

Article



The Effect of Various Hydroxide and Salt Additives on the Reduction of Fluoride Ion Mobility in Industrial Waste

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Abstract: In this work, the influence of various hydroxide and salt additives on the removal of F^- ions from silica gel waste, which is obtained during the production of AlF₃, was examined. The leaching of the mentioned ions from silica gel waste to the liquid medium was achieved by the application of different techniques: (1) leaching under static conditions; (2) leaching under dynamic conditions by the use of continuous liquid medium flow; and (3) leaching in cycles under dynamic conditions. It was determined that the efficiency of the fluoride removal from this waste depends on the w/s ratio, the leaching conditions, and the additives used. It was proven that it is possible to reduce the concentration of fluorine ions from 10% to <5% by changing the treatment conditions and by adding alkaline compounds. The silica gel obtained after the leaching is a promising silicon dioxide source.

Keywords: fluorine ions; silica gel waste; leaching; hydroxide additives



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1. Introduction

Waste management and the reduction of pollution are the priority areas of environmental protection in the World [1–4]. According to the data of Eurostat [5], the European Union generates approximately 180 million tons of manufacturing waste every year. From an economic point of view, it is preferable to store waste in landfill sites, but they occupy large areas, and are concentrated sources of air, groundwater and soil pollution [6–10]. Therefore, the search for attractive industrial waste recycling treatments, which will allow us to develop products of high value, has become very important.

The global production of aluminum fluoride (AlF₃) reaches 1 million tons per year, while the amount of generated waste is more than 3 million tons [11–14]. It is worth noting that more than 60% of this waste is contaminated with fluorine ions, the concentrations of which can reach up to 10%. According to the literature, more than 20% of the aluminum fluoride in the world is produced by neutralizing hexafluorosilicic acid with aluminum hydroxide [11,13,15]:

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

However, during the acid neutralization, about 0.67 tons of silica gel contaminated with fluoride ions are generated and stored in the landfill sites [11,13,15-17]. Furthermore, many manufacturers use an amount of hexafluorosilicic acid (H₂SiF₆) in excess of the amount that the added aluminum hydroxide would fully react, and the yield of aluminum fluoride would increase [11-18]. However, very low pH values of the obtained system are produced, leading to the strong chemisorption properties of silica gel for fluoride ions [17,19-21]. For this reason, the purification of this material has become a great challenge [19]. Few attempts have been made to reduce the amount of fluoride ions in silica gel waste by leaching [22,23]. None of the experiments were successful enough.

For this reason, the scientific literature is mostly focused on the search for alternative routes, using silica gel waste as a raw material for the synthesis of commercial value products, or as an additive in binding materials [17,20–22,24,25]. Vaiciukyniene et al. [17,26] investigated the possibility of the utilization of silica gel waste in cement stone. The authors found that the compressive strength of the standard concrete samples decreased by increasing the amount of silica gel waste (up to 15%). Furthermore, these authors determined that the addition of 10% silica gel waste calcined at 800 °C (1 h) had a positive effect on the compressive strength values of the samples, which increased by ~5–7 MPa. However, these studies did not provide any data on the stability of the fluoride ions in cement stone or during calcination.

In other research, silica gel waste was used for the production of alkali-activated blends [27]. It was found that the compressive strength values of hardened samples of silica gel and clay, which were additionally treated with sodium hydroxide and calcined at 600 °C (3 h), were equal to 6–17.50 MPa. Krivenko et al. [28] investigated the influence of sodium silicate (Na₂SiO₄) activated silica gel waste on the hydration characteristics of cement samples. It was found that the additive changes the mechanism of early hydration: (1) increase the amount of heat released during the main hydration reaction; (2) prolong the duration of the induction period; and (3) promote the crystallization of both crystalline and amorphous calcium silicates hydrates and calcium aluminate hydrates. The discussed studies [17,26–28] did not determine the durability of the samples or the stability of the fluorine ions.

R. Kaminskas et al. [21,25,29,30] found that, after the calcination of a mixture containing 20% clay and 80% silica gel waste at 600 °C, its pozzolanic activity increased two times, equal to 230–260 mg CaO/g. Further studies have shown that, in order to bind fluorine ions to the stable compounds, 10–20% limestone must be used in the production of the pozzolanic additive. It was also found that by replacing a part of the cement with a synthetic additive (5–15 wt%) in the concrete products, the compressive strength values of the samples increased to 5%.

