

The study of the process of alkaline precipitation purification of solutions from silicon macroscales in the ammonium-fluoride processing of beryllium-containing materials

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Abstract. The ammonium-fluoride method of beryllium materials processing is examined. An analysis of the existing sulfuric-acid and fluoride processing scheme of beryllium-containing concentrates processing is described; advantages of the proposed ammonium-fluoride scheme and possible problems that may occur when testing a new technique are discussed. Studies on determining the effect of silicon macroscales on the behavior of beryllium in fluoride solutions at an increased pH, as well as on establishing the distribution of beryllium and silicon by phases in laboratory testing of the technology on model mixtures, are described. As a result of the studies, it is found that precipitation purification of solutions from silicon with a solution of ammonia is possible at a temperature of 20-25 °C. The paper presents data on the effect of an excessive concentration of ion-fluoride in a solution on the pH level of silicon precipitation; and on the hydrolysis degree of beryllium and silicon during the precipitation.

1 Introduction

Beryllium in nature mainly represented about 30 minerals, the most important of them are: beryl, chrysoberyl, behoit, bertrandite, phenacite [1-3]. The volume of metallic beryllium production amounts to nearly 300 tons/year. The main source of beryllium is a bertrandite-phenacite concentrate which is produced using methods of flotation from the beryllium-fluorite-containing ore; the concentrate from the Ermakovskiy deposit, which has been used for following researches, contains up to 4 % of beryllium (Table 1) [4].

Table 1. Chemical composition of phenacite concentrate

Substance	Be	SiO ₂	CaF ₂	F	Al ₂ O ₃ ; Fe ₂ O ₃ ; CaO
Content, %	4	29	20	5	40

To date, two ways of hydrometallurgical processing of beryllium concentrates have been designed and developed: sulfuric-acid and fluoride (Table 2) [2].

Table 2. Description of existing methods of hydrometallurgical processing of beryllium concentrates

Parameters	Processing method	
	Sulfuric-acid	Fluoride
1	2	3
Basic reagents	93% sulfuric acid, water, ammonium sulphate, caustic soda, EDTA, ammonium bifluoride solution	Sodium hexafluorosilicate, soda ash, caustic soda, iron sulfate (III), water, ammonium bifluoride
Stages	Melting in an arc furnace, thermal activation of the concentrate, sulfuric-acid interaction, water leaching of beryllium, purification from Al and Fe, formation and hydrolysis of sodium beryllate, production of beryllium hydroxide	Mixing of reagents, briquetting, sintering, water leaching, alkaline precipitation, production of beryllium hydroxide
Process conditions	Melting point of the concentrate in an arc furnace – 1700 °C, heat treatment – 900-950 °C, sulfation – 200 °C; Process duration – 20 hours.	Sintering temperature – 750 °C; Process duration – 32 hours.
Energy intensity	High-energy	High-energy
Environmental risks	High Utilization of volatile fluorides (SiF ₄ , HF), utilization of ferrous sulphate solutions	High Potential emissions of beryllium compounds during crushing and grinding
Possibility of reagent regeneration	Absent	Partially in the form of (NH ₄) ₂ FeF ₆
The volume of the liquid phase in the process	High	Average
Beryllium recovery, %	80	70
Commercial products	Beryllium metal, plaster	Beryllium metal

Disadvantages of the sulfuric-acid method: huge water consumption; multistage processing; necessity in high-temperature two-stage activation of concentrates; large amount of impurities passes into the target solution in the form of sulphates; necessity to produce intermediate highly-toxic beryllium compounds (Be(OH)₂).

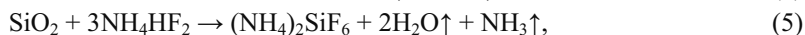
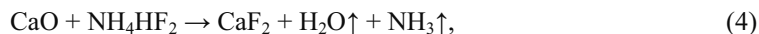
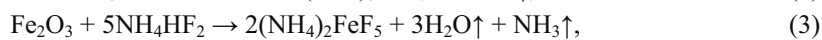
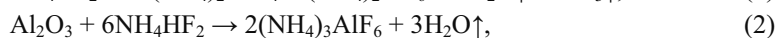
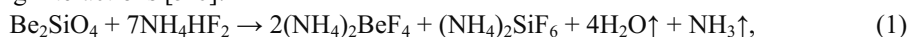
As compared to the sulfuric-acid scheme, the fluoride processing does not include high-temperature, energy-intensive stages of concentrate activation, and there is a possibility to

regenerate the fluorinating reagent in the form of ferrous cryolite (Na_3FeF_6) evolved from mother solutions of sodium fluoride which remained after separation of the amorphous $\text{Be}(\text{OH})_2$. Disadvantages of the fluoride method: multistaging of the hydrometallurgical process, costly leaching reagent – Na_2SiF_6 , high consumption of sodium hexafluorosilicate as a result of its intensive decomposition and volatilization of the produced SiF_4 from the reaction zone, necessity in a high-temperature stage of concentrate fluorination, necessity to produce highly toxic beryllium compounds – $\text{Be}(\text{OH})_2$.

