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Preparation and Swelling Inhibition of Mixed Metal Hydroxide to Bentonite Clay

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Abstract: In this paper, mixed metal hydroxide (MMH) was prepared via $MgCl_2$ and $AlCl_3$ by the co-precipitation method and characterized by XRD, TGA laser and particle size analysis. The inhibitory effect of MMH on the swelling of clay was evaluated by linear expansion, mud ball, laser particle size analysis, X-ray diffraction analysis and TGA. The linear expansion experiment showed that MMH with a ratio of Mg:Al = 3:1 displayed a strong inhibitory effect on bentonite expansion when 0.3% MMH was added to the drilling fluid, demonstrating better inhibition than 4.0% KCl. Within 48 h, only a few cracks were visible on the mud ball surface in the 0.3% MMH suspension, which indicates that MMH can inhibit wet bentonite for deep hydration. X-ray diffraction and particle size analyses of bentonite were conducted before and after MMH was added to illustrate the inhibition. MMH also displayed high temperature resistance in water-based drilling fluid as a shear strength-improving agent, and its dynamic plastic ratio and shear force were stable after aging at 200 °C for 16 h.

Keywords: mixed metal hydroxide; bentonite clay; swelling; inhibitors; montmorillonite; drilling fluid

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1. Introduction

Mixed metal hydroxide (MMH) is a layered hydroxide composed of mixed metal hydroxide crystal ions with positive charges [1–3]. In 1942, Feitknecht [4] stated that the structure of these compounds was double-layered, with one regular triakisoctahedral layer containing divalent cations, and another regular dioctahedral layer containing trivalent cations. Compositions of chemicals can generally be described as follows:

$$\left[M^{2+}_{1-X}M^{3+}_{X}(OH)_2\right]^{x+}A^{n-}_{x/n}\cdot mH_2O$$

In its chemical formula, the cation M^{2+} is bivalent, similar to Mg^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Zn^{2+}, etc. M^{3+} is a trivalent metal cation, such as Al^{3+}, Cr^{3+}, Mn^{3+}, Fe^{3+}, Co^{3+}, Ni^{3+}, and so on. A^{n-} is an anion with a valence of n, such as Cl^-, $NO_3{}^-$, etc. [5]. In 1988, Burba et al. [6] first proposed the use of mixed metal-layered MMH in oilfield drilling. In 1989, the Dow Company developed an MMH material as a new type of mud treatment agent. Later, significant research was conducted on MMH in China [7–10]. MMH drilling fluid has a strong ability to inhibit the hydration swelling of clay and prevent well diameter reduction caused by the hydration swelling of mud shale. It is especially effective in preventing well diameter enlargement and collapse in muddy and loose sandstone formations [11–19]. Due

to its ability to stabilize well walls, carry chips and inhibit chip dispersion, MMH is widely used in oilfield drilling fluid. MMH also reduces drilling fluid costs [1].

The MMH products widely used in Chinese oil fields are typically magnesium–aluminum hydroxide (Mg-Al MMH), also known as magnesium hydroxide-positive gel, which contains Mg^{2+}, Al^{3+}, OH^{-} and Cl^{-}. However, our understanding of the inhibitory effect of raw materials on MMH remains incomplete, and the inhibition has not been fully characterized. In this paper, MMH was prepared via $MgCl_2$ and $AlCl_3$ by the co-precipitation method [20]. Then, its inhibitory effect on the swelling of clay was characterized and evaluated in detail. The inhibitory effect of MMH on the swelling of clay was evaluated by linear expansion, mud ball, laser particle size, X-ray, and TGA diffraction experiments. At present, there is no literature report on the temperature resistance testing of MMH. In this study, we tested the temperature resistance and drilling fluid performance of MMH for the first time, contributing to new knowledge on the subject.

2. Experimental

2.1. Materials

Sodium bentonite (technical grade Mineralogical composition: 70% montmorillonite, 20% Quartz, 10% Feldspar) and calcium bentonite (Technical grade. Mineralogical composition: 60% montmorillonite, 25% quartz, 15% feldspar) were purchased from Xi'an Chanqing Chemical Co., Ltd., Xi'an, China. $MgCl_2 \cdot 6H_2O$, $AlCl_3 \cdot 6H_2O$ and NaOH were purchased from Tianjin Shengao Chemical Reagent Co., Ltd., Tianjin, China.

2.2. Preparation of MMH

In this experiment, the different ratios of $MgCl_2 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$ were dissolved in 100 mL of water at room temperature (MMH-1, Mg:Al = 1:1; MMH-2, Mg:Al = 1:2; MMH-3, Mg:Al = 1:3). Immediately after dissolution, the magnesium chloride solution and aluminum chloride solution were poured into the NaOH solution while stirring. We stirred well to thoroughly mix the solutions. Eventually, a white precipitate was observed in the beaker. The obtained mixed precipitate was sealed and aged at room temperature for 1 h. The aged precipitate was then subjected to centrifugation. It was repeatedly centrifuged and washed with distilled water until its pH was between 8 and 9. Subsequently, the solution was heated in a water bath at 75 °C for 5 h for softening. After 5 h of softening, magnesium–aluminum MMH sols were obtained. The obtained sol was placed in an oven and dried at 105 °C. After 24 h, a dried solid was obtained. The solid was ground through a 160-mesh sieve to obtain inorganic Mg-Al MMH dry powder.

