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USE OF ULTRASOUND FOR STABILISATION OF NANODISPERSED STRUCTURE OF ALUMOSILICIC REAGENTS FOR WASTEWATER TREATMENT

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Abstract. The complex reagent, sold under the trade mark AKFK – a new alumosilicic flocculant-coagulant – has both coagulating and flocculating properties. It ensures higher level of water purification from petroleum products in comparison with reagents that are conventionally used in Russia. The wide use of AKFK is constrained by the ability of the reagent to form a gel, which leads to a loss of its commercial characteristics. Short-term ultrasonic treatment facilitates the preservation of an active silicic acid sol and prolongs the shelf life of AKFK more than twofold.

Keywords: wastewater treatment, ultrasound, flocculation, coagulation.

AIMS AND BACKGROUND

Crude oil and petroleum products are one of the most widespread sources of contamination in natural water reservoirs and wastewater. Normally mechanical devices are used at the pretreatment stage for purification of such water. Therefore, further wastewater treatment often involves reagent methods, such as coagulation, flocculation, reagent flotation[1,2].

Aluminum- and iron-containing compounds such as aluminum sulphate (AS), aluminum oxychloride (AOC), sodium aluminate (SA), and ferric chloride (FC) are normally used as coagulants. Active silicic acid (ASA), organic compounds, etc. are typically used as flocculants. Active silicic acid is a silica sol, the properties of which (isoelectric point, degree of polymerisation, etc.) depend on the technology of its production and storage conditions. This flocculant has advantages over other reagents, since its use in water purification systems, especially in water treatment systems, is harmless and cheap.

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Using reagents obtained from industrial wastes would make it possible to reduce the cost of water purification, while maintaining its efficiency. In some cases, this can be achieved by combining up-to-date physicochemical methods of purification with efficient ultrasonic pretreatment of such reagents[3].

Taking this into account, a new alumosilicic flocculant-coagulant AKFK was developed, which is one of few binary compositions that contain only inorganic components: the aluminum sulphate as the coagulant and the active silicic acid as the anionic flocculant[4]. The presence of aluminum sulphate (up to 20 g/l) and ASA (up to 40 g/l silicon oxide) in the AKFK solution ensures the efficiency of removing various contaminants. The high efficiency of AKFK is caused, on the one hand, by the additive (independent) properties of the composite components. On the other hand, chemical interaction between its components takes place in AKFK. This leads to the formation of alumosilicic zeolite-like structures with a developed interfacial area and increased absorption capacity. In other words enhancement of the flocculating action due to the participation of reactions products in the process (a synergistic effect) is observed[5].

Zeolite-like structures ensure high efficiency of AKFK, which is comparable to other aluminum-containing coagulants. The use of AKFK in water purification can yield a substantial economic effect, since one of the options for producing such low-cost and high-efficiency reagents is the use of the wastes of apatite production.

The AKFK solution can be produced by acidising nepheline-containing raw materials (syenite, urtite, and nepheline) or the tailings of apatite-nepheline flotation. When 1 t of apatite concentrate is produced at OJSC Apatit, about 1.2 t of tailings are formed as a by-product. The total resources of tailings containing valuable and useful components are more than 1 billion t and annually increase by 12–15 million t.

Processing of the tailings of apatite flotation makes it possible to obtain a solution of AKFK in the form of a system, in which aluminum is present in an ionic form and ASA is present in the form of a sol. In addition, an acid-proof material Si-stoff is formed. Thus, AKFK is a multipurpose reagent for the purification of natural water and wastewater from petroleum products, heavy metals, and certain radionuclides, for colour reduction, and for iron removal.

However, wide application of AKFK is constrained by the ability of the reagent to form a gel and, consequently, to lose its commercial characteristics. Under laboratory conditions, AKFK is produced in the form of an off-the-shelf aqueous solution with a shelf life of no more than two weeks. Apart of that, the low activity of AKFK at low temperatures is a problem.

In view of the above, the objective of this study is to analyse the possibility of using ultrasound, to increase the stability of the AKFK reagent. At present, ultrasound has already been used successfully for the intensification of a number of processes[6–8].

