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Calcined Attapulgite Clay as Supplementary Cementing Material: Thermal Treatment, Hydration Activity and Mechanical Properties

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Abstract

The present paper studied the effects of calcination temperatures (200–800 °C) on the appearance, mineral composition, and active SiO_2 content in attapulgite and investigated the effects of attapulgite before and after calcination on the chemically bonded water content, the degree of reaction of cement paste, and the mechanical properties such as the flexural strength, compressive strength, and splitting-tensile strength of cement mortar. The results indicate that the calcination temperature changes the mineral composition of attapulgite, thereby affecting the hydration activity of cement-based materials. The attapulgite calcined at 500 °C (AT500) has the best enhancement on the hydration activity of cement-based materials. The calcination at 500 °C is most beneficial to the dissolution of SiO_2, and the content of SiO_2 reaches 20.96%. The contents of chemically bonded water in the samples incorporated with calcined attapulgite reduced and that of the samples incorporated with AT500 at 28 d is the same as that of the control group. The reaction degree of AT500 is 78.61% at 28 days. Calcined attapulgite clay can reduce the energy consumption of the cement industry and promote the sustainable development of attapulgite clay.

Keywords: attapulgite clay, supplementary cementing material, calcination temperature, hydration activity, mechanical properties

1 Introduction

Attapulgite is a type of fibrous rod-shaped clay, with palygorskite as the main mineral component. Palygorskite has a chain-layered structure and is composed of a water-containing magnesium-rich aluminosilicate with a chemical formula of $(Mg, Al)_5\ [(OH)_2(Si, Al)_8O_{20}]\cdot 8H_2O$ (Shi et al., 2009, 2017). Attapulgite is distributed in many places in the world. China is very rich in reserves. Its proven reserves in Jiangsu Province are as high as 272 million tons, accounting for nearly 50% of the global total reserves of attapulgite (Wu, 2019). The attapulgite has many applications owing to its excellent adsorption properties. The application of attapulgite in China is mainly based on additives and adsorbents, including paint, drilling mud, edible oil decolorization and so on.

The current research on attapulgite clay in cement-based materials mainly focuses on the direct use of attapulgite clay as an admixture to study its adsorption, colloid, filling, and pozzolanic effect. The research on attapulgite clay in cement-based materials mainly includes rheological properties, mechanical properties and deformation properties. However, there is a lack of studies on the hydration process of attapulgite clay in cementitious materials.

Tregger and Kawashima (Kawashima et al., 2016; Tregger et al., 2010; Yuan et al., 2017, 2018) have demonstrated that low amounts of attapulgite remarkably modified yield stress and viscosity of cement pastes. Varela et al. (2020) investigated flowability and rheology parameters of cement-limestone filler blended SCC

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pastes with attapulgite nanoclay, and found that water adsorbed by attapulgite nanoclay reduced the water available in the paste, reducing paste flowability, especially for low *w*/*b* (0.35) and that the alkaline pH of the cement pore solution greatly increased substantially adsorption nanoclay water adsorption. Shiho Kawashima et al. (2013) studied the effect of attapulgite clay on the recovery rate of the rheological properties of cementitious materials by comparing strain rate decay curves and relaxation times, and found that the rate of recovery after shear-induced breakdown exhibited by the clay-modified pastes was very rapid compared to the plain cement pastes, especially at early ages (0 and 120 s resting times). Panda B (2018) investigated the effect of nano-attapulgite clay (NC) addition on the fresh, hardened and microstructural properties of high volume fly ash (HVFA) mixes designed for 3D printing. The experimental results show that the addition of 0.1–0.5 wt% of NC increased the static yield stress of HVFA mortars without significantly affecting the apparent viscosity, due to particle reflocculation and enhanced thixotropy. Shiho Kawashima et al. (2014) investigated the effect of adding 0.2 wt% and 0.5 wt% attapulgite clay on the adhesion properties of cement pastes by viscosity test measurements and found that at additions of 0.2% and 0.5%, the clay increases the peak normal force experienced by cement pastes at all plate velocities, indicating increase in cohesion and viscosity.

