The effect of interlayer cations on the expansion of vermiculite

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Three kinds of salt solutions including NaCl, CaCl2 and MgCl2 were used to modify the expansion of vermiculite. X-ray diffraction results indicate that vermiculites have been successfully modified by salt solutions. The d\(_{002}\) reflection spacings of Na-vermiculite, Ca-vermiculite and Mg-vermiculite corresponding to different salt solution modifications are 1.223 nm, 1.474 nm and 1.448 nm, respectively. Expansion ratio experiment results show that the as-obtained vermiculite modified by NaCl solution can lower the beginning expansion temperature, while the vermiculites modified by CaCl2 and MgCl2 solutions can show high expansion ratio. The combined thermogravimetric-differential thermal analysis and infrared spectroscopy analysis reveal that electrostatic attraction force between interlayer cations and interlayer water plays the key factor in the expansion ratio of vermiculite. Compared with Ca and Mg cations, the electrostatic attraction force between Na cation and interlayer water is weak and Na-vermiculite has less interlayer water than that of Ca-vermiculite and Mg-vermiculite.

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1. Introduction

Vermiculite can be expanded by several times in volume when heated rapidly due to the sudden release of interlayer water [1,2]. The expanded vermiculite has many remarkable physical and chemical properties, such as low density, good chemical stability, high cation exchange capacity and good adsorption ability, and so on [3–5], which lead to various application fields such as environmental protection, agriculture, building materials and chemical industry [6–13]. Generally speaking, industrial vermiculite and mineralogical vermiculite have different definition, and the latter generally refers to the biotectahedral or trioctahedral layered aluminum silicate mineral with 2:1 layers structure which has water molecular and exchangeable cations in the interlayer spacing. However, the industrial vermiculite is a kind of mineral aggregates composed of vermiculite and vermiculite mixed layer minerals. Actually, “Qeganbulak vermiculite” from Yuli, Xinjiang used in the present study is a kind of industrial vermiculite.

The expanded vermiculite is mainly prepared by three methods: chemical expansion method, microwave expansion method and high temperature calcination expansion method, respectively. For chemical expansion method, some activated reagents such as sulfuric acid, hydrochloric acid, nitric acid, phosphoric acid and hydrogen peroxide solution are usually used to exfoliate phyllosilicate, while hydrogen peroxide solution is the most commonly used one since it has the best expansion effect among them. When the vermiculite and hydrogen peroxide react, hydrogen peroxide molecule will exchange with interlayer water molecular and then decomposes, so that the vermiculite will be expanded [14]. It is also found that hydrogen peroxide concentration, reaction time, reaction temperature and solid–liquid ratios have great impact on the expansion process. As far as microwave expansion method is concerned, water molecular is firstly penetrated by high frequency electromagnetic microwave, and then it begins to vibrate with high-frequency and then collides with each other to produce friction heat, finally it leads to the expansion compared to the starting vermiculite [15,16]. In this method the expansion behavior of vermiculite is mainly affected by microwave heating time and microwave power [17]. High temperature calcination expansion method can be described that the interlayer water quickly converts into steam when vermiculite is placed in high temperature furnace, and then the formed high vaporization pressure exfoliates promptly from the interlayer of the vermiculite [18–23].

Interlayer water molecular is partly attracted by interlayer cations because of the electrostatic attraction force, and the attracted interlayer water plays a key role in the expansion properties. One kind of vermiculite often contains various interlayer cations, which show different electrostatic attraction force with interlayer water, so that the interlayer water molecular escapes from the interlayer cations in turn and further vaporizes gradually when the vermiculite is heated at high temperature. Therefore the sudden expansibility cannot be expected. In this study, the interlayer cations in vermiculite are unified through salt solution modification in order to obtain good expansibility, furthermore the effect of different interlayer cations on the expansion of vermiculite expansion is also studied in detail.
2. Experimental

2.1. Sample preparation

In this study, three kinds of industrial vermiculite samples with different compositions were collected from “Qeganbulak vermiculite” deposit, Yuli, Xinjiang, which were labeled as XJ-1, XJ-2 and XJ-3, corresponding to original particle size of 0.3–1.0 mm, 0.7–2.0 mm and 1.4–4.0 mm, respectively. All the samples were treated by grinding and sifting to get the vermiculites samples with the same particle size range of 0.5–1.0 mm and later were dried at 60 °C for 48 hours.

