ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 5, pp. 810−814. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © A.P. Zosin, T.I. Priimak, V.A. Masloboev, L.B. Koshkina, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 5, pp. 757−761.

PHYSICOCHEMICAL STUDIES OF SYSTEMS AND PROCESSES

Synthesis of Thin-Layer Oxyhydrate Sorbents Based on Aluminosilicate Minerals

A. P. Zosin, T. I. Priimak, V. A. Masloboev, and L. B. Koshkina

Institute for Problems of Industrial Ecology of the North, Kola Scientific Center, Russian Academy of Sciences, Apatity, Murmansk oblast, Russia

Received May 15, 2008

Abstract—A procedure was developed for preparing sorption-active materials based on hardening mineral dispersion eudialyte–aqueous acid solution. The hardening processes and conditions for formation of sorption-active compounds were studied.

DOI: 10.1134/S1070427209050115

Granulated oxyhydrates are used as sorbents in some specific fields of industry, due to their high mechanical strength, selectivity, and high radiation resistance. The most widely used oxyhydrates are hydrated zirconium dioxide, hydrated titanium dioxide, and hydrated iron(III) oxide [1]. Synthesis of oxyhydrate sorbents consists, as a rule, in precipitation of hydroxides with alkali from solutions of salts of metals in intermediate oxidation states. Hydrolysis and maturing of the precipitate are the main procedures for preparing crystalline oxyhydrate sorbents.

Extensive studies performed in the field of synthesis of oxyhydrate sorbents [1] showed that ion-exchange specificity of an oxyhydrate arises if ordering of the structure of the polymeric matrix does not reach the step of formation of the crystalline phase. Oxyhydrate sorbents with high sorption characteristics consist of globules 4–6 nm in size, linked in a three-dimensional network. The raw materials for preparing oxyhydrate sorbents by this process are pure salts containing the required elements. This leads to high cost of oxyhydrate sorbents. As a result, they are of limited use.

For wide use in treatment of large amounts of industrial wastewaters, sorbents should be cheap and effective. To solve this problem, we suggest a procedure for preparing sorption-active materials using the technology of self-hardening binding systems. By binding systems are understood systems containing in definite proportions liquid and solid phases capable of physicochemical interaction to form new condensed phases and of hardening [2]. Materials prepared by this technology are hardened dispersions consisting of particles of the initial mineral dispersed phase coated with condensed products of its reaction with the dispersion medium. As a rule, the thickness of the layer of reaction products is 5 to 100 nm, and they act as binder. It is known that, in hardening of water-containing binding systems using aluminosilicates as solid phase, condensed reaction products are salts of complex composition, containing oxyhydrates, hydrosilicates, and hydroaluminates exhibiting sorption properties under definite conditions [3].

The raw material for preparing such materials should contain cations or anions of elements whose oxyhydrates are to be prepared. It is not necessary to isolate a pure salt of the corresponding element, which considerably decreases the cost of adsorbents. Therefore, these materials can be recommended for wide use in treatment of large amount of wastewaters and in construction of various geochemical barriers in disposal of hazardous wastes.

The main sources of environmentally hazardous wastes subject to long-term disposal are mining enterprises. The wastes interact with atmospheric precipitations and groundwater, forming dissemina-tion streams of environmentally hazardous components, which requires construction of special geochemical barriers on storage

sites. One of regions with the developed mining complex is Murmansk oblast. Extraction and processing of rare-metal raw materials is accompanied by formation of process wastewaters containing such environmentally hazardous components as fluoride ions. The use of traditional sorbents for defluorination of large-tonnage wastes is complicated not only by their high cost but also by technological problems related to regeneration of traditional sorbents. Therefore, development of economically efficient and environmentally sound procedures for defluorination of process wastes, taking into account regional features of raw materials, is a topical problem.

We took advantage of eudialyte concentrate, a zirconium-containing raw material formed by reprocessing of apatite–nepheline ores of Khibiny deposit. Eudialyte concentrate contains 72% eudialyte. The remaining mineral components are nepheline, aegirite, and feldspars. The chemical composition of the eudialyte concentrate is as follows, wt %: SiO_2 51.4, Na_2O 13.4, ZrO_2 9.59, Al_2O_3 5.73, CaO 4.68, Fe_2O_3 4.44, TiO_2 1.09, K_2O 1.32, MnO 1.80, and REE 1.64. Experiments were performed with eudialyte pulverized to a surface area of 2600 $cm^2\ g^{-1}$. Based on the experience in preparation of oxyhydrate sorbents and hardening of binding systems, we chose as second component of the eudialyte-based self-hardening system an acid solution [1, 3, 4]. We studied the hardening of a binding system based on sulfuric, hydrochloric, nitric, and phosphoric acids.

