



Research of fluoride ions removal from post-absorption solutions from flue gases desulfurization process by the wet ammonia method using fossil calcium sulfate – studies on model systems

Anna Zdunek^{a,*}, Dorota Kołodzyńska^b, Krzysztof Borowik^a, Aleksandra Bińczak^a, Piotr Rusek^a

^aŁukasiewicz Research Network - New Chemical Syntheses Institute, Al. Tysiąclecia Państwa Polskiego 13a, 24-110 Puławy, Poland, Tel.: +48814731429; email: anna.zdunek@ins.lukasiewicz.gov.pl (A. Zdunek), Tel.: +48814731764; email: krzysztof.borowik@ins.lukasiewicz.gov.pl (K. Borowik), Tel.: +48814731458; email: aleksandra.binczak@ins.lukasiewicz.gov.pl (A. Bińczak), Tel.: +48814731473; email: piotr.rusek@ins.lukasiewicz.gov.pl (P. Rusek)

^bMaria Curie-Skłodowska University, pl. M. Curie Skłodowskiej 2, 20-031 Lublin, Poland, Tel.: +48815375770; email: dorota.kolodynska@mail.umcs.pl

Received 24 March 2023; Accepted 3 July 2023

ABSTRACT

The paper presents the study on the removal of fluoride ions in the form of NH_4F from the ammonium sulfate solutions compared with the aqueous solutions using the calcium sulfate samples of fossil origin. The effect of ammonium sulfate on fluoride ion uptake by the calcium sulfate samples was investigated as a function of calcium sulfate mass and initial fluoride concentration, at 295 K. The results of X-ray diffraction and Fourier-transform infrared spectroscopy analyses of the calcium sulfate samples as well as of the solid residue obtained after the contact with the $\text{NH}_4\text{F} + \text{H}_2\text{O}$ and $\text{NH}_4\text{F} + (\text{NH}_4)_2\text{SO}_4$ solutions are presented. The changes in fluoride removal efficiency and the amount of fluoride ions combined by the calcium sulfate were analyzed. It was found that the effect of $(\text{NH}_4)_2\text{SO}_4$ was particularly unfavourable for the solutions with the fluoride concentration $0.05 \text{ mg}\cdot\text{L}^{-1}$ causing a decrease of fluoride removal efficiency. When the initial fluoride concentration increased to $0.5 \text{ mg}\cdot\text{L}^{-1}$, the negative effect of the presence of ammonium sulfate became weaker and it was possible to remove significant amounts of fluoride; however, it was necessary to adjust the dose of calcium sulfate precisely to the fluoride concentration. It was concluded that the fluoride removal onto calcium sulfate is a complex process.

Keywords: Fluoride removal; Ammonium sulfate from flue gases desulfurization; Calcium sulfate for fluoride removal

1. Introduction

The issue of fluoride removal from the liquid phase generally applies to drinking water [1–4]. The literature reports on numerous methods of fluoride removal from water, from the amount about 30 to $1.5 \text{ mg}\cdot\text{L}^{-1}$ that have been approved by the World Health Organization as safe for human health [5,6]. These studies take into account also the effects of the

presence of anions other than fluorides that naturally occur in drinking water, such as sulfate, chloride and nitrate anions at their actual concentrations [7,8]. A more complex issue is fluoride removal from the industrial solutions because of both higher concentrations of fluoride and the presence of accompanying ions.

One of the industrial processes that generates solutions containing fluoride ions is the flue gas desulfurization using

* Corresponding author.

the wet ammonia method. In this case, some types of solutions are generated as a result of absorption of sulfur oxides in the ammonia water. Apart from ammonium sulfate (AS) as the main product of reaction of sulfur oxides with the absorption solution, ammonium fluoride is also present as one of the products of the absorbent reaction with the components of the purified gas other than sulfur oxides.

Both crystal AS and AS solutions generated in the desulfurization process can be used as components of solid and liquid fertilizer products. The presence of fluoride ions in AS, obtained as the product of the wet ammonia-based desulfurization process can affect adversely both the conditions of the fertilizer production process and the physicochemical properties of these fertilizer products [9]. One of the most important aspects is the effect on the corrosive properties of ammonium sulfate-based liquid fertilizers, which in and of themselves create an aggressive environment for plant construction materials [10,11]. However, ammonium sulfate solutions, generated during the desulfurization process, are a very difficult system to defluorinate because of their high ionic strength value due to the large content of ammonia and sulfate ions as well as the presence of other impurities.

Many of the fluoride removal methods are based on the affinity of fluoride ions for calcium ions. They include precipitation and sorption methods as well as those based on ionic exchange [12–14]. Apart from such materials as calcium phosphates [15–18], calcium carbonates [19–21], and waste materials containing calcium [22], the literature reports also the studies on the calcium sulfate use for fluoride removal from water [23–26].

Al-Rawajfeh et al. [25] presented the mechanism of fluoride binding by calcium sulfate. After introducing ions competitive to fluoride into the purified solution in the process of fluoride adsorption by calcium sulfate, no decrease in the fluoride removal efficiency was found. On the contrary, the efficiency even increased. Therefore, it was determined that the main mechanism of fluoride removal by calcium sulfate is not the adsorption process but the process of calcium fluoride precipitation. The results of the studies by Kang et al. [26] on the fluoride ion removal using gypsum derived from the flue gas desulfurization technology using the limestone method revealed that gypsum from the flue gas desulfurization removes fluoride by binding it with calcium and through further calcium fluoride precipitation. The thermodynamic analysis confirmed the possibility of converting calcium sulfate into calcium fluoride at $\text{pH} > 5$. Reducing the pH below 5 is unsuitable for calcium fluoride formation, but its increase above 11 hinders the release of calcium from gypsum. The research showed that gypsum formed in the flue gas desulfurization process can be an attractive material for fluoride removal.

When considering the possibility of using calcium sulfate for fluoride removal from the ammonium sulfate solutions, an important aspect is the effect of ammonium sulfate presence on solubility of calcium sulfate in these solutions compared to water. Calcium sulfate is known as a sparingly soluble compound whose solubility after reaching the maximum value at the temperature of about 313 K, decreases with a further increase in temperature [27], in contrast to most substances. The literature data also show that calcium

sulfate is much more soluble in the concentrated solutions of ammonium sulfate than in water [27]. At the temperature of 298 K, the solubility of calcium sulfate in the diluted AS solutions equals about 2/3 of the solubility value in water while in the concentrated AS solutions, this value is about twice as high as in water. The solubility of calcium sulfate in the AS solutions decreases as the temperature increases, in the same way as its solubility in water.

Apart from the increased gypsum solubility in the AS solutions relative to water, as it was already mentioned, the use of gypsum for purification of ammonium sulfate solutions seems to be greatly beneficial due to the fact that the only introduced ions are those of calcium, which are desirable for fluoride binding, and sulfate ions, already present in these solutions. Taking these advantages into account, analyses were carried out to find out the calcium sulfate application for fluoride removal from the ammonium sulfate solutions. The novelty of this paper is not only the study of the effects of the ammonium sulfate presence, but also the examination of the efficiency of fluoride removal methods in a much wider range of fluoride concentrations in the process solutions compared to drinking water.

2. Materials and methods

2.1. Properties of calcium sulfate

Studies on the removal of fluoride ions by calcium sulfate were carried out using two types of fossil calcium sulfate samples, containing different amounts of crystalline water. One of them was dihydrate $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, hereinafter referred to as gypsum, and the other one was CaSO_4 , hereinafter referred to as anhydrite. The physicochemical properties of these materials such as the chemical composition obtained by the X-ray fluorescence (XRF) method, porosity and the specific surface area as well as size grains were described by the study of Zdunek et al. [28]. The X-ray diffraction (XRD) and the Fourier-transform infrared spectroscopy (FTIR) analyses were performed for both the calcium sulfate samples and the solid residue, obtained after the contact of these materials with the aqueous fluoride solutions and the ammonium sulfate solutions at the concentration of 40% by mass containing fluorides. The XRD analysis was performed using the X-ray diffractometry (PANalytical Empyrean, The Netherlands). The FTIR analysis was conducted using the Nicolet iS10 spectrometer (Thermo Scientific, United States). The spectra were recorded using the appropriate ATR technique (attenuated total reflection) at room temperature with 4 cm^{-1} resolution in the mid-infrared spectral range of $400\text{--}4,000 \text{ cm}^{-1}$.

To characterize the effects of ammonium sulfate on the fluoride removal by calcium sulfates and to identify the mechanism of this process, the pH of the point of zero charge (pH_{PZC}) and the solubility of calcium sulfates used in the AS solutions, at different concentrations of AS, were determined.

The purpose of determining the pH_{PZC} at which the surface of gypsum has an electric charge of zero was to find the pH range within which the surface of these gypsum samples is positively charged and will be able to bind negatively charged fluoride ions. It was determined according to the method described by the study of Lopez-Ramon et al. [29], by measuring the pH of the suspension obtained by mixing

0.2 g of gypsum with 50 mL of 0.05 M NaCl solution with various pH values for 24 h. The initial pH was adjusted to the values from 2 to 12 adding either the 0.1 M HCl solution or the 0.1 M NaOH solution. The final pH (pH_e) was measured after 24 h and the difference between this value and the pH of the initial solution was plotted against the initial pH (pH_0). The pH value for which the curve crosses the line that corresponds to $pH_e - pH_0 = 0$ was taken as the pH_{PZC} of the gypsum samples.

The effect of the presence of ammonium sulfate on the calcium sulfate solubility was determined adding 1 g of each gypsum material to 100 mL of water and ammonium sulfate solutions at the concentrations of 10%–40% by mass and stirring it at ambient temperature for 1 h. Then, the liquid phase was separated from the solid residue and the obtained solution was analyzed for the concentration of calcium ions using the atomic absorption spectrometry with flame atomization (Varian AA 240FS, United States).

2.2. Batch experiments

In the first stage of the experiments the samples of calcium sulfate were dried in a laboratory dryer for about 4 h at the temperature of 343 K until a constant mass value was obtained. Ammonium fluoride, as the source of fluoride ions (NH_4F a.g. Acros Organics, Belgium) was also dried at 343 K for about 2 h. The fluoride removal studies were carried out for various fluoride concentrations in the range of 0.05–5 $g \cdot L^{-1}$ in the aqueous systems and the ammonium sulfate solutions ($(NH_4)_2SO_4$ a.g. POCH, Poland) at the concentrations of 10%, 20%, 30%, and 40% by mass. The fluoride concentrations in the test solutions were measured using the direct potentiometric method. The fluoride selective electrode of the Monokrystaly 09–37 type (made of lanthanum fluoride single crystal) was used as the indicating electrode combined with the AgCl electrode used as the reference one. A citrate buffer was used to maintain the required pH value for the linear relationship between the measured signal and \log_{10} of the molar concentration of the standard fluoride solutions. The standard fluoride solution of 1,000 $mg \cdot L^{-1}$ was prepared by dissolving 2.21 g of sodium fluoride (NaF a.g. Acros Organics, Belgium) (dried at 353 K) in the 1,000 mL volumetric flask and the volume was made up to mark with ultrapure water from the Milli-Q ultrapure water system. The experimental solutions of desired concentrations were prepared by diluting the standard solution.