Chai et al. (2017) investigated the effect of attapulgite clay as a cement additive on the unconfined compressive strength (UCS) of warm and ice-rich frozen soils. After curing at − 1 °C for 7 days, changes in UCS at − 1 °C, freezing point depression and water content of soil samples were measured and it was found that the attapulgite clay increased the UCS by reducing the water content of frozen soils. Pan (2006a, b) et al. studied the effect of calcined attapulgite clay mixed with 20% of the cement mass on the item properties of dry mortar, and found that mixing with attapulgite clay calcined below 450 °C did not significantly improve mortar strength, shrinkage and bond strength; mortar mixed with attapulgite clay calcined above 450 °C increased the 28 days compressive strength by 102.1%, bond strength by 39.7% and impermeability by 25% compared to blank mortar. Jian et al. (2019) investigated the early cracking process of nano-clay cement mortar by incorporating nano-clay attapulgite, and the results showed that the nano-clay caused the crack initiation moment of cement mortar to be 16–18 h earlier, effectively inhibited the expansion of mortar cracks, and the cracking area per unit of nano-clay cement mortar surface was reduced by 72.3% (3 days) and 50.8% compared to normal cement mortar specimens (28 days).

In addition, attapulgite clay is modified as an admixture are used in cement-based materials. The modification methods of attapulgite mainly include purification, thermal activation, acid modification, and surface organic modification. With increasing calcination temperature, the mineral structure of attapulgite is affected because of the gradual dehydration of the adsorbed water, pore water, coordinated water, and structured water on the inner and outer surfaces of the attapulgite (Chen et al., 2006). Therefore, calcination can be used to enhance the hydration activity of attapulgite (Guo et al., 2018) and reduce the impact of a large dosage of attapulgite on the fluidity of cement paste. Attapulgite is composed of water containing magnesium aluminosilicate, so it may have properties similar to cement cementitious materials after high-temperature calcination, so it has potential application in cement concrete materials. The mineral attapulgite, which has a wide range of sources, low price, rich in minerals and environmental protection, can reduce the energy consumption of the cement industry and promote the sustainable development of attapulgite. Therefore, it has important practical significance and application potential.

In this paper, the attapulgite was calcined, the appearance and particle size of attapulgite before and after calcination were studied, and the change of mineral composition of attapulgite before and after calcination was analyzed by XRD. The effect of calcination temperature on the content of active SiO_2 in attapulgite was studied by the color reaction of SiO_2 with ammonium molybdate solution. Attapulgite calcined at different temperatures was used to replace part of cement, and the effect of calcination temperature on the chemically bound water content and hydration reaction degree of attapulgite in cement paste was studied. Attapulgite calcined at different temperatures was added into cement mortar instead of part of cement. The influence of calcination temperature of Attapulgite on compressive strength, flexural strength, and splitting tensile strength of cement mortar was studied.

2 Materials and Methods

2.1 Materials

The high purity attapulgite (Fig. 1) produced by Jiangsu Xuyi Weina Technology & Trade Co., Ltd. and the P·I 42.5 cement produced by Shandong Lucheng Cement Co., Ltd. were used as the raw material, and their chemical compositions are listed in Table 1.

2.2 Methods

2.2.1 The Calcination of Attapulgite

The attapulgite was placed in a corundum crucible and calcined in a muffle furnace. During the entire

Fig. 1 Picture of concave bumpy clay powder.

heating process, the working current of the muffle furnace remained unchanged. After reaching the set heating temperature, the attapulgite sample was calcined for 2 h, and then the muffle furnace was shut down. After the furnace was cooled to room temperature, the sample was taken out and stored in a sealed bag. The attapulgite samples were calcined at 200, 300, 400, 500, 600, 700, and 800 °C, and the corresponding calcined attapulgite samples were named AT200, AT300, AT400, AT500, AT600, AT700, and AT800, respectively. LAP-WA2000H automatic laser particle size analyzer was used to test the particle size distribution of attapulgite before and after calcination.

