The Prospective Approach for the Reduction of Fluoride Ions Mobility in Industrial Waste by Creating Products of Commercial Value

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Abstract: In this work, we present the possibility to reduce the amount of fluoride ions in silica gel waste by using different techniques or to immobilize these ions by creating products of commercial value. The leaching of fluoride ions from silica gel waste to the liquid medium was done under static and dynamic conditions. It was determined that the removal of fluoride ions from this compound depends on various factors, such as dissociation, solubility, the w/s ratio, reaction temperature, leaching conditions, the adsorption properties of silica gel waste, and others. The obtained results showed that, by applying different techniques, the quantity of fluoride ions can be reduced by 60%, while obtained water was neutralized by calcium hydroxide. Additionally, it was determined that silica gel waste is a promising raw material for the hydrothermal synthesis of a stable compound containing fluoride ions–cuspidine.

Keywords: fluoride ions; silica gel waste; leaching; hydrothermal synthesis; cuspidine

1. Introduction

The disposal of industrial by-products is becoming an increasing concern for many industries due to the large amounts of wastes generated and increasing costs of operating landfills in combination with the scarcity of landfill sites [1–8]. Accordingly, the recycling and reutilization of industrial waste and by-products are a subject of great importance [9–12].

Large amounts of silica gel waste contaminated with fluoride ions are generated in the industrial production of aluminum fluoride [13,14]. In fact, one of the main fertilizer producers in Lithuania, a joint-stock company "Lifosa", generates approximately 15 thousand tons per year of the mentioned waste during the manufacture of 17 thousand tons of AlF_3 [15]. In the process of obtaining AlF_3, the latter compound is formed in the reaction of neutralizing hexafluorosilicic acid with aluminum hydroxide [13,14]:

$$H_2SiF_6 + 2Al(OH)_3 \rightarrow 2AlF_3 + SiO_2 \cdot nH_2O + H_2O + Q \tag{1}$$

The structure of the precipitated silica gel waste depends on many variables: the duration of the reaction, the temperature, the way in which reagents are dosed, the structure of $Al(OH)_3$ used in the process, and the purity of the applied fluorosilicic acid [13]. However, due to the strong bonding of fluoride ions to the crystal structure of the latter compound, the purification of silica gel waste poses a great challenge. Thus, because of the high cost of silica gel waste processing, it is preferably discharged in landfill sites [13,16–18]. For this reason, long-term storage and maintenance of silica gel waste are currently facing many environmental concerns, which are associated with the dumps and disposal sites of this by-product due to the leaching of fluoride into the surface and underground water [13,16].

According to literature [12,19–24], the content of toxic ions can be reduced in two ways: by removing them from waste or by reducing their mobility in the environment–immobilization.

The removal or reduction of fluoride ions from silica gel waste is a complex process, thus there is a lack of data in the literature. To our knowledge, in 2014, Iljina et al. tried to purify silica gel waste by performing leaching experiments [17]. However, the results of these experiments demonstrated that the concentration of F^- ions was only decreased from 8.64% to 8.03% and the remaining amount of fluoride ions was adsorbed by the main compound–silica dioxide. In the case of success, silica gel with a low content of F^- ions and water contaminated with F^- ions can be obtained. The silica gel with a lower content of F^- ions (<5%) can be used as an SiO_2 source in some industries [25–29], and only LTD "Alufluor AB" [30] sells this product worldwide. Meanwhile, wastewater contaminated with F^- ions can be neutralized by adding $Ca(OH)_2$ or $CaCO_3$ [31,32]. During neutralization, the obtained CaF_2 may be reused as a raw material or an additive in several industrial applications. Mainly, CaF_2 is used for the manufacture of hydrofluoric acid and as a flux in steel or ceramic industries [31,33]. The manufacture of HF requires a high purity of calcium fluoride, while steel or ceramic industries require only 60–97% purity.

According to the literature, untreated silica gel waste can be immobilized in concrete stone [14,19]; however, due to effect of F^- ions on the environment, the application in cement industry is limited. Also, F^- ions can be bound into stable compounds during the hydrothermal synthesis of lower basicity calcium silicates hydrates [17,18,34]. For these reasons, it may be possible to use silica gel waste for the synthesis of cuspidine ($3CaO \cdot 2SiO_2 \cdot CaF_2$). This compound is generally used as mold flux, which controls the horizontal mold heat transfer and lubricates the solidified steel shell from the oscillating mold [35,36]. According to Jung et al. [37], cuspidine is a key ingredient in the continuous casting process to improve the quality of the cast slabs.

As a matter of fact, in the context of reducing environmental issues and enhancing economic benefits, technologies for converting waste materials into products of commercial value are in great demand [14,17,18,29,34,38]. However, the literature concerning the successful application of silica gel waste contaminated with F^- ions is scarce.

For this reason, the aim of this work is to reduce F^- ions in silica gel waste by using different techniques and/or immobilize these ions by creating products of commercial value.

2. Materials and Methods

2.1. Raw Materials

In this work, the following reagents were used: silica gel waste (SGW), i.e., a waste product of AlF_3 production in the chemical plant of Lifosa (Kėdainiai, Lithuania), which was dried for 48 h at 50 °C, with a specific surface area S_a of 281.01 m^2/kg, by a CILAS LD 1090 granulometer; and calcium oxide from $Ca(OH)_2$ ("Stanchem", Poland), additionally burned at 550 °C temperature for 1 h and ground for 30 s in a vibrating cup "Pulverisette 9" mill at 600 rpm, with a quantity of free CaO equal to 98.7%.

2.2. Methodology

2.2.1. The Chemical Analysis

A standard method of SiO_2 chemical analysis. A total of 1 g of the sample was mixed with sodium and potassium carbonate mixture (6 g) and put in a platinum crucible. The crucible was placed in a furnace and melted at a 900–1000 °C temperature for 1 h. After fusion, in order to solidify the melt on the crucible walls, the sample was placed on a 200 cm^3 porcelain plate with distilled water. Then, the distilled water was removed and a required amount of 10% of HCl was added and mixed until almost all the CO_2 gas had been released from the solution. After that, the solution in the porcelain plate was heated on the sand bath until it evaporated. The residue formed was mixed with a few drops of concentrated HCl acid and left to cool down. After 30 min, in order to dissolve chlorides,

hot distilled water was added to the porcelain plate. Then, the solution with residue consisting of SiO_2 was filtered through an ash-free filter and rinsed with distilled water to eliminate chloride ions (the presence of chloride ions was tested by adding one drop of clean filtrate and a drop of 1% $AgNO_3$ solution on a glass). The obtained filtrate was used for the second chemical analysis of SiO_2 and, finally, both filtrate papers were put in the crucibles and heated at 1000 °C for 1 h. The amount of SiO_2 was calculated by using the equation:

$$SiO_2 = (a_1 \cdot 100)/a, \, \% \qquad (2)$$

where a_1 is the mass of heated residue after the experiment, g; and a is the initial mass of the sample, g.