2.3. Inhibitory Evaluation

The hydrated expansion of sodium bentonite was determined using a shale expander (NP01, Chuangmeng Ltd., Qingdao, China), according to the Chinese Petroleum and Natural Gas Industry Standards SY/T59711994 and SY/T63351997. Using a 2:1 mass ratio, we dried the sodium bentonite at 105 °C for 2 h, then mixed it with water to form mud balls with a mass of about 10 g each. Then, we immersed the mud balls (sodium bentonite) in the same volume of different MMH treatment agents. After a certain period of time, we captured a photo to observe the shape changes and evaluate the MMH inhibition by the appearance changes and surface changes of the mud balls [21].

2.4. Drilling Fluid Evaluation

Calcium bentonite (4%) and sodium carbonate (0.2%) were added to tap water (350 mL), stirred for 30 min and aged for 16 h at 298 K [22]. The rheological, filtration and lubrication properties of drilling fluid, such as AV (apparent viscosity), PV (plastic viscosity), YP (yield point), FL (API filtration) and Tg (friction coefficient), were evaluated using a viscometer (ZNN-D6S, Hetongda Co., Ltd., Qingdao, China), medium-pressure filtration instrument (GJSS-B12K, Haitongda Co., Ltd., Qingdao, China) and viscosity coefficient instrument

(Qingdao Hetongda Co., Ltd., Qingdao, China), according to the formulas in Chinese National Standard GB/T 16783.1-2006.

2.5. Particle Size Experiment

The particle size of each sample was measured with a laser particle sizer to determine the median and mean particle diameter of each sample. The data were used to analyze the variation in sodium bentonite particle size, which was measured with a LS-13320 (Beckman Coulter, Inc., Brea, CA, USA) [23].

2.6. X-ray Diffraction

The samples were analyzed by using a D8ADVAHCL X-ray diffractometer of the Bruker company from Germany. A Cu target, ceramic X-ray tube, tube current of 40 mA, tube voltage of 40 kV, step size of 0.02° and scanning range of 5~90° (2θ) were used for measurements. The synthesis result was determined as MMH. At the same time, the variation of the interlayer spacing of the sodium bentonite under different conditions was calculated by the Bragg equation (n λ = 2 sinθ) [24].

2.7. TGA and SEM

Sodium bentonite was dispersed in MMH suspensions for 24 h. Bentonite was separated and dried at 378 K for TGA and SEM. TGA was performed with a TGA/DSC1/1600 thermal analysis machine (Mettler Toledo Inc., Zurich, Switzerland). The surface morphology of samples was investigated using a digital imaging scanning electron microscope (model SU6600, serial no. HI-2102-0003, Hitachi, Japan) [25].

3. Results and Discussion

3.1. X-ray Diffraction Analysis

Multiple studies have shown that MMH has the crystal structure of hydrotalcite [25]. X-ray diffraction was conducted on the three prepared samples, as shown in Figure 1. It can be seen from Figure 1 that the characteristic peaks of the X-ray diffraction patterns of the three synthesized samples were different from the characteristic peaks of $Mg(OH)_2$. The peak of $Al(OH)_3$ is relatively broad, while the peaks of the three samples in the figure were very sharp, so the synthesized sample was different from $Al(OH)_3$. Therefore, our synthesized MMH was not a separate precipitate of $Mg(OH)_2$ and $Al(OH)_3$, but a new substance different from $Mg(OH)_2$ and $Al(OH)_3$. Comparing the PDF card (89–460) of the X-ray diffraction pattern of hydrotalcite, the characteristic peaks 003, 006, and 012 of hydrotalcite appeared in all three samples.

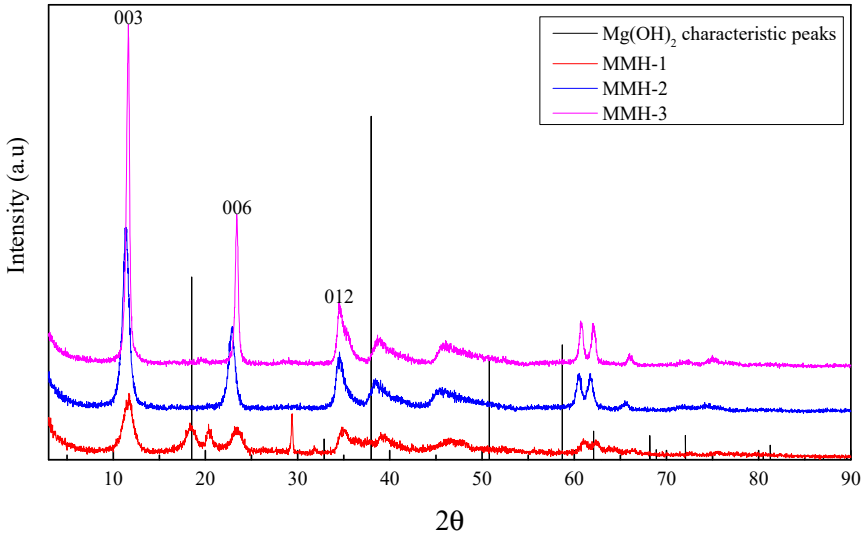

Figure 1. X-ray diffraction patterns of MMH and $Mg(OH)_2$.