The tests were carried out in the consecutive series, in which the calcium sulfate dose and NH_4F solution concentration were the variable parameters. All tests were carried out in the fluoride solutions in the amount of 50 mL placed in the PE flasks with caps. They were put on the multiposition magnetic stirrer to obtain the same mixing conditions (speed of 550 rpm). After carrying out the tests under the assumed conditions, the final concentration of fluoride ions in the tested solutions was determined.

2.3. Evaluation of the effectiveness of fluoride removal and the mechanism of this process

Based on the initial fluoride concentration of the tested solutions and the values obtained for them after the contact

with the calcium sulfate doses, the percentage removal of fluoride, described further as fluoride removal efficiency (%), was calculated according to the following equation:

$$\text{Fluoride removal efficiency} = \frac{c_0 - c_t}{c_0} \times 100\% \quad (1)$$

where c_0 and c_t are the fluoride concentrations in the working solution – initial and at time t , respectively – in $mg \cdot L^{-1}$.

All experiments were done in triplicate and the presented results are the mean values. To express the reproducibility of these results, the graphs include the error bars showing the average deviation of each result from the mean, and for the results presented in the tables, the values of the standard deviation, calculated according to the formula:

$$s = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{n - 1}} \quad (2)$$

where s is the sample standard deviation, x_i is each value, \bar{x} is the sample mean, n is the number of values in the sample.

On the basis of the average value of fluoride removal efficiency, the ability of calcium sulfate used for fluoride removal q_e ($mg \cdot g^{-1}$) in the presence and absence of ammonium sulfate was defined as follows:

$$q_e = \frac{(c_0 - c_e)}{m} \times V \quad (3)$$

where c_0 and c_e are the initial and equilibrium fluoride concentrations in the working solution, respectively, in $mg \cdot L^{-1}$, V is the volume of the fluoride ion solution, in L, m is the dose of calcium sulfate, in g.

For better understanding the nature of fluoride ions interactions with the calcium sulfate samples, the obtained experimental values of fluoride removal efficiency were fitted to the adsorption equations of the most common adsorption models, that is, Langmuir isotherm [Eq. (4)], Freundlich isotherm [Eq. (5)], Temkin isotherm [Eq. (6)] and Dubinin–Radushkevich isotherm [Eq. (7)] [30].

$$\frac{1}{q_e} = \frac{1}{K_L q_t c_e} + \frac{1}{q_t} \quad (4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln c_e \quad (5)$$

$$q_e = B_T (\ln A_T + \ln c_e) \quad (6)$$

$$\frac{q_e}{X_m} = e^{-\beta \epsilon^2} \quad (7)$$

where K_L is the Langmuir constant related to the binding energy or the affinity parameter, K_F is the Freundlich constant associated with the sorption capacity, n is the Freundlich constant referring to the adsorbate and adsorbent affinity, B_T is the Temkin constant related to the heat of adsorption, A_T is the Temkin equilibrium binding constant corresponding to the maximum binding energy,

X_m is the theoretical saturation capacity, \mathcal{E} is the Polanyi potential, β is the constant related to the adsorption energy.

3. Results and discussion

3.1. Physicochemical properties of calcium sulfate samples

Fig. 1 shows the results of the tests determining the point of zero charge of the calcium sulfate surface. The presented values of pH changes for gypsum show that the value of pH_{PZC} is 2.59. For the solutions in the pH range of 2.59–9.94, its surface has a negative charge. As pH increases, the charge becomes positive. In the case of anhydrite, the value of pH_{PZC} is 6.23, which is close to that established for $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ equal 6.72 by the study of Gopal and Elango [23]. In the pH range of 2–4.06 and above 6.23, the surface of anhydrite reveals a negative charge and in the range of 4.06–6.23, it has a positive charge. On the basis of pH changes of the solutions after the contact with gypsum and anhydrite, it can be concluded that in the concentrated solution of ammonium sulfate, that is, with pH at about 4–5, the capacity for fluoride removal by the reaction with calcium ions occurs only when anhydrite is used and in the case of gypsum, for that pH range, the potential fluoride binding ability is due to the exchange of fluoride ions for such anions as SO_4^{2-} and OH^- .

The XRF results presented by the study of Zdunek et al. [28] show that besides the significant differences in the content of main ingredients of the calcium sulfate samples, such as CaO , SO_3 and water (loss on ignition), additionally the gypsum sample contains 1.24% of silicon by mass, 0.91% of phosphorus by mass and 1.24% of sodium by mass. The sample of anhydrite contains only 0.22% of silicon by mass and 0.83% of magnesium by mass. A small amount of strontium oxide has also been observed. On the basis of the XRF results, it can be concluded that apart from the reaction with calcium, some amounts of fluoride ions can be bound by silicon and aluminum in the case of gypsum, while in the case of anhydrite, reactions with magnesium are also possible.

Figs. 2a and 3a show that the main crystalline phase identified for the gypsum sample is $\text{CaSO}_4(\text{H}_2\text{O})_2$ while for anhydrite it is CaSO_4 but also some amounts of $\text{CaSO}_4(\text{H}_2\text{O})_2$ are present. After the contact with the $\text{NH}_4\text{F} + \text{H}_2\text{O}$ solution, the main crystalline phase present in the solid state obtained as

a result of adding gypsum is CaF_2 but some amounts of the remaining $\text{CaSO}_4(\text{H}_2\text{O})_2$ are also observed. When the anhydrite sample is used, CaF_2 is almost the only crystalline phase. This observation is consistent with the results described by the study of Gopal and Elango [23], where after the contact of water containing fluoride ions with $\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$, the only crystalline phase found in the solid residue is CaF_2 .

As a result of the calcium sulfates contact with the $\text{NH}_4\text{F} + (\text{NH}_4)_2\text{SO}_4$ solution, in the case of gypsum, there were observed only two crystalline phases: CaF_2 and $(\text{NH}_4)_2\text{SO}_4$, when using anhydrite, some amounts of CaSO_4 were bound in the phase of $(\text{NH}_4)_2\text{Ca}(\text{SO}_4)_2\text{H}_2\text{O}$ called koktaite. Apart from CaF_2 and $(\text{NH}_4)_2\text{SO}_4$, significant amounts of CaSO_4 were also recorded that can be related to dissolving calcium fluoride formed in the ammonium sulfate solution and rebirthing of calcium sulfate.

As follows from Figs. 4 and 5, the changes in the FTIR spectra of the applied calcium sulfate samples after the contact with $\text{NH}_4\text{F} + \text{H}_2\text{O}$ and $\text{NH}_4\text{F} + (\text{NH}_4)_2\text{SO}_4$ are very similar for both gypsum and anhydrite. After the contact with the $\text{NH}_4\text{F} + \text{H}_2\text{O}$ solution, in place of the bands in the 3,503; 3,396 and 3,242 cm^{-1} region, broad, fuzzy and significantly reduced bands appear in the 3,527 and 3,402 cm^{-1} regions, prominent in the case of gypsum and somewhat weaker in the case of anhydrite. These bands correspond to the stretching vibrations of the bonds in the free O–H groups and the hydrogen bonds [31,32]. This may be the result of the exchange of the O–H groups with the F^- [33,34]. Similarly, a notable decrease of the bands related to the bending vibrations of the bonds in the molecule of H_2O (1,682 and 1,619 cm^{-1}) present in the gypsum is observed and can be also associated with their replacement with F^- .

A significant decrease is also observed for the bands related to the stretching vibrations of the bands in the SO_4^{2-} groups present at 1,096–1,097 cm^{-1} and in the range of 665–592 cm^{-1} . At 1,010 cm^{-1} for gypsum and 1,031 cm^{-1} for anhydrite, the bands associated with the vibrations of the Si–F bonds appeared. After the contact with the $\text{NH}_4\text{F} + (\text{NH}_4)_2\text{SO}_4$ (40% by mass) solution, the bands at 3,209; 3,054 and 2,750 cm^{-1} in the case of gypsum and at 3,201; 3,046 and 2,850 cm^{-1} in the case of anhydrite are observed, related to the vibrations bands of hydrogen bonds of OH group and $\text{OH} \cdots \text{F}$. These bands are much weaker in the case of anhydrite than in the case of gypsum. The bands also come up at 1,422 and 1,417 cm^{-1} for gypsum and anhydrite, respectively, related to the bending vibrations of the bands in NH_4^+ .

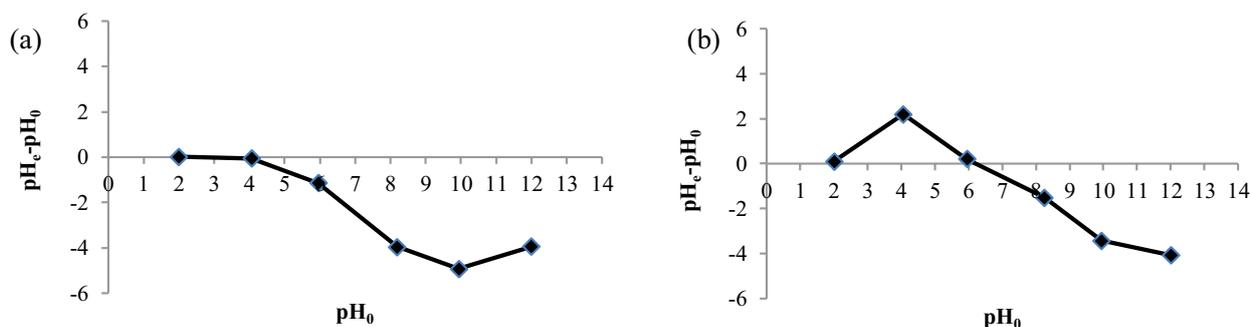


Fig. 1. Determination of pH_{PZC} for gypsum (a) and anhydrite (b).

