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Removal of Fluoride from Ammonium Sulphate Solutions Using Bentonite

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Flue gases desulphurization process by the wet ammonia method as the source of ammonium sulphate solutions containing fluoride

One of the flue gases desulphurization methods is the wet ammonia method, which relies on the following reactions [1]:

$$SO_2 + 2NH_3 + H_2O \rightleftarrows (NH_4)_2SO_3$$

$$(NH_4)_2SO_3 + ½O_2 \rightleftarrows (NH_4)_2SO_4$$

In addition to SO_2, the components of the flue gases such as HF and HCl are also absorbed in the ammonia solution according to the following reactions [2]:

$$HF + (NH_4)_2SO_3 \rightarrow NH_4HSO_3 + NH_4F$$

$$HCl + (NH_4)_2SO_3 \rightarrow NH_4HSO_3 + NH_4Cl$$

As the result of this process the ammonium sulphate solutions are generated, which undergo a crystallization process to obtain an ammonium sulphate in the solid state.
Both crystalline ammonium sulphate and ammonium sulphate solutions derived from the flue gases desulphurization process could be used as the components of solid and liquid fertilizers.
The presence of fluoride ions in ammonium sulphate obtained as the product of the wet ammonia-based desulphurization process can adversely affect both the conditions of the fertilizer production process and the physicochemical properties of these fertilizer products. One of the most important aspect is the effect on corrosion properties of liquid fertilizers based on ammonium sulphate, which in themselves constitute an aggresive environment for plant construction materials.

Fluoride removal methods

Among various kinds of known defluoridation methods like: precipitation and coagulation, ion-exchange, electrodialysis and electrolysis, membrane processes, adsorption method seems to be one of the most suitable technique for fluoride removal because it is economical, environmental friendly and efficient.

Many kinds of adsorbents have been reported to be effective for fluoride removal like: activated carbon, activated alumina, low-cost type sorbents. calcite, tricalcium phosphate, natural materials like zeolites or bentonites [3].

Bentonites, in addition to such materials as claay pottery, activated clay, kaolinite or illite-goehite soils are known as natural adsopbents used to fluoride removal from drinking water, especially in India, Kenya or China [4]. In the case of these kinds of materials, solution pH, surface area, structure, aluminium content and the presence of certain exchangable cations capable of forming fluoride precipitates are significant in defluoridation process. Though ion-exchange reactions are believed to be the predominant form of fluoride sorption, they may also be immobilized through the formation of complexes or precipitates with exchangeable cations such as: magnesium, iron and calcium. There may be an electrostatic attraction to the surface through which F^- may be retained in the electric double layer [4]. Like most of the low-cost type adsorbents, bentonites reveal rather low fluoride adsorption capacity, around several mg/g, hence they are usually subjected to various modifications to increase this value.

Impact of ammonium sulphate solutions environment on the fluoride removal efficiency

Fluoride removal from the ammonium sulphate solutions seems to be much more difficult than from the drinking water, mainly because of:
- high value of ionic strength,
- strictly defined pH without the possibility of correction of it,
- competitiveness of SO_4^{2-} in relations to F^-.

Additionally, in the case of real ammonium sulphate solutions derived from flue gases desulphurization plant, there are also present other ions which may hinder the removal of fluoride. These solutions are under high temperture that also influence the fluoride removal efficacy.

Bentonites as the fluoride adsorbent

Goal of the experiments

- Study on fluoride removal in the form of NH_4F from ammonium sulphate solutions compared to aqueous fluoride solutions, using two samples of bentonite.
- Examine the properties of bentonites like: chemical composition by XRF method, BET Surface and pores volume, value of pH pzc.
- Analysis of bentonites before and after contact with fluoride solutions by XRD method.
- Investigation of the effect on fluoride removal efficiency of such factors as: bentonite dosage, initial fluoride concentration, contact time, and temperature.

Methodology

- All the adsorption tests were carried out in batch mode, in 100 mL plastic containers with caps, with 50 mL of ammonium fluoride test solutions, using multi-station magnetic stirrer, with the same agitation speed.
- The fluoride concentration in the test solutions was measured by the direct potentiometric method, using a fluoride selective electrode, made of lanthanum fluoride single crystal (LaF_3) as the indicating electrode.
- To optimize certain parameter, one parameter was changed and all other variables were kept constant.

