

## Article

# Composite Hydration Process of Clay Minerals Simulating Mineral Clay Components and Influence Mechanism of Cations

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**Abstract:** Clay minerals are an important part of the mud shale reservoir, and their type of content has a great impact on the hydration of the formation. The hydration of clay minerals causes a decrease in drilling fluid performance, an increase in pore pressure, and a decrease in rock strength, leading to wellbore wall collapse. Therefore, it is important to study the influence of clay mineral hydration on well-wall stability. In this paper, we analyze the hydration process of clay minerals qualitatively and quantitatively by simulating the mineral clay fraction and the effect of the change in cations on their hydration and clarify the difference in the hydration of different clay minerals. The results show the following: (1) montmorillonite has the most obvious hydration and swelling effect, while the hydration of illite is mainly based on hydration and dispersion, which easily produce exfoliations and fall off in the stratum; kaolinite has poor hydration performance, while chlorite shows certain hydration but low hydration degree. (2) Cations have a certain inhibitory effect on the hydration of clay minerals, and the degree of hydration inhibition is different for different types. (3) Different clay minerals also differ in the form of state after water exposure, as montmorillonite shows swelling, while illite has no swelling, but its dispersion is stronger.

**Keywords:** clay minerals; mud shale hydration; hydration; bentonite



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## 1. Introduction

As the economy continues to grow, the demand for oil and gas continues to become greater, but due to the increasing number of problems encountered in exploration and development, the drilling environment is becoming more and more complex, and problems, such as wellbore wall stability, are still not well resolved. Additionally, as the application of water-based drilling fluids becomes more and more widespread, it is widely believed that water-based drilling fluids are more environmentally friendly than oil-based drilling fluids, but that their use promotes the hydration and swelling of clay minerals, causing wellbore wall instability [1–3]. Therefore, the study of the influence of clay minerals on wellbore wall stability is being explored and deepened.

Clay minerals are an important part of soils and rocks and have a wide range of applications in various projects. Clay minerals carry a negative charge between layers, so to balance the charge, when water is present, they tend to exchange with positively charged cations in water, a process known as clay hydration. After a period of hydration, isolated microcracks in local areas of the formation are communicated to form macroscopic cracks through the whole rock, providing a channel for water to enter the rock, further aggravating the hydration of organic-rich shale, reducing the cohesion between the rock particles, and leading to a decrease in the overall strength of the rock. In addition, clay minerals play a role in the hydraulic fracturing stage to communicate the fractures and form an effective fracture network, which is beneficial to increasing the production of shale gas from a single well. Therefore, the study of the inhibitory effect of cations on

the hydration of different clay minerals is also of great significance to solve the problem of wellbore wall destabilization during drilling and the reasonable stewing period after hydraulic fracturing [4–6].

Clay minerals are widely present in the formation and their different hydration properties will affect the wellbore and drilling fluid performance, which will have a great impact on oil and gas extraction and construction [7,8]. These formations exhibit strong water absorption due to clay minerals, resulting in structural damage to the formation, causing wellbore wall instability and collapse during drilling. This leads to softening of the rock formation and reduction in rock strength, which affects the engineering construction efficiency and economic benefits. Therefore, a reasonable assessment of the hydration process of clay minerals and the study of its hydration mechanism can provide a theoretical basis for engineering [9,10]. According to relevant statistics, among these formations, mud shale accounts for about 75% of instability, and nearly 90% of wellbore wall instability occurs in shale formations [11,12].

In recent years, many scholars have primarily analyzed clay minerals by focusing on the following aspects: concentrating on the hydration experiments on a specific block of strata to study its macro-, micro-, and other characteristics, such as its mineral components, microstructural characteristics, mechanical characteristics, etc. [13,14]; using some experimental instruments, such as XRD, FTIR, scanning electron microscopes, microscopes, etc., to analyze its microstructural characteristics or its changes in hydration characteristics [15–18]. Some scholars have also carried out molecular simulations of clay minerals and studied the hydration swelling and interlayer structure of clay, the relationship between clay swelling process and relative humidity, the diffusion process of interlayer water and ions in clay, etc., such as Monte Carlo (MC) simulations and molecular dynamics (MD) simulations, or by using AI techniques to predict and simulate the dynamic linear swelling of minerals [19–23]. Studies have also been conducted to verify the causes of hydration mechanism of clay minerals or to explore the experimental methods [22,24] or the analysis and characterization of a single clay mineral or a single reservoir [25]. The study of hydration inhibition mechanism on the surface of clay minerals has proposed new hydration principles and established corresponding evaluation methods [19,26], while some scholars have also studied the hydration inhibition mechanism on the surface of clay minerals and proposed new hydration principles and established corresponding evaluation methods. Some scholars also analyzed the differences in the microstructural properties of different clay minerals themselves, revealing that the mechanical properties of clay minerals are affected by their location, type, density, and other factors, such as the relationship between the internal characteristics of the structure and mechanical properties and the type of interlayer cations [27,28]. As such, they studied the influencing factors on the hydration and swelling of clay minerals, such as the influence of pressure and temperature on their hydration [29–31], or the interaction of their hydration with the surrounding rock as well as the mud properties [32–37]. In drilling fluid research, different additives have been added to drilling or completion fluids to inhibit mud shale hydration and optimize its performance, such as the addition of surfactants or environmentally friendly shale swell inhibitors [38–40].

In the study of microstructures, scholars have used different methods to study the expansion mechanism of clay minerals in the early days. For example, using low-angle X-ray diffraction to study the swelling characteristics of montmorillonite in water, these studies have carried out certain quantitative analyses in the microscopic aspect [41–43]. Most of the studies on clay minerals' hydration swelling crystal layer spacing provide the test results after a long time of soaking, and most of them focus on sodium montmorillonite hydration swelling. In contrast, the main clay minerals in mud shale are illite, ilmenite, chlorite, and little or no montmorillonite, and the ilmenite can be regarded as a mixture of montmorillonite and illite in a certain ratio [44,45]. It can be seen that the study of the hydration and hydration mechanism of clay minerals at the macroscopic level, especially for different clay minerals after different composite components, is still of great significance

for subsequent research in mineralogy and molecular dynamics. In this study, not only were hydration experiments on different clay minerals, namely montmorillonite, illite, kaolinite, and chlorite, conducted, including the changes in hydration swelling morphology, hydration dispersion morphology, and the strength of cationic inhibition of hydration, but hydration experiments of different proportions of illite and montmorillonite were also conducted to simulate the different mineral compositions in the stratum more intuitively. To simulate the different mineral compositions in the formation, the hydration experiments of the composite components were carried out, including the changes in hydration state and quantitative analysis [4]. Therefore, in this paper, based on the existing research results, aiming at the hydration mechanism of different clay mineral fabrics, a more intuitive hydration analysis experiment was carried out on clay minerals, and quantitative analysis was carried out in terms of appearance and hydration degree.

## 2. Materials and Instruments

### 2.1. Experimental Materials

The study was mainly carried out using analytical pure clay minerals and experimental samples, and the experimental samples used for the experiments in the paper are shown in Table 1.

