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SORPTION AND ION-EXCHANGE PROCESSES

Sorption-Active Materials Based on an Acid-Nonresistant Aluminosilicate Nepheline, Used for Defluorination of Industrial Sewage

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Abstract—A method for obtaining sorption-active materials based on a solidifying mineral dispersion composed of nepheline, hydrochloric acid, and water was suggested. The hardening processes and conditions under which sorption-active compounds are formed were studied. The mechanism of sorption of F- ions on the sorbents developed was determined.

A topical environmental problem of the Kola region is purification of mine water and underground water to remove fluoride ions. All the methods presently used for this purpose can be divided into two groups: (1) coprecipitation and coagulation on freshly synthesized aluminum and magnesium hydroxides and calcium phosphate and (2) ion exchange of fluorineselective ion exchangers, e.g., activated aluminum oxide, which is a strongly basic anion exchanger. However, use of these expensive ways to defluorinate water is unacceptable in the case of large-tonnage wastes. Defluorination of sewage from mining plants require granulated sorbents, which can be used by creating check dams before discharging, e.g., mine water into natural water basins. To solve this problem, it is suggested to prepare sorption-active materials by the technology of self-hardening binder systems. By binders (self-hardening) are understood systems containing, in certain relative amounts, the solid and liquid phases that can interact to give new condensed phases and are capable of hardening [1, 2]. It is known that condensed reaction products formed in hardening of water-containing binder systems, with aluminosilicates used as a solid phase, are salts of complex composition. These salts contain oxyhydrates, hydrosilicates, and hydroaluminates, which exhibit sorption properties under certain conditions [5].

In development of sorbents for defluorination of wastewater, the mineral phase of the self-hardening binder system should be composed of acid-nonresistant aluminum-containing minerals that can interact with aqueous solutions of acids to give hydroxo compounds of aluminum, which are anion-active sorbents under certain conditions [4]. The search for starting raw materials was limited to the natural resources of the Kola Peninsula. Preference was given to nepheline-containing raw materials, whose advantage over other types of raw materials consists in larger resources, fast decomposition by acids, and high content of alumina (up to 30 wt % Al₂O₃). In view of the fact that aluminum hydroxides exhibiting the highest activity toward fluoride ions are formed in hydrolysis of its oxychlorides [4], a hydrochloric acid solution was chosen as the second component of the binder system for synthesis of a fluorine-selective sorbent.

The aim of this study was to find conditions under which granulated sorption-active materials to be used in treatment of mine wastewater can be formed by the binder technology in the system constituted by nepheline, hydrochloric acid, and water and to determine the optimal application conditions of the materials obtained.

We used a nepheleine concentrate produced by the Apatit Open Joint-Stock Company, ground to a specific surface area of 2600 cm² g⁻¹. The concentrate contained up to 80-81 wt % nepheline and had the following chemical composition (wt %): SiO₂ 42.60, Al₂O₃ 29.30, Na₂O 13.96, and K₂O 7.13. The concentration of hydrochloric acid was varied from 5 to 35%. The degree of nepheline decomposition was controlled by changing the amount of HCl contained in the starting binder system and calculated in accor-

Sam- ple no.	α	c _{HCl} %	s : 1	$c_{\mathrm{F}^-},$ mg g ⁻¹	R _{comp} , MPa
1	6–7	17	3:1	20.7	2.5-3.5
2	25	17	1:1.5	33.0	1.0
3	50	17	1:3	64.5	0.4
4	75	17	1:4	65.0	0.2
5	100	39	1:4	52.0	0.2
6	100	17	1:5.5	22.0	Less than 0.2
7	100	17	1:15	24.0	" "
8	75	9.5	1:8	33.0	" "
9	50	3.5	1:15	32.0	" "

 Table 1. Synthesis conditions and strength characteristics of sorbents

dance with the reaction of complete (stoichiometric) decomposition of nepheline:

$$(\text{Na}_3\text{K})\text{O}_2 \cdot 2\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 + 16\text{HCl} \rightarrow 3\text{NaCl} + \text{KCl}$$
$$+ 4\text{AlCl}_3 + 4\text{SiO}_2 + 8\text{H}_2\text{O}.$$

It was assumed that 100% decomposition of nepheline occurs in those reaction mixtures in which the amount of hydrochloric acid corresponded to that required by the stoichiometry. In what follows, the degree of decomposition α is given in percent relative to total decomposition.

