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THE INFLUENCE OF SALT IONS ON THE BOUND WATER IN THE MONTMORILLONITE

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ABSTRACT

The content of bound water in the montmorillonite soaked in NaCl solution is measured by thermogravimetric analysis. The variation of NaCl solution concentration and bound water content is discussed. The results show that the bound water content of the montmorillonite decreases with the increase of salt ion concentration. The experimental drying temperature and heating rate has little effect on the bound water content. It is concluded that ions have a great influence on the water content in porous media, which provides guidance for the research on the influence of ions on the formation of hydrate in porous media.

Keywords: methane hydrate, porous media, montmorillonite, ion, bound water

1. INTRODUCTION

The behavior of hydrate formation in porous sediment is important in the investigation of reservoirs and in the drilling of natural gas hydrate. The capillary force and the rock and fluid characteristics in the porous media have great influence on the phase equilibrium conditions of the hydrate formation [1-3]. Recently, the decomposition conditions of hydrate in artificial porous media, such as quartz sand, have been studied by experiment and simulation [4, 5]. Due to the complex physical and chemical properties of natural sediments and the diversity of the conditions, there are few studies on hydrate formation in natural porous media. As a kind of porous media, the montmorillonite has good characteristic on adsorption, hydration, expansion and plasticity. Meanwhile it's physical and chemical properties are similar to the deep-sea mud. The analysis of sea mud samples from South China illustrate that most areas contain more than 20% montmorillonite, and the samples of the land slope and the outer shelf in the west of DONGSHA contain more than 40% montmorillonite [6, 7]. As a result, the study on the formation of hydrate in montmorillonite is representative.

In addition, the water in the montmorillonite sample is made up of free water and bound water. With different structure and property in the hydration stage, the bound water can be divided into strong bound water and weak bound water. The presence of bound water in the montmorillonite has an impact on hydrate formation[8]. In the same time, the salinity of bound water affects directly the formation and decomposition of hydrate [9, 10]. The chemical composition and concentration of pore water in marine sediments not only affect the stability of marine natural gas hydrate[11], but also inhibit the hydration of the montmorillonite. Therefore, the investigation of the content of bound water in the montmorillonite with salt ions solution is of great significance to study the effect of ions on the formation of hydrate in porous media. In this work, the content of bound water in the montmorillonite soaked in NaCl solution is measured by thermogravimetric (TG) analysis. The discipline of bound water content which changes with the concentration of NaCl solution is discussed.

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2. EXPERIMENTAL SECTION

2.1 Materials

99.999% pure methane is supplied by Foshan MS Messer Gas Co., Ltd. and the 98% pure montmorillonite is supplied by American NANOCOR Company. The NaCl is supplied by Shanghai Aladdin Bio-Chem Technology Co., Ltd. with a purity of 99.8%.

2.2 Procedure

The montmorillonite is put into the NaCl solution of corresponding concentration. And the montmorillonite samples are sealed at the room temperature (25℃) for 48 hours to fully hydrate. The bottom montmorillonite samples are dried at a certain temperature until keep its weight constantly. Thermal decomposition of the bound water adsorbed on the montmorillonite is carried out in a thermal analysis-gas chromatography system (the STA 409 PC, which is produced by NETZSCH Scientific Instrument Trading Co., Ltd.) in a flowing nitrogen atmosphere. Approximately 20mg of samples were heated in an open crucible at a rate of 5.0 C/min up to 300 ℃.

