KAUNAS UNIVERSITY OF TECHNOLOGY

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INNOVATIVE REPROCESSING TECHNOLOGIES OF SILICA GEL WITH INCORPORATED ALUMINUM AND FLUORINE IONS

Doctoral dissertation
Technological Sciences, Chemical Engineering (T 005)

2020, Kaunas

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KAUNO TECHNOLOGIJOS UNIVERSITETAS

VALDAS RUDELIS

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1. INTRODUCTION

Relevance of the work

Waste management and the reduction of pollution are the priority areas of environmental protection in the Republic of Lithuania and the European Union. These areas are regulated by Law, and their importance is outlined in the *Environmental Strategy* and the *EU Waste Statistics Action Plan* (EU Implementation of the Circular Economy Action Plan; Eurostat Waste Statistics) (1, 2). According to the data of Eurostat, the European Union generates more than 184 million tons of manufacturing waste every year, while it reaches ~2.6 million tons in Lithuania (2). From the economic point of view, it is preferable to store waste in landfill sites, but they occupy large areas and are rendered into concentrated sources of air, groundwater and soil pollution (3). Therefore, the search for attractive industrial waste recycling treatment, which will allow developing products of high value, is fundamentally important (1–3).

Global production of aluminum fluoride (AlF_3) reaches 1 million tons per year, while the amount of the generated hazardous waste is more than 3 million tons (4, 5). It is worth noting that more than 60% of this waste is contaminated with fluorine ions whose concentrations can reach up to 10%. The amount of waste and its toxicity depends on the selected production method: dry fluorite (calcium fluoride, CaF_2) or from hexafluorosilicic acid (6, 7). Aluminum fluoride is mainly produced (~60%) by applying the dry fluorite method from calcium fluoride, aluminum hydroxide and sulfuric acid (7). The production process consists of the production of hydrogen fluoride gas from fluorite and the neutralization reaction between the latter acid and aluminum hydroxide. This method of production of AlF_3 requires costly natural raw materials and energy resources, i.e., the preparation of 1 metric ton of AlF_3 consumes ~4.4 metric tons of feedstock and ~1.5 MWh (~5 MJ) of energy (5–7). For this reason, due to the rising fluorite (~2-fold increase in the recent years) and energy prices, this method is becoming economically unattractive (8, 9). Besides, the dry production method also generates huge amounts of waste, i.e., the production of 1 metric ton of AlF_3 produces ~3.3 tons of waste. Most of it (~2.7 tons) is composed of gypsum contaminated with sulfuric acid and fluorine ions (6, 7). Often, this waste is transported to a landfill site without any further treatment or neutralization. It should be noted that the use of calcium sulphate is limited by the formation of sulfuric acid and fluorine ion residues.

Therefore, alternative cheaper raw materials and more profitable production technologies, such as the treatment of hexafluorosilicic acid, are becoming increasingly attractive (10–12). It is estimated that around 20% of global production of AlF_3 is obtained in this way. According to various literature sources, up to 3 million metric tons of hexafluorosilicic acid is produced annually in the world (13–15). Although this acid is a concentrated source of fluorine ions, most of it is stored in landfill sites, and only 0.5 million metric tons is used for fluoridation of drinking water (heavy metals or other impurities have to be removed), silicate synthesis, and the production of aluminum fluoride. Most of this acid (~0.2 million metric tons) is used in the above outlined process.

Currently, two major technologies for the production of AlF_3 from hexafluorosilicic acid are applied (6, 16, 17). The first technology is based on the conversion of hexafluorosilicic acid into hydrogen fluoride, which is further used to produce AlF_3. The production of hydrogen fluoride from hexafluorosilicic acid is a complex process involving many stages and specific aggregates. Besides, 1 metric ton of anhydrous hydrogen fluoride produces up to 30 metric tons of pure sulfuric acid, which is difficult to recycle. Also, the production of 1 metric ton of HF produces about 0.55 metric tons of silica gel contaminated with fluorine ions. Therefore, the most widely used aluminum fluoride preparation method is based on direct neutralization of hexafluorosilicic acid with aluminum hydroxide (the wet process) (16, 17). According to the literature, more than 17% of aluminum fluoride in the world is prepared by this process. The production of 1 metric ton of aluminum fluoride consumes about 1.2 tons of hexafluorosilicic acid and ~1 metric ton of aluminum hydroxide. The total amount of raw materials used to prepare 1 metric ton of the product by the wet process is lower than that required for the dry method. However, during acid neutralization, about 0.67 metric tons of silica gel contaminated with fluoride ions is generated and stored in landfill sites. The total amount of waste produced per 1 metric ton of aluminum fluoride ranges from 1 to 1.3 tons, which is about 3 times lower in comparison to the dry method.

In addition, with the development and application of innovative technologies, the amount of waste from 1 metric ton of aluminum fluoride, during the wet process can be reduced to 0.3 metric tons by (6, 15–17):

- using filter and absorption systems which can reduce fluorine emissions to air up to 0.015 kg per 1 metric ton of AlF_3;
- treating aqueous waste flows with lime, which can minimize fluoride emissions to water up to 0.1 kg per 1 metric ton of AlF_3;
- using leaching and other treatment technologies, which will reduce the fluorine content in silica gel to acceptable levels (GOST 3956-76).

It should be indicated that, due to dissociation, solubility, W/S ratio and SiO_2 adsorption properties, the reduction of fluorine ion concentration in silica gel is a complex technological problem.

The aim of this work is to determine the influence of the peculiarities of AlF_3 production process on the chemical and mineral composition of silica gel waste and its properties.

In order to achieve the aim of the work, the following goals had to be completed:

1. To examine the effect of the calcination temperature to 1000 °C on the composition and properties of contaminated silica gel samples.
2. To investigate the influence of static and dynamic treatment as well as the mechanical activation conditions and the addition of alkaline compounds on the chemical and mineral composition of contaminated silica gel samples.
3. To determine the stability temperature intervals and properties of treated contaminated silica gel samples which show the best results.
4. To apply the optimum treatment conditions of silica gel in the industrial production line of aluminum fluoride.

Scientific novelty of the dissertation

It was proven that it is possible to reduce the concentration of fluorine ions to 1.5% by changing the treatment conditions (leaching under static and dynamic conditions or mechanical activation), and by adding alkaline compounds (NH_4OH, $Ca(OH)_2$, NaOH, Al_2O_3). For the first time, it was determined that the compounds containing aluminum and fluorine ions, such as aluminum fluoride, calcium fluoride and/or katoite, are crystallized in the liquid medium which was separated from silica gel by using mechanical treatment or by leaching with alkaline solutions.

Practical significance of the dissertation

Fluorine ions removal technology was proposed; it not only allowed reducing the concentration of fluoride ions in silica gel to 1.5%, but also increased the yield of aluminum fluoride. Based on the results of the work, additional equipment was installed, and industrial tests were carried out in the AlF_3 production line of Lifosa, JSC.

Approval and publication of research results

The results of the research have been presented in 6 publications: 2 papers were included into the *Clarivate Analytics Web of Science* database and 4 were reported at international conferences.

Structure and contents of the dissertation

The dissertation consists of the introduction, literature review, experimental part, results and discussion, conclusions, list of references and publications on the dissertation topic and appendixes. The list of references includes 89 bibliographic sources. The main results are discussed on 107 pages and illustrated in 40 tables and 57 figures.

Statements presented for the defence

Contaminated silica gel waste is a mesoporous material whose structure and the values of the specific surface area change during calcination.

The most effective method for the removal of fluoride ions from the structure of AlF_3 production waste – silica gel – are the treatment of silica gel samples with ammonium water under static conditions.

2. EXPERIMENTAL PART

Raw materials

Silica gel waste (SGW), i.e., a waste product of AlF_3 production in the chemical plant of JSC "Lifosa" (Kėdainiai, Lithuania) which was dried for 48 hours at 50 °C.

Comparative substance, whose properties correspond to the requirements of GOST 3956-76. Dried for 48 hours at 50 °C, $S_a = 456$ m^2/kg.

Aluminum hydroxide (*Honeywell*, Germany) – purity >99%.

Calcium hydroxide (*Stanchem Sp. J.*, Poland) – purity >97%.

KOH (*Reachem*, Slovakia) purity >99%.

NaOH (*Reachem*, Slovakia) purity >99%.

NH_4OH (*Lachema*, Czech Republic) and JSC Lifosa.

$(NH_4)_2CO_3$ (*Reachem*, Slovakia). NH_3 – 30–34%.

NaF (*Lachema*, Czech Republic) purity >99%.

Na_2CO_3 (*Reachem*, Slovakia) purity >99%.

K_2CO_3 (*Reachem*, Slovakia) purity >99%.

NaX zeolite (*Reaktiv*, Russia).

Limestone (*Naujasis kalcitas*, Lithuania) dried for 24 h at 100±2 °C temperature, crushed with a jaw crusher (*Fritsch 01.5030*, Germany). $1<x<1.2$ mm fraction was used for the experiments. The chemical composition of limestone is presented in Table 1, while the properties of calcined (900 °C) limestone were determined according to Standard LST EN 459-1:2010 in Table 2.