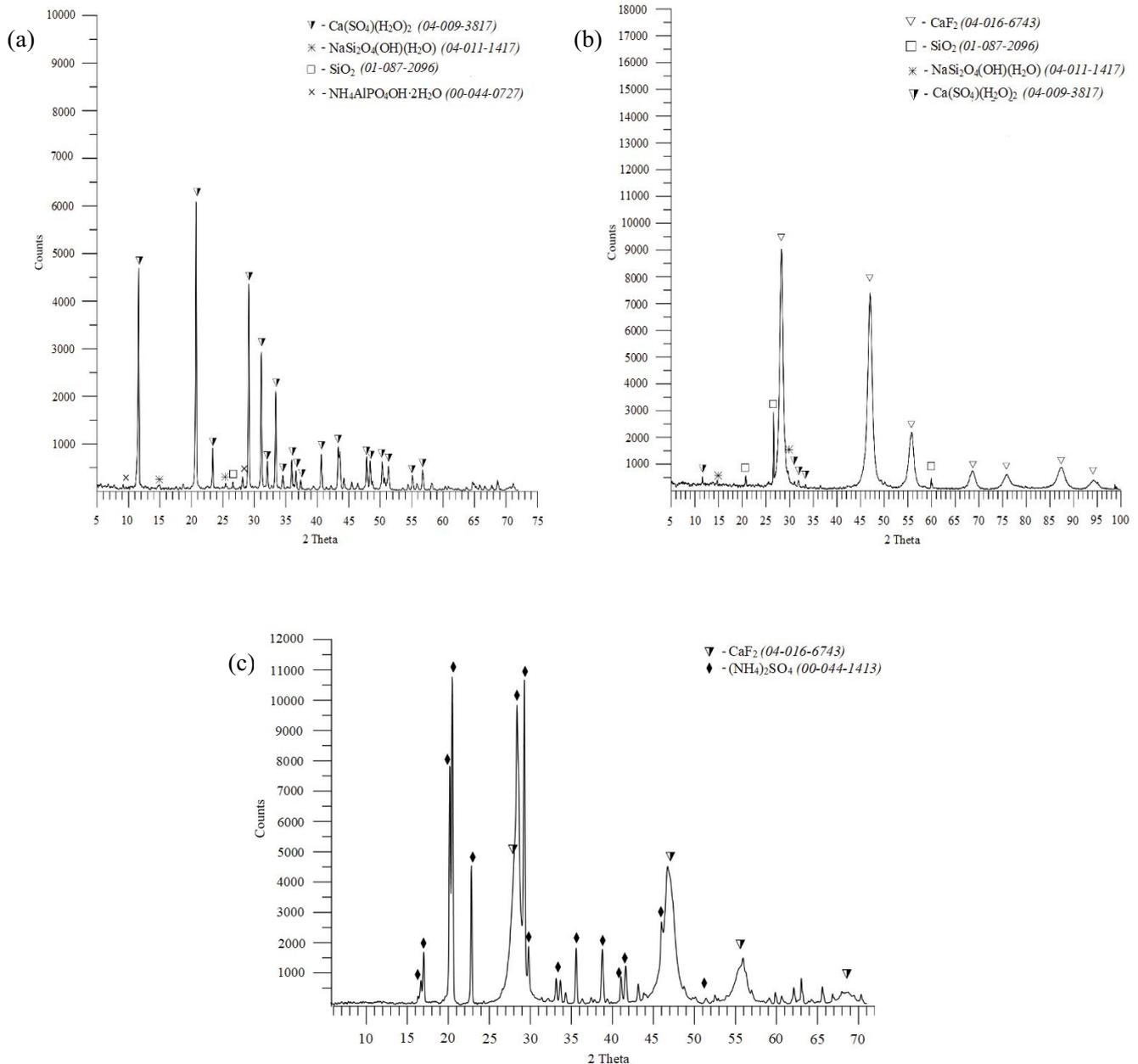


Fig. 2. X-ray diffraction analysis of gypsum (a), solid residue after the gypsum contact with the $\text{NH}_4\text{F} + \text{H}_2\text{O}$ solution (b), solid residue after the gypsum contact with the $\text{NH}_4\text{F} + (\text{NH}_4)_2\text{SO}_4$ solution (40% by mass) (c).

The bands associated with the vibrations of the bonds of Si–F are recorded at 990 and 992 cm^{-1} for gypsum and for anhydrite, respectively. The bands related to the vibrations of the bonds in SO_4^{2-} are also observed once more.

3.2. Effect of the ammonium sulfate presence on the solubility of calcium sulfate samples

Fig. 6 shows the results regarding the change in solubility of calcium sulfate samples in the ammonium sulfate solutions, in comparison to solubility in water. The solubility of the tested gypsum samples in the ammonium sulfate solution at the concentration of 10%, 20% and 30% by

mass is much smaller than in water. Simultaneously, a gradual increase of solubility is observed with the increasing ammonium sulfate concentration. In the ammonium sulfate solution, at the concentration of 40% by mass, the increase of both gypsum and anhydrite solubility is observed from the value of 0.19 and 0.14 g in water to the value of 0.38 and 0.58 g of CaSO_4 , respectively. The effect of the AS content on the solubility of calcium sulfate is consistent with the results of the studies presented by the study of Azimi et al. [27].

Reduction of gypsum solubility in the ammonium sulfate solutions at the concentrations of 10%–30% by mass, compared to water, results from the common ion effect, that is,

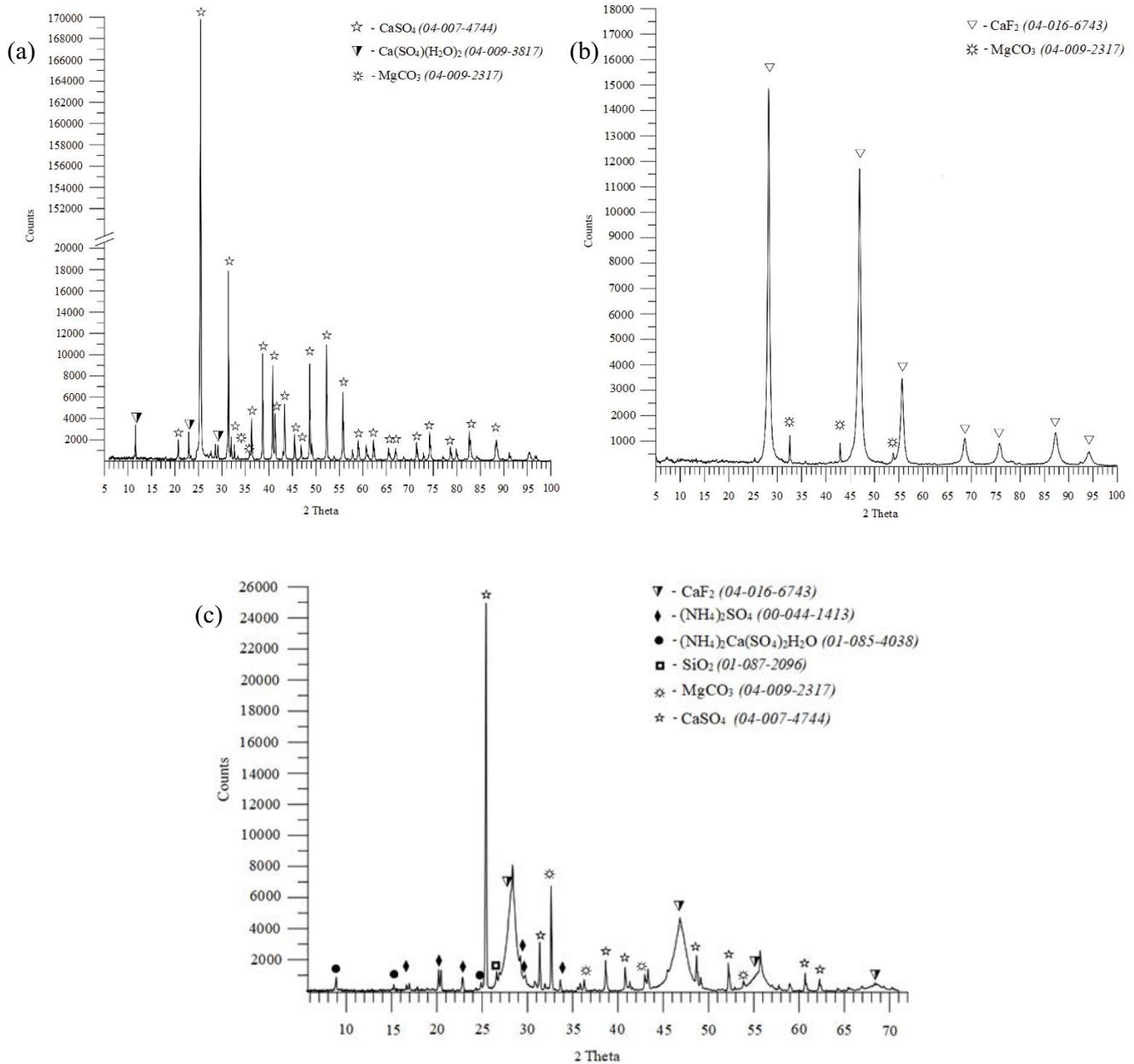
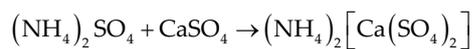


Fig. 3. X-ray diffraction analysis of anhydrite (a), solid residue after the anhydrite contact with the NH₄F + H₂O solution (b), solid residue after the anhydrite contact with the NH₄F + (NH₄)₂SO₄ solution (40% by mass) (c).

decreased solubility in the presence of other ingredients of the solution containing the same ion. As the concentration of one of the ions increases, a decrease of concentration of other ions is observed, according to the value of solubility product in the equilibrium state.

For the multicomponent solutions, the effect of the presence of the common ion with a sparingly soluble material overlaps with the phenomenon of complexed compounds creation, which is characteristic especially of high concentrations of electrolytes with the same anions. In the concentrated solutions of ammonium sulfate, calcium sulfate reveals a tendency towards creating complexed compounds, according to the formula [35]:



The phenomenon of complexed compounds creation influences the solubility of sediments of electrolytes. When a complexed ion is created, a decrease in the ions concentration is observed in the solution which increases the solubility of substances in order to restore the balance state value.

According to the calcium sulfate tendency towards creating a complex ion [Ca(SO₄)₂]²⁻, in the presence of ammonium sulfate, the amount of calcium sulfate dissolved in that solution will be the resultant value of two phenomena: the

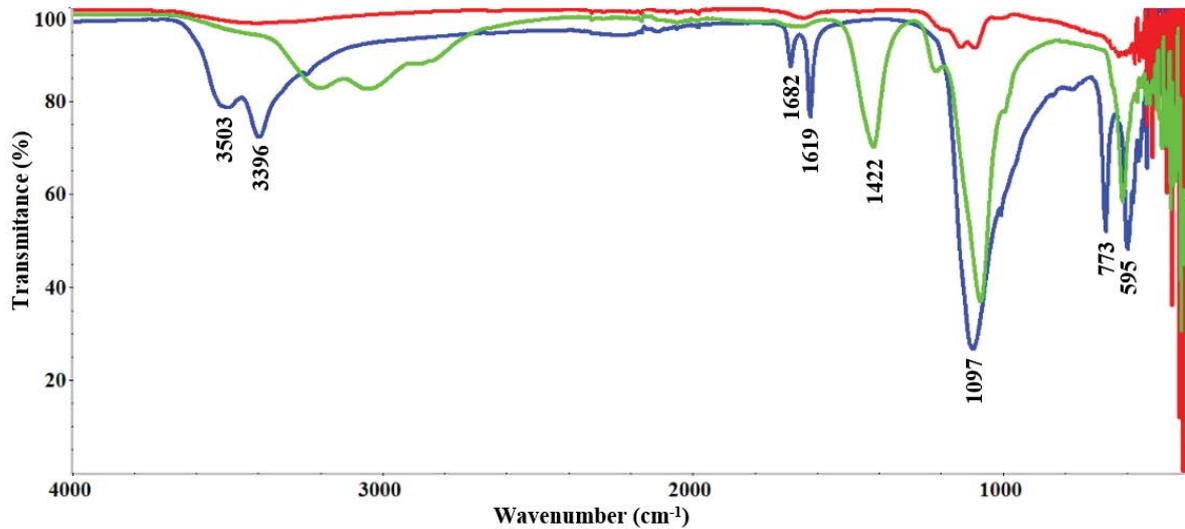


Fig. 4. Fourier-transform infrared spectra of gypsum (—), solid residue after the gypsum contact with the NH₄F + H₂O (—), solid residue after the gypsum contact with the NH₄F + (NH₄)₂SO₄ solution (40% by mass) (—).

