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Structural evolution of kaolinite in muddy intercalation under microwave heating

Qijun Hu, Qin Yong, Leping He, Yucheng Gu and Junsen Zeng

1 School of Civil Engineering and Geomatic, Southwest Petroleum University, Chengdu 610500, People’s Republic of China
2 School of Geoscience and Technology, Southwest Petroleum University, Chengdu 610500, People’s Republic of China
3 School of Mechatronic Engineering, Southwest Petroleum University, Chengdu 610500, People’s Republic of China

E-mail: 201231010028@swpu.edu.cn

Abstract

The failure of muddy intercalation in the slope is mainly due to the clay minerals which mainly contains the kaolinite. This study investigates the structural evolution of kaolinite in muddy intercalation exposed to the microwave heating of 300 °C–800 °C by evaluating the uniaxial compressive strength, morphology, mineralogical composition, and water stability. Results show that the crystal structural evolution of kaolinite can be divided into four stages, which are 300 °C–400 °C, 400 °C–500 °C, 500 °C–700 °C, and 700 °C–800 °C. The kaolinite undertakes the thermal expansion, dehydroxylation-induced crack, kaolinite-metakaolinite transition, and two-step transition of metakaolinite - silica spinel (γ-alumina) - mullite. The mechanical performance increasing consists of three stages. At 300 °C–400 °C, the uniaxial compressive strength increases about 38.7% due to thermal expansion. At 400 °C–700 °C, the uniaxial compressive strength is unchanged due to the balance between the positive side due to thermal expansion and semi-liquid metakaolinite and the negative side due to the dehydroxylation-induced crack propagation. At 700 °C–800 °C, the re-increase of 35.8% is mainly due to the two-step transition of metakaolinite-silica spinel (γ-alumina)-mullite. Water leaching test shows that the kaolinite over 500 °C present well integrity.

1. Introduction

The muddy intercalation is a type of weak thin layer between the hard and soft layers in the slope [1]. It mainly consists of clay minerals which takes account for 60–70 wt%, including kaolinite, mullite [2–4]. Accompanying the porous structure, the muddy intercalation’s low mechanical performance and poor water resistance usually induce structural failure to cause the landslide [5–7]. The industry has been sought for approaches to replace the conventional grouting and roasting methods due to their unknown penetrating path and low reinforcing efficiency. Microwave heating treatment is efficient and environmental-friendly reinforcing method for muddy intercalation.

To prevent the landslides, the reinforcement can be summarized into two types: (1) improving the whole slope structure, e.g., anti-slide piles and retaining walls; (2) directly reinforcing the muddy intercalation, e.g., grouting method [8, 9] and roasting method. The grouting method reinforces the muddy intercalation by injecting the cement mortar into the pores and fracture to cohesive the loose particles. Although the grouting method advantages in the cost and raw materials, the reinforcement effect is guaranteed due to the complex pore and fracture structure. The metakaolinite predominated in cement mortar presents good cohesion in water conditions [10–12]. The kaolinite transforms into the metakaolinite over 600 °C [13]. Therefore, it is necessary to find efficient and environmental-friendly approaches to heat the muddy intercalation and drive the kaolinite to transform into metakaolinite.

The conventional heat treatment indeed reinforces the muddy intercalation [14, 15]. However, its operation is hard to introduce into the slope reinforcement. Microwave heating is widely applied to the materials heat
treatment which advances in its selective, efficient, uniform, and environmental-friendly heating. In our previous study, microwave heating is proved a potential and efficient method to reinforce the muddy intercalation [16]. The XRD results revealed the kaolinite transformed into metakaolinite. However, it fails to rule out the influence of other components. To promote the microwave heating into reinforcing more types of muddy intercalation, it is necessary to study the structural evolution of kaolinite under microwave heating.

This work emphasizes the structural evolution of kaolinite in muddy intercalation under microwave heating. The individual kaolinite samples are heated by microwave heating. The macro- and meso-morphologies, crystal phases, mechanical performance, and water stability are characterized in detail by scanning electronic microscopy, x-ray diffraction, uniaxial compression test, and leaching experiment, respectively.

2. Material and methods

2.1. Material properties and specimen preparation

The raw kaolinite powder sample was provided by the Chengdu Hongyun Chemical Co.Ltd, Sichuan, China. The elemental composition is identified by x-ray fluorescence spectroscopy, as listed in Table 1. The crystal phases are measured by x-ray diffraction, which comprises 85.0 wt% kaolinite, 7.4 wt% illite, and 7.6 wt% quartz (Figure 3). Specimens preparation follows the GB/T50123-2019 that: first, dry sample of 178 g was ground to 200 mesh and mixed with deionized water at a mass ratio of 1:0.2; then, remolded sample ware compacted with a 2.0 MPa pressure to the cylindrical specimen with a 50 mm diameter and 50 mm height; finally, the specimen was sealed with plastic wrap.

