STRUCTURAL AND FUNCTIONAL FEATURES OF ANIONIC ACRYLAMIDE COPOLYMERS IN THE FLOCCULATION OF MODEL MINERAL AND OIL-CONTAINING SYSTEMS.

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Abstract. The study presents the results of research on the synthesis and application of anionic copolymers of acrylamide with acrylic and maleic acids for the flocculation of mineral suspensions and oil-containing emulsions. The structural features of the copolymers were confirmed by IR spectroscopy, thermal analysis, and powder X-ray diffraction. The phase and particle-size composition of model mineral dispersions (bentonite and calcium carbonate) was examined, as well as their clarification kinetics in the presence of various flocculants. It was shown that calcite systems tend to undergo rapid sedimentation and require minimal flocculant dosages, whereas smectite-containing dispersions exhibit high stability and strong sensitivity to environmental conditions. In “oil–water” emulsion systems, the synthesized copolymers provided deeper clarification and a faster breakdown of droplet structures compared to industrial analogues. Optimal dosages were identified in the range of 0.2–0.3 %, above which restabilization was observed. The obtained results substantiate the use of the new anionic acrylamide copolymers in the treatment of wastewater with mixed organo-mineral composition.

Keywords: flocculation, polyacrylamide, copolymers, bentonite, calcium carbonate, oil-containing emulsions, IR spectroscopy, X-ray diffraction, thermal analysis.

Annotatsiya. Ushbu tadqiqotda akrilamidning akril va malein kislotalari bilan olinadigan anion sopolimerlarini mineral suspenziyalar va neft tarkibli

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emulsiyalarni flokulyatsiyalashda qo‘llash va ularni sintez qilish bo‘yicha olingan natijalar keltirilgan. Sopolimerlarning strukturaviy xususiyatlari IK-spektroskopiya, termoanaliz va kukunsimon rentgen difraksiyasi orqali tasdiqlandi. Model mineral dispersiyalar (bentonit va kaltsiy karbonat)ning fazaviy va granulometrik tarkibi hamda turli flokulyantlar ishtirokidagi tiniqlashish kinetikasi o‘rganildi. Kaltsit tizimlari tez cho‘kishga moyil bo‘lib, minimal flokulyant miqdorini talab qilishi aniqlandi; smektit tarkibli dispersiyalar esa yuqori barqarorlik va muhit sharoitlariga sezgirlik bilan ajralib turadi. “Neft–suv” tipidagi emulsiyalarda sintez qilingan sopolimerlar sanoat analoglariga nisbatan chuqurroq tiniqlashish va tomchi strukturasi tezroq buzilishini ta’minladi. Optimal dozalash 0,2–0,3 % oralig‘ida bo‘lib, undan oshirilganda qayta barqarorlashish kuzatildi. Olingan natijalar organo-mineral tarkibli oqova suvlarni tozalashda yangi anion akrilamid sopolimerlaridan foydalanish imkoniyatlarini asoslaydi.

Kalit so‘zlar: flokulyatsiya, poliacrilamid, sopolimerlar, bentonit, kaltsiy karbonat, neft tarkibli emulsiyalar, IK-spektroskopiya, rentgen difraksiyasi, termoanaliz.

Аннотация. Представлены результаты исследований по синтезу и применению анионных сополимеров акриламида с акриловой и малеиновой кислотами для флокуляции минеральных суспензий и нефтесодержащих эмульсий. Структурные особенности сополимеров подтверждены методами ИК-спектроскопии, термоанализа и порошковой рентгенографии. Изучены фазовый и гранулометрический состав модельных минеральных дисперсий (бентонит и карбонат кальция), а также их кинетика осветления в присутствии различных флокулянтов. Показано, что кальцитовые системы склонны к быстрой седиментации и требуют минимальных доз флокулянта, тогда как смектитсодержащие дисперсии характеризуются высокой устойчивостью и выраженной чувствительностью к условиям среды. В эмульсионных системах типа «нефть–вода» синтезированные сополимеры обеспечили более глубокое осветление и ускоренное разрушение капельных структур по сравнению с промышленными аналогами. Оптимальные дозы составили 0,2–0,3 %, при превышении которых наблюдается рестабилизация. Полученные результаты обосновывают применение новых анионных сополимеров акриламида в процессах очистки сточных вод смешанного органо-минерального состава.