Table 1. Concentration of major oxides in limestone as determined by XRF

Concentration, %						Loss on ignition, %
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3^{2-}	
50.88	4.38	0.22	0.70	1.67	0.53	41.62

Table 2. The properties of calcined limestone

Parameter	Value
Quantity of free CaO + MgO, %	84.3
Quantity of total CaO + MgO, %	90.3
Quantity of free CaO, %	81.6
MgO, %	2.52
CO_2, %	2.65
SO_3, %	0.48
Loss on ignition, %	3.16
Duration of extinction, min	3.5
Temperature of extinction, °C	86

Opoka (Stoniškių–Žemaitkiemio Quarry, Lithuania) was dried for 24 h at 100±2 °C temperature, and crushed with a jaw crusher (*Fritsch 01.5030*, Germany). 1<x<1.2 mm fraction was used for the experiments. The chemical composition of opoka is presented in Table 3.

Table 3. Concentration of major oxides in opoka as determined by XRF

Concentration, %							Loss on ignition, %
CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	K_2O	SO_3^{2-}	
22.64	52.56	2.42	0.78	0.61	0.62	0.45	18.97

Other chemical reagents (acetone, HCl, $AgNO_3$, NH_4Cl, AgCl, HNO_3)

Methodology

The chemical analysis of the silica gel waste was carried out according to the methodology developed by Alekin (18).

The concentration of fluoride ions in the solution was measured by using a *Mettler Toledo T70* potentiometer. The error of the selective electrode for F^- ions is <1ppm (0.0001%). The concentration of F^- was calculated as the arithmetic mean of the 3 individual results. The measurement deviations were below 3%.

The leaching of F^- ions from silica gel waste to the liquid medium was done by applying various techniques:

1) leaching of F^- ions under static conditions; in order to reach the water-to-solid (w/s) ratios of 2–100, 10 g of silica gel waste was mixed with distilled water and kept for 24 h at 25 °C and 55 °C temperatures. After leaching, the suspensions were filtered off, the products were dried at 50 °C ± 5 °C temperature for 24 h.

2) leaching of F^- ions under dynamic conditions by using the continuous distilled water *(25 °C, by applying vacuum 0.6–0.7 bar*) flow which was applied on 10 g of silica gel waste till the water-to-solid (w/s) ratio reached the value of 20–200. After the process, the products were dried at 50 °C ± 5 °C temperature for 24 h.

3) F^- ions leaching in cycles under dynamic conditions. A total count of 20 cycles were carried out during this experiment, in which, the total amount of 10 g of SGW was treated with 50 ml of distilled water in each step till the w/s ratio reached 100. Water of various temperatures was used (25, 35, 45 and 55 °C) for this experiment. After each cycle, the obtained products were filtered off and dried (50 °C ± 5 °C; 24 h) at the end of the process.

Treatment under hydrothermal conditions was performed in the mixtures with molar ratio of C/S (CaO/SiO_2) equal to 0.55, 0.66, 0.83, 1.0, 1.75, 2.0 and 2.5. The hydrothermal treatment was carried out in unstirred suspensions under saturated steam pressure at 200 °C temperature for 16 hours by applying extra argon gas (10 bar). After the experiment, the autoclave was quenched to room temperature. The suspensions were filtered, the products were rinsed with acetone, dried at 50 ºC ± 5 °C temperature for 24 h, and sieved through a sieve with a size width of 80 µm.

X-ray diffraction analysis (XRD) was performed on a D8 Advance diffractometer (*Bruker AXS*, Karlsruhe, Germany) operating at the tube voltage of 40 kV and tube current of 40 mA. The X-ray beam was filtered with Ni 0.02 mm filter to select the CuKα wavelength. The diffraction patterns were recorded in a Bragg-Brentano geometry by using a fast counting detector *Bruker LynxEye* based on the silicon strip technology. The samples were scanned over the range $2\theta = 3–70°$ at a scanning speed of $6° \text{ min}^{-1}$ by using a coupled two theta/theta scan type

The quantitative chemical composition analysis of the samples was performed by X-ray fluorescence spectroscopy (XRF) on a *Bruker X-ray S8 Tiger WD* spectrometer equipped with an Rh tube with the energy of up to 60 keV. Powder samples were measured in the Helium atmosphere, and the data was analyzed with *SPECTRAPlus QUANT EXPRESS* standard less software.

The measurements of the thermal stability and phase transformation were prepared with a *Netzcsh Polyma DSC 214* instrument (*Netzsch*, Germany): at a heating rate of 10 °C/min, the temperature ranged from 30 °C up to 600 °C under nitrogen atmosphere. Ceramic sample handlers and aluminum crucibles were used.

The particle size distribution was measured by using a CILAS 1090 LD grain-size analyzer which has a sensitivity range from 0.04 to 500 µm. The particles were dispersed by ultrasound for 2 min while the obscuration of particles in water reached 14%. The ultrasound duration during the measurement was 70 s. The standard operating procedure in use was the Fraunhöfer method.

The density of the samples was measured by using a *Quantachrome Ultrapyc 1200e* gas pycnometer under helium atmosphere; the number of measurements was 5; the accuracy was 0.1 kg/m^3.

The values of pH were measured with a *Hanna* instrument (Hi 9321, microprocessor pH meter, *Hanna Instruments*, Woonsocket, RI, USA). The measurements of the values of pH were repeated three times, and the deviations were below 2%.

Scanning electron microscopy (SEM) was performed by using a *JEOL JSM-7600F* (Japan) instrument at an accelerating voltage of 10 kV, at a working distance of 8.6 mm.

The surface area of the samples was measured with a BET surface area analyzer (Nitrogen adsorption porosimeter) *Nova 1200 E-Series* (*Quantachrome Instruments*, USA). Prior to nitrogen adsorption analysis, the samples were degassed under vacuum at 100 °C temperature. The specific surface area of the samples was calculated with the BET equation by using the data of the lower part of the N_2 adsorption isotherm ($0.05 < P/P_0 < 0.35$).

The total pore volume and the pore size distribution were calculated according to the corrected Kelvin equation and the scheme developed by Orr *et al.* by using the entire N_2 desorption isotherm at 77 K.

3. RESULTS AND DISCUSSION

3.1. Properties of silica gel waste

The chemical analysis data showed that dried (50 °C, 48 h) SGW consists of 79.01% of SiO_2 and 10.03% of F^- ions (Fig. 1 a). Yet, almost the same tendency was observed by applying XRF: it was determined that SGW contains 36.2% of silica, which is equivalent to 78.9% of SiO_2 (Fig. 1, a). Moreover, 2.48% of Al^{3+} ions and traces of other elements are also present in the above mentioned compound. These results were in good agreement with the data of XRD analysis. $AlF_3{\cdot}3H_2O$ and amorphous silicon dioxide, which corresponds to a broad basal reflection in the 18–37° diffraction angle range, were observed in the XRD pattern of SGW (Fig. 1, b).

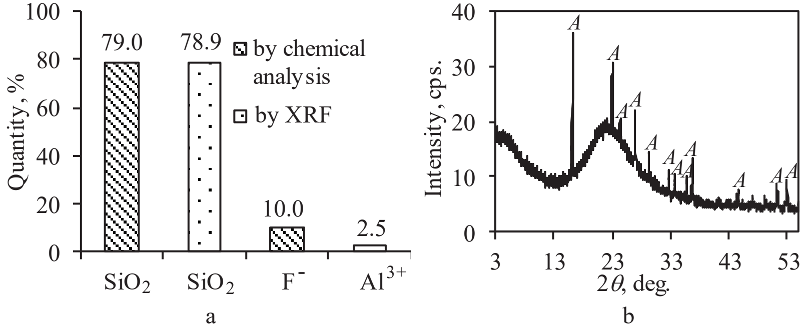


Fig. 1. Chemical composition (a) and the XRD pattern (b) of dried silica gel waste. Indexes: A – $AlF_3{\cdot}3H_2O$

The results of the particle size distribution analysis showed that the diameter of SGW particles varied within the 0.03–170 µm range, while the particles with a size of 34–72 µm were dominant. It was also determined that the surface area and the density of silica gel waste were equal to 281.01 m^2/kg and 2141 kg/m^3, respectively.

The results of chemical composition were proved by the data of differential scanning calorimetry. In the DSC curve, two-step decomposition of $AlF_3{\cdot}3H_2O$ was observed at 146 °C and 165 °C temperatures, in which, the quantity of the heat flow was equal to: 2.78 J/g – for $AlF_3{\cdot}3H_2O \rightarrow AlF_3{\cdot}0.5H_2O + 2.5H_2O$ and 33.62 J/g – for $AlF_3{\cdot}0.5H_2O \rightarrow AlF_3 + 0.5H_2O$, respectively (Fig. 2, a). Meanwhile, the third endothermic effect, which is assigned to dehydration of silica gel ($SiO_2{\cdot}nH_2O \rightarrow SiO_2 + nH_2O$), was observed at 188 °C

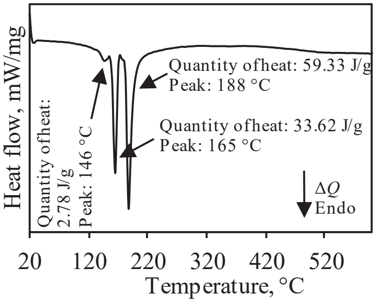


Fig. 2. DSC curve of dried silica gel waste

In order to fully understand the thermal behavior of SGW, the calcination of this compound was carried out within the 50–1000 °C temperature range (Fig. 3). Although the typical diffraction maximums characteristic to $AlF_3·3H_2O$ slightly decreased with the increasing temperature, it remained stable till 165 °C and fully decomposed at 188 °C (Fig. 3). In a higher temperature range (188–550 °C), a low-intensity peak (*d*-spacing of 0.355 nm) at ~25° diffraction angle was detected and could be assigned to other anhydrous aluminum fluoride phases. Besides, when the temperature of calcination was increased to 1000 °C, due to the reaction between aluminum containing components and SiO_2, mullite was formed in the calcination products (Fig. 3). It is worth mentioning that F^- ions are strongly bound in the structure of silica gel waste because the performed chemical analysis data of calcined SGW (188 and 550 °C) showed that the quantity of fluoride ions in solid is equal to ~9.8%.