The goal of our study was to reveal conditions for preparing granulated sorption-active materials for defluorination of mine wastewater by the binder technology using the eudialyte–hydrochloric acid–water system and to determine the best conditions for application of these materials. The synthesis conditions determine such properties of the material as sorption capacity, kinetic parameters of the sorption process, strength of granules, and their water resistance. The concentration $c(F^-)$ was measured potentiometrically using an EF-VI fluorine-selective electrode in the presence of a citrate buffer solution. Citrate buffer solution was used for decomposing complexes of F^- ions with aluminum cations which may be present in the solution. Products of the reaction of eudialyte with hydrochloric acid were studied by X-ray diffractometry, IR spectroscopy, and mass spectrometry.

Table 1. Influence of the kind of the acid on the rate of decationization of eudialyte concentrate (S : L = 1 : 100)

Initial acid	SiO_2 content in precipitate in 24 h, %	Time complete decomposition, h
31HNO_3	62.18	120
20 HCl	66.71	36
30 H_2SO_4	71.15	28
50 H_3P0_4	50.13	180

EXPERIMENTAL

The materials were prepared by the procedures similar for all the compositions: Finely divided eudialyte concentrate was poured over with an HCl solution and stirred for 15 min. The resulting mass was kept at 22°C for 24 h, after which it was subjected to thermolysis at 105°C to constant weight. To determine the strength characteristics (compression strength R_c), we prepared from synthesized materials 2 × 2 × 2-cm specimens. For this purpose, the mass was poured into molds, kept there at 22°C for 24 h, and then heat-treated at 105–110°C for 1 h. The water resistance of the synthesized materials was evaluated by the loss of the strength of the samples kept in water for 7 days. The sorption and the kinetics of leaching of the sorbent components were determined under static conditions at sorbent to sorbate ratio of 1 : 100 and a temperature of 22°C, with intermittent stirring. The contact time was varied from 15 min to 72 h.

The phase composition of reaction products in the system eudialyte–mineral acid solution should be affected by the rate of decationization of particular components of the eudialyte structure, which, in turn, is determined by crystal chemistry of the starting material and nature of the acid used in the synthesis. Therefore, we examined the stability of eudialyte at various phase ratios (S : L from 1 : 100 to 1 : 5). The acid concentration was chosen so as to ensure its highest protolytic activity. Namely, the concentrations were as follows, %: 31 HNO_3, 20 HCl, 30 H_2SO_4, and 50 H_3PO_4. In addition, to examine the effect of the acid anion, we examined acid concentrations equivalent in the protolytic strength, namely, %: 30 HNO_3, 19 HCl, and 24 H_2SO_4. The cationization rate was judged from an increase in the SiO_2 content in the precipitate. Data on the SiO_2 content in the eudialyte concentrate after its contact for 24 h with acid solutions and on the time of complete decomposition of soluble components of eudialyte concentrate are given in Table 1.

Our results show that the rate of eudialyte decationization in mineral acids decreases in the order $SO_4^{2-} > Cl^-$, NO_3^-, PO_4^{3-}. Thus, the stability of eudialyte in acids is determined by the structure of the acid anion, rather than by the protolytic activity. The kinetic curves of egress of the main structural elements of eudialyte into HCl solution (Fig. 1) show that leaching of cations is essentially congruent. The leading egress of sodium and aluminum in the first step is determined by dissolution of the nepheline component, which is less resistant to acid treatment. The subsequent reprecipitation of the Ca^{2+}, Zr^{4+}, Na^+, and Al^{3+} cations is due to polymerization of silica in solution and to probable involvement of the cations in the process.

To study the reaction products in highly concentrated dispersions (S : L > 1 : 5), we used the developed procedure for preparing gels over the surface of unchanged precipitate of the solid phase. The conditions for preparing gels were as follows: reaction time 24 h, S : L = 1 : 3, acid concentrations corresponded to their maximal protolytic activity. The isolated gels were analyzed to determine their chemical and phase composition. We found that, in going to highly concentrated dispersions, the character of eudialyte dissolution changes. Aluminum undergoes leading egress relative to the other cations. The content of the other elements in the gel (Zr, Na, Ca) depends on particular acid and is apparently determined by the solubility of the forming compounds. With a decrease in the solubility, their fraction in the gel relative to the initial content in the mineral decreases. For example, for gels based on nitric and hydrochloric acids, this quantity for sodium and calcium is 2.8–3.0 and 2.2–2.7, and for gels based on phosphoric and sulfuric acids, 1.5–1.8 and 0.4–0.6, respectively. That is, dissolution of eudialyte is incongruent.