2.2. Microwave instrument and experimental design

A 2.45 GHz microwave instrument was employed, as shown in Figure 1. It comprises a single magnetron tube, BJ-26 waveguide, metal-clad cavity, water coolant, control system and power supply, alumina for thermal insulation, and infrared thermometer. The microwaves are generated from the magnetron tube, then propagate through the waveguide, and finally entered the cavity. The microwave power level is adjustable from 0.25 to 1.40 kW based on the preset temperature curve. The range of the infrared thermometer is 0 °C–1000 °C with an accuracy of ±1 °C. Regarding the microwave experimental design, the target temperatures were preset to cover
the interval 300 °C–800 °C at 100 °C increments. Note that each group contained three specimens for comparison, e.g., a total of 18 specimens were treated. Besides, only one specimen was exposed to microwave in each experiment. The kaolinite specimen was heated to the target temperature with a heating rate of 4 °C min\(^{-1}\) and held for 30 min. Then, the power supply was shut down, and the specimen was cooled to room temperature in the cavity.

2.3. Characterization
To comprehensively analyze the mineralogical composition, micromorphology, and mechanical performance of kaolinite after microwave heating, the characterization covered the x-ray diffraction (XRD), scanning electronic microscopy (SEM), uniaxial compressive test, and leaching test in water. The XRD was measured by a Netherlands X'Pert PRO XRD instrument with Cu-K\(\alpha\) heating (\(\lambda = 1.54184 \text{ Å}\)). The XRD patterns were recorded at 2\(\theta\) values ranging between 3 and 80° at a 2° min\(^{-1}\) scanning rate. Subsequent analysis of the XRD data was performed using JADE software. The micromorphology was observed by a ZEISS EVO MA15 SEM instrument with 15 kV accelerated voltage, 50 Ma emission current, and 10 mm working distance. A total of 21 specimens were carried out in the uniaxial compressive test. It was employed by an MTS SHT4106 computer controlled electro-hydraulic servo pressure testing machine with a constant loading rate of 0.005 mm s\(^{-1}\). Regarding the leaching test, the specimen fragments were soaked in deionized water for 48 h to evaluate its structural integrity.
3. Results

3.1. Physical properties after microwave heating

Figure 2 exhibits the morphology of kaolinite after microwave heating. The color of kaolinite keeps in faint yellow after microwave heating, where the grey film attached on the specimen surface at 300 °C is identified as the residual wax during the preparation. We further measured the mass loss of specimens after microwave heating, as shown in Figure 2. It can be summarized into three stages: (i) the interlayer water loss at 300 °C–400 °C; (ii) the dehydration of kaolinite at 400 °C–600 °C; (iii) the formation of mullite at 600 °C–800 °C.
$7.5\%$; (ii) the dehydroxylation of kaolinite at $400\,^\circ\text{C}–600\,^\circ\text{C} (6.8\%)$; and (iii) the transition from metakaolinite to the mullite at $600\,^\circ\text{C}–800\,^\circ\text{C} (2.15\%)$.

### 3.2. Mineralogical composition

Figure 3 shows the XRD patterns of kaolinite before and after microwave heating. The kaolinite diffraction peaks’ intensity reduces at $300\,^\circ\text{C}–400\,^\circ\text{C}$ owing to the dehydroxylation of kaolinite transferring to amorphous metakaolinite. Subsequently, it further reduces because the layer structure of kaolinite fails at $500\,^\circ\text{C}$. With the temperature in excess of $600\,^\circ\text{C}$, the diffraction peaks of kaolinite vanish while the amorphous metakaolinite content is almost unchanged. Meanwhile, the mullite peaks occur which reveals the transition from metakaolinite to the mullite. This transition continuously runs at $600\,^\circ\text{C}–800\,^\circ\text{C}$.

### 3.3. Micromorphology

Figure 4 presents the micromorphology of kaolinite after microwave heating at different magnifications. As shown in figure 3(a), the kaolinite at $400\,^\circ\text{C}$ absorbs numerous tiny particles on the surface. Higher magnifications illustrate that the kaolinite maintains the layer structure at $400\,^\circ\text{C}$. Brigatti et al. declared that this temperature enlarges the kaolinite lattice which present heat expansion on macroscopy. However, it fails to induce the phase transition. The SEM images at $600\,^\circ\text{C}$ show that the layer structure was destroyed. Although the dehydroxylation destroys the aloxy octahedron, the silicon tetrahedron still maintain the layer structure.

