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THE KAZAKHSTAN CLAY FOR DRILLING MUDS

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ABSTRACT
This paper presents the results of studying the physical–chemical, physical–mechanical, structure–mechanical and technological properties of Kazakhstan bentonite clay of Taganskoye deposit.

KEYWORDS: bentonite, montmorillonite, Kazakhstan, deposits, mineralogical and granulometric composition, physical and chemical properties

1. INTRODUCTION

As it is known, the natural bentonites are the materials for drilling mud preparation on water basis. In the former Soviet Union countries the most various kinds of clays (alkaline and alkaline-earth bentonites, attapulgite, kaolinite, hydromicaceous and polymineral materials) have been applied in drilling muds preparation. Moreover, sometimes the drilling muds are prepared on the base of any clay available in the area of drilling works. The majority of these clays, except for alkaline and alkaline-earth bentonites and attapulgite, give the drilling muds which quality is very far from the world standards.

The basic indicator of the clay grade quality is a clay suspension yield, what is the amount of cubic meters clay suspension with the given viscosity and sand contents received from one ton of a clay (m^3/t).

According to the specification API 13A the clays giving a clay suspension yield not less than 16 m^3/t, are suitable for drilling muds. The alkaline bentonite clays from Wyoming deposit (USA) having a clay suspension yield about 20 m^3/t, Georgia (USA) attapulgite clays, the hectorite (lithium magnesium bentonite) deposit Hector (USA, California) with a clay suspension yield more than 25 m^3/t meet these parameters.

In the former Soviet Union countries, the alkaline bentonite of Sarigyukhskoye (Armenia), Askanskoye, Oglanlinskoye (Turkmenistan), Dash-Salakhlinskoye (Azerbaijan) and Cherkassk (Ukraine) deposits are referred to be clays of high quality. These clays create well structured suspensions; a clay suspension yield from such clays achieves 20 m^3/t. Attapulgite clays of Borshchevskoye deposit should be mentioned here. The clay suspension yield is equal to 16 m^3/t.

Among 11 Russian bentonite deposits, only Gerpegezhskoye deposit (Kabardin-Balkarskaya Republic) contains alkaline bentonite; on the other deposits, alkaline-earth bentonites are explored in Khakassiya and in Primorye territories with rather increased contents of alkaline cations.

In Kazakhstan, such large bentonite deposits as Monrakskoye or Taganskoye (East Kazakhstan), Kysyl-Zharskoye (Western Kazakhstan), Kyngrakskoye, Darbazinskoye, Chardarinskoye (Southern Kazakhstan) are known. The large bentonite stocks are concentrated in the Taldy-Kurgan area (Ildersaiskoye, Andreevskoye, Dzerjinskoye, Gerasimovskoye deposits).

Bentonites of Mangushlak peninsula (Western Kazakhstan) have a favorable geographical situation (they are situated nearby to places of drilling oil-gas wells), favorable mine-technical conditions, significant capacities and good technological parameters.

Bentonite massive capacity of various deposits makes up to 100 meters. However, it is necessary to note, that the majority of Kazakhstan bentonites are refered to alkaline-earth bentonites.

As is known, alkaline-earth calcium bentonites bind water more strongly in comparison with alkaline bentonites, they are peptized very badly, forming strong rigid structure in water. Moreover, such bentonites are required much more than natrium ones.

To get bentonite products with alkaline bentonite properties, in world practice, the alkaline-earth bentonites are subjected to modification by clay processing with various reagents. The best qualities of bentonite clay powders, for example, are received by introducing calcinating soda and acryl polymers.

The effect of modification is shown in increasing viscosity of clay suspension at the expense of additional clay dispersion, in increasing of the connected water volume, dispersion medium of viscosity and gel-formation strengthening. The calcinating soda additives are necessary for bentonite transmitting into natrium form, which is better dispersed in water. Due to it an active surface of bentonite and the amount of adsorbed polymer are increased, qualitatively changing character of interaction between contacting particles. Such processing allows increasing of the clay suspension yield from 10 up to 18 – 20 m^3/t and more.