The determination of fluoride. A total of 1 g of sample was put on a platinum plate and mixed with 10 g of sodium and potassium hydroxide mixture (5:7 of NaOH and KOH). After that, the platinum plate was put on the sand bath and heated till the mixture was melted. During the heating, the melt was vigorously stirred with a platinum spatula and then, it was left to cool down. Afterwards, 150 cm^3 of distilled water was poured onto the platinum plate and heated on the sand bath till the formed salts were melted. Then, in order to bind the fluoride ions, 15 g of chemically pure $(NH_4)_2CO_3$ powder was added into the solution and evaporated till the dry salt was formed. After that, the residue was mixed with 150 cm^3 of distilled water and heated. A hot solution with precipitates was poured into a 250 cm^3 flask and cooled down. Then, it was diluted with water to the indicated level and filtered off. Before measurements, TISAB II was added to each sample (volume ratio 1:1). The concentrations of fluoride ions in the solution were measured by using a Metler Toledo T70 potentiometer. The error of the selective electrode for F^- ions is ±1 ppm (0.0001%). The concentration of F^- was calculated as the arithmetic mean of the three individual results. The measurement deviations were below 3%.

2.2.2. The Leaching of Fluoride Ions

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

(1) Leaching of F^- ions under static conditions; in order to reach the water-to-solid (w/s) ratios of 2, 4, 6, 8, and 100, 10 g of silica gel waste was mixed with distilled water and kept for 24 h at 25 and 55 °C temperatures. After leaching, the suspensions were filtered off, and the products were dried at a 50 °C ± 5 temperature for 24 h.

(2) Leaching of F^- ions under dynamic conditions by using 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 25, 50, 100, and 200. After the process, the products were dried at a 50 °C ± 5 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 a 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. Different temperature water 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; 24 h) at the end of the process.

2.2.3. The Application of Silica Gel Waste

The synthesis of dibasic calcium silicate hydrates by using silica gel waste was performed in the mixture, with a molar ratio of C/S (CaO/SiO_2) that was equal to 2. The hydrothermal synthesis was carried out in unstirred suspensions, under saturated steam pressure at 200 °C temperature for 16, 24, 48, and 72 h by applying extra argon gas (10 bar) [39].

2.3. Instrumental Analysis

The samples were characterised by powder X-ray diffraction (XRD; with a D8 Advance X-ray diffractometer), differential scanning calorimetry (DSC; with Netzsch DSC214 Polyma instrument), X-ray fluorescence spectroscopy (XRF; with a Bruker X-ray S8 Tiger WD spectrometer), a grain-size

analyzer (CILAS 1090 LD), and scanning electron microscopy (SEM; with a JEOL JSM-7600F instrument) [17,18,34,39].

The density of samples was measured using a Quantachrome "Ultrapyc 1200e" gas pycnometer under helium atmosphere; the number of measurements was 5 and accuracy—0.1 kg/m^3. The value of pH was measured with a Hanna instrument (Hi 9321, microprocessor pH meter, Hanna Instruments, Woonsocket, RI, USA). The measurements of the value of pH were repeated three times, and deviations were below 2%.

3. Results and Discussion

3.1. The Properties of Silica Gel Waste (SGW)

In the first part of this work, the properties of silica gel waste (SGW) were examined in detail. The chemical analysis data showed that dried (50 °C, 48 h) SGW consists of 79.0% SiO_2 and 10.0% F^- ions (Figure 1a). Yet almost the same tendency was observed by applying XRF: it was determined that SGW contains 36.2% silica, which is equivalent to 78.9% SiO_2 (Figure 1a). Moreover, 2.5% of Al^{3+} ions and traces of other elements are also present in the mentioned compound (Figure 1a). As other authors' work showed, the chemical composition of SGW strongly depends on the conditions of AlF_3 manufacture [17,18].

The previous results were in a good agreement with the data of XRD analysis. $AlF_3 \cdot 3H_2O$ (PDF 00-035-0827, *d*-spacing = 0.545; 0.386; 0.329; 0.244 nm) and the amorphous silicon dioxide, which corresponds to a broad basal reflection in a 18–37° diffraction angle range, were observed in the XRD pattern of SGW (Figure 1b).

Moreover, the results of particle size distribution analysis showed that the diameter of the latter compound particles varied in a 0.03–170 μm range, while the particles with a size of 34–72 μm were dominant (Figure 1c). It was also determined that the surface area and density of silica gel waste were equal to 281.01 m^2/kg and 2141 kg/m^3, respectively.
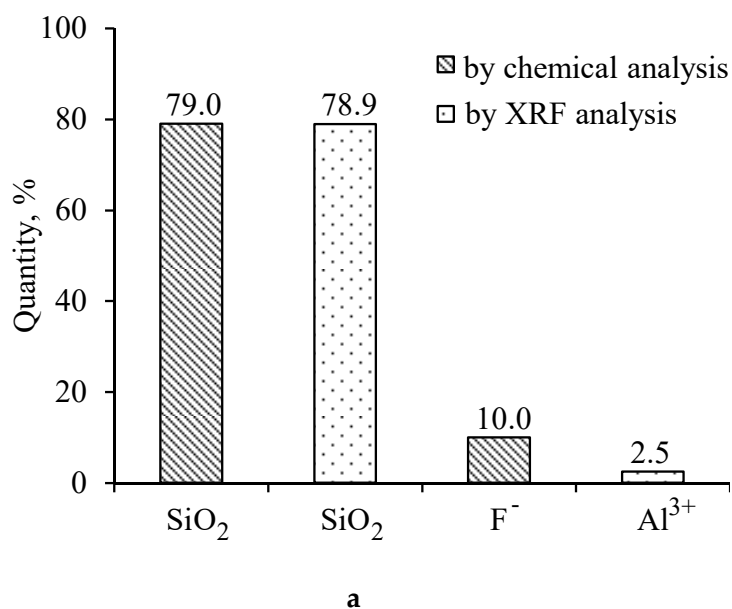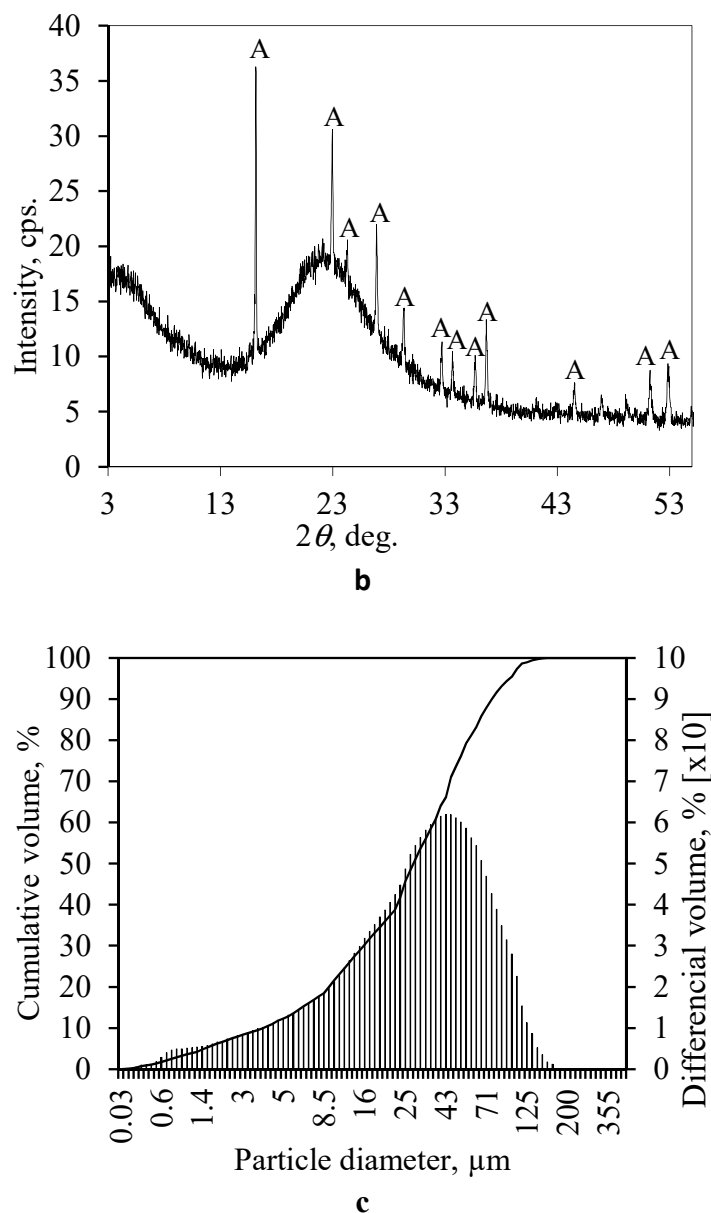

