, 1225.5 cm<sup>-1</sup>, 1063.4 cm<sup>-1</sup>, 1011.1 cm<sup>-1</sup>, 878.5 cm<sup>-1</sup>, 852.4 cm<sup>-1</sup>.

The absorption band at 1173.8 cm<sup>-1</sup> can refer to the valence vibrations of [HSO<sub>4</sub>]<sup>-</sup> ion, as well as to the deformation vibrations of the SiO<sub>4</sub>-tetrahedron. The absorption bands at 608.2 cm<sup>-1</sup> and 584.6 cm<sup>-1</sup> in the field of deformation vibrations of [HSO<sub>4</sub>]<sup>-</sup> also indicate hydrosulfate formation. Alongside hydrosulfate ion absorption bands, absorption bands are observed at 1121.9 cm<sup>-1</sup> and 1063.4 cm<sup>-1</sup> which are characteristic of fluorosulfonic acid salts. Fluorosulfonic acid formation is possible as a result of the interaction between the formed during sulfatization hydrogen fluoride and excess sulfuric acid as follows:



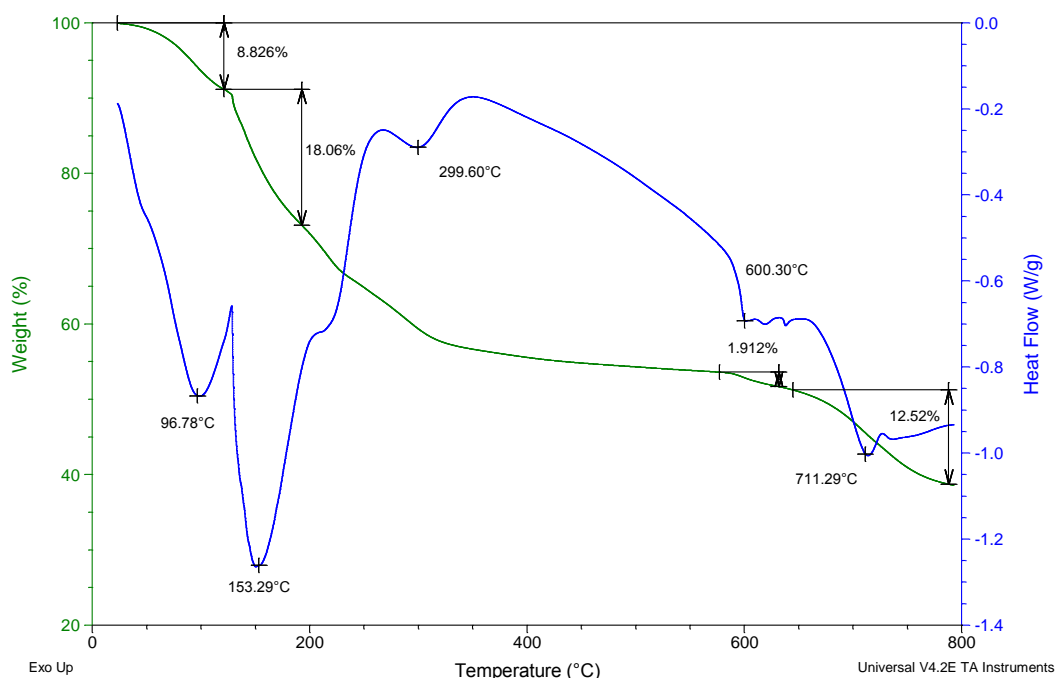
A diffused band in the frequency range of 650-800 cm<sup>-1</sup>, as in case of the melt, reveals the presence of SiF<sub>6</sub><sup>2-</sup>-ion, although it is partially overlapped by S-O deformation vibrations. Thus, the infrared spectra of the fluorosilicates are characterized by the valence vibration absorption band in the 740-750 cm<sup>-1</sup> region. The deformation vibration band at 527.8 cm<sup>-1</sup> points at the presence of sodium fluorosilicate. This band coincides with the deformation vibration of [HSO<sub>4</sub>]<sup>-</sup> for calcium fluorosilicate.