**Table 1.** List of experimental materials.

Material Name	Material Grade	Manufacturers
NaCl	Analytical purity	China Jingzhou Jiahua Technology Co., Ltd., Jingzhou, China
CaCl <sub>2</sub>	Analytical purity	China Jingzhou Jiahua Technology Co., Ltd., Jingzhou, China
KCl	Analytical purity	China Jingzhou Jiahua Technology Co., Ltd., Jingzhou, China
Montmorillonite	Analytical purity	Shuolong Mineral Processing Plant, Lingshou, China
Illite	Analytical purity	Shuolong Mineral Processing Plant, Lingshou, China
Kaolinite	Analytical purity	Shuolong Mineral Processing Plant, Lingshou, China
Chlorite	Analytical purity	Shuolong Mineral Processing Plant, Lingshou, China
Sodium bentonite	Analytical purity	Shuolong Mineral Processing Plant, Lingshou, China
Distilled water	Analytical purity	Shuolong Mineral Processing Plant, Lingshou, China

### 2.2. Experimental Instruments

The experiments were carried out mainly using pressed mud cakes, and experiments, such as soaking and CST, were carried out using the main experimental apparatus as shown in Table 2 in order to obtain and support the experimental conclusions.

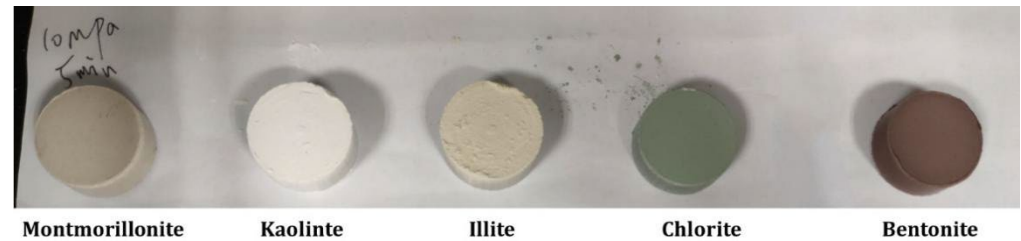
**Table 2.** List of experimental instruments.

Instrument Name	Model	Manufacturers
Electronic scale	FA	Qingdao Jiaonan Analytical Instrument Factory, Qingdao, China
Liquid pressure machine	YLJ600	Qingdao Haitongda Special Instrument Co., Qingdao, China
Constant speed stirrer	GJS-B12K	Qingdao Paradigma Petroleum Machinery Manufacturing Co., Qingdao, China
CST capillary absorption time tester	Fann440	Fann Instrument Company, Houston, TX, USA

In addition to the apparatus shown in Table 2, vernier calipers, Petri dishes, medicine spoons, measuring cylinders, etc., were also used.

### 3. Experimental Methods

- (1) Preparation of mud cake. We selected montmorillonite, illite, kaolinite, chlorite, and bentonite samples, weighed 10 g of each into the press container, applied 10 MPa pressure to the samples, held the pressure for 5 min to press them into mud cakes, and then used vernier calipers to record their initial diameter and height. The prepared mud cake is shown in Figure 1.



**Figure 1.** Photo of the prepared mud cakes.

- (2) Hydration swelling test. The pressed mud cake was placed in a measuring cylinder and immersed in water at room temperature under static conditions. We observed the experimental phenomenon and recorded the expansion height of the cake at different times with vernier calipers.
- (3) Hydration and dispersion experiment. ① The pressed mud cakes were put into petri dishes, then poured into distilled water and soaked at room temperature under static conditions. ② We observed the phenomenon, and vernier calipers were used to record the dispersion of the collapsed diameter of mud cake after different soaking times. The measured dispersion diameter values are the maximum diameter.
- (4) Hydration and dispersion experiments of different components. ① We placed the mud cakes into the Petri dishes with water, and soaked them under the condition of standing at room temperature. ② We observed the phenomenon and recorded the mud cake dispersion collapse diameter with vernier calipers. The dispersion of the collapsed diameter of the cake was measured at different soaking times. The measured dispersion diameter value has two values, in that the inner diameter of the mud cake is the diameter of the dispersion collapse part in the middle of the mud cake in water, and the outer diameter of the mud cake is the maximum diameter of the overall dispersion of the mud cake. Thus, the difference between the inner diameter and the outer diameter of the mud cake is the difference between the values of the outer diameter and the inner diameter, and a larger value indicates stronger dispersion of the mud cake.
- (5) Hydration experiments of different cation solutions. ① We used distilled water to prepare a 10% concentration of NaCl, CaCl<sub>2</sub>, and KCl solution. ② The pressed mud cake was put into the Petri dish, then poured into different solutions, soaked at room temperature under static conditions after we had observed the phenomenon and used vernier calipers to measure the height of the expansion of the mud cake at different soaking times and the diameter of mud cake dispersion collapse. The measured values of dispersion diameter are the maximum diameter.
- (6) A CST test. In this experiment, the effect of different metal ion concentrations and types on CST was measured to evaluate its dispersibility. This index describes the dispersion ability of mud, which can be used to evaluate the ability of mud to inhibit dispersion, the anti-swelling ability of drill fluid, the ability of drill fluid to inhibit hydration and dispersion, and to optimize the formulation of working fluid into the well, such as dosage and ratio, type of treatment agent, etc. It is also a new method to analyze and evaluate the classification of shale. Given that the hydration properties

of bentonite and montmorillonite are very similar, the effect of different metal ions on their dispersion performance was further investigated using sodium-based bentonite, and the base slurry was formulated to test its capillary absorption time (CST). The smaller the CST, the better the inhibition of montmorillonite dispersion and, vice versa, the worse the inhibition of its dewatering performance. The experimental steps are as follows:

Base slurry: 100 mL distilled water + 10% bentonite; with 5 groups of base slurry, add +3% KCl (NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, AlCl<sub>3</sub>); with 5 groups of base slurry, add +9% KCl (NaCl, CaCl<sub>2</sub>, MgCl<sub>2</sub>, AlCl<sub>3</sub>) solution, respectively. The configured solutions were stirred at high speed for 20 min with a constant speed stirrer in three gears according to the standard procedure of API RP 13B and aged for 16 h at room temperature (24 ± 3) °C. The experimental apparatus was assembled according to the device diagram. After the mud was stirred sufficiently, 5 mL of the solution was quickly taken with a dropper and immediately added to the circular casing, the CST tester was turned on. The timing started when the wet circle diffused to the first electrode, the timing was terminated after penetrating to the second electrode, and the time shown on the CST meter in this matter was the CST of the mud.

## 4. Results and Discussion

### 4.1. Trend of Hydration and Swelling of Clay Minerals

Since different clay minerals exhibit different states of hydration dispersion and swelling, the different states of clay minerals after exposure to water were experimentally analyzed and investigated. The swelling of montmorillonite, illite, chlorite, kaolinite, and sodium bentonite was tested indoors.

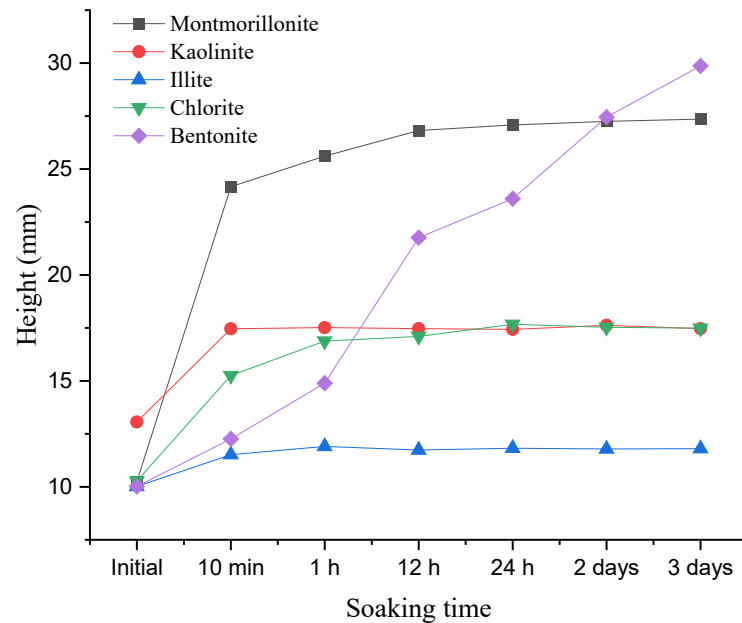
Clay mineral crystals are mainly composed of water-bearing layered silica-aluminate facets with amorphous silicates, and the unit crystal layer has a negative charge on its surface, due to which its crystal layer adsorbs hydrated cations and forms a hydration film on the surface [1,46]. The hydration properties of the clay minerals differ due to their different types. Montmorillonite interlayer cations together with some water molecules constitute hydrated cations, and cations can be exchanged with each other in different media, so it has high cation exchangeability, and its high specific surface area can reach 800 m<sup>2</sup>/g. Exchangeable cations affect its swelling degree, and it belongs to the swelling class of clay minerals, which is the most injurious water-sensitive clay mineral in the reservoir.