Another potential application of silica gel waste is the synthesis of calcium silicates hydrates [21,31]. However, the obtained products contain fluoride ions which limit their application. Furthermore, silica gel waste can be used for the synthesis of NaA zeolite [20]. The authors found that this zeolite can be synthesized by the sonication of suspensions of silica gel, aluminum hydroxide, sodium hydroxide, and water. Finally, Sarkar et al. [32] found that the use of silica gel with impurities in the production of white porcelain can reduce the burning temperature of products without compromising their performance.

However, the applicability of the mentioned products is limited due to the presence of fluorine ions in the structure of the final product. Therefore, another method could be to leach it from silica gel waste, which later on could be used as an adsorbent or silica source. In the previous work [19], it was determined that it is possible to reduce the quantity of F^- ions by more than two times by applying different leaching techniques. However, due to the strong adsorption properties of silica gel waste, the amount of water required for the leaching process is very high (w/s = 100). It is known that, by increasing the pH values of system up to >4, the framework of silica gel is destroyed and it loses its adsorption properties. In order to increase the mentioned value, silica gel waste should be treated using alkaline (various synthetic or natural) additives, which could improve the physicochemical properties of amorphous silicon dioxide (SiO₂·nH₂O). On the other hand, by using additives at the same time, the formation of other by-products could be avoided.

For this reason, the aim of this work is to determine the influence of various hydroxide and salt additives on the removal of F^- ions from the silica gel waste obtained from the production of AlF₃.

2. Materials and Methods

2.1. Materials

Silica gel waste (SGW)—i.e., a waste product of the production of AlF₃ in the chemical plant of JSC 'Lifosa' (Kėdainiai, Lithuania)—was dried for 48 h at 50 °C. The XRF analysis data showed that SGW consists of 36.2% silica (which is equivalent to 78.9% SiO₂), 2.5% Al³⁺ ions, and traces of other elements. Meanwhile, the chemical analysis data showed that SGW contains 10.0% F⁻ ions. These results were in good agreement with the data of the XRD analysis: aluminum fluoride trihydrate (AlF₃·3H₂O) 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 (Figure 1). The results of the particle size distribution analysis showed that the diameter of the SGW particles varied within the 0.03–170 µm range, while particles with a size of 34–72 µm were dominant. It was also determined that the surface area and the density of the silica gel waste were equal to 281.01 m²/kg and 2141 kg/m³, respectively. The detailed description of the SGW's chemical and physical properties are available in reference [19].



Figure 1. XRD patterns of the SGW. Indexes: A—AlF₃·3H₂O.

Chemicals of the following characteristics were used: aluminum hydroxide (Al(OH)₃, 'Honeywell', Düsseldorf, Germany) purity > 99%; calcium hydroxide (Ca(OH)₂, 'Stanchem Sp. J.', Niemce, Poland), purity > 97%; potassium hydroxide (KOH, 'Reachem', Petrzalka, Slovakia), purity > 99%; sodium hydroxide (NaOH, 'Reachem', Petrzalka, Slovakia), purity > 99%; potassium chloride (KCl, 'Honeywell', Düsseldorf, Germany), purity > 99%; ammonium hydroxide (NH₄OH, 'Lachema', Reckovice, Czech Republic, and JSC 'Lifosa').

2.2. Methodology

In this work, the following leaching experiments were performed:

(1) The leaching of F⁻ ions under static conditions: silica gel waste was mixed with the required amount of additive and liquid medium, and kept for 24 h at 25 °C. After the leaching, the suspensions were filtered off, and the products were dried at 50 \pm 5 °C for 24 h.

(2) The leaching of F⁻ ions by the use of continuous liquid medium (by applying vacuum 0.6–0.7 bar) flow, which was applied to silica gel waste. After the process, the products were dried at 50 \pm 5 °C for 24 h.

(3) The leaching of F^- ions in cycles by the use of continuous liquid medium flow. In total, 10 g SGW was treated with 50 mL liquid medium in each step until the w/s

ratio reached 10–100. After each cycle, the obtained products were filtered off and dried (50 \pm 5 °C; 24 h) at the end of the process.

The X-ray diffraction analysis (XRD) was performed on a D8 Advance diffractometer (Bruker AXS, Karlsruhe, Germany) operating at U = 40 kV and I = 40 mA. The X-ray beam was filtered with Ni 0.02 mm filter in order to select the CuK α wavelength. The diffraction patterns were recorded in a Bragg–Brentano geometry by the use of a fast counting detector Bruker LynxEye. The samples were scanned over the range $2\theta = 3-70^{\circ}$ at a scanning speed of 6° min⁻¹.