In addition, it can be seen from Figure 1 that, when the raw material ratio was 1:1, the crystallinity of the synthesized MMH-1 was poor. Although the characteristic peaks 003, 006 and 012 of the hydrotalcite-like compounds appeared, the characteristic peak intensity did not meet strict multiples. The relationship indicates that the layered performance of MMH-1 was poor. Therefore, the effect of MMH-1 was not ideal. As the ratio of the Mg and Al raw materials increased, the sharpness of the diffraction peaks in the spectra of MMH-2 and MMH-3 gradually increased, indicating that the synthesized sample had high crystallinity and a complete crystal form. The intensities of the characteristic peaks 003, 006 and 012 of MMH-2 and MMH-3 all had strict multiple relationships, indicating that MMH-2 and MMH-3 had a good layered structure, and the synthesis result was ideal. The Bragg equation can be used to calculate the basal spacing (d_{001}) of the three samples. MMH-1: $d_{(003)}$ = 0.759 nm, MMH-2: $d_{(003)}$ = 0.758 nm, MMH-3: $d_{(003)}$ = 0.776 nm.

3.2. SEM Experiment

Figure 2 shows SEM images of the three MMH samples, where a, b and c represent MMH-1, 2 and 3, respectively. They clearly illustrate the laminate structure and appearance of the three synthetic samples. When comparing the SEM images of the three samples, it is clear that MMH-3 had a more complete layer structure and crystallinity. As reported in Section 3.1, this result was consistent with the X-ray diffraction data.

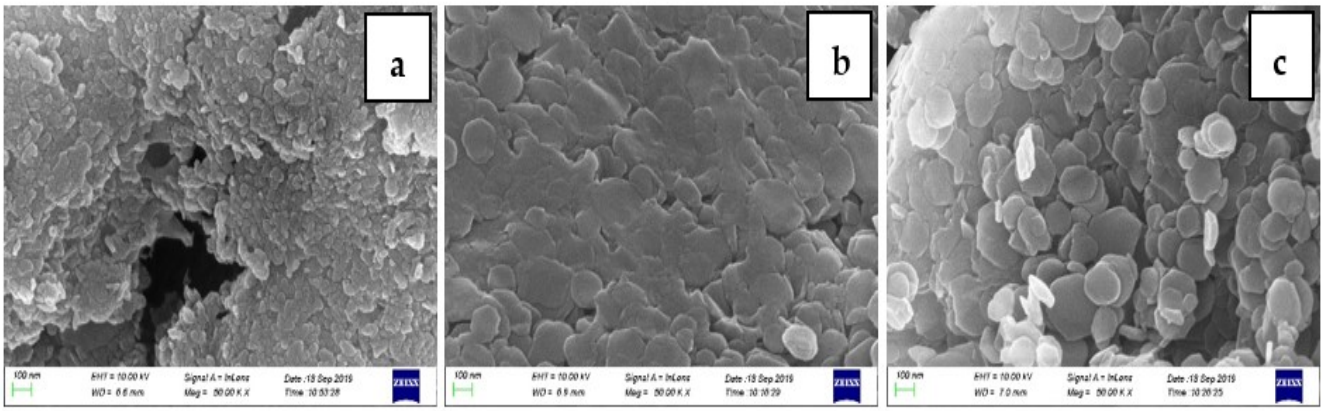

Figure 2. SEM of different MMH samples (**a**): MMH-1, (**b**): MMH-2, (**c**): MMH-3.

3.3. Linear Swelling Experiment

Bentonite is a type of clay rock, also called montmorillonite clay rock, that often contains small amounts of illite, kaolinite, quartz, feldspar, etc. Bentonite has strong hygroscopicity and swelling. It can adsorb between 8- and 15-times its own volume in water, and volume expansion ranges from several times up to 30 times. Therefore, bentonite was selected for this experiment. MMH particles can repel cations on the surface of bentonite and replace them with cations between bentonite layers. The negative charge resulting from the lattice replacement of montmorillonite must adsorb ions of opposite electrical properties to balance the electrical properties of the solution. The thickness of the double electric layer is inversely proportional to twice the square of the counter ion valence, i.e., high cation valence, thin hydration film and low expansion multiplier. Therefore, MMH has strong inhibitory properties. Linear expansion experiments were performed on three samples. The optimal concentrations of the three samples were selected, and the results of the linear expansion experiments were as follows. It can be seen from Figures 3–5 that MMH had a clear inhibitory effect on the hydration and swelling of bentonite. The inhibitory effect of the 0.1%~0.5% concentrations of the three samples on the hydration and swelling of bentonite was better than the 4.0% KCl solution.