Ключевые слова: флокуляция, полиакриламид, сополимеры, бентонит, карбонат кальция, нефтесодержащие эмульсии, ИК-спектроскопия, рентгенография, термоанализ.

Introduction

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The problem of treating wastewater containing mineral and organo-mineral dispersions remains highly relevant due to increasing anthropogenic pressure and the need for resource conservation. Mineral suspensions formed during ore processing, the manufacture of construction materials, and the treatment of industrial effluents, as well as “oil–water” emulsions characteristic of the petrochemical and energy sectors, represent stable dispersed systems that hinder clarification and filtration processes.

One of the most effective approaches to destabilizing such systems involves the use of polymeric flocculants capable of inducing particle agglomeration through adsorption on particle surfaces and the formation of inter-particle bridges. Of particular interest are anionic acrylamide copolymers, which combine high molecular weight, water solubility, and the presence of functional groups capable of electrostatic and coordination interactions. Their efficiency is determined not only by molecular weight and degree of ionization, but also by the distribution of carboxyl units along the macromolecular chain, which directly affects adsorption behavior and the resistance of flocs to shear forces.

LITERATURE REVIEW AND METHODS

The literature indicates that the flocculation activity of polyacrylamides and their copolymers depends strongly on the nature of the mineral phase. Clay minerals containing montmorillonite exhibit high negative charge density, necessitating significant reagent dosages and an extended slow-mixing stage [1–3]. In carbonate systems, surface calcium centers play a key role, being capable of forming coordination bonds with polymer carboxyl groups [4–6]. In the presence of organic components (oil, surfactants, natural organic matter), additional complications arise due to competitive adsorption and shielding of active sites [7–9].

The aim of this work is to establish the relationship between the structure of anionic acrylamide copolymers and their efficiency in the flocculation of model mineral and organo-mineral systems, and to identify the interaction mechanisms that determine optimal dosing regimes and the stability of the resulting flocs.

Bentonite from the Navbakhor deposit (a smectite-containing clay) and calcium carbonate (commercial chalk, predominantly calcite) were used as model mineral dispersions. Mineral characterization included determination of phase composition by X-ray diffraction analysis (XRD, Cu Kα radiation), measurement of interplanar spacings, and estimation of impurity phase content.

Particle-size distribution was determined by sieve analysis across standard fractions (>0.42 mm; 0.42–0.297 mm; 0.297–0.105 mm; 0.105–0.062 mm; 0.062–0.044 mm; <0.044 mm).

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Acrylamide copolymers with acrylic (AA–AC, 8FAK) and maleic (AA–MC, 8FMK) acids were synthesized via radical polymerization in aqueous medium. Commercial analogues used for comparison included polyacrylamide (RAAM) and hydrolyzed polyacrylonitrile (GIPAN).

Clarification kinetics of mineral suspensions was evaluated in cylindrical tubes by monitoring the evolution of the clarified layer volume over time. The influence of organic impurities was studied using model oil-in-water emulsions (40:60) stabilized with sodium stearate (1%). The effect of the flocculants was assessed by measuring changes in optical density (UV-5100 spectrophotometer, λ = 600 nm) during storage of the samples at 25 °C.

RESULTS AND DISCUSSION

Structural and phase characteristics of mineral dispersions.

According to X-ray diffraction data, calcium carbonate is predominantly represented by calcite (space group R-3c). The diffractogram exhibits distinct reflections at 2θ ≈ 39.5° (plane (113)), as well as peaks in the regions 31.3–31.5° and 71.6–71.8°, characteristic of calcite (Fig. 1). The low background intensity and absence of additional maxima confirm the high purity and crystallinity of the sample.