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

For the determination of the fluoride in the solid, a 1 g sample was placed on a platinum plate and mixed with 10 g NaOH and KOH mixture (5:7). After that, the platinum plate was placed on the sand bath and heated until the mixture was melted. During the heating, the mixture was vigorously stirred with a platinum spatula before being left to cool down. Afterward, 150 cm³ distilled water was poured into the platinum plate and heated on the sand bath until the formed salts were melted. Then, in order to bind the fluoride ions, 15 g chemically pure (NH₄)₂CO₃ powder was added into the solution and evaporated until a dry salt was formed. After that, the residue was mixed with 150 cm³ distilled water and heated. A hot solution with precipitates was poured into a 250 cm³ flask and cooled down. Then, it was diluted with water to the indicated level and filtered off. Before the measurements were taken, TISAB II was added to each sample (volume ratio 1:1).

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

3. Results and Discussion

3.1. The Effect of Aluminium Hydroxide on the Mobility of F^- Ions in the Silica Gel Waste Samples

It is known that aluminum hydroxide has amphoteric properties, i.e., it is able to donate or accept protons and react with both acids and bases. Furthermore, $Al(OH)_3$ dissolves in water, and—under certain conditions—produces H⁺ or OH⁻ ions:

$$3\mathrm{H}^{+} + \mathrm{AlO}_{3}^{3-} \leftrightarrow \mathrm{Al}^{3+} + 3\mathrm{OH}^{-}$$
⁽²⁾

As the pH of the silica gel waste is strongly acidic, different amounts of aluminum hydroxide, which were equivalent to 2.5, 5, 7.5 and 10% Al³⁺ ions from the mass of the dry materials, were added to the SGW samples and mixed in a homogenizer (Turbula type T2F) for 1 h at 30 rpm. Later, the samples were treated with water under static and dynamic conditions.

It was determined that, after 24 h of the treatment of the SGW with Al(OH)₃ additive (2.5–10%) under static conditions, the intensity of the diffraction peaks characteristic to AlF₃·3H₂O only slightly decreased, when the water-to-solid ratio was equal to 6 (Figure 2). Meanwhile, the intensity of the main diffraction maximum of Al(OH)₃ (d-spacing: 0.547 nm) increased from 0 (without additive) to 185 cps (when 10% additive was used). Meanwhile, the increment of the water-to-solid ratio to 100 had a positive effect on the decomposition of the AlF₃·3H₂O in the mixtures with 2.5% Al³⁺ ions, because the intensities of the diffraction maximums typical to the latter compound decreased more than five times (Figure 2). It should be noted that, when the Al(OH)₃ additive is not used and the SGW is treated with water (w/s = 100, 24 h), the intensity of the diffraction peaks characteristic of AlF₃·3H₂O decreased only three times [19].



Figure 2. XRD patterns of the products obtained after the treatment of SGW with Al^{3+} ions under static conditions. Indexes: *A*—AlF₃·3H₂O; *g*—Al(OH)₃.

Moreover, it was found that the pH values of the liquid medium separated from the SGW samples after the treatment with water (w/s = 6) depended on the amount of Al³⁺ ions used (Table 1). When 2.5% of the mentioned ions were added to the system, the pH of the liquid medium reached 2.54; meanwhile, at higher concentrations of Al³⁺ ions (\geq 5%), this parameter was increased to 4.41–4.73 (Table 1). It should be noted that, in the same treatment conditions, the pH value of the liquid medium was ~2.4 times higher in comparison with the samples without aluminum ions [19]. However, the amount of F⁻ ions released to the liquid medium was insignificant (Table 1).

Table 1. The amount of F^- ions and the pH values of the liquid medium after the treatment of the SGW with Al^{3+} ions under static conditions.

The Amount of Al ³⁺ Additive, %	w/s Ratio	The Concentration of F^- Ions in the Sample, %	The Amount of Released F ⁻ Ions, %	The pH Value of the Liquid Medium
2.5	6	-	-	2.54
5	6	-	-	4.41
7.5	6	-	-	4.60
10	6	9.51	5.18	4.73
2.5	100	4.47	55.43	3.06

Furthermore, when the w/s ratio was increased to 100 and 2.5% Al^{3+} ions were used, the pH value of the liquid medium reached 3.06 (Table 1). In this case, more than 55% of the initial amount of F^- ions were released from the structure of the sample into the liquid medium (Table 1). It should be noted that this is ~6% more than in the samples without an additive [19].