Table 1. Chemical composition (by XRF method) and loss of ignition (1273 K) of bentonites

	Ingredient content [% by weight]	
	Bentonite I	Bentonite II
CaO	1.65	1.63
SiO_2	53.56	57.69
Al_2O_3	15.24	16.92
MgO	3.51	3.36
Fe_2O_3	1.88	2.30
SO_3	0.37	0.29
Na_2O	4.92	2.79
K_2O	1.16	1.19
TiO_2	0.12	0.15
Mn_2O_3	0.13	0.15
Loss of ignition	14.81	13.90

Table 2. BET Surface (S_{BET}), total pore volume (V_T) and volume of mesopores (V_M) of bentonites

	Bentonite I	Bentonite II
S_{BET} [m²/g]	5.9	43.0
V_T [cm³/g]	0.03	0.09
V_{MES}	0.02	0.06

Table 3. pH $_{PZC}$ values of bentonites

	Bentonite I	Bentonite II
pH_{PZC}	10.2	9.7

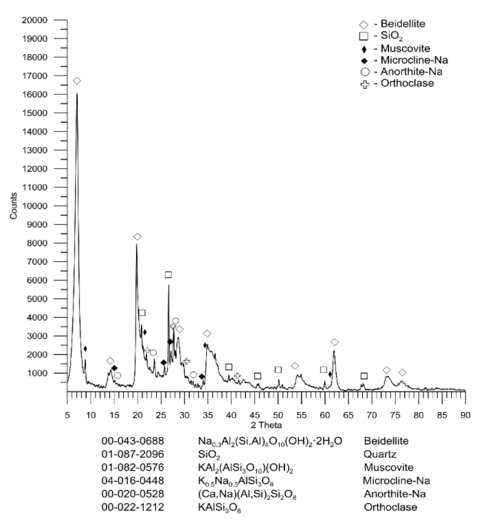

Fig. 1. XRD pattern of bentonite I

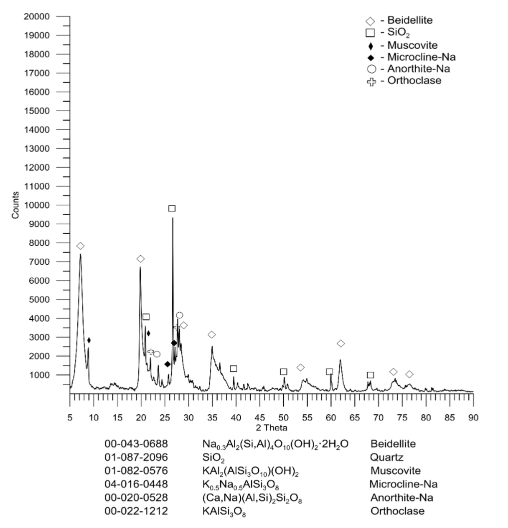

Fig. 2. XRD pattern of solid state obtained after contact of bentonite I with NH_4F+H_2O

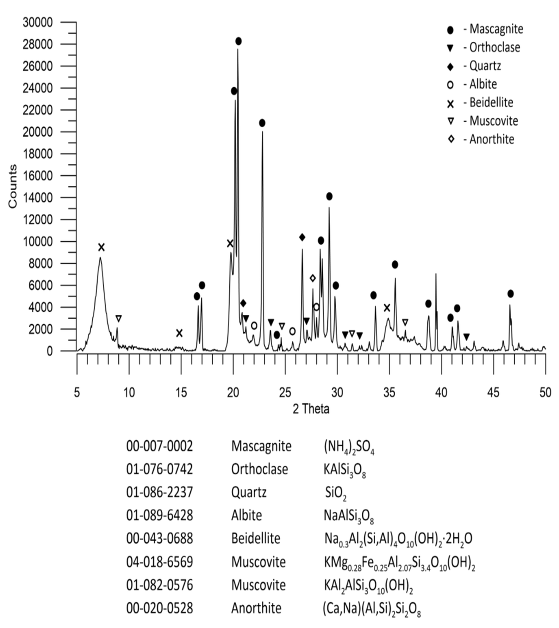

Fig. 3. XRD pattern of solid state obtained after contact of bentonite I with $NH_4F+(NH_4)_2SO_4$

