


## STUDY OF COLLOIDAL-CHEMICAL PROPERTIES OF CLAY HYDRODISPERSIONS OBTAINED FROM THE SOUTHERN REGION OF KAZAKHSTAN

ASSANOV AMANKAIT   
MAMESHOVA SAYAT ALISHERIEVNA 

Taraz Regional University named after M. Kh. Dulati, Professor, Honorary Professor of the Russian Academy of Natural Sciences, Academician of the Regional Academy of Management, Taraz, Kazakhstan, e-mail:asanovamankait@mail.ru,

Taraz Regional University named after M. Kh. Dulati, senior lecture, Associate Professor of the Regional Academy of Management, Advisor to the Russian Academy of Natural Sciences, Taraz, Kazakhstan, e-mail:saya8383@mail.ru

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### KEYWORDS

*clay, bentonite, hydrodispersion, filtration, clarification.*

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### ABSTRACT

*A study of the colloidal and chemical properties of hydrodispersed clay from the Southern region of the Republic of Kazakhstan revealed variations in sediment volume, optical density, and filtration process depending on the clay sample's type, origin, and settling time. These differences were attributed to factors such as chemical composition, particle size, and the interaction between solid-phase particles and the dispersing medium. Additionally, the study comprehensively examined various characteristics of the clay samples, including zeta potential, colloidity, electrical conductivity, salt content, and pH.*

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## Introduction

Clay hydrodispersions possess significant colloidal and chemical properties that contribute to their diverse applications across various industries and agriculture. Notably, these properties enable the production of stable clay systems exhibiting unique rheological behaviors (Luckham & Rossi, 1999), (Murray, 1999), (Moraes и др., 2017).

The widespread availability and diverse properties of clay minerals have established them as valuable resources across numerous industries. This study aims to investigate the colloidal and chemical properties of hydrodispersions prepared from clays extracted from Southern Kazakhstan (Liu и др., 2021), (Murray, 2006).

This work investigates the colloidal chemical properties of hydrodispersions composed of clay minerals sourced from Southern Kazakhstan. These clays offer both ample reserves and convenient access, and exhibit variations in chemical composition, particle size, and hydration ability.

## Methodology

Natural bentonite clays from the Moldagash (Turkestan, Sozak district), Urangai (Turkestan, Sozak district), Keles (Turkestan, Saryagash region), and Kyzylorda (Kyzylorda oblast) deposits were used as research objects. An FTIR spectrometer (Cary 660 Agilent, USA) was employed to determine the functional groups in the samples. Electrophoretic mobility was measured using a Zetasizer Nano device (Malvern, UK). Optical densities were determined with a PE-5300VI spectrophotometer (EKROSCHEM, St. Petersburg, Russia). Specific electrical

conductivity and salt content were measured with a Conductivity meter-salinometer MARK-603 (Nizhny Novgorod, Russia), and the pH of the clay hydrodispersions was determined with an ITAN pH meter/ionomer (Tomsk, Russia). Additionally, the colloidal chemical properties of selected clay hydrodispersion samples were examined.

## Research results and discussion

Clays typically have three distinct surfaces: interlayers, edges, and outer surfaces of the clay mineral layers. The interlayer and outer surfaces are susceptible to changes during ion exchange and adsorption processes (Luckham & Rossi, 1999). Clay minerals exhibit a small net negative surface charge due to isomorphic substitution. Furthermore, the edges of clay mineral particles can develop charges depending on the pH of the suspension, resulting from the rupture of primary bonds such as Si-O and Al-O (De Paiva и др., 2008).