As typical experimental process for the preparation of Na-vermiculite (Ca-vermiculite and Mg-vermiculite) is as follows, 25 g vermiculite sample (such as XJ-1) was firstly washed by distilled water for three times, then 250 ml NaCl (CaCl2 and MgCl2) solution with the content of 20 g/L were mixed with the washed vermiculite sample in a conical flask for modification. The mixture were stirred for 4 hours at 25 °C and then centrifuged with supernatant replaced by fresh NaCl (CaCl2 and MgCl2) solution. This modification was carried out twice. After modification, vermiculites were washed again with distilled water and then dried at 60 °C for 48 hours. Na-XJ-1(Ca-XJ-1 and Mg-XJ-1) was finally obtained. The same modification method was used for the preparation of Na-XJ-2(Ca-XJ-2 and Mg-XJ-2) and Na-XJ-3 (Ca-XJ-3 and Mg-XJ-3).

2.2. Characterizations

X-ray diffraction (XRD) was obtained on a Rigaku Dmax 12 KW diffractometer with CuKα radiation, 40 kV, 100 mA and a scanning speed of 4.0° (2θ)/min from 2.5 to 30°. Thermogravimetric-differential thermal analysis (TG-DTA) was performed on a TA Q600 instrument at a certain speed of 4.0° (2θ)/min from 2.6 to 30°. Thermogravimetric-differential thermal analysis (TG-DTA) was performed on a TA Q600 instrument with heating temperature range from 25 to 1200 °C and heating rate of 20 °C/min under air atmosphere. Fourier-transform infrared spectroscopy (FTIR) was recorded by PerkinElmer spectrum100 infrared spectroscopy.

2.3. Expansion ratios test of vermiculite

A certain volume of vermiculite was rapidly put in the burning evaporating dish in a muffle furnace. After sintering for 3 minutes at a fixed temperature, the vermiculite was removed away and cooled to room temperature. The expansion ratio were measured by the following formula $K = \frac{V}{V_0}$ and $V_0$ represents the volume of vermiculite before expansion; $V$ represents the sample volume after expansion. $K$ represents the measured expansion ratio.

3. Results and discussion

3.1. XRD analysis

The compositions of vermiculite from “Qeganbulak vermiculite” deposit, Yuli, Xinjiang, have been studied and found that the studied vermiculite contains two kind of mixed-layer vermiculite-mica mixed minerals, Hy-a and Hy-b, in which Hy-a contains 60/40 vermiculite/mica (6:4 layer) and Hy-b contains 40/60 vermiculite/mica (4:6 layer). As shown in Table 1, it shows that XJ-1, XJ-2 and XJ-3 have the same phase compositions but different relative content. Vermiculite content and mixed layer minerals content are both negatively correlated with the content of phlogopite. All the three samples have few vermiculite content, with the highest content of 5.8% in XJ-1 and large mixed-layer minerals content ranging from 59.4% to 71.6%.

Vermiculite is typically formed by mica through hydrothermal alteration or weathering, so that the smaller the particle size is, the more complete the hydrothermal alteration or weathering of mica is, therefore high content of vermiculite and mixed-layer minerals will obtain.