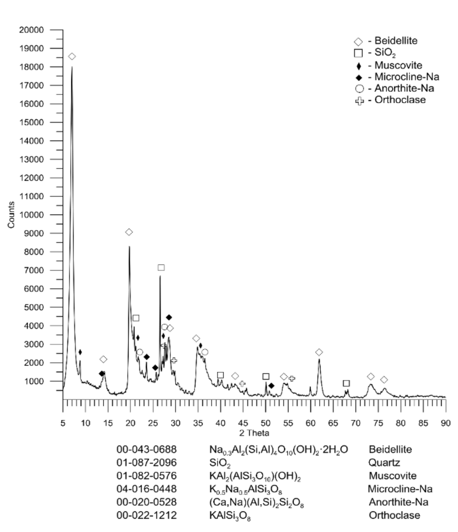

Fig. 4. XRD pattern of bentonite II

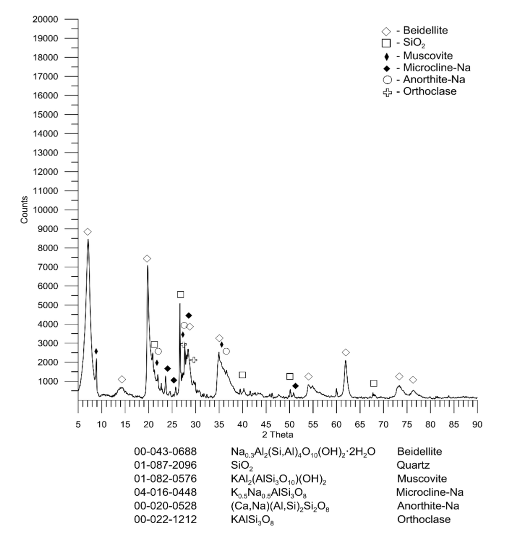

Fig. 5. XRD pattern of solid state obtained after contact of bentonite II with NH_4F+H_2O

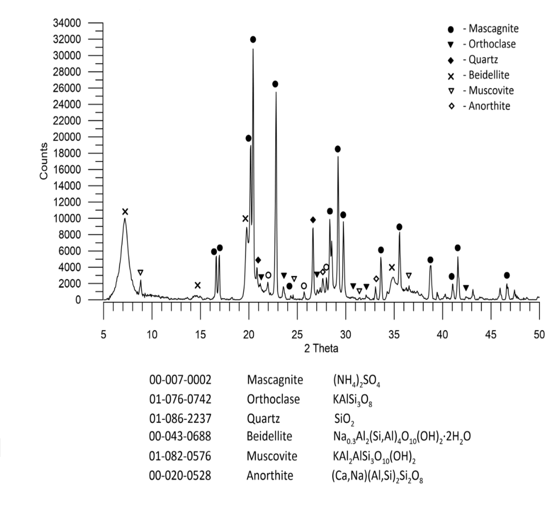

Fig. 6. XRD pattern of solid state obtained after contact of bentonite II with $NH_4F+(NH_4)_2SO_4$

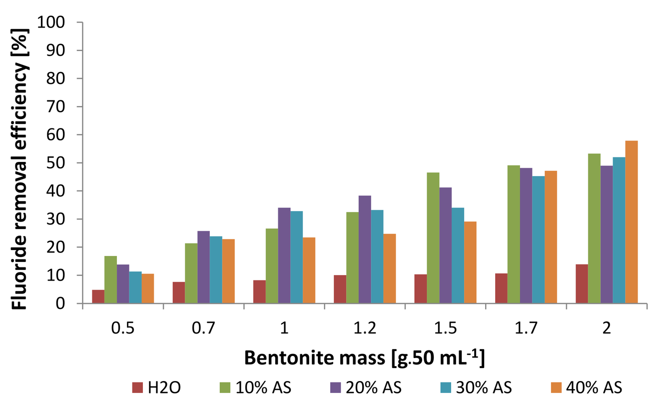

Fig. 8. Effect of bentonite I dose on fluoride removal efficiency, initial fluoride concentration 0.5 g L⁻¹, contact time 1 hour, temperature 298 K

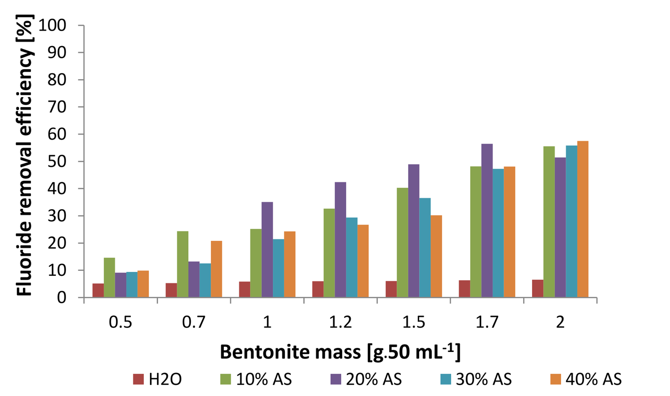

Fig. 9. Effect of bentonite II dose on fluoride removal efficiency, initial fluoride concentration 0.5 g L⁻¹, contact time 1 hour, temperature 298 K

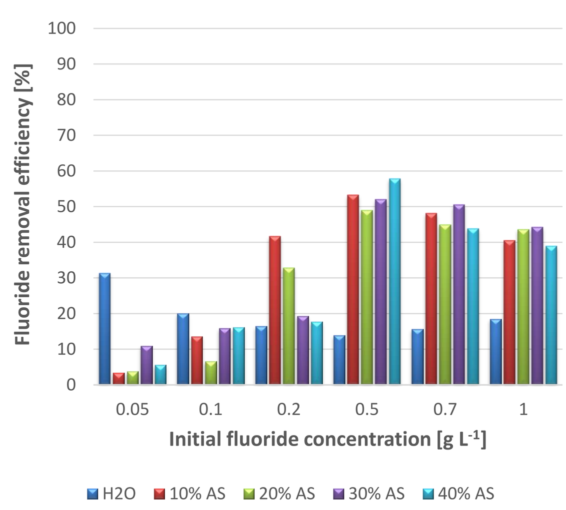

Fig. 10. Effect of initial fluoride concentration on fluoride removal efficiency using bentonite I, bentonite dose 2 g/50 mL, contact time 1 hour, temperature 298 K.