Bentonite is a layered silicate adsorbent of aluminum, consisting mainly of montmorillonite. It is a type of sedimentary rock consisting mainly of clay, with a typical 2:1 layered structure (smectites) and high concentrations of Na<sup>+</sup>, Ca<sup>2+</sup> ions located between the layers. Octahedral and tetrahedral sheets are arranged in such a way that the vertices of the tetrahedra in each silica sheet and one of the hydroxyl layers in

the octahedral sheet make up one layer (Muhammad & Siddiqua, 2022), (Borah и др., 2022). Montmorillonites are unique smectite clays that are widespread in the natural environment. Montmorillonite is a rather delicate layered silicate. It consists of lamellar particles with an average diameter of about 1  $\mu\text{m}$  and is chemically represented as  $(\text{Na,Ca})_{0.33}(\text{Al,Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot n\text{H}_2\text{O}$ , which is formed by changing volcanic ash (Park et al., 2016), and has three layers: one octahedral layer of aluminum in the center, surrounded by two tetrahedral layers of silica. The interactions between the sheets usually occur through groups  $-\text{OH}$  in the octahedral layer and the vertices of the tetrahedral layer.

Clay is primarily composed of silica, alumina, and water, with trace amounts of iron, alkali metals, and alkaline earth metals (Kumari & Mohan, 2021).

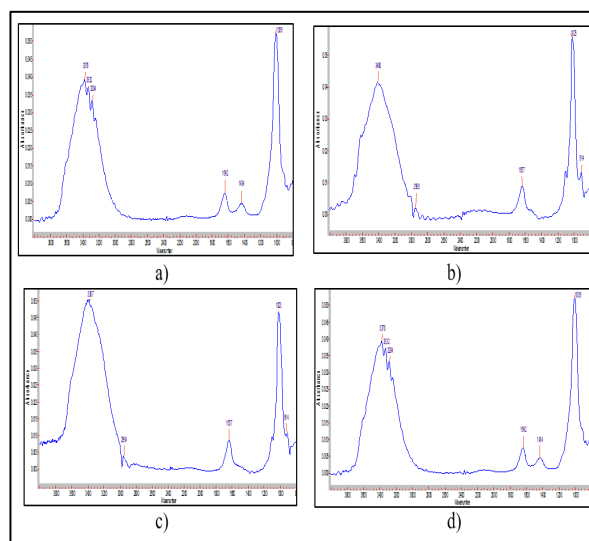
The clay samples were analyzed by Fourier-transform infrared spectroscopy (FT-IR) on the Agilent Cary 660 spectrometer within the  $4000 - 800 \text{ cm}^{-1}$  range. The FT-IR analysis revealed characteristic absorption bands, indicating the presence of specific vibrational modes within the clay structure (Zhirong и др., 2011).

**Fig.1** – FT-IR for natural bentonite clays

a) Keles, b) Kyzylorda, c) Urangay, d) Moldyagash

The results of the experimental data showed that the main absorption bands in the infrared spectrum (FT-IR spectrum) of the studied clay sample (Fig.1) relate to valence vibrations. These fluctuations are characteristic of the bonds of silicon with oxygen and hydrogen with oxygen. The