EXPERIMENTAL

To investigate the effect of ultrasound on the efficiency of AKFK, the purification of wastewater from petroleum products was studied using model emulsions. We used emulsions that change their optical transparency by no more than 10% for three days. To prepare such an emulsion, water and a small amount of oil were placed into the cup of an MPW-303 homogeniser and were subjected to intensive agitation for 15 min at a rotational speed of 12 000 min^{-1}. After that the prepared emulsion was placed into a separating funnel and was pre-settled for 24 h in order to remove coarsely dispersed droplets of oil. In this way, relatively concentrated emulsions were prepared, which were then diluted with water. The size of oil particles after emulsion pre-settling was in the range of 1–5 μm, which reduced the probability of the collision of droplets and coagulation in the bulk of the liquid to a minimum. The initial concentration of petroleum products in the obtained emulsion was 30 mg/l.

In some experiments, AKFK was subjected to ultrasonic pretreatment. Experiments were performed for five days after single ultrasonic activation of the reagent at a frequency of 25 kHz and an acoustic intensity of 5 W/cm^2 for 30 s – 3 min. Ultrasonic treatment was conducted in 72 h after the preparation of reagent solutions.

A laboratory flocculator designed for performing trial coagulation during the purification of natural water and wastewater was used to study the dependence of the degree of water purification on the dose of the coagulant. The flocculator was a device that ensured mixing of reagents with the water under treatment using a mechanical stirrer for specified time intervals. Two modes were used: rapid agitation at a stirrer speed of 150–200 rpm and slow agitation at a stirrer speed of 30–100 rpm. In the study, the agitation of wastewater with the coagulant solution was conducted sequentially for 15 s at a stirrer speed of 200 rpm and for 1 min at a stirrer speed of 30 rpm with subsequent settling for 30 min. Samples of treated water were taken from the middle section of the vessel.

A KN-3 concentration meter (manufactured by SIBEKOPRIBOR) designed for measuring the weight concentrations of petroleum products in samples of potable, natural, waste and treated water was used to analyse the efficiency of purification when using the AKFK reagent obtained and treated under different operating conditions. The operating principle of the instrument is based on measuring the optical densities of the solution in carbon tetrachloride in the infrared spectrum by a photometer. The two-wave mode was used in measurements: the difference of optical densities of the solution under analysis at two wavelengths was measured. In the first (measuring) channel, the spectral range of radiation (2930 ± 70) cm^{-1} (3.42 μm) was used. In the second (reference) channel, the spectral range (3333 ± 70) cm^{-1} (3.0 μm) in which petroleum products, grease, and surfactants do not absorb infrared radiation was used.

To study the effect of ultrasound on the stability of AKFK, the starting time of gelation and the ultimate rupture stress of the formed gel were determined using rotational viscosimeter.

The electrophoretic scattering of light that is incident on a standard cuvette containing a sample of the liquid under study at an angle of 20 degrees was used to determine the zeta potential. Measurements were conducted using a Photocor Compact-Z instrument with a built-in Photocor-FC correlator for auto- and cross-correlation measurements. In this instrument, a thermally stabilised diode laser with a wavelength of 650 nm and a power of 30 mW was used as an excitation source. Electrophoretic light scattering (ELS) and phase analysis light scattering (PALS) were used in measurements. The typical error of measurement was ±1%.

RESULTS AND DISCUSSION

Monomeric, dimeric, tetrameric, and other forms of silica with a low molecular weight constitute a considerable fraction in freshly prepared AKFK. An increase in the 'age' of AKFK (i.e. the time *t* passed from the moment of AKFK preparation to the moment of its use as a flocculant-coagulant) is accompanied by the transition of silica to compounds with a high molecular weight, which plays a crucial role in flocculation processes. The mechanism of the effect of AKFK consists of three stages: (1) the coagulation of dispersed contaminants (rapid process), (2) the formation of primary flocs, and (3) the formation of macroflocs. The dynamics of the synergistic effect in AKFK is hardly studied; however, it is assumed[4] that porous honeycomb nanostructures are formed first and, after that, more complex three-dimensional structures that have a flocculating activity appear due to self-organisation processes. Thus, the important task is the selection of methods for stabilising the original nanodispersed structures in order to increase the working life of the reagent. Solving these problems will make it possible to determine optimum conditions for the organisation of the purification process.

