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INVESTIGATION ON THE PHYSICO - CHEMICAL PROPERTIES OF MAGNETIC CLAY COMPOSITES

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Abstract. *This article studies the main physical and chemical properties of magnetic clays. Structural changes in magnetic clay composite suspensions were evaluated by measuring the permittivity through direct measurement of the sensor capacitance and through computer measurement of the frequency of the electric signal inversely proportional to the sensor capacitance. Natural bentonite clay of the Tagan field (East Kazakhstan region) was used in this study. Magnetite synthesized by the method of co-precipitation of iron salts with magnetite-clay composites. Different compositions of clay-magnetite compounds were investigated to study the magnetic properties of the samples. According to the study, with the increasing of magnetite in the composition the magnetic properties increase. However, increasing the magnetite in the composition leads to lose the stability of the suspension. The stability of the suspension also investigated by measuring of the size of the particles. Depending on the findings of the study 20% magnetite-clay composition was the optimal value for the magnetic solution.*

Key words: *magnetic properties, bentonite, magnetic permeability, magnetic particles.*

МАГНИТТІ САЗДЫ КОМПОЗИТТЕРДІҢ ФИЗИКА-ХИМИЯЛЫҚ ҚАСИЕТТЕРІН ЗЕРТТЕУ

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Аңдатпа: *Бұл мақалада магниттік саздардың негізгі физика-химиялық қасиеттері зерттелінді. Магниттік сазды композициялық суспензиялардың құрылымдық өзгерістері сенсордың сыйымдылығын тікелей өлшеу және магниттік өткізгіштігін өлшеу арқылы зерттелінді. Осы зерттеуде Таган кен орнының (Шығыс Қазақстан облысы) табиғи бентонитті сазы пайдаланылды. Магнетит темір тұздарын магнетит-сазды композиттермен бірге тұндыру әдісімен синтезделеді. Үлгілердің магниттік қасиеттерін зерттеу үшін саз-магнетит қосылыстарының әртүрлі композиттері қарастырылды. Зерттеулерге сәйкес, композициядағы магнетит құрамының жоғарылауымен магниттік қасиеттер артады. Алайда композициядағы магнетиттің жоғарылауы суспензияның тұрақтылығын жоғалтуға әкеледі. Суспензияның тұрақтылығы бөлшектердің мөлшерін өлшеу арқылы да зерттелді. Зерттеу нәтижелеріне байланысты 20% магнетит-саз құрамы магниттік ерітінді үшін оңтайлы мән болды.*

Түйінді сөздер: *магниттік қасиеттер, бентонит, магниттік өткізгіштігі, магниттік бөлшектер.*

ИССЛЕДОВАНИЕ ФИЗИКО-ХИМИЧЕСКИХ СВОЙСТВ КОМПОЗИТОВ МАГНИТНЫХ ГЛИН

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Аннотация. *В статье исследуются основные физико-химические свойства магнитных глин. Структурные изменения в суспензиях магнитно-глинистых композиционных материалов оценивали путем измерения электрической проницаемости путем прямого измерения емкости датчика и путем компьютерного измерения частоты электрического сигнала, обратно пропорциональной емкости датчика. В исследовании использовалась природная бентонитовая глина Таганского месторождения (Восточно-Казахстанская область). Магнетит синтезирован методом соосаждения солей железа с магнитными-глинистыми композитами. Были исследованы различные составы глинисто-магнетитовых соединений для изучения магнитных свойств образцов. Согласно исследованию, с увеличением содержания магнетита в составе магнитные свойства увеличиваются. Однако увеличение количества магнетита в составе приводит к потере устойчивости суспензии. Стабильность суспензии также исследовали путем измерения размера частиц. В зависимости от результатов исследования 20% магнетит-глинистый состав был оптимальным значением для магнитного раствора.*

Ключевые слова: *магнитные свойства, бентонит, магнитная проницаемость, магнитные частицы.*

Introduction

Nowadays, the study of water-based magnetic fluids is one of the interesting topics on the scientific field. Water-based magnetic fluids (MF) and magnetite, used as a dispersed phase in a magnetic fluid, are practically harmless to the human body, and water is a unique medium with a number of anomalous properties. Therefore,water-based magnetic fluid is an interesting object for use in medical purposes [1].