2.2.2 *XRD Test of Attapulgite*

The attapulgite powders before and after calcination were subjected to XRD test using an X-ray diffractometer (X, Pert PRO, PNAlytical, Netherlands) equipped with Cu ($\lambda = 0.1541$ nm) radiation, in the scanning range 2θ of 5–80° at a scanning step of 0.05°. The specimens were dried in a vacuum oven at 60 °C for 8 h. After drying, the specimens were finely ground in an agate mortar and tested after passing through a 200 mesh standard sieve.

2.2.3 *Determination of Active SiO_2 Content*

Through the chromogenic reaction between the sample and the ammonium molybdate solution (Li et al., 2009; Surana & Joshi, 1988), the absorbance of the sample at 410 nm ultraviolet light was measured using a spectrophotometer. After that, the absorbance was compared to the standard absorbance curve obtained by the solutions with different SiO_2 concentrations to determine the content of active SiO_2. Firstly, the absorbance values of 1 ppm, 2 ppm, 3 ppm, 5 ppm, 7 ppm, 9 ppm, 11 ppm, 13 ppm standard SiO_2 solution and ammonium molybdate solution after color reaction were measured respectively. Then calculate the standard curve of SiO_2, obtain the calculation formula of absorbance and SiO_2 concentration. Finally, the absorbance value of the attapulgite solution sample was measured, and the active SiO_2 concentration of the sample was calculated using the standard curve formula. Equation (1) was used to calculate the active SiO_2 content. The uncalcined attapulgite samples were named AT00, and the samples calcined at 200–800 °C were named AT200, AT300, AT400, AT500, AT600, AT700 and AT800, respectively.

$$z = \frac{x \times 250\mathrm{mL}}{200\mathrm{mg}} \times 100\% \tag{1}$$

x: the concentration of SiO_2 solution, ppm; z: the content of active SiO_2, %

2.2.4 *Measurement of Chemically Bound Water Content and Degree of Hydration Reaction of Calcined Attapulgite in Cement Paste*

The test method of chemically bound water content was referred to as reference (Guo et al., 2018). The control paste and cement paste samples with 10% calcined attapulgite were prepared. The water-binder ratio of the samples was 0.4. After the samples cured to the specified age (3 days, 7 days and 28 days) were broken, the middle pieces were taken and soaked in absolute ethanol. During the test, the finely ground sample was dried in an oven at 65 °C for 24 h and dried for 24 h to a constant mass. It was then calcined at 950 °C for 3 h to constant mass. The content of chemically bonded water was calculated by Eqs. (2) and (3).

$$W_{\mathrm{ne}} = \frac{m_1 - m_2}{m_2} - \frac{W_{\mathrm{AT,c}}}{1 - W_{\mathrm{AT,c}}} \tag{2}$$

$$W_{\mathrm{AT,c}} = f_{\mathrm{AT}} \cdot W_{\mathrm{AT,I}} + f_{\mathrm{c}} \cdot W_{\mathrm{c,I}} \tag{3}$$

W_{ne}: chemically bonded water content; m_1: mass of the sample after drying at 65 ℃, g; m_2: mass of the sample

Table 1 Chemical composition of attapulgite and cement (wt%).