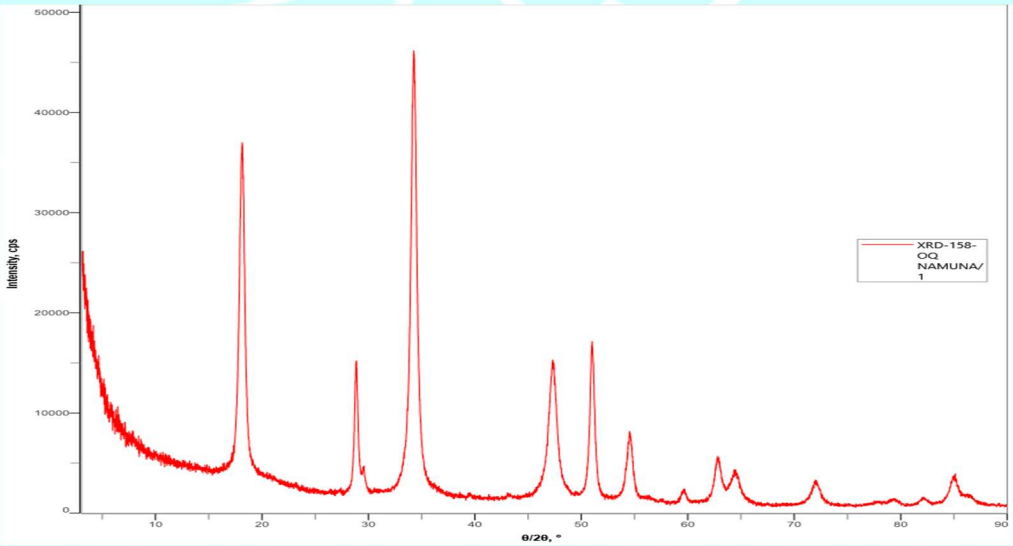


Fig. 1. X-ray diffractogram of calcium carbonate.

For bentonite (Fig. 2), low-angle reflections at d001 ≈ 16.6–13.6 Å are characteristic, indicating interlayer hydration of montmorillonite. In the mid-angle range, reflections corresponding to illite (d ≈ 10 Å) and kaolinite (d ≈ 7.1 Å) are observed, as well as intense quartz lines (2θ ≈ 26.6°) and calcite reflections (2θ ≈ 29.5°). Thus, the examined bentonite represents a smectite-containing material with quartz and carbonate impurities, typical of natural clays.

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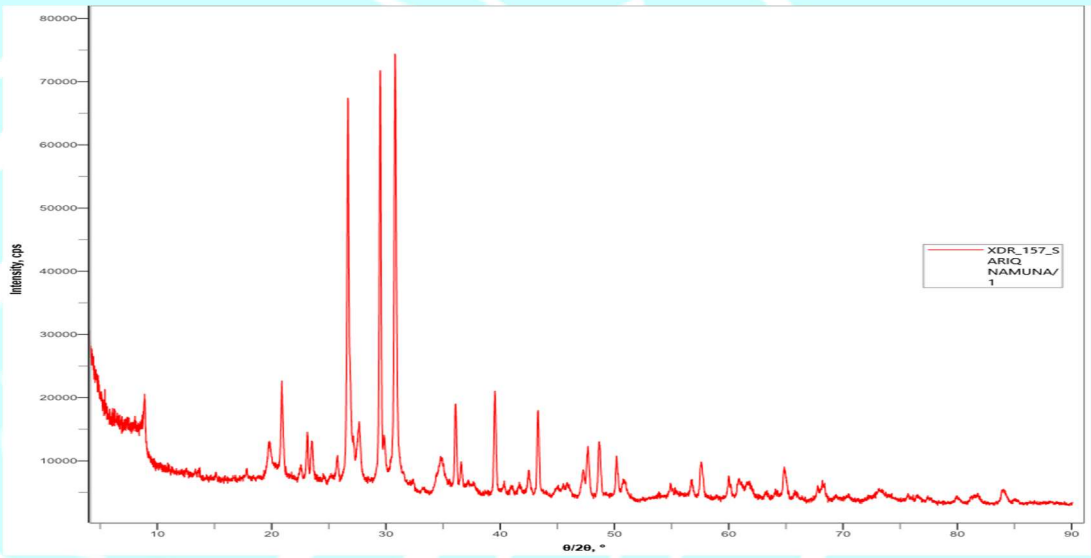


