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Improving the Quality of Clay Powders by Mechanoactivation

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ABSTRACT

The ability to effectively use mineral resources is the key to the sustainable development of industry in modern conditions of environmental protection. High-quality bentonites are rarely found in nature, so technologies for improving the quality of clay powders are quite relevant today. The article considers the possibility of improving the quality of clays obtained from candidate quarries for the purpose of further use as components of drilling fluids. The filtration and rheological characteristics of drilling fluids obtained on the basis of activated clay powder were also investigated by Benta Limited Liability Company.

Keywords: clay, bentonite, swelling index, cation exchange capacity, drilling fluid, rheology.

INTRODUCTION

A large number of clay minerals exist in nature. Quite often, the properties of natural minerals do not fully satisfy the needs of industry according to certain criteria. In this case, technological schemes and methods for modification or activation of clay powders are developed, the purpose of which is to acquire certain regulated properties by the material. Reagents-modifiers or activators can be various compounds, for example (Ratkievicius et al., 2017; Silva et al., 2014; Tyagi et al., 2006; Zhuang G. et al., 2019) anionic, amphoteric, cationic, nonionic surfactants, acids (H_2SO_4, etc.), alcohols (Kafashi et al., 2014) (polyvinyl, etc.), salts (alkylammonium, etc.) (de Paiva et al., 2008) or biomolecules (proteins, enzymes, amino acids, peptides).

Modified clays are currently widely used by industry as structure-forming reagents and reagents that increase the thermal and sedimentation stability of drilling fluids, in lubricants, adhesives, paints, cosmetics, composite materials, and for soil reclamation (de Paiva et al., 2008; Ratkievicius et al., 2017; Vipulanandan & Mohammed, 2020; Zhuang G. et al., 2018).

Also, in recent years, significant attention has been paid to clay nanomaterials with sizes of 10–100 nm, the properties of which differ significantly from ordinary materials, which makes them promising in the development of advanced materials with specific properties (Cortés et al., 2010; Silva et al., 2014; Vipulanandan & Mohammed, 2020). Clay nanoparticles also effectively affect the quality of drilling fluids under HPHT conditions (Barry et al., 2015). Organophilic clays are often used as components of ecological solutions based on a hydrocarbon synthetic base, in particular, based on biodiesel (Li et al., 2018).

Various methods can be used to modify clays and clay minerals, such as adsorption, infusion, intercalation, ion exchange with organic and inorganic cations, grafting of organic compounds, polymerization, dehydroxylation, calcination, lyophilization, ultrasound, and plasma.

The most common clay minerals are divided into four groups (Bridges & Robinson, 2020; Zhuang G. et al., 2019): montmorillonites - montmorillonite ($Al_2O_3 . 4SiO_2 . H_2O$), sapenite, vermiculite, nontrenite; kaolinitic – kaolinite ($Al_2O_3 . 2SiO_2 . 2H_2O$), nakrite, schisite, dickite, anoxite and endelite; hydromica – hydromuscovite, illite (general formula $Ky(Si_8\text{-}y\ Al\ y)(Al_4Fe_4 \cdot Mg_4 \cdot Mg_6)O_{20} \cdot (OH)_4$.

y = 2 for hydromuscovite y = 1.0 ... 1.5 for illite), palygorskite – sepiolite ($2MgO_3SiO_2 \cdot 4H_2O$) and palygorskite (atapulgite).

The crystal lattice of clay minerals of different groups has different structures, sizes, and features of the placement of oxygen atoms and covalent or ionic bonds. According to these features, the degree of expression of the main technological properties is different.

Under the action of electrostatic and surface forces, the crystal lattice attracts exchangeable cations from the aqueous medium Na^+, K^+, Ca^{+2}, Mg^{+2}, which were adsorbed on its surface, but do not change its structure (Teixeira-Neto E. & Teixeira-Neto A., 2009). These cations are not part of the crystal lattice and can be replaced by other ions, therefore they are called swelling index (SI), which can be organic and inorganic (Teixeira-Neto E. & Teixeira-Neto A.,2009). Each clay mineral has a certain amount of exchangeable cations, also called exchange capacity or cation exchange capacity (*CEC*). In most cases, the exchange complex consists of cations Na^+ and Ca^{+2}. The physical and chemical properties of clays and, accordingly, their technological application strongly depend on *CEC* and *SI* (Cortés et al., 2010).