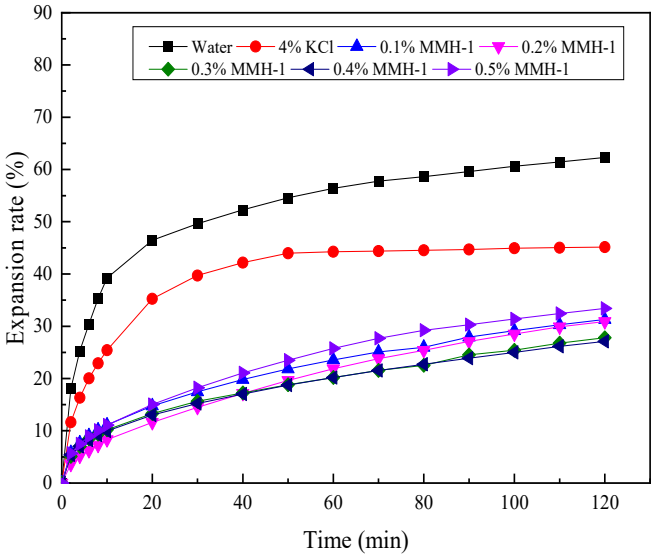

Figure 3. Swelling of bentonite in the MMH-1 suspension.

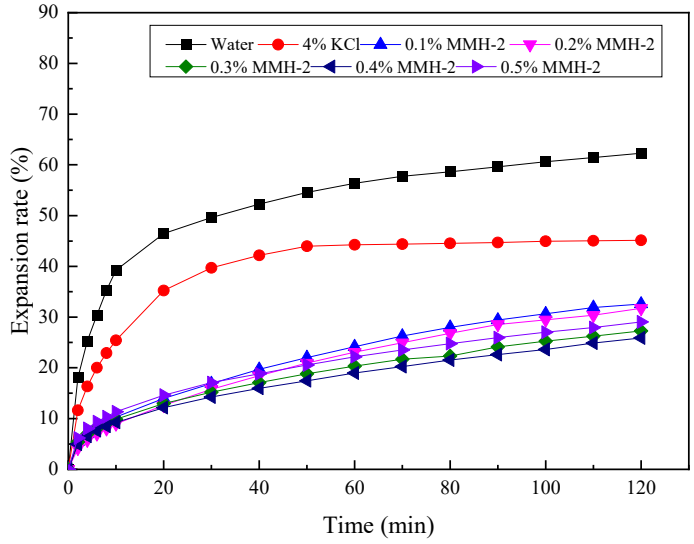

Figure 4. Swelling of bentonite in the MMH-2 suspension.

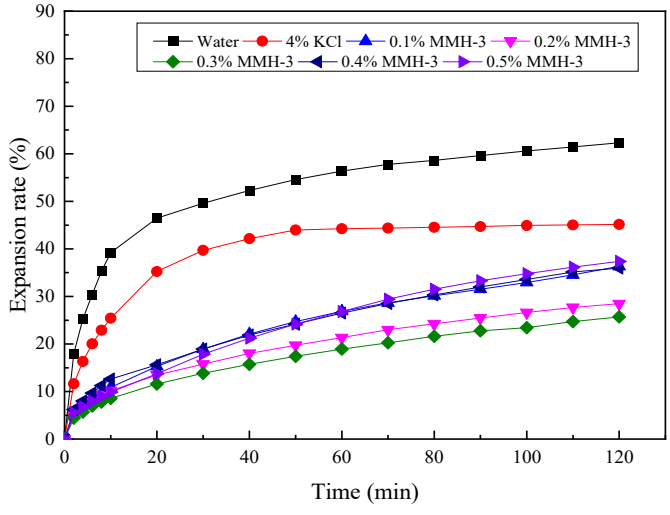

Figure 5. Swelling of bentonite in the MMH-3 suspension.

Among the different concentrations, the effect of 0.3% MMH-3, as shown in Figure 5, was the best. The expansion rate at 120 min was only 25.71%, which was significantly lower than the expansion rate at 120 min in clean water (63.21%), and the suppression effect was far greater than the 4.0% KCl solution. The experimental results show that with the increase in the ratio of Mg and Al raw materials, the inhibitory ability of synthetic samples on the hydration and swelling of bentonite gradually increases. As the concentration of MMH increases, the inhibitory ability of MMH on the hydration and swelling of bentonite increases first, and then gradually decreases.

3.4. Mud Ball Experiment

The results of the linear expansion experiment showed that MMH significantly inhibited the hydration expansion of bentonite. In the next step, the mud ball experiment was used to further evaluate their inhibitory properties. The changes in the mud ball were observed after 24 h and 48 h immersion in different MMH suspensions (0.3%). The results are shown in Figure 6.