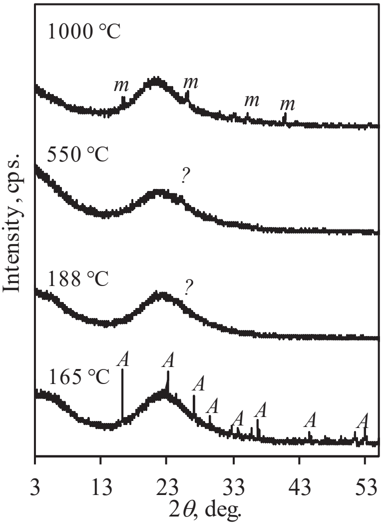


Fig. 3. XRD patterns of calcined silica gel waste samples at various temperatures. Indexes: A – $AlF_3·3H_2O$, m – mullite.

3.2. Effect of the calcination temperature on the porosity of silica gel waste

The N_2 adsorption/desorption isotherm of the calcined SGW samples is presented in Figure 4. According to IUPAC classification, the adsorption isotherm corresponds to Type IV which occurs in mesoporous materials (pore diameter 2–50 nm) when capillary condensation or pore filling occurs. In addition, the hysteresis loop can be classified as Type H3, which means that samples have slit-shaped (parallel plates) pores or disordered aggregates of plate-like particles. Meanwhile, the rapidly increasing adsorption isotherm above $P/P_0 = 0.9$ shows the existence of macropores (Fig. 4).

It was examined that, after calcination at 550 °C, the shape of the adsorption isotherm significantly changed, although the type of the isotherm and the hysteresis loop remained the same (Fig. 4). The linear increment of adsorption isotherms of the samples calcined at 100, 188 and 1000 °C was observed till $P/P_0 = 0.9$, and, at higher relative pressure values ($P/P_0 = 0.9$), the curves increased more rapidly (Fig. 4, a, b and d). Meanwhile, in the case of the sample calcined at 550 °C, and a rapid increase was noticed above $P/P_0 = 0.7$ (Fig. 4, c). These differences can be explained by the removal of structural water from SGW during calcination, which can lead to an increased pore diameter and/or formation of new pores.

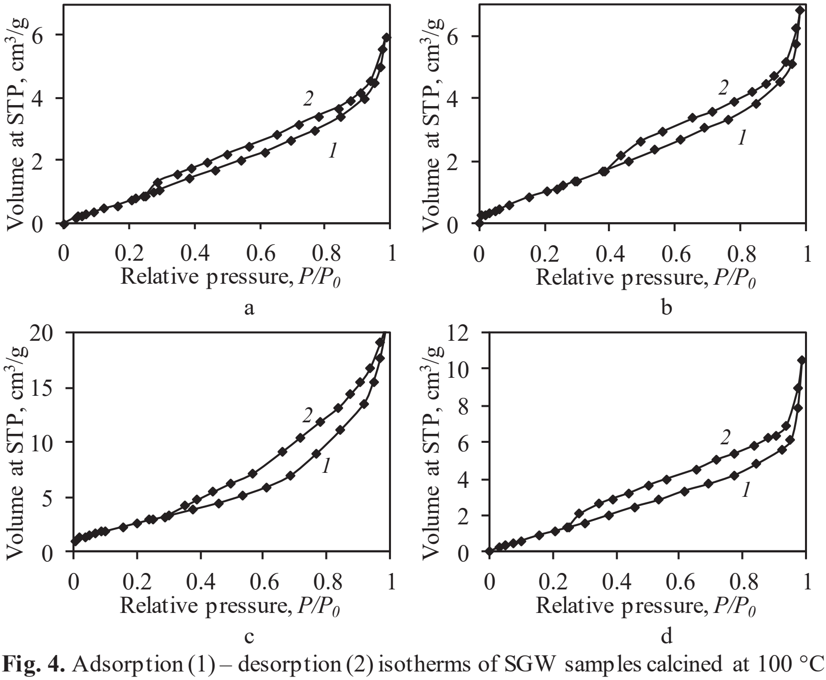


Fig. 4. Adsorption (1) – desorption (2) isotherms of SGW samples calcined at 100 °C (a), 188 °C (b), 550 °C (c) and 1000 °C (d) temperatures

The calculations revealed that the surface area (S_{BET}) of the SGW sample is equal to 4.61 m^2/g (Table 4). After calcination at 188 °C and 550 °C temperatures, the value of the surface area increased to 5.43 m^2/g and 11.32 m^2/g, respectively. Meanwhile, after calcination at 1000 °C, the value of S_{BET} decreased to 7.73 m^2/g because solid sintering proceeded in the SGW sample.

The calculations of desorption isotherms by using the cylindrical pore model showed high errors between the measured S_{BET} and the calculated ΣA (more than 40% in all cases) (Table 4). Meanwhile, by using the parallel plates pores model, the difference between S_{BET} and $\sum A$ was not significant (up to 8%) and confirmed that the selected model is valid. It is worth mentioning that, by raising the calcination temperature, the errors increased from 1.77% (100 °C) to 7.74% (550 °C), which can be explained by the formation of new pores during calcination (Table 4). These results were in good agreement with the data obtained from hysteresis where slit-shaped pores were observed (Fig. 4).

It was calculated that the total pore volume of the SGW sample is equal to $9.01 \cdot 10^{-3}$ mm^3/g and increased more than 3 times after calcination at 550 °C (Table 4). Meanwhile, at a higher calcination temperature (1000 °C), the solid sintering proceeded in the SGW sample, and, as a result, the total pore volume decreased from $30.06 \cdot 10^{-3}$ mm^3/g to $16.38 \cdot 10^{-3}$ mm^3/g (Table 4).

Table 4. The data of ΣA and ΣV_P calculations of calcined SGW samples

T, °C	S_{BET}, m^2/g	Results using cylindrical pores model			Results using between parallel plates pores model			
		ΣA, m^2/g	$\lvert S_{BET} - \Sigma A \rvert$, m^2/g	$\lvert S_{BET} - \Sigma A \rvert$, %	ΣA, m^2/g	$\lvert S_{BET} - \Sigma A \rvert$, m^2/g	$\lvert S_{BET} - \Sigma A \rvert$, %	$\Sigma V_P /\times 10^3$ cm^3/g
100	4.61	8.15	3.54	43.44	4.53	0.08	1.77	9.01
188	5.43	9.20	3.77	40.98	5.04	0.39	7.74	10.31
550	11.32	20.90	9.58	45.84	11.75	0.43	3.66	30.06
1000	7.73	13.20	5.47	41.44	7.33	0.4	5.46	16.38

It should be underlined that the pores with 1.5–4.0 nm radius were dominating in all SGW samples. It can be assumed that silica gel waste is a mesoporous material, and the temperature of calcination influenced only the surface area and the total pore volume.

3.3. Leaching peculiarities of F^- ions under static and dynamic conditions

It was determined that under static conditions, the water-to-solid (w/s) ratio, as well as the reaction temperature, strongly affected the stability of the main compound containing F^- ions in SGW, $AlF_3 \cdot 3H_2O$ (Fig. 5). At 25 °C temperature, when the w/s ratio reached 100, the intensity of diffraction peaks characteristic to $AlF_3 \cdot 3H_2O$ decreased by 3.1 times. It was determined that, even when the w/s ratio was equal to 200, a small amount of the above mentioned compound is presented in SGW. Meanwhile, an increase of the reaction temperature positively affects the decomposition of $AlF_3 \cdot 3H_2O$: when the temperature was equal to 45–55 °C, $AlF_3 \cdot 3H_2O$ was fully removed from the solid (Fig. 5).

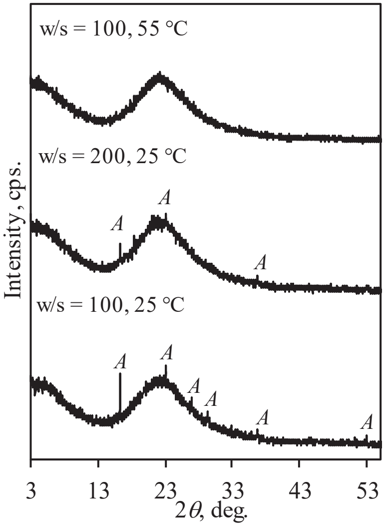


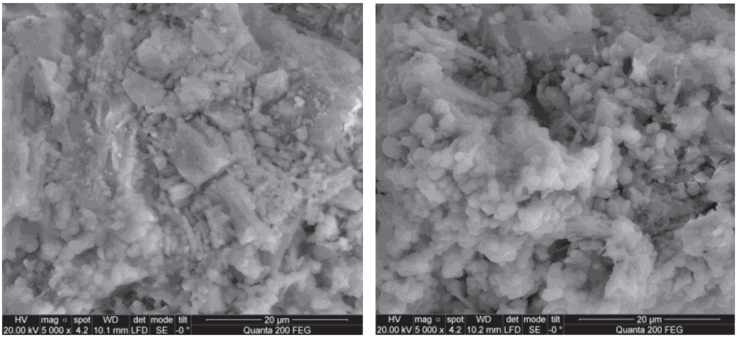
Fig. 5. XRD patterns of silica gel waste samples after 24 h of leaching under static conditions. Indexes: A – $AlF_3 \cdot 3H_2O$

The data of the chemical analysis of SGW treated at 25 °C (w/s = 100) showed that the amount of the released F^- ions into the liquid medium was equal to ~49% from the total amount of F^- ions in SGW (Table 5). It is worth noting that a higher reaction temperature has a positive effect on the quantity of the released F^- ions as it increased by 9% after treatment at 55 °C temperature.