XJ-1 sample and its corresponding modified sample were investigated by XRD to make sure the modification effect. Fig. 1 gives the XRD patterns of XJ-1 and its salt-modified samples. As shown in Fig. 1, the observed diffraction lines for XJ-1 at 1.223 nm, 1.114 nm and 1.012 nm correspond to the (002) reflection of vermiculite, (002) reflection of mixed-layer mineral and (001) reflection of mica, respectively. After modification treatment, the diffraction peaks of the mixed layer minerals and vermiculite split and become sharper and its intensity become stronger than those of the original sample. However, no obvious change can be observed for mica in the XRD pattern. For example, through NaCl modification, the diffraction peak at 1.114 nm for the mixed layer mineral splits into 1.137 nm and 1.104 nm, which are corresponding to Hy-a and Hy-b, respectively. The d-spacing 1.223 nm of vermiculite corresponding to (002) reflection decreases to 1.214 nm due to the substitution of interlayer Na+ cations (Fig. 1, Na-XJ-1). Through CaCl2 modification, the diffraction peak at 1.114 nm for the mixed layer mineral splits into 1.251 nm and 1.211 nm corresponding to Hy-a and Hy-b, respectively. While the d-spacing 1.223 nm of vermiculite (002) reflection increases to 1.474 nm which is associated with the replacement of interlayer Ca2+ cations (Fig. 1, Ca-XJ-1). Similarly, after MgCl2 modification, the peak at 1.114 nm splits into 1.251 nm (Hy-a) and 1.200 nm (Hy-b), and the d-spacing 1.223 nm increases to 1.448 nm owing to the substitution of interlayer Mg2+ cations (Fig. 1, Mg-XJ-1).

After modification, various interlayer cations of vermiculite and mixed layer minerals are replaced by uniform cation (such as Na+, Ca2+ or Mg2+) and the structural unit thickness for the modified vermiculite tends to identical. Therefore, the crystal structure of the as-obtained product is more periodic and the crystallinity is higher than that of the original vermiculite and mixed layer minerals. Consequently the observed diffraction peaks becomes sharp and the intensity becomes strong as mentioned above. Compared to Ca and Mg, the electrostatic attraction force between Na cation and interlayer water is relatively weak. Therefore, Na-vermiculite has a monomolecular
layer of water while both Ca-vermiculite and Mg-vermiculite have two monomolecular layer of water, suggesting that interlayer spacing of Na-vermiculite is smaller than that of Ca-vermiculite and Mg-vermiculite. Furthermore, Ca-vermiculite interlayer spacing is larger than that of Mg-vermiculite since the ionic radius of Ca is larger than that of Mg.

3.2. Expansion ratio tests

Fig. 2 gives the expansion ratio of XJ-1, XJ-2 and XJ-3 at different temperature, respectively. It is found that the expansion ratios of XJ-1, XJ-2 and XJ-3 are larger at high temperature (Fig. 2) and all the three samples have low content of vermiculite but high content of mixed layer minerals (Table 1). Herein, we conclude that the expansion capacity is mainly affected by the mixed layer minerals. As shown in Fig. 2, the expansion ratio of XJ-1 is close to that of XJ-2, and both of them are obviously larger than that of XJ-3. As also shown in Table 1, the Hy-a content of XJ-1 is close to that of XJ-2, and obviously larger than that of XJ-3. From these comparative data, it can be speculated that expansion capacity is mainly determined by mixed-layer mineral Hy-a rather than Hy-b.

Fig. 3 shows the expansion ratios of different salt solution modified samples of XJ-1, XJ-2 and XJ-3 at different temperature, respectively. It can be found that the modification treatment by NaCl solution can lower the onset expansion temperature of vermiculite, the NaCl modified vermiculite display good expansion effect at low temperature (500 °C). However, the modification treatment by CaCl₂ and MgCl₂ solutions can improve vermiculite expansion ratio obviously compared to the original vermiculite samples, as given in Fig. 3.

The increased percentage of expansion ratio is calculated by following formula:

\[ K\% = \left( \frac{K_{m-v} - K_v}{K_v} \right) \times 100 \]  

(1)

Where \( K\% \) represents the increased percentage of expansion ratio; \( K_{m-v} \) represents the expansion ratio of modified vermiculite; \( K_v \) represents the expansion ratio of the original vermiculite without modification. From the above Fig. 3, the calculated results are shown in Table 2. Furthermore, the relationships between expansion temperature and \( K\% \) of Na-vermiculite, Ca-vermiculite and Mg-vermiculite are depicted in Fig. 4 for a comparison.

