Features of the chemical composition and colloidal-chemical properties of local clays of Uzbekistan and their comparison with other clays

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Abstract. This article examines the study of the chemical composition and colloidal-chemical properties of local clays of Uzbekistan and their comparison with other clays. As well as the features of the chemical composition and colloidal - chemical properties of local palygorskite clays. The distinctive features of the chemical composition and properties of local palygorskite clays of the Navai deposit (Uzbekistan) in comparison with the Cherkassky palygorskite (Ukraine) have been studied. Palygorskite clays are considered a valuable raw material for the production of special types of drilling fluids used in drilling deep salt-bearing formations.

1. Introduction

The literature contains information about the process of mechanical and chemical dispersion of polymineral clays and their influence on the technological characteristics of the resulting drilling fluids.

Of all the types of drill fluids, clayey drill fluids are used most often and in large volumes.

Back in 1929, a patent for Kross and Hart was obtained on a clayey brown solution, where bentonite clay is used in a mixture with magnesium oxide.

Palygorskite clays are considered a valuable raw material for producing special types of drilling fluids used for drilling high-depth salt-bearing formations.

It should be noted that not all types of palygorskite clays allow obtaining high-quality drilling fluids, which is directly related to their chemical composition. The presence of even a small amount of salts and other substances can degrade the quality of the clay suspension created. Therefore, initially new types of clays are subjected to chemical analysis [1].

We have established the chemical compositions of the palygorskites considered in this paper from new deposits in Uzbekistan.

Analyses of clays was carried out in the laboratory of non-metallic materials of the Ministry of Geology of Uzbekistan, where the quantitative composition of silicon dioxide (SiO\textsubscript{2}) was established by coagulation using gelatin [2], Sesqui-oxides (Fe\textsubscript{2}O\textsubscript{3} and Al\textsubscript{2}O\textsubscript{3}) – complexmetrically method [3], titanium oxide (TiO\textsubscript{2}) - colorimetric method acidically and magnesium (CaO and MgO) - complex metrically methods [4], the iron oxide (FeO) – titration [3], potassium oxide (K\textsubscript{2}O) and sodium (Na\textsubscript{2}O) – by flame photometry [4], the manganese oxide (MnO) - colorimetric method [3].

Previously, [4] noted that it is advisable to use suspensions of palygorskite clays from the Cherkassk deposit (Ukraine) for drilling salt-bearing rocks. In Uzbekistan, oil and gas drilling is carried out in complicated conditions, often in salt-bearing formations. Import of palygorskite from abroad requires
significant material and transportation costs, which negatively affects the cost of drilling fluids. Therefore, the search for local palygorskite clays and their use in drilling operations is certainly relevant and economically rational. For this purpose, we have studied some types of local palygorskite clays. Table 1 shows the chemical composition of the local palygorskites considered in this paper. At the same time, Cherkassy palygorskite purchased from Ukraine [5] was used as a reference material for comparison.

The Navbakhor clay deposit is located in the Navbakhor district of Navoi region and was discovered in 1998. This deposit is unique and consists simultaneously of three natural varieties of clays: alkaline-alkaline-earth bentonites, as well as carbonate palygorskites, which significantly expands the scope of their application for drilling operations.

2. Methods

From the data in table 1 it can be seen that the local palygorskite clays of the Tulsokh (Ferghana region) and Navbakhor (Navoi region) deposits are close in chemical composition to the well-known in the CIS countries-Cherkassy palygorskite, which is widely used for drilling operations [6].

Table 1. Chemical composition of selected local palygorskites promising for producing clay drilling fluids.

| Clay deposit                          | SiO₂ | TiO₂ | Al₂O₃ | Fe₂O₃ | MgO | CaO | Na₂O | K₂O | P₂O₅ | FeO | P.P.P | %P |
|--------------------------------------|------|------|-------|-------|-----|-----|------|-----|------|-----|-------|-----|
| Cherkassky palygorskite (Ukraine, for comparison) | 54.70 | 0.36 | 11.52 | 6.36 | 5.75 | 0.74 | 0.25 | 1.2 | 0.11 | 9.74 | 99.63 |
| Tulsokh palygorskite (Ferghana region) | 50.9 | -    | 9.45  | 3.8  | 9.25 | 12.3 | 0.01 | 1.4 | 0.71 | 10.2 | 99.82 |
| Navbakhor carbonate palygorskite (Navoi region) | 46.79 | -    | 8.63  | -    | 2.74 | 10.08 | -    | 1.6 | 1.9  | 3.41 | 24.33 | 99.75 |

However, the efficiency of using bentonites and palygorskites from different deposits in the production of clay powders for drilling fluids can be completely different, due to the variability of the composition and characteristics of the raw material used.