pronounced band with a frequency of



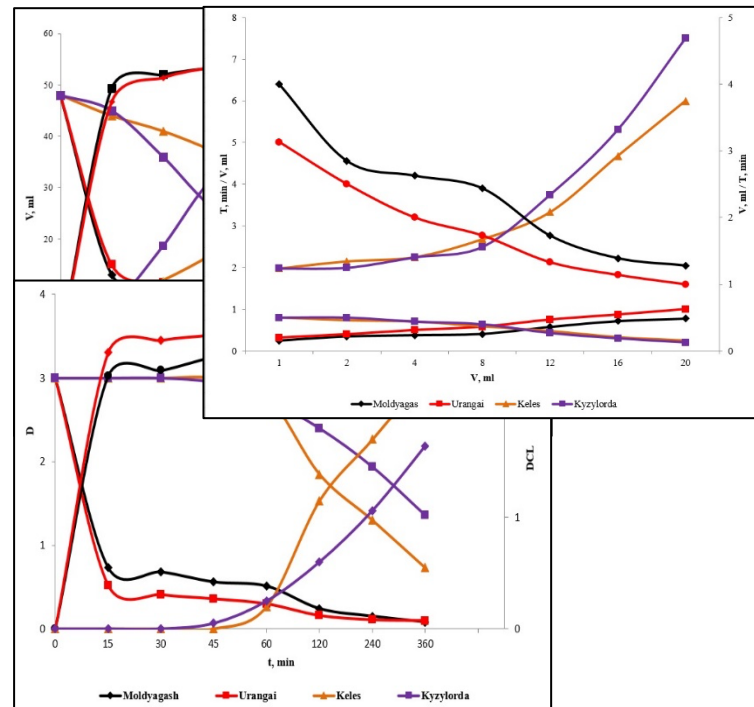
$1630 \text{ cm}^{-1}$  is due to the absorption of deformation vibrations of hydroxyl groups. Deformation vibrations are vibrations in which atoms or groups of atoms inside a molecule or crystal move relative to each other, but do not break the bonds between them. The appearance of absorption bands in the region of  $1000-1100 \text{ cm}^{-1}$  corresponds to the valence vibrations of the Si-O group. In the clay of the Moldagash deposit, Si-O is in the region of  $1009 \text{ cm}^{-1}$ , in the samples of Kyzylorda, Kolyanskaya and Urangai, it is observed in the regions of  $1023-1027 \text{ cm}^{-1}$ .

The hydrodispersion behavior of these clay minerals, particularly their colloidal properties, has been understudied (Asanov & Mameshova, 2021). To address this gap in knowledge, we investigated the changes in sediment volume ( $V, \text{ml}$ ), liquid height above sediment ( $h, \text{ml}$ ) (Fig. 2a), and optical density ( $D$ ), representing the degree of liquid clarification ( $D_{lc}$ ) (Fig. 2b), over time ( $t, \text{min}$ ) for clay hydrodispersions (CHD) from various locations. Our data reveal significant differences in these parameters, dependent on the

specific clay mineral and its origin. Notably, the rate of change in sediment volume and optical density, as well as the corresponding changes in liquid height and clarification, vary considerably between samples. Kyzylorda and Keles samples exhibit the highest sediment volume and lowest liquid height, while Urangai and Moldyagash samples demonstrate the opposite trend. Further research is necessary to elucidate the underlying mechanisms responsible for these observed variations.

Along with this, a higher value of optical density ( $D$ ) and a lower degree of clarification ( $D_{clc}$ ) were found in the Kyzylorda and Keles hydrodispersions, respectively. In this case, the value of optical density ( $D$ ) not only depends on the type of clay being studied, but also on the territory and location of the collected sample and the settling time. This is evidenced by a comparison of the value of optical density ( $D$ ), the volume of sediment ( $V$ , ml) which were determined after 60 minutes of settling, the value of optical density ( $D$ ) of the hydrodispersion of clay (HDC) from Kyzylorda, Keles. The same features can be observed when studying the change in sediment volume ( $V$ , ml), optical density ( $D$ ) of liquid over the sediment of clay samples from the Moldyagash, Urangai deposits and other clay samples (Fig. 1 a, b).

**Fig.2** - Changes in sediment volume ( $V$ , ml), height of liquid above sediment ( $h$ , ml) (a), optical density ( $D$ ), degree of liquid clarification ( $D_{clc}$ ) (b) on the surface of sediment of clay hydrodispersions from time ( $t$ , min.) This is especially clearly seen when comparing the rate of separation of the solid phase of hydrodispersion



over time. In this case, the highest rate of separation and formation of sediment, as well as clarification of the liquid above the sediments, occurs in the Moldyagash and Urangai samples. And the slowest process of separation of the solid phase from the liquid medium occurs in clay samples from the Kyzylorda and Keles deposits.

The identified differences are mainly related to the particle size of the solid phase and the interacting ability of the dispersed medium. Since, as the dispersion of the solid phase increases, the surface area of the particles increases, which leads to an intensification of the process of contact of the dispersed medium with particles of the solid phase, which leads to an improvement in hydrophilicity (Асанов и др., 2023).