The influence of the kind of the acid on the features of dissolution of the main structure-forming elements of eudialyte in concentrated dispersions is reflected in sorption and strength properties of the synthesized material. Figures 2 and 3 show how the strength and sorption capacity depend on the kind of the acid and degree of eudialyte breakdown. The concentration of the initial acids in the hardening dispersion corresponds to their maximal protolytic activity. As seen from Fig. 3, the dependence of the sorption capacity of the synthesized material on particular acid correlates with the stability of eudialyte in this acid. The series given below corresponds to a decrease in the sorption ability of materials containing

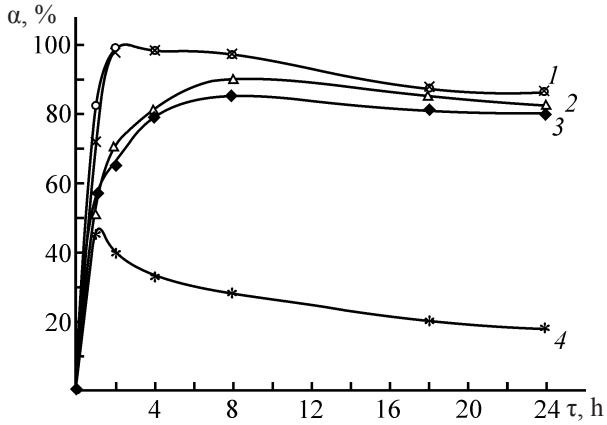

Fig. 1. Kinetic curves of the egress of the main structure-forming elements of eudialyte in the course of its dissolution in hydrochloric acid. (α) Weight fraction of elements that passed into the solution and (τ) dissolution time. Soluble component: (*1*) Na_2O, Al_2O_3; (*2*) CaO; (*3*) ZrO_2; and (*4*) SiO_2.

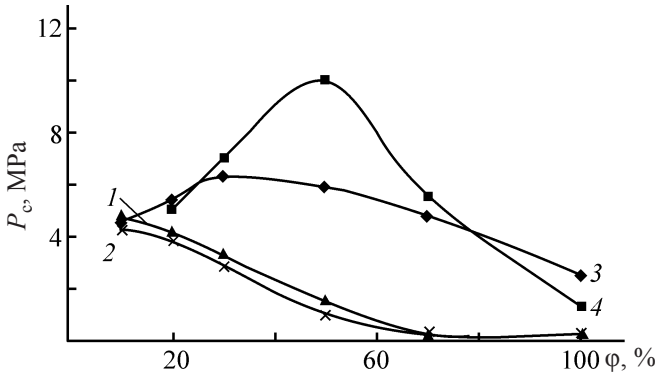

Fig. 2. Influence of the kind of the acid on the strength properties of eudialyte-based adsorbents: (P_c) Compression strength and (φ) degree of breakdown. Acid: (*1*) HCl, (*2*) HNO_3, (*3*) H_2SO_4, and (*4*) H_3PO_4; the same for Fig. 3.

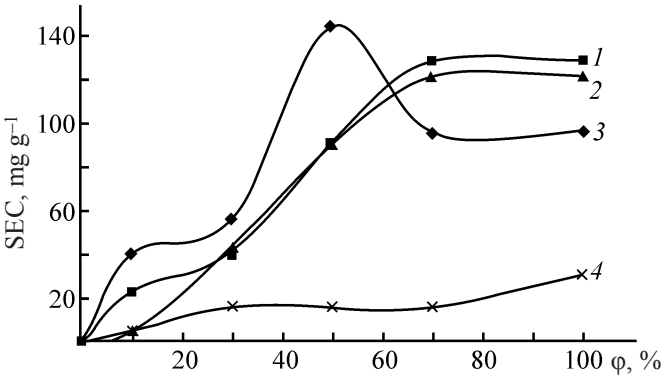

Fig. 3. Influence of the kind of the acid on the sorption capacity of eudialyte-based adsorbents (c_F = 190 mg l^{-1}). (SEC) Sorption capacity and (φ) degree of breakdown.

Table 2. Ratio of the main structure-forming elements in gels isolated from the reaction mixture eudialyte–mineral acid solution

Acid, %	SiO_2	ZrO_2	Al_2O_3	Na_2O	CaO
Eudialyte	1	0.16	0.11	0.34	0.11
20 HCl	1	0.16	0.53	0.90	0.27
31 HNO_3	1	0.20	0.41	1.00	0.30
24 H_2SO_4	1	0.30	0.30	0.60	0.07
50 H_3P0_4	1	0.13	0.24	0.52	0.04

the anion of the corresponding acid: $SO_4^{2-} > Cl^- > NO_3^- > PO_4^{3-}$. The materials prepared by treatment of eudialyte with sulfuric acid exhibit the highest sorption capacity for fluoride ions, reaching 143 mg g^{-1}, and those prepared by treatment with orthophosphoric acid exhibit the lowest capacity, 30 mg g^{-1}. It should be particularly noted that the solubility of Zr(IV) compounds decreases in the same order (Table 2). It is known that zirconium ions having high valence but, at the same time, relatively large radius (0.8 E) tend to form stable complexes with small anions, especially with fluoride ions. With an increase in the degree of eudialyte breakdown, the sorption of fluoride ions increases (the materials treated with sulfuric acid are an exception).