If in an exchange complex predominate cations Na^+ then such a clay mineral is called sodium, if it Ca^{+2} is calcium (Teixeira-Neto E. & Teixeira-Neto A., 2009). Sodium clay minerals swell more, disperse faster, and the final particle size is smaller compared to calcium (magnesium) minerals, which, on the contrary, have less swelling, worse dispersion, and a larger final particle size (Cortés et al., 2010; Teixeira-Neto E. & Teixeira-Neto A., 2009).

It is worth noting that all clay minerals have in their composition one or another amount of impurities (Kafashi et al., 2014; Cortés et al., 2010; Tyagi et al., 2006; Vipulanandan & Mohammed, 2020; Zhuang G. et al., 2018) such as CaO, $CaCO_3$, MgO, MnO, K_2O, Na_2O, Fe_2O_3, SiO_2, SiO_3, Al_2O_3, TiO_2 P_2O_5, LOI the ratio of which determines the quality of clay powder and its properties.

High-quality bentonites are rarely found in nature, so specialists use technologies to improve the quality of clay powders, for example, various enrichment procedures (Afolabi et al., 2017), precipitation (Mohammadi et al., 2015) or fractionation and physico-chemical processing for the purpose of activation (Teixeira-Neto E. & Teixeira-Neto A., 2009).

The process of activation of clay materials can be carried out by various methods. Three methods are most widely used (Zhuang G. et al., 2019): “wet”, “dry” and “method of activation in suspension”. It is also possible to combine these methods with the heating of raw materials to certain temperatures (50–80°C) and with the use of various catalysts.

With “wet” activation, a paste is prepared from bentonite, water and a given amount of soda, the mixture is dried and then crushed. At the same time, activated bentonite and sediment from insoluble and slightly soluble salts such as $CaCO_3$ and $MgCO_3$ are obtained. “Dry” activation is carried out by mechanically mixing soda with bentonite in a certain proportion. Activation in this case occurs due to the moisture content of the bentonite itself.

The method of activation in suspension consists in dissolving the clay in a layer mill with water and soda. A soda solution was used for activation. Activation was carried out according to the following reaction: Na, Ca, Mg - bentonite + Na_2CO_3 (solution) = Na-bentonite + Ca, Mg (solution).

The experience of using different methods of activating lumpy clays indicates the maximum efficiency of the method of activation in an aqueous solution (wet activation) (Afolabi et al., 2017; Zhuang G. et al., 2019).

A minor disadvantage in the implementation of activation technologies is the time of standing of the formed samples (first for activation), and then to get rid of excess moisture in a drying cabinet.

MATERIALS AND METHODS

For the modification and activation process by the limited liability company “Benta” provided samples (Figure 1) in the form of lumpy clay obtained from various layers of a promising career-candidate in the Cherkasy region, Ukraine. Each of the three types of samples contained some amount of moisture, as the material has hygroscopic properties. These clay samples were obtained without any data on the reference to a specific deposit. Therefore, to determine the main directions of research and the selection of the necessary chemical reagents-activators, the mass concentrations of chemical compounds present in the test samples were first determined (Table 1).

Figure 1. Clay samples obtained for research; (a) horizon 1, (b) horizon 2, (c) horizon 3

Table 1. Mass concentrations of chemical compounds for clay test samples

Chemical formula	Concentration, %			
	1	2	3	4
Al_2O_3	16.250	15.167	12.536	9.288
MgO	4.565	3.643	2.537	1.672
SiO_2	56.798	55.100	48.732	34.555
Nb_2O_5	ppm 25	ppm 41	–	ppm 36
P_2O_5	5.615	–	–	0.771
RuO_3	ppm 25	–	–	–
PbO	ppm 56	–	–	–
Ag_2O	ppm 20	–	ppm 40	–
CaO	14.066	24.688	33.962	50.090
Fe_2O_3	2.435	1.061	1.809	3.080
ZnO	ppm 85	ppm 44	ppm 76	ppm 58
TiO_2	0.123	0.159	0.162	0.164
MnO_2	–	ppm 259	ppm 496	0.062
SrO	–	0.112	0.170	0.264
ZrO_2	–	ppm 135	ppm 189	ppm 134

According to Table 1, the main impurities in the samples are CaO, MgO, Fe_2O_3 and P_2O_5. The presence of these impurities indicates that it is a calcium form of clay that requires treatment with soda ash.