The optimum clay-powder moisture is one of the important conditions of clay interaction with chemical reagents, which allow the increase of the clay suspension yield of a drilling mud several times.

In the present work, physical-chemical, physical-mechanical, technological and other parameters of Taganskoye bentonite clays (East Kazakhstan) are defined by the various methods.

2. EXPERIMENTAL WORKS

2.1. BENTONITE SAMPLE PREPARATION

The clay samples from various lithologic horizons (horizon 12, horizon 13, horizon 14, horizon 15), and also of geological-industrial bench (GIB) from horizons 12 + 13 + 14 - GIB“G” and horizon 15-GIB“D” from Taganskoye quarry (East Kazakhstan) were used.

The natural bentonites are used for the preparation of the drilling muds. Cleared from sand particles, mica and crushed in a mill they were used for complex study by different methods. The fraction of 0.25 mm is selected after sifting for making the analyses.

2.2. MINERALOGICAL AND GRANULOMETRIC COMPOSITION

For receiving the clay suspension of good quality, used at drilling works, the mineralogical clay composition and the amount of thick-dispersed particles, i.e. of colloid fractions, play the main role. By its activity, colloid fraction is basically obliged to a very small size of particles in ratio to their mass. Due to the large specific surface the particles behavior of this fraction is mainly determined by electrostatic charges on their surfaces that promote development of attraction forces and pushing away between separate particles. As is known, the clays are active colloids (Grim, 1956). It is explained both by the form (the smallest crystal plates or packages of such plates) and by molecular structure of particles what results in formation of strong negative charges on their basal surfaces and positive charges on edges. The interaction between these opposite charges at low speeds of flow strongly influences drilling muds clay viscosity and it is the reason of convertible structure forming when the mud rests.

As is known, the bentonites have the greatest activity of clays. From the literary data, the contents of thick-dispersed particles with the sizes 1.0 – 5.0 μm in alkaline bentonites of good quality make up more than 90 % (Litayeva and Raybchenko, 1992).

To study the mineral structure of investigated materials, the X-ray diffraction analysis, which was carried out by the automatic diffractometer of the Mineralogical Institute of Technical University in Freiberg Mining Academy, was used. The sample consisting of a mixture of bentonites from horizons 12, 13 and 14 (GIB“G”) was subjected to the analysis.

Granulometric composition of clays was determined according to the techniques of State Committee USSR on Standards. The method is based on defining the quantitative distribution of particles according to the size by a method of dry sifting on a sieve with the following weight determination of the received size classis and calculation of their output in percentages of total weight taken for sieve analysis.

2.3. PHYSICAL PROPERTIES

These properties include the determination of the moisture of bentonite samples, swelling, weight losses at heating up to 800 °C, number of plasticity, and structure-adsorbing properties, including total volume of pores and volume of connected water.

As it was already mentioned, the important condition of clay interaction with chemical reagents is clay powder of the optimal moisture, giving the increase of a clay suspension yield at the increased moisture.

The research of swelling processes of clays with various crystal structure has shown that montmorillonite clays differ with the greatest swelling ability (Ovcharenko, 1961). The montmorillonite swelling is accompanied by two phenomena: by introducing of water layers between lattice planes of clay mineral and by capillary absorption water inside a clay crystal. Thus, interpackage distance is increased from 0.96 up to 2.84 nm, depending on the amount of absorbed water (Bradley, Clark and Grim, 1937).

The nature of clay swelling is still insufficiently investigated and serves as an object for various hypotheses. It is the most probable, as Ovcharenko has found (Ovcharenko, 1961), the base of this phenomenon is the action of adsorbing, osmotic and capillary forces determining a pressure with the help of water kept in the structure system. The basic component of clay swelling is water absorbed on an internal surface of mineral. Osmotic forces are shown more or less capillary forces. The action of capillary forces is limited by the period of material sample impregnation, including dispersion processes of clay particles under action of a medium. At significant permeability of samples (the absence of semi-permeable membrane), the influence of osmotic forces also has the limited character. The adsorbed forces play the main role in interpackage swelling.

