

MODIFICATION OF BENTONITES INOCULATION WITH IRON COMPOUNDS TO AFFORD MAGNETITE CLAYS

BAKYTGUL ASKAPOVA^{a*}, KUANYSHBEK MUSABEKOV^a

ABSTRACT. Bentonites refer to the class of argilliferous folded silicate rocks, which as a whole have such common characteristics, as dispersion (fragmentation), colloidal properties, propensity to wetness, and adsorption properties. The importance of this paper, as it follows from the conclusion, is connected with the study of synthesizing of magnetic clay composites which have high adsorption capacity, as well as with systematization of their properties. Bentonite magnetic composites are among those which can be stabilized using sodium alginate. Magnetic composites synthesized on the basis of bentonite showed the proportion of magnetite corresponding to the proportion of Fe in the composition of the initial clays. Sodium alginate-based stabilization method is an effective one for bentonite magnetic composites.

Keywords: *bentonite, iron impurities, magnetic composite*

INTRODUCTION

All the existing large ore deposits of bentonite clays were formed because of decomposition of volcanic ash and peat water. The total world reserves of bentonite clays make about 5.5 billion tons. China accounts for 2.4 billion tons (about 45%) of the total, the United States accounts for about 15%, and such countries as Turkey, Greece, India and Russia account for 5-7% each of the total reserves. Most of the ore deposits in the world coincide with alkaline earth bentonites, while high-quality bentonites reservoirs are limited due to their concentration in volcanic sedimentary deposits and hydrothermal-metasomatic, geological-industrial areas.

In the world environmentally safe multifunctional hybrid materials get development for using them in biotechnology, medicine, and ecology is solve an urgent problem. Aluminosilicates, montmorillonite and bentonite clays widely occurring in nature those contain at least 70% mineral montmorillonite are

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most promising for production of new composites [1]. They exhibit unique texture and physical-chemical properties, such as a developed specific surface area, a regular distribution of meso- and micropores, thermal stability, and the presence of various active centers of different nature. One method for obtaining composites based on bentonite consists in the modification of aluminosilicate by iron metal particles [2]. The addition of such metal particles promotes destruction of the hierarchical structure formed because of the coalescence of individual crystallites in the layerwise silicate and can cause changing in the texture and physical-chemical properties of the resulting composite. Using iron oxides, as initial magnetite Fe_3O_4 is characterized by a positive magnetic susceptibility. Iron metal particles give control for formation magnetic compounds with in intensification of the solid-liquid separation process.

As for Kazakhstan the reserves of bentonite clays there are rather large [3]. The productive intervals of Kazakhstan's bentonitic montmorillonite deposits are widely developed. They are limited by the folded belt, the Turanian Plate and lowlands, as well as by the basing bordering the Caspian lowland. The deposits of Southern and Eastern Kazakhstan cause the greatest practical interest. In Southern Kazakhstan they are the Darbaza and Kele deposits, whose total reserve makes 58 million tons. Besides, there are the Andreev, Dzerzhinsk and Ildersay deposits, with the total reserve making more than 100 million tons. Eastern Kazakhstan known reservoirs of bentonite clay are those of the Manrak group deposits, whose total reserves make about 50 million tons. The Tagan deposit bentonites (10.6 million tons) and those of the Dinosaur deposit (about 4 million tons) are of high quality [1]. The study of the Tagan deposit has revealed the genesis and distribution pattern of montmorillonitic mudstone varieties, the reserves and nature of bentonites, and the minerals extraction methods.

According to the research results there are three types of bentonite clays including alkaline, alkaline-earth and pharmaceutical one. Due to the special properties of montmorillonites and bentonite clays conditioned by the genesis of the Tagan deposit, the clays can be used in various industrial technologies. Alkaline bentonites are suitable to produce drilling solvents, while the sodium-free montmorillonites are usable in the production of catalysts. The pharmaceutical variety is represented by alkaline montmorillonites of the 12th horizon. The raw material extracted from this horizon is used in production of enterosorbents, capable to withdraw heavy metal ions and radionuclides from the human body [4]. Bentonite clays are usually called fine-dispersed clays, and their main components are montmorillonite ($\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot \text{H}_2\text{O}$) and beidellite ($\text{Al}_2\text{O}_3 \cdot 3\text{SiO}_2 \cdot n\text{H}_2\text{O}$). The montmorillonitic group minerals (smectites) have high binding, adsorption and catalytic

abilities. The structure of bentonite rock consists of smectite minerals whose tier-structured crystal lattice is arranged of a single cell frame, each having 3 layers. The upper and lower layers of the AlSiO_4 frame are formed from tetrahedras and are called tetrahedral.