a

Figure 1. *Cont.*

Figure 1. The chemical composition (**a**), XRD pattern (**b**), and particle size distribution (**c**) of dried silica gel waste. Indexes: A—AlF$_3\cdot$3H$_2$O.

The results of chemical composition were proved by the data of differential scanning calorimetry. In the DSC curve, a two-step decomposition of AlF$_3\cdot$3H$_2$O was observed at 146 and 165 °C temperatures, in which the quantity of the heat flow was equal to: 2.78 J/g for AlF$_3\cdot$3H$_2$O → AlF$_3\cdot$0.5H$_2$O + 2.5H$_2$O and 33.62 J/g for AlF$_3\cdot$0.5H$_2$O → AlF$_3$ + 0.5H$_2$O, respectively (Figure 2a) [40,41]. Meanwhile, the third endothermic effect, which is assigned to the dehydration of silica gel (SiO$_2\cdot$nH$_2$O → SiO$_2$ + nH$_2$O), was noticed at 188 °C. These results were confirmed by the experiment of water vapor adsorption: when the ratio of relative water vapor pressure (p/p_0) was equal to 1.0, the dehydration heat of silica gel waste significantly increased from 59 to 189 J/g (Figure 2b), and this process overlapped with the endothermic effect assigned to the decomposition of AlF$_3\cdot$3H$_2$O (Figure 2).

Heat: 2.78 J/g
Peak: 146 °C
Onset: 138 °C
End: 154 °C

Heat: 33.62 J/g
Peak: 165 °C
Onset: 159 °C
End: 170 °C

Heat: 59.33 J/g
Peak: 188 °C
Onset: 182 °C
End: 196 °C

↑ Exo
ΔQ
↓ Endo

a

Peak: 157 °C

Heat: 189 J/g
Peak: 175 °C
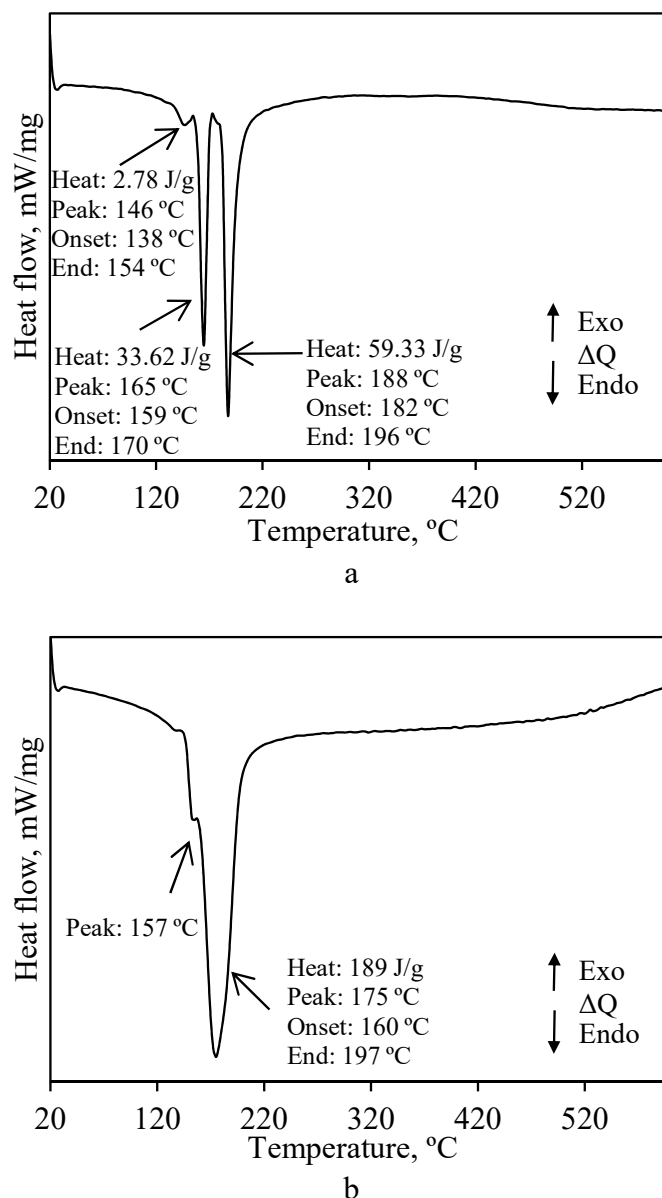Onset: 160 °C
End: 197 °C

↑ Exo
ΔQ
↓ Endo

b

Figure 2. DSC curves of silica gel waste samples before (**a**) and after water vapor adsorption (p/p_0 = 1.0) (**b**).