The solvate (hydrate) layers, which thickness between two plates for separate hard bodies is experimentally defined, are formed because of the not- compensated molecular forces on a surface of a hard phase. It is known, that the properties of a liquid in a solvate layer, considerably differ from its properties in a mud volume. Its viscosity, resistance to shift, elasticity, and other properties considerably rise. These layers, despite of their small size, essentially change a nature of surfaces interaction.

Bradley, Clark and Grim's (1937) careful researches, devoted to montmorillonite hydration have shown, that swelling of a lattice during hydration is the same. A series of 4 apparently various and dispersed hydrates, having cell height of 12.4, 15.4, 18.4 and 21.4 Å was established. Near every area, where a given hydrate is stable, the sequence of reflection orders (00l) corresponds only to it. In intermediate areas two groups of reflections (00l) simultaneously appear, one is identified with the following higher hydrate, another – with next, the lower hydrate.

Bradley, Clark and Grim (1937) in their researches used oriented units, in which plane joins were almost parallel. Hofmann and Hausdorf (1942), using oriented units, have concluded that montmorillonite hydration takes place at formation of water alternating monomolecular layers. Further, it was proved, that the change of inter-planar distances according to the contents of water in a direction of c-axis goes continuously, but it is not monotonous. Apparently, it is the result of the average effect caused by a lattice containing various numbers of water layers in various places. Thus, apparent continuous change of an c-axis size is the result of the disordered changes of discrete hydration following one after another.

Processes occurring at heating of clay minerals play the great role. Water, which can be kept in clay minerals at rather low temperatures, leaves them at heating approximately between 100 – 150 °C. A nature of low temperature water and the factors revealing its features, have the great importance. They essentially determine such properties of clay materials, as are plasticity, viscosity, density etc., resulting in industrial importance of clay materials.

Water lost in clay minerals at low temperatures, depending on its relation to mineral components and a temperature of clay materials, can be subdivided in: 1) water in pores, on a surface and on edges of separate particles of minerals and 2) inter-plane water between layers of an elementary cell of a clay mineral (water causing montmorillonite swelling) (Grim, 1956). Water removals of the first type usually need little energy, and drying at the temperature, which is a little bit higher than usual room temperature, is already enough for its almost complete removal. Water removals of the second type need a certain amount of energy. Temperature not below 100 °C is necessary for complete evaporation of internal water in montmorillonite clays. Under temperature increasing the removal speed of interplane water is also increased.

Dehydration causes significant changes in the structure of clay minerals. These changes can be connected not only to dehydration processes. Such features of minerals, as are the size of grains, decrystallization degree, and nature of adsorbed ions influence the results of dehydration.

The plasticity of a clay material is characterized as property allowing it to be deformed under influence of a pressure (of external force) without entire breakage, i.e. without formation of cracks and in general without complete separation of particles of the given material, and to keep the acquired form after a pressure removal. Clays receive properties of body plasticity only when they are mixed with the known amount of water, and also with some other liquids, but not with all of them. With wetting the dry clay by water and with increasing the amount of water the clay reaches a working condition, i.e. gets ability to change the form without breakage. This working condition and ability to keep the form are characteristic for a very narrow limit of moisture. The introduction of superfluous amount of water gives the large mobility to a mass; it does not keep the form, and gets ability to flow as a liquid.

There exist many techniques defining the value of plasticity. The most widespread method of plasticity limit definition and the number of plasticity are described in Atterberg's works (Atterberg, 1911; Atterberg, 1912), and also in Litayeva and Raybchenko (1992); Zemaytchenskiy (1935).

2.4. CHEMICAL PROPERTIES

Correct definition of isomorphous replacements, nature, finding a charge place in a lattice and hence cation changeability capacity and activity of samples depends on the realization of the chemical analysis.

The components of samples chemical structure are defined by well-known methods according to the specification API.