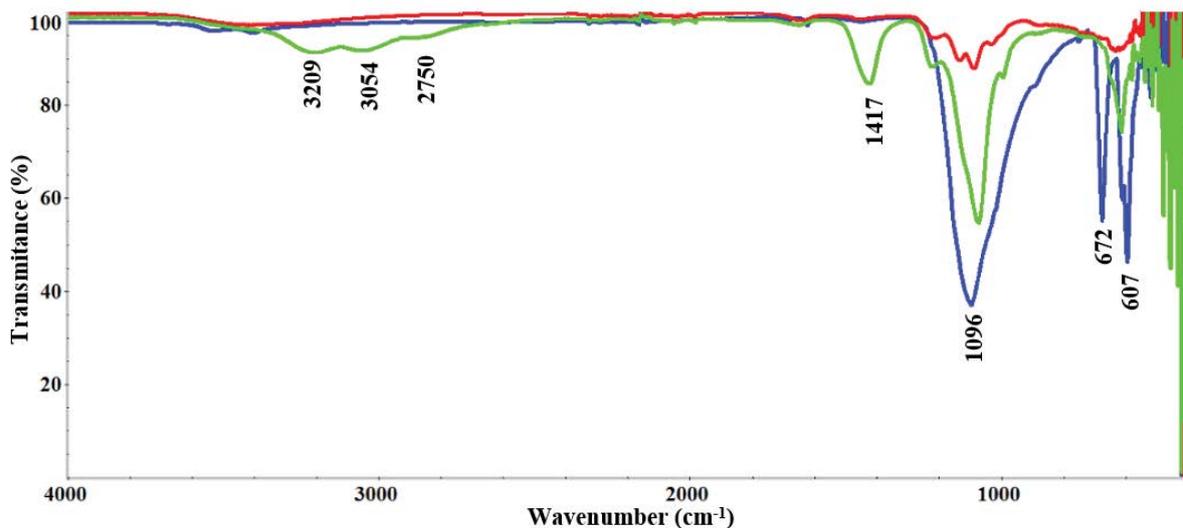


Fig. 5. Fourier-transform infrared spectra of anhydrite (—), solid residue after the anhydrite contact with the NH₄F + H₂O (—), solid residue after the anhydrite contact with the NH₄F + (NH₄)₂SO₄ solution (40% by mass) (—).

presence of the same ion and the tendency towards complexed compounds creation. With the increase of concentration of ammonium sulfate there can be seen the predominance of the complexing phenomenon, but in the ammonium sulfate solution at the concentration of 40% by mass, this phenomenon is superior to the common ion effect. The amount of calcium ions derived from calcium sulfates present in the ammonium sulfate solution will therefore result from the value of solubility product reduced by the value of decrease in solubility influenced by the common ion effect SO₄²⁻ as well as from the amount of calcium ions derived from the complex compound that has been generated, related to the value of stability constant of the complex compound. Therefore, the observed change in the solubility of calcium sulfate in the ammonium sulfate solutions compared to

the solubility in water (Fig. 6) is the resultant value of the effect of all phenomena occurring in the SO₄²⁻ ions containing systems.

3.3. Effect of the calcium sulfate dose on the fluoride removal efficiency

The effect of the amount of calcium sulfate on the efficiency of fluoride removal from the aqueous and ammonium sulfate solutions was analyzed for three significantly different values of the fluoride ion solution concentration, that is, 0.05, 0.5, and 1 g·L⁻¹. For each of fluoride concentrations, the effect of added calcium sulfates was examined at the quantity of 0.05, 0.1, 0.2, 0.5, 0.7, and 1 g per 50 mL of solution and over the period of 15 min. The values obtained for the reduction

in the fluoride ion content in the individual systems are presented in Tables 1–3. It can be observed that the effect of calcium sulfate doses on the fluoride removal efficiency depends precisely on the initial fluoride concentration. For the low concentration at $0.05 \text{ g}\cdot\text{L}^{-1}$, a significant reduction of fluoride concentration over 70% was observed only for the aqueous solutions, using the dose of just 0.05 g per 50 mL of solution (Table 1). In the case of gypsum, a further increase of the dose over 0.2 g caused a significant decrease of fluoride removal, and for 0.7 g and more, no decrease in the fluoride content was observed. When anhydrite was used, a significant degree of fluoride removal was observed, irrespective of its amount but when the dose of 0.7 g and larger was used, a slight decrease in the fluoride removal was observed. According to Gopal and Elango [23], the optimal dose of $\text{CaSO}_4\cdot 0.5\text{H}_2\text{O}$ for the effective removal of fluoride ions from the solutions of $4 \text{ mg}\cdot\text{L}^{-1}$ was determined to be equal to 1 g/50 mL.

The presence of ammonium sulfate at the fluoride concentration of $0.05 \text{ g}\cdot\text{L}^{-1}$ caused the removal of fluorides to be stopped completely when gypsum was used and resulted in a significant decrease in the fluoride removal efficacy in the case of anhydrite, depending on the concentration of ammonium sulfate. Similarly, a strong effect of the presence of SO_4^{2-} ions on reducing the removal rate of F^- ions was observed by the study of Gopal and Elango [23], where the initial fluoride concentration was $4 \text{ mg}\cdot\text{L}^{-1}$. In the case of the increase of the initial fluoride concentration to $0.5 \text{ g}\cdot\text{L}^{-1}$, it proved possible to obtain large levels of fluoride removal from aqueous solutions as well as from ammonium sulfate solutions when using an adequately large amount of calcium sulfate (Table 2). A significant fluoride removal efficiency when using both gypsum as anhydrite was obtained at the dose of 0.2 g per 50 mL of solution, and was equal to 94.3% and 96.7% for the aqueous solutions, respectively. In

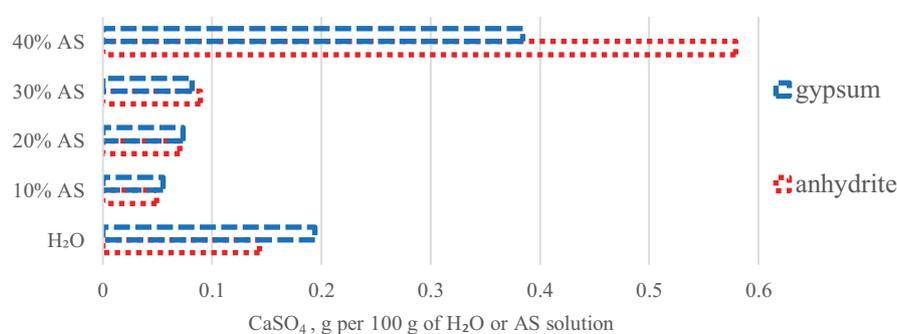


Fig. 6. Change in the solubility of the tested calcium sulfates in water compared to the ammonium sulfate solutions (temperature 298 K, contact time 1 h).

Table 1

Effect of the calcium sulfate dose on the fluoride removal efficiency from the $\text{NH}_4\text{F} + \text{H}_2\text{O}$ and $\text{NH}_4\text{F} + \text{AS}$ solutions (initial concentration of fluoride: $0.05 \text{ g}\cdot\text{L}^{-1}$, volume: 50 mL, contact time: 15 min) with the standard deviation(s) values

Dose (g)	Fluoride removal efficiency (%) (s)				
	Gypsum				
	$\text{NH}_4\text{F} + \text{H}_2\text{O}$	$\text{NH}_4\text{F} + 10\% \text{ AS}$	$\text{NH}_4\text{F} + 20\% \text{ AS}$	$\text{NH}_4\text{F} + 30\% \text{ AS}$	$\text{NH}_4\text{F} + 40\% \text{ AS}$
0.05	69.8 (2.2)	0.0	0.0	0.0	0.0
0.1	70.2 (0.9)	0.0	0.0	0.0	0.0
0.2	74.4 (1.8)	0.0	0.0	0.0	0.0
0.5	20.5 (1.2)	0.0	0.0	0.0	x
0.7	0.0	0.0	0.0	0.0	x
1	0.0	0.0	0.0	0.0	x
Anhydrite					
	$\text{NH}_4\text{F} + \text{H}_2\text{O}$	$\text{NH}_4\text{F} + 10\% \text{ AS}$	$\text{NH}_4\text{F} + 20\% \text{ AS}$	$\text{NH}_4\text{F} + 30\% \text{ AS}$	$\text{NH}_4\text{F} + 40\% \text{ AS}$
0.05	77.3 (2.4)	0.0	0.0	3.5 (0.2)	22.9 (1.2)
0.1	88.0 (1.4)	0.0	0.0	3.8 (0.3)	25.3 (1.6)
0.2	89.6 (1.1)	0.0	9.2 (0.8)	8.9 (0.9)	4.5 (0.3)
0.5	89.4 (0.8)	0.0	13.7 (1.1)	13.6 (1.1)	1.6 (0.2)
0.7	86.6 (0.4)	0.0	4.9 (0.7)	14.9 (0.7)	x
1	86.1 (0.3)	11.7 (1.1)	0.1 (0.02)	20.4 (1.4)	x

x – coagulation was observed.

Table 2

Effect of the calcium sulfate dose on the fluoride removal efficiency from the $\text{NH}_4\text{F} + \text{H}_2\text{O}$ and $\text{NH}_4\text{F} + \text{AS}$ solutions (initial concentration of fluoride: $0.5 \text{ g}\cdot\text{L}^{-1}$, volume: 50 mL, contact time: 15 min) with the standard deviation(s) values

Dose (g)	Fluoride removal efficiency (%) (s)				
	Gypsum				
	$\text{NH}_4\text{F} + \text{H}_2\text{O}$	$\text{NH}_4\text{F} + 10\% \text{ AS}$	$\text{NH}_4\text{F} + 20\% \text{ AS}$	$\text{NH}_4\text{F} + 30\% \text{ AS}$	$\text{NH}_4\text{F} + 40\% \text{ AS}$
0.05	39.2 (1.8)	34.5 (1.3)	30.4 (1.2)	32.7 (1.3)	34.6 (1.1)
0.1	75.5 (2.3)	64.2 (1.4)	50.8 (1.9)	57.0 (2.2)	58.3 (1.3)
0.2	94.3 (1.7)	86.5 (1.1)	83.6 (1.1)	75.2 (1.1)	77.6 (0.9)
0.5	91.4 (1.9)	82.4 (0.9)	81.1 (0.8)	78.9 (1.5)	x
0.7	89.3 (1.2)	80.6 (2.1)	85.4 (2.1)	79.2 (2.2)	x
1	83.7 (1.3)	82.5 (0.8)	78.2 (1.3)	79.5 (2.3)	x
	Anhydrite				
	$\text{NH}_4\text{F} + \text{H}_2\text{O}$	$\text{NH}_4\text{F} + 10\% \text{ AS}$	$\text{NH}_4\text{F} + 20\% \text{ AS}$	$\text{NH}_4\text{F} + 30\% \text{ AS}$	$\text{NH}_4\text{F} + 40\% \text{ AS}$
	0.05	62.8 (2.3)	45.9 (2.5)	31.2 (1.5)	35.0 (1.2)
0.1	80.7 (2.5)	74.7 (2.1)	59.3 (0.9)	58.9 (0.7)	62.6 (0.8)
0.2	96.1 (2.1)	86.7 (0.8)	83.7 (0.7)	83.0 (1.3)	76.7 (1.2)
0.5	97.3 (1.3)	89.0 (0.3)	83.7 (0.5)	85.4 (0.9)	x
0.7	97.5 (0.4)	88.7 (0.6)	84.5 (1.1)	82.3 (1.1)	x
1	97.7 (0.8)	89.3 (1.1)	85.7 (0.9)	82.0 (0.7)	x

x – coagulation was observed.