Table 5. Amount of F^- ions after leaching under static conditions

Conditions of treatment	The amount of F^- ions in solid, %	The amount of released F^- ions, %
25 °C, w/s = 100	5.08	49.3
55 °C, w/s = 100	4.21	58.0

The effect of F^- ions leaching under static conditions is clearly seen in SEM micrographs: the untreated SGW sample showed an amorphous mass of $SiO_2 \cdot nH_2O$ and uncertain form agglomerates – crystals (Fig. 6, a). Meanwhile, in the sample after the treatment (w/s = 100, 25 °C), the above mentioned agglomerates were disrupted, and only globules with a size of ~0.5–1 μm of $SiO_2 \cdot nH_2O$ were observed (Fig. 6, b).



a b

Fig. 6. SEM micrographs of SGW (a) and treated SGW (w/s = 100, 25 °C) (b) samples

Thus, it is clearly seen that, after leaching under static conditions, the amount of F^- ions in SGW can be reduced from 10% to a value lower than 5%. However, the leaching process under static conditions requires a high amount of water (w/s=100) and is time-consuming. For this reason, in order to reduce the water to solid ratio and to shorten the interaction time, in the next stage of this research, leaching of F^- ions was performed under dynamic conditions.

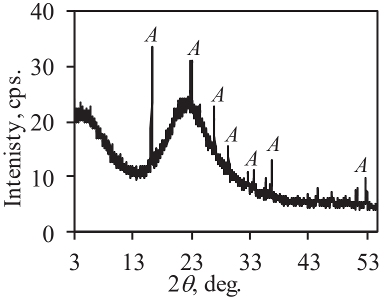


Fig. 7. XRD patterns of silica gel waste samples after leaching (w/s = 200) under dynamic conditions at 25 °C. Indexes: A – $AlF_3{\cdot}3H_2O$

It was examined that the change in the leaching conditions had a negative effect on the stability of $AlF_3{\cdot}3H_2O$ because the intensity of diffraction peaks characteristic to $AlF_3{\cdot}3H_2O$ decreased only 1.73 times (w/s = 200) (Fig. 7). The XRD results were verified by chemical analysis. It was determined that the leaching of F^- ions into the liquid medium proceeded heavily as only ~16.9% (w/s = 100) and ~32.3% (w/s = 200) of F^- ions from the total amount in silica gel waste were released into the reaction medium. This observation can be explained by the short duration of interaction (100–200 s) between the latter compound and the liquid medium.

In order to prolong the duration of interaction, leaching under dynamic conditions was performed in cycles. As expected, due to a ~5 times longer interaction time, at 25 °C temperature, the decomposition of $AlF_3{\cdot}3H_2O$ is more intensive compared with the previous results (Figs. 7 and 8). It was determined that $AlF_3{\cdot}3H_2O$ fully decomposed when the reaction temperature reached 45 °C and 55 °C because only a broad reflection typical to amorphous SiO_2 in a 18°–26° diffraction angle range was visible in the XRD pattern (Fig. 8). It is worth noting that a similar trend was observed under static conditions (Fig. 5), however, in this case, the interaction time is extremely shortened. i.e., from 24 h at static conditions to 0.14 h at dynamic conditions in cycles.

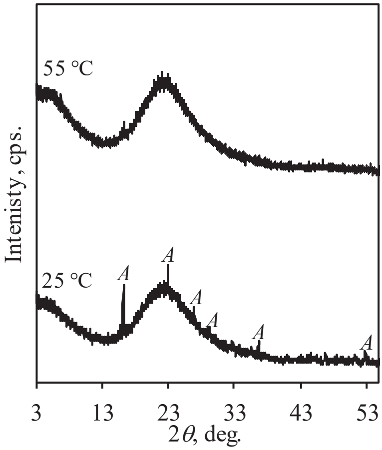


Fig. 8. XRD patterns of silica gel waste samples after leaching in cycles (w/s=100) under dynamic conditions at various temperatures. Indexes: A – $AlF_3{\cdot}3H_2O$

The chemical analysis data of SGW showed that, after leaching in cycles at 25 °C, the quantity of the released F^- ions was equal to ~45.6% (w/s = 100) from the total amount of F^- ions (Table 6), which was almost the same as under static conditions (Table 5). Moreover, the reaction temperature had a positive effect on the amount of the released F^- ions in the liquid medium (Table 6) because the best results (55.7%) were obtained after leaching at 55 °C temperature.

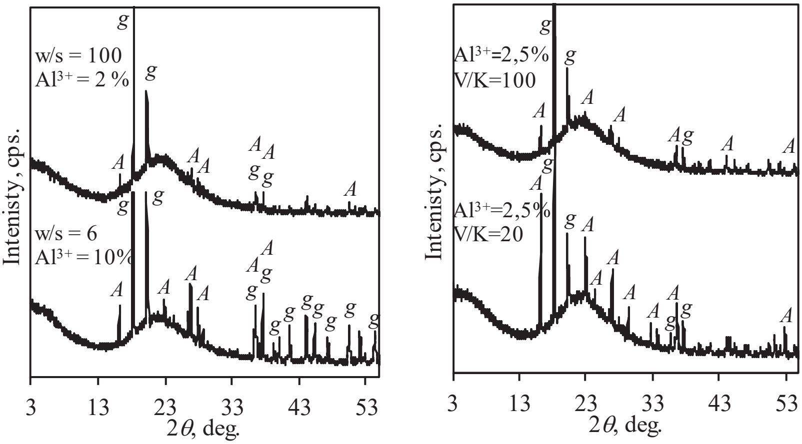
Table 6. Amount of F^- ions after leaching in cycles

Conditions of treatment	Amount of F^- ions in solid, %	Amount of released F^- ions, %
25 °C, w/s = 100	5.08	49.3
55 °C, w/s = 100	4.21	58.0

By summarizing the leaching results, it can be stated that the removal of fluoride ions from this compound to the liquid medium depends on various factors, such as dissociation, solubility, w/s ratio, reaction temperature, leaching conditions, adsorption properties of silica gel waste, and others. Despite the above outlined factors, the quantity of F^- can be reduced more than two times.

3.4. Effect of alkaline compounds on the concentration of F⁻ ions in silica gel waste

Treatment of silica gel waste with Al^{3+} ions under static conditions. The results of XRD analysis showed that the used aluminum hydroxide additive did not significantly affect the stability of $AlF_3·3H_2O$ (Fig. 9, a). Meanwhile, the intensity of the main diffraction maximum of $Al(OH)_3$ (*d*-spacing – 0.547 nm) increased from 0 (without additive) to 185 relative units (when 10% of additive was used). Since the intensity of the above mentioned diffraction peak in the control substance is equal to 38 relative units, the amount of Al^{3+} ions added to silica gel should not exceed 2.5%. It should be noted that, after SGW with 2% of Al^{3+} ions leaching (w/s – 100), the intensities of the diffraction maximums typical to $AlF_3·3H_2O$ decreased more than 3 times (Fig. 9, a) in comparison to the samples without an additive (Fig. 5). In this case, more than 55% of the initial amount of F^- ions was released from the structure of the sample into the liquid medium



a b

Fig. 9. XRD patterns of products obtained after SGW with Al^{3+} ions leaching under static (a) and in cycles under dynamic (b) conditions. Indexes: *A* – $AlF_3·3H_2O$; *g* – $Al(OH)_3$

Treatment of silica gel waste with Al^{3+} ions under dynamic conditions. The treatment of silica gel with 2% of Al^{3+} ions under dynamic conditions was carried out in cycles. It was determined that, after leaching (w/s – 100), a small amount of $AlF_3·3H_2O$ is still present in the sample (Fig. 9, b), but the amount of the released F^- ions was 57.93% from the total amount of F^- ions. Moreover, the latter value was estimated to be 12.33% higher than in the samples without an additive (Table 5).

The obtained results showed that the aluminum additive positively affected the removal of F^- ions from the structure of SGW into the liquid medium.

Therefore, it was decided to investigate the influence of calcium hydroxide on the presently outlined process. According to the literature, the application of calcium hydroxide not only induces the release of F⁻ ions, but can also bind these ions into stable compounds.

Treatment of silica gel waste with a saturated calcium hydroxide solution under dynamic conditions. It was obtained that, when the SGW sample was treated in cycles (w/s = 100), $AlF_3 \cdot 3H_2O$ was completely decomposed (Fig. 10). As expected, after treatment, calcium fluoride and calcium carbonate were formed. However, alongside the above mentioned compounds, two diffraction peaks (*d*-spacing – 0.762, 0.385 nm), which did not correspond to any compound indexed in the PDF-4 database, were observed (Fig. 10).