Since the amount of Al(OH)₃ additive does not affect the stability of AlF₃·3H₂O, the leaching in cycles under dynamic conditions (10 g SGW was treated with 50 mL liquid medium) was achieved by the use of Al(OH)₃, the quantity of which corresponded to 2.5% Al³⁺ ions. It was determined that the intensities of the diffraction peaks characteristic to AlF₃·3H₂O only slightly decreased, and the concentration of F⁻ ions decreased only to ~9% when the w/s ratio was equal to 20 (Figure 3, Table 2). By increasing the w/s ratio to 100, it was observed that a small amount of AlF₃·3H₂O was still present in the sample,

because only low intensity diffraction peaks were identified in the XRD patterns (Figure 3). Moreover, the quantity of the fluorine ions released into the liquid medium was estimated to be ~2.5% higher (Table 2) than in the samples treated under static conditions (Table 1).



Figure 3. XRD patterns of the products obtained after the treatment of SGW with Al^{3+} ions in cycles under dynamic conditions. Indexes: *A*—AlF₃·3H₂O; *g*—Al(OH)₃.

Table 2. The concentration of F^- ions in the SGW with 2.5% Al³⁺ ions after treatment in cycles under dynamic conditions.

Number of Cycles	w/s Ratio	The Concentration of F^- Ions in the Sample, %	The Amount of Released F^- Ions, %
4	20	9.06	9.67
20	100	4.22	57.93

The results of the liquid medium analysis showed that the duration of one cycle (filtration/interaction) was equal to ~40 s; thus, the total interaction time was 13 min, which is significantly shorter in comparison to the static conditions (24 h). Moreover, the pH value of the liquid medium reached ~3 when the w/s ratio was equal to 10 (Figure 4). The further increment in the w/s ratio (30–100) resulted in a pH value of 4.2.



Figure 4. The change in the pH values of the liquid medium during the treatment in cycles.

In a previous work, it was determined that, by the use of treatment with water at 25 °C, the F⁻ ion concentration in silica gel waste can be reduced by up to 49% [19]. Meanwhile, by adding 2.5% Al³⁺ ions to SGW, the F⁻ ion concentration can be reduced by up to 58% (Tables 1 and 2). Thus, it can be stated that the Al(OH)₃ additive positively affected the removal of F⁻ ions from the structure of the silica gel in the liquid medium.

In the next part of this work, it was decided to investigate the influence of another hydroxide (calcium hydroxide) on the mentioned process.

3.2. The Effect of Calcium Hydroxide on the Mobility of F^- Ions in Silica Gel Waste Samples

According to the literature [33,34], the application of $Ca(OH)_2$ can not only induce the release of F^- ions, but can also bind these ions into a stable calcium fluoride compound (CaF₂).

The treatment of contaminated silica gel with a Ca(OH)₂ additive was first performed under static conditions. In order to decrease the amount of F⁻ ions, 6.5 and 20% Ca(OH)₂ were added to the SGW sample, along with a w/s ratio equal to 10 and a treatment temperature of 25 °C. It is worth noting that the maximum amount of the additive (20%) was sufficient enough to combine all of the fluorine ions into CaF₂. It was determined that, after the treatment of the SGW samples with 6.5% Ca(OH)₂, the AlF₃·3H₂O was fully decomposed, and the F⁻ ions were bound into CaF₂ (Figure 5). Furthermore, aluminum fluoride hydroxide hydrate (AlF_{1.5}(OH)_{1.5}·0.375H₂O; *d*-spacing: 0.568, 0.296, 0.284 nm), a product of AlF₃·3H₂O decomposition, was identified in the XRD patterns. Moreover, the increment in the quantity of the additive to 20% did not affect the mineral composition of the formed compounds (Figure 5). The results of chemical analysis showed that, in both cases, F⁻ ions were not released into the liquid medium. Furthermore, it was found that the amount of the additive determined the pH of the liquid medium, the values of which were equal to 7.1 (by the use of 6.5% Ca(OH)₂) and 11.7 (by the use of 20% Ca(OH)₂).



Figure 5. XRD patterns of the products obtained after the treatment of SGW with 6.5% Ca(OH)₂ under static conditions (24 h, w/s = 10). Indexes: n—CaF₂; x—AlF_{1.5}(OH)_{1.5}·0.375H₂O; k—CaCO₃.

It can be stated that the Ca(OH)₂ additive has a positive effect on AlF₃·3H₂O decomposition; however, the F⁻ ions were bound into CaF₂, or were absorbed into the silica gel sample and remained in the solid material. Similar results were obtained by Iljina et al. [22]. These authors showed that, by treating SGW under static conditions at different temperatures and w/s ratios, the F⁻ ion concentration can be reduced to only 6–7 wt%. For this reason, in the next stage of this work, the silica gel samples were treated with a saturated Ca(OH)₂ solution under dynamic conditions.