The concentration of fluoride ions, $c_{\rm F}$, was measured potentiometrically with an EF-VI fluorine-selective electrode in the presence of a citrate buffer solution. The citrate buffer solution was used to break down complexes formed by F⁻ ions with aluminum cations, which may be present in solution.

The products formed in the reaction of nepheline with hydrochloric acid were studied by X-ray diffraction analysis, IR spectroscopy, and mass spectrometry.

EXPERIMENTAL

The technique used to obtain materials was the same for all the compositions: finely ground nepheline concentrate was poured-over with an HCl solution, the mixture was agitated for 15 min, and the resulting mass was kept at 22°C for 24 h, and then thermolysis was performed at 105°C to constant weight.

To determine the strength characteristics (compression strength R_{comp}) of the materials synthesized, $2 \times 2 \times 2$ -cm samples were fabricated. For this purpose,

the mass formed was cast into molds, kept at 22° C for 24 h, and then heat-treated at $105-110^{\circ}$ C for 1 h. The water resistance of the materials synthesized was evaluated by the loss of strength by the samples kept in water for 7 days.

The sorption and the kinetics of leaching-out of the sorbent components were determined under static conditions at a sorbent : sorbate ratio of 1 : 100, temperature of 22°C, and intermittent agitation, with the time of contact varied from 15 min to 72 h. The data obtained are listed in Table 1. The results of the study demonstrated that a granulated water-resistant material should be synthesized in a narrow range of compositions of the starting binder system: the amount of hydrochloric acid corresponds to $\alpha = 6$ -7%, and the concentration of water, to an s : 1 ratio of 2.8:1 to 3:1. As α increases, the strength and water resistance of grains decrease dramatically. The technique that can be used to obtain the sorbent includes the following operations: grinding of the nepheline concentrate to a specific surface area of 2500- $3000 \text{ cm}^2 \text{g}^{-1}$, mixing of the ground concentrate with a 7% HCl solution at a phase ratio of 3 : 1, granulation of the resulting mass, and thermolysis at 105°C.

The reaction products responsible for formation of a strong water-resistant stone and sorption-active phases were for the most part studied using physicochemical methods. This is due to difficulties in isolation of the newly formed phases from the whole mass of a solidified dispersion. To make simpler the identification of the reaction products, all the physicochemical studies were carried out with samples synthesized on nepheline crystals ground to a specific surface area of 2600 cm² g⁻¹. This is justified by the fact that the main impurity minerals (feldspar, titanomagnetite) contained in the nepheline concentrate are considerably more resistant to solutions of acids, compared with nepheline, and have no effect on the hardening processes.

It is known that the key role in hardening of binder formulations and in sorption interactions in materials synthesized by the technology of binder systems is played by water molecules, which are in a firmly bound state in the reaction products [3–4]. The role played by water molecules in the sorbent synthesized from nepheline was revealed using mass-spectrometric analysis, which makes it possible to record not only the loss of mass by a sample, but also the molecular weight of the thermolysis products being removed and their qualitative composition. The results obtained demonstrated that three temperatures of water removal can be distinguished in the mass spectrum of the *p*, relative partial pressure units



Fig. 1. Mass-spectrometric monitoring of thermal removal of water from the nepheline sorbent synthesized at various α and s : 1 ratios. (*p*) Relative pressure and (*T*) temperature. (*1*) $\alpha = 7\%$ at s : 1 = 3 : 1, (2) $\alpha = 50\%$ at s : 1 = 1 : 2.5, and (3) $\alpha = 50\%$ at s : 1 = 1 : 5.

sample obtained at $\alpha = 7\%$ (s : 1 = 3 : 1), with the following distribution of intensities: 120 > 175 > 320°C (Fig. 1). As α increases to 50%, an increase in the amount of OH_n groups removed at at T > 320°C and a decrease in that of OH_n groups removed at 175°C are observed at a water deficiency (s : 1 = 1 : 2.5). As the content of water in the starting dispersion increases ($\alpha = 50\%$ at s : 1 = 1 : 5), the fraction of water removed at 175–180°C increases, and the content of firmly bound OH_n groups decreases.

The mass spectra of hydrogen chloride demonstrate that chlorides and hydroxochlorides decomposing at 320, 410, and 520°C are present in a weakly treated material ($\alpha = 7\%$).