At the present time, in the process of drilling, the greatest interest is represented by three groups of clay minerals: bentonite (montmorillonite, beidellite, nontronite, saponite, etc.), caolinic (kaolinite, glularite and hydrolite). Montmorillonite and other bentonite minerals possess the best qualities from the point of view of preparation of boring mortar. So, from 1 ton of bentonite clay it is possible to obtain about 15 m³ of high-quality clay solution, then as from clay of medium quality it is 4-8 m³ and from low-grade clay [7].

Two aluminosilicate compounds are known: orthoclase \(K_2Al_2Si_6O_{18}\) and albite \(Na_2Al_2Si_6O_{18}\) / Most of the clays are a product of natural decomposition (weathering process) of these miner

\[K_2Al_2Si_6O_{18} + H_2O + CO_2 = K_2CO_3 + H_2Al_2Si_6O_{22} + 2SiO_2\text{-montmorillonite},\text{ or depending on the conditions: } K_2Al_2Si_6O_{18} + H_2O + CO_2 = K_2CO_3 + H_2Al_2Si_6O_{22} + 4SiO_2 - caolinite.\]

It is customary to write down the formulas of clay materials in the following form: \(Al_2O_3 \cdot 4SiO_2 \cdot 2H_2O - \text{montmorillonite}, Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O - \text{caolinite}.\]
Today more than 40 aluminosilicates are known, which are included in the composition of natural clay. The most important and widely distributed groups of minerals, which differ from each other in the chemical composition and the structure of the crystal lattice, are montmorillonite, caolinitic, hydromicaceous [6].

To determine their suitability for obtaining multifunctional drilling fluids, a special study of their mineralogical and chemical compositions, as well as their physicochemical properties, is required. It should be noted that Uzbekistan has significant reserves of bentonite, palygorskite and hydro-mica clays that are not used as raw materials due to: insufficient knowledge of their compositions and physical and chemical properties, as well as the lack of scientifically based technology and recipes for obtaining thermo-and salt-resistant drilling fluids [8].

Naturally, in order to identify effective local palygorskite for the preparation of salt-resistant drilling fluids, it is necessary to study their colloidal-chemical and technological properties. At the same time, information about their chemical and mineralogical compositions allows you to select the necessary chemical reagent for processing.

As noted earlier, there is very little information in the literature about the colloidal-chemical properties of local clays, especially palygorskite clays. From the colloidal-chemical properties of clays, we studied the dispersed composition, porosity, swelling, heat of wetting with water, ion exchange capacity, etc. [7,8].

In the table, 2 shows the results of a dispersed analysis of local palygorskites, which are compared with similar characteristics of known analogues.

**Table 2.** Indicators of the dispersed composition volume of total and transition pores and specific surface area of local palygorskite clays.

| Name of clay                      | Fraction content, % | Pore volume, sm³/g | Specific surface area, 10³ m²/kg |
|----------------------------------|---------------------|--------------------|----------------------------------|
|                                  | Less than 0.01 mm   | Less than 0.1 mm   | Less than 1.0 mm                 |                          |
| Cherkassy palygorskite (Ukraine, for comparison) | 65.1                | 31.3               | 3.6                              | 0.18 0.14 395           |
| Tulsox palygorskite (Ferghana region)  | 71.3                | 26                 | 2.7                              | 0.21 0.12 373           |
| Navbahor carbonate palygorskite (Navoi region)  | 76.5                | 21.4               | 2.1                              | 0.15 0.15 386           |

3. Results and discussion

Sedimentation analysis performed by the Sabanin-Robinson method showed that all the samples of the studied palygorskites have a granulometric composition (table 2) refer to fine raw materials, represented mainly by particles ranging in size from 1.0 to 10 microns [9].

The porosity of palygorskite clays determines their moisture capacity, swelling capacity, and structural and rheological properties. In practice, the volumes of common and transition pores with effective radii ranging from 2·10⁻⁹ to 20·10⁻⁸ m are more often studied [10]. The mercury porometry method makes it possible to study macro-, micro-, and transition pores of bentonites and palygorskites at various pressures (from 500 to 1000 MPa).