Magnetic fluids consist of a dispersed solid magnetic phase, a dispersion medium and stabilization. The fluid components' cumulative characteristics significantly affect the overall properties of the fluid. In the dispersed magnetic phase ferromagnetic and ferrimagnetic metals and metal oxides are often used. For the synthesizing purposes such metals, as Fe, Co, Ni, Gd; nitrides of these metals (for example, Fe_xN); metal oxides (primarily magnetite Fe_3O_4 and maghemite $\gamma\text{-Fe}_2\text{O}_3$); and parts of bimetallic alloys (Ni-Fe, Fe-Pt, Fe-Co, Sn-Co) are used. Ferrites, for example, chemical compounds, are also afforded from iron oxide Fe_2O_3 ore (ferrimagnets) with other metals oxides including special magnetic additives [5-7]. Despite the maximum magnetic saturation of metals, they are very sensitive to oxidation, especially in a highly dispersed state. Therefore, ferrite particles including magnetite, which is often used among ferrites (Fe_3O_4), are used here as the magnetically dispersed phase. The magnetic properties of magnetic liquids are determined by the weight composition of the solid phase, which can reach 25%.

The choice of magneto-containing materials is rather wide, and it can be greatly simplified, if such a question, as good compatibility of surfactants with the particles transporting fluid, as an important factor for stable colloidal suspensions extraction is taken into consideration.

Currently, a wide range of carrier products is used, as follow: water, ethanol, pentanol, glycol, perfluoropolyethylene, synthetic esters, transformer oils, freons, styrene, methylethylketone, kerosene, various synthetic hydrocarbons and organic solvents, vegetable and silicone oils [8-12]. Chemical interaction of the transporting fluid with the magnetic phase and the materials used in the mechanical device is inadmissible and is to be avoided. Stabilizer of magnetic particles in the transportation fluid is an indispensable element for magnetic fluids. The magnetic particles collision triggered off by their intense Brownian motion in the fluid is induced by the magnetic force, thus resulting in coagulation of magnetic particles. Therefore, stabilizing substances are required to prevent the particles collision and oxidation of the surface of the magnetic particles as well [13].

The magnetic particles in the fluid have doubled protective coating each, so that they are prevented from the adhesion effect, and due to the thermal disorder, they are dispersed through the fluid. Therefore, unlike a standard suspension, magnetic fluid particles do not settle to the bottom and remain effective for many years [14]. Stabilizing agents are important in the

synthesizing process of magnetic fluids, as they ensure coagulation stability of the system. The transporting fluid [magnetic particles], i.e., its properties, are critical for the choice of a particular stabilizer. Hence, magnetic fluids based on hydrocarbons (kerosene, marginal hydrocarbons, cold paraffin, vacuum oils) require such stabilizers, as higher alcohols, amines, fatty acids and surfactants (olein, stearin, laurine) [15].

Magnetic fluids and water-based magnetite used as a dispersed phase are practically harmless to the human body. As for water it is a special medium with a number of specific properties. Therefore, water-based magnetic fluids can be used for medical purposes [16]. For instance, a drop of a magnetic fluid is capable to transport the required medicine to the diseased area of a human body [17]. When biocompatible water- and ascorbic acid-based magnetite fluids are introduced into blood vessels as a stabilizer [18], they are capable to remove liposome, which now are controlled magnetically, as the magnetite particles inside them are encapsulated by the introduced drug [19, 20]. Ophthalmology is one more sphere, in which applicability of magnetic fluids is patented.

The aim of this work consisted in obtaining composites based on bentonite and magnetite and in studying their structure, stabilizing and sorption properties.

RESULTS AND DISCUSSION

In Fig. 1 the X-ray phase spectra of magnetite-clay composites are shown. The diffractograms of the composites confirm occurrence of the peaks corresponding to the structure of the mineral type montmorillonite and 8-silicon-oxygen and aluminum–oxygen groups included in the iron oxides γ - Fe_2O_3 (hematite) and $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ (Fe_3O_4 -magnetite). An increase in magnetite concentration in the composite gives an increase in the height of iron oxides peaks (30.6° and 37.2°), and the decrease in the height of the Silicon and aluminum oxygen groups of montmorillonite peaks (6.8° and 20.1°).

Penetration of oxides into the clay structure is determined by its iron exchange capacity. The introduction of bentonite into the inter-pack space is provided not only by the physical correspondence of the space between the magnetite particles and the clay layers, but also by chemical interaction, accompanied by significant changes in the structure of bentonite, leading to the formation of new phases. Changes observed on bentonite X-ray diffractograms.