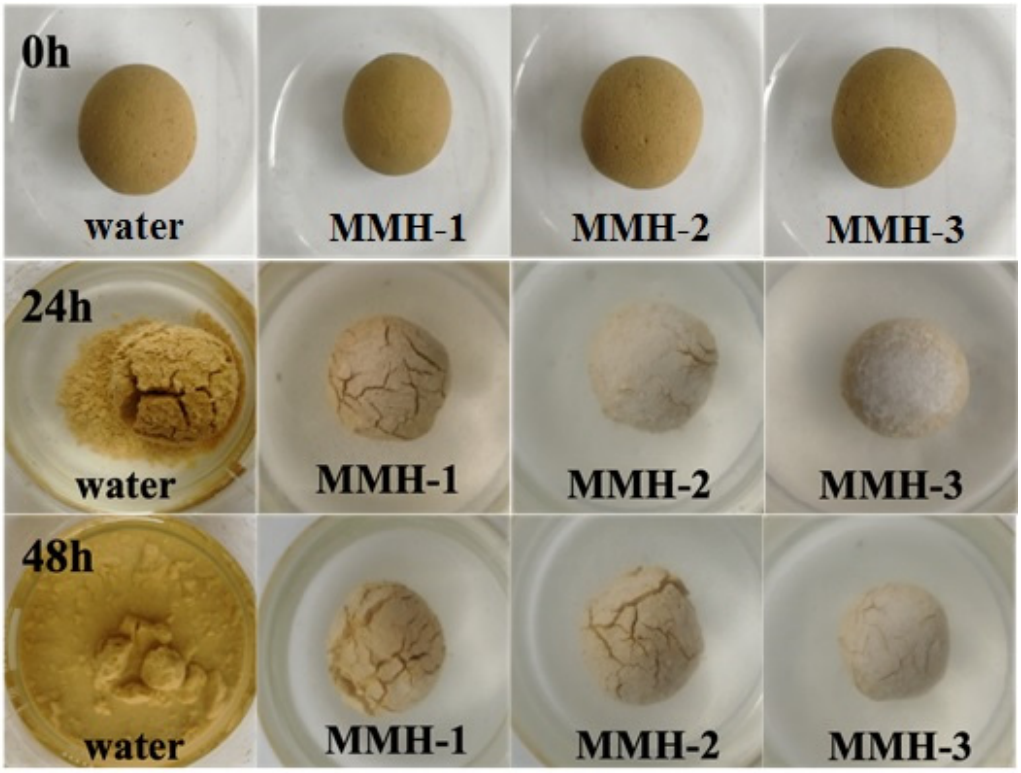

Figure 6. Appearance of mud balls after soaking in three MMH suspensions at different times.

The results showed that the MMH suspensions inhibited the swelling of hydration and the dispersal of the hydration of bentonite mud balls (Figure 6). The suspension with MMH-3 as 0.3% of its content showed the greatest inhibitory effect. In MMH-1, 2 and 3, the mud ball maintained its spherical appearance after being submerged in 0.3% suspensions for 48 h. After 48 h, the mud ball in clear water collapsed more severely, and it could no longer maintain its spherical shape. In addition, the mud ball experiment demonstrates that MMH has a strong inhibitory effect on bentonite.

3.5. Particle Size Measurement

Particle size analysis was performed on bentonite treated with different samples. The analysis results are shown in Table 1. As can be seen in Table 1, the average size of the particles of unhydrated bentonite and hydrated bentonite decreased from 34.62 μm to 16.92 μm. The addition of three MMH samples to the hydrated bentonite base slurry

significantly increased the bentonite particles' size, indicating that MMH had a better inhibitory effect on the hydration and dispersion of bentonite, causing the dispersed bentonite particles to aggregate, while MMH-3 had the best effect.

Table 1. Average and median particle size of bentonite under different treatments.

Clay	Average Particle Size/μm	Median Particle Size/μm
Original bentonite	34.62	30.18
Bentonite + water	16.92	11.33
Bentonite + MMH-1	22.74	15.16
Bentonite +MMH-2	35.75	24.54
Bentonite +MMH-3	36.86	24.59

3.6. X-ray Diffraction of Modified Samples

X-ray diffraction experiments were carried out on bentonite particles under different treatment conditions. From Figure 7, it is clear that the 001 characteristic peak of bentonite was $2\theta = 5.9^\circ$ after hydration expansion. The interlayer distance $d_{(001)} = 14.96$ nm can be calculated following the Bragg equation ($n\lambda = 2 \sin\theta$).

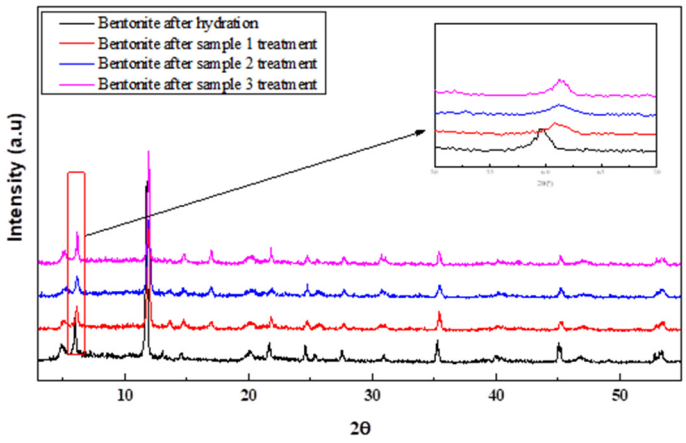

Figure 7. X-ray diffraction patterns of bentonite under different treatments.