Materials	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	K_2O	P_2O_5	SO_3	Na_2O_{eq}	f-CaO	Loss
Attapulgite	55.82	9.40	4.06	12.24	1.43	0.86	0.23	0.01	–	–	15.00
Cement	22.10	4.43	3.13	2.28	62.38	–	–	2.62	0.53	0.78	2.04

after drying at 950 ℃, g; $W_{\mathrm{AT,c}}$: loss on ignition of composite cementitious materials; f_{AT}: mass fraction of attapulgite, wt%; $W_{\mathrm{AT,I}}$: loss on ignition of attapulgite; f_{c}: mass fraction of cement, wt%; $W_{\mathrm{c,I}}$: loss on ignition of cement, wt%

The hydrochloric acid dissolution method was used to test the reaction degree of attapulgite in the composite cementing material slurry. The determination process refers to GB/T 12,960-2007 "Quantitative Determination of Constituents of Cement". The degree of attapulgite reaction was calculated according to Eq. (4).

$$\alpha_{\mathrm{AT}} = 1 - \frac{\frac{n_{\mathrm{AT,c}}}{1-W_{\mathrm{ne}}} - f_{\mathrm{c}} \cdot n_{\mathrm{c}}}{f_{\mathrm{AT}} \cdot n_{\mathrm{AT}}} \tag{4}$$

α_{AT}: reaction degree of attapulgite; W_{ne}: chemically bonded water content; f_{AT}: mass fraction of attapulgite, wt%; $n_{\mathrm{AT,c}}$: residual mass fraction of paste dissolved by hydrochloric acid, wt%; n_{c}: residual mass fraction of cement dissolved by hydrochloric acid, wt%; n_{AT}: residual mass fraction of attapulgite dissolved by hydrochloric acid, wt%.

2.2.5 Mechanical Properties of the Mortar Specimens with Calcined Attapulgite Added

The effects of incorporation of 10 wt% calcined attapulgites on the flexural strength, compressive strength, and splitting-tensile strength of cement mortar were studied. The flexural strength and compressive strength were measured by the cement mortar strength test method (ISO method) referring to GB/T 17671-1999 (China State Bureau of Quality and Technical Supervision, 1999). The specimens were cured for 3 days, 7 days, 28 days and 90 days under an environment of 20 ± 1 ℃ and relative humidity over 90% to test their flexural strength and compressive strength. Concerning GB/T 50081-2002, the standard test method for mechanical properties of ordinary concrete was used to measure the splitting-tensile strength of mortar with water-cement ratio of 0.5 (China State Bureau of Quality & Technical Supervision, 2003). The samples were cured for 28 days, 90 days and 180 days and tested their splitting tensile strength. The cement mortar was indexed as M0, M200, M300, M400, M500, M600, M700, and M800. M0 was the control group, and M200–M800 is the test groups incorporated with 10 wt% attapulgites calcined at different temperatures in the range 200–800 °C.

3 Results and Discussions

3.1 Effects of Calcination Temperature on the Appearance and Particle Diameter of Attapulgite

Fig. 2 The color change of attapulgite before and after calcination.

Fig. 3 Attapulgite calcined at 700 ℃ for 2 h (fully sintered).

The appearance and morphology, such as color and particle diameter, of the calcined attapulgite, changed significantly after calcination at different temperatures. When calcinating, sintering does not occur in attapulgite samples calcined in the range 200–500 °C, while sintering occurs partly at 600 °C and 700 °C. The completely melted sintering phenomenon occurs at 800 °C. The color change of the calcined attapulgite is shown in Fig. 2.

The color of the non-calcined attapulgite is gray–white, which gradually becomes orange with increasing calcination temperature (Fig. 3). When the temperature reaches 800 °C, the sample is completely sintered with a deep brown color (as shown in Fig. 4), which turned to gray–black after grinding. The color change of attapulgite may be caused by Magnetite (Fe_3O_4) produced by high-temperature calcination. The XRD pattern in Fig. 5 also confirms the above phenomenon. Besides, the gradual dehydration of attapulgite at high temperatures causes the pores to collapse and the rod-like structure to sinter and shrink; therefore, the volume of the attapulgite decreases significantly after calcination.

Fig. 4 Attapulgite calcined at 800 ℃ for 2 h (fully sintered).