Table 3

Effect of the calcium sulfate dose on the fluoride removal efficiency from the $\text{NH}_4\text{F} + \text{H}_2\text{O}$ and $\text{NH}_4\text{F} + \text{AS}$ solutions (initial concentration of fluoride: $1 \text{ g}\cdot\text{L}^{-1}$, volume: 50 mL, contact time: 15 min) with the standard deviation(s) values

Dose (g)	Fluoride removal efficiency (%) (s)				
	Gypsum				
	$\text{NH}_4\text{F} + \text{H}_2\text{O}$	$\text{NH}_4\text{F} + 10\% \text{ AS}$	$\text{NH}_4\text{F} + 20\% \text{ AS}$	$\text{NH}_4\text{F} + 30\% \text{ AS}$	$\text{NH}_4\text{F} + 40\% \text{ AS}$
0.05	11.6 (1.1)	21.0 (1.2)	26.5 (1.3)	10.6 (1.3)	20.4 (1.3)
0.1	31.5 (1.5)	38.6 (1.8)	33.9 (1.5)	31.9 (2.1)	36.6 (2.2)
0.2	71.6 (1.8)	69.5 (2.1)	69.1 (2.3)	73.7 (2.2)	71.5 (0.7)
0.5	96.9 (0.9)	92.5 (1.4)	92.9 (2.1)	91.9 (1.3)	84.1 (1.1)
0.7	96.6 (0.3)	89.2 (3.2)	91.0 (1.5)	91.0 (1.1)	x
1	93.6 (0.7)	91.0 (1.1)	89.3 (0.8)	90.1 (0.8)	x
	Anhydrite				
	$\text{NH}_4\text{F} + \text{H}_2\text{O}$	$\text{NH}_4\text{F} + 10\% \text{ AS}$	$\text{NH}_4\text{F} + 20\% \text{ AS}$	$\text{NH}_4\text{F} + 30\% \text{ AS}$	$\text{NH}_4\text{F} + 40\% \text{ AS}$
	0.05	36.0 (2.1)	20.7 (0.5)	21.3 (1.4)	17.3 (1.3)
0.1	52.1 (1.2)	49.4 (0.8)	39.9 (1.1)	36.2 (2.1)	44.2 (1.4)
0.2	96.2 (1.9)	80.3 (1.3)	62.6 (1.5)	82.7 (2.4)	74.8 (1.6)
0.5	97.7 (1.4)	93.3 (1.5)	93.5 (1.6)	91.2 (1.8)	86.5 (1.1)
0.7	97.6 (1.5)	93.4 (1.3)	94.4 (1.1)	93.3 (1.1)	88.2 (0.9)
1	95.8 (0.7)	95.8 (1.8)	94.6 (0.8)	94.4 (1.9)	82.1 (0.7)

x – coagulation was observed.

the ammonium sulfate solutions, it was equal to 86.5% and 86.7% for 10% of AS, 83.6% and 83.7% for 20% of AS, 75.2% and 83.0% for 30% of AS, 77.6% and 76.7% for 40% of AS, for gypsum and anhydrite, respectively. With the initial fluoride concentration increased to $1 \text{ g}\cdot\text{L}^{-1}$, a further increase of

removal efficiency was observed at the calcium sulfate dose of 0.5 g per 50 mL of solution. It amounted to over 90%, in both the aqueous solutions and ammonium sulfate solutions with the concentrations in the range of 10%–30% (Table 3). Only for the solutions with the largest concentration of AS

a slight decrease of removal efficiency was recorded at the same dose of calcium sulfate samples; however, it was still considerable and was equal to 84.1% and 86.5% for gypsum and anhydrite, respectively.

Summing up the studies of the effects of calcium sulfate dose, it can be concluded that the larger the initial concentration of fluoride was, the smaller the negative effect of the ammonium sulfate presence on the fluoride removal efficiency was observed. To obtain a significant fluoride removal efficiency, it is necessary to match the calcium sulfate dose properly to the value of the initial fluoride concentration because its overuse decreases the amount of fluoride uptake. Additionally, in the case of ammonium sulfate solutions at the concentration of 40% by mass, it was found that when higher doses of calcium sulfates were used, the coagulation process occurred, and the fluoride concentration measurement was impossible.

One can observe that despite the fact that the amount of fluoride being removed rises with the increase of the calcium sulfate dose, the amount of fluoride uptake (in mg) by 1 g of calcium sulfate q_e decreases, particularly for the initial fluorides concentrations of 0.05 g·L⁻¹ (Fig. 7) and 0.5 g·L⁻¹ (Fig. 8). Only at the initial concentration of fluorides of 1 g·L⁻¹ (Fig. 9) an increase of the q_e value is observed with the calcium sulfate dose of 0.1 or 0.2 g per 50 mL of the solution,

depending on the system. With further increases of the dose, a decrease of q_e is observed. In the aqueous solutions with the initial fluoride concentration of 0.05 g·L⁻¹, the maximum amount of fluoride ions uptake by 1 g of calcium sulfate is equal to about 40 mg·g⁻¹ (Fig. 7). The kinetic analysis presented by the study of Kang et al. [26] indicates that the theoretical fluoride capacity at 1 g·L⁻¹ flue gas desulfurization gypsum is 97 mg·g⁻¹. This value is more than twice as large as that obtained in the presented studies, but it was also determined at the twice larger initial fluoride content being 0.109 mg·L⁻¹. In the fluoride ions containing solutions the concentrations of 0.5 g·L⁻¹ (Fig. 8) and 1 g·L⁻¹ (Fig. 9), it is over 100 mg·g⁻¹ in both the aqueous solutions and in the ammonium sulfate solutions. In the case of smaller doses of calcium sulfate samples, significant differences in the q_e values for the aqueous solutions compared to the ammonium sulfate solutions are observed, which were much smaller when larger doses of calcium sulfate samples were applied. When comparing the amounts of fluoride ions combined by the gypsum and the anhydrite sample, it can be stated that the anhydrite revealed a slightly larger capacity for the fluoride ions, which can be seen particularly in the aqueous solutions and in the ammonium sulfate solutions at the concentration of 40% by mass, in the case of smaller anhydrite doses.

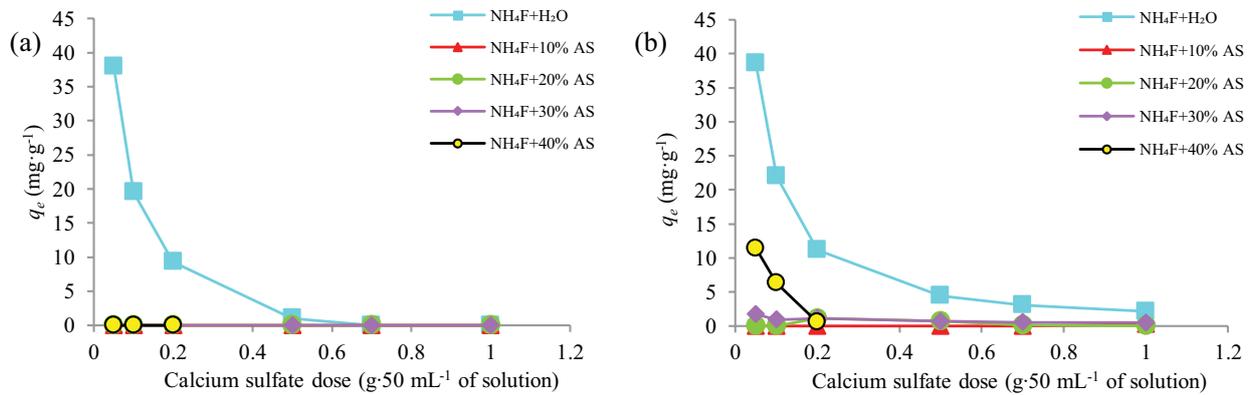


Fig. 7. Effect of the calcium sulfate dose on the value of capacity for fluoride ions using gypsum (a), anhydrite (b) (initial fluoride concentration 0.05 g·L⁻¹).

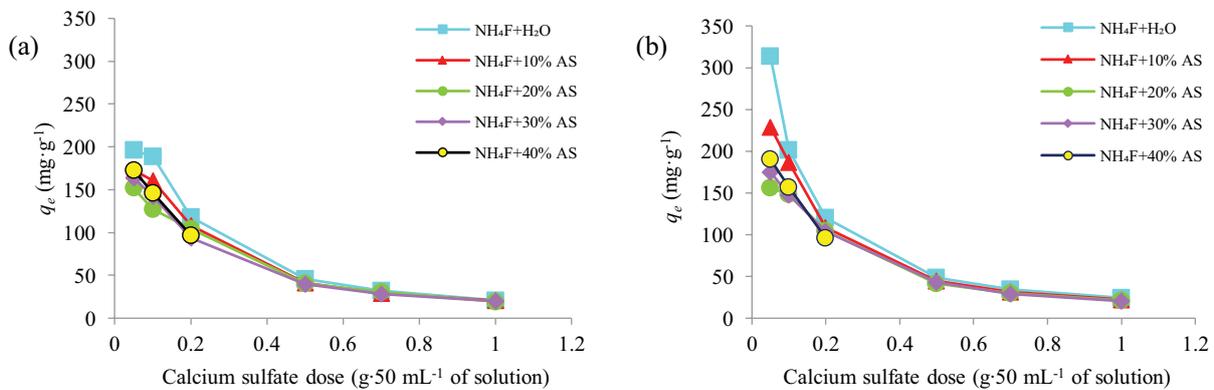


Fig. 8. Effect of the calcium sulfate dose on the value of capacity for fluoride ions using gypsum (a), anhydrite (b) (initial fluoride concentration 0.5 g·L⁻¹).

3.4. Effect of initial fluoride concentration on the fluoride removal efficiency

Based on the results concerning the effect of the amount of calcium sulfate added to the purified solution at the fluoride concentration of up to $0.5 \text{ g}\cdot\text{L}^{-1}$, it can be assumed that significant effects of fluoride removal can already be obtained using calcium sulfate at the dose of 0.1 g per 50 mL of solution. However, as the initial fluoride concentration increased to $1 \text{ g}\cdot\text{L}^{-1}$, the removal efficiency decreased significantly. Therefore, the studies on the effect of initial

fluoride concentration were carried out for a large range of fluoride concentrations ($0.05\text{--}5 \text{ g}\cdot\text{L}^{-1}$) with the calcium sulfate dose of 0.2 g per 50 mL of solution. The obtained results are shown in Fig. 10a and b. For both tested calcium sulfates, the presence of AS caused a decrease in the fluoride removal efficiency in comparison with the aqueous solutions when the initial fluoride concentration was smaller than $0.7 \text{ g}\cdot\text{L}^{-1}$ while for the larger concentrations of F^- , some fluctuations were observed. In some cases, the efficiency of fluoride removal from the AS solutions was greater than from the aqueous ones. Using calcium sulfates at the

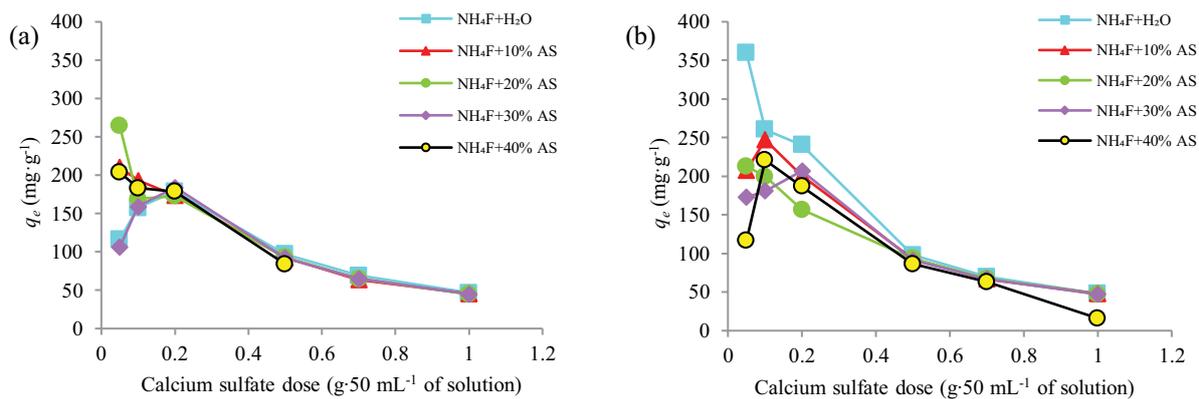


Fig. 9. Effect of the calcium sulfate dose on the value of capacity for fluoride ions using gypsum (a), anhydrite (b) (initial fluoride concentration $1 \text{ g}\cdot\text{L}^{-1}$).