RESULTS

Raw materials for obtaining industrial clay powders are special lumpy clays from the quarry: bentonite, palyhorskite, kaolinite and hydromica. Such raw materials go through several stages of preparation (Figure 2) in order to obtain clay powder of industrial quality.

In order to improve the quality of the initial product, it is necessary first of all to carefully select clay and sort it in the quarry, rejecting lots with a significant amount of foreign impurities.

The maximum dispersion of clay powders is achieved by coarse (using a disintegrator) and

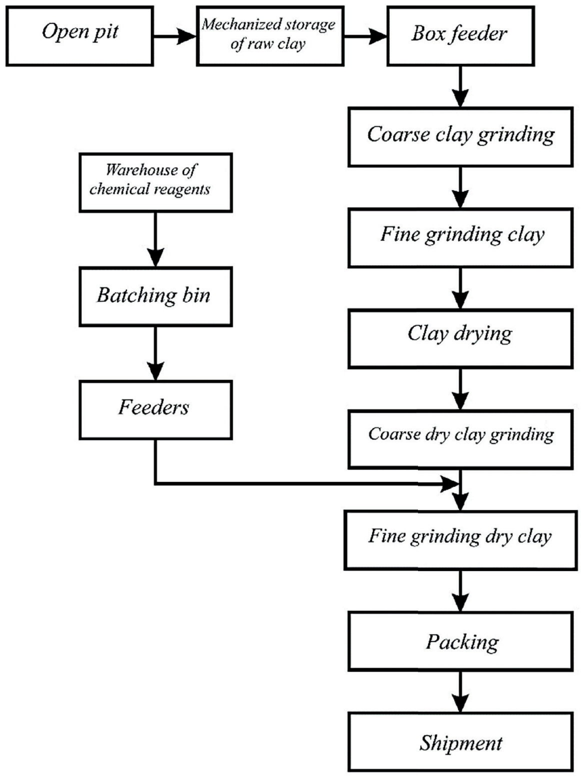

Figure 2. Technological diagram of the production of clay powders

fine (using a roller-pendulum mill) grinding. Reliable aspiration is also important, especially during chemical processing. Double grinding of raw clay allows more efficient drying.

At the same time, the limit of fine grinding and the drying mode of the raw material should be correctly selected. It is known that excessive grinding can damage the quality of clay powder, because during grinding the crystal lattice of clay minerals is partially destroyed, which leads to a decrease in the hydrophilicity of the powders.

At the stage of fine grinding, chemical reagents are added to the clay powder, which significantly improve the yield of drilling fluid from 1 ton of clay powder. Usually (15)% of soda ash is added to clay powder, which is especially effective for bentonite clays of the calcium type, because it allows you to convert them into sodium.

$$\boxed{\text{clay}} - Ca^{+2} + Na_2CO_3 \rightarrow \boxed{\text{clay}} - Na^+ + \frac{CaCO_3}{\downarrow}$$

In addition, 0.2–0.5% of metas or 1.0–2.5% of magnesium oxide, M-14, etc. are added to clay powders to increase the liquid yield.

To ensure optimal moisture content of the mixture during activation, sodium carbonate in the form of an aqueous solution is introduced into the clay, which facilitates and accelerates the active interaction and change in the properties of clay particles: Na^+ ions replace exchangeable Ca^{2+} ions. After placing such clay in an aqueous solution, the clay particles go into a highly dispersed state with a maximally active surface for binding water, which entails swelling of the clay particles and an increase in the viscosity of the clay solution.

There is a limit of dehydration, below which the quality of clay slurry deteriorates sharply. Such a limit is considered to be the presence of water in the crystal lattice of clay minerals, which is 4÷8% for bentonite clay powders and much higher for palyhorskite clays. Therefore, the main criterion for the rehydration of clay powder is not the temperature and duration of drying, but the residual moisture.

At a lower moisture content of the clay and especially when air-dry samples are used during grinding, there is almost no exchange of Ca^{2+} for Na^+. Their interaction occurs only after mixing clay powder with water, but mechanically absorbed salts interact very weakly with clay particles under these conditions; the yield of drilling fluid is several times lower than that of clay powders subjected to mechanical activation at higher humidity.

From part of the source material of lumpy clay samples (Figure 1) about 1 kg., selected for activation with soda ash (Figure 3a).