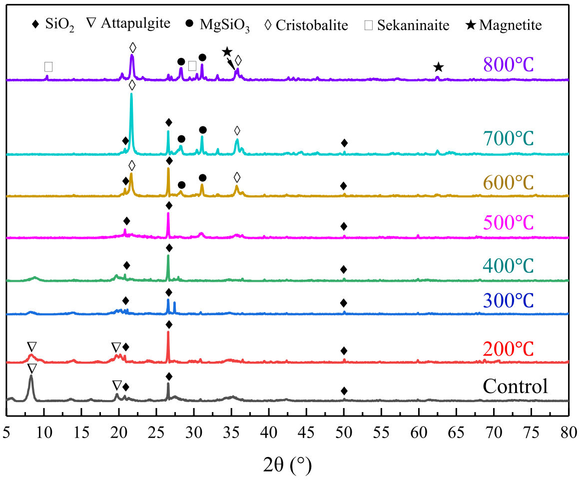

Fig. 5 XRD pattern of attapulgite.

As listed in Table 2, with increasing calcination temperature, the average particle diameter of the attapulgite increased. Partial sintering takes place in AT600 and AT700. Severe sintering and hard texture occurred in AT800. AT600 and AT700 samples were ground in a small vibration mill in a laboratory for 20 min, and the AT800 sample was ground for 1 h. The ground attapulgite was incorporated into the cement-based material before performing mechanical tests.

3.2 XRD Characterization on the Mineral Composition of Attapulgite Before and After Calcination

Fig. 5 shows the changes of the XRD pattern in attapulgite before and after calcination. The uncalcined and calcined attapulgite samples at 200 ℃ mainly contain attapulgite minerals and SiO_2 (Alpha quartz α-SiO_2). At 200 ℃, the SiO_2 diffraction peak intensity increased significantly, but the attapulgite diffraction peak intensity decreased. When the calcination temperature exceeded 200 ℃, the attapulgite diffraction peak disappeared. This is because the crystal structure of the attapulgite was destroyed during the calcination process, and SiO_2 was formed. When the calcination temperature is 200–500 ℃, the XRD pattern of the sample mainly contains SiO_2, which may be due to the formation of SiO_2 crystals after the crystal structure of attapulgite is destroyed. The diffraction peak intensity of the sample SiO_2 is the highest at 500 ℃. This may be because 500 ℃ is the most suitable temperature for calcining attapulgite as an auxiliary cementing material. The SiO_2 activity test also shows the active SiO_2 content when the calcination temperature of the sample is 500 ℃ highest.

When the calcination temperature exceeds 500 ℃, the diffraction peak intensity of Alpha quartz (α-SiO_2) in the sample gradually decreases, and the diffraction peak intensity of Alpha cristobalite (α-SiO_2) increases, and the diffraction peak of $MgSiO_3$ appears in the sample. The intensity of the diffraction peak gradually increases with the calcination temperature, which may be caused by the reaction of quartz and MgO at high temperatures. In this process, SiO_2 (Alpha quartz α-SiO_2) is consumed, and its crystal structure is transformed into SiO_2 (Alpha quartz α-SiO_2) as the calcination temperature rises. At 800 °C, the diffraction peaks of Sekaninaite ($Fe_2Al_4Si_5O_{18}$) and Magnetite (Fe_3O_4) appeared in the sample, both of which are black minerals, which exactly explains the reason why the sample turned black. Pan (2006b) explored the influence of the calcination temperature on the structure and composition of the attapulgite. The XRD test results of the sample found iron-containing oxides, which confirmed the experimental conclusions inferred above.

3.3 Effect of Calcination Temperature on the Content of Active SiO_2 Content of Attapulgite

The absorbance of attapulgite after the chromogenic reaction, the SiO_2 concentration corresponding to the standard curve, and the calculated content of active SiO_2 are listed in Table 3. The SiO_2 content of the non-calcined attapulgite is 3.56%. The content of the active SiO_2 in attapulgite increases with increasing calcination temperature, which reaches a maximum of 20.96% at 500 °C and decreases significantly over 500 °C. The main reason for the change of active SiO_2 content in attapulgite may be that the temperature changes the mineral structure of palygorskite and reduces its crystallinity, making it easier to dissolve more SiO_2 under alkaline conditions. The dehydration of attapulgite during the calcination process may increase the relative content of SiO_2. When the temperature rises, SiO_2 and MgO react to form $MgSiO_3$ during the calcination process, which causes SiO_2 to be consumed, so the active SiO_2 content in the attapulgite

Table 2 Average particle size color and grind condition of attapulgite at different calcination temperatures.