The porosity, in particular, of the transition pores of the selected palygorskites was analyzed by the standard method on a model - 200 mercury porometer manufactured by Carlo Erba Strumontazion (Italy). At the same time, the duration of the experiments was 30 minutes, the maximum mercury pressure was 20x10⁵ KPa and the mass of the studied clays was 0.977 g. table 2 shows the results of studying the total and transition pores of samples of selected palygorskites.
From the data in Table. 2 shows that the Navbakhor carbonate palygorskite in terms of transition pore volume (0.15 sm$^3$/g) and Tulsokhsky in terms of total pore volume (0.21 sm$^3$/g) are superior to the well-known Cherkassy Palygorskite (Ukraine), which has the following parameters (0.14 sm$^3$/g and 0.18 sm$^3$/g), respectively. Consequently, local palygorskites can be used to produce clay drilling fluids for special purposes based on their general porosity and the content of transition pores.

The specific surface area of clays determines the depth of their dispersion. We have studied the specific surface area of palygorskites by the standard method [11]. The results obtained are presented in table 2. As can be seen from the data in table 2, local palygorskites are not inferior to their foreign counterparts in terms of their specific surface area.

Determining the amount of palygorskite swelling is very important, especially at the stages of well drilling, since the drilled rock, being peptized, can lead to an undesirable increase in the viscosity of the drilling mud. Therefore, reducing the amount of swelling of the used clays is one of the main tasks of obtaining efficient drilling fluids.

In the literature, there are many methods for assessing the degree of clay swelling, which depend on taking into account factors affecting this process. Of course, the amount of bound water depends on the type of clay, its mineralogical and chemical composition, porosity, specific surface area, and others.

The maximum swelling of clays $H$ (sm$^3$/g) was calculated by the formula (4):

$$H = \frac{h \cdot S}{F}$$  \hspace{1cm} (1)

Where: $h$ - is the swelling height, sm; $S$ - is the area of the ring, sm$^2$; $F$ - is the sample weight, g.

We have studied the maximum water uptake by local palygorskites under normal conditions. The results obtained are presented in table 3.

| Name of clay                  | $h$, sm$^3$/g | $\tau$, h | $\omega_{sp}$·10$^{-3}$, sm$^3$/g·h | $P_m$, g·s/sm$^2$ | Heat of wetting (Q), cal/g |
|-------------------------------|--------------|----------|-------------------------------------|-------------------|----------------------|
| Tulsokh palygorskite          | 1.213        | 650      | 1.674                               | 121               | 17.3                 |
| Navbakhor palygorskite        | 1.235        | 675      | 1.689                               | 127               | 19.5                 |
| (carbonate)                   |              |          |                                     |                   |                      |

Where: $h$ - is the degree of swelling, $\tau$ - is the swelling period, $\omega_{sp}$ - is the average swelling rate, $P_m$ - is the ultimate shear stress.

Table 3 shows that local palygorskites are close to each other in terms of the intensity of swelling, but they differ in the degree of swelling.

As expected, palygorskites swell to a lesser extent than betonies. The data obtained above on the specific surfaces $S$, allowed us to calculate the heat of water wetting of local palygorskites $Q$ under the condition of the total surface energy $q = 116$ Erg/sm$^2$, [6]:

$$Q = S \cdot q$$  \hspace{1cm} (2)

In the case of measuring $S$ (specific surface area) in units of m$^2$/g, formula (2) has the following form (4):

$$S = \frac{Q}{q} = \frac{Q \cdot 4.186 \cdot 10^7}{116}$$  \hspace{1cm} (3)

Table 3 shows the wetting heat data for selected local palygorskites.

Using the heat of wetting of clays, it is possible to calculate the amount of water $A$ bound by them according to the formula (4):

$$A = Q \cdot d(\%)$$  \hspace{1cm} (4)

Where: $Q$ – heat of wetting of clay, cal/h; $d$ is the density of bound water ($d = 1.3$ g /sm$^3$) (4).
The amount of bound water makes it possible to judge the degree of hydrophilicity of clays. For the studied local palygorskites, this indicator varies from 8 to 16 %.

4. Conclusion
Thus, based on the study of the chemical composition and colloidal-chemical properties of local palygorskites, it can be concluded that they are not inferior in their studied parameters to the well-known Cherkassy palygorskite imported from Ukraine. They can be effectively used in the production of drilling fluids for special purposes, instead of imported ones.

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