Silicon dioxide is determined by a gravimetric method. For this purpose a sample is decomposed by melting with soda, the alloy is dissolved in a hydrochlorid acid and the received solution is evaporated until drying. Thus the basic amount of silicon acids is dehydrated and transforms in a sediment, and silicic acid remained as ash in the solution is coagulated by gelatine. The determination is finished by a gravimetric method.

The determination of the titanium dioxide extract is based on formation of the complex titanium compound with hydrogen peroxide in yellow color. Measurement of its coloring intensity in the sulphuric environment is taken in area of optical transmission 400 – 450 nm at using the dark blue filter.

Trivalent iron is determined by a complexon-metric method in a hydrochlorid solution received after silicic acid separation. Iron is titrated by EDTA in an acid solution (pH = 1.0 - 1.5) with sulphosalicylic acid as the indicator forming with iron (III) the colored complex compound.

Table 1 Bentonite granulometric composition (%)

Bentonite lithologic horizons, GIB	Sandy particles (above 0.1 mm)	Dusty particles (below 0.1 mm)	Clay particles (fraction below 60 µm)	Clay particles (fraction below 15 µm)	Clay particles (fraction below 1.5 µm)	Sum
horizon 12	6	6.5	3.6	6.6	77.3	100
horizon 13	5.3	6.7	4.2	7.9	75.9	100
horizon 14	4.3	4	3.7	8.4	79.6	100
GIB“G”	4.68	4.96	3.86	8.17	78.33	100
horizon 15 GIB“D”	6.5	6.7	5.42	8.68	72.7	100

Aluminium oxide is determined by a complexonmetric method in solutions where iron is titrated. The method is based on the ability of aluminium to form complexes (at pH = 5 – 5.5) at taking the precise volume of EDTA to the solution and heating. Excess of EDTA is titrated by solution of zinc salt.

Calcium oxide is determined by a complexonmetric method in aliquot part of filtrate after the silicic acid separation. Fluorexon (a dry mixture with potassium chloride) is used as the indicator. It is also possible to use methyltimol blue or thymolftalexon in a mixture with methylrot. The pH value at titrating by complexon should be 13 – 13.5.

Magnesium oxide is determined in aliquot part of filtrate after the hydroxide sediment separation together with calcium (barium and strontium) and manganese by titrating with the indicator chromogen black ET-00 at pH = 9.5. To warn oxidation of manganese (II) to manganese (IV) in alkaline environment by air oxygen, hydrochloride hydroxylamine (or ascorbic acid) is previously added into the solution and then all other reagents just before titrating of each solution. The magnesium content is calculated from the difference between the results of the determination of calcium, magnesium and manganese sums and the sum of complexonmetric results of calcium determination (barium and strontium) and the photocolorimetric of determination of manganese.

The determination of natrium and potassium is based on the measurement of atomic radiation intensity of these elements in the acetylene-air flame by an atomic absorption method after acid decomposition of a sample portion.

Gravimetric method of sulphur determination consists of transmitting of all sulphur, contained in the examined material, (sulphate, sulphide and sulphur of organic compounds) into soluble alkaline sulphate by fusion and then of its isolation as barium sulphate and weighing of the incinerated rest. Sulphide sulphur is defined as a difference between the total sulphur content and sulphate sulphur content.

The water content in clay samples is determined as the loss of mass after drying at the temperature 105 – 110 °C up to constant weight.

The loss of mass at the incineration (LI), expressed in percentages, is caused by water volatilization, carbon dioxide or organic substances release. Incineration was carried out at high temperature (1050 °C) up to constant weight.

Cation exchangeability of the examined bentonite was determined by replacement of exchanged cations by processing of dissolved samples with neutral salts of the appropriate metals at achieving the balance establishment. The equilibrium condition was considered to be established at reaching the initial pH value of salt. At defining the cation exchange capacity the presence of gypsum, carbonates and water-soluble salts was always considered.

3. CLAY AS A MATERIAL FOR THE PREPARATION OF DRILLING MUDS

Bentonite sample GIB“G” for a drilling mud was estimated according to the standard of the API 13A and Oil Companies Materials Association (OCMA) and the comparison was made with a standard Wyoming bentonite.