The cleavage of the absorption bands in the region of deformation vibrations of water (1600-1700 cm<sup>-1</sup>) demonstrates the presence of several types of nonequivalent crystallochemical water molecules.

A wide band in the region of 3500-2900 cm<sup>-1</sup> also proves the presence of several crystallization water modes. In the region of valence O-H vibrations the referred modes are difficult to distinguish. It is believed that weakly polarized in the field of cations water usually absorbs in the 3650-3400 cm<sup>-1</sup> region, more strongly polarized, participating in stronger H-bonds, water usually gives broad diffused absorption bands lying below 3400 cm<sup>-1</sup>. In addition, valence O-H oscillation frequencies of water shift to a low frequency oscillation spectrum due to strengthening of H-bonds. In the IR spectrum of sulfate mass two bands at 2483.4 cm<sup>-1</sup> and 2325.1 cm<sup>-1</sup> corresponding to a composite tone δ<sub>H<sub>2</sub>O</sub> + ν<sub>L</sub> (deformation + libration) are observed. Since libration vibrations occur only with the participation of H<sub>2</sub>O molecules in hydrogen bonds, the appearance of composite tone in IR spectrum proves the presence of free unbound water in the substance. The presence of unbound water in the sulfate mass was confirmed by thermal analysis data, represented in Figure 1.

Heating sulfate-silicate mass at 10 °C/min in the atmosphere is accompanied with a series of endothermic processes followed by weight loss. Mass spectra library NIST 08 was employed for the identification of gaseous products; mass spectrum of sulfuric acid decomposition products at atmospheric pressure in the air was determined experimentally and appeared identical to SO<sub>2</sub> spectrum. On the basis of the mass spectra investigated, the identification of water, sulfurous anhydride and silicon tetrafluoride in the reaction products was carried out by the presence of ions with M/Z= 18; 64; 85 in the mass spectra.

The processes with a maximum gas emission rate of 96 °C and 153 °C are caused by the loss of free (96 °C) and bound (153 °C) water, which is confirmed by mass spectrometry analysis. The content of free (unbound) water is about 9%, and the hydrated crystalline water content is 18% of the sample weight.



**Figure 1.** Sulfate-silicate mass thermogram at the rate of 1.6 g of 60% sulfuric acid per 1 g of melt

The endothermic process occurring in the temperature interval of 600-800 °C with 12.5% weight loss and the evolution of gaseous  $\text{SO}_3$  indicate decomposition of sulfates. According to the gas phase analysis, an endothermic process with 1.9% mass loss in the temperature range of 580-650 °C is followed by  $\text{SiF}_4$  evolution. This confirms the IR analysis data of the presence of fluorosilicates in the sulfate-silicate mass composition. According to mass spectrometry analysis, in the interval of 200-300 °C the occurring in the system process is accompanied with a simultaneous release of water,  $\text{SiF}_4$  and  $\text{SO}_3$ .

The IR spectrum of the sulfate-silicate mass calcinated at 300 °C revealed that the absorption band of sodium (calcium) fluorosilicates disappears in the interval of  $740\text{-}750\text{ cm}^{-1}$  as a result of thermal treatment at 300 °C. The reduction of the absorption band at  $\sim 3400\text{ cm}^{-1}$  indicates the removal of crystallization water weakly bound with crystal lattice. The dehydration of hydrosulfate leads to a peak at  $1024.3\text{ cm}^{-1}$ , associated with valence vibrations of a sulfate anion. Both the peak at  $674.5\text{ cm}^{-1}$ , characteristic of Si-O-Mg(Na) bonds, and a diffused absorption band at  $792.9\text{ cm}^{-1}$ , characteristic of Si-O-Si bridging bonds, are observed.