Figure 2 shows the dependence of the time of gelation start of AKFK solutions (which was obtained from the tailings of apatite-nepheline flotation) from the concentration of sulphuric acid after ultrasonic pretreatment and without it. It follows from the presented data that the maximum time of gel formation start in sulphuric acid solutions is observed when the concentration of the acid in the leaching solution is 10 wt.% regardless of the temperature of the reaction mixture. In this case, the pH value of the filtered solution of AKFK is 1.8–2, which is also close to the isoelectric point of silicate sols. At a temperature of 25ºC and a sulphuric acid concentration of 10 wt.%, the time of gel formation is 352 h. The time of gel formation start substantially decreases with an increase in temperature, which leads to noticeable complications in the organisation of a technological cycle in industrial use. Ultrasonic treatment leads to an increase in the start time

of gel formation. Curve 3 of Fig. 1 shows the time of gel formation start of the ultrasonically treated reagent as a function of the concentration of sulphuric acid. The time of ultrasonic activation of the reagent in this case was 1 min.

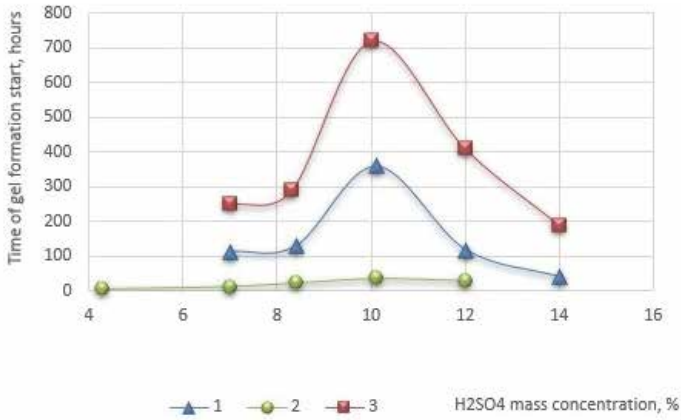

Fig. 1. Time of gel formation start in AKFK solutions as a function of sulphuric acid concentration: (1) when holding at $T = 25$ºC, (2) when holding at $T = 60$ºC, and (3) after ultrasonic treatment and holding at $T = 25$ºC

To study the effect of ultrasound on the efficiency of AKFK, a large number of experiments on the purification of model emulsions were performed both at room temperature and at reduced temperatures. The results of the experiments are given in Table 1 and Fig. 2. The concentration of AKFK in terms of Al_2O_3 was 20 mg/l when conducting experiments on the purification of model mixtures at a temperature of 25°C and 40 mg/l at a temperature of 6°C. Ultrasonic treatment of the reagent was performed before its mixing with the polluted water 72 h after reagent preparation.

Table 1. Efficiency of purification of the model emulsions as a function of ultrasonic treatment time

Time of ultrasonic treatment	0	30 s	1 min	2 min	3 min
Degree of purification with the use of the reagent immediately after treatment (%)	84	81	80	78	78
Degree of purification with the use of the reagent in 48 h after treatment (%)	–	90	93	94	94

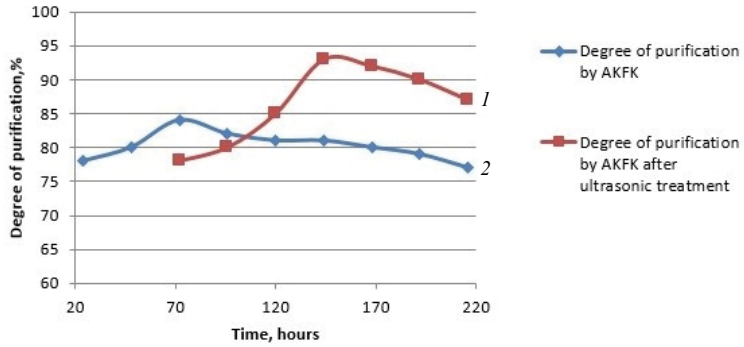

Fig. 2. Degree of purification versus the time of AKFK ageing: (*1*) without ultrasonic treatment and (*2*) after single ultrasonic activation (t = 1 min and I = 4 W/cm^2)