To fully understand the thermal behavior of SGW, the calcination of this compound was carried out in a 50–1000 °C temperature range (Figure 3). Although the typical diffraction maximum characteristic of $AlF_3 \cdot 3H_2O$ slightly decreased with increasing temperature, it remained stable till 165 °C and fully decomposed at 188 °C (Figure 3). In a higher temperature range (188–550 °C), a low-intensity peak (d-spacing = 0.355 nm) at a ~25° diffraction angle was noticed 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 aluminium containing components and SiO_2, mullite ($Al_{4.95} \cdot Si_{1.05} \cdot O_{9.52}$; PDF 00-015-0776; d-spacing = 0.341; 0.541; 0.270 nm) was formed in calcination products (Figure 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 a solid is equal to ~9.8%.
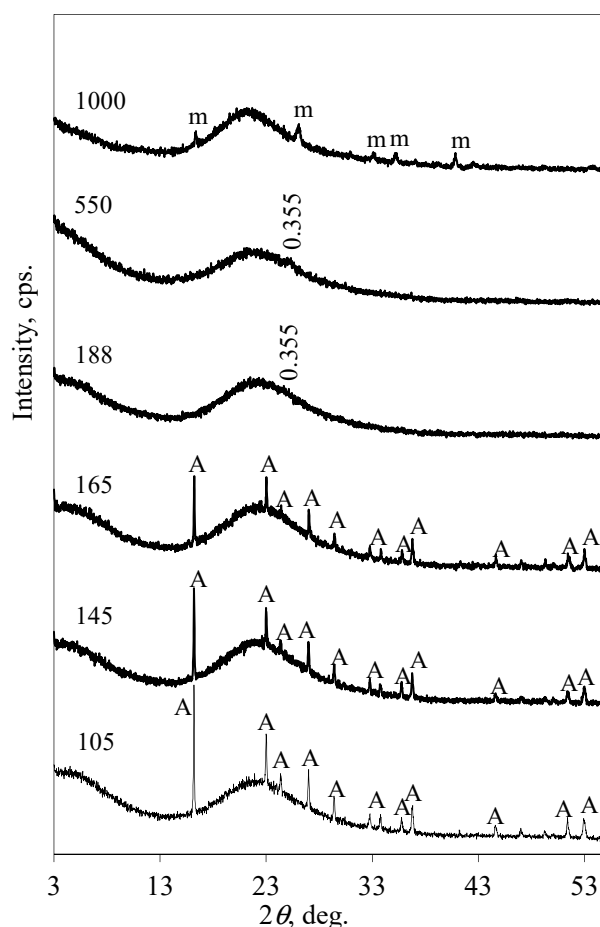
Figure 3. XRD patterns of calcined in a 50–1000 °C temperature range for 1 h silica gel waste samples. Indexes: A—$AlF_3 \cdot 3H_2O$, m—mullite.

3.2. The Leaching Peculiarities of F⁻ Ions under Static and Dynamic Conditions

In the second part of this work, the leaching peculiarities of F^- ions under static and dynamic conditions were examined by using dried SGW, when the water-to-solid (w/s) ratios varied from 2 to 200 and the temperature of the reaction was equal to 25, 35, 45, and 55 °C. 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, $AlF_3 \cdot 3H_2O$ (Figure 4). At a 25 °C temperature, when the w/s ratio reached 100, the intensity of diffraction peaks characteristic of $AlF_3 \cdot 3H_2O$ decreased by 3.1 times (Figure 4). It was determined that, even when the w/s ratio was equal to 200, a small amount of the mentioned compound was present in SGW. Meanwhile, the increase of reaction temperature positively affected the decomposition of $AlF_3 \cdot 3H_2O$: when the temperature was equal to 45–55 °C, and $AlF_3 \cdot 3H_2O$ was fully removed from the solid (Figure 4).

Furthermore, the data of the chemical analysis of silica gel waste treated under static conditions at 25 °C (w/s = 100) showed that the amount of F^- ions released into the liquid medium was equal to ~49% from the total amount of mentioned ions in SGW (Table 1). However, when the water-to-solid ratio was increased two times, the amount of F^- ions released into the liquid medium increased slightly. It was also observed that, by increasing the w/s ratio from 2 to 100, the value of the pH of the liquid medium rose by two times (Table 1). It is worth noting that a higher reaction temperature has a positive effect on the quantity of released F^- ions as it increased by 4% and 9% after treatment at a 45 °C and 55 °C temperature, respectively. In spite of the mentioned fact, the value of the pH of the liquid medium was kept almost the same (Table 1). It is worth mentioning that Iljina et al. [17], reported that during the leaching of SGW, $AlF_3 \cdot 3H_2O$ fully decomposed when the water to solid ratio

was equal to 500; however, the concentration of F^- ions decreased slightly (~6% from total amount of F^- ions). The differences between the amount of F^- ions released from SGW (~8 times lower according to Iljina et al. [17]) can be explained by the short time of leaching (1 h), and as a result, compounds containing fluoride ions were not destructed. In addition, more successful results were obtained by Krysztafkiewicz et al. [42], where the F^- ions concentration was reduced by eight times; however, the initial concentration of mentioned ions was only equal to 1.6%, and there is no data about the water to solid ratio.
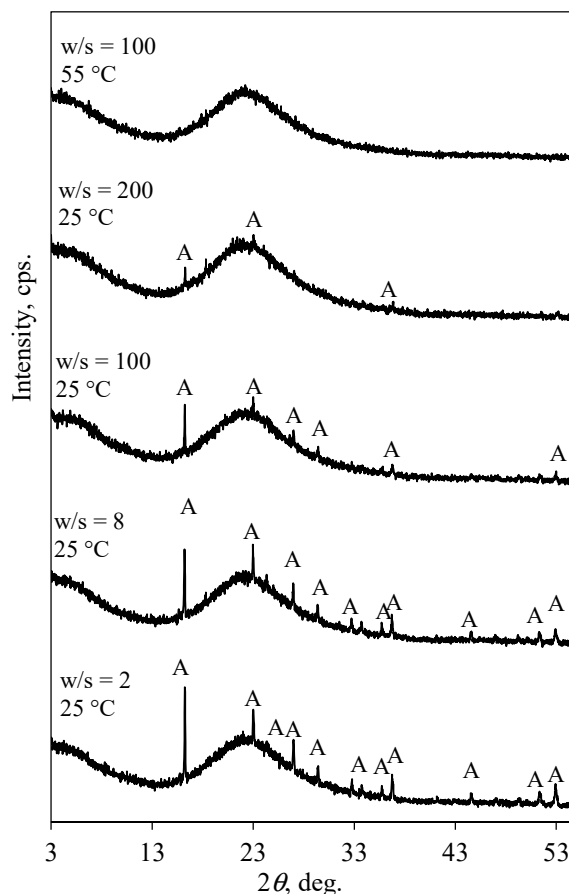

Figure 4. XRD patterns of silica gel waste samples after 24 h of leaching under static conditions. Indexes: A—AlF$_3$·3H$_2$O.

Table 1. The parameters of fluoride ions leaching under static conditions.

Sample Name *	The Amount of F^- Ions in Solid, %	The Amount of Released F^- Ions, %	pH of Liquid Medium
SGW-25 °C-2	-		1.53
SGW-25 °C-4	-		1.76
SGW-25 °C-6	-		1.95
SGW-25 °C-8	-		2.06
SGW-25 °C-100	5.08	49.3	2.94
SGW-25 °C-200	4.71	53.1	3.02
SGW-35 °C-100	4.92	50.9	2.94
SGW-45 °C-100	4.68	53.3	2.92
SGW-55 °C-100	4.21	58.0	2.90

*: the sample names were chosen according to the conditions of the experiment: SGW-25 °C-2—silica gel waste sample, when leaching temperature was equal to 25 °C and w/s ratio—2; SGW-25 °C-4—silica gel waste sample, when leaching temperature was equal to 25 °C and w/s ratio—4 and etc. While the label SGW-55 °C-100 meant the silica gel waste sample, when leaching temperature was equal to 55 °C and w/s ratio—100.