3. RESULT AND ANALYSIS

3.1 Effects of salt solution on the bound water content in the montmorillonite

The montmorillonite is a kind of hydrated aluminosilicate, which is comprised of layers. Each layer formed by one central octahedral Al oxide layer sandwiched between two tetrahedral silicate layers, shown in Figure 1. Therefore, the clay is described as 2:1 hydrated aluminosilicate or TOT (tetrahedral octahedral tetrahedral) layer mineral. The TOT structure holds the net negative structural charge, which is balanced by the interlayer cation, such as Na^+ and Ca^{2+}. When the montmorillonite soaks in the pure water, some water intercalates in the interlayer of the montmorillonite due to differential concentration of the ions between the interlayer of the montmorillonite and the pure water solution. When the montmorillonite soaks in the NaCl solution, the differential concentration of the ions between the interlayer of the montmorillonite and the pure water solution decreased. Therefore, the expansion of the montmorillonite also decreased.

In this experiment, the montmorillonite samples soak in the different concentration NaCl solution， which concentrations are shown in Table 1. The montmorillonite samples are obviously expanded by soaking with the solutions, shown in Figure 2. In Figure 2, we can see the expansion of the montmorillonite decrease with the increase of the NaCl solution concentrations. It indicates that the salt solution have inhibit for the expansion of the montmorillonite.

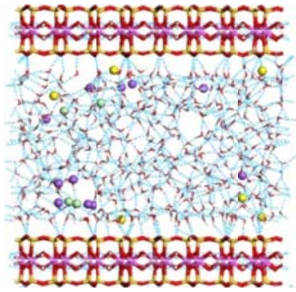

Fig 1 Configuration of the montmorillonite soaded by Nacl solution. Yellow sphere indicates Na+ ions in the montmorillonite; purple sphere indicates Na+ ions in the Nacl solution; green sphere indicates cl- ions in the Nacl solution; red stick and white stick indicate H_2O molecules, respectively; yellow stick and purple stick indicate Si and Al atoms of the montmorillonite molecule, respectively; the blue dashed line represents the hydrogen bounds

Tab 1 The weight loss rate and inflection point of the montmorillonite samples

Number	Sample	weight loss rattio（%）	inflection point（℃）
1	pure water	5.85	90.94
2	0.1mol/L NaCl	5.01	89.23
3	0.2mol/L NaCl	4.28	86.75
4	0.3mol/L NaCl	3.92	78.074
5	0.4mol/L NaCl	2.07	76.274
6	0.5mol/L NaCl	1.41	65.728

Fig 2 The montmorillonite samples soaked in the NaCl solution at the different concentrations

The montmorillonite samples are dried at 75 ℃ to remove the free water. And then, the lose weight of the bound water of the montmorillonite samples are measured by TG. Figure 3 shows the TG curves of the montmorillonite samples. In Figure 3, the mass of the montmorillonite samples reduces with the temperature increase. It indicates that the bound water of the montmorillonite is evaporated with the temperature increase. When the mass of the montmorillonite is no change, the bound water of the montmorillonite is completely dried. From Figure 3, we can see the mass of the bound water of the montmorillonite samples decreased with the increase of the salt solution concentration. In the montmorillonite, the combined action of hydrogen bound force and electrostatic attraction between the montmorillonite surface and the bound water cause the hydration effect. The salt ions have great influence on the balance of hydrogen bound between the montmorillonite surface and the bound water [12]. Therefore, the ability of the montmorillonite to binding water is affected by the salt ions. The higher concentration of the salt solution is the greater effect on the mass of the bound water of the montmorillonite. The dehydration temperature of the bound water in the montmorillonite decreased with the increase of the salt solution concentration. DTG curve is obtained by first derivative of TG curve. The inflection point temperature is the temperature at the peak on the DTG curve, which reflects the dry reaches the maximum reaction rate. In Figure 4 and Table 1, we can see the inflection point temperature decrease with the increase of NaCl solution concentration. It is concluded that the bound water content of the montmorillonite is affected by the salt ion concentration. However, the mass of the strongly bound water and weakly bound water in the montmorillonite samples are difficult to distinguish in this measure. The separation of the strongly bound water and the weakly bound water will be carried in the future work.