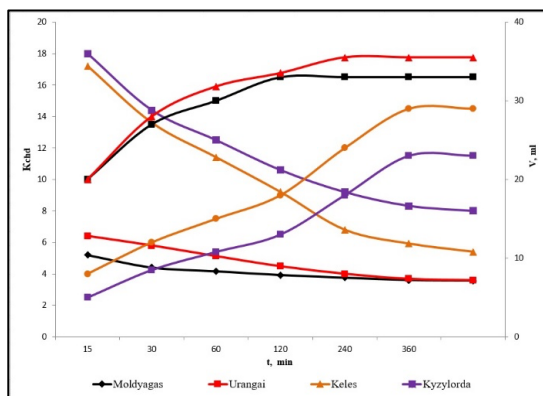
This leads to a decrease in sediment volume ( $V$ , ml) and a slowdown in the solid phase separation process. Consequently, the height of the clarified liquid above the sediment decreases, while the optical density ( $D$ ) of the liquid above the sediment

remains sufficiently high at a given settling time (Fig. 2 a, b). Comparative data on the change in  $V$  of the CHD samples after 4, 6, and 24 hours of settling time clearly demonstrate this phenomenon.

Samples of clay hydrodispersion with identical solid phase content exhibited varying rates of sediment volume decrease over time. Generally, sediment volume decreased gradually with increasing settling time, but the rate of decrease differed between samples. This pattern was consistent across all analyzed clay hydrodispersion samples. The most evident differences were observed when comparing the changes in the volume coefficient of precipitation ( $K_s$ ) of samples with identical solid phase content over time (Fig. 3a). This decrease in sediment volume can be attributed to the release of liquid bound to the surface of the solid phase with varying degrees of strength. Notably, the release of this liquid is also influenced by the type, nature, and surface properties of the solid phase during clay hydrodispersion.

**Fig.3** - Change in sediment volume coefficient ( $K_{chd}$ ), filtration process ( $V$ , ml) over time (a)

Coefficient ( $K = T_{min} / V_{ml}$ ,  $K = V_{ml} / T_{min}$ ) depending on the volume of liquid ( $V$ , ml) clay hydrodispersion (b)



This is evidenced by the kinetics of the change in the solid phase coefficient ( $K_{vc}$ ) over time. A decrease in the volume of sediment over time leads not only to a thinning of the liquid part on the interphase surface and thickening, bringing the particles of the solid phase closer together, as a result of which the filtration rate decreases over time. A comparison of the decrease in filtration rate over time clearly shows the numerical amount of filtrate, which differs not only in time but also in type and nature, as well as the place where the clay samples under study were obtained (Fig. 2 a). For example, for samples obtained from the Moldyagash and Urangai deposits, the filtration process generally ends within 60 minutes. Unlike the Moldyagash and Urangai samples, the filtration process in the Keles and Kyzylorda samples continues for up to 6 hours. These differences are observed not only in the filtration time, but also in the amount of filtered liquid (Fig. 3 a). This can also be detected by determining the ratio  $T_{min} / V_{ml}$  and  $V_{ml} / T_{min}$  (Fig. 3 b). Analysis of the numerical value of the coefficient ( $K = T_{min} / V_{ml}$ ,  $K = V_{ml} / T_{min}$ ) the ratio  $T_{min} / V_{ml}$  shows that As the filtration time increases, to release the same amount of liquid, the required time gradually increases. When determining the ratio  $V_{ml} / T_{min}$ , it indicates that as the time of the filtration process increases, the numerical value, on the contrary, decreases. This is due to the fact that at the initial stage of filtration, the resulting sediment consists mainly of larger particles containing less adsorbed liquid and a thin adsorption layer, which has better permeability of the liquid medium through the sediment layer. In addition, at this stage, the thickness of