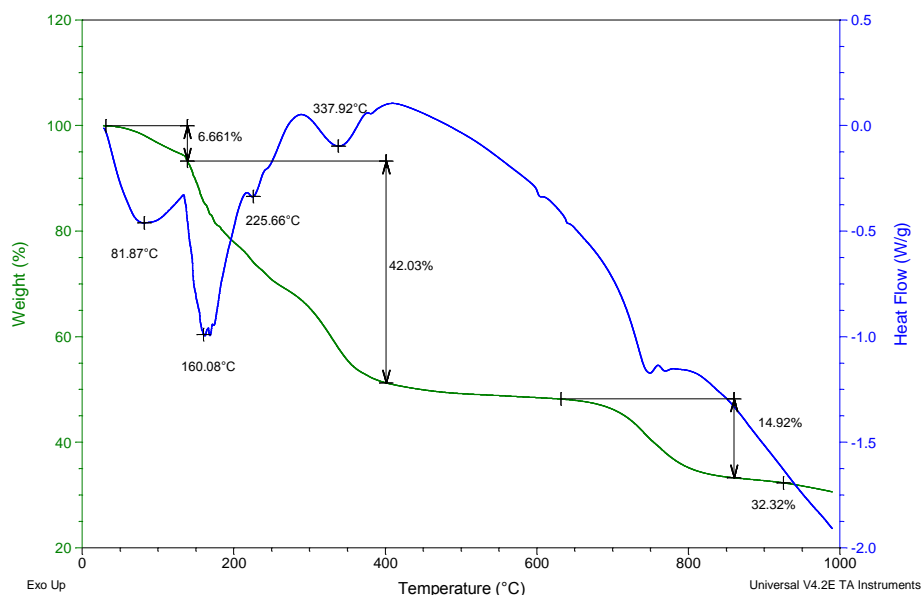
Thermal analysis and IR spectroscopy results demonstrate that the process occurring in the system in the range of 200-300 °C is determined by the interaction between melt sulphatization products according to the reaction scheme:



Thereby, sulfate-silicate mass examination revealed that the main reaction products of the melt and sulfuric acid solution interaction are crystalline hydrates of calcium and sodium hydrosulfates with a portion of water remaining in the unbound state. In the reaction products fluorine is represented in the form of fluorosilicates and fluorosulfonic acid salts.

Further investigation was focused on the study of the characteristics of sulfuric decomposition of fluorosilicates. For this purpose, the influence of sulfuric acid amount on the process of granulate

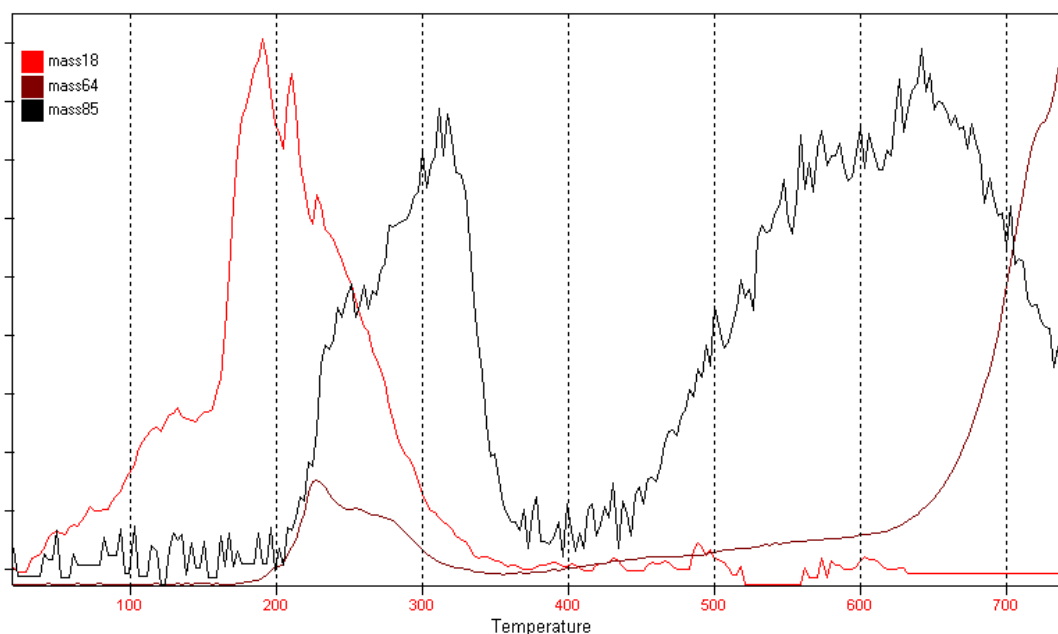
desulfurization was studied. Leaching was done with 60% sulfuric acid solution. The amount of sulfuric acid solution was varied in the interval of 1.35 – 3.24 g per 1 g of the melt. Typical thermogram of the obtained sulfate-silicate masses is represented in Figure 2.