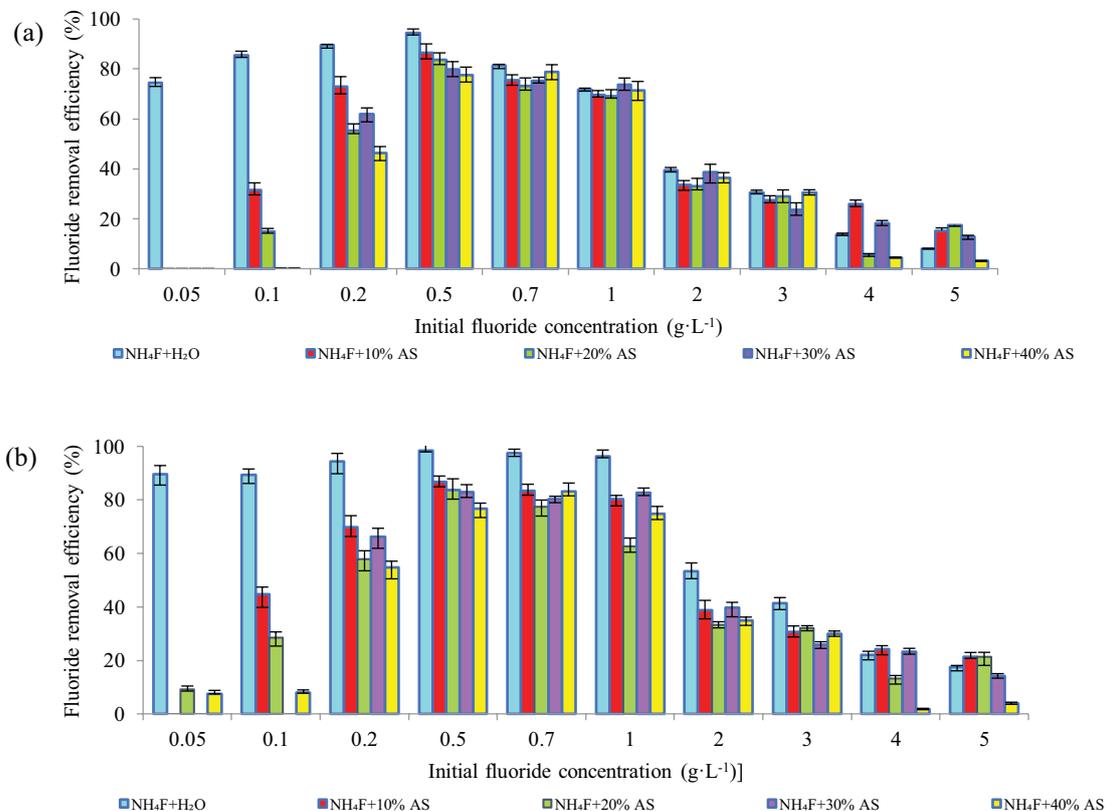


Fig. 10. Effect of the initial fluoride concentration on the fluoride removal efficiency using gypsum (a), anhydrite (b) (calcium sulfate dose: 0.2 g).

dose of 0.2 g resulted in the significant effects of fluoride removal from the AS solutions in the range of 10%–40% by mass only at the initial fluoride ion concentration of at least 0.2 g·L⁻¹. In the case of smaller fluoride concentrations, there was a significant decrease of fluoride removal along with the increasing AS concentration in the purified solution. With the further increase in the fluoride concentration, an increase in the fluoride removal was observed regardless of the AS concentration. However, at the initial fluoride concentration of 2 g·L⁻¹ and higher, this tendency changed and there was a significant decrease in the fluoride removal from both aqueous and AS containing solutions.

Due to the fact that at the 0.2 g dose of calcium sulfates and the initial fluoride concentration of at least 2 g·L⁻¹, a significant decrease in the amount of removed fluoride ions was observed. The tests were carried out with an increased amount of calcium sulfate at the doses of 0.5, 0.7 and 1 g for the fluoride solutions at the concentrations of 2, 3, 4, and 5 g·L⁻¹. The results show that the increase of the calcium sulfate dose to 0.5 g causes a significant increase of fluoride removal efficiency compared to the results obtained for the dose of 0.2 g, for both aqueous and ammonium sulfate solutions. This effect is enhanced at the dose of 0.7 g. However, it turned out that in order to obtain a high value of fluoride removal with an increase of fluoride ion concentration above 3 g·L⁻¹, it is necessary to use calcium sulfate at the dose of 1 g (Fig. 11a and b). When gypsum was used, the efficiency of fluoride removal from the solution at the concentration of 2 g·L⁻¹ equalled 96% for NH₄F + H₂O and 94% for

NH₄F + 40% by mass of AS, and at the concentration of 4 g·L⁻¹, it was 91% for NH₄F + H₂O and 89% for NH₄F + 40% by mass of AS. However, as the initial fluoride concentration increased to 5 g·L⁻¹, the efficacy decreased to 78% for NH₄F + H₂O and to 70% for NH₄F + 40% by mass of AS. In the case of anhydrite, the values of efficiency were 98% for NH₄F + H₂O and 93% for NH₄F + 40% by mass of AS, and at the concentration of 4 g·L⁻¹, they were 95% for NH₄F + H₂O and 66% for NH₄F + 40% by mass of AS. Upon the increase of the initial fluoride concentration to 5 g·L⁻¹, the values of efficacy for both NH₄F + H₂O and NH₄F + 40% by mass of AS were nearly the same, 92% and 62%, respectively.

The results proved that when the concentration of fluoride ions exceeds a certain level, it is necessary to use larger doses of calcium sulfate. It is also important to take into consideration that when the dose of calcium sulfate is properly matched to the initial concentration of fluoride, the phenomenon of coagulation is not observed, even for the solutions containing ammonium sulfate at the concentration of 40% by mass.

On the basis of the results obtained for the effect of initial fluoride concentration using various calcium sulfate doses, the values of calcium sulfate capacity for fluoride ions were also determined. The maximum values of q_e (q_e max.) obtained for 0.2 g, 0.5 g, 0.7 g, and 1 g of the calcium sulfate doses for the range of the initial concentrations of fluoride of 0.05–5 g·L⁻¹ are shown in Table 4.

The maximum capacity value for fluoride ions of calcium sulfates was different in the case of the aqueous solution

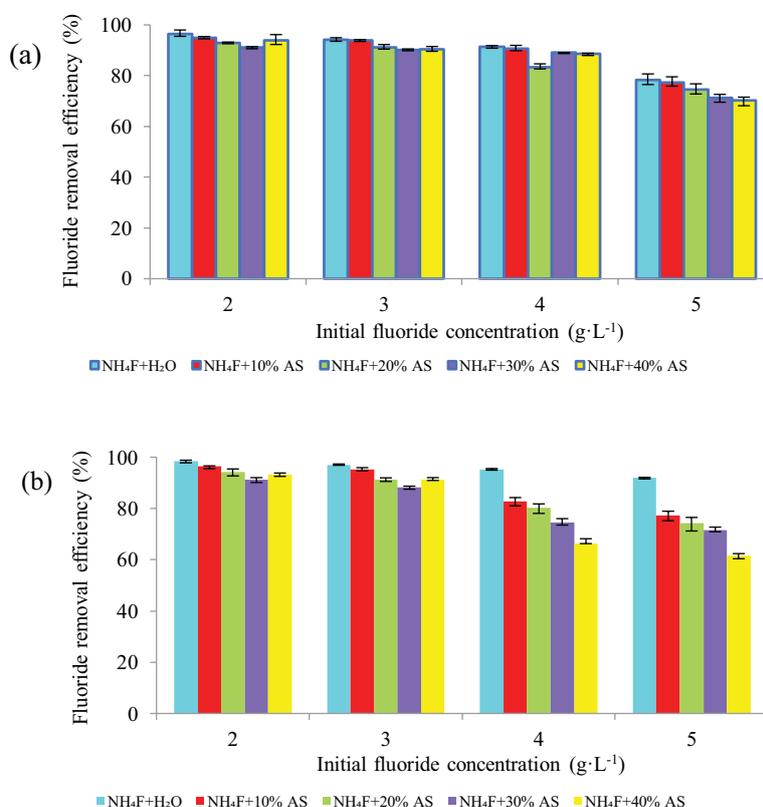


Fig. 11. Effect of the initial fluoride concentration on the fluoride removal efficiency using gypsum (a), anhydrite (b) (calcium sulfate dose: 1 g).

Table 4

Maximum values of q_e obtained for 0.2, 0.5, 0.7, and 1 g of calcium sulfate doses for the range of the initial concentrations of fluoride of 0.05–5 g·L⁻¹

Type of calcium sulfate sample	Dose of calcium sulfate (g)	q_e max. (mg·g ⁻¹)				
		NH ₄ F + H ₂ O	NH ₄ F + 10% AS	NH ₄ F + 20% AS	NH ₄ F + 30% AS	NH ₄ F + 40% AS
Gypsum	0.2	229	258	219	193	228
	0.5	248	240	212	193	176
	0.7	208	193	183	172	171
	1	196	193	186	178	177
Anhydrite	0.2	310	267	265	232	224
	0.5	196	173	169	189	180
	0.7	198	173	165	165	155
	1	230	193	186	179	154

and in the presence of ammonium sulfate both for gypsum and anhydrite. In the case of gypsum, the value of q_e max. was equal to 229 mg·g⁻¹ for NH₄F + H₂O, 258 mg·g⁻¹ for NH₄F + 10% by mass of AS, 219 mg·g⁻¹ for NH₄F + 20% by mass of AS, 193 mg·g⁻¹ for NH₄F + 30% by mass of AS and 228 mg·g⁻¹ for NH₄F + 40% by mass of AS. When anhydrite was used, the value of q_e max. was slightly higher and was equal to 310 mg·g⁻¹ for NH₄F + H₂O, 267 mg·g⁻¹ for NH₄F + 10% by mass of AS, 265 mg·g⁻¹ for NH₄F + 20% by mass of AS, 232 mg·g⁻¹ for NH₄F + 30% by mass of AS and 224 mg·g⁻¹ for NH₄F + 40% by mass of AS. These maximum values were obtained for the dose of 0.2 g. Although with the increasing calcium sulfate doses, the fluoride removal efficiency increased significantly for the dose of 1 g compared to 0.2 g, the capacity of calcium sulfates for fluoride ions decreased for both aqueous and ammonium sulfate solutions.