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 (Figure 5a). Meanwhile, in the sample after the treatment (w/s = 100, 25 °C), the mentioned agglomerates were disrupted and only globules with a size of ~0.5–1 μm of $SiO_2 \cdot nH_2O$ were observed (Figure 5b). Besides, the results of EDX analysis showed that F^- ions are distributed over the whole structure of silica gel waste (Figure 5c); while in a case of the treated sample, they are removed from its surface and are more concentrated in the center of the particles (Figure 5d).
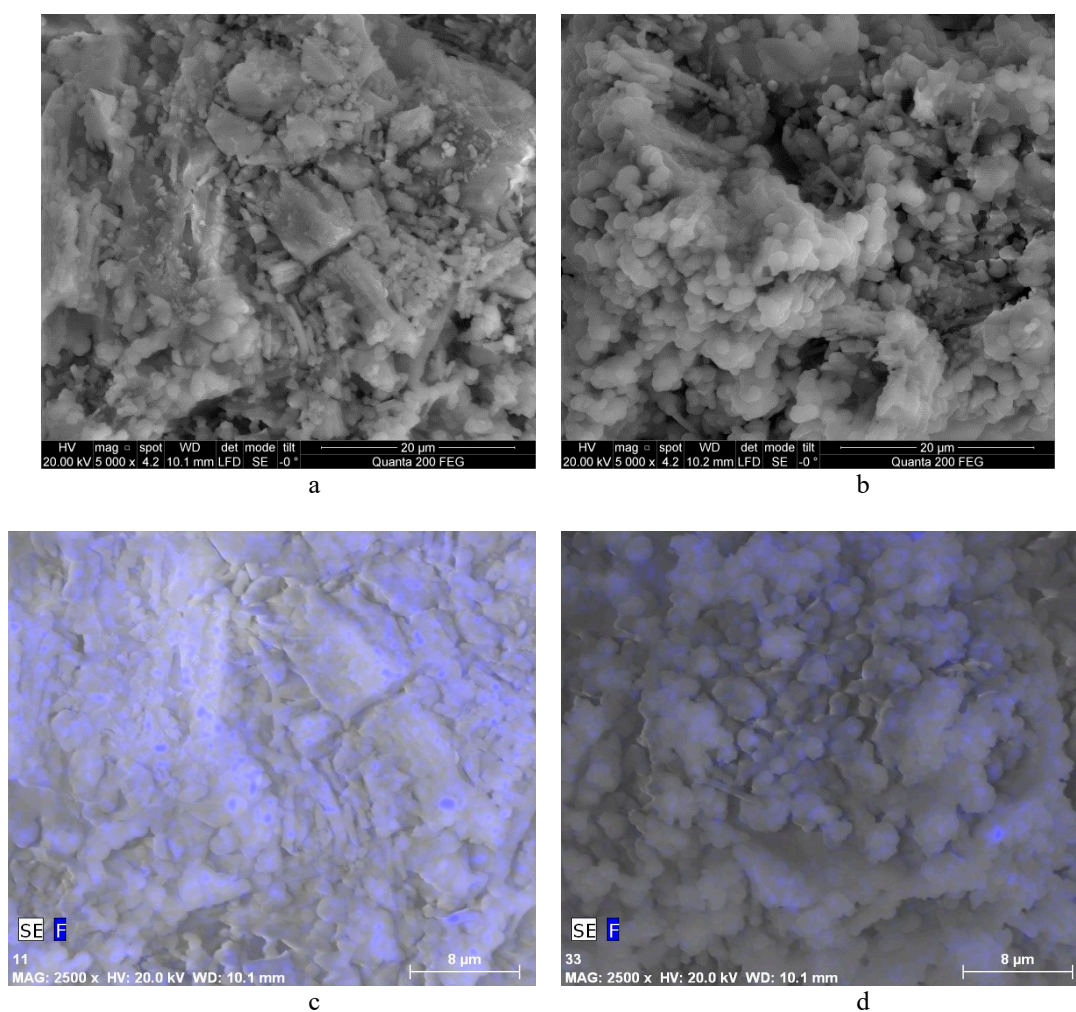

Figure 5. SEM micrographs (**a**,**b**) and EDX mapping (**c**,**d**) of SGW (**a**,**c**) and treated SGW (under static conditions, w/s = 100, 25 °C) (**b**,**d**) samples.

According to the previous results given in Figure 3, the influence of F^- ions leaching on the properties of SGW was examined at 50 and 188 °C temperatures. It was determined that both the density and loss on ignition strongly depend on the w/s ratio and temperature of the reaction. In comparison with untreated samples, due to the structural alterations of silica gel waste during the leaching of F^- ions, the density of the latter compound significantly increased from 2140 to 2708 kg/m^3 (Table 2). Meanwhile, the loss on ignition decreased with an increasing w/s ratio and temperature of the reaction (Table 2).

Table 2. The density and loss on ignition of silica gel waste before and after the leaching and calcination in a 50–188 °C temperature range.

Sample Name [*]	Density, kg/m^3	Loss on Ignition, %	
		Temperature, °C	
		50	188
Untreated SGW	2141	50.81	53.39
SGW-25 °C-2	2263	44.33	49.70
SGW-25 °C-100	2457	35.16	39.23
SGW-55 °C-100	2708	32.28	37.55

*: the sample names were chosen according to the conditions of the experiment: SGW-25 °C-20—silica gel waste sample, when leaching temperature was equal to 25 °C and w/s ratio—20; SGW-25 °C-100—silica gel waste sample, when leaching temperature was equal to 25 °C and w/s ratio—100; and SGW-55 °C-100—the silica gel waste sample, when leaching temperature was equal to 55 °C and w/s ratio—100.

Thus, it is clearly seen that after leaching under static conditions, the amount of F$^-$ ions in SGW can be reduced from 10% to lower than 5% and such a product can be sold worldwide [30]. 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 shorten the interaction time, in the next stage of this research, the leaching of F$^-$ ions was performed under dynamic conditions.

It was examined that the change in leaching conditions had an effect on the stability of AlF$_3$·3H$_2$O: under static conditions; when the w/s ratio was equal to 100, the intensity of diffraction peaks characteristic of AlF$_3$·3H$_2$O decreased by 3.1 times (Figure 4), while under dynamic conditions, by 1.23 times (w/s = 100) and 1.73 times (w/s = 200) (Figure 6). The XRD results were verified by the 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 (Table 3). This observation can be explained by the short interaction duration between the latter compound and liquid medium (Table 3).

Table 3. The parameters of F$^-$ ions leaching under dynamic conditions at 25 °C temperature by using different w/s ratios.

Sample Name [*]	The Amount of F$^-$ Ions in Solid, %	The Amount of Released F$^-$ Ions, %	pH of Liquid Medium	The Duration of Interaction, s
SGW-25	9.60	4.2	2.45	40
SGW-50	-	-	2.67	69
SGW-100	8.33	16.9	2.90	108
SGW-200	6.78	32.3	3.11	215

*: the sample names were chosen according to the conditions of the experiment: SGW-25—silica gel waste sample, in which w/s ratio was equal to 25; SGW-50—silica gel waste sample, in which w/s ratio was equal to 50; SGW-100—silica gel waste sample, in which w/s ratio was equal to 100; and SGW-200—silica gel waste sample, in which w/s ratio was equal to 200.