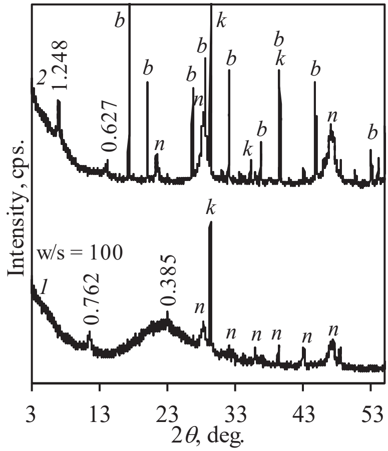


Fig. 10. XRD patterns of products obtained after treatment SGW with a saturated $Ca(OH)_2$ solution under dynamic conditions (1st curve) and precipitates formed in the liquid medium (2nd. curve). Indexes: *A* – $AlF_3 \cdot 3H_2O$; *n* – CaF_2; *x* – $AlF_{1.5}(OH)_{1.5} \cdot 0.375H_2O$; *b* – $Ca_3Al_{2.85}O_{2.55}(OH)_{9.45}$; *k* – $CaCO_3$

Regardless of the chosen treatment method (in cycles or not cyclic), fine solid particles were formed after filtration in the liquid medium (Fig. 10, b). For this reason, in order to avoid sedimentation and induce a chemical reaction, the liquid medium was additionally maintained for 24 h under static conditions. By performing XRD analysis of the precipitates, it was determined that calcium hydroxide reacted with both fluoride and aluminum ions, which led to the formation of calcium fluoride and katoite ($Ca_3Al_{2.85}O_{2.55}(OH)_{9.45}$) in the products (Fig. 10).

It was determined that, after treatment of the samples in cycles, at the beginning of the process (w/s = 10), the pH of the liquid medium was alkaline, i.e., pH >7. A further increment in the w/s ratio had no significant effect on the values of pH of the liquid medium. It was measured that the amount of F⁻ ions released into the liquid medium during the treatment was equal to 39.98%, which is ~18% lower than by using $Al(OH)_3$ additive.

Treatment of silica gel waste with calcium hydroxide under hydrothermal conditions. It was determined that in CaO–silica gel waste–H_2O system, when the molar ratio of C/S was equal to 0.55; 0.66; 0.83; 1.0; 1.75; 2.0 or 2.5, after 16 h of isothermal curing at 200 °C, $AlF_3 \cdot 3H_2O$ was unstable and decomposed. For this reason, due to the interaction between fluoride, calcium, and silicon ions, cuspidine (C/S $\geq$1.75) and calcium fluoride were formed (C/S <1.75) (Fig. 11). It was observed that, together with the mentioned compounds, calcium silicate hydrates and hydrogarnet were also formed in the products (Fig. 11). It addition, the data of liquid medium analysis showed that, during hydrothermal synthesis, F^- ions were not released into the liquid medium, but instead they were combined into stable compounds.

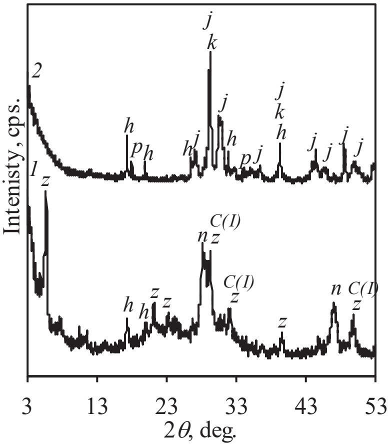


Fig. 11. XRD patterns of the synthesis products obtained in the mixtures with C/S 0.55 (a) and 1.75 (b) after 16 h of hydrothermal treatment. Indexes: j – cuspidine, p – portlandite, h – hydrogarnet, z – Z-phase, n – calcium fluoride, C(I) – C-S-H(I)

Thus, calcium ions influenced both the composition (mineral and chemical) and the properties of the liquid medium; therefore, in the next stage of this work, the effect of other calcium-containing additives on the removal of fluorine ions was investigated. The natural raw materials, which are widely used in Lithuania, i.e., opoka and limestone, and zeolite NaX were used for the research.

Treatment of silica gel waste with NaX zeolite, limestone and opoka additives under static conditions. The experiment was carried out by using fine (~1 mm) additive particles which were mixed with the investigated sample at a ratio of 1:1. The prepared mixture was poured into distilled water (w/s = 100), maintained for 1 h (25 °C), filtered and dried. After drying, SGW was separated from the additives by using sieves. It was determined that the natural additives did not significantly influence the mineral composition of the silica gel: after the reaction, the intensity of the diffraction peaks typical to $AlF_3 \cdot 3H_2O$ was slightly changed, and, in the samples with limestone and opoka, low intensity diffraction maximums characteristic to calcium carbonate and CaF_2 were detected. The results of quantitative chemical analysis showed that the concentration of F^- ions in the silica gel waste sample only slightly decreased to the level of 9.8%. Thus, it can be stated that the above mentioned additives are suitable for the removal of fluorine ions from the silica gel sample.

As it can be seen from the obtained results, alkaline additives not only promoted the release of fluorine ions into the liquid medium, but also altered the mineral composition of the contaminated silica gel samples. Therefore, it was decided to treat the investigated samples with soluble alkali solutions.

Treatment of silica gel waste with NaOH solution under dynamic conditions. It was determined that the intensities of the diffraction maximums typical to $AlF_3·3H_2O$ only slightly decreased when contaminated silica gel samples were treated with NaOH solution (w/s = 20) (Fig. 12). Also, low intensity diffractions peaks characteristic to $AlF_{1.5}(OH)_{1.5}·0.375H_2O$ were detected.

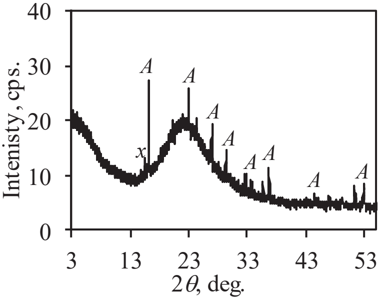


Fig. 12. XRD patterns of products obtained after treatment of SGW with 0.05% NaOH solution in cycles (w/s = 20). Indexes: *A* – $AlF_3·3H_2O$; *x* – $AlF_{1.5}(OH)_{1.5}·0.375H_2O$

The results of the examination of the sample which was treated with 0.05% sodium hydroxide solution (w/s = 20), showed that the concentration of fluorine ions in the sample decreased by ~1.6 times, i.e. to 6.23%. Due to the intense release of fluorine ions into the liquid medium during the treatment of SGW samples with NaOH solution, it was decided to use 0.01% and 0.5% ammonia water solutions which are used at JSC *Lifosa* for further research.

Treatment of silica gel waste with NH_4OH solution under dynamic conditions. The treatment of SGW samples was performed in cycles when the maximum w/s ratio 20 was used (4 cycles in total). It was determined that a slight decrease in the intensities of the diffraction peaks typical to $AlF_3·3H_2O$ was observed in XRD patterns when the sample was treated with 0.01% ammonia water solution (w/s = 20) (Fig. 13). Meanwhile, after treatment with a higher concentration solution (0.5 %, w/s = 10), it was noted that $AlF_3·3H_2O$ recrystallized to $Al(OH,F)_3$.

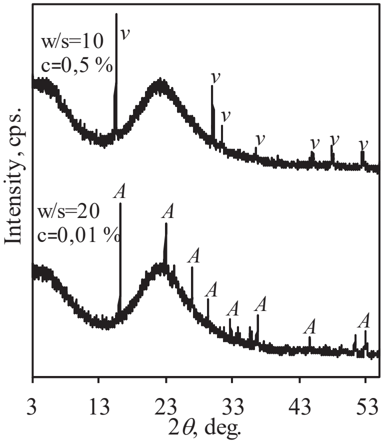


Fig. 13. XRD patterns of products obtained after treatment of silica gel waste with NH_4OH solution in cycles. Indexes: *A* – $AlF_3·3H_2O$; *v* – $Al(OH,F)_3$

It was determined that the amount of $F^–$ ions released from the structure of the SGW sample into the liquid medium depends on the concentration of ammonia water (Table 7). It was found that, after treatment with 0.01% ammonia water (w/s = 20), the amount of the released $F^–$ ions was almost 3 times lower than in the sample which was treated with 0.5% ammonia water (w/s = 10) (55.04%). It should be indicated that a similar amount of fluorine ions released into the liquid medium (>50%) was obtained by treating SGW with a high volume of water (w/s = 100) (Table 5 and Table 6).

Table. 7. Amount of $F^–$ ions after treatment with NH_4OH solution under dynamic conditions

Treatment conditions			Concentration of F^- ions in the sample, %	Amount of released F^- ions, %
w/s	No. of cycles	Concentration of NH_4OH solution, %		
20	4	0.01	8.02	20.04
10	2	0.5	4.51	55.04

Influence of the sample temperature on fluoride ion concentration. During the research, it was observed that the temperature of the liquid medium influences the amount of the released $F^–$ ions. Thus it was decided to investigate the possibility to remove fluorine ions from hot (65 °C) silica gel samples in the company’s laboratory. Experiments were performed on October 3, 2017. It was observed that SGW used for experiments contained 10.42% fluorine ions. It was determined that, after SGW treatment with water or 0.1% ammonia water solution (w/s = 20) under static or dynamic conditions, aluminum hydroxide and aluminum fluoride fully decomposed. It should be noted that, in order to remove the latter compound from cold SGW samples, a higher quantity of the liquid medium should be used. Thus it can be stated that the temperature of the SGW sample influences the stability of aluminum fluoride.

The chemical analysis data of SGW treated with water under static conditions showed that the quantity of the released F^- ions was equal to 45.88% (w/s = 20) from the total amount of F^- ions (Table 8). Moreover, the nature of the liquid medium had a positive effect on the amount of the released F^- ions in the liquid medium (Table 8) because, after treatment with ammonia water solution, this value increased to 60.25%. Unexpected results were obtained after SGW treatment with ammonia water solution under dynamic conditions: the concentration of fluoride ions in silica gel waste decreased to 0.55% (Table 8). It is worth mentioning that, by treating cold SGW samples, the amount of the released F^- ions in the liquid medium did not exceed 60%; thus, it can be stated that the properties of SGW samples strongly depend on the temperature and the duration of senescence.