The measurements were carried out using FANN 35 SA Viscometer and FANN Filter Press of American production.

4. RESULTS AND DISCUSSIONS

The investigated bentonite sample is represented as alkaline earth montmorillonite (91 - 93 %) with 7 – 9 % of quartz.

The granulometric data of the analyses are given in Table 1. As it can be shown from the table, the main clay mass is made of fractions below 15 µm that define their high dispersion, being characteristic for bentonite, with montmorillonite basic mineral component.

The amount of large particles of sandy fraction, depending on the sample type, should be 6 up to 10 %. The excessive contents of sand result in abrasive wear of the hydraulic equipment and drilling assembly, reduction of mechanical speed of drilling.

The amount of sandy particles in the investigated bentonite clay samples (see Table 1) varies from 4.3 up to 6.5 % that corresponds to the requirements of a sandy fraction.

In Table 2 the bentonite clay physical properties of the quarry are given. Comparing swelling value of

Table 2 Physical-mechanical and physical-chemical properties of bentonite clays in the quarry

Indicators, measurement units	**horizon 12**	**horizon 13**	**horizon 14**	**GIB “G”**	**GIB “D”**
Volume of mass, t/m^3	1.7	1.7	1.7	1.7	1.8
Natural moisture, %	21	23	25	24	25
Air-dry bentonite swelling, number of times	6.7	7.5	8.8	8.3	7.6
Bentonite swelling value (at t 0°C up to 200°C)	6.4	7.2	8.5	8	7.1
Mass loss at heating up to 100 °C	59.94	60.98	64.14	62.96	
Mass loss at heating up to 200 °C	70.11	72.65	74.48	73.72	
Mass loss at heating up to 300 °C	78.91	83.47	83.07	83.02	
Mass loss at heating up to 400 °C	89.56	96.24	94.29	94.8	
Mass loss at heating up to 500 °C	94.53	97.6	96.31	96.65	
Mass loss at heating up to 600 °C	96.5	98.57	98.62	98.52	
Mass loss at heating up to 700 °C	97.81	98.89	99.69	99.3	
Mass loss at heating up to 800 °C	100	100	100	100	

Table 3 Bentonite structure-adsorbed properties

Indicators, measurement units	**horizon 12**	**horizon 13**	**horizon 14**	**GIB“G”**	**GIB“D”**
Total pores volume, cm^3/g	0.407	0.389	0.405	0.4	0.475
Volume of connected water, cm^3/g	0.295	0.279	0.285	0.286	0.289
Number of plasticity	50	49	51	51	48

air-dry bentonite samples and samples dried at temperature up to 200 °C, it is clear that these values differ insignificantly, i.e. show enough steady hydration properties. The plenty of researchers have shown that bentonite clay swelling during the hydration is typical. It means, that bentonite hydration takes place at formation of alternating monomolecular water layers.

Besides, concerning montmorillonite hydration stability, it is important to note the following. If the dried mineral is placed in water, it can adsorb very fast up to the certain stage, and then mass becomes to be paste-like. Water is not more adsorbed, if mass is not stirred intensively. The ability to adsorption in this point stops, and the balance is kept at very high moisture contents. The similar property appears, by the way, in case of Wyoming bentonite. Practically it is desirable to use this mineral as a waterproof material.

It may be shown from the Table 2 that the significant loss of water is observed at low temperatures (up to 200 °C). The amount of this water being mainly present as interlayer water, located between silicate layers, depends on the nature of absorbed ions and preliminary processing of a sample (character of drying, relative moisture etc.). Bentonite dehydration finishes at 800 °C.

The volume of pores, ensuring availability and transport of reacting molecules, plays the essential role at clay swelling. The comparison of the bentonite structural characteristics of various lithologic horizons shows, that the total volume of pores and the volume of connected water within the limits of various horizons have approximately identical values. These data are well coordinated with bentonite swelling processes.