Attapulgite sample	Calcination temperature	Average particle size/μm	Color	Grind condition
AT00	No calcination	6.81	White grey	–
AT200	Calcination at 200 ℃	11.90	Grey	–
AT300	Calcination at 300 ℃	11.82	Yellowish–grey	–
AT400	Calcination at 400 ℃	12.39	Yellow pale	–
AT500	Calcination at 500 ℃	10.28	Yellow mid	–
AT600	Calcination at 600 ℃	5.38	Orange–yellow	Easy grind
AT700	Calcination at 700 ℃	6.57	Orange	Easy grind
AT800	Calcination at 800 ℃	3.33	Black grey	Difficult grind

Table 3 Absorption and SiO_2 concentration and mass fraction of SiO_2 of attapulgite solution.

Clay sample	Average abs	SiO_2 concentration (mg/L)	Mass fraction of SiO_2 (%)
AT00	0.3880	28.4787	3.56
AT200	0.4790	35.5275	4.44
AT300	1.0727	81.5125	10.19
AT400	1.1443	87.0573	10.88
AT500	2.1854	167.7041	20.96
AT600	0.7103	53.4400	6.68
AT700	0.3247	23.5729	2.95
AT800	0.6353	47.6370	5.95

decreases. XRD test results also confirmed the change of active SiO_2 content in attapulgite.

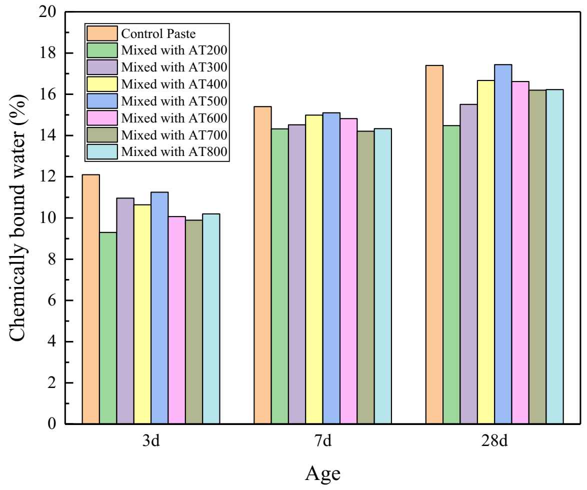

Fig. 6 Chemical bound water content of paste mixed with calcined attapulgite at different ages.

3.4 Effect of Incorporating Calcined Attapulgite on the Chemically Bonded Water Content of Paste Samples and the Reaction Degree of Attapulgite

Fig. 6 shows that the amount of chemically bonded water in pure cement paste is higher than that in the paste with calcined attapulgite. At the same age, with increasing calcination temperature, the content of chemically bonded water in the paste with attapulgite also increases. It reaches the maximum when the calcination temperature is 500 °C and then decreases with increasing calcination temperature. When the calcination temperature reaches 800 °C, the content of chemically bonded water increases slightly again. Among the samples with calcined attapulgite, the contents of chemically bonded water all increase with the age, and the paste with AT500 always has the highest chemically bonded water content. At 28 days, the content of chemically bonded water in the sample with AT500 is equivalent to that of the pure cement paste. For the sample calcined at different temperatures, the variation in the chemically bonded water contents in samples with attapulgite calcined at different temperatures is consistent with that of the active SiO_2 content. Feng believed that the low-temperature calcined attapulgite generally hindered the hydration of the cement particles (Feng & Sun, 2007; Han & Yan, 2010). It might be that the attapulgite adsorbed a large amount of water and relatively reduced the water–cement ratio, resulting in an environment where the cement particles were not sufficiently dissolved to hydrate, leading to a reduction in overall hydration.