In this experiment, the changes in the swelling degree of montmorillonite, illite, chlorite, kaolinite, and sodium-based bentonite were tested after immersion in water.

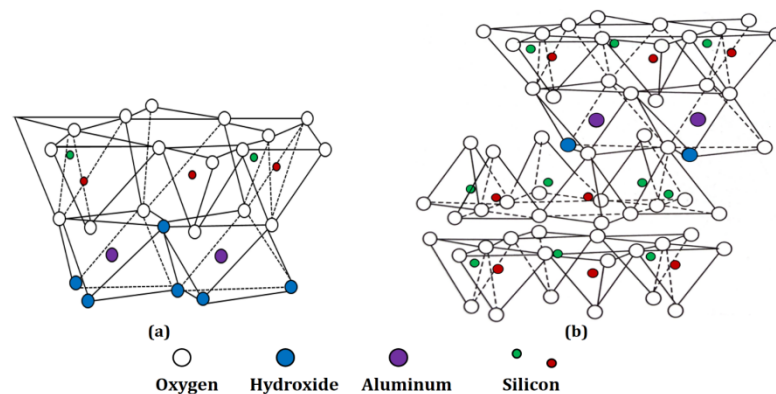
The variation curve of the swelling height of each clay mineral in water is shown in Figure 2. From the experimental data, due to the adsorption of water molecules on the surface of clay minerals, the mud cakes all underwent different degrees of swelling. The degree of swelling in order of magnitude is as follows: bentonite > montmorillonite > chlorite > kaolinite > illite. After soaking in water, montmorillonite swelled the most and was on average twice as swollen as the other clay minerals. Chlorite swelled less, kaolinite and illite did not swell easily as a result of hydration, and the swelling degree of all four clay minerals stabilized after 12 h immersion. The swelling height of bentonite increased with time, and its water absorption and swelling rate were slow, but its swelling height growth data in 3 days showed a continuous growth trend, the swelling degree by hydration exceeded that of montmorillonite after 2 days of immersion, and the final swelling degree was greater than that of the four clay minerals at 1 to 2 times higher. The final state of bentonite is highly dependent on the type of clay chosen, but this result reflects the true trend.

This is mainly because montmorillonite is a clay mineral with a 2:1 type of three-layer structure. Its structure is shown in Figure 3b; this structure is mainly composed of two silica–oxygen tetrahedra sandwiched by one aluminum–oxygen octahedron as a unitary structural layer. This structure is characterized by the partial replacement of cations (Al<sup>3+</sup>, Si<sup>4+</sup>) by other cations (Mg<sup>2+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, etc.). The replacement of high valence cations by

low valence ions, such as  $\text{Al}^{3+}$  by  $\text{Mg}^{2+}$ ,  $\text{Mg}^{2+}$  by  $\text{Na}^+$ , etc., occurs mainly in the octahedron. For example, the d001 of montmorillonite is  $(9.7\sim 12.2) \times 10^{-1}$  nm, while the d of kaolinite is about  $(7.15\sim 7.2) \times 10^{-1}$  nm. In addition, the two adjacent crystalline layers of this structure are adjacent to each other with an oxygen atom and oxygen atom face, and there is no hydrogen bonding between the layers, but only van der Waals force, thus, when the cation carries a large number of water molecules and other polar molecules into the crystal layer, it will exhibit obvious swelling characteristics.



**Figure 2.** Height curve of hydration swelling of different clay minerals.



**Figure 3.** Schematic of the lamellar structure of different types of clays: (a) 1:1 type laminated clay minerals. (b) 2:1 type laminated clay minerals.

Illite structure is similar to montmorillonite and also belongs to the 2:1 type of three-layer structured clay minerals. Lattice substitution mainly occurs in the silica–oxygen tetrahedral body, and the cations adsorbed are mainly  $\text{K}^+$ . When  $\text{K}^+$  is adsorbed on the tetrahedral wafer, its size is just embedded in the mesh space formed by the oxygen ions between the crystal layers, meaning that, due to the mere adsorption between the crystal layers, it is difficult for water molecules to enter the crystal layers, and the interlayer structure becomes very solid, thus, making it difficult to absorb water and swell. Thus, its swelling and compaction kink is between kaolinite and montmorillonite. The hydration of illite is only limited to the surface and if it encounters a formation with high illite content during the drilling process, the wellbore wall is prone to flaking off the block, and its dispersion is strong.

Kaolin is not easily swollen by hydration and belongs to the 1:1 type of laminated clay minerals. The main connection force between the layers of kaolinite is the van der Waals force and hydrogen bonding force, and the strong hydrogen bonding makes it difficult for water molecules to enter between the crystal layers. As shown in Figure 3a, due to the crystal layer on one side of the (OH) atomic surface on the other side of the O atomic surface, and the stacking, in addition to the Van der Waals gravitational expansion of electrostatic energy between the two adjacent crystal layers, there is a certain proportion of (OH) atomic group formation of hydrogen bonding forces, so that the two adjacent crystal layers are closely bound. Thus, water molecules find it difficult to enter between the crystal layers. Even if there is surface hydration energy to hold open the crystal layer, this hydration energy is not enough for large cohesion between the crystal layer, so there is almost no cation exchange.

Chlorite swells less, as its structure is similar to illite, with the difference being that its interlayer is filled with a layer of hydromagnesite wafers. In the silica–oxygen tetrahedra, part of the silicon is replaced by aluminum to generate a negative charge while, in the hydromagnesite wafers, some of the magnesium ions are replaced by aluminum ions and, thus, is positively charged, and these two charges balance each other so that the net charge of chlorite wafers is very low. Usually, the chlorite wafer has no interlayer water, but in some degraded chlorite parts of the hydromagnesite, the wafer is removed, which can produce some degree of interlayer water and lattice expansion.

The height variation of the hydration swelling produced by this experiment is mainly due to the lattice swelling caused by the surface hydration of the clay minerals. The lattice expansion occurs in all clays, and at this stage, water is adsorbed by the interlayer region, resulting in the hydration of interlayer cations and the subsequent formation of hydrate layers. These hydrate layers force the mineral layers apart, thus, leading to the expansion of the clay mineral. In general, all clay minerals show some hydration in water immersion, but due to their different hydration characteristics, their swelling changes are different. The contrast between the changes in montmorillonite and illite is the most obvious. It can also be seen that the swelling height of the bentonite used in the laboratory showed a continuous increase with the change in soaking time, and the height was almost three times the original height after three days of soaking. Its hydration swelling effect was very strong; montmorillonite also swelled very strongly, and its swelling height increased to twice the original height; kaolinite and chlorite eventually swelled to a comparable height after three days of soaking, and illite had the smallest swelling performance.