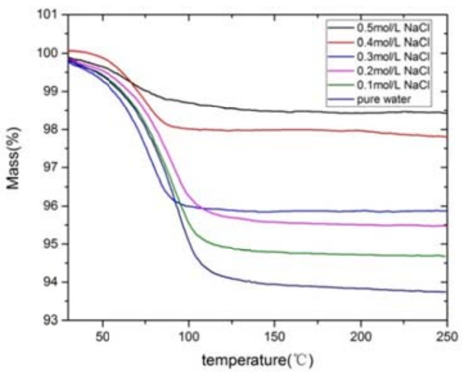

Fig 3 TG curves of the montmorillonite samples

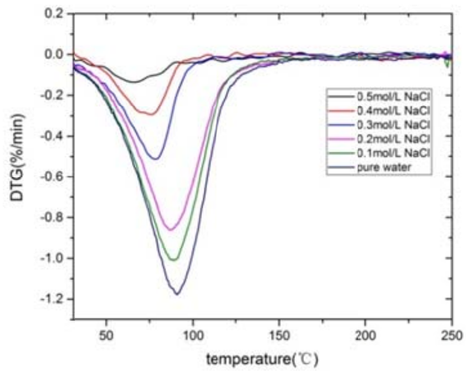

Fig 4 DTG curves of the montmorillonite samples

3.2 *Effects of different heating rates on removing bound water in the montmorillonite*

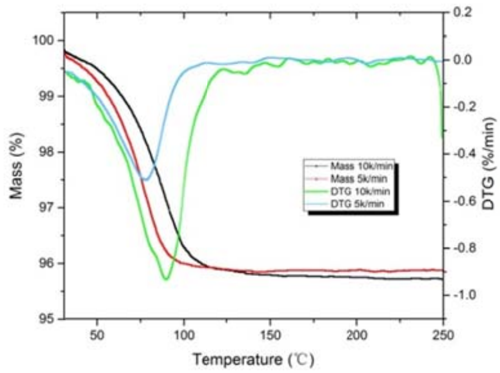

Fig 5 TG and DTG curves of the montmorillonite sample 4 with the different heating rates

Figure 5 shows the TG and DTG curves of the montmorillonite sample 4 with different heating rates. From Figure 5, we can see the inflection point temperature is lower at the heating rates of 5k/min than that at the heating rates of 10k/min. It indicates the temperature of removing the montmorillonite bound water decrease with the decrease of the heating rate. It is because the dehydration of the montmorillonite has a certain lag with the increase of the experimental temperature. On the other hand, it can be seen from Figure 5 the masses ratio of the montmorillonite samples after the dried temperature at 150℃ are coincidence. Therefore the heating rate has no effect on the content of bound water of the montmorillonite sample.

3.3 *Effects of the different drying temperatures on the content of the montmorillonite bound water*

The montmorillonite sample 1 and the montmorillonite sample 2 are dried at 75℃ and 50 ℃.

The measure results of TG on the two montmorillonite samples are shown in Table 2. It can be seen from Table 2, the weight loss rations of the montmorillonite are same with the different drying temperature. It means that the drying temperature has little effect on the contents measure of the bound water in the montmorillonite within a certain range.

Tab 2 Weight loss rate of the montmorillonite samples dried at the different temperatures

drying temp. (℃)	sample	weight loss ratio (%)
75	0.1mol/L NaCl	5.01
	pure water	5.85
50	0.1mol/L NaCl	4.92
	pure water	5.78

4. CONCLUSION

The montmorillonite samples soaked in sodium chloride solution are measured by TG. The effect of the concentration of the NaCl solution on the expansion of the montmorillonite is discussed. The results shows that the expansion of the montmorillonite on the different concentration of the ions between the interlayer of the montmorillonite and the pure water solution. The bound water content of the montmorillonite decreases with the increase of salt ion concentration. The experimental drying temperature and heating rate has little effect on the bound water content. It is concluded that ions have a great influence on the water content in porous media. The investigation provides guidance for the research on the influence of ions on the formation of hydrate in porous media.

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