It was determined that the treatment conditions affect the stability of $AlF_3 \cdot 3H_2O$ and the removal of F^- ions. After the leaching of the F^- ions by the use of continuous liquid medium flow (w/s = 25, 50, 100), low diffraction peaks characteristic of $AlF_3 \cdot 3H_2O$ and its decomposition product, $AlF_{1.5}(OH)_{1.5} \cdot 0.375H_2O$, were still observed in the XRD patterns (Figure 6, curves 1–4). As expected, together with the mentioned compounds, CaF_2 and $CaCO_3$ (formed due to the interaction between $Ca(OH)_2$ and atmospheric CO_2) were detected. Meanwhile, when the silica gel waste was treated in cycles (w/s = 100), $AlF_3 \cdot 3H_2O$ was completely decomposed. However, alongside CaF_2 and $CaCO_3$, two diffraction peaks (*d*-spacing: 0.762, 0.385 nm)—which did not correspond to any compound indexed in the PDF–4 database—were also noted (Figure 6). Calcium aluminates with unknown structures and compositions were probably formed during the leaching.



Figure 6. XRD patterns of the products obtained after the treatment of SGW with saturated Ca(OH)₂ solution (curves 1–4) under dynamic conditions, and the precipitates formed in the liquid medium (curve 5). Indexes: *A*—AlF₃·3H₂O; *n*—CaF₂; *x*—AlF_{1.5}(OH)_{1.5}·0.375H₂O; *b*—Ca₃Al_{2.85}O_{2.55}(OH)_{9.45}; *k*—CaCO₃.

Regardless of the chosen treatment method (in cycles or not), fine solid particles were formed after the filtration in the liquid medium (Figure 7). For this reason, in order to induce the sedimentation and chemical reaction, the liquid medium was additionally maintained for 24 h under static conditions. Later on, the obtained precipitates were filtered and dried at 50 ± 5 °C for 24 h. The XRD analysis of the precipitates showed that, during the leaching experiments, Ca(OH)₂ reacted with both fluoride and aluminum ions (formed by the decomposition of AlF₃·3H₂O) ions, which lead to the formation of CaF₂ and katoite (Ca₃Al_{2.85}O_{2.55}(OH)_{9.45}, *d*-spacing: 0.509, 0.333, 0.279 nm) in the products

(Figure 6, curve 5). It is worth mentioning that $CaCO_3$ and two diffraction maximums (d-spacing: 1.248, 0.627 nm), which did not correspond to any compound indexed in the PDF–4 database, were observed in the XRD patterns of the obtained precipitates as well (Figure 6, curve 5). Based on the obtained results, it can be stated that the rate of CaF_2 crystallization was great; therefore, this compound was detected in both the solid material and the precipitates. The obtained results were in good agreement with the literature data [23,33,34].



Figure 7. The optical images of the liquid medium obtained after the treatment of SGW with saturated Ca(OH)₂ solution under dynamic conditions: (**a**) leaching by the use of continuous liquid medium flow (w/s = 100); (**b**) leaching in cycles (w/s = 100).

It was determined that, after the treatment of the SGW with the saturated Ca(OH)₂ solution under dynamic conditions, the pH values of the liquid medium were greater than 8, i.e., the liquid medium had alkaline properties (Table 3). Meanwhile, in a case of the samples with Al(OH)₃, the pH of the liquid medium was acidic (Table 1). It was measured that the duration of the interaction (filtration) depends on the amount of water, and it increased from 55 s (w/s = 25) to 283 s (w/s = 100) (Table 3). The chemical analysis data of the treated SGW (w/s = 100) showed that the amount of F⁻ ions released into the liquid medium was two times higher in comparison to the value obtained after the treatment of SGW without the additives (16.9%) [19].

Table 3. The amount of F^- ions and the pH values of the liquid medium in the SGW samples after the treatment with a saturated Ca(OH)₂ solution under dynamic conditions.

No. of Cycles	w/s Ratio	The Concentration of F ⁻ Ions in the Sample, %	The Amount of Released F Ions, %	The pH Value of the Liquid Medium	The Duration of Interaction, s
25	1	-	-	8.61	55
50	1	-	-	11.67	107
100	1	6.50	35.19	12.03	283
100	20	6.02	39.98	-	-