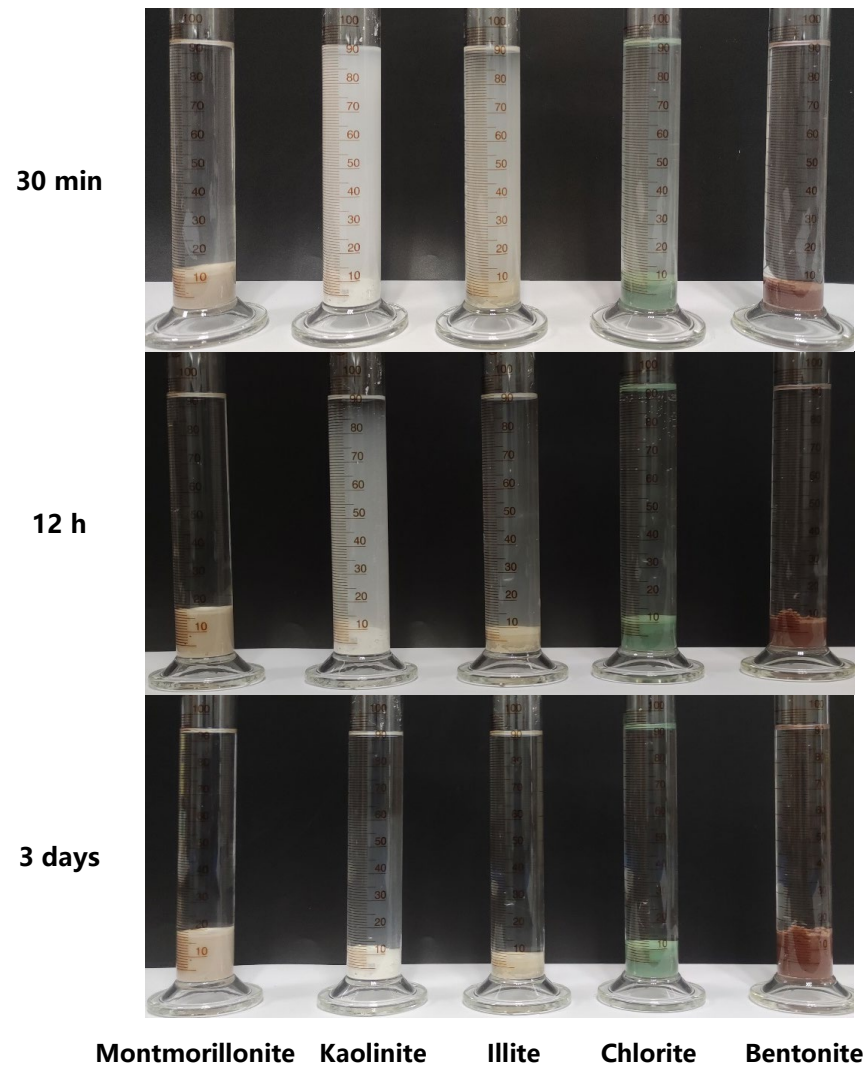
Figure 4 shows the apparent state changes in the mud cakes during the soaking process. During the experiment, by observing the experimental phenomena and the apparent swelling state of the mud cakes, the following can be found: the height of the mud cake of montmorillonite is 13 mm after 30 min of soaking in water, it swells to 17 mm after 12 h, and it swells to nearly 20 mm after 3 days.

By observing the changing state of the mud cake, the compactness of the mud cake varied among different clay minerals in the mud cake pressed into 10 g samples. Among them, illite has the best compactness, followed by montmorillonite and bentonite, chlorite is slightly worse, and kaolinite has the worst compactness and collapses easily, with an initial cake height of 13 mm, while the initial height of the rest of the cakes is between 10 and 11 mm. This is mainly due to the poor interparticle adhesion of kaolinite, which is not swelling in itself, but the poor interparticle adhesion causes the water molecules on the surface of the cake to invade so that the cake is scoured by the water flow after the water is put into the measuring cylinder, resulting in a certain degree of dispersion and the change in swelling height. The swelling height variation of illite is similar to that of kaolinite, which shows a certain variation in the swelling height, mainly due to its dispersibility.

#### 4.2. Hydration Dispersion of Single Clay Minerals

Clay minerals undergo hydration and swelling when they are exposed to water. When their swelling exceeds their cementation degree, the particles will enter the mud, so

dispersion is an important index to judge the hydration of clay minerals. The experiment was conducted to quantify the dispersion of different clay minerals in the water.

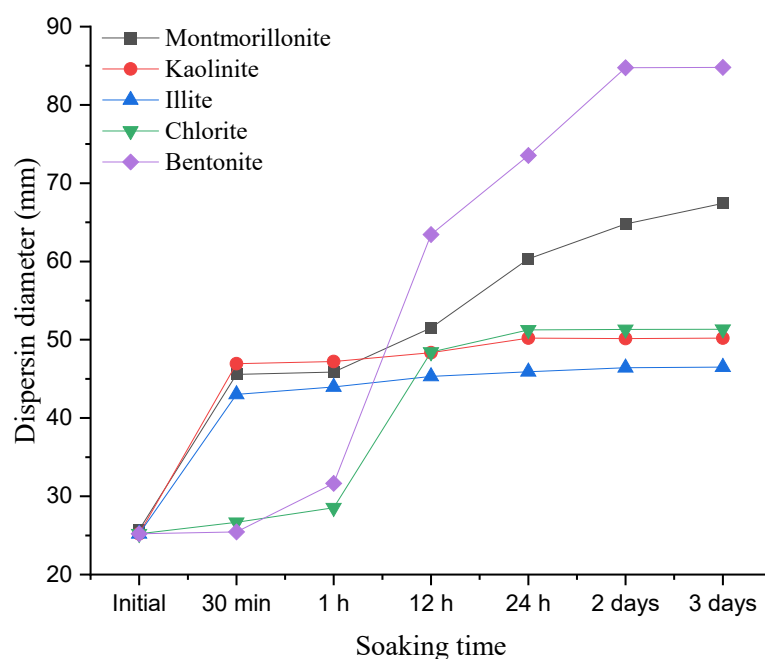


**Figure 4.** The state of the mud cakes immersed in water for different times.

Figure 5 shows the trend of mud cakes after soaking in water, as follows: the dispersion of mud cake all increases with time, and from the stable values, montmorillonite is the most dispersed, followed by chlorite and kaolinite, and illite is the least dispersed. The degree of hydration dispersion and collapse of montmorillonite is much greater than that of kaolinite, illite, and chlorite, and the rate of hydration dispersion and swelling is much greater than that of the other three clay minerals.

Since montmorillonite has extremely strong water absorption and swelling properties and high slurry-making ability, hydration experiments were also conducted to compare montmorillonite with the sodium-based bentonite used in the laboratory. From Figure 4, it can be found that the bentonite water absorption and swelling compared to the montmorillonite water absorption and swelling are better, due to the continuous water absorption and swelling of bentonite resulting in its volume change. Thus, the mud cake diameter is also larger, as is the degree of dispersion collapse. In addition, the bentonite water absorption and swelling rate in the first period was slower than for the montmorillonite, but after 12 h its swelling and dispersion rate accelerated, and the degree of swelling with time enhanced. After 3 days of soaking, the volume change growth was no longer accelerated because most of the water had been absorbed.