In order to prolong the duration of the interaction, the leaching under dynamic conditions was performed in cycles. A total count of 20 cycles were carried out during this experiment, in which a total amount of 10 g of SGW was treated with 50 mL of H$_2$O in each step (till the w/s ratio reached 100). The duration of each cycle lasted approximately 25 s, i.e., the total duration of the reaction was equal to ~500 s. It is worth mentioning that after each step, the liquid medium obtained was neutralized by passing it through calcium hydroxide. The neutralized water was returned to the leaching of SGW.
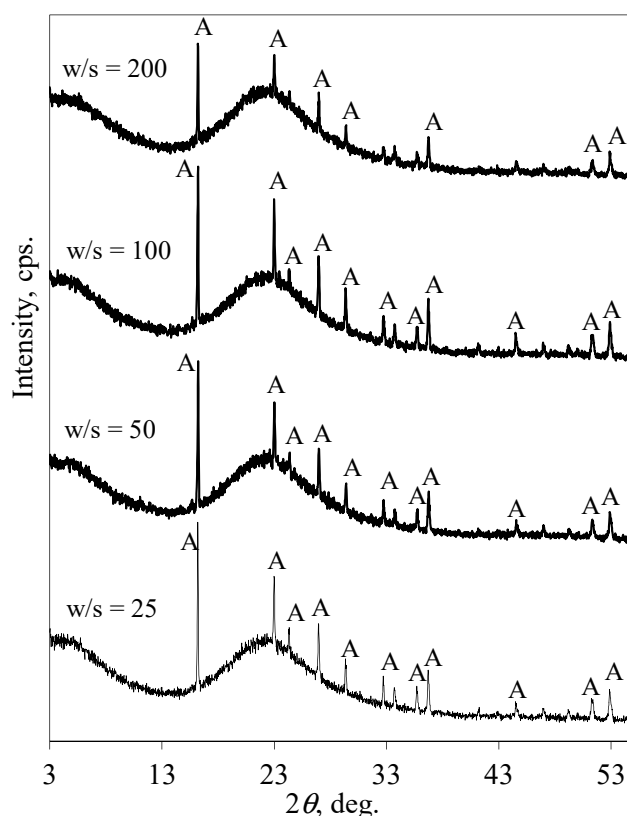
Figure 6. XRD patterns of silica gel waste samples after leaching under dynamic conditions at 25 °C. Indexes: A—$AlF_3 \cdot 3H_2O$.

As expected, due to the ~5 times longer interaction time, at a 25 °C temperature, the decomposition of $AlF_3 \cdot 3H_2O$ is more intensive compared with the previous results (Figures 6 and 7). To completely destroy the structure of crystalline compounds, the reaction temperature was increased to 35, 45, and 55 °C. It was determined that $AlF_3 \cdot 3H_2O$ became unstable in SGW, when the reaction temperature reached 45 and 55 °C, because only a broad peak typical to amorphous SiO_2 in a 18°–26° diffraction angle range was visible in the XRD pattern (Figure 7). It is worth mentioning that a similar tendency was obtained under static conditions (Figure 4); 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.

The results of the XRD analysis were in good agreement with the data of differential scanning calorimetry. When the reaction temperature was equal to 25 °C, the amount of adsorbed heat attributed to the dehydration of $AlF_3 \cdot 3H_2O$ at 180 °C decreased by almost two times: from 33.62 to 18.26 J/g, and at 35 °C—to 12.69 J/g (Figure 2; Figure 7). However, at a higher leaching temperature (45 and 55 °C), the dehydration of $AlF_3 \cdot 3H_2O$ was no longer observed (Figure 7). This fact allowed us to state that the latter compound is fully removed from silica gel waste. Moreover, due to the structural alterations of the mentioned compound, an endothermic effect at a ~182 °C temperature, which is assigned to the dehydration of silica gel waste, shifted to a higher temperature range (Figure 2; Figure 7). Besides, the amount of adsorbed heat during this process decreased from 59.33 to 39.68 J/g as a smaller quantity of moisture was present in this compound after leaching.

At the beginning of leaching in cycles, the value of the liquid medium pH rapidly increased until it reached a w/s ratio of 25 (Figure 8). However, when the duration of the reaction was extended, the mentioned values only slightly increased and at the end of the process, they were equal to 4.4–4.7. Presumably, at the beginning of the leaching, hexafluorosilicic acid and/or HF was removed from SGW and by continuing the mentioned process, the amount of released F^- ions strongly depended on the solubility of compounds, which contained F^- ions.
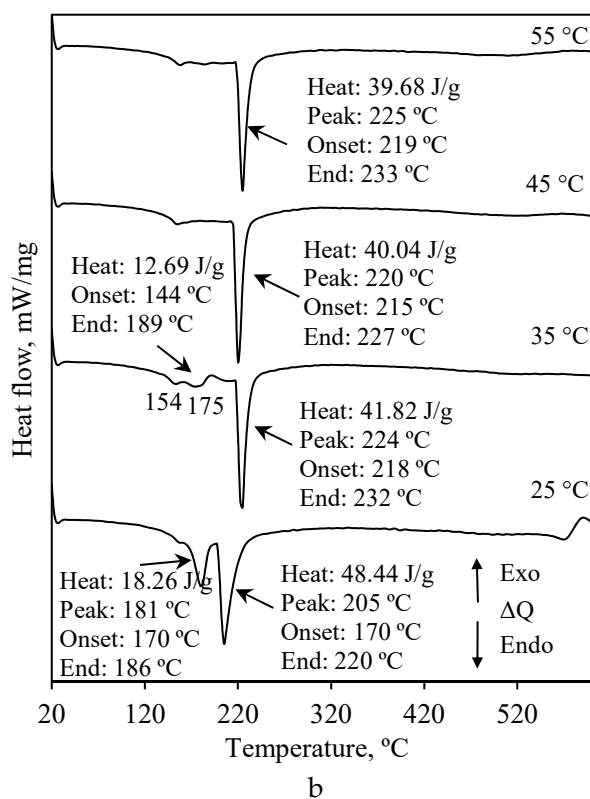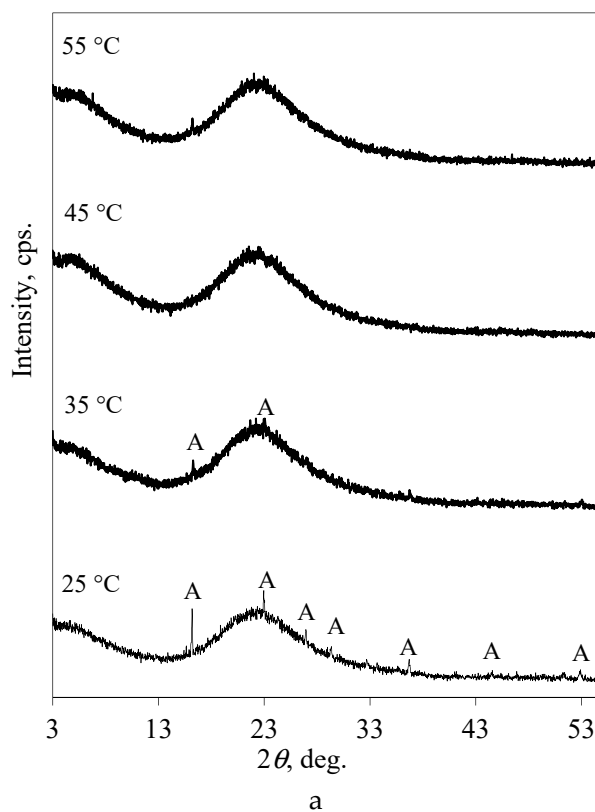
Figure 7. XRD patterns (**a**) and DSC curves (**b**) of silica gel waste samples after leaching in cycles (w/s = 100) under dynamic conditions at different temperatures. Indexes: A—$AlF_3 \cdot 3H_2O$.
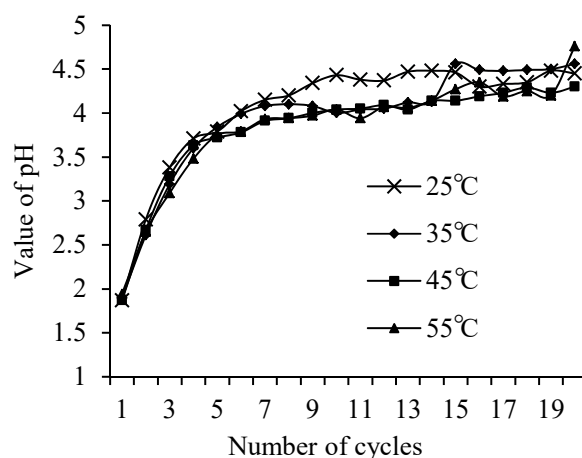
Figure 8. The change in the values of pH of liquid medium during leaching in cycles.