Thus, the materials synthesized on the basis of binder systems with a low degree of nepheline decomposition contain, in contrast to materials with a high degree of decomposition, H_2O and HCl in



Fig. 2. X-ray diffraction patterns of nepheline and the nepheline sorbent synthesized at various s:1 ratios. (1) Starting nepheline, (2) $\alpha = 50\%$ at s:1 = 1:2.5, and (3) $\alpha = 50\%$ at s:1 = 1:5. (1) Nepheline, (11) sodium chloride, and (111) hydrated aluminum chloride.

a firmly bound state, which are removed at temperatures exceeding 350°C. This is in agreement with the variation of the strength characteristics of samples with their synthesis conditions (Table 1).

X-ray diffraction studies of the products formed in the reaction of nepheline with a hydrochloric acid solution demonstrated (Fig. 2) that the phase composition of the compounds formed is primarily determined by the amount of water contained in the starting dispersion, which presumably affects the diffusion of mobile elements in the nepheline structure. In the case of an excess of water, separate phases recorded in the X-ray diffraction pattern are formed. In the dispersions synthesized at s : 1 = 1 : 5, the reflections associated with nepheline disappear already at $\alpha = 50\%$ and the phase of aluminum hydrochlorides (Fig. 2, X-ray diffraction pattern 3) and that of amorphous hydrated silicon oxide are formed in the reaction prod-

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Fig. 3. IR spectra of nepheline and the nepheline sorbent synthesized at $\alpha = 50\%$ and s : 1 = 1 : 2.5. (*T*) Transmission and (v) wave number. (*1*) Nepheline, (2) nepheline sorbent, and (3) the sorbent heat-treated at 400°C.

ucts in addition to chlorides of alkali metals. In the case of deficiency of water (s : 1 = 1 : 2.5), formation of reaction products as separate phases is hindered and a broad band centered at about 3.7 Å is observed on the background of reflections associated with nepheline and alkali metal compounds. This band characterizes the amorphization of the aluminosilicate skeleton: reflections related to AlCl₃ · 6H₂O are absent (Fig. 2, pattern 2).

The behavior revealed was also observed in a study of the reaction products formed at $\alpha = 100\%$ at various s : 1 ratios: 17% HCl at s : 1 = 1 : 15 and 36% HCl at s : 1 = 1 : 3. The X-ray diffraction patterns of the samples obtained with excess water (s : 1 = 1 : 15) contain reflections associated with chlorides of alkali metals, hydrated aluminum chloride, and hydrated amorphous silicon oxide. With a deficiency of water, only NaCl, KCl, and amorphous aluminosilicates are manifested in the X-ray diffraction patterns. After washing of the reaction products with water, only a broad band associated with amorphous aluminosilicates is observed in both cases. The shift of its center from 3.7 to 3.3 Å in water-deficient systems indicates that this phase is enriched with aluminum oxides [5]. The SiO₂ : Al₂O₃ ratio in the reaction products is 1 : 0.04 in the system with an excess of water and 1 : 0.25 in that with a deficiency of water. This indicates that the extent to which aluminum oxides are removed from the aluminosilicate skeleton decreases as the concentration of H₂O in the starting dispersion becomes lower. The nepheline structure disintegrates incongruently: the egress of alkaline cations is ahead of the diffusion of Al³⁺ from the nepheline structure, which leads to formation of a sparingly soluble amorphous phase of aluminosilicates.

The results of X-ray diffraction studies are confirmed by the IR data (Fig. 3). A pronounced increase in the absorption at 960 cm^{-1} and in the range 540- 640 cm^{-1} in nepheline treated with hydrochloric acid under conditions of water deficiency (s : 1 = 1 : 2.5) is due to hydroxylation of the surface and formation of Al-OH and Si-OH bonds [6]. The presence of hydrated aluminosilicates in the products formed in the reaction of nepheline with hydrochloric acid under conditions of water deficiency is indicated by the fact that the IR spectra contain a broad band at 2800-3740 cm⁻¹. The shoulders at 3560–3680 cm⁻¹ correspond to stretching vibrations of silanol groups involved in hydrogen bonding and to isolated silanol groups. This interpretation is supported by the fact that the absorption in these spectral ranges decreases upon removal of water from the samples at 400°C. The partial cleavage of Si-O-Al bonds characterizing the ordered isomorphism in the aluminosilicate skeleton of nepheline and the appearance of purely Si-O and Al-O bonds is confirmed by broadening of the band of symmetric stretching vibrations v_{as} of Si–O–Si and Si–O–Al bonds (920–1200 cm⁻¹) and by weakening of doublets of bending vibrations v_s (690–710 cm⁻¹) and δ (470–510 cm⁻¹) of these bonds [6]. It should also be noted that all the samples under study exhibit absorption at $590-650 \text{ cm}^{-1}$, suggesting the presence of aluminum compounds with an octahedral coordination [6–9].