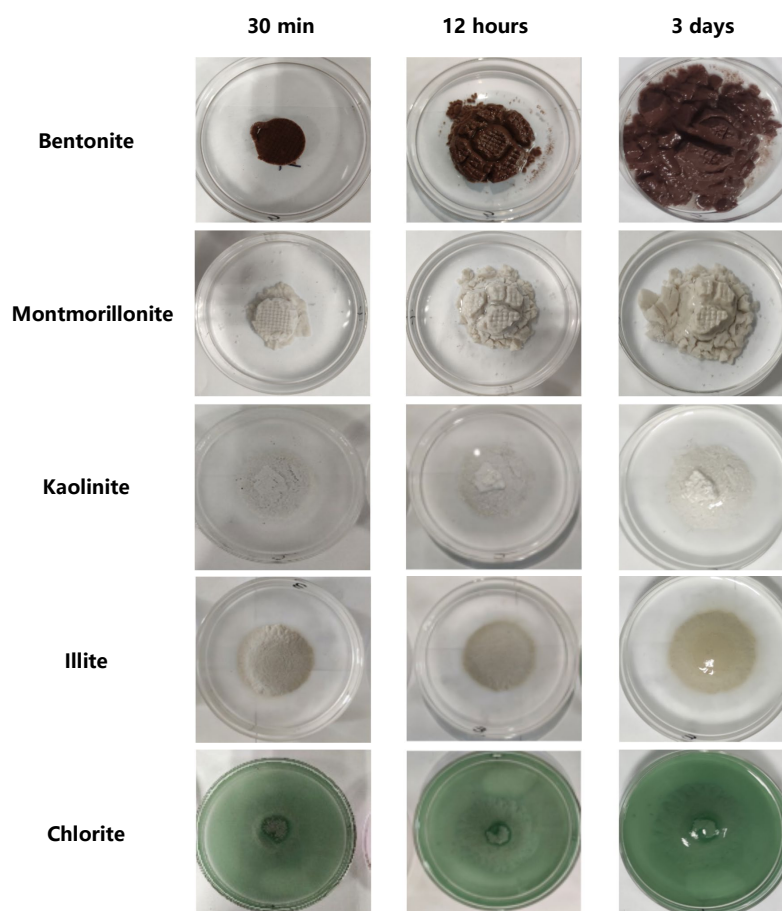
**Figure 5.** Variation curve of hydration dispersion of different clay minerals.

By observing the change in the state of the mud cakes immersed in water in Figure 6 and combining the phenomena observed in the experiment, the following was found: in the instant after pouring water into it, illite dispersion collapsed most obviously and rapidly, and its hydration was only limited to the surface, and in the drilling process, if it encountered a formation with high illite content, the wellbore wall was prone to spalling and falling off, and its dispersion was stronger. Additionally, kaolinite collapsed instantly, while montmorillonite and bentonite were able to maintain their original forms. After 30 min of soaking, the edges of the bentonite and montmorillonite mud cakes collapsed to a small extent, and the dispersion of the other three clay minerals mud cake also increased to a small extent. After 12 h of soaking, it is obvious that the surface of bentonite and montmorillonite cake produced cracks, and the top of kaolinite cake still has a part of the cake pieces, while the state of illite and chlorite cake is almost completely dispersed into powder from the surface. With the change in time, the degree of dispersion and collapse of each mud cake increased, the cracks on the surface of the bentonite and montmorillonite mud cakes increased, the volume expanded due to the continuous water absorption and expansion, and the mud pieces were flaked off from the mud cake continuously. Among them, bentonite and montmorillonite mainly showed water absorption and swelling characteristics, bentonite showed strong water absorption and swelling characteristics and, after 3 days of immersion, the water in the bentonite mud cake container was absorbed the most and the fastest. Montmorillonite water absorption and swelling is also strong, while the remaining three types of clay minerals mainly showed dispersion, and their mud cake states were mainly expressed as water absorption and dispersion.

The hydration form of the kaolinite, illite, and chlorite mud cakes are mainly presented as hydration dispersion, and easily collapse and disperse in water, without swelling. The dispersion and collapse state of mud cake tend to be stable after 24 h of immersion. Montmorillonite, on the other hand, mainly shows the characteristics of swelling in water, and its swelling property increases with time and reaches stability after a certain period. The number of exchangeable cations on the surface of clay minerals is large enough at this stage, so its volume change no longer increases sharply.

Compared with four kinds of clay minerals, bentonite is in a state of continuous dispersion collapse during the process of immersion, and its water absorption and swelling performance are stronger. This is mainly due to the strong adsorption and swelling properties of bentonite. It has a good cation exchange effect, and its crystal layer spacing is less,

meaning that water can penetrate the crystal layer spacing to make the internal crystal spacing become fully expanded.



**Figure 6.** State change in the mud cakes after soaking in water.

#### 4.3. Effect of the Clay Fraction of Simulated Minerals on Hydration

For the special nature of the hydration of montmorillonite and illite, the effect of montmorillonite to illite change on the change in hydration of the formation was simulated, and the effect of the change in montmorillonite and illite components on the hydration dispersion of the formation was investigated.

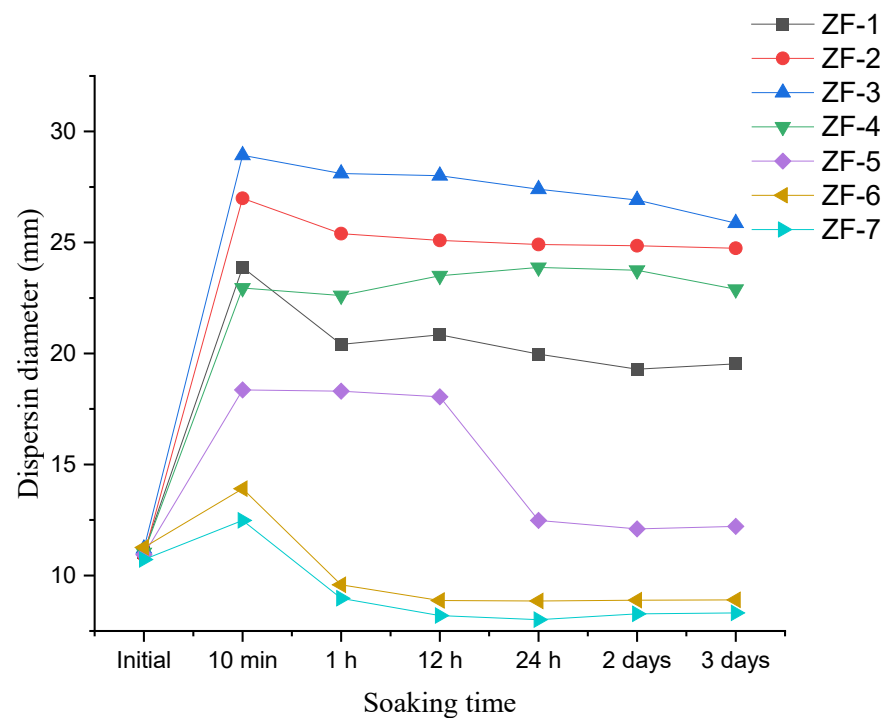
From Experiments 4.1 and 4.2, it can be seen that montmorillonite and illite have contrasting hydration, i.e., montmorillonite is easy to hydrate and swell, while illite is weakly affected by hydration. Therefore, comparative experiments were conducted on the hydration of different ratios of montmorillonite and illite. To simulate the different components of clay minerals in mud shale formations and, thus, their different degrees of hydration, a set of comparative experiments was conducted mainly for the different components of montmorillonite and illite in clay minerals. The mineral formulations of different component clays are shown in Table 3.