Clay is crushed, moistened and treated with soda ash in the amount of 4% of the mass of clay. The mass is reduced in viscosity to the state of the dough (Figure 3b) and repeatedly kneaded for a more complete passage of the sodium calcium substitution reaction. In order for the activation process to be successful, it is necessary to withstand the minimum time for the interaction of the components and the replacement of Na^+ and Ca^{2+} ions. Thus, 4 days turned out to be insufficient time necessary for exchange processes to take place in the entire volume of the prepared test samples, so the exposure time was increased to 6 days. After 6 days, the reacted material is crushed and sifted through sieve No. 008 (Figure 3c). Since the material is hygroscopic and the exposure time was quite long, to remove the moisture absorbed from the environment, the samples were kept for 2 hours in a drying cabinet at a temperature of 60°C. This step is necessary to ensure the reproducibility of the experiments,

Figure 3. Production of bentonite clay powder

because the amount of moisture in the samples must be the same for this.

The amount of Ca and Mg that went into the solution was determined chemically. At a two percent concentration, soda replaces approximately 75% of the amount of exchangeable cations. As a result of the conducted experiments, it was established that at a low concentration of soda (0.1%) the substitution does not occur completely. An excess of soda in the solution (concentration 2–5%) negatively affects the process of replacing calcium cations with sodium cations. Precipitation from insoluble $CaCO_3$ salts and free soda residues in the resulting activated clay powder negatively affect the process of preparing and using the drilling fluid when drilling wells.

Bentonite that underwent mechanoactivation at a soda concentration of 2% showed almost complete replacement of cations and the absence of insoluble $CaCO_3$ salts and traces of free soda.

The next stage was the assessment of the quality of the obtained material and the possibility of its use as a component of drilling fluids. The quality of clay powders is a complex of physico-chemical and technological indicators of clay powder, which allows you to fully evaluate it as a material for the preparation of drilling fluid and take into account its influence on the efficiency of drilling. The quality indicators include the minimum permissible effective viscosity, the dispersion of clay powder for the standardized shear rate, the maximum permissible static shear stress in the minimum time; the maximum permissible coefficient of thixotropic structure formation (km), etc (Table 2).

Determination of the quality of clay powder suitable for the preparation and processing of drilling fluids was carried out in accordance with the industry standard GOST 28177-89 and API Specification 13A/ISO 13500:2010. Technical requirements for bentonite clay powders (including those based on bentonites, modifie Na_2CO_3). For activated bentonite, the Swelling index (SI) was determined according to the ASTM D5890 method (Figure 4) and the "Water absorption" indicator according to the GOST 28177-89 method (Table 3). When determining water absorption, Bulgarian bentonite clay powder, which is available in the laboratory and is used in the preparation of clay solutions by the Limited Liability Company "GEOSINTEZ ENGINEERING", was chosen as the standard. According to the requirements of the ASTM D5890 methodology, SI should be min. 27 ml. The bentonite sample from Benta Limited

Table 2. Properties of activated clay powder

Sample	Method of activation (modification)	Index of free swelling, $cm^3/2g$	Water absorption, time	Method of activation (modification)
1 horizon top	4,0% Na_2CO_3	11.0	5.0	8,0
1 horizon below	4,0% Na_2CO_3	12.5	5.0	9,0
2 horizon top	4,0% Na_2CO_3	8.5	3.0	11,0
2 horizon below	4,0% Na_2CO_3	9.2	3.0	10,0
3 horizon top	4,0% Na_2CO_3	10.0	4.0	10,0
3 horizon below	4,0% Na_2CO_3	11.0	4.0	10,0
1 horizon top	4,0% Na_2CO_3+3%MgO	12.0	3.0	10,0
1 horizon below	4,0% Na_2CO_3+3%MgO	12.5	3.0	11,0
2 horizon top	4,0% Na_2CO_3+3%MgO	8.0	3.0	9,0
2 horizon below	4,0% Na_2CO_3+3%MgO	9.0	4.0	10,0
3 horizon top	4,0% Na_2CO_3+3%MgO	10.5	4.0	10,0
3 horizon below	4,0% Na_2CO_3+3%MgO	11.5	4.0	10,0
Clay powder Bentonite (Bulgarian)		27,0	11.0	10.0

Table 3. Clay powder indicators

Sample	Swelling, units	Index of free swelling, $cm^3/2g$	Water supply claying, once	Mass fraction of moisture, %	Mass fraction of montmorillonite, %
Sample 1	2.8	4.0	1.5	7.74	42.59
Sample 2	4.5	5.0	1.7	11.10	44.44
Sample 3	3.4	6.0	1.6	10.00	42.59