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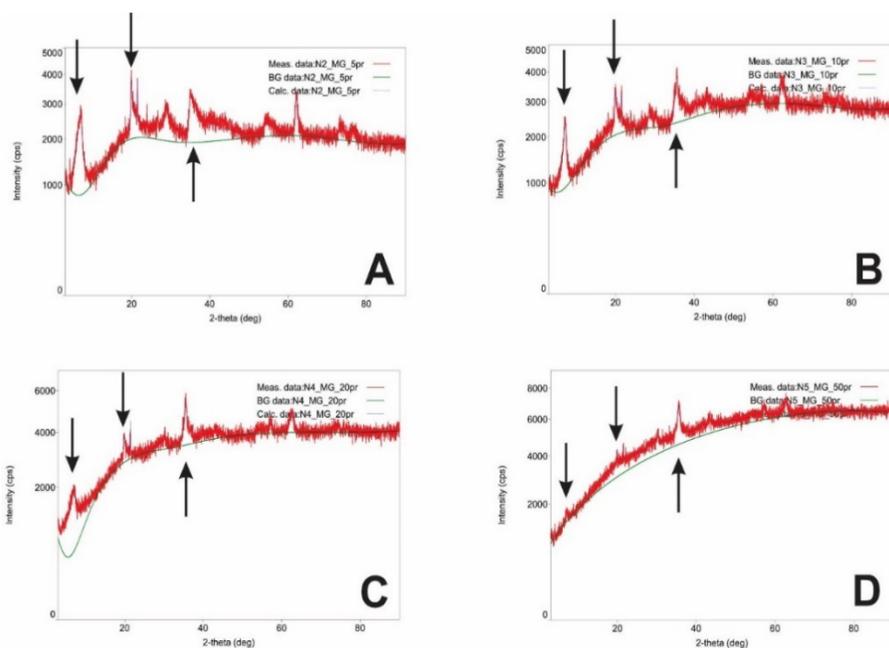


Figure 1. Diffractogram of X-ray phase composites: 5% (A); 10% (B); 20% (C); 50% (D)

Introduction of bentonite into the inter-frame space is adequate to the space between the magnetite particles and the clay layers and the chemical interaction occurring there and causing significant changes in the structure of bentonite leads to formation of new phases.

Ultrasonic dispersion of the afforded clay-magnetite composites, pure bentonite clay and magnetite allowed to obtain water suspensions by crushing the particles to a powdery state. The Figurovsky method of study of the magnetite effect on the hydrosuspensions shrinkage stability and granulometric composition of the Tagan bentonite included investigation of the sedimentation kinetics of the clay particles, which contain various quantities of magnetite (Figure 2). Hydrostatic microbalance captures the change in the mass of composites in size which during the experiment is fixed using a cathetometer through a sieve. The main indicator of the method is the ability to study the sedimentation of dilute suspensions over time. It was found that the increase in the content of magnetic structures increases the size of the particles.

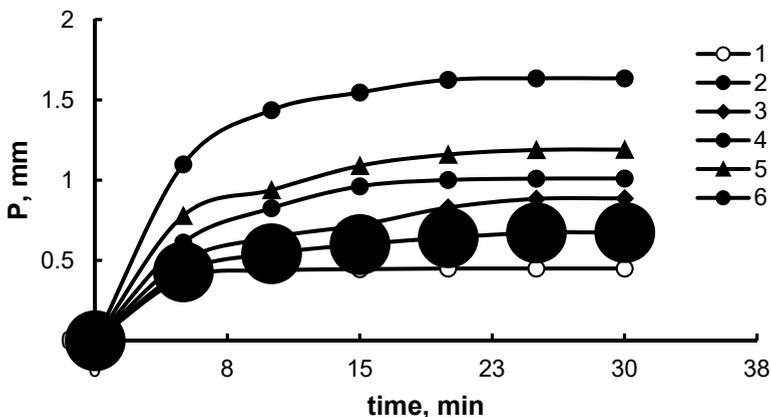


Figure 2. Particles sedimentation curves in hydrosuspension: 1 – bentonite clay, 2 – clay magnetic composite (5 %), 3 – clay magnetic composite (10 %), 4 – clay magnetic composite (20 %), 5 – clay magnetic composite (50 %), 6 – magnetite.