It was determined that, after the treatment of the samples in cycles—already at the beginning of the process (w/s = 10)—the pH of the liquid medium was alkaline, i.e., pH > 7 (Figure 8, curve 2). Meanwhile, after 4 cycles (w/s = 20), the values of the pH of the liquid

medium became equal to the ones of the initial solution, and the further increment in the w/s ratio had no effect on the latter values. It was observed that, under these experimental conditions, the duration of the interaction (filtration) depended on the number of cycles, i.e., the duration increased with each cycle, and was more than five times longer at the end of the process (112 s) than at the beginning (21 s) (Figure 8, curve 1). Presumably, this was caused by the crystallization of CaF₂ and/or Ca₃Al_{2.85}O_{2.55}(OH)_{9.45} in the filter pores. Although the duration of the interaction (filtration) was longer than it was in the samples with Al(OH)₃ (40 s), the amount of F⁻ ions released into the liquid medium (39.98%) during the treatment in cycles was ~18% lower than the amount formed by the use of the Al(OH)₃ additive (Tables 2 and 3). The greater amount of residual F⁻ ions can be explained by the fact that CaF₂ remains in the sample (Figure 6). The chemical analysis data of the liquid medium showed that all of the F⁻ ions were combined to CaF₂, because the mentioned ions' concentration did not exceed 0.001%. Thus, the calcium ions influenced both the composition (mineral and chemical) and the properties of the silica gel waste and the liquid medium.



Figure 8. The change in the duration of the filtration (curve 1) and the pH values of the liquid medium (curve 2) during the treatment of the SGW with a saturated Ca(OH)₂ solution in cycles.

As can be seen from the results obtained in parts 3.1 and 3.2, the hydroxide additives not only promote the release of fluorine ions into the liquid medium but also alter the mineral composition of the silica gel waste. Therefore, it was decided to treat the investigated samples with soluble alkaline solutions.

3.3. The Effect of Alkaline Solutions on the Mobility of F^- Ions in Silica Gel Waste Samples

In this part of work, the NaOH and NH₄OH solutions were used for the leaching of the F⁻ ions in the experiments. At the beginning, the treatment of the SGW with 0.01% and 0.05% NaOH solutions under dynamic conditions was performed. It was determined that the NaOH solutions (w/s = 20) do not have a significant influence on the stability of AlF₃·3H₂O, because the intensities of the diffraction maximums typical to the latter only slightly decreased (Figure 9). Furthermore, low intensity diffraction peaks characteristic of AlF_{1.5}(OH)_{1.5}·0.375H₂O were detected.





Figure 9. XRD patterns of the products obtained after the treatment of SGW with an NaOH solution in cycles. Indexes: A—AlF₃·3H₂O; x—AlF_{1.5}(OH)_{1.5}·0.375H₂O.

Moreover, it was found that the duration of the interaction (Table 4) was very close to the one obtained by the treatment of the SGW sample with distillated water (20–30 s). Meanwhile, the pH value of the liquid medium had already reached more than 3 at the beginning of the process (w/s = 10). It should be indicated that the pH values of the initial NaOH solutions were equal to 11.17 (0.01%) and 11.73 (0.05%).

Table 4. The change in the pH values of the liquid medium and the duration of the interaction during the treatment with an NaOH solution in cycles.

	The Concentration of NaOH Solution, %				
No. of Cycles	0.01		0.05		
	The pH Values of the Liquid Medium	The Duration of Interaction, s	The pH Values of the Liquid Medium	The Duration of Interaction, s	
1	2.08	29	2.13	24	
2	3.03	28	3.96	22	
3	4.15	27	6.92	34	
4	6.38	30	7.06	30	

The results of the chemical analysis showed that, after treatment with a 0.05% NaOH solution (w/s = 20), the concentration of fluorine ions in the SGW sample decreased by ~1.6 times, i.e., to 6.23%. Although the diffraction peaks characteristic of $AlF_3 \cdot 3H_2O$ remained intensive, the intense release of fluorine ions into the liquid medium proceeded.

Due to the intense release of fluorine ions into the liquid medium, during the leaching experiments with the NaOH solution, it was decided to use 0.01% and 0.5% ammonia water solutions—which are currently applied in JSC 'Lifosa'—for further research.

The treatment of the SGW samples was performed in cycles when the maximum w/s ratio 20 was used (four cycles in total). It was determined that a slight decrease in the intensities of the diffraction peaks typical to $AlF_3 \cdot 3H_2O$ was observed in the XRD patterns when the sample was treated with a 0.01% ammonia water solution (w/s = 20) (Figure 10). Meanwhile, after the treatment with a more highly-concentrated solution (0.5%, w/s = 10), it was noted that $AlF_3 \cdot 3H_2O$ fully recrystallized to $Al(OH,F)_3$ (*d*-spacing: 0.570, 0.289, 0.284, 0.189 nm).