After adding three MMH samples to the bentonite slurry, the 001 characteristic peak shifted slightly to the right, with peaks of 2θ: MMH-1 $2\theta = 6.08^\circ$, MMH-2 $2\theta = 6.10^\circ$ and MMH-3 $2\theta = 6.11^\circ$, which can be calculated separately. The interlayer spacing of bentonite after the three sample treatments was MMH-1 $d_{(001)} = 14.52$ nm, MMH-2 $d_{(001)} = 14.48$ nm and MMH-3 $d_{(001)} = 14.45$ nm. After adding the MMH samples, the interlayer spacing of bentonite was clearly reduced, which further illustrates that MMH has a strong ability to suppress the hydration expansion and hydration dispersion of bentonite. In addition, the increase in the Mg and Al raw material ratio increased the MMH's inhibitory function.

3.7. TGA Measurement

By analyzing the performance of the samples at room temperature, we concluded that the solution with the addition of 0.3% of MMH-3 achieved the best performance. In order to verify the temperature resistance of MMH-3, thermogravimetric analysis was performed on MMH-3-treated bentonite and water-treated bentonite, and the results are shown in Figure 8. As can be seen in Figure 8, the water content in the MMH-3-treated bentonite was significantly smaller than that of the tap water-treated bentonite, which further indicates that the MMH has a strong inhibitory effect on the hydration swelling and hydration dispersion of bentonite.

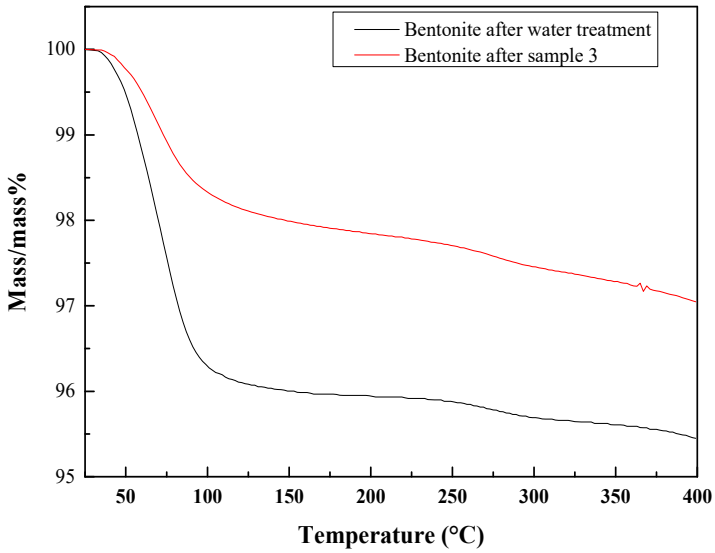

Figure 8. TG curves of bentonite particles after treatment with different treatment agents.

3.8. Performance in Drilling Fluid

The above experiments show that MMH-3 has the best inhibitory properties. Since MMH is an inorganic type of treatment agent, this experiment investigated the temperature resistance of MMH by evaluating the effect of MMH on the rheology of drilling fluid. The rheological properties of MMH water-based drilling fluid after hot rolling aging tests at different temperatures are shown in Table 2.

Table 2. Drilling fluid performance of MMH-3 treatment at different temperatures.

MMH Dosage (%)	Temperature (°C)	PV (mPa·s)	YP (Pa)	AV (mPa·s)	YP/PV (Pa/mPa·s)	FL (mL, 7.5 min)
0.0	30	3.00	0.00	3.00	0.00	16.5
0.3		3.25	1.00	4.25	0.31	16.2
0.0	150	3.00	0.25	3.25	0.08	18.4
0.3		3.25	0.75	4.00	0.21	21.5
0.0	180	3.00	0.00	3.00	0.00	20.1
0.3		4.00	0.75	4.75	0.18	23.3
0.0	190	3.25	0.25	3.50	0.08	22.3
0.3		3.50	1.00	4.50	0.29	24.2
0.0	200	3.00	0.00	3.00	0.00	24.5
0.3		4.00	1.00	5.00	0.25	15.5

As can be seen from Table 2, 0.3% of MMH-3 at 150 °C increased the drilling fluid YP from 0.25 to 0.75 and the YP/PV from 0.08 to 0.21; 0.3% of MMH-3 at 180 °C increased the drilling fluid yield YP from 0 to 0.75, and the yield point and YP/PV from 0 to 0.18; 0.3% of MMH-3 at 190 °C increased the YP from 0.25 to 1.00 and the YP/PV from 0.08 to 0.29; 0.3% of MMH-3 increased the drilling fluid YP from 0.25 to 1.00, and the yield point and the YP/PV from 0.08 to 0.29; and 0.3% of MMH-3 at 200 °C increased the drilling fluid YP from 0 to 1.00 and the YP/PV from 0 to 0.25. Combined with the suitable addition amount selected in the inhibition evaluation of MMH-3, the effects of temperature on the yield point and YP/PV are presented in Figure 9. The results indicate that MMH has good temperature resistance and can improve the YP and YP/PV.