The chemical analysis data of SGW showed that, after leaching in cycles at 25 °C, the quantity of released F^- ions was equal to ~45.6% (w/s = 100) from the total amount of F^- ions in silica gel waste, which was almost the same as under the static conditions (Table 1) and ~2.7 times greater than under dynamic conditions (Table 3). The same tendency was observed at a higher temperature (Tables 3 and 4). Moreover, the reaction temperature had a positive effect on the amount of F^- ions released in the liquid medium (Table 4), because the best results (55.7%) were obtained after leaching at a 55 °C temperature.

Table 4. The amount of F^- ions in solid after leaching in cycles at different reaction temperatures, when the w/s ratio was equal to 100.

Sample Name [*]	The Amount of F^- Ions in Solid, %	The Amount of Released F^- Ions, %
SGW-25 °C	5.45	45.6
SGW-35 °C	4.92	50.9
SGW-45 °C	4.68	53.3
SGW-55 °C	4.44	55.7

[*]: the sample names were chosen according to the conditions of the experiment: SGW-25 °C—silica gel waste sample, when the reaction temperature was equal to 25 °C; SGW-35 °C—silica gel waste sample, when the reaction temperature was equal to 35 °C; SGW-45 °C—silica gel waste sample, when the reaction temperature was equal to 45 °C; and SGW-55 °C—silica gel waste sample, when the reaction temperature was equal to 55 °C.

As it was mentioned before, in order to neutralize the liquid medium obtained after leaching experiments, calcium hydroxide was used [31,32]. It was determined that calcium hydroxide reacted with both F^- and Al^{3+} ions as calcium fluoride (CaF_2; PDF 04-002-2191, *d*-spacing = 0.315, 0.193, 0.165 nm) and katoite ($Ca_3Al_{2.85}O_{2.55}(OH)_{9.45}$ PDF 04-017-1504, *d*-spacing = 0.509, 0.333, 0.279 nm) were identified in the XRD pattern after the experiment (Figure 9). The mentioned compounds formed under all experimental conditions. The obtained results were in good agreement with the literature data [31,32,42]. Meanwhile, the different results obtained by Iljina et al. [17] can be explained by their use of a different leaching technique: SGW with CaO additive (6.5–20%) was treated under static conditions (1 h, w/s-500), thus CaF_2 crystallized in solid and cannot be distinguished.

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, the w/s ratio, reaction temperature, leaching conditions, the adsorption properties of silica gel waste, and others. Despite the mentioned factors, the quantity of F^- can be reduced more than two times and the obtained products of SGW with a lower content of F^- (>5%) and CaF_2 can be reused in other industries.
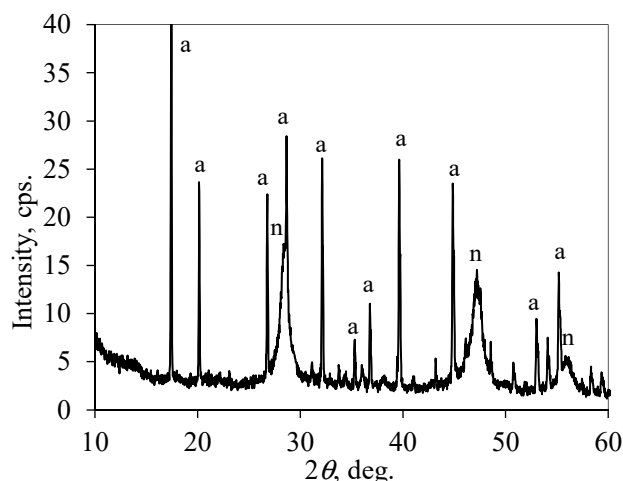
Figure 9. XRD patterns of calcium hydroxide after the neutralization experiment. Indexes: n—calcium fluoride, a—katoite.

3.3. Application of SGW for the Direct Hydrothermal Synthesis of Cuspidine

It is known that toxic ions can be reduced in two ways: by removing them or by reducing their mobility–immobilization. As the 3.2 part showed, the quantity of F^- was successfully reduced to less than 5% in SGW, while wastewater was neutralized with calcium hydroxide. Meanwhile, in order to expand the application areas of SGW, in the third part of this work, the possibility to reuse SGW for the synthesis of a stable compound containing F^- ions was determined.