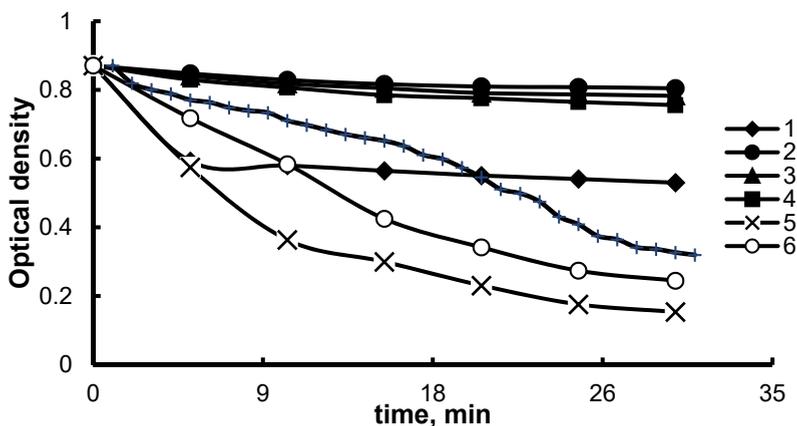


Figure 3. Changes in optical density kinetics of the bentonite hydrosuspension added with sodium alginate and chitosan at different concentrations. 1 – bentonite clay, 2 – 0.25 % Na alginate, 3 – 0.125 % Na alginate, 4 – 0.0625 % Na alginate, 5 – 0.25 % chitosan, 6 – 0.125 % chitosan, 7 – 0.0625 % chitosan

The decrease in the swelling of clay is explained by the water molecules displacement from the inter-frame space, when magnetite is introduced into the structure of bentonite clay. Since the growth of magnetite particles occurs directly in the inter-frame space, and the particle sizes correspond to the inter-frame space dimensions, then almost complete displacement of water molecules takes place there. The effect of stabilizers on the sedimentation

curves was studied in order to afford a stable bentonite hydrosuspension in aqueous medium. The following figure shows the effect on the shrinkage which the bentonite clay particles have in an aqueous medium at different concentrations of chitosan and sodium alginate (Figure 3).

As it follows from the Figure, the effect of sodium alginate on this process is very large, namely: first, a decrease in concentration of sodium alginate by 0.0625% results in a decrease in the deposition rate (Curve 4) and further increase in concentration, i.e. sodium alginate with a concentration of 0.25% leads to a long-term stabilization. When chitosan concentration is equal to 0.25%, the maximum accumulation of sediment is 5 times less than that in pure water. The effect of chitosan on the bentonite particles sedimentation can be explained by the water-soluble polymer's mechanism changes. It is known, in particular, that low concentrated chitosan has a flocculatory effect.

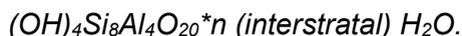
Table 1. Bentonite and its composites' surfaces values

Composite	Content of Fe ₃ O ₄ , %	The surface area determined by the thermal desorption method, m ² /g	The surface area determined by the sedimentation method, m ² /g
Bentonite	-	278.5	243.8
MC 1	4.37	305.3	289.7
MC 2	9.62	368.5	355.4
MC 3	24.44	282.7	271.6
MC 4	27.78	189.9	185.6

As it follows from the Table 1, an increase in the amount of magnetite in the composites MC 1 and MC 2 gives the values increase of a certain surface due to the particle sizes decrease. However, the values of the specific surface areas of the MC 3 and MC 4 compositions decrease, despite the small-sized particles of the composites. The reason of this lies in the fact that increased magnetite concentration in this composite gives the pores clogged, since the Fe₃O₄ particles in this composite are located not only on the coating of bentonite clay (like composites MC 1 and MC 2) but in the interplanar space too.

EXPERIMENTAL

The objects of the study were bentonite clay from the Tagan ore deposit (East Kazakhstan oblast) used as clay minerals has the formula, as follows:



Heaving properties of the Tagan bentonite clays are of great importance, as they indicate the suitability of the clay raw for solvents preparing. Moreover, the raw material does not lose its properties for a long time, even when preserved in a smaller amount in the dispersed phase. For the synthesis of magnetite particles iron salts, as $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ are used.

Carboxymethyl cellulose (Na-CMC), Na-alginate (Na-ALG), methylcellulose and chitosan are used as stabilizing agents for the magnetite dispersion. Due to the ability of sodium alginate to retain water this substance is used in the manufacture of medicines to improve their dissolving ability. Along with the water-absorbing capacity the agent is good enough to sorb radionuclides from the human body. The substance is resistant to high temperatures, and since the density of Na-CMC is 1590 kg/m^3 , this fibrous material has a high stabilizing ability.