The dependence of the strength properties on the kind of the acid is different. The strength decreases in the order $H_3PO_4 > H_2SO_4 > HCl > HNO_3$. The maximal strength is shown by samples prepared by treatment with 50% orthophoshoric acid, with the degree of eudialyte breakdown of 40% (compression strength 10.0 MPa).

Treatment of eudialyte concentrate with hydrochloric or nitric acid does not result in formation of a strong water-resistant stone, irrespective of the phase ratio in the initial dispersion.

The strength and sorption properties correlate with the X-ray diffraction data. X-ray diffraction studies of the synthesized materials reveal the following trends. As the degree of breakdown of eudialyte concentrate increases, an amorphous colloidal phase is manifested, the reflections of aegirite and feldspars become clearer, and the reflections of sodium salts of the corresponding acids grow in intensity. The degree of breakdown of the eudialyte structure was judged from the intensity ratio of the main reflections of eudialyte and orthoclase (potassium feldspar). The rate of these processes depends on the kind of the acid used in the synthesis. The trend is the same as in decationization in thin dispersions: decrease in the rate of eudialyte dissolution in the order $H_2SO_4 > HCl > HNO_3 > H_3PO_4$.

The following differences, depending on particular acid, are observed in the X-ray diffraction patterns. With sulfuric acid used as dispersion medium, the main reflections of calcium sulfates and hydrosulfates appear in the X-ray diffraction patterns. These components apparently impart strength to the materials. With orthophosphoric acid, insoluble zirconium phosphates are formed in the reaction products. These compounds are manifested particularly clearly in gels isolated from the reaction mixture. In addition, all the gels exhibit in the X-ray diffraction patterns the main reflections of calcium silicates and hydrosilicates (e.g., $2CaO{\cdot}3SiO_2{\cdot}3H_2O$ and α-Ca_2SiO_4). In gels obtained by treatment of the eudialyte concentrate with hydrochloric acid, aluminum hexachloride complexes are formed.

Interaction of the synthesized materials with the adsorbate medium (0.1 M NaF) leads to appearance of reflections of sodium tetrafluoroaluminate, whereas the reflections belonging to soluble sodium salts of the corresponding acids disappear. Appearance of a band of an amorphous colloidal phase after the sorption indicates that the reaction products contain soluble X-ray amorphous aluminum compounds.

CONCLUSIONS

(1) The breaking-down effect of acids on eudialyte is determined by the structure of the acid anion, rather than by the protolytic activity of the acid, and decreases in the order $SO_4^{2-} > Cl^- > NO_3^- > PO_4^{3-}$.

(2) Zirconium-containing granulated adsorbents in the system eudialyte concentrate–mineral acid solution can be prepared with a sulfuric or phosphoric acid solution used as dispersion medium.

(3) With an increase in the degree of breakdown of eudialyte, the sorption capacity increases, but the solid is formed only at S : L > 1 : 2.

(4) The reaction products on the surface of unchanged grain in the hardened mineral dispersion based on eudialyte consist of an amorphous colloidal phase, alkali metal sulfates or phosphates, calcium hydrosulfates or hydrophosphates, and zirconium hydroxy salts.

REFERENCES

1. Sukharev, Yu.I., *Sintez i primenenie spetsificheskikh oksigidratnykh sorbentov* (Synthesis and Use of Specific Oxyhydrate Sorbents), Moscow: Energoatomizdat, 1987.
2. Fedorov, N.F., *Vvedenie v khimiyu i tekhnologiyu spetsial'nykh vyazhushchikh* (Introduction to Chemistry and Technology of Specialty Binders), Leningrad: Leningrad. Tekhnol. Inst. im. Lensoveta, 1976, part 1.
3. Granovskii, I.G., *Strukturoobrazovanie v mineral'nykh vyazhushchikh sistemakh* (Structure Formation in Mineral Binding Systems), Kiev: Naukova Dumka, 1984.
4. Zosin, A.P., Priimak, T.I., Koshkina, L.B., and Masloboev, V.A., *Ekol. Prom. Proizv*., 2007, no. 2, pp. 37–41.