Today, only the sulfuric-acid method is commonly used in processing of concentrates, because it is more economically viable, environmentally sound, and allows producing a cleaner beryllium hydroxide.

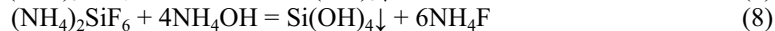
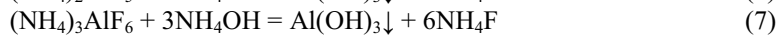
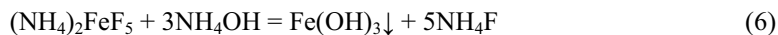
2 Theory section

In order to improve the profitability and to reduce the risks at production of beryllium metal, a method of ammonium-fluoride processing of beryllium concentrates is being developed. The method is based on the interaction of the concentrate components with ammonium bifluoride (NH_4HF_2) at 210 °C, omitting stages of concentrate activation. The main component of the ore concentrate from the Ermakovskiy deposit is fluorite – CaF_2 , which does not react with ammonium bifluoride and is separated at the filtration stage after water leaching of the sinter. The remaining components of the concentrate come into the following interactions [5-6]:



With further aqueous leaching of the sinter the following compounds go into the solution: beryllium, silicon, partially iron and aluminum, excessive ammonium bifluoride. Fluorides of calcium, partially of aluminum and iron, remain in the insoluble precipitate.

The next stage of the process is the alkaline precipitation purification of the beryllium solution from impurities. Beryllium remains in the solution in the form of BeF_4^{2-} - ion, and impurities (the main impurity is silicon) precipitate as a result of hydrolysis under the following reactions:



The purified solution $(\text{NH}_4)_2\text{BeF}_4$, omitting the stage of production of highly toxic $\text{Be}(\text{OH})_2$, goes to crystallization. The formed crystals of ammonium fluoroberyllate are subjected to thermal decomposition to produce BeF_2 [5].

The aim of this research was the study the influence of silicon macroscales on the behavior of beryllium in fluoride solutions at an increased pH, as well as the establishment of the distribution of beryllium and silicon by phases in laboratory testing of the described ammonium-fluoride technology on model mixtures.

3 Material and methods

The prepared model mixture, consisting of BeO and SiO₂, was combined with ammonium bifluoride taken with a 50 % excess relative to the stoichiometric amount. The load was placed into a laboratory shaft furnace, where the fluorination process of the model mixture took place during 1 hour at a temperature of 210 °C. The produced sinter was crushed and dissolved in 200 ml of water. The sinter dissolved completely. The pH level of the solution was equal to 3. A complete dissolution of the fluorinated product demonstrates the importance of the fluorination degree approximately equal to 100%.

Precipitation was carried out with an ammonia solution at room temperature; the pH value was gradually increased until a white precipitate. The pulp was settled at each pH unit for 1 hour. Precipitation was observed during the transition of pH level from 7 to 8. The produced pulp was filtered, and the clarified solution was brought up to pH = 9, the precipitate no longer formed. The precipitate after the filtration was pulped in 100 ml of water; the formed on the filter cake was washed with another 100 ml of water. The washed precipitate was removed together with the filter and transferred to a platinum cup. The precipitate was dried at 150 °C for 2 hours, then calcined at 700 °C.

Crystallization of (NH₄)₂BeF₄ from the filtrate was carried out until a gelatinous mass was obtained. Then, amorphous crystals were dried for 3 hours without heating using an air extraction system. Thermal decomposition of (NH₄)₂BeF₄ was carried out at 500 °C in a platinum cup.

The elemental analysis of liquid and solid samples was carried out using an atomic-emission spectrometer with an inductive coupled plasma iCAP 6300 Duo. To dissolve solid samples, the microwave system MARS 6 was used. A scandium solution with a concentration of 100 ppm was used as an internal standard. To calibrate the method, state standard reference samples (GSO) were used: for silicon – GSO 8934-2008, beryllium – GSO 7759-2000. In sample preparation the following acids were used: hydrochloric (GOST 14261-77), nitric (GOST 4461-77), and hydrofluoric (TU 2612-007-56853252-2010). The analysis was carried out under the following lines: for beryllium – 234.8; 249.4; 265.0 nm; silicon – 198.8; 251.6; 288.1 nm.

4 Results and discussion

As a result of the precipitation purification of beryllium fluoride solutions from silicon macrosales, more than 21 % of beryllium removes together with a gelatinous precipitate of polysilicon acids. But, during washing of the produced cake with ordinary distilled water it is possible to recover 18.5% of beryllium into the solution, which indicates the absence of a large-scale hydrolysis of BeF₄²⁻ - ion at pH equal to 9 and a ratio of a free fluoride-ion to beryllium equal to Be:F = 1:6. Fluoroberyllate ion in the basic amount is drawn into a jelly-like precipitate together with moisture; as a result of alkali hydrolysis 2.7 % of beryllium is precipitated.

Approximately 2 % of silicon remains in the clarified solution at a pH level equal to 9.

An incomplete removal of silicon, as well as a very high pH of silicon hydrolysis (pH = 7), is associated with a large excess of fluoride-ion present in the solution. Part of silicon can be removed in the form of (NH₄)₂SiF₆ at the stage of thermal decomposition of (NH₄)₂BeF₄ (Fig. 1).