**Figure 2.** Sulfate-silicate mass thermogram at the rate of 3.24 g of 60% sulfuric acid per 1 g of melt.

It was established that the increase in the amount of sulfuric acid solution does not cause any significant change to the amount of free unbound water and sulfates. The reduction of the residue after calcination is determined by significant differences in the processes in the range of 100-400 °C indicating the formation of chemical compounds with decomposition temperature from 100 to 400 °C. In this area of the thermograms 3 occurring processes can be allocated, the speed peaks of which are observed at 150-160 °C, 215-240 °C and 300-330 °C. Increasing the amount of acid has a positive effect on the process that takes place in the range of 300-400 °C, it inhibits the process in the range of 200-300 °C and does not affect the process in the range of 130-200 °C.

Mass spectrometry analysis of gaseous reaction products was carried out to identify separate stages. Typical mass-spectrum of gaseous products is shown in Figure 3. It was depicted above that the process occurring in the interval of 200-300 °C is caused by the interaction between sodium and calcium fluorosilicates and sulfuric acid followed by sodium hydrosulfate decomposition. The product of the process occurring in the range of 300-400 °C is  $\text{SiF}_4$ .  $\text{SO}_3$  and water are not available, what indicates the occurrence of thermal dissociation of calcium fluorosilicate. In the region of about 600 °C thermal dissociation of sodium hexafluorosilicate  $\text{Na}_2\text{SiF}_6$  proceeds and at temperatures above 700 °C the decomposition of sulfates occurs.



**Figure 3.** Formation of gaseous products after thermal treatment of sulfate-silicate masses in the course of granulate leaching with 60% sulfuric acid solution at the rate of 3.24 g per 1 g of the melt

Generally sulfate-silicate mass defluorination is possible by thermal dissociation of fluorosilicates at temperatures of 550-650 °C, or by acid leaching of fluorosilicates at 200-300 °C. Defluorination by thermal dissociation can destroy soluble beryllium compounds, resulting in a significant loss of beryllium at the subsequent leaching step. Therefore, acid leaching of sodium and calcium fluorosilicates with concentrated sulfuric acid at 200-300 °C is preferred.

#### 4. Conclusion

X-ray diffraction, infrared spectroscopy, thermogravimetry and mass spectrometry were employed to study the behavior and distribution of fluorine in sulfuric acid treatment of the melt of beryl-bertrandite-phenakite-fluorite concentrates with alkali fluxes. It was established that fluorine in a solid phase is predominantly present in the form of sodium and calcium fluorosilicates, and in a gaseous phase it is evolved in the form of silicon tetrafluoride and fluorosulfonic acid. The preferred method of defluorination is acid decomposition of sodium and calcium fluorosilicates with concentrated sulfuric acid at 200-300 °C. The obtained results are the basis for detailed kinetic studies to determine the optimal technological conditions for fluorine removal process.

#### References

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