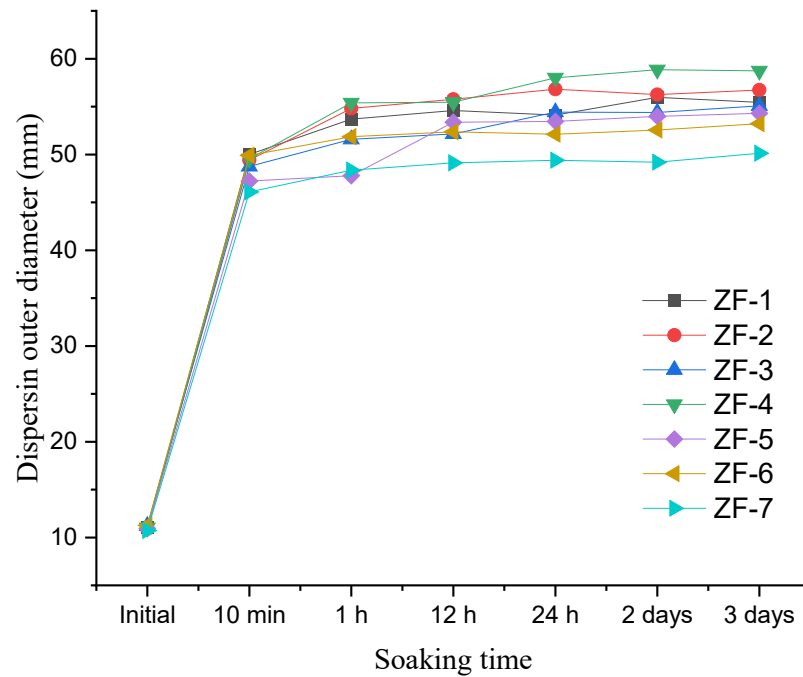
During the experiment, it was observed that, after the hydration of the mud cake, the difference in the maximum diameter change in its dispersion state from the center of the mud cake to the outward diffusion was small, but the contrast of its central part collapse dispersion state was more obvious, and it can be seen that the greater the degree of collapse of the central part, i.e., the smaller the diameter of the central part of the undispersed mud cake, the greater the dispersion of the hydration of the mud cake, while the smaller diameter indicates that it does not disperse easily. Therefore, the numerical changes in the innermost circle diameter and the outermost circle diameter of the mud cake were measured separately.

**Table 3.** Proportion of different components in clay minerals.

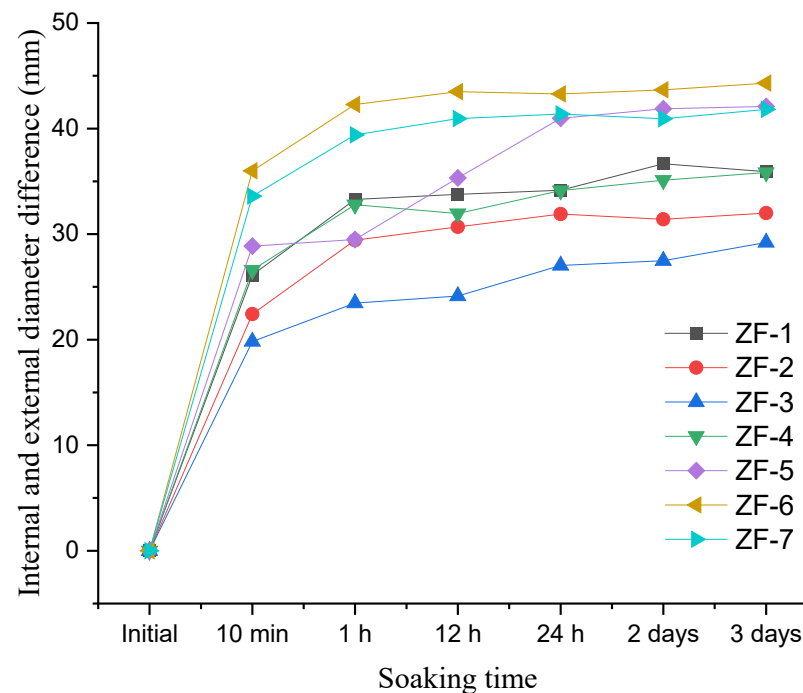
Mud Cake Number	Clay Mineral Composition (%)			
	Montmorillonite	Illite	Kaolinite	Chlorite
ZF-1	25	25	25	25
ZF-2	30	20	25	25
ZF-3	40	10	25	25
ZF-4	50	0	25	25
ZF-5	20	30	25	25
ZF-6	10	40	25	25
ZF-7	0	50	25	25

From Figures 7 and 8, it can be seen that, after soaking in water for 3 days, the diameter of the ZF-4 mud cake is the largest and that the diameter of the ZF-7 mud cake is the smallest, that is, when the content of montmorillonite in clay minerals is larger, the stronger the degree of hydration, and when the proportion of illite is large, it is less affected by hydration. As shown in Figure 9, by observing the state of mud cake, it is found that the higher the proportion of montmorillonite, the larger the inner diameter of the mud cake, and the middle of the mud cake is less dispersed, mainly showing that when the proportion of illite is high, the mud cake mainly shows a dispersed state, its inner diameter is smaller, and the ZF-7 mud cake is dispersed immediately when water is poured into it. When the difference between the innermost and outermost diameter of the mud cake is changed, Figure 9 shows that, the larger the difference, the greater the dispersion of the mud cake. It can be seen that when the proportion of illite is larger, the larger the difference, i.e., the mud cake is easily dispersed by hydration; when the proportion of montmorillonite is higher, the smaller the difference, i.e., the hydration of the mud cake is mainly hydration swelling rather than hydration dispersion, so the outermost diameter of the mud cake is relatively higher.

**Figure 7.** Variation of the inner diameter of hydration and dispersion of mineral mud cakes with different components.



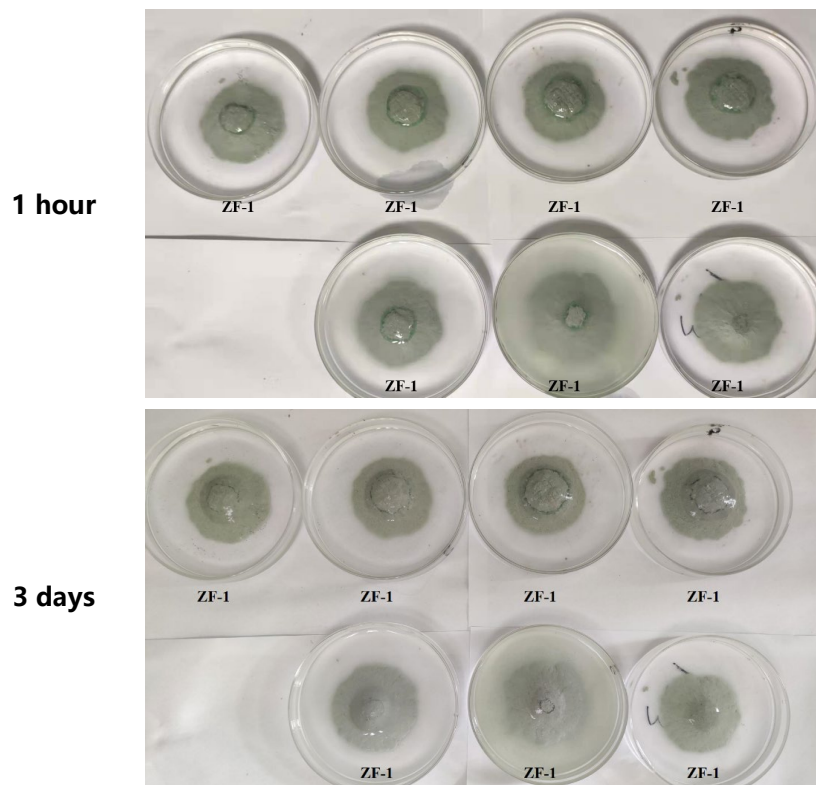
**Figure 8.** Variation of the outer diameter of hydration and dispersion of mineral mud cakes with different components.