Table 8. Amount of F^- ions after treatment of hot SGW samples

Conditions of treatment	Amount of F^- ions in solid, %	Amount of released F^- ions, %
Untreated SGW (Oct 03, 2017)	10.42	-
After treatment with water (w/s = 20) under static conditions	5.64	45.88
After treatment with 0.1% NH_4OH solution (w/s = 20) under static conditions	4.14	60.25
After treatment with 0.1% NH_4OH solution (w/s = 20) under dynamic conditions	0.55	94.72

Influence of mechanical treatment on F^- ion concentration in SGW samples. The experiments in the laboratory were performed by using SGW obtained in December 2016, while the experiments with hot SGW were done in June 2018. It was determined that the properties of SGW samples were changing during mechanical treatment despite the temperature and duration of senescence of SGW. It should be noted that the force of mechanical treatment must be very high because the properties of SGW do not change in vibration or impact (stroke direction ↔). Meanwhile, by vigorous mixing SGW samples with an *AT-M S157-06* laboratory mixer (140–240 rpm; 30–60 s) or by treating with a disintegrator *DEZI-14* (3000 rpm), the solid and liquid phases separate from each other (Fig. 14).

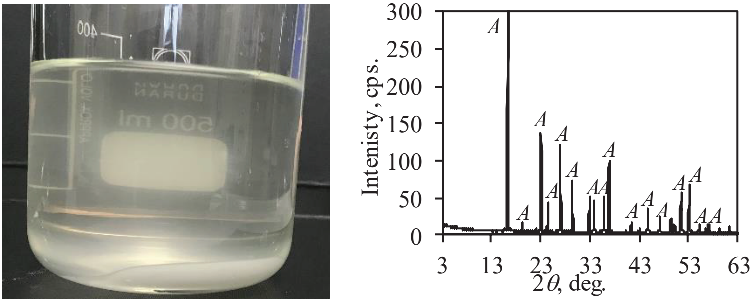

a b

Fig. 14. Images of untreated (a) and mechanically treated (b) SGW samples

It was determined that, after filtration of mechanically treated SGW, the quantity of the obtained liquid phase was equal from 16% to 30% of the original weight of the sample. In this way, the moisture content of undried SGW is reduced from ~50% to 28–40%. It was measured that fluoride ion concentration and the pH value of the liquid phase was equal to 0.5–0.6% and 1.38–1.89, respectively.

The chemical analysis data showed that, after mechanical treatment and separation of the liquid medium, the concentration of F^- ions in the SGW sample is ~1.5 times lower (6.63%) than in the untreated SGW (9.87%). Furthermore, after additional treatment of samples with water (w/s = 0.5), the concentration of F^- ions in SGW decreased to 4.31% which is 56% less than in untreated SGW. It should be noted that, by increasing the water to solid ratio to 1, the concentration of fluoride ions in SGW slightly changes. Thus, it can be stated that, during mechanical treatment, the structure of SGW samples is disturbed, and fluoride ions are released within the liquid medium. However, in order to completely remove fluoride ions, additional treatment with water is required.

It was determined that, despite the equipment in use, the intensity of mechanical treatment, the temperature of SGW samples and the w/s ratio in the obtained liquid phase, precipitates formed (Fig. 15, a). It should be noted that the rate of sedimentation is low as it finished within 24 h. The data of XRD analysis showed that precipitates consisted solely of aluminum fluoride trihydrate (Fig. 15, b).



a b

Fig. 15. Optical image (a) and XRD pattern (B) of precipitates formed in the liquid phase. Indexes: *A* – $AlF_3{\cdot}3H_2O$

It was determined that the most effective method for the removal of fluoride ions from the structure of SGW samples are the treatment of hot samples with 0.1% NH_4OH solution under static conditions (w/s = 3, 60 min) since the amount of fluorine ions released into the liquid reaches >90%. The experiments involving the use of ammonium water solution were performed in the production line of JSC *Lifosa*.

3.4. Removal of fluoride ions in industrial AlF_3 production line

Experiments of the removal of fluoride ions in the industrial AlF_3 production line were carried out at JSC *Lifosa* in October and November, 2017. The aim of the research was:

1) to reduce fluoride ion concentration to 5% (by dry weight) in AlF_3 production waste – silica gel;
2) to determine the influence of ammonia water on the crystallization and filtration processes of aluminum fluoride by using the available equipment in the production line.

During the experiments, when the electrical conductivity in the aluminum fluoride suspension reached 30–60 mS/cm (which corresponds to the residual acid content in the aluminum fluoride pulp from 1 g/dm^3 to 7 g/dm^3), it was supplied:

1) on the vacuum belt filter for dynamic treatment with 0.15% ammonia water (w/s = 3) (Fig. 16);
2) on the vacuum belt filter to separate AlF_3 solution from silica gel. Later on, the obtained silica gel was supplied to a reactor filled with 0.15% ammonia water (w/s = 3) for static treatment (Fig. 18).

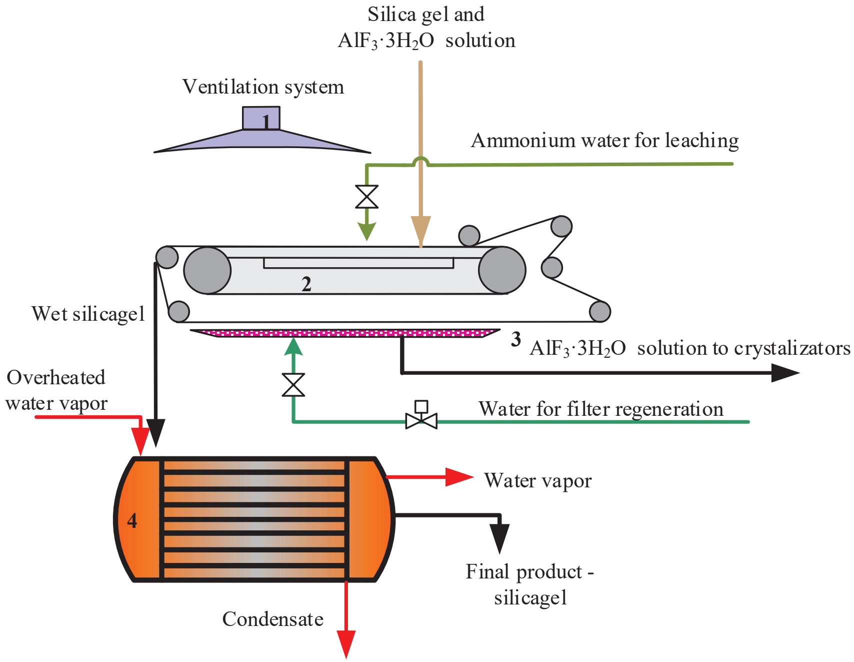


Fig. 16. Principal technological scheme of silica gel waste treatment with ammonium water under dynamic conditions. Here: 1 – Ventilation system; 2 – vacuum belt filter; 3 – collector for $AlF_3 \cdot 3H_2O$ solution; 4 – dryer.

It is known that the duration of AlF_3 solution filtration depends on the pH of the liquid medium and must not exceed 4. It was measured that, during the treatment with ammonia water under dynamic conditions, the pH values of the suspension were equal to ~3, and the duration of filtration was the same as when using water (Fig. 17).

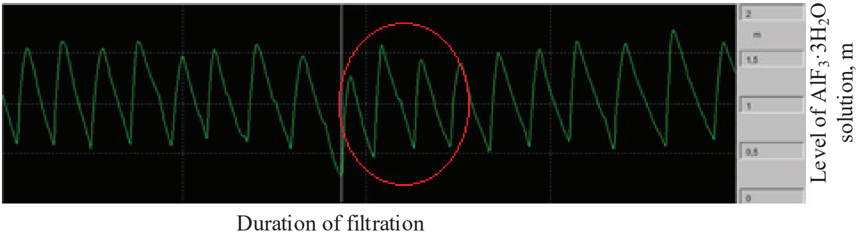


Fig. 17. Duration of AlF_3 solution filtration during experiments

The XRD results showed that, after the experiment, the intensity of the diffraction peaks corresponding to aluminum fluoride trihydrate decreased ~8 times in comparison to untreated SGW. Furthermore, the data of chemical analysis showed that the concentration of fluoride ions in treated SGW was equal to 3.1–5.2% (by dry weight). As expected, treatment with 0.15% ammonia water increased the yield of AlF_3 in the crystallizers to 3% compared to the results obtained by treating with water. However, under these treatment conditions, it is difficult to assure stable supply of NH_4OH as well as pH values equal to 3. Thus, the experiments were performed under static conditions (Fig. 18): firstly, silica gel was treated under regular production conditions, i.e., AlF_3 solution and SGW are separate on the vacuum belt filter, and, additionally, treatment with water (w/s = 3) was conducted. Later on, SGW was supplied to the reactor with 0.15% ammonium water (w/s = 3) for treatment under static conditions for 15 min. After the treatment, the obtained suspension was separated on the filter, and the liquid medium was maintained in the crystallizer.