Fig. 2. X-ray diffractogram of bentonite.

Particle-size analysis (Table 1) revealed notable differences in dispersity: bentonite contains a substantial proportion of fine particles (<0.105 mm — 37.4 %), including 22.4 % of the <0.044 mm subfraction, which determines its high specific surface area and negative charge. Calcium carbonate, by contrast, is dominated by coarser fractions (>0.297 mm — 52.3 %), which explains its rapid sedimentation and low colloidal component.

Table 1.

Particle-size distribution of the samples

Sample	>0,42 mm	0,42–0,297 mm	0,297–0,105 mm	0,105–0,062 mm	0,062–0,044 mm	<0,044 mm
Bentonite	10,32	31,94	20,34	13,25	1,71	22,44
Chalk	9,94	42,35	34,14	5,24	0,74	7,59

These differences in mineralogy and dispersity determine fundamentally different mechanisms of interaction with flocculants: bentonite requires higher dosages and longer polymer bridges, while calcite is efficiently flocculated at low dosages due to coordination of polymer carboxyl groups with Ca^{2+} ions.

Clarification kinetics of mineral suspensions.

In the absence of flocculants, the calcite suspension clarifies rapidly (Fig. 3): the clarified layer reaches 90 % in under 100 min. For bentonite, the process is significantly slower: the plateau is reached only at ~40 %, and the half-clarification time is four times longer than for calcite.

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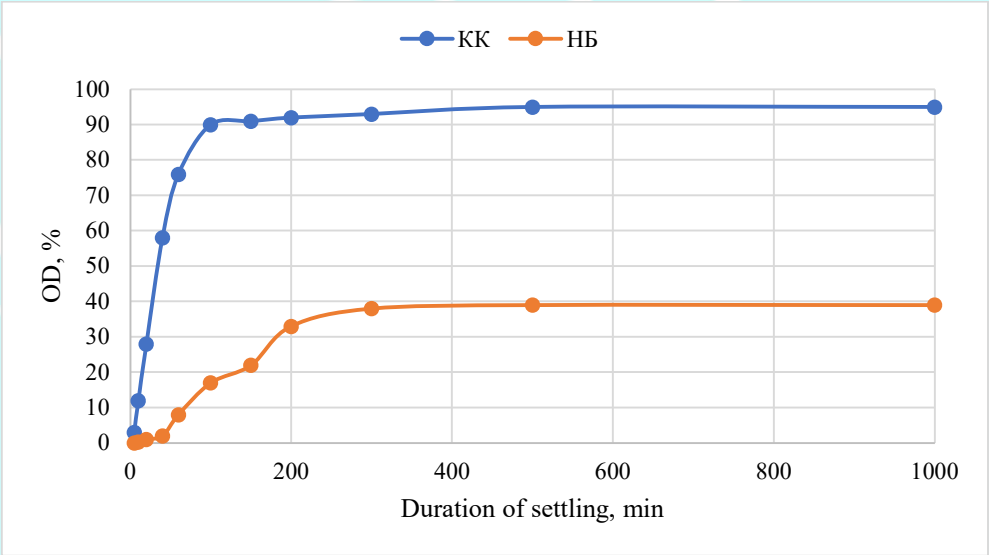


Fig. 3. Clarification kinetics without flocculant.