Magnetic fluids have a unique combination of fluidity and the ability to interact with a magnetic field. Their properties are determined by a set of characteristics of its constituent components (solid magnetic phase, dispersion medium and stabilizer), varying which, within a wide range, the physicochemical parameters of MF can be changed depending on the conditions of their application. A list of many of these characteristics was given in a number of works [2-3], however, the main colloidal-chemical property that determines the conditions for using MF as intended is the aggregative stability of this colloidal system in combination with a high dispersion of the magnetic phase.

Currently, a lot of research is being carried out in this direction [3-5]. So, for example, with the help of magnetic fluid, drugs are delivered to the targeted area, biologically compatible water-based magnetite liquids with ascorbic acid as a stabilizer were created, which were injected into blood vessels, magnetically controlled liposomes were obtained, in which fine particles of magnetite were simultaneously encapsulated with a drug [6].The use of magnetic fluid and ophthalmology is patented, in particular for the treatment of retinal detachment [7]. Magnetic sorbents, which have the general name "ferrocarbon", obtained on the basis of carbon with included iron particles, are described [8]. Magnetic particles are used to create artificial muscles, magnetic fluids, magnetically controlled adsorbents [9-10]. Of great interest is the use of magnetic particles in medicine for the delivery of drugs to organs [11-12]. Recently, bentonite clays, in particular, montmorillonite particles bearing magnetite nanoparticles (Fe_3O_4), have been used quite often as magnetic particles.

Materials and methods of research

X-ray diffraction analysis of a sample of this clay was carried out on an automated DRON-3 diffractometer with $Cu_{K\alpha}$ - radiation, β-filter. Conditions for recording diffraction patterns: U = 35 kV; I = 20 mA; shooting θ-2θ; detector 2 deg / min. The quantitative ratios of the crystalline phases were determined. Interpretation of diffractograms was carried out using data from the ICDD card index: the database of powder diffractometric data PDF2 (PowderDiffractionFile) and diffractograms of minerals free of impurities. The research results are presented in Table 1.

Table 1. Results of semi-quantitative X-ray phase analysis of crystalline phases

Phase name	Formula	Concen-tration, %
bentonite	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot xH_2O$	97.7
silica	SiO_2	2.3

Montmorillonite was dispersed in water at pH = 7 and fractionated by sedimentation. A fraction stable for 1 day with an average particle diameter of 1.9 ± 0.2 μm was used.

Samples of magnetite-clay (MC) composites were obtained according to the modified method of Elmore [13] by chemical condensation, which is based on the reaction $2FeCl_3 \cdot 6H_2O + FeSO_4 \cdot 7H_2O + 8NH_4OH \rightarrow Fe_3O_4\downarrow + 6NH_4Cl + (NH_4)_2SO_4 + 23H_2O$

The reaction was carried out at a ratio of salts Fe +3/Fe +2 2: 1, with a 1.5-fold excess of ammonium hydroxide and with stirring of the solution in order to limit the growth of particles when obtaining a highly dispersed precipitate. To obtain clays, according to the Elmore method, the amounts of the initial salts of iron (II, III) were taken on the basis of the stoichiometry of the reaction of obtaining magnetite according to the Elmore method (in an equivalent ratio). Since the theoretical mass of the magnetite formed as a result of the reaction is known, and considering that the same amount of it should have been formed "inside the structure" of the clay, to obtain magnetic clays, theoretically containing 5, 10, 20 and 50% magnetite, we took the corresponding weighed portions of clay.

Sedimentation analysis was performed. The particle size was determined using a ZetaSizer device (Malvern) [14].