As shown in Table 2 and Fig. 4(A), it can be found that modification of NaCl solution significantly increases the vermiculite expansion ratio at low temperature, such as 500 °C. The \( K\% \) values at 500 °C for Na-XJ-1, Na-XJ-2 and Na-XJ-3 are 78.57%, 20.00% and 35.71%, respectively.

Table 2 and Fig. 4(B) show the modification effect of CaCl₂ solution on vermiculite. It is found that the \( K\% \) of Ca²⁺ modified samples increases with the increase of operating temperature and becomes stable at 700–1000 °C. It can be explained by two stages, the first stage
from 500 to 600 °C and the second from 700 to 1000 °C. CaCl₂ solution modification treatment fails to improve vermiculite expansion ratio at first stage. K% at 500 °C of Ca-XJ-1, Ca-XJ-2 and Ca-XJ-3 are reduced by 28.57%, 33.33% and 28.57%, respectively. K% increases with increasing expansion temperature in the range of 700–1000 °C. At 900 °C K% of Ca-XJ-1, Ca-XJ-2 and Ca-XJ-3 are 16.22%, 18.42% and 15.63%, respectively, and further increase to 17.50%, 20.51% and 15.63%, respectively, at 1000 °C. So it can be concluded that modification of CaCl₂ solution on vermiculite has a good effect at 900 and 1000 °C.

Similarly results can be obtained from the MgCl₂ solution modified vermiculite samples. As shown in Table 2 and Fig. 4(C), the expansion process can also be divided into two stages, from 500 to 700 °C and from 800 to 1000 °C. At the second stage, K% increases with the increase of expansion temperature and modification of MgCl₂ solution on vermiculite also has a good effect to its expansion behavior.

On the basis of the above results, three samples of XJ-1, XJ-2 and XJ-3 with different relative composition have similar expansion tests results by different modification reagents, such as NaCl, CaCl₂ and MgCl₂ solutions. It is believed that the present conclusion can be accepted and widely used. Therefore, the possible mechanism on the effect of the expansion of vermiculite can be expected. Usually, there are various interlayer cations except for Na⁺, Ca²⁺ and Mg²⁺ in the interlayer of the original vermiculite. Interlayer cations can be replaced by other cations through ions’ exchange. Na-vermiculite, Ca-vermiculite and Mg-vermiculite are often produced by salt solution modification, as presented in this study. Na-vermiculite with single Na cation in the interlayer displays good expansion property at low temperature since it has monomolecular layer of water and the electrostatic attraction force between Na cation and interlayer water is weak, which makes it easy to lose water molecular at low temperature. However, both Ca-vermiculite and Mg-vermiculite have two monomolecular layers of water and the electrostatic attraction force between Ca or Mg cations and interlayer water are strong, so that the two kinds of vermiculites have large expansion ratio and high expansion temperature.

Fig. 5 reveals the possible ions’ exchange process of the present modification experiments for vermiculites. In the interlayer structure of vermiculite, many cations, such as Na⁺, Ca²⁺, Mg²⁺, [Na(H₂O)₃]⁺, [Ca(H₂O)₆]²⁺, [Mg(H₂O)₆]²⁺ and H₂O moleculars are adsorbed in the interlayer spacing. As an example, when vermiculite is modified by MgCl₂ solution, the following reaction can be formed:

\[ X - \text{vermiculite}(s) + MgCl₂(l) \xrightarrow{25 \degree C, 4 h} Mg - \text{vermiculite}(s) + XCl_n(l) \quad (2) \]

For scheme(2), X represents the possible interlayer cations, such as Na⁺, Ca²⁺ or other cations, n represents charge number of X. Vermiculite interlayer cations are unified after cation exchange process and Mg-vermiculite is obtained with interlayer spacing increasing from 1.223 nm to 1.448 nm. Mg-vermiculite is further calcited at high temperature with the following reaction:

\[ Mg - \text{vermiculite} \xrightarrow{\text{high temperature}} Mg - \text{vermiculite} + H₂O(g) \quad (3) \]
For scheme (3), the interlayer water vaporizes simultaneously and the formed high vaporization pressure promptly exfoliates vermiculite when vermiculite is calcited, so that the expanded vermiculites are produced. After this expansion process vermiculite interlayer spacing increases from 1.448 nm to larger sizes depending from different expansion temperature.