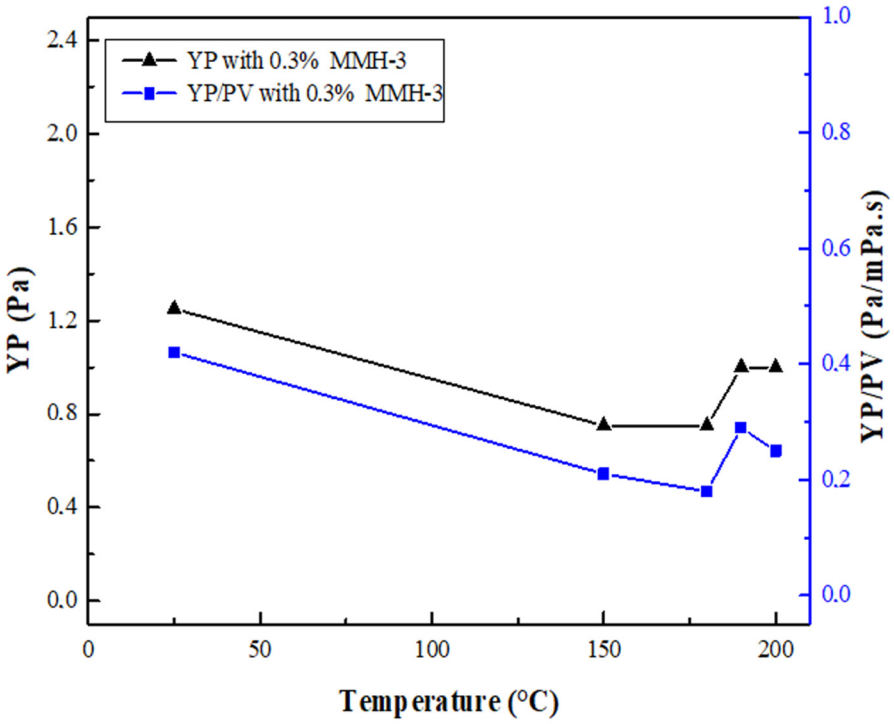

Figure 9. Effect of temperature on the drilling fluid YP and YP/PV with 0.3% MMH-3.

3.9. Mechanism Discussion

MMH has a strong ability to inhibit the hydration expansion and dispersion of bentonite. Meanwhile, MMH has good temperature resistance, which can improve the yield point of drilling fluid. MMH has a hydrotalcite-like structure. During the formation process, the Mg^{2+} in brucite is replaced by an Al^{3+} isomorph, the crystal structure does not change, and a magnesium–aluminum hydroxide octahedral structure layer is formed. This structure layer is a hydrotalcite-like structure, with a unit crystal layer of hydrotalcite. Hydrotalcite is a type of one-sided brucite-like surface-overlapping structure, as shown in Figure 10.

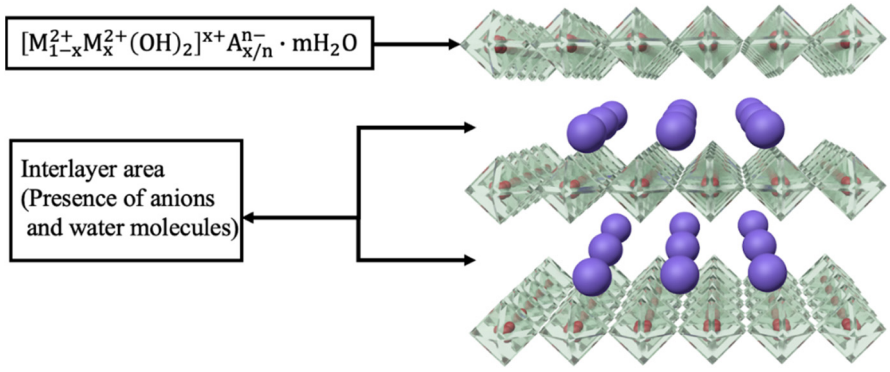

Figure 10. MMH crystal structure diagram.

As shown in Figure 11, the expansiveness of bentonite is strongly related to the montmorillonite content. Montmorillonite is composed of a lattice of aluminum octahedrons and silicon oxygen tetrahedra. The constant negative charge of the montmorillonite layer arises due to the isomorphic replacements of Al^{3+} by Fe^{2+} or Mg^{2+} in octahedrons, and/or as a result of isomorphic Si^{4+} replacement by Al^{3+} in tetrahedrons [25]. When bentonite is dispersed in water, charged particles will form. A negative outer edge will form around the particles; this is due to the hydration film formed on the surface of the bentonite particles,

caused by the electrical property. The repellent effect of hydration film disperses bentonite particles. MMH particles have a higher positive charge, while the surface of bentonite has a negative charge. Therefore, MMH adsorbs on the surface of bentonite and prevents water molecules from entering the interlayer of bentonite, as shown in Figure 12, thus inhibiting the hydration and dispersion of bentonite.