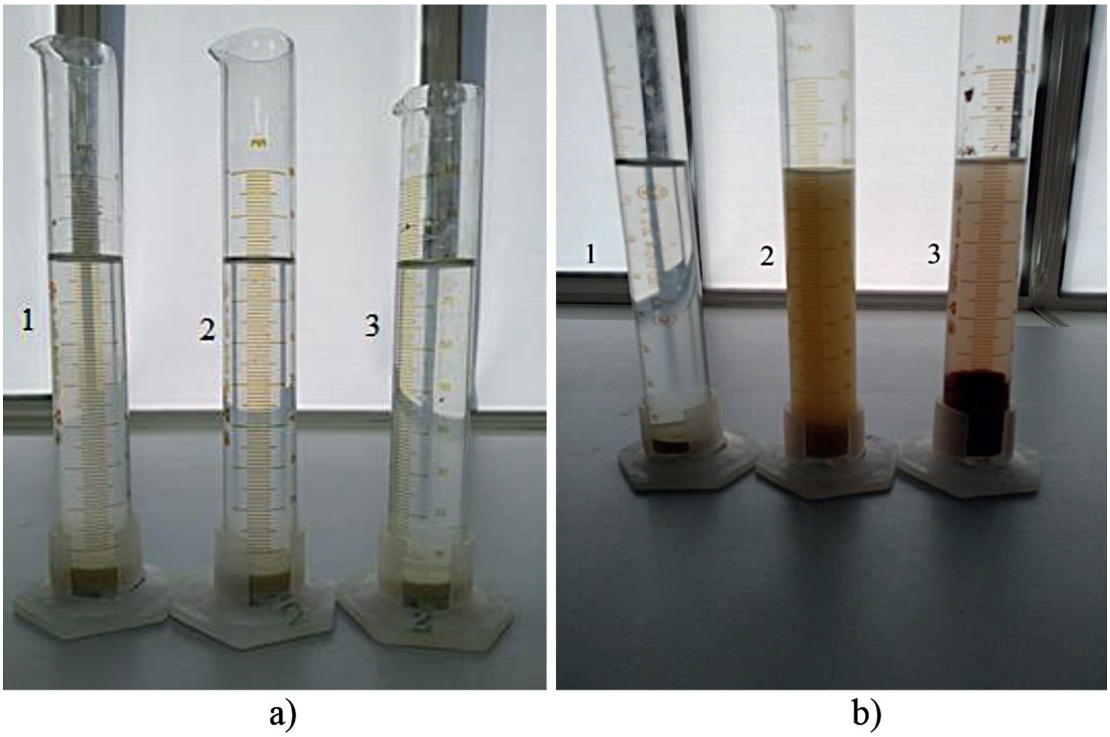

Figure 4. Swelling index of clay powder; a) clay powder not activated with soda ash from "Benta Utility Company" – 4 - 6 units: 1 – horizon 1 (sample 1); 2 – horizon (sample 2) 2; 3 – horizon 3 (sample 3); b) comparison of IS clay powder "Communal enterprise Benta" and Bulgarian: 1– clay powder " Communal enterprise Benta " is not activated with soda ash; 2– clay powder " Communal enterprise Benta " activated with soda ash; 3 – Bulgarian bentonite clay powder

Liability Company is a pure calcium form and requires treatment with soda ash.

The sodium form of bentonite has a "Swelling Index" value of about 24–36 ml/2g according to ASTM D5890-06, rarely higher. Calcium bentonite has a "Swelling Index" value of about 4.5–8 ml/2g.

After activation with soda, the IS indicator increased from 4.0–6.0 to 14.0 ml./2g. Comparing the IS of activated bentonite from "Bent" and Bulgarian bentonite clay powder, as well as the parameters of the clay suspension (Table 4) prepared on this clay powder, it is possible to assert the low quality of this raw material. Without treatment with soda and magnesium oxide, this clay powder cannot be used as a component of drilling mud.

Three clay samples were prepared to study the interaction of activated clay powder with water and to select the concentrations of chemical reagents for the preparation of test formulations of drilling fluids. In each experiment, the main technological properties were measured (density, conditional viscosity, filtration index, CH_3 after 1 and 10 minutes, rheological properties). Table 5 shows the results of the measurements.