The measurements of the efficiency of purification of model solutions have shown that, in the absence of ultrasonic treatment, the reagent reaches the maximum of its activity when it is kept at a temperature of 25°C, 72 h after its preparation (curve *1* of Fig. 2); then, its efficiency decreases. At the maximum efficiency, it was possible to remove 84% of petroleum products from the model mixture.

After ultrasonic activation of the reagent, its efficiency was periodically measured for five days. Even a single short-term ultrasonic treatment affects the efficiency of the reagent. If the reagent was used immediately after ultrasonic treatment, its efficiency was lower compared to the maximum efficiency, which AKFK demonstrated without ultrasonic treatment 72 h after its preparation. However, after treatment the efficiency of AKFK starts to raise and reaches values higher than all values reached by the untreated reagent. As shown in Fig. 2, the efficiency of the treated AKFK reaches its maximum in 36–48 h after ultrasonic treatment. Under the conditions of treatment for 1 min and subsequent reagent ageing for 2 days, the degree of purification reached was 93%. As can be seen from Fig. 2, the increased activity of AKFK after ultrasonic treatment remains as such level for at least 4 days. After that, the activity returns to the initial values and then decreases.

The short duration of the time of treatment makes it possible to use ultrasound in water treatment processes, treatment for only 1 min is sufficient. This can be seen in Table 1.

One more result is important: the degree of purification of polluted water at reduced temperature (+6°C) using AKFK (40 mg/l in terms of Al_2O_3) without ultrasonic treatment did not exceed 80% (the concentration of petroleum products decreased from 30 to 6 mg/l). In this case, ultrasonic treatment made it possible to achieve the degree of purification 98.9%, which corresponds to the residual concentration of petroleum products in treated water 0.33 mg/l.

To reveal the effect of ultrasonic treatment on the properties of the reagent before and after treatment, its zeta potential, which determines the degree and

character of interaction between the particles of a disperse system, was measured. When the zeta potential is low, attraction exceeds repulsion and the stability of a dispersion is disturbed. For instance, colloids with a high zeta potential are electrically stabilised, whereas colloids with a low zeta potential tend to coagulate or flocculate. After ultrasonic treatment of AKFK solutions, an increase in the zeta potential from 4 to 12 mV was observed, which indicates the stabilisation of a nanodispersed structure. A more than twofold increase in the time required for gel formation was simultaneously observed (curve 2 in Fig. 2).

Analysing the obtained result on the basis of the Smoluchowski formula and the observed increase in the zeta potential, it can be assumed that this can be associated both with an increase in the concentration of coagulation centres and with a change in the radius of the sphere of particle attraction.

Thus, the obtained data indicate that the ultrasonic treatment of AKFK solutions for 1 min substantially retards the gelation and polycondensation of ASA by breaking down silica nuclei to the nanodispersed state and facilitating the preservation of an ASA sol, which substantially prolongs the shelf life of the reagent and is accompanied by a noticeable increase in its efficiency.

CONCLUSIONS

The complex reagent AKFK has both coagulating and flocculating properties. The cheapness of AKFK as compared with other coagulants is determined by the low cost of the feedstock and the simple technology of its production. The wide use of AKFK is constrained by the ability of the reagent to form a gel, which leads to a loss of its commercial characteristics. Another drawback of the reagent is the low activity at low temperatures.

Short-term ultrasonic treatment facilitates the preservation of an ASA sol and prolongs its shelf life more than twofold, which can be associated both with an increase in the concentration of coagulation centres and with a change in the radius of the sphere of particle attraction.

Results of experiments indicate a noticeable increase in the efficiency of the AKFK flocculant-coagulant after relatively short ultrasonic treatment. At reduced temperatures the use of AKFK for the fine purification of oil-contaminated water is possible only after ultrasonic pretreatment, since otherwise the required efficiency of purification is not reached.

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