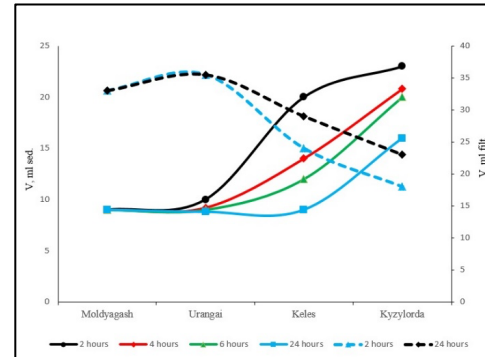
the adsorption layer is also smaller. As the filtration process grows, the height of the sediment layer above the filter gradually increases. Along with this, the pores existing between large sediment particles are filled with smaller particles and a large adsorption layer. As a result, to pass the same volume of liquid, the required filtration time gradually increases, and with the same filtration time, the volume of filtered liquid decreases (Fig. 3 b). As a result, the volume of filtrate after 24 hours has a different amount depending on the type of clay, which is slightly different in chemical composition, dispersity, and hydrophilicity. This is evidenced by the fact that to achieve a constant volume of CHD sediment for a clay sample from the Moldyagash deposit, 2 hours is enough.

For clay samples from the Urangai deposit, the change in the volume of the CHD sediment, even after 2 hours, slowly continues up to 24 hours.

Fig.4 - Variation of solid phase precipitation and filtrates of clay hydrodispersions (CHD) with time

Along with this, for clay samples from the Keles deposit, the volume of sediment changes noticeably during settling time up to 24 hours. In contrast to these samples, for clays from the Kyzylorda deposit, the volume of sediment after 4 hours is twice as large, while the height of the sediment volume is almost twice as high. The detected difference persists even after 24 hours of settling. The same differences were also found when determining the volume of the amount of liquid filtered depending on time. That is, to achieve the same amount of filtrate volume, 2 hours are generally sufficient for samples of Moldyagash and Urangai clays, and 4 hours for Keles. For the Kyzylorda clay sample,

the filtration process is very slow and very difficult. Since, when assessing



the filtered liquid, it is clear that the maximum amount for Kyzylorda is reached in 4 hours, and as the filtration process continues, the volume of the filtered liquid remains constant even for 24 hours. The observed volume of sediment and the filtration process once again indicates that these studied clay samples have unequal hydrophilicity. This is indicated by the amount of filtrate ( $V$ , ml ft) as well as the volume of sediment ( $V$ , ml os) of the studied clay samples (Fig.4). The electrokinetic potential (zeta potential) of the studied samples was measured to determine the surface energy of clay particles in water, its values are shown in

Table 1. The table shows that the samples have a negative charge. This indicates that water molecules (cations) cannot fully compensate for the negative charge of a clay particle during the formation of a colloidal adsorption layer (Zhirong и др., 2011). It should be noted that the measured values of the zeta potential describe the energy state on the surface of the adsorbed (fixed) colloidal layer. Therefore, the higher the value of the zeta potential, the stronger the diffusion (mobile) layer formed by the colloid.

In addition, the colloidity of the natural clay samples was determined. As a result, it was confirmed that the highest index among the studied samples was observed in Kyzylorda, followed by Keless clay, and in Molagash and Urangay it was significantly lower (Table 1).

The determination of some physicochemical characteristics of CHD also showed that there are noticeable differences in the numerical values of specific electrical conductivity ( $\chi_{sp}$ ), salt content and pH of the filtrates (Table 1). From the above data it is clear that the filtrates of the Urangai and Moldyagash clay samples have the highest value of specific electrical conductivity ( $\chi_{sp}$ ), the lowest value of specific electrical conductivity ( $\chi_{sp}$ ) corresponds to the Kyzylorda sample. The same pattern of patterns is observed in the numerical values of salt content. These patterns, to a certain extent, correspond to changes in the stability of clay hydrodispersion and the ability to interact with the aquatic environment

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