Figure 6. Water stability of kaolinite before after microwave heating
3.4. Mechanical performance

Figure 5 illustrates the mechanical performance enhancement of kaolinite after microwave heating. The virgin specimen without microwave heating fails to measure the uniaxial compressive strength. However, the microwave heating significantly promotes its mechanical resistance. The values at 300 °C–800 °C are fitted in Origin Pro 2020 by the quintic polynomial with a good correlation coefficient of 1.00. The enhancement can be divided into three stages. In the first stage (300 °C–400 °C), the uniaxial compressive strength increases from the 1.6 MPa to 2.2 MPa, which is about 37.4%. In the second stage (500 °C–700 °C), the mechanical performance keeps in constant of 2.2–2.5 MPa. In the third stage, the uniaxial compressive strength increases further to 3.3 MPa at 800 °C, which is about 35.8%.

3.5. Water stability

Figure 6 shows the leaching test results of kaolinite before and after microwave heating. The virgin specimen fails to maintain structural integrity just in few minutes. The microwave heating apparently promotes the water stability of kaolinite. Although the partial softening is observed at the edge of the specimen, the kaolinite structure exposed to 300 °C–400 °C still keeps integrity well in the test time. It should be noted that some powders are also found in the deionized water. No collapse and powders are found when the temperature exceeds 500 °C–800 °C.

4. Discussion

4.1. Structural evolution

Kaolinite is a 1:1 layered structure of dioctahedral silicate mineral, which belongs to a triclinic system comprised of silicon–oxygen tetrahedral layer and aluminum oxide octahedral layer [17]. It contains five chemical bonds, i.e., Si–O, Al–O, Al–O–H, O–H, and O–H·O. Following the mineralogical quantification results, the structural evolution at 300 °C–800 °C can be divided into four stages, which are 300 °C–400 °C, 400 °C–500 °C, 500 °C–700 °C, and 700 °C–800 °C. Note that the temperature quantity is the surface temperature, while the internal temperature is higher than the surface.

In the first stage, the heat treatment induces the thermal expansion where the crystal structure stretches along the OA, OB, and OC orientations. The interactions of the Si–O, Al–O, Al–O–H, and O–H decrease, and the lattice constant non-linearly increase. Although the expansion occurs, the layered structure still locates in the elastic stage and maintains integrity [18, 19]. This can be evidenced by the SEM images (400 °C) of dense surface and fewer pores between particles. However, the thermal expansion gradually destroys the structure in the second stage. The micro fractures in SEM images are induced by the tensile failure of the crystal cracking along OA and OB orientations. The most significant influence occurs in the OC orientation that the whole layer detaches [18]. Combined with the XRD patterns, the diffraction peaks’ intensity decreases, indicating the layered structure is failing. Furthermore, the quantification identifies the amorphous substance to form. It is known that the metakaolinite presents the disorder non-definite form at high temperatures [20]. The kaolinite dehydrates at 400 °C–700 °C and transfers to the metakaolinite [21]. During the dehydroxylation, the hydroxyl bond breaking lead to the bond water [22] losing which is consistent with the mass loss curve (figure 3) [20]. The kaolinite contains two types of hydroxyl bonds [19]. The first type is called the external hydroxyl bonds located in the two bottom surfaces of the cover layer. In contrast, the second type is between the flakes of aluminum octahedron called internal one. Since the crystal expands and stretches at microwave heating function, the external hydroxyl bonds easily break rather than the internal bonds [23]. The dehydroxylation gradually diffuses to internal at 500 °C–700 °C. The initial layered structure suffers the local buckling due to external hydroxyl groups losing [24]. This shuts down the interlayered tunnel to form the metakaolinite [23], which remains the kaolinite particles. These closed particles require a higher temperature to dehydroxylate because the kaolinite-metakaolinite transition needs a stronger activation energy [25]. According to the XRD patterns, the diffraction peaks of kaolinite vanish over 600 °C, which is replaced by the metakaolinite. The molecular distance of kaolinite significantly decreases as temperature increased and it transfers from solid to semi-liquid. Consequently, the thermal cracks are filled with the semi-liquid metakaolinite [26] during the heat treatment, and the structure becomes dense during the solidification. In the last stage, the XRD quantification shows the mullite occurs at 700 °C–800 °C due to the further transition of metakaolinite. The metakaolinite initially decomposes to the γ-alumina and silica spinel, and then further decompose to the mullite [27, 28]. The γ-alumina advantages in the high activation and absorption. Therefore, the γ-alumina can absorb the neighbor particles together to form the mullite with temperature increasing. The structure densification can be observed in the figure 5 (a-3, b-3, c-3) where numerous tiny particles attach on the surface of mullite particles.
4.2. Reinforcement of mechanical performance