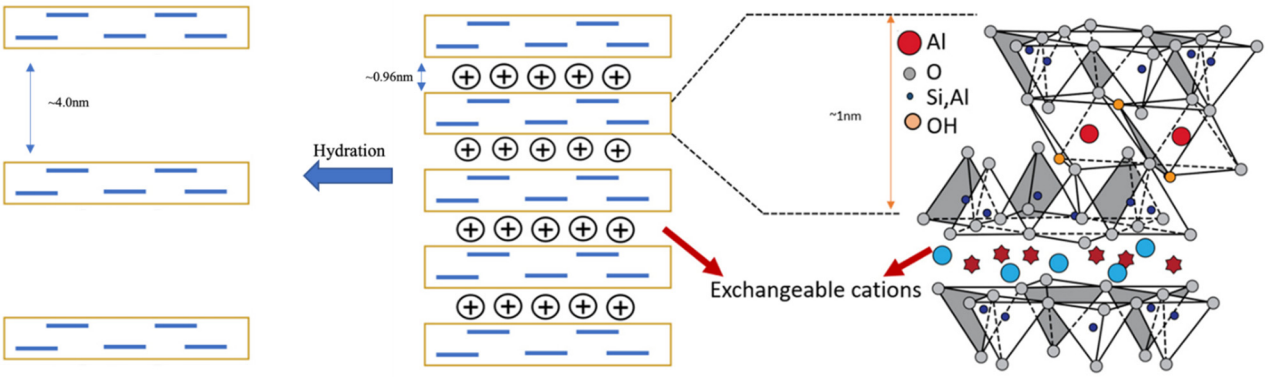

Figure 11. Structure of montmorillonite.

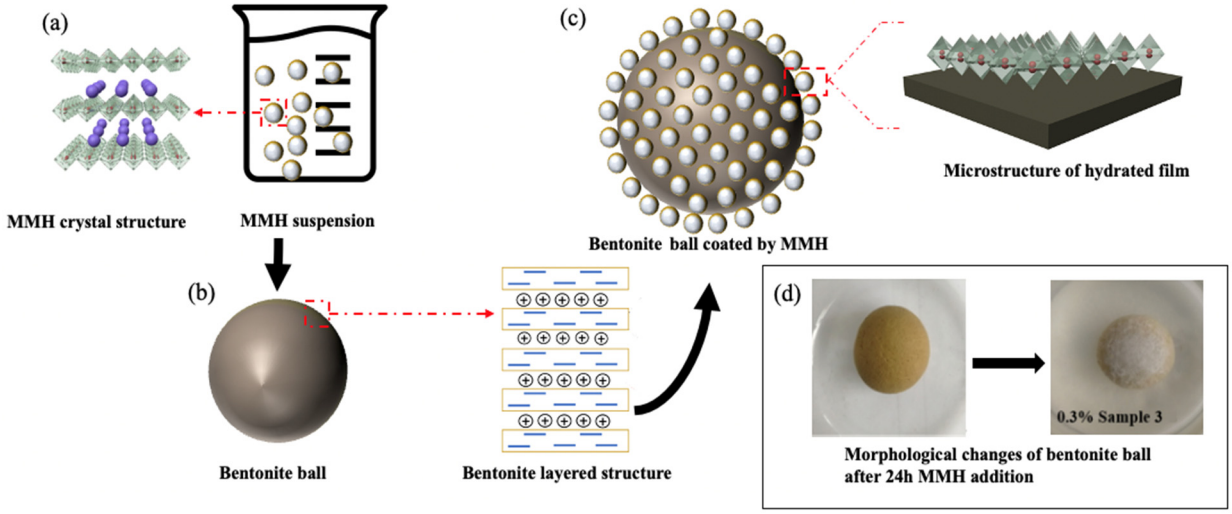

Figure 12. Principle of action of the MMH inhibitor: (**a**) crystal structure of MMH in water, (**b**) bentonite-layered structure, (**c**) microstructure of hydrated film and (**d**) morphological changes of the bentonite ball after 24 h of MMH addition.

4. Conclusions

Considering the results of the experiments above, the Mg-Al ratio had a strong influence on the results of the synthesis of MMH. According to the experiment results, the crystallinity and layer structure of MMH synthesized with a Mg:Al ratio of 3:1 was more complete. In addition, its X-ray diffraction peaks were more consistent with the characteristic peaks of hydrotalcite. The inhibition of MMH-3 at a concentration of 0.3% was proven to be the best, displaying a significantly better inhibitory effect than the 4% KCl solution. Similarly, MMH with a larger Mg-Al ratio inhibited bentonite hydration and dispersion more effectively. Meanwhile, with its more pronounced reticular structure, temperature resistance and improved viscosity, the MMH with a larger Mg-Al ratio displayed a better performance. After hot rolling at 200 °C for 16 h, MMH still displayed a good effect on the reduction of the PV and improvement of the YP of drilling fluid. Consequently, when synthesizing MMH, the ratio between Mg and Al had a greater impact on the properties of the final product.

Author Contributions: Data curation, investigation, writing—original draft. B.Z.; Formal analysis, data curation. Q.W.; Investigation, software. Y.W.; Data curation, validation. W.W.; Formal analysis, investigation. W.D.; Supervision, validation, project administration. J.Z.; Methodology, project administration, funding acquisition, writing—review and editing. G.C.; Investigation, formal analysis, supervision, writing—review and editing. M.S. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available on request from the corresponding authors.

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