### 3.3. TG-DTA analysis

In order to further understand the effect of interlayer cations on the expansion of vermiculite, TG-DTA and FTIR measurements were used to verify the expansion process of the vermiculite. It is accepted that there are two kinds of interlayer water in the layer of the vermiculite, the bounded water and the free water. DTA curves of XJ-1 and its modified samples are shown in Fig. 6(A). All DTA curves can be divided into three stages. The first stage is from 30 to 200 °C corresponding to the releasing of the interlayer water, and the second stage from 200 to 800 °C has no obvious heat effect, finally the third stage from 800 to 1200 °C will lead to the releasing of the structure water releasing and the collapse of the crystal structure. Endothermic valleys at 86 °C for four samples are associated with the releasing of free water, and the weak valleys near 187 °C correspond to interlayer bounded water releasing temperature. As also given in the TG curves (Fig. 6(B)), the interlayer free water and bounded water molecular release completely when the samples are heated at 200 °C. The total mass loss for the interlayer water of XJ-1, Na-XJ-1, Ca-XJ-1 and Mg-XJ-1 are 4.70%, 3.57%, 5.88% and 5.43%, respectively. Na-vermiculite has least water content as it has monomolecular layer of water. Ca-vermiculite and Mg-vermiculite have more water content as they have two monomolecular layer of water as mentioned above.

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**Fig. 5.** Ions’ exchange of vermiculite modification and its expansion process.

**Fig. 6.** DTA (A) and TG (B) curves of XJ-1 and its modified samples.

**Fig. 7.** FTIR curves of XJ-1 and its modified samples.
Vermiculite without modification has moderate content water as it has different interlayer cations with the interlayer water between one and two layers.

3.4. FTIR analysis

Fig. 7 shows the FTIR curves of XJ-1 and its modified samples. The band at 3716 cm⁻¹ is attributed to O—H stretching vibration of Mg₃OH (or Mg₂FeOH) groups corresponding to phlogopite. The bands at 3436 cm⁻¹ and 1646 cm⁻¹ are due to the stretching vibration and bending vibration of the interlayer water, respectively. At 1429 cm⁻¹ there is a band ascribed to CO₃ stretching vibration of calcite. Other bands are observed at 990 cm⁻¹ and 685 cm⁻¹ corresponding to strong absorption region and weak absorption region of Si-O (or AlIV-O) stretching vibration, respectively. Those bands at 3436 cm⁻¹ of original vermiculite without modification and Na-vermiculite are relatively weak means they have less water molecular in the interlayer. Comparatively, the bands at 3436 cm⁻¹ of Ca-vermiculite and Mg-vermiculite are strong, suggesting that they have more water in the interlayer. These above results are also consistent with that of TG-DTA analysis.

4. Conclusions

Vermiculites have been successfully modified by NaCl, CaCl₂ and MgCl₂ solutions, and the single cation exchanged Na-vermiculite, Ca-vermiculite and Mg-vermiculite are obtained. Electrostatic attraction force between interlayer cations and interlayer water play the key role in the expansion behavior of the vermiculite. Na-vermiculite has a monomolecular layer of water while both Ca-vermiculite and Mg-vermiculite have two monomolecular layer of water, suggesting that interlayer spacing of Na-vermiculite is smaller than that of Ca-vermiculite and Mg-vermiculite. Expansion ratio experiment results show that the as-obtained vermiculite modified by NaCl solution can lower the beginning expansion temperature, while the vermiculites modified by CaCl₂ and MgCl₂ solutions can show high expansion ratio. The combined thermogravimetric-differential thermal analysis and infrared spectroscopy analysis reveal that electrostatic attraction force between interlayer cations and interlayer water plays the key role in the expansion ratio of vermiculite. The possible ions' exchange and expansion process of vermiculite modification have also been discussed.

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