Upon addition of flocculants (Fig. 4), the kinetics accelerate considerably, but the dose dependence differs. For calcite, optimal dosages range from 0.1–0.25 %, at which the AA–MC copolymer provides up to 88 % clarification. For bentonite, maximum efficiency is achieved at 0.2–0.5 %, where the AA–AC copolymer yields up to 88 % clarification. When optimal dosages are exceeded, restabilization occurs due to surface saturation and the onset of electrosteric stabilization.

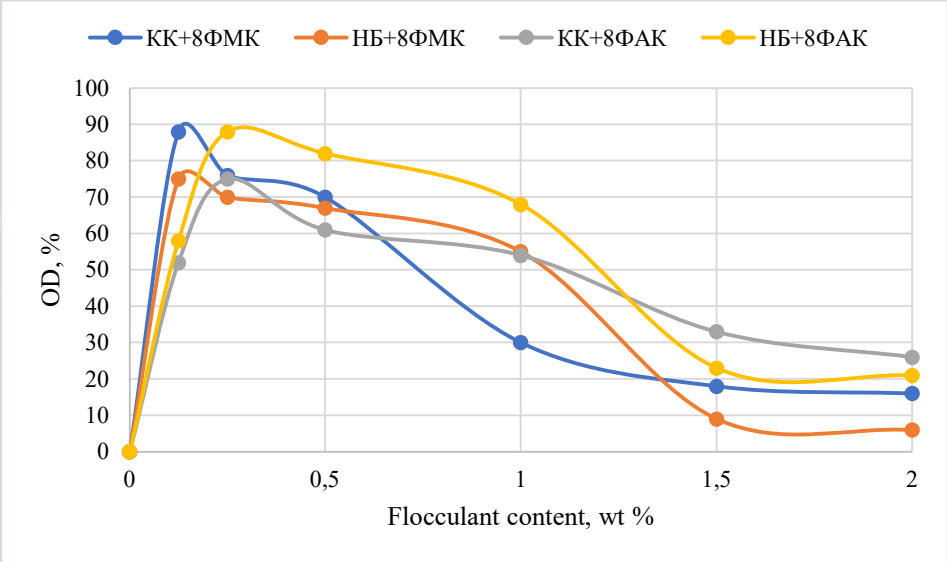


Fig. 4. Flocculation kinetics at different flocculant concentrations. Influence of organic components.

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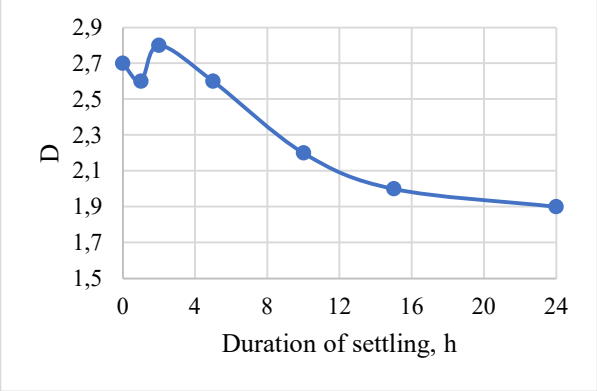


Fig. 5. Change in optical density during storage (25 °C).

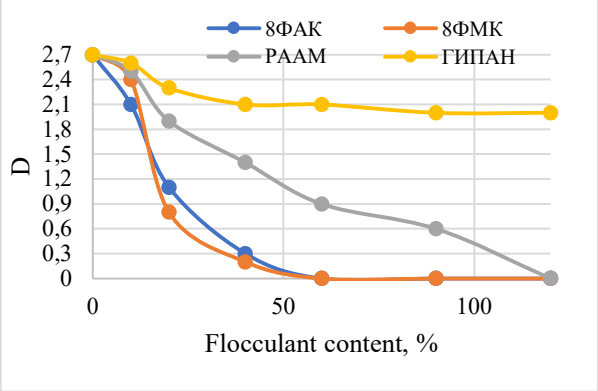


Fig. 6. Change in optical density under the action of flocculants at 0.25 wt% (25 °C).