Figure 10. XRD patterns of products obtained after the treatment of SGW with NH₄OH solution in cycles. Indexes: A—AlF₃·3H₂O; v—Al(OH,F)₃.

It was measured that, when the silica gel waste was treated with 0.01% ammonia water, the filtration time and the pH values increased with the increasing w/s ratio, and at the end of the experiment (w/s = 20) were equal to 55 and 6.54 s, respectively (Table 5). Meanwhile, after the treatment with a higher concentration of the solution, the structure of the silica gel was destroyed, and fine particles clogged the pores of the filter, because even by applying vacuum 0.6–0.7 bar, ~900 s (cycle 1) and ~6000 s (cycle 2) filtration durations were reached (Table 5). Thus, the w/s ratio was not increased to 20. It is worth noting that the pH values obtained in these conditions were >8.

Table 5. The change in the pH values of the liquid medium and the duration of the interaction during the treatment wi	th
NH ₄ OH solution in cycles.	

	The Concentration of NH ₄ OH Solution, %			
No. of Cycles	0.01		0.5	
	The pH Values of the Liquid Medium	The Duration of Interaction, s	The pH Values of the Liquid Medium	The Duration of Interaction, s
1	2.02	26	8.51	900
2	3.36	34	9.59	6000
3	6.30	40	-	-
4	6.54	55	-	-

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 the NH₄OH solution (Table 6). It was found that, after treatment with 0.01% ammonia water (w/s = 20), the amount of F^- ions released was almost three times lower that than in the sample which was treated with 0.5% ammonia water (w/s = 10) (55.04%). It should be noted that a similar amount of fluorine ions were released into the liquid medium (>50%) obtained by treating the SGW only with a high volume of water (w/s = 100) (Tables 1 and 2). Thus, it can be stated that the structure of the SGW decomposes in NH₄OH solution, and that the SGW lost its adsorption properties.

No. of Cycles	w/s Ratio	The Concentration of NH4OH Solution, %	The Concentration of F ⁻ Ions in the Sample, %	The Amount of Released F^- Ions, %
4	20 10	0.01	8.02	20.04
Z	10	0.5	4.51	55.04

Table 6. The amount of F^- ions in contaminated silica gel samples after treatment with NH₄OH solution under dynamic conditions.

3.4. The Effect of a Combined Treatment on the Mobility of F^- Ions in Silica Gel Waste Samples

As can be seen from the results discussed above that the pH value of the liquid medium obtained after the treatment increases significantly with the addition of different hydroxide additives (NH₄OH, Ca(OH)₂, NaOH) (Tables 3–6 and Figure 8). This is likely due to the peculiarities of the AlF₃ production process; a significant amount of one of the starting materials, H_2SiF_6 acid, remained in the investigated sample, and it can theoretically be converted into soluble compounds only by the use of KCl and NaOH solutions:

$$2KCl + H_2SiF_6 \rightarrow K_2SiF_6 + 2HCl$$
(3)

$$4NaOH + K_2SiF_6 \rightarrow 2KF + 4NaF + SiO_2 + 2H_2O$$

$$(4)$$

Therefore, in the last stage of this research, the SGW was treated with 5% KCl and 5% NaOH solutions: the KCl solution (w/s = 0.5) was poured onto the sample, stirred vigorously for 5 min (60 rpm), and filtered off; later, the same procedure was repeated with an NaOH solution (w/s = 0.5), and, in the final step, the sample was treated with water (w/s = 0.5).

The results of the XRD analysis show that a slight decrease in the intensities of $AlF_3 \cdot 3H_2O$ diffraction peaks was observed, when the SGW sample was treated with KCl solution (Figure 11). Meanwhile, $AlF_3 \cdot 3H_2O$ recrystallized to a related compound, $Al_2(OH)_{2.76}F_{3.24}(H_2O)$, after treatment with an NaOH solution (Figure 11). It was found that, due to the presence of Al^{3+} ions in the silica gel samples, the F⁻ ions were bound to low solubility compounds— K_2NaAlF_6 (*d*-spacing: 0.287, 0.234, 0.203 nm) and Na₃AlF₆ (*d*-spacing: 0.194, 0.275, 0.157 nm)—therefore, they were identified even after the treatment with water (Figure 11).



Figure 11. XRD patterns of the products obtained after the combined treatment of SGW with KCl and NaOH. Indexes: *A*—AlF₃·3H₂O; *x*—Al₂(OH)_{2.76}F_{3.24}(H₂O); *e*—K₂NaAlF₆; *c*—Na₃AlF₆.