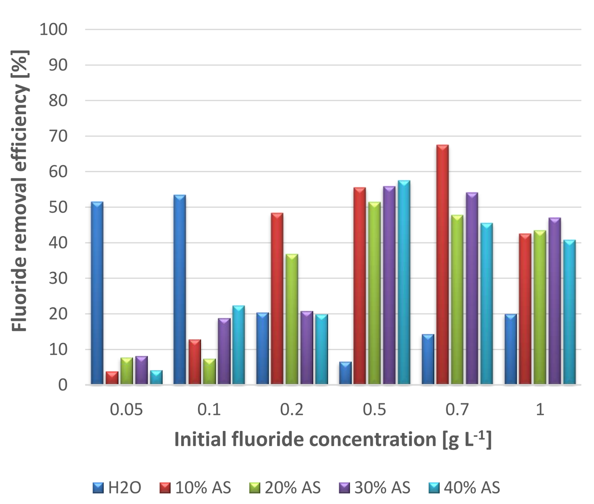

Fig. 11. Effect of initial fluoride concentration on fluoride removal efficiency using bentonite II, bentonite dose 2 g/50 mL, contact time 1 hour, temperature 298 K.

- **Effect of contact time on fluoride removal efficiency**

The conducted reserach have proved that about 60 minutes of bentonites contact time with the fluoride solution is needed to remove of considerable amounts of fluorides, for both aqueous and ammonium sulphate solutions. Extending of time contact over 60 minutes is unreasonable.

- **Effect of temperature on fluoride removal efficiency**

Investigations on the impact of temperature in the range of 298-353 K on fluoride removal effciency using bentonites have shown that the most temperature effect has been observed in the case of NH_4F+H_2O solutions for which, the fluoride removal effciciency has rised with the increase of the temperature from 298 K to 313 K from 12% to 61% in the case of bentonite I sample, and with the increase of the temperature from 298 K to 323 K from 6% to 66% in the case of bentonite II sample. For higher values of temperatures, the quantity of fluoride ions removed has decreased considerably.

In the case of ammonium sulphate solutions, with the increase of temperature the fluoride emoval efficiency has increased slightly, but for temperature value of 343 K, this parameter has decreased. The highest decreased has been observed for solutions containing 30% and 40% by mass of ammonium sulphate.

Conclusions:

- Both samples of bentonites used contain over 50% of SiO_2 and over 15% of Al_2O_3, over 3% of MgO, about 2% of Fe_2O_3 and about 1.6% of CaO. Every of these ingredients can take part in the bindinf of fluoride.
- Each of bentonites samples revealed various size of BET surface. Bentonite II has much bigger S_{BET} and this sample is more porous than bentonite I.
- Values of pH_{PZC} of bentonites indicate that for pH of solution below about 10, the fluoride binding ability is due to exchange with other anions.
- The XRD analysis revealed that the main crystalline phase present in bentonites is beidellite. After contact of bentonites with NH4F+H2O solution there is no new phases present, but the peak derived from beidellite is much lower than in bentonites. After contact with $NH_4F+(NH_4)_2SO_4$ solution there were new phases noticed like anorthite and albite. No fluoride-containing crystalline phases were found in any of the tested samples obtained after contact of bentonites with fluoride solutions.
- The results of studies on effect of bentonites dose on fluoride removal have proved that in the case of aqueous solutions of fluoride increasing of bentonites dosage did not increase effectively the fluoride removal efficiency. In the case of ammonium sulphate solutions, with increasing of bentonites dosage a significant increase of fluoride removal efficacy has been noticed.
- The results of studies on effect of initial concentration of fluoride have proved that in the case of aqueous solutions of fluoride, the fluoride removal efficiency is the greater the lower is the initial fluoride concentration. But for the ammonium sulphate solutions containing fluoride, a positive effect of increase in the initial concentration of fluoride was noticed.
- 60 minutes of contact time turn out to be sufficient to achieve considerable degree of fluoride binding by bentonites both from aqueous and ammonium sulphate solutions.
- Temperature affects the fluoride removal efficiency epecially in the aqueous solutions, but in the case of ammonium sulphate solutions, this impact is much lower.

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