In the model "oil–water" emulsion stabilized with sodium stearate, the system remains stable in the absence of reagents: optical density decreases by only ~30 % in 24 h (Fig. 5). Upon addition of AA–AC and AA–MC copolymers, the process accelerates sharply: within 40 h the optical density decreases by more than 70 %, and by 60 h complete clarification is achieved (Fig. 6).

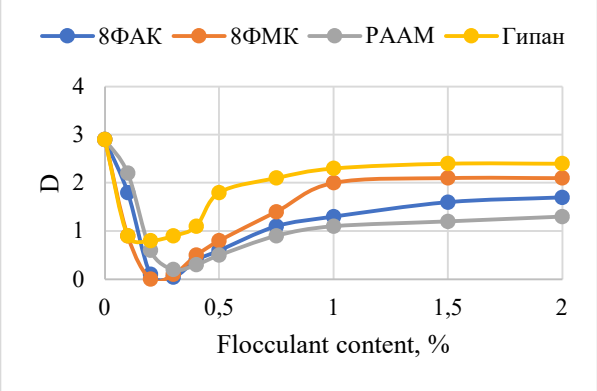


Fig. 7. Change in optical density of the oil–water–bentonite (0.05 %) system under different flocculant concentrations (25 °C).

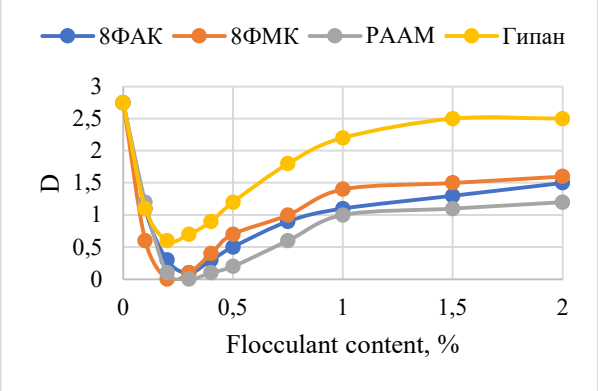


Fig. 8. Change in optical density of the oil–water–$CaCO_3$ (0.05 %) system under different flocculant concentrations (25 °C).

In the three-phase systems "oil–water–bentonite" (Fig. 7) and "oil–water–$CaCO_3$" (Fig. 8), the influence of the mineral phase becomes evident. In the presence of bentonite, optimal dosages of the copolymers shift to the range 0.2–0.3 %, where minimal turbidity is achieved. In the calcite system, the effect is more pronounced for the AA–MC copolymer: due to coordination interactions with calcium ions, the operating dosage window broadens and restabilization becomes less abrupt.

Thus, the interaction of flocculants in organo-mineral systems is governed by both the polymer's chemistry and the nature of the mineral matrix.

CONCLUSION

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The study demonstrates that the efficiency of anionic acrylamide copolymers in flocculation depends on the structure of the mineral phase and environmental conditions. For calcite dispersions, the copolymer containing maleic acid is the most effective at low dosages (0.1–0.2 %), ensuring rapid formation of calcium coordination bridges. For smectite-containing systems, the copolymer with acrylic acid is optimal at dosages of 0.2–0.5 %, where the dominant factor is the formation of long interparticle polymer bridges.

In oil-containing emulsions, the synthesized copolymers outperform industrial analogues: they provide deeper clarification, shorter demulsification times, and lower residual turbidity. Polyacrylamide acts more slowly, while hydrolyzed polyacrylonitrile exhibits a stabilizing effect, making it unsuitable for such applications.

The practical significance of the work lies in the fact that the identified mechanisms justify the selection of copolymer type and dosage range depending on the mineralogy and organic composition of wastewater. The results can be used to design flocculation-based treatment technologies for complex multicomponent systems.

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