The microwave indeed significantly reinforces the structure resistance to load function. The mechanical performance reinforcement can be divided into three stages as the structural evolution that are 300 °C–400 °C, 400 °C–700 °C, and 700 °C–800 °C. The reinforcement of 37.4% in the first stage is mainly due to the thermal expansion [19]. The enlarged particles narrow the pores to increase the structural integrity. However, the second stage at 400 °C–700 °C is balanced by the positive thermal expansion for reinforcement and the negative crack to reduce the integrity. Although the thermal expansion continues during the whole heating treatment, the fracture due to the dehydroxylation over 400 °C cannot be ignored. The kaolinite crystal’s tensile resistance decreases with temperature increasing and reaches the tensile strength over 400 °C. Since the metakaolinite forms at 500 °C–700 °C, the cracks can be filled by the semi-liquid so that to dense the structure integrity [29–31]. As a result, the mechanical performance slowly re-increases. Note that this solidified structure still presents a well water resistance with soaking over ten days. Note that the metakaolinite can form the calcium silicate hydrate cement under the alkaline condition to further reinforce the structure. In the third stage, the reinforcement of about 35.8% can be summarized into the two-step transition of metakaolinite - silica spinel (γ-alumina) - mullite that: first, the semi-liquid metakaolinite fills the cracks to dense the structure; next, meanwhile, the formation of mullite forms the major skeleton; and meanwhile, the porous γ-alumina absorbs the neighbor particles together to further strengthen the major skeleton [27, 28].

Mechanical performance is one of the most important facets to evaluate the degree to reinforce the muddy intercalation by microwaves. However, measuring the mechanical performance after water soaking is less meaningful without analyzing the kaolinite and water interaction. To reveal the water effects on the microwave-treated kaolinite, it requires a fine characterization, including the contact angle, water film thickness, molecular dynamics simulation, water-stress coupled simulation, etc. This is beyond this study’s scope, but the future study will investigate the water-kaolinite interaction after microwave heating. Besides, the muddy intercalation contains several minerals. The multiple interactions among different minerals should also be considered.

4.3. Practical application

The muddy intercalation is widely distributed near the edge of the basin. It is a thin weak intercalation with poor mechanical properties and strong hydrophilicity. This study has verified that microwave heating can improve the mechanical properties and water stability of kaolinite. Figure 7 shows the schematic diagram of in situ microwave reinforcement for the muddy intercalation.

The microwave system mainly consists of a power supply, magnetron tube, cooling system, and waveguide. The microwave source power and the waveguide are deployed according to the distribution of the muddy intercalation. The specific reinforcement steps are as follows:

1. Determine the distribution of the muddy intercalation in the slope.

2. The microwave equipment is modified according to the specific engineering condition. Since the microwave power is negatively related to the propagating length, the higher output power is required.
3. The waveguide is inserted into the borehole and extended to the intercalation. Then, the heating procedure follows the preset temperature curve. Finally, the microwave power supply and cooling system are switched on to finish the heating procedure automatically.

5. Conclusions

This study investigates the structural evolution of kaolinite in muddy intercalation exposed to the microwave heating of 300 °C–800 °C by evaluating the uniaxial compressive strength, morphology, mineralogical composition, and water stability. The conclusions can be drawn as follows:

The crystal structural evolution of kaolinite can be divided into four stages: In the first stage (300 °C–400 °C), the thermal expansion promotes the structural integrity; In the second stage (400 °C–500 °C), the crystal tensile failure induces cracks to occur; In the third stage (500 °C–700 °C), the hydroxyl bonds break to loss the bond water and the kaolinite gradually transfers to the metakaolinite; In the last stage (700 °C–800 °C), the metakaolinite decomposes into γ-alumina and silica spinel, and the silica spinel further decomposes into mullite.

The kaolinite without microwave heating fails to measure the uniaxial compressive strength, where the microwave heating increases the uniaxial compressive strength from 1.6 MPa of 300 °C to 3.4 MPa of 800 °C. Furthermore, it can be divided into three stages. First, the uniaxial compressive strength increases about 37.4% at 300 °C–400 °C because of the thermal expansion. Next, the uniaxial compressive strength almost keeps in constant at 400 °C–700 °C. This is balanced by the positive side due to thermal expansion and semi-liquid metakaolinite and the negative side due to the dehydroxylation-induced crack propagation. At 700 °C–800 °C, the re-increase of 35.8% is mainly due to the two-step transition of metakaolinite - silica spinel (γ-alumina) - mullite.

The microwave heating promotes the kaolinite water resistance. Although the kaolinite fails to maintain the integrity after microwave heating with 300 °C, the kaolinite over 500 °C presents well integrity over six days. In the future study, the interaction between microwave-treated kaolinite and water and the multi-interactions among different minerals should be further investigated.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

ORCID iDs

Leping He https://orcid.org/0000-0002-2566-487X

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