The rheological properties of clayey solutions were determined based on rotational viscometry data on the OFITE 800 device. Data processing was performed using the Rheometry 2.0 program (Myslyuk, 2012; Myslyuk & Salyzhyn, 2007) in the class of rheologically stationary Shvedov–Bingham, Ostwald, Herschel–Bulkley, and Shulman–Kesson models.

As can be seen from the rheograms (Figure 5), the rheological profile of "Benta" clay powder in comparison with the reference Bulgarian clay powder is unstable and has half the shear stress. These phenomena are most likely related to the

Table 4. Study of the main indicators of the Benta clay suspension in comparison with the API 13A standard

Main properties	Activated clay powder «Utility enterprise of Bent»	Standard API 13A
Fann figures at 600 rpm for 22.5 grams/350 cm^3	5	At least 30
YP/PV	0.2	No more than 3,0
Filtration API 13A, ml/30 min	25	No more than 15
Mass fraction of moisture, %	7.7	10
The balance on the sieve 200 mesh, %	3.0	No more than 4,0
Plastic viscosity PV, mPa * c	2.5	-
Dynamic Shear Stress YP, lb/100 ft^2	0.5	-
Conditional viscosity, s (Marsh Funnel)	16	-
Montmorillonite content, %	43	-
pH indicator, unit	7.7	-
$CaCO_3$ content, kg/m^3	35	-
Sand content, %	1.3	-

Table 5. Results of experiments for clay solutions

The composition of the drilling mud	Properties of the solution					
	Density, kg/m^3	*T*, with VP5	*F*, cm^3/30 min	$SNZ_{1/10}$, dPa	Rheological properties of the most adequate model	pH
Sample 1 (Top) activated Na_2CO_3 4% + NaOH 0.1% + Praestol 0.05%, Water - the rest	1020	18	16.5	2.39/2.86	*Ostwald model* k = 0.976 Pa·c^n n = 0.500	10.0
Sample 2 (Bottom) activated Na_2CO_3 4% + NaOH 0.1% + Praestol 0.05%, Water - the rest	1020	16	17.5	1.91/2.15	*Ostwald model* k = 0.182 Pa ·c^n n = 0.475	10.0
Sample 3 (Top) activated Na_2CO_3 4% + NaOH 0.1% + Praestol 0.05% Water - the rest	1020	16	17	2.15/2.39	*Ostwald model* k = 0.06 Pa·c^n n = 0.602	10.0
Bulgarian clay powder + NaOH 0.1% + Praestol 0.05% Water - the rest	1050	32	8	9.56/19.2	*Herschel–Bulkley model* τ_o=1.73 Pa k = 0.17 Pa ·c^n n = 0.59	10.5