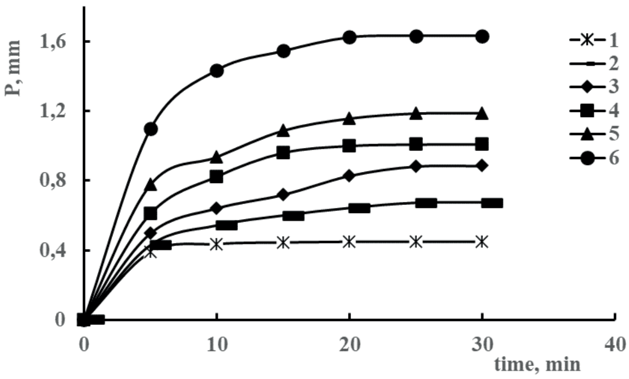
The stability of the magnetic hydro suspension was studied by the kinetics of changes in its optical density (D) [15]. The optical density (A) was measured on a PD-303 spectrophotometer (Japan) at a wavelength of 540 nm with constant slow stirring of the system with a magnetic stirrer.

The magnetic permeability was measured using a computer measuring complex using a controller - "USB - frequency meter PM 732" [16], the software of which shows the signal frequency on the monitor screen inversely proportional to the dielectric constant of the measured substance. For this, the measuring capacitor was included in the circuit of the electric pulse generator. At each value of R, by measuring the frequency of generation with a filled measured substance, its relative magnetic permeability is calculated. It should be emphasized that important parameters of magnetic substances are relative magnetic permeability μ, magnetization İ, magnetic moment of domains and etc.

Results and discussion

Determination of the particle size of the dispersed phase and the construction of particle size distribution curves are the essence of the analysis of variance.

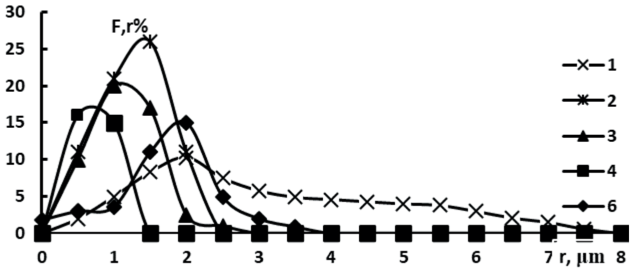
According to the results of sedimentation analysis, the preferred particle size of montmorillonite was 1-2 microns. The results of the studies are shown in Figure 1.



1 - bentonite clay, 2 - composite MC 5%, 3 - composite MC 10%, 4 - composite MC 20%, 5 - composite MC 50%, 6 – magnetite

Figgure 1. Sedimentation curve of deposition of 0.05% suspensions of composites of MC and pure magnetite

As can be seen from the figure 1, pure clay has the lowest rate of sediment accumulation (curve 1), with an increase in the magnetite content, the rate of particle settling and their accumulation increases (curves 2 - 6). It was found that the original clay is characterized by a wide particle size distribution (r = 0.1 ÷ 7.8 μm). Differential particle size distribution curves results are shown in Figure 2.



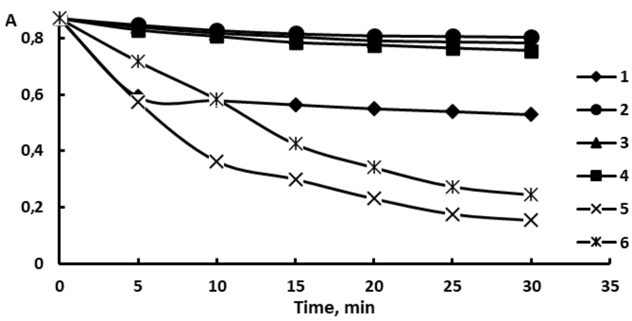
1 - bentonite clay, 2 - composite MC 5%, 3 - composite MC 10%, 4 - composite MC 20%, 5 - composite MC 50%, 6 – magnetite

Figgure 2. Differential curves of particle size distribution in aqueous suspensions

It was found that the original clay is characterized by a wide particle size distribution (r = 0.1 ÷ 7.8 μm).The introduction of magnetite particles into clay leads, on the one hand, to a shift of the maxima of the differential distribution curves of particles in the region of small values of r, to a narrowing of these curves.