As JSC 'Lifosa' preferentially uses NH_4OH in the production process, the NaOH solution was replaced with 5% ammonia water. It was found that the $AlF_3 \cdot 3H_2O$ remained stable, as a slight decrease in the intensities of the diffraction peaks typical to the mentioned compound was observed in the XRD patterns (Figure 12). Besides this, K_2NaAlF_6 or Na_3AlF_6 did not form under these treatment conditions.



Figure 12. XRD patterns of the products obtained after the combined treatment of SGW with KCl and NH_4OH . Indexes: A—AlF₃·3H₂O.

It was also found that the SGW sample was neutralized when KCl and NaOH solutions were used together, as the pH value of the liquid medium was equal to 6.69 after the treatment with water (Table 7). Meanwhile, when the NaOH solution was replaced with 5% ammonia, the pH values were equal to 2.36 and 3.01. It should be noted that, after the leaching of the silica gel samples with ammonia water (without KCl), the pH value of the liquid medium had already reached >6 at the beginning of the process (Table 5).

Table 7. The amount of F^- ions and the pH values of the liquid medium in the SGW samples after the treatment with saturated Ca(OH)₂ solution under dynamic conditions.

The Treatment Conditions	The Concentration of F^- Ions in the Sample, %	The Amount of Released F ⁻ Ions, %	The pH Value of the Liquid Medium
SGW + KCl	-	-	1.96
SGW + KCl + NaOH	-	-	8.13
$SGW + KCl + NaOH + H_2O$	8.44	15.86	6.69
$SGW + KCl + NH_4OH$	-	-	2.36
$SGW + KCl + NH_4OH + H_2O$	8.73	12.97	3.01

Thus, a combined treatment method was found to have no significant effect on the fluorine ion content in the investigated sample, as the concentration of these ions in the sample was reduced only by 13–16% (Table 7), which was four times lower than that in the sample which was treated with NH_4OH (Table 6).

To summarise the results, it can be stated that, by the use of an Al(OH)₃ additive, it is possible to reduce the concentration of F^- ions in the sample from 10.0% to ~4.5%; however, a large amount of water is required for this process (w/s > 100) (Table 8). The amount of liquid medium required can be significantly reduced by the use of an NH₄OH solution (Table 8). To our knowledge, the more successful results were obtained only by

Krysztafkiewicz et al. [23]; the F^- ions' concentration was reduced by eight times; however, the initial concentration of the mentioned ions was equal only to 1.6%, and there is no data about the water-to-solid ratio.

Table 8. The treatment conditions under which the concentration of F^- ions in the sample was reduced twice.

Additive	w/s Ratio	Treatment Conditions	The Duration of Interaction	The pH Value of the Liquid Medium	The Concentration of F ⁻ Ions in the Sample, %
-	-	-	-	-	10.0
Al(OH) ₃	100	Static	24 h	3.06	4.47
Al(OH) ₃	100	Dynamic	13 min	4.2	4.22
NH ₄ OH solution	10	Dynamic	2 h	>7	4.51

In the future research, the treated silica gel waste will be used as an SiO_2 source for the production of environmentally-friendly cementitious materials.

4. Conclusions

(1) The treatment method and additives were found to have a significant effect on the mineralogical composition of the silica gel waste samples. It was determined that the amount of the Al(OH)₃ additive did not affect the stability of the AlF₃·3H₂O; however, by increasing w/s ratio from 20 to 100, only a small amount of AlF₃·3H₂O was present in the sample. Meanwhile, when a Ca(OH)₂ additive or a saturated Ca(OH)₂ solution were used, the formation of CaF₂ in the silica gel waste was observed.

(2) It was found that, in the case of $Al(OH)_3$ or $Ca(OH)_2$ additives, a significant reduction (~2 times) of the fluorine ions in the silica gel waste can be achieved only by applying the treatment with a high quantity of liquid medium (w/s = 100). Meanwhile, by the use of NaOH or NH₄OH solutions (w/s = 20), the concentration of fluorine ions in the silica gel waste can be reduced by 1.6 and 2.2 times, respectively.

(3) It was determined that the compounds containing aluminum and fluorine ions such as AlF_3 , CaF_2 and/or $Ca_3Al_{2.85}O_{2.55}(OH)_{9.45}$ —were crystallized in the liquid medium, which was separated from the silica gel by the application of leaching with alkaline solutions.

(4) The fluoride ions were found to be most efficiently removed from the silica gel waste when treatment with an NH₄OH solution under dynamic conditions (w/s = 10) was applied, as the amount of fluorine ions released into the liquid medium was >50%. The resulting reaction medium, after the precipitation of aluminum fluoride trihydrate, can be reused for the treatment of contaminated silica gel samples.

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