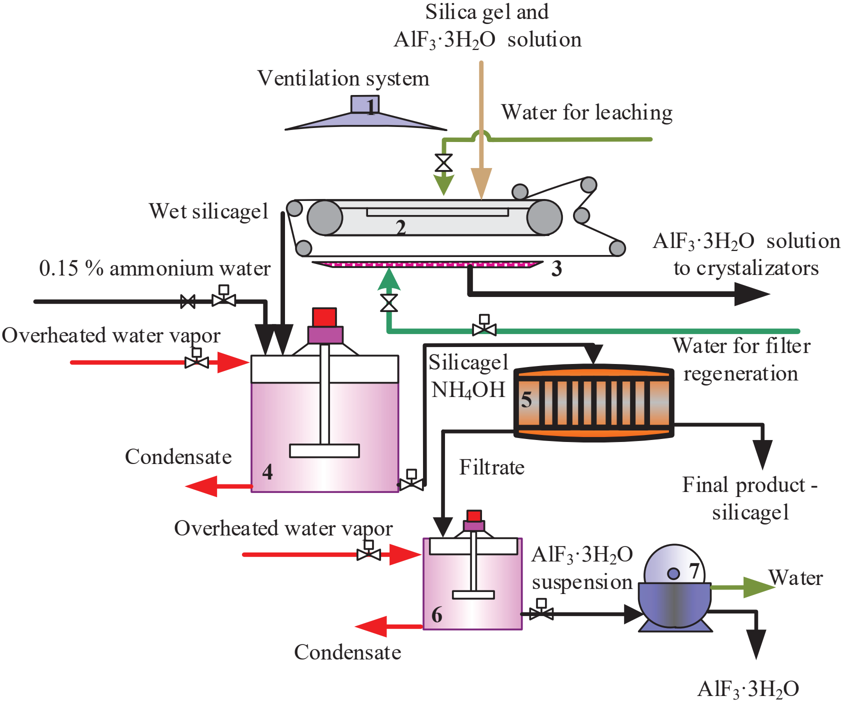


Fig. 18. Principal technological scheme of silica gel waste treatment with 0.15% ammonium water under static conditions. Here: 1 – ventilation system; 2 – vacuum belt filter; 3 – collector for $AlF_3·3H_2O$ solution; 4 – reactor, 5 – frame filter press, 6 – AlF_3 crystallizer; 7 – drum filter.

It was determined that aluminum fluoride was fully removed from SGW after treatment under static conditions. As expected, the chemical analysis data showed that the concentration of F^- ions in silica gel waste did not exceed 1.42–1.49% (by dry weight). In addition, after 24 h of crystallization in the liquid medium, precipitation of $AlF_3 \cdot 3H_2O$, which can be separated by filtration, was formed. Although additional equipment (reactor (4), filter press (5), crystallizer (6)) is required when using the static processing scheme (Fig. 18), it is still preferable in comparison to the dynamic processing scheme because, under static conditions:

- F^- ions content in silica gel waste is reduced to 1.5%;
- It is easier to control the pH value of the liquid medium which is supplied in the crystallizer;
- It is easier to control the treatment of SGW by ammonia water.

4. CONCLUSIONS

1) The peculiarities of the AlF_3 production process affect the chemical and mineral composition of the resulting waste, i.e., silica gel, because the concentration of fluorine ions in it changes from 9.8% to 10.5%, Al_2O_3 from 1% to 2.5%, while the amount of the major component of amorphous structure, SiO_2, varies from 78% to 80%. It was measured that the diameter of silica gel particles ranges from 0.4 to 170 μm, while the surface area and the density are equal to 281 m^2/kg and 2141 kg/m^3, respectively. It was found that, during calcination (550 °C), F^- ions remain bound into the composition of the investigated samples although the main crystalline compound containing fluorine ions, aluminum fluoride trihydrate, is decomposed.
2) Contaminated silica gel waste is a mesoporous material, in which, the dominant pores are formed between parallel crystal planes, and their radius r_p varies within the 1.5–4 nm range. The obtained specific surface area (S_{BET}) of this compound is equal to 4.61 m^2g^{-1}, while the total pore volume (ΣV_P) is equal to $9.01 \cdot 10^{-3}$ cm^3g^{-1}. The calcination temperature (100–1000 °C) influences both the porosity and the specific surface area (from 4.6 m^2/g to 11.3 m^2/g) of contaminated silica gel waste.
3) The treatment method and conditions were found to exert a significant effect on the stability of $AlF_3 \cdot 3H_2O$ and the content of fluorine ions in the investigated sample. Significant reduction (more than 2 times) of fluorine ions in contaminated silica gel samples under laboratory conditions can be achieved by the treatment with water or by addition of alkaline additives. It should be indicated that, if leaching of these ions with water under static conditions is applied (with or without additives), F^- ions can only be removed from the silica gel samples at a very high water content (water/solid ratio >100).
4) The treatment of contaminated silica gel affected both the thermal stability and morphology of the samples: particles of an undefined form and agglomerates of $SiO_2 \cdot nH_2O$ and spherical particles of ~0.5–1 μm were observed. It was determined that moisture/humidity in silica gel waste can be reduced up to 2 times by treating the samples with water or other additives.
5) Fluoride ions were found to be most efficiently removed from contaminated silica gel at the industrial scale when treatment with NH_4OH solution under static conditions (W/S = 3, 60 min) is applied because the amount of the released fluorine ions into the liquid medium is >90%. The resulting reaction medium, after precipitation of aluminum fluoride trihydrate, can be reused for the treatment of contaminated silica gel samples.

6) By applying the established optimum treatment conditions of silica gel with ammonia water (0.15%) under static conditions in the industrial AlF_3 production line, it is possible not only to reduce the concentration of fluoride ions in silica gel by >90%, but also to increase the yield of aluminum fluoride.

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REZIUMĖ

Temos aktualumas

Atliekų tvarkymas ir taršos mažinimas Lietuvos Respublikoje ir Europos Sąjungoje yra prioritetinės aplinkos apsaugos sritys. Jos yra reglamentuotos įstatymais, o jų svarba nurodyta aplinkos apsaugos strategijoje ir veiksmų programoje (EU Implementation of the Circular Economy Action Plan; Eurostat Waste Statistics). Eurostat‘o duomenimis, Europos Sąjungoje kasmet susidaro daugiau kaip 184 mln. tonų gamybos atliekų, o štai Lietuvoje – ~2,6 mln. tonų. Ekonominiu požiūriu, priimtiniausia atliekas kaupti sąvartynuose, tačiau jie užima didelius plotus, yra koncentruoti oro, gruntinių vandenų bei grunto taršos šaltiniai. Todėl ieškoma patrauklių technogeninių atliekų perdirbimo būdų, kurie leistų sukurti pridėtinės vertės produktus.

Aliuminio fluorido gamyba yra susijusi su didžiuliais toksiškų ir aplinkai pavojingų atliekų kiekiais, t. y. pasaulyje per metus pagaminama apie 1 mln. tonų aliuminio fluorido bei generuojama apie 3 mln. tonų atliekų. Pažymėtina, kad daugiau nei 60 % minėtų atliekų yra užteršta fluoro jonais, kurių koncentracija gali siekti net iki 10 %. Atliekų kiekis ir jų toksiškumas priklauso nuo pasirinkto gamybos būdo: sausojo fluorito (kalcio fluorido – CaF_2) ar iš heksafluorsilicio rūgšties. Aliuminio fluoridas dažniausiai gaminamas (~60 %) sausuoju fluorito būdu naudojant kalcio fluoridą, aliuminio hidroksidą ir sieros rūgštį. Gamybos procesą sudaro: dujinio vandenilio fluorido gavimas iš fluorito ir šios rūgšties neutralizacija aliuminio hidroksidu. Šitoks AlF_3 gamybos būdas pasižymi didelėmis gamtinių žaliavų ir energijos sąnaudomis, t. y. gaminant 1 toną AlF_3 yra sunaudojama ~4,4 tonos žaliavų ir ~1,5 MWh (~5 MJ) energijos. Taigi dėl didėjančių fluorito (per pastaruosius metus pakilo ~2 kartus) ir energijos kainų šis metodas tampa ekonomiškai nepatrauklus. Be to, sausasis gamybos būdas ne tik imlus žaliavoms, bet ir išmetami didžiuliai kiekiai atliekų, t. y. gaminant 1 toną AlF_3 produkcijos susidaro ~3,3 tonos atliekų. Didžiąją dalį atliekų (~2,7 tonos) sudaro sieros rūgštimi ir fluoro jonais užterštas gipsas. Dažniausiai ši atlieka be papildomo apdorojimo ar neutralizavimo transportuojama į sąvartynus. Pažymėtina, kad kalcio sulfato panaudojimą riboja sieros rūgšties ir fluoro jonų likučiai. Todėl alternatyvių pigesnių žaliavų bei pelningesnės gamybos technologijos, tokios kaip heksafluorsilicio rūgšties perdirbimas, tampa vis patrauklesnės. Literatūros duomenimis, apie 20 % pasaulinės AlF_3 produkcijos gaminama minėtu būdu.