Chitosan is a polymer rather coherent to hydrophilic sedimentary shells of hydrophilic adsorptive assemblages. Taking into consideration the anti-allergic properties of chitosan and its ability to deliver biopolymer drugs to diseased areas of human bodies and dose them, the potential of the biopolymer to taken as a polymer matrix is also among the objects of research.

The mineral bentonite extracted at the Tagan deposit was purified from various solid sand impurities and then subjected to heat treatment in a vacuum drying oven at a temperature of 220°C for two hours. In the paper a highly dispersed fraction of the Tagan montmorillonite, with an average radius of $1.4 \pm 0.2 \text{ nm}$, measured by the ZetaSizer device (Malvern-NanoZS, England) is described. Montmorillonite was subjected to dispersion in water at pH 7 and fractionation by sedimentation method for 24 hours. The particles that remained unsettled after 24 hours of settling were used then for the research purposes. The turbidimetric method was used to study the suspensions stability. The optical density (A) was measured on a PD-303 spectrophotometer (Japan). The system was subjected to constant slow stirring at a magnetic stirrer, at a wavelength of 540 nm. The kinetics of the optical density changes depending on the electrolyte and flocculant concentration showed the sedimentation rate.

The prepared suspension and stabilizers were stirred in a magnetic stirrer for one minute. The finished system was filled into the cuvette of PD-303 spectrophotometer, and observed for the changes in its optical density with recording them every 40 minutes.

The magnetite particles have been released by the sedimentation method. For this purpose an aqueous solution of ammonium (15%) was added to $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ solutions, whose pH were 9.5-11.0, in a molar ratio of 2:1, at indoor temperature and normal pressure. The resulting suspension was stirred at ambient temperature for 30 minutes, then filtered, washed with distilled water and dried at 130°C . The simplest and most sensitive device is

Figurovsky's hydrostatic microbalance, the change in the deformation of the rocker during the experiment is recorded using a reference microscope or cathetometer. The sensitivity of the device depends on the length and thickness of the rocker arm. The main advantage of the method is the possibility of studying dilute suspensions with concentrations from 0.2 to 0.001%.

The resulting suspension of magnetite first acquires a black color, but after drying it turns into a dark brown powder. The process reaction equation is, as follows:

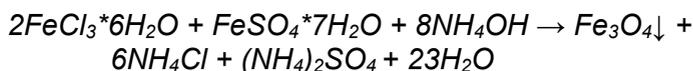
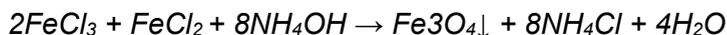


Introduction of magnetite into the clay structure is an effective way to afford magnetic fluids. According to this method the bentonite clay hydrosuspension was added with a solution of divalent iron and settled for 24 hours. Then it was kept in a solution of FeCl₃ for about 2 more hours, then settled at the air temperature of 25 °C, using ammonia water with a pH of 9.5-11.0. Finally, there were obtained clay-magnetite composites of brown–black color. This increases the absorption capacity of iron ions on the clay surface and turns them into exchange cations, and displacing water molecules contributes to the expansion of the space between them. Since we knew the theoretical mass of magnetite resulted from the reaction, and assumed that the same amount of it should be formed in the clay structure, appropriate amounts of clay were afforded to produce magnetic clay with a mass of 5, 10, 20 and 50% of magnetite (Table 2).

Table 2. Elemental composition of primary bentonite and magnetic composite samples

Sample	Composite	Share of Fe, %	Share of Fe ₃ O ₄ , %
Bentonite		–	–
Magnetic composite 5 %	MC 1	0,74	4,37
Magnetic composite 10 %	MC 2	1,84	9,62
Magnetic composite 25 %	MC 3	5,89	24,44
Magnetic composite 50 %	MC 4	6,70	27,78

Synthesizing of magnetite is determined to be according to the reaction, as follows:



CONCLUSION

For the study purposes of magnetic montmorillonite physicochemical properties in water, the Elmore method [23] was used to afford magnetic montmorillonites with different magnetite (Fe_3O_4) concentrations (5%, 10%, 20% and 50%) from two (Fe^{2+}) and three (Fe^{3+}) valence iron salts in a weak alkaline medium (in an aqueous solution of ammonium hydroxide). The obtained magnetic montmorillonites were studied by the X-ray phase method and proved to contain hematite and magnetite. Natural polymers of sodium alginate and chitosan have been studied for the effect they have on the stability of magnetic montmorillonite hydrosuspension. The maximum stability was observed in the presence of 0.25 % sodium alginate. The flocculation properties of chitosan have been observed at lower concentrations.

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