3.5. Equilibrium studies on the sorption process of fluoride ions with calcium sulfate

Assuming that the uptake of fluoride ions by calcium sulfate is partially caused by the adsorption process, the estimation how the equilibrium matches the isotherm models of Langmuir, Freundlich, Temkin and Dubinin–Radushkevich was made. The main parameter confirming a good match between the experimental data and the models of isotherms was the correlation coefficient, designated R^2 . For the research systems for which the values of R^2 were the highest, the values of q_e theoretical and q_e experimental were compared. The values of q_e theoretical were determined based on the isotherm Eqs. (3)–(6). A high value of the R^2 coefficient and consistency between q_e theoretical and q_e experimental were taken as a sufficient confirmation of the fluoride ion adsorption mechanism matching the particular isotherm model.

The data summarized in Tables 5 and 6 show that the nature of the mechanism of fluoride ions uptake by the calcium sulfate samples is largely dependent on the environment of the reaction, aqueous or ammonium sulfate solution of fluorides as well as on the dose of calcium sulfate. The general tendency is that the highest values of the correlation coefficient R^2 for every type of isotherm model were

obtained when larger doses of calcium sulfates were used. In some cases, the value of R^2 decreased with the increase of the calcium sulfate dose from 0.2 to 0.5 g, but upon further increase of the dose, it increased significantly. This is probably due to the overlapping of various factors influencing the fluoride binding by calcium sulfates.

Based on the data presented in Tables 5 and 6, it can be concluded that for each of the adsorption models under consideration, the largest degree of conformity of q_e theoretical and q_e experimental was reached for the ammonium sulfate solutions at the concentration of 40% by mass. It was found that these values were consistent even though the values of the R^2 coefficient were not the highest. For example, for the Langmuir isotherm model, when anhydrite was used in the aqueous solution of ammonium fluoride with the R^2 coefficient equal to 0.98, the values of q_e theoretical and q_e experimental were equal to 213.94 and 229.88, respectively. However, in the ammonium sulfate solution of ammonium fluoride at the concentration of 40% by mass of AS, for which R^2 was equal to only 0.66, the values of q_e theoretical and q_e experimental were equal to 9.23 and 10.00, respectively.

Among the considered isotherm models, the Langmuir model seems to be best suited to describe the mechanism of fluoride uptake from the ammonium sulfate solutions by gypsum since the better consistency with this model was achieved, when the concentration of ammonium sulfate was higher. In the case of anhydrite, it appears that the Freundlich model is the most appropriate one, particularly when fluoride ions are removed from the ammonium sulfate solutions. The Temkin isotherm model also proved to be useful in describing the fluoride ions uptake by anhydrite, but only from the aqueous and ammonium sulfate solutions at the concentration of 10%–30% by mass, as well as by gypsum, but only for the concentrated solutions of ammonium sulfate. The Dubinin–Radushkevich isotherm model is not suitable for describing the mechanism of fluoride ions uptake by anhydrite, but in the case of gypsum, it is the better the higher the concentration of ammonium sulfate is. For the aqueous solutions, despite the high values of the R^2 coefficient, none of the isotherm models under consideration is adequate to describe the mechanism of uptake of fluoride ions from these solutions except the Temkin model, but only when anhydrite was used.

Table 5

Values of the correlation coefficient R^2 and sorption capacities q_e theoretical and experimental obtained for the Langmuir and Freundlich isotherm models

Purified solution	Dose (g)	Gypsum			Anhydrite		
		Langmuir isotherm model					
		R^2	q_e theoretical ($\text{mg}\cdot\text{g}^{-1}$)	q_e experimental ($\text{mg}\cdot\text{g}^{-1}$)	R^2	q_e theoretical ($\text{mg}\cdot\text{g}^{-1}$)	q_e experimental ($\text{mg}\cdot\text{g}^{-1}$)
NH ₄ F + H ₂ O	0.2	0.71	–	–	0.67	–	–
	0.5	0.11	–	–	0.68	–	–
	0.7	0.87	–	–	0.94	–	–
	1	0.99	204.98	195.95	0.98	213.94	229.88
NH ₄ F + 10% AS	0.2	0.13	–	–	0.24	–	–
	0.5	0.20	–	–	0.35	–	–
	0.7	0.91	–	–	0.81	–	–
	1	0.97	211.19	193.13	0.96	187.28	193.35
NH ₄ F + 20% AS	0.2	0.08	–	–	0.57	–	–
	0.5	0.09	–	–	0.78	–	–
	0.7	0.95	–	–	0.79	–	–
	1	0.98	193.02	186.45	0.99	178.69	185.78
NH ₄ F + 30% AS	0.2	0.03	–	–	0.06	–	–
	0.5	0.05	–	–	0.06	–	–
	0.7	0.97	170.73	172.14	0.52	–	–
	1	0.89	–	–	0.96	170.10	179.08
NH ₄ F + 40% AS	0.2	0.05	–	–	0.66	9.23	10.00
	0.5	0.99	177.03	176.00	0.09	–	–
	0.7	0.43	–	–	0.62	–	–
	1	0.68	–	–	0.14	–	–
Freundlich isotherm model							
Purified solution	Dose (g)	R^2	q_e theoretical ($\text{mg}\cdot\text{g}^{-1}$)	q_e experimental ($\text{mg}\cdot\text{g}^{-1}$)	R^2	q_e theoretical ($\text{mg}\cdot\text{g}^{-1}$)	q_e experimental ($\text{mg}\cdot\text{g}^{-1}$)
NH ₄ F + H ₂ O	0.2	0.52	–	–	0.50	–	–
	0.5	0.96	847.97	248.00	0.67	–	–
	0.7	0.88	–	–	0.97	–	–
	1	0.87	–	–	0.99	244.22	229.88
NH ₄ F + 10% AS	0.2	0.48	–	–	0.46	–	–
	0.5	0.36	–	–	0.58	–	–
	0.7	0.87	189.84	193.21	0.62	–	–
	1	0.81	–	–	0.88	195.73	193.35
NH ₄ F + 20% AS	0.2	0.41	–	–	0.53	–	–
	0.5	0.23	–	–	0.94	–	–
	0.7	0.88	–	–	0.51	–	–
	1	0.91	191.29	186.45	0.95	183.78	185.78
NH ₄ F + 30% AS	0.2	0.43	–	–	0.38	–	–
	0.5	0.18	–	–	0.03	–	–
	0.7	0.84	179.16	172.14	0.20	–	–
	1	0.66	–	–	0.91	175.56	179.08
NH ₄ F + 40% AS	0.2	0.25	–	–	0.17	–	–
	0.5	0.65	–	–	0.06	–	–
	0.7	0.86	173.44	171.43	0.00	–	–
	1	0.77	–	–	0.64	155.94	153.98

Table 6

Values of the correlation coefficient R^2 and sorption capacities q_e theoretical and experimental obtained for the Temkin and Dubinin–Radushkievich isotherm models

Purified solution	Dose (g)	Gypsum			Anhydrite		
		Temkin isotherm model					
		R^2	q_e theoretical ($\text{mg}\cdot\text{g}^{-1}$)	q_e experimental ($\text{mg}\cdot\text{g}^{-1}$)	R^2	q_e theoretical ($\text{mg}\cdot\text{g}^{-1}$)	q_e experimental ($\text{mg}\cdot\text{g}^{-1}$)
NH ₄ F + H ₂ O	0.2	0.50	–	–	0.62	–	–
	0.5	0.24	–	–	0.66	–	–
	0.7	0.85	–	–	0.98	–	–
	1	0.91	207.46	195.95	1.00	226.82	229.88
NH ₄ F + 10% AS	0.2	0.79	–	–	0.81	–	–
	0.5	0.37	–	–	0.59	–	–
	0.7	0.86	–	–	0.91	–	–
	1	0.86	205.13	193.13	0.92	190.02	193.35
NH ₄ F + 20% AS	0.2	0.45	–	–	0.72	–	–
	0.5	0.26	–	–	0.94	–	–
	0.7	0.88	–	–	0.48	–	–
	1	0.96	191.43	186.45	0.97	184.37	185.78
NH ₄ F + 30% AS	0.2	0.64	–	–	0.61	–	–
	0.5	0.20	–	–	0.03	–	–
	0.7	0.85	174.77	172.14	0.18	–	–
	1	0.69	–	–	0.92	171.33	179.08
NH ₄ F + 40% AS	0.2	0.15	–	–	0.07	–	–
	0.5	0.61	–	–	0.05	–	–
	0.7	0.87	173.56	171.43	0.00	–	–
	1	0.78	–	–	0.65	149.47	153.98
Dubinin–Radushkievich isotherm model							
Purified solution	Dose (g)	R^2	q_e theoretical ($\text{mg}\cdot\text{g}^{-1}$)	q_e experimental ($\text{mg}\cdot\text{g}^{-1}$)	R^2	q_e theoretical ($\text{mg}\cdot\text{g}^{-1}$)	q_e experimental ($\text{mg}\cdot\text{g}^{-1}$)
NH ₄ F + H ₂ O	0.2	0.94	162.43	99.63	0.69	–	–
	0.5	0.10	–	–	0.63	–	–
	0.7	0.81	–	–	0.89	184.31	197.86
	1	0.91	–	–	0.83	–	–
NH ₄ F + 10% AS	0.2	0.72	–	–	0.83	–	–
	0.5	0.16	–	–	0.29	–	–
	0.7	0.85	–	–	0.84	–	–
	1	0.98	186.57	193.13	0.94	175.78	193.35
NH ₄ F + 20% AS	0.2	0.76	–	–	0.90	–	–
	0.5	0.07	–	–	0.71	–	–
	0.7	0.92	–	–	0.85	–	–
	1	0.97	175.10	178.33	0.92	167.18	185.78
NH ₄ F + 30% AS	0.2	0.62	–	–	0.56	–	–
	0.5	0.04	–	–	0.08	–	–
	0.7	0.98	168.52	172.14	0.62	–	–
	1	0.97	–	–	0.92	160.48	179.08
NH ₄ F + 40% AS	0.2	0.56	–	–	0.58	–	–
	0.5	0.33	–	–	0.11	–	–
	0.7	0.98	167.22	171.43	0.14	–	–
	1	0.91	–	–	0.90	145.85	153.98

Gopal and Elango [23] showed a great fit of experimental data of fluoride ion removal from water onto $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ to both Langmuir and Freundlich models. The high value of the correlation coefficient was justified by the fact that under the given experimental conditions they favour both the monolayer adsorption and that on the heterogeneous surfaces. It was concluded that $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ used in the study exhibited complex adsorption properties, and the adsorption of fluoride ions involved more than one mechanism.

Summarizing the results of equilibrium studies of the process of sorption of fluoride ions with calcium sulfate, it can be concluded that the essence of the process is not explicit for the $\text{NH}_4\text{F} + \text{H}_2\text{O}$ and $\text{NH}_4\text{F} + (\text{NH}_4)_2\text{SO}_4$ systems. Based on the largely varying values of the coefficient of determination for these systems, for different calcium sulfate dosages, it can be also concluded that the mechanism depends not only on the environment from which fluoride ions are removed but also on the amount of calcium sulfate. The significantly smaller values of the determination coefficient for each of the sorption models under consideration when smaller amounts of calcium sulfate are used, and the significant increase in these values with the increasing amounts, indicate that in the presence of smaller amounts of gypsum, the dominant process responsible for the removal of fluoride ions from the treated solutions is not sorption but precipitation of fluoride in the form of CaF_2 . Taking into account how the solubility of the different types of calcium sulfate used in the study changes as well as the values of the coefficients of matching the size of the sorption capacities determined experimentally with those determined on the basis of individual adsorption models, it should be concluded that the process of precipitation of fluoride ions and their adsorption overlap, and the observed effect in the form of the number of mg of fluoride removed using 1 g of calcium sulfate is the resultant of these two processes.