It was determined that in a CaO–silica gel waste–H_2O mixture, when the molar ratio of CaO/SiO_2 was equal to 2, after 16 h of isothermal curing at 200 °C, the main compound containing F^- ions in silica gel waste, $AlF_3 \cdot 3H_2O$, was unstable and decomposed (Figure 10, curve 1). For this reason, due to the interaction between fluoride, calcium, and silicon ions, cuspidine (PDF 04-015-0711, *d*-spacing = 0.306, 0.290, 0.287 nm) was formed (Figure 10, curve 1). Together with this compound, 1.1 nm tobermorite (PDF 04-011-0271, *d*-spacing = 1.139, 0.308, 0.298 nm), katoite (PDF 00-024-0217, *d*-spacing = 0.513, 0.230, 0.204 nm), and traces of grossular (PDF 00-038-0368, *d*-spacing = 0.276, 0.226, 0.200 nm) were also identified in XRD patterns (Figure 10, curve 1). Furthermore, basic reflections (*d*-spacing = 0.493; 0.193; 0.179 nm) of partially unreacted portlandite (PDF 01-078-0315) were also noticed (Figure 10, curve 1). However, when the duration of synthesis was extended to 48 h, 1.1 nm tobermorite became metastable and recrystallized to other synthesis products (Figure 10, curve 3). Meanwhile, cuspidine remained stable under all hydrothermal synthesis conditions (Figure 10). The data of liquid medium analysis showed that during the hydrothermal synthesis, F^- ions were not released into the liquid medium, but instead, were combined into a stable compound.

Thus, the experimental studies showed that the reduction of mobility and/or removal of F^- ions from the SGW can be carried out under dynamic or hydrothermal conditions. Based on the data obtained in this study and already existing equipment in a Joint stock Company "Lifosa" [15], a principal technological scheme for reducing the quantity of F^- ions in silica gel waste or for its immobilization has been designed (Figure 11). For the synthesis of cuspidine, the required amount of SGW and lime is weighed (CaO/SiO_2 = 2.0), and supplied to a mixer (3), in which an appropriate quantity of water (w/s = 10) is added from the reservoir (2). The mixture of raw materials is then supplied to an autoclave (4) and the hydrothermal treatment is carried out: the synthesis temperature and duration are equal to 200 °C and 16 h, respectively. After isothermal curing, the product is filtered off by a vacuum belt filter (6). For the leaching of silica gel waste, SGW is supplied from the weight dispensers to a vacuum belt filter (6), where it is treated by adding a required amount of water (55 °C, w/s = 100). The obtained liquid medium with F^- ions is neutralized with calcium hydroxide on the second vacuum belt filter (6). Later on, liquid medium is returned to the water reservoir (2).

The obtained products (cuspidine, silica gel with a lower content of fluoride ions, and calcium fluoride) are stored in products silos (7).
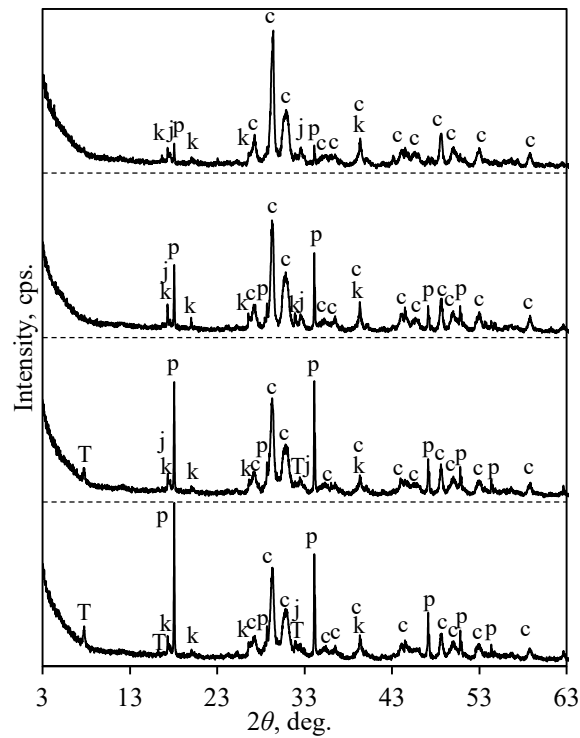

Figure 10. XRD patterns of synthesis products after 16 h (curve 1), 24 h (curve 2), 48 h (curve 3), and 72 h (curve 4) of isothermal curing. Indexes: c—cuspidine, p—portlandite, k—katoite, j—grossular, T—1.1 nm tobermorite.
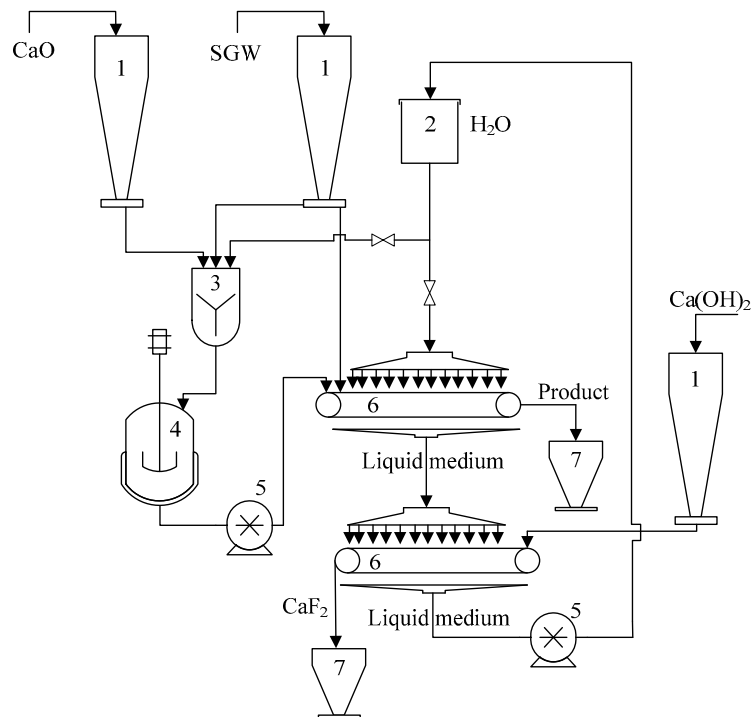

Figure 11. A principal technological scheme for silica gel waste neutralization/utilization: 1—raw materials silos, 2—water reservoir, 3—mixer, 4—autoclave, 5—pump, 6—vacuum belt filter, 7—products silos.

4. Conclusions

1. It was determined that silica gel waste mainly consists of silicon dioxide (79%) and other compounds containing 10% F^- and 2.5% Al^{3+} ions. It was observed that three endothermic effects are characteristic of this compound: a two-step decomposition of $AlF_3 \cdot 3H_2O$ at 146 and 165 °C temperatures and the dehydration of silica gel at 188 °C. Moreover, the evaluation of the thermal stability of SGW showed that $AlF_3 \cdot 3H_2O$ was fully decomposed at 188 °C, while at a higher calcination temperature (1000 °C), mullite was formed due to the reaction between aluminium-containing components and SiO_2.

2. The findings revealed that, by applying different leaching techniques of F^- ions (leaching under static and dynamic in cycles conditions), it is possible to reduce the amount of mentioned ions in silica gel waste to less than 5%. The obtained water contaminated with F^- ions was neutralized with calcium hydroxide and as a result, calcium fluoride and katoite were produced.

3. Silica gel waste is a promising raw material for the hydrothermal synthesis of cuspidine ($3CaO \cdot 2SiO_2 \cdot CaF_2$), because this compound formed after 16 h and remained stable till 72 h of synthesis. The data of the liquid medium analysis showed that during synthesis, F^- ions were not released into the liquid medium, but instead, were combined into a structure of cuspidine. A principal technological scheme has been designed for the products of commercial value.

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