Remiantis skirtingais literatūros šaltiniais, pasaulyje per metus pagaminama iki 3 mln. tonų heksafluorsilicio rūgšties. Nors ši rūgštis yra koncentruotas fluoro jonų šaltinis, didžioji dalis utilizuojama sąvartynuose ir tik 0,5 mln. tonų panaudojama geriamojo vandens fluoravimui (turi būti išvalyta nuo sunkiųjų metalų ir kt. priemaišų), silikatų sintezėje ir aliuminio fluorido gamyboje. Didžiausia dalis, ~0,2 mln. tonų, naudojama aliuminio fluorido gamyboje. Šiuo metu yra taikomos 2 pagrindinės AlF_3 gamybos iš heksafluorsilicio rūgšties technologijos. Pirmoji technologija paremta heksafluorsilicio rūgšties konversija į vandenilio fluoridą, kuris toliau naudojamas AlF_3 gamybai. Vandenilio fluorido gamyba iš heksafluorsilicio rūgšties yra sudėtingas procesas, apimantis daug stadijų ir agregatų. Be to, gaminant vieną toną bevandenio vandenilio fluorido, sunaudojama iki 30 tonų grynos sieros rūgšties, kurios regeneracija yra sudėtinga. Be to gaminant 1 toną HF susidaro apie 0,55 tonos silikagelio, užteršto fluoro jonais. Todėl plačiausiai taikoma aliuminio fluorido gamyba paremta tiesiogine heksafluorsilicio rūgšties neutralizacija aliuminio hidroksidu (šlapiuoju būdu).

Literatūros duomenimis, pasaulyje daugiau nei 17 % aliuminio fluorido gaminama minėtu būdu. Gaminant 1 toną aliuminio fluorido šlapiuoju būdu, sunaudojama apie 1,2 tonos heksafluorsilicio rūgšties ir ~1 tona aliuminio hidroksido. Bendras žaliavų kiekis, sunaudojamas 1 tonai produkcijos pagaminti šlapiuoju būdu, yra beveik 2 kartus mažesnis nei reikalingas taikant sausąjį gamybos būdą. Tačiau, rūgšties neutralizacijos metu susidaro apie 0,67 tonos silikagelio, užteršto fluoro jonais, kuris tiekiamas į sąvartynus. Bendras susidarančių atliekų kiekis gaminant 1 toną aliuminio fluorido svyruoja nuo 1 iki 1,3 tonos, o tai yra apie 3 kartus mažiau lyginant su sausuoju gamybos būdu. Be to, sukūrus ir pritaikius inovatyvias technologijas atliekų kiekis, susidarantis gaminant 1 toną aliuminio fluorido šlapiuoju būdu, gali būti sumažintas iki 0,3 tonos:

1) naudojant filtrų ir absorbcijos sistemas, fluoro emisija į orą gali būti sumažinta iki 0,015 kg tonai AlF_3 pagaminti;
2) apdorojant vandeninius atliekų srautus kalkėmis, fluoro emisija į vandenį gali būti sumažinta iki 0,1 kg tonai AlF_3 pagaminti;
3) panaudojant atplovimo ir kitas apdorojimo technologijas fluoro kiekis silikagelyje gali būti sumažintas iki leistinų normų (GOST 3956-76).

Pažymėtina, kad dėl disociacijos, tirpumo, V/K santykio bei SiO_2 adsorbcinių savybių fluoro jonų koncentracijos sumažinimas silikagelyje yra sudėtinga technologinė problema.

Darbo tikslas – nustatyti AlF_3 gamybos technologinių parametrų įtaką susidarančios atliekos – silikagelio su aliuminio ir fluoro jonais – cheminei bei mineralinei sudėčiai ir jo savybėms.

Darbo uždaviniai:

1) Išnagrinėti terminio apdorojimo iki 1000 °C temperatūros įtaką silikagelio su aliuminio ir fluoro jonais bandinių sandarai ir savybėms;
2) Ištirti statinių, dinaminių ir mechaninės aktyvacijos apdorojimo sąlygų bei šarminės prigimties junginių įtaką silikagelio su priemaišomis bandinių cheminei ir mineralinei sudėčiai;

3) Nustatyti geriausių apdorotų silikagelio su priemaišomis bandinių stabilaus egzistavimo temperatūrinį intervalą ir fizikines savybes;
4) Pritaikyti optimalias silikagelio apdorojimo sąlygas aliuminio fluorido pramoninės gamybos linijoje.

Mokslinis darbo naujumas

Įrodyta, kad keičiant apdorojimo sąlygas (statines, dinamines ir mechaninę aktyvaciją) bei šarminės prigimties junginius (NH_4OH, $Ca(OH)_2$, NaOH, Al_2O_3) galima silikagelio sudėtyje minimizuoti fluoro jonų koncentraciją iki 1,5 %. Pirmą kartą nustatyta, kad skystojoje terpėje, atskirtoje taikant mechaninį apdorojimą ar atplovimą šarminės prigimties tirpalais nuo AlF_3 gamybos atliekos – silikagelio, kristalizuojasi aliuminio ir fluoro jonų turintys junginiai – aliuminio fluoridas, kalcio fluoridas ir/arba katoitas.

Praktinė vertė

Pasiūlyta priemaišų pašalinimo iš silikagelio technologija, pagal kurią fluoro jonų koncentraciją silikagelyje galima sumažinti iki 1,5 % bei padidinti tikslinio produkto (aliuminio fluorido) išeigą. Remiantis gautais darbo rezultatais, AB „Lifosa“ pramoninėje aliuminio fluorido gamybos linijoje buvo sumontuota papildoma įranga ir atlikti gamybiniai bandymai.

Darbo aprobavimas ir publikavimas

Disertacinio darbo tema paskelbtos 2 mokslinės publikacijos leidiniuose su citavimo indeksu, įtrauktuose į *Clarivate Analytics Web of Science* duomenų bazę. Darbo rezultatai pristatyti 4 tarptautinėse mokslinėse konferencijose.

Darbo apimtis

Disertaciją sudaro įvadas, literatūrinių duomenų analizė, eksperimentinė dalis, tyrimų rezultatai bei jų aptarimas, išvados, 89 literatūros šaltinių sąrašas, mokslinių publikacijų sąrašas, priedų sąrašas. Pagrindinė medžiaga išdėstyta 107 puslapiuose, įskaitant 40 lentelių ir 57 paveikslus.

Disertacijos ginamieji teiginiai

1) Silikagelis su aliuminio ir fluoro jonais yra mezoporė medžiaga, kurią degant kinta jos struktūra ir savitasis paviršiaus plotas.
2) Efektyviausia F^- jonų šalinimo iš AlF_3 gamybos atliekos – silikagelio – technologija yra silikagelio apdorojimas amoniakiniu vandeniu esant statinėms sąlygoms.

IŠVADOS

1) AlF_3 gamybos technologiniai parametrai keičia susidarančios atliekos – silikagelio – cheminę ir mineralinę sudėtį, nes kinta: fluoro jonų koncentracija 9,8–10,5 %, Al_2O_3 kiekis 1–2,5 %, o pagrindinio amorfinės struktūros komponento SiO_2 kiekis 78–80 %. Išmatuota, kad silikagelyje esančių dalelių skersmuo kinta nuo 0,4 µm iki 170 µm, paviršiaus ploto vertė yra lygi 281 m^2/kg, o tankis 2141 kg/m^3. Degimo metu (550 °C) $F^–$ jonai lieka tiriamųjų bandinių sudėtyje, nors ir skyla pagrindinis kristalinis junginys, turintis fluoro jonų – aliuminio fluorido trihidratas.
2) Silikagelis su priemaišomis yra mezoporė medžiaga su 1,5–4,0 nm skersmens dominuojančiomis tarp lygiagrečiųjų kristalinių plokštumų poromis. Šios medžiagos savitasis paviršiaus plotas S_{BET} lygus 4,61 m^2/g, o suminis porų tūris ΣV_P – $9{,}01 \cdot 10^{-3}$ cm^3/g. Didinant degimo temperatūrą iki 1000 °C, kinta silikagelio su priemaišomis akytumas bei savitojo paviršiaus ploto vertės nuo 4,6 m^2/g iki 11,3 m^2/g.
3) Apdorojimo metodas ir sąlygos turi pastebimą įtaką tiek silikagelyje esančio $AlF_3 \cdot 3H_2O$ stabilumui, tiek fluoro jonų koncentracijai bandinyje. Reikšmingai sumažinti fluoro jonų kiekį (daugiau nei 2 kartus) silikagelio su priemaišomis bandiniuose laboratorinėmis sąlygomis galima juos apdorojant vandeniu ar įmaišant šarminės prigimties priedų. Pažymėtina, kad taikant dinaminio srauto išplovimo technologiją (su priedais arba be) fluoro jonus iš silikagelio galima pašalinti tik labai dideliu vandens kiekiu (kai vandens/kietųjų medžiagų santykis >100).
4) Silikagelio su priemaišomis bandinių apdorojimas turi įtakos tiek bandinių terminiam stabilumui, tiek morfologijai: neaiškios formos $SiO_2 \cdot nH_2O$ dalelių aglomeratai suyra ir identifikuojamos sferinės ~0,5–1 µm skersmens dalelės. Be to, silikagelio bandiniuose esantis drėgmės kiekis gali būti sumažintas iki 2 kartų juos apdorojant vandeniu ar kitais priedais.
5) Efektyviausia fluoro jonus gamybinėmis sąlygomis pašalinti iš silikagelio su priemaišomis, jį apdorojant NH_4OH tirpalu statinėmis sąlygomis (V/K = 3, 60 min), nes atpalaiduotų į skystąją terpę fluoro jonų kiekis yra daugiau nei 90 %. Gauta skystoji terpė po aliuminio fluorido trihidrato nusodinimo gali būti grąžinama silikagelio su priemaišomis bandinių apdorojimui.
6) Įdiegus nustatytą optimalią silikagelio apdorojimo amoniakiniu vandeniu (0,15 %) statinėmis sąlygomis technologiją pramoninėje AlF_3 gamybos linijoje, galima ne tik sumažinti fluoro jonų koncentraciją susidarančioje atliekoje >90 %, bet ir padidinti aliuminio fluorido išeigą.

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