**Figure 9.** Variation of the inner and outer diameter difference of hydration and dispersion of mineral mud cakes with different components.

As shown in Figure 10, in the hydration state of the mud cakes after soaking, ZF-2~ZF-4 are the components with higher montmorillonite and ZF-5~ZF-6 are the components with higher illite. The difference between ZF-4 and ZF-7 can be seen by observing the state of the mud cakes. When the proportion of illite in the mud cake is higher, the diameter of its innermost circle is smaller, that is, the higher its degree of hydration and dispersion, thus, combined with the previous experiments, it can be concluded that the hydration and dispersion of illite are relatively strong. Additionally, when the content of montmorillonite

is higher, the dispersion of the center part of the mud cake is smaller, and the hydration form is mainly hydration swelling, so its hydration degree is stronger. Furthermore, when illite is higher in the component, the hydration dispersion state of the mud cake is more obvious.



**Figure 10.** Soaking state of mud cakes with different mineral clay fractions in water.

Through the above experimental data, it can be seen that the presence of montmorillonite and illite both have an effect on the hydration and swelling of clay, i.e., montmorillonite is mainly manifested as enabling hydration and swelling after encountering water, i.e., the volume of mud cake increases after hydration, while illite is mainly manifested as water dispersion, i.e., the collapse of the mud cake itself, and the phenomenon of flaking off the block. In fact, the hydration of montmorillonite is more intense compared with illite, that is, the presence of montmorillonite has a more serious effect on the expansion of clay minerals.

#### 4.4. Effect of Cations on the Hydration of Clay Minerals

##### 4.4.1. Hydration Dispersion Effect

The study used 10% NaCl, 10% CaCl<sub>2</sub>, and 10% KCl solutions as soaking solutions to observe the soaking hydration trends of different types of clay minerals. The experimental results are shown in Figures 11–13.

From the data in Figures 11–13, it can be seen that the dispersion of the mud cakes all increased with time, except for bentonite, whose dispersion degree stabilized after 1 h. From the stable values, montmorillonite dispersion is the largest, followed by chlorite and kaolinite, and illite dispersion is the smallest. The degree of hydration dispersion and collapse of montmorillonite is much greater than that of kaolinite, illite, and chlorite, and the rate of hydration dispersion and swelling is much greater than that of the other three clay minerals. The dispersion and collapse of sodium bentonite are very strong, and the dispersion of the mud cake does not stabilize with time but strengthens continuously.

Since montmorillonite has extremely strong water absorption and swelling properties, has a high slurry making ability, and is a material for formulating drilling fluids, hydration

experiments were also conducted to compare montmorillonite with the sodium-based bentonite used in the laboratory. It was found that the bentonite used in the laboratory had better water absorption and swelling than that of montmorillonite, but in terms of time, the water absorption and swelling of bentonite was slower than that of montmorillonite. However, its degree of swelling increased with time, while the water absorption and swelling of montmorillonite were more limited.

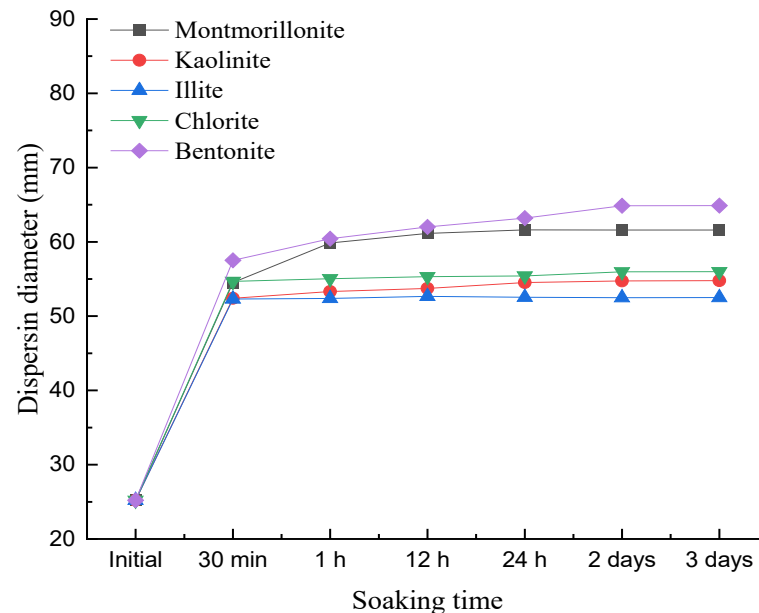


Figure 11. Dispersion trend of clay minerals immersed in 10% NaCl solution.

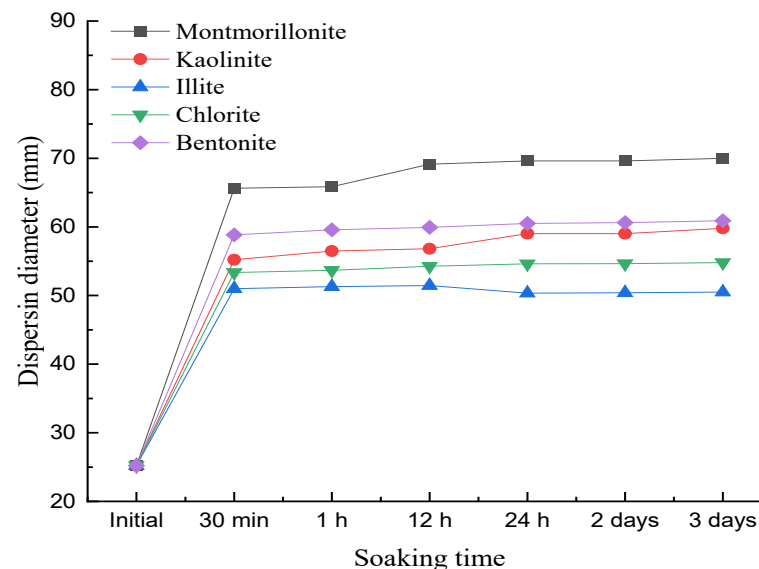
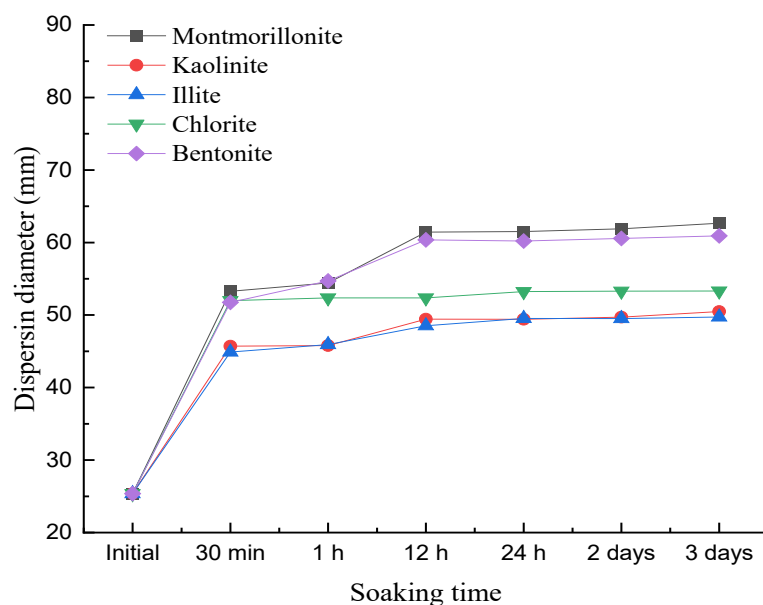


Figure 12. Dispersion trend of clay minerals immersed in 10% CaCl<sub>2</sub> solution.