As shown in Fig. 7, the uncalcined attapulgite samples were named AT00, and the samples calcined at 200 °C–800°C were named AT200, AT300, AT400, AT500, AT600, AT700 and AT800, respectively. The reaction degree of attapulgite in the sample gradually increased with the increase of curing age. With the progress of the hydration reaction, the pozzolanic effect of the attapulgite gradually increased, resulting in a gradual increase in the reaction degree of the attapulgite in the sample. The reaction degree of attapulgite shows a trend of first increasing and then decreasing with the increase

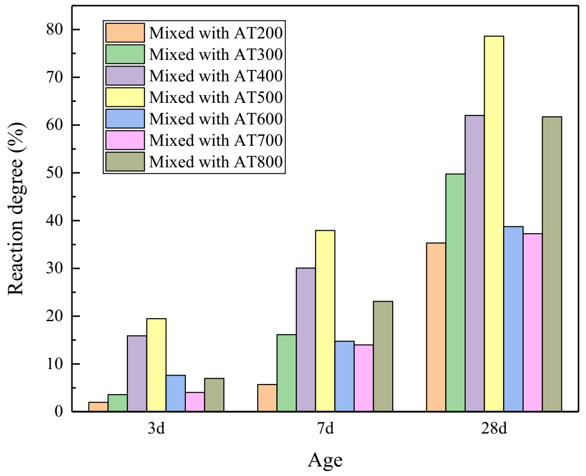

Fig. 7 Reaction degree table of attapulgite at different ages.

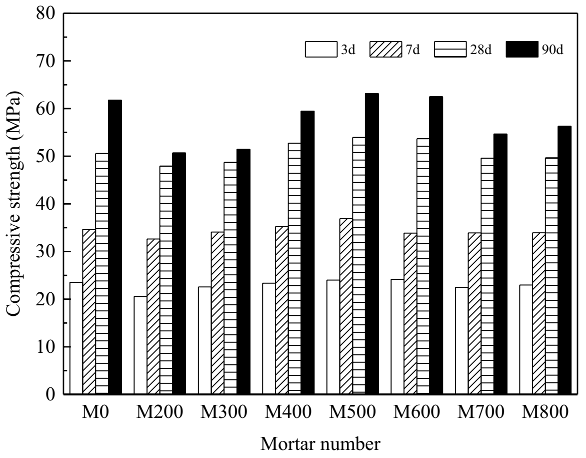

Fig. 8 Compressive strength of attapulgite mortar.

of calcination temperature, which is caused by the content of active SiO_2 in attapulgite. The attapulgite calcined at 500 °C has the greatest degree of reaction in all ages. At 28 days, the reaction degree of attapulgite calcined at 500 ℃ is 78.61%, which is about twice the reaction degree of attapulgite calcined at 200 ℃ and 700 ℃. This is because the active SiO_2 content of the attapulgite calcined at 500 °C is the largest, and its excellent pozzolanic activity improves the reaction degree of the attapulgite. Many researchers have reached similar conclusions. Pan (2006a) found that when attapulgite clay calcined at a temperature higher than 450 °C was added, the compressive strength, bonding strength, shrinkage and impermeability of the mortar were significantly improved due to the loss of bound water and crystal water. However, due to the limitations of experimental conditions and methods, the heat of hydration test and thermal analysis of the sample are expected to be further tested to confirm the influence of the calcined attapulgite on the hydration process of the sample.