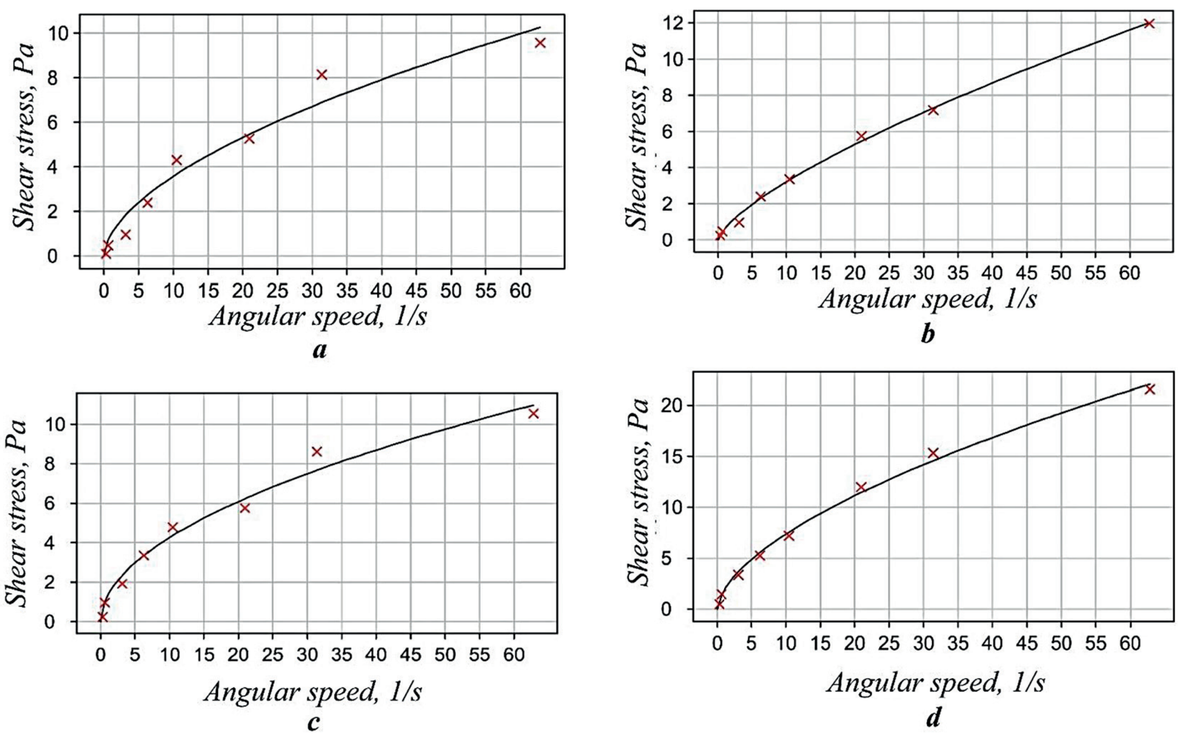

Figure 5. Rheological curves of drilling fluids: a) activated clay powder KP Benta sample 1 (Top); b) activated clay powder KP Benta sample 2 (Bottom); c) activated clay powder KP Benta sample 3 (Top); d) Bulgarian clay powder

Table 6. Formulation of humate-acrylo-potassium drilling fluid

Reagent	Content, kg/m³	Function
Bentonite clay loam KP Benta1 sample	70	Structure former
Polygamous	40	Regulator of filtration and conditional viscosity
Condensed sulphite alcohol bard	30	Conditional viscosity regulator
Calcined soda	4	pH regulator
Caustic soda	0.5	pH regulator
Carboxymethyl cellulose HV	3	Filter reducer
Carboxymethyl cellulose LV	4	Filter reducer
KCl	50	Clay inhibitor

presence of foreign impurities and the purity of the source material, which is high in Bulgarian bentonite. Therefore, clay powder "Benta" at the stage of purification from impurities requires more careful control of the types and sizes of extraneous materials.

In addition, in order to evaluate the impact of clay powder on the technological properties of a typical drilling mud, we decided to prepare in laboratory conditions a humate-acrylopotassium drilling mud based on clay powder of KP "Benta", sample 1 (horizon 1), which showed the highest swelling index (see Table 2). The recipe of the solution is given in Table 6, and its technological parameters are measured according to DSTU and ARI standards in Table 7.

From Table 7, we can draw a conclusion about the possibility of using activated clay powder as a component of typical drilling fluids, subject to careful laboratory control of technological parameters and timely chemical treatment of the solution.

CONCLUSIONS

The modification of clay materials makes it possible to use bentonites of degraded "primary"

Table 7. Technological properties of humate-acrylo-potassium solution

Properties of drilling fluid		DSTU	Units measurement	API	Units measurement
Density of the solution		1120	kg/m^3	1.12	g/cm^3
Conditional viscosity		43	s	150	Marsh. s
CH_3 (Gel)	10 s	dPa	dPa	1	lb/100ft^2
	10 min	dPa	dPa	2.5	lb/100ft^2
Effective viscosity (AV)		24.5	mPa·s	49	cP
Plastic viscosity (PV)		19	mPa·s	19	cP
DNZ (YP)		52.3	dPa	11	lb/100ft^2
Filtration		5	cm^3/30 min	6.5	mL/30 min
Crust thickness		1.5	mm	1.5	mm
Friction coefficient of the crust		0.0875	–	0.0875	–
Breakdown filtering (HTNR)		−	cm^3/30 min	12	ml/30 min
Sand content		−	% vol.	-	% by vol
Solution temperature		20	^{o}C	20	Deg C
pH of the solution		10.5	–	10.7	–
Rheological properties					
Rheological model		Ostwald			
A measure of consistency k, Pa·c^n		0.279			
Non-linearity index n		0.635			

quality as components of drilling fluids, which allows more rational use of natural resources. A condition for the effective use of such materials is preliminary laboratory research according to classical schemes and procedures. Therefore, the interaction of the academic and industrial sectors is the foundation for the development of new technologies for the processing of natural resources.

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