The trend of hydration and dispersion in NaCl, CaCl<sub>2</sub>, and KCl solutions shows that the hydration and dispersion of clay minerals are suppressed. Additionally, by observing the state of mud cake, it can be found that although montmorillonite and bentonite displayed a swollen collapse state in water, this changed to the main dispersion state in the cationic solution, especially with the bentonite hydration dispersion performance. Compared to in water, its hydration dispersion degree under the action of cations was inhibited to a stronger extent. It can be seen that when the concentration is 10% in these three solutions, the hydration inhibition effect is  $K^+ > Na^+ > Ca^{2+}$ , the degree of dispersion

in KCl solution soaked for 1 h tends to be smooth, and the mud cake dispersion diameter is small.



**Figure 13.** Dispersion trend of clay minerals immersed in 10% KCl solution.

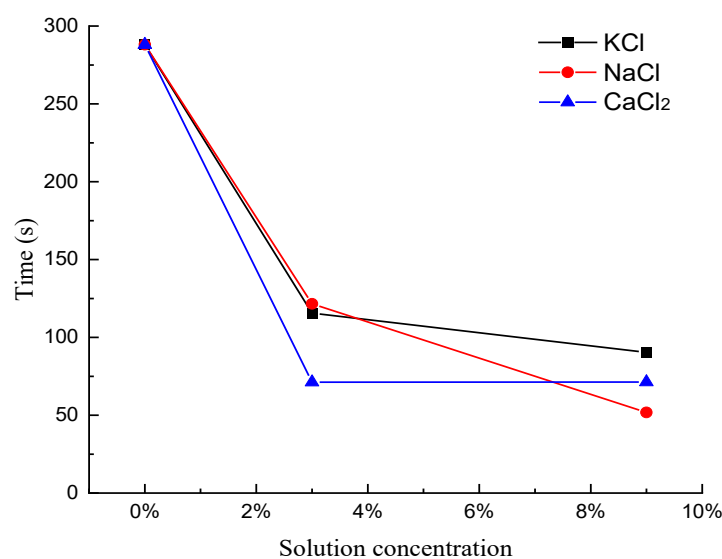
#### 4.4.2. CST Capillary Absorption Time

On the contrary, the above experimental phenomena and their results show that the sodium-based bentonite has the most obvious hydration effect, so it was used to test the effect of different cations on inhibiting the hydration of clay minerals by configuring a certain percentage of its base slurry.

In this experiment, the effect of different metal ion concentrations and types on CST was measured to evaluate its dispersibility. This index describes the dispersion ability of mud, which can be used to evaluate the ability of mud to inhibit dispersion, the anti-swelling ability of drilling fluid, the ability of drilling fluid to inhibit hydration and dispersion, and to optimize the formulation of working fluid into the well, such as dosage and ratio, type of treatment agent, etc. It is also a new method to analyze and evaluate the classification of shale. Given that the hydration properties of bentonite and montmorillonite are very similar, the effect of different metal ions on their dispersion performance was further investigated using sodium-based bentonite, and the base slurry was formulated to test its capillary absorption time (CST). The smaller the CST, the better the inhibition of montmorillonite dispersion and, vice versa, the worse the inhibition of its dewatering performance.

As shown in Figure 14, the measured relationship curves for different ion concentrations of CST are shown, and it can be seen from the figure that the dispersion is substantially inhibited regardless of the metal ions added.

When the concentration is 3%, the inhibition effect is  $\text{Ca}^{2+} > \text{K}^+ > \text{Na}^+$ . At a concentration of 9%, the inhibition effect was  $\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+$ . At lower concentrations of inorganic salt solution,  $\text{K}^+$ ,  $\text{Na}^+$ , and  $\text{Ca}^{2+}$ , the ion concentration in the solution increased as the CST test value decreased significantly, i.e., the dispersibility decreased significantly and the inhibition effect was obvious. However, as the ion concentration continued to increase the dispersibility of potassium and calcium ions decreased slowly, and the inhibitory effect was no longer obvious. Additionally, sodium ion dispersion at low concentrations will be significantly reduced with the increase in ion concentration characteristics, as when the concentration continues to increase, the CST value does not always show a slow decrease in the trend but will instead appear to increase the dispersion.



**Figure 14.** Relationship curves of CST with different ion concentrations.

Therefore, it seems that all three cations have a certain inhibitory effect on the hydration dispersibility of clay. At lower concentrations of these three cations,  $\text{Ca}^{2+}$  has the best inhibitory effect, when the solution concentration reaches 9%,  $\text{Na}^{+}$  has the best inhibitory effect, and when the concentration is greater, then  $\text{K}^{+}$  has the best inhibitory effect

## 5. Conclusions

In this study, by simulating the hydration process of clay minerals and their cationic influence mechanism, the clay mineral mud cake variables were controlled in a certain range, the states of clay minerals and bentonite in different soaking times in water and different cationic solutions were characterized, and the hydration process of different components of clay minerals was simulated. Thus, the following conclusions were drawn:

- (1) Clay minerals in contact with water reach the early stage of hydration faster when the hydration is gradually stabilized to a certain extent. The hydration of sodium bentonite and montmorillonite is the strongest.
- (2) Different clay minerals show different states after encountering water. Of these, montmorillonite and illite hydration are the most obvious, and montmorillonite mainly shows hydration swelling. Illite has no water absorption and swelling but mainly shows dispersion. Kaolinite collapses very easily after encountering water, and chlorite has almost no hydration swelling.
- (3) Through qualitative and quantitative analysis of water absorption processes of different clay minerals, and different mineral components, the changes in the water absorption states of clay minerals and their influence laws were obtained. By comparing the difference between illite and montmorillonite content, it is found that illite and montmorillonite hydration show different states. When illite content is high, mainly for hydration dispersion, it is not easily swollen by hydration. On the other hand, when montmorillonite content is higher, the degree of hydration is greater, and it is mainly affected by the swelling of hydration.
- (4) Cations in solution have a certain inhibitory effect on the hydration of clay minerals, and different cations have different degrees of inhibition. The inhibition effect of  $\text{Ca}^{2+}$  is best when the concentration of cations is low, the inhibition effect of  $\text{Na}^{+}$  is best when the concentration of solution reaches 9%, and the inhibition effect of  $\text{K}^{+}$  is best when the concentration is greater.

It can be observed that the hydration state of clays is influenced by the type, charge, etc., and a complex hydration process is formed by the interaction with ions in solution, which has been intensively studied in the characterization of clay mineral hydration. However,



there are still limitations in experimental methods, and better methods for the dynamic characterization of clay mineral hydration processes in macroscopic aspects have not been found yet. Therefore, in future research, we should try to reduce the simulation of complex formation mineral composition, focusing on the interaction between clay minerals and cations and the influence of different components of clay on hydration. Given the previous research results, combined with the actual engineering situation, it is expected that we will establish a new hydration model which can be better used in engineering.

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