In other words, in the presence of magnetite, the particles of bentonite clays become more monodisperse and finer than the original clay. This may be due to an increase in the density of clay particles and a decrease in their swelling when introducing magnetite.

To study the effect of water-soluble polymers (WSP) on the stability of a hydrosuspension of magnetic clays obtained by the formation of magnetite (Mgt) Fe_3O_4 nanoparticles in the interpacket space of Na - montmorillonite. More accurate information on the flocculating effect of the considered polyelectrolytes was obtained by studying this process spectrophotometrically. The research results are shown in Figure 3.

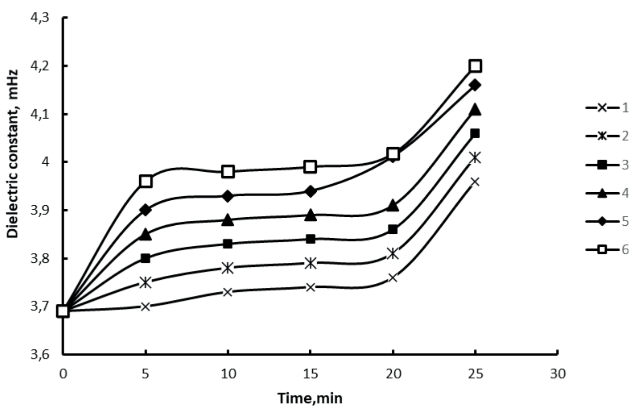


1 - bentonite clay, 2 - composite MC 5%, 3 - composite MC 10%, 4 - composite MC 20%, 5 - composite MC 50%, 6 – magnetite

Figgure 3. Kinetics of the change in optical density (A540) of a hydro suspension of the MC composite with the addition of sodium alginate and chitosan of various concentrations

It was found that at a concentration of 0.25%, both WSP significantly stabilize 0.05% hydrosuspension of magnetic clay composites. Chitosan at the same concentration has no significant effect on the stability of the suspension under consideration.The condition for effective stabilization of particles is the compatibility of the ferro phase, stabilizer and dispersion medium, while the best stabilizers are substances such as Na alginate in 0.25% concentrations, which dissolve well in the dispersion medium. Stabilization is explained by a decrease in the surface energy of dispersed particles and an increase in the absolute value of their electro kinetic potential, as well as due to structural-mechanical and steric factors.

The experimental data on the magnetic permeability of MC composites are shown in Figure 4.



1 - bentonite clay, 2 - composite MC 5%, 3 - composite MC 10%, 4 - composite MC 20%, 5 - composite MC 50%, 6 – magnetite

Figgure 4. Dependence of magnetic permeability on time of 5% suspensions of MG composites

Figure 4 shows that with an increase in the concentration of magnetite in the composition of clay composites in a ratio of 5, 10, 20, 50%, the values of the magnetic permeability are increased. This is due to the different ratio between the components of the conductivity due to the mobility of the magnetic particles. Magnetic susceptibility is the proportionality coefficient between magnetization and the external magnetic field that created it, and is numerically equal to the ratio of magnetization to magnetic field strength. Most iron minerals are ferromagnetic (magnetite, titanium-magnetite, pyrrhotite, etc.). Thus, the magnetic properties of composites of magnetic clays show the influence on the formation of the mesostructured not only in strong fields, but also in the geomagnetic field.

Conclusion

The experimental results obtained using a complex of modern physicochemical methods and their interpretation allow us to draw the following conclusions:

It was found that the values of the maximum magnetization of composites synthesized by the Elmore method significantly exceed the values of magnetization for samples containing iron oxide in the form of Fe_2O_3. It was shown that the use of composites containing Fe_3O_4 makes it possible to obtain materials with pronounced magnetic properties at a low iron content, which is explained by the presence nano-sized particles.

The introduction of magnetite particles into the structure of bentonite clay leads to a decrease in the stability of hydraulic suspensions of composites and a decrease in the size of composites, which is caused by an increase in the density of clay particles and a decrease in their swelling upon the introduction of magnetite. Magnetic properties of fluid increased by adding more magnetite.

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