The results of physicochemical studies of the reaction products formed in the dispersions composed of nepheline, hydrochloric acid, and water indicate that the amorphous phase of oxyhydrate aluminumcontaining compounds is formed on the sorbent surface. These compounds incorporate H_nO and HCl in a bound state, which are removed at temperatures higher than 350°C. These reaction products, formed in a narrow range of compositions, are responsible for the dispersion hardening and sorption processes.

To determine the optimal application conditions of

nepheline sorbents, the kinetics of leaching-out of the main components of the sorbent and its sorption characteristics were studied under varied conditions [4]. As is known, sorption of fluoride ions on oxyhydrate aluminum-containing sorbents occurs via formation of insoluble polymolecular fluoroaluminate complexes AlF_x^{3-x} (x = 1-6) through ion exchange or chemical interaction. The main exchange centers in amorphous aluminum oxyhydrates are molecules of coordination water and bridged and terminal OH groups [10]. Formation of various types of centers and occurrence of one or another sorption mechanism are affected by the solution pH, concentration of active Al³⁺ on the sorbent surface, and concentration of F^- in solution [10]. In the case of the nepheline concentrate, as active aluminum was regarded that contained in the reaction products, i.e., in the active phase. The amount of the active phase was evaluated by the degree of nepheline breakdown, α , i.e., by the amount of hydrochloric acid, with water contained in the dispersion disregarded. The study was carried out with a nepheline concentrate of the optimal composition. The kinetics of leaching-out of the main components was examined under static conditions. The concentration of fluoride ions in solutions, varied from 19 to 190 mg l^{-1} , was measured in the presence of a citrate buffer solution and without this solution. The difference between the concentrations of fluoride ions measured with and without the citrate buffer solution corresponded to the content of fluorine bound in fluoroaluminate complexes [8]. The solution pH was adjusted on the background of a constant concentration of NaCl (1 N solution) by adding NaOH and HCl.

Sorption of fluoride ions is primarily governed by the fundamental aspects of dissolution of aluminum from the active phase under the given conditions. The degree of dissolution of aluminum from the active phase of the sorbent was determined in percent relative to the total amount of aluminum in the active phase and was denoted by $\beta = Al_{in \ sol}^{3+} /Al_{act}^{3+}$. A study of the kinetics of leaching-out of aluminum from the active phase of the sorbent into solution and of the hydrolytic equilibrium at various pH values and concentrations of the F⁻ ion revealed the following pattern (Figs. 4, 5; Table 2). It was established that, at $4 < pH_{in} < 10$, the fraction of Al^{3+} ions that passed into solution in the absence of fluoride ions is 20% of their total amount in the active phase (Fig. 4). The pH of the equilibrium solution in this range is 4.8– 5.0 (Fig. 5), which indicates that compounds that can be hydrolyzed by the acid or base mechanism, depending on pH_{in} , are contained in the sorbent.



Fig. 4. Kinetic curves of redistribution β of active aluminum in relation to the solution pH and $c_{\rm F}$ in the contact solution. (τ) Time. $c_{\rm F}$, mg g⁻¹: (a) 80, (b) 19, and (c) 0. pH: (a) (1) 3.08, (2) 11.18, (3) 4.35, and (4) 9.78; (b) (1) 3.01, (2) 10.81, (3) 3.88, and (4) 9.17; (c) (1) 3.02, (2) 5.93, and (3) 9.08.



Fig. 5. Effect of pH and c_{F^-} in solution on the hydrolytic equilibrium in a system. (*I*-4) Nepheline sorbent and sodium fluoride solution and (5) activated aluminum oxide and sodium fluoride solution. c_{F^-} , mg g⁻¹: (*I*) 0, (2) 19, (3) 30, (4) 80, and (5) 19.