Clay plasticity is defined by a method based on finding the difference value of clay mass moisture corresponding to the bottom border of fluidity and pasting border. According to results received in the present work (Table 3), studied clay samples are highly plastic, the number of plasticity is ~ 50, that is in agreement with the literary data (Litayeva and Raybchenko, 1992).

In the Table 4 the data on chemical composition of the investigated bentonite samples are submitted.

The sample in item GIB“G” taken for technological researches has lower contents of silicon than API-bentonite. The aluminium contents exceed the iron contents three times, it is supposed that iron

Table 4 Chemical composition of the bentonite clay

Component content %	horizon 12	horizon 13	horizon 14	GIB “G”	GIB “D”	API bentonite
SiO_2	52.54	56.06	55.48	55.5	59.56	62.16
TiO_2	0.2	0.63	0.3	0.4	0.48	0.31
Al_2O_3	21.11	16.11	19.38	18.4	14.92	19.31
Fe_2O_3	2.6	8.0	4.4	5.48	4.27	2.60
CaO	2.06	1.96	1.98	1.97	2.12	2.57
MgO	2.82	2.63	2.18	2.35	2.26	0.30
Na_2O	1.43	1.36	1.24	1.3	0.17	2.32
K_2O	0.58	0.45	0.51	0.49	0.27	0.65
SO_3	0.32	0.17	0.18	0.18	0.11	0.22
H_2O	11.34	7.15	8.49	8.17	9.47	–
LI (Mass loss at incineration)	12.37	10.97	11.31	11.24	–	9.0

Table 5 Cation-exchange capacities of the examined bentonites

Bentonite samples	Cation-exchange capacities, meq/100 grams					Coefficient of alkaline Na^++ $K^+/Ca^{2+}+Mg^{2+}$	Module Ca^{2+}/Na^+
	Na^+	K^+	Ca^{2+}	Mg^{2+}	Sum		
horizon 12	40.6	0.3	25.8	21.3	88.0	0.88	0.63
horizon 13	35.5	0.3	22.3	17.7	75.8	0.89	0.63
horizon 14	25.9	0.2	42.9	27.8	96.8	0.37	1.6
GIB“G”	29.5	0.2	35.6	24.3	89.6	0.5	1.21
GIB“D”	30.5	0.5	23.4	21.9	76.3	0.68	0.77

Table 6 Bentonite technological parameters

Clay sample	600 rpm	300 rpm	200 rpm	100 rpm	6 rpm	3 rpm	Plastic Bingam viscosity mPa s	Apparent viscosity mPa s	Water loss
GIB“G”	65	64	64	63	61	60	1	64	15
«Tixoton»	30	26	24	23	23	22.5	4	26	19
API 13A	30								15

was replaced by aluminium in octahedral coordination. This phenomenon is known as “isomorphous replacement”. As to alkaline exchange of natrium and potassium cations, their contents are lower than in case of API-bentonite. Calcium is the main exchangeable cation instead of natrium. The contents of alkaline earth magnesium slightly exceed calcium contents. They characterize the examined bentonite as alkaline earth bentonite of the calcium-magnesium form.

The data of Table 5 confirm that the investigated bentonite clay samples have high values of the cation exchange capacities (from 75.8 up to 96.8 meq/100 grams). The cation exchange capacity of Wyoming bentonite is 76.65 meq/100 grams of clay (Merabishvili, 1979).

The technological examinations were carried out for the Kazakhstan bentonite clay GIB“G” and German activated bentonite “Tixoton”. They are compared with API 13A specification (Table 6).

The results in Table 6 indicated that the suspension properties of Kazakhstan bentonite successfully met the API 13A specification with such parameters as are viscosimeter dial reading at 600 rpm and water loss.

Table 7 Technological parameters of bentonite clays

Clay sample	Gel Strength 10 s, Pa	Gel Strength 10 min, Pa	Tixotropy, Pa	Density, g/cm^3	pH	Filter cake, mm
GIB"G"	28.8	29.04	0.24	1.03	8.37	2.1
«Tixoton»	9.6	12	2.4	1.0	10.6	1.7

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