4. Conclusions

Based on the obtained results, it can be concluded that calcium sulfate of fossil origin can be effective in fluoride ions removal in the presence of ammonium sulfate only with a sufficiently large F^- ions content. With the F^- ion content of $0.05 \text{ g}\cdot\text{L}^{-1}$, the presence of AS prevents completely from their binding by gypsum and reduces this ability significantly in the case of anhydrite. As the initial fluoride content increases to $0.5 \text{ g}\cdot\text{L}^{-1}$, the presence of AS causes a reduction in the removal efficiency in relation to the aqueous solutions but still allows large removal values to be achieved. At the dose of 0.2 g per 50 mL of solution containing 40% of AS and at the initial fluoride concentration of $0.05 \text{ g}\cdot\text{L}^{-1}$, the fluoride removal efficiency using gypsum was zero and it was 4.5% for anhydrite. When the initial fluoride concentration was $0.5 \text{ g}\cdot\text{L}^{-1}$, it increased to 77.6% with gypsum and to 76.7% with anhydrite. Similar observations were made at the initial fluoride content of $1 \text{ g}\cdot\text{L}^{-1}$. Hence, calcium sulfate can be considered as a material for removing F^- from the ammonium sulfate solutions, but only at the sufficiently large contents of these ions. Choosing the right dose of calcium sulfate, it is possible to obtain more than 70% removal efficiency of fluoride ions from the $\text{NH}_4\text{F} + 40\%$ AS solution

containing $0.5 \text{ g}\cdot\text{L}^{-1} \text{ F}^-$ and more than 80% efficiency at the fluoride content of $1 \text{ g}\cdot\text{L}^{-1}$, both with gypsum and anhydrite. However, using a too large dose of calcium sulfate in relation to the amount of fluoride ions results in thickening of the purified solution due to coagulation. As the dose of calcium sulfate increased, a decrease in the amount of mg of F^- removed per 1 g of calcium sulfate was observed in the solutions with the increasing fluoride concentration. The maximum amount of mg of F^- bound by 1 g of calcium sulfate from the $\text{NH}_4\text{F} + 40\%$ AS solution was $228 \text{ mg}\cdot\text{g}^{-1}$ for gypsum and $224 \text{ mg}\cdot\text{g}^{-1}$ for anhydrite.

Of the isotherm models that were considered, the Langmuir model seems to be the best for describing the fluorides binding on gypsum and the Freundlich model – for anhydrite. However, in the absence of perfect matching of these values, overlap between the precipitation and adsorption of fluorides, as well as a complexation process between the ions of calcium sulfate and ammonium sulfate are assumed.

References

- [1] A. Meenakshi, R.C. Maheshwari, Fluoride in drinking water and its removal, *J. Hazard. Mater.*, 137 (2006) 456–463.
- [2] M. Mohapatra, S. Anand, B.K. Mishra, D.E. Giles, P. Singh, Review of fluoride removal from drinking water, *J. Environ. Manage.*, 91 (2009) 67–77.
- [3] M.A. Tikki, Fluoride removal from water – a review, *Int. J. Sci. Eng. Res.*, 5 (2014) 515–518.
- [4] A.K. Gupta, S. Ayoob, *Fluoride in Drinking Water. Status, Issues and Solutions*, CRC Press Taylor & Francis Group, Boca Raton, 2016.
- [5] K. Singh, D.H. Lataye, K.L. Wasewar, C.K. Yoo, Removal of fluoride from aqueous solution: status and techniques, *Desal. Water Treat.*, 51 (2013) 3233–3247.
- [6] J. Singh, P. Singh, A. Singh, Fluoride ions vs removal technologies: a study, *Arabian J. Chem.*, 9 (2016) 815–824.
- [7] WHO, *Guidelines for Drinking-Water Quality*, 4th ed., World Health Organization, Malta, Gutenberg, 2011. Available at: https://www.academia.edu/38907437/guidelines_for_drinking-waterquality
- [8] G.C. Velazquez-Pena, M. Solache-Rios, V. Martinez-Miranda, Competing effects of chloride, nitrate and sulfate ions on the removal of fluoride by a modified zeolitic tuff, *Water Air Soil Pollut.*, 226 (2015) 1–15.
- [9] A. Zdunek, D. Kołodźńska, P. Rusek, Z. Hubicki, Ammonium sulfate from flue gases desulfurization by the wet ammonia method as the new nitrogen and sulfur source for production of mineral fertilizers, *Przem. Chem.*, 96 (2017) 660–671 (in Polish).
- [10] J.R. Cahoon, Corrosion characteristics of mild steel in urea ammonium nitrate fertilizer solutions, *Corrosion*, 58 (2002) 166–174.
- [11] P.K. Sundaram, I. Mani, R.A. Parrray, Effect of urea ammonium nitrogen fertilizer on corrosion of different materials, *Int. J. Chem. Stud.*, 7 (2019) 2256–2259.
- [12] B.D. Turner, P. Binning, S.L.S. Stipp, Fluoride removal by calcite: evidence for fluoride precipitation and surface adsorption, *Environ. Sci. Technol.*, 39 (2005) 9561–9568.
- [13] A. Djamel, B.A. Abdelhafidh, Defluoridation of water by precipitation with calcium sulfate and calcium chloride, *Int. J. Chem. Stud.*, 1 (2013) 39–44.
- [14] S.S. Waghmare, T. Arfin, Fluoride removal from water by calcium materials: a state-of-the-art review, *Int. J. Innovation Res. Sci. Eng. Technol.*, 4 (2015) 8090–8102.
- [15] H. Korir, K. Mueller, L. Korir, J. Kubai, E. Wanja, N. Wanjiku, J. Waweru, M.J. Mattle, L. Osterwalder, C.A. Johnson, The Development of Bone Char-Based Filters for the Removal of Fluoride from Drinking Water, Refereed Paper 189, 3th WEDC International Conference, Addis Ababa, Ethiopia,

2009. Available at: https://repository.lboro.ac.uk/articles/The_development_of_bone_char-based_filters_for_the_removal_of_fluoride_from_drinking_water/9585764
- [16] J. Fawell, K. Bailey, J. Chilton, E. Dahi, L. Fewtrell, Y. Magara, Fluoride in Drinking-Water, World Health Organisation, TJ International (Ltd.), Padstow, Cornwall, UK, 2006.
- [17] V.E. Badillo-Almaraz, J.A. Flores, H. Arriola, F.A. Lopez, L. Ruiz-Ramirez, Elimination of fluoride ions in water for human consumption using hydroxyapatite as an adsorbent, *J. Radioanal. Nucl. Chem.*, 271 (2007) 741–744.
- [18] L. Li, Z.L. Zhu, Y.L. Qiu, Adsorption of fluoride ions on a Ca-deficient hydroxyapatite, *Huan Jing Ke Xue*, 31 (2010) 1554–1559 (Abstract in English).
- [19] B.D. Turner, P. Binning, S.L.S. Stipp, Fluoride removal by calcite: evidence for fluorite precipitation and surface adsorption, *Environ. Sci. Technol.*, 39 (2005) 9561–9568.
- [20] M. Yang, T. Hashimoto, N. Hoshi, H. Myoga, Fluoride removal in a fixed bed packed with granular calcite, *Water Res.*, 33 (1999) 3395–3402.
- [21] S.K. Nath, R.K. Dutta, Fluoride removal from water using crushed limestone, *Indian J. Chem. Technol.*, 17 (2010) 120–125.
- [22] M. Srimurali, A. Pragathi, J. Karthikeyan, A study on removal of fluorides from drinking water by adsorption onto low-cost materials, *Environ. Pollut.*, 99 (1998) 285–289.
- [23] V. Gopal, K.P. Elango, Equilibrium, kinetic and thermodynamic studies of adsorption of fluoride onto plaster of Paris, *J. Hazard. Mater.*, 141 (2007) 98–105.
- [24] B. Thole, F. Mitalo, W. Masamba, Groundwater defluoridation with raw bauxite, gypsum, magnesite and their composites, *Clean*, 40 (2012) 1222–1228.
- [25] A.E. Al-Rawajfeh, S. Al-Hawamdeh, S. Al-Dharaba'a, Defluoridation of Water by Natural Materials: Is It Adsorption?, Proceedings of the 13th International Conference of Environmental Science and Technology, Athens, Greece, 5–7 September 2013. Available at: <https://www.researchgate.net/publication/319154811>
- [26] J. Kang, X. Gou, Y. Hu, W. Sun, R. Liu, Z. Gao, Q. Guan, Efficient utilisation of flue gas desulfurization gypsum as a potential material for fluoride removal, *Sci. Total Environ.*, 649 (2019) 344–352.
- [27] G. Azimi, V.G. Papangelakis, J.E. Dutrizac, Modelling of calcium sulphate solubility in concentrated multi-component sulphate solutions, *Fluid Phase Equilib.*, 260 (2007) 300–315.
- [28] A. Zdunek, K. Borowik, D. Kołodyńska, Application of Spectroscopic Methods for the Study of the Possibilities of Fluoride Removal From Aqueous Solutions with Calcium Sulfates of Various Origin, Z. Hubicki, Ed., Science and Industry – Spectroscopic Methods in Practice, New Challenges and Opportunities, UMCS Publishing House, Lublin, 2019, pp. 564–568 (in Polish).
- [29] M.V. Lopez-Ramon, F. Stoeckli, C. Moreno-Castilla, F. Carras-Marín, On the characterization of acidic and basic surface sites on carbons by various techniques, *Carbon*, 37 (1999) 1215–1221.
- [30] A.O. Dada, A.P. Olalekan, A.M. Olatunya, Langmuir, Freundlich, Temkin and Dubinin–Radushkevich isotherms studies of equilibrium sorption of Zn²⁺ onto phosphoric acid modified rice husk, *IOSR J. Appl. Chem.*, 3 (2012) 38–45.
- [31] R.M. Silverstein, F.X. Webster, D.J. Kiemle, Spectrometric Identification of Organic Compounds, PWN, Warszawa, 2012 (in Polish).
- [32] R.A. Meyers, Encyclopedia of Analytical Chemistry, John Wiley & Sons Ltd., Chichester, 2000.
- [33] Y. Liu, A. Wang, J.J. Freeman, Raman, MIN and NIR Spectroscopic Study of Calcium Sulfates: Gypsum, Basanite, and Anhydrite, 40th Lunar and Planetary Science Conference, 2009. Available at: <https://www.semanticscholar.org/paper/Raman%2C-MIR%2C-and-NIR-Spectroscopic-study-of-Calcium-Liu%20Wang/bfb66f30b51761fecec40af2530694b8b46f7a00>, (Accessed on 20.05.2021).
- [34] M. Azami, S. Jalilifiroozinezhad, M. Mozafari, M. Rabiee, Synthesis and solubility of calcium fluoride/hydroxy-fluorapatite nanocrystals for dental applications, *Ceram. Int.*, 37 (2011) 2007–2014.
- [35] R. Kocjan, Analytical Chemistry. Qualitative Analysis. Classical Analysis, Vol. 1, PZWL, Warszawa, 2000 (in Polish).