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Initial solution		Time of contact, h								
c _F -, mg g ⁻¹	рН	1		4	1	24				
		β, %	A, mg g ⁻¹	β, %	A, mg g ⁻¹	β, %	A, mg g ⁻¹			
80	2.0	36.0	0.0	38.0	0.10	45.0	0.17			
	4.0-4.3	10.2	1.3	13.0	1.73	9.7	4.11			
	7.0-7.2	11.7	1.3	13.2	2.25	9.2	4.11			
	9.8-10.1	11.7	1.7	12.1	3.11	8.4	4.43			
	10.8-11.2	10.7	1.3	12.2	1.73	12.9	3.57			
19	2.0	43.0	0.0	47.0	0.10	49.0	0.15			
	4.0-4.3	16.5	0.37	15.0	0.37	12.6	0.99			
	7.0-7.2	16.3	0.4	16.5	0.98	15.0	0.97			
	9.8-10.1	16.5	0.59	14.7	0.62	13.2	1.23			
	10.8–11.2	12.6	0.0	15.2	0.27	16.3	0.27			

Table 2. Kinetics of sorption of fluoride ions by the nepheline sorbent in relation to the pH of the initial solution

Table 3. Change in the chemical composition of mine water after its treatment with the nepheline adsorbent

Chanastaristic of motor	Content of indicated components, mg g ⁻¹									
Characteristic of water	Na ⁺	Al ³⁺	Ca ²⁺	Mg ²⁺	Cl-	SO_4^{2-}	HCO ₃	F ⁻	suspension	рп
Before treatment After treatment to breakthrough	600 600	1.8 2.9	0.7 0.7	1.0 1.0	5 15.0	10.5 10.5	20.1 20.1	60 0.5	465 1.2	10.15 8.6

In the nepheline sorbent, these salts are, probably, hydrated aluminum oxychlorides. At pH < 3 and pH >10, the active phase dissolves and the fraction of aluminum passing into solution increases dramatically. In the presence of fluoride ions in solution, the fundamental aspects of aluminum leaching-out from the sorbent vary over the entire range of pH values studied. At pH < 3 and pH > 10, the solubility of aluminum in the presence of fluoride ions somewhat decreases, although no sorption of the fluoride ion occurs. At $4 < pH_{in} < 10$, the solubility of aluminum from the active phase decreases substantially, and this decrease is the stronger, the higher the concentration of fluorine (Fig. 4, Table 2). In this pH range, sorption of fluoride ions is observed. The sorption capacity A (mg g^{-1}) is at a maximum at pH in the range from 9 to 10 (Table 2). The correlation between the sorption processes and the solubility of aluminum belonging to the active phase confirms the previously made assumption that aluminum-containing compounds are responsible for sorption processes involving fluoride ions.

The study performed made it possible to develop a technique for defluorination of mine and pit waste-

water from plants for mining and dressing of phosphate and rare-metal raw materials at the Kola Peninsula. The mine wastewater from the Lovozero ore mining and processing combine contains up to 60 mg g^{-1} of fluoride ions at a high total salinity of the discharged water. The defluorination technique developed is based on synthesis and use of nephelinecontaining sorbents in sorption filters with a fixed filtering bed, mounted as cartridges in gallery drains. The degree of purification of process wastewater to remove fluoride ions was 98.5-99.0% (Table 3). Spent sorbents are used to fill worked out mine spaces at mines of the Lovozero combine as a fluorine-containing additive to portland cement fill mixtures, which leads to an increase in the strength and water resistance of the fill [2].

CONCLUSIONS

(1) To prepare sorbents for defluorination of largetonnage sewage formed in mining and processing of rare-metal and phosphate raw materials at the Kola peninsula, a procedure involving the use of a selfhardening dispersed system constituted by a nepheline-containing waste, hydrochloric acid, and water is suggested. The synthesis of a solid product exhibiting a sorption activity is governed by incongruent dissolution of nepheline at a high concentration of the solid phase in the initial dispersion (s : 1 = 3 : 1) and small value of α (7% anhydrous HCl relative to the amount required by stoichiometry for complete decomposition of nepheline). The adsorption-active phase formed under the given conditions is composed of the amorphous phase of aluminosilicates, which contains bound H₂O and HCl (removed at $T > 350^{\circ}$ C). Adsorption of fluoride ions presumably occurs via formation of sparingly soluble aluminosilicofluorides.

(2) The sorbent passed semicommercial tests at the Lovozero ore mining and processing combine. Implementation of the technique suggested in the study makes it possible to organize a closed cycle of processing of mined raw materials.

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