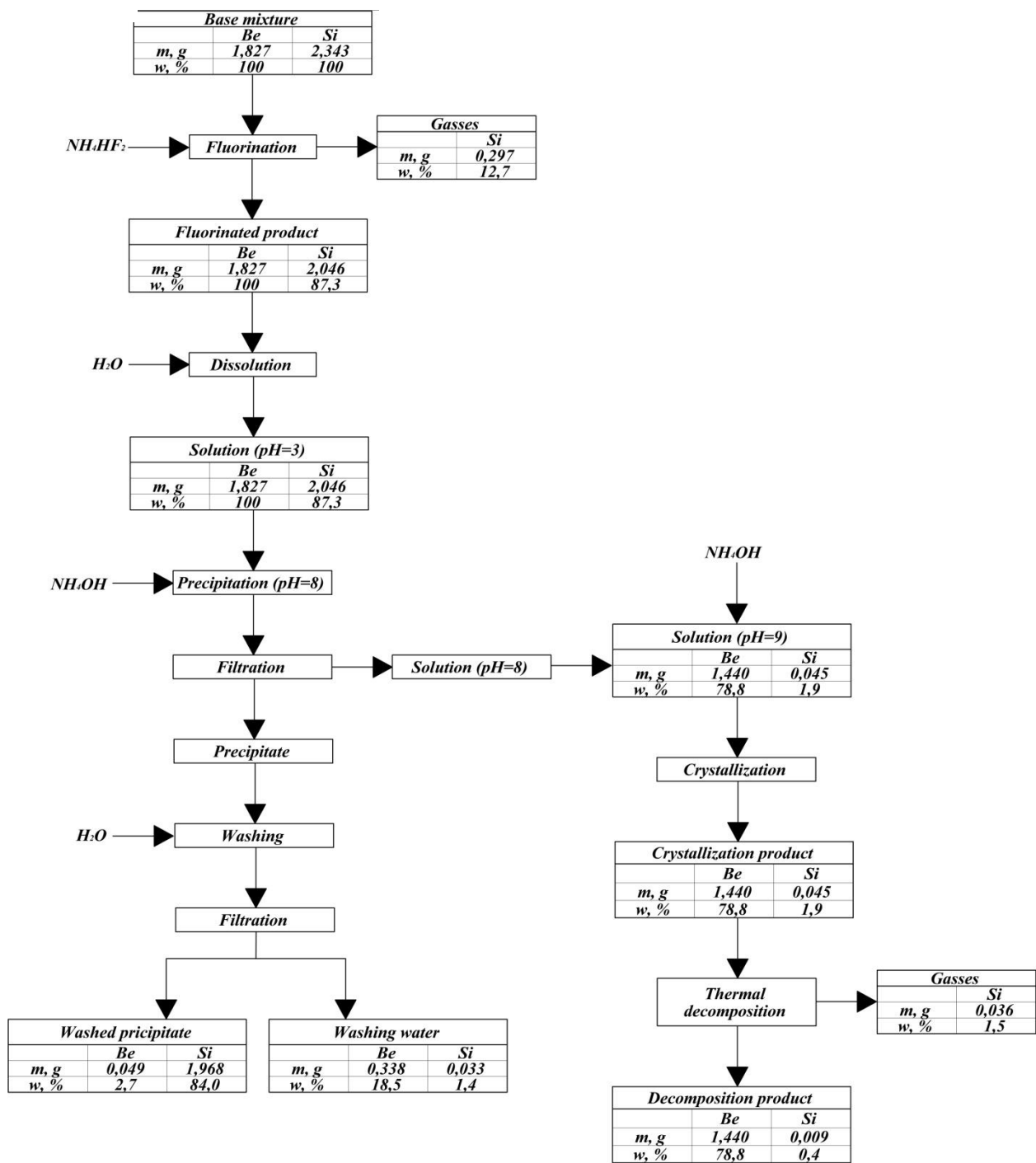


Figure 1. Distribution of beryllium and silicon by phases

5 Conclusion

1. Precipitation purification of beryllium fluoride solutions from silicon macroscales is feasible at room temperature (20-25 °C) and at a ratio Be:F = 1:6.
2. Co-precipitation of beryllium and silicon was not established. Approximately 18.5 % of beryllium removes together with the precipitate of polysilicic acids in the composition of the adsorbed by the cake moisture. During the purification 2.7 % of beryllium hydrolyzes and precipitates in the form of $\text{Be}(\text{OH})_2$.
3. Due to a significant amount of fluoride-ion present in the productive solutions, the pH of hydrolysis SiF_6^{2-} - ion increases up to 7.
4. It was impossible to completely remove silicon at the stage of precipitation purification: 1.9 % of silicon remains in the solution of ammonium fluoroberyllate. It is possible to remove the remaining portion of silicon at the stage of thermal decomposition in the form of $(\text{NH}_4)_2\text{SiF}_6$.
5. The purity of beryllium fluoride produced during the study was 99.7 %. The amount of SiO_2 in the product was 0.3 %.

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