3.5 Effects of Incorporating Calcined Attapulgite on the Mechanical Properties of Cement Mortar

Figs. 8 and 9 respectively show the changing trend of compressive strength and flexural strength of calcined attapulgite cement mortar and blank mortar group. In general, the changing trend of strength is consistent with the changing trend of active SiO_2 content, chemical bond water content, and reaction degree of attapulgite. With the increase of the calcination temperature, the compressive strength and flexural strength of cement mortar generally show a trend of first increasing and then decreasing. When the calcining temperature of attapulgite is 500 ℃, the cement mortar shows excellent mechanical properties, while the strength and growth rate at other calcining temperatures are smaller. The strength of calcined attapulgite cement mortar is lower in the early stage (such as 3 days and 7 days). With the increase of curing age, the compressive strength and flexural strength of calcined attapulgite cement mortar are close to those of the blank group. At 90 d, the compressive strengths of AT500 mortar and blank samples were 63.1 MPa and 61.8 MPa, and the flexural strengths were 8.23 and 8.27 MPa, respectively. When the calcination temperature is 500 °C, the active SiO_2 content of attapulgite is the largest, and its pozzolanic activity is the largest, which leads to the largest reaction degree of attapulgite (Feng et al., 2004; Tironi et al., 2017). Therefore, when

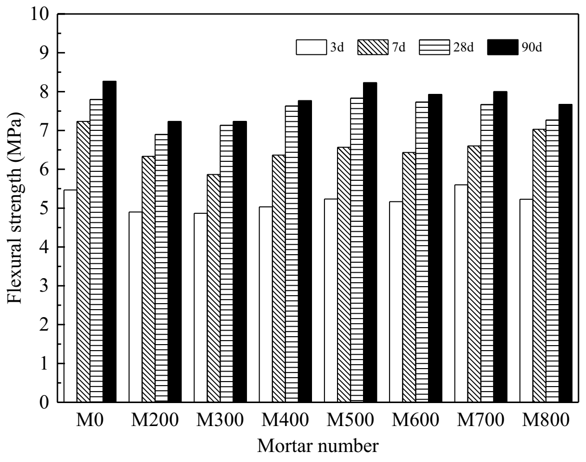

Fig. 9 Flexural strength of attapulgite mortar.

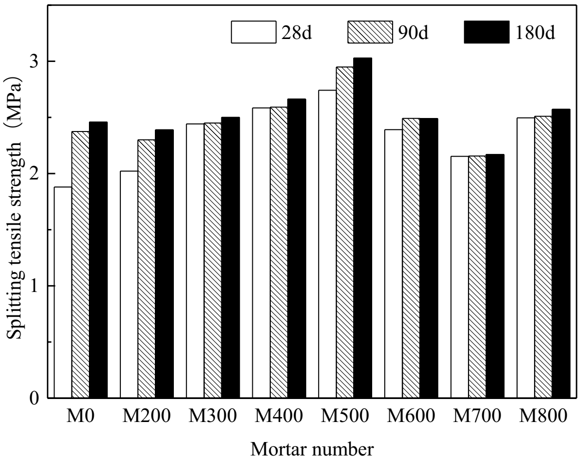

Fig. 10 Splitting tensile strength of attapulgite mortar.

the calcination temperature is 500 °C, the cement mortar exhibits excellent mechanical properties.

As shown in Fig. 10, the splitting-tensile property can be enhanced by incorporating calcined attapulgite. At 28 days, the splitting tensile strength of the blank group is 1.88 MPa, while that of the mortar with AT200 reaches 2.02 MPa, the minimum value of all groups with calcined attapulgite. The sample with AT500 has the maximum splitting-tensile strength of 2.74 MPa. The splitting-tensile strength of the sample with AT500 maintains the same strength development trend as the flexural strength and compressive strength. The splitting-tensile strength of the sample with AT500 continues to increase with age and reaches 3.03 MPa at 180 days. Except for the attapulgite calcined at 500 °C, although the splitting-tensile strengths of the samples with attapulgite calcined at the other temperatures are also higher, the strength and the growth rate are not as good as that with AT500. The reasons why attapulgite enhances the splitting-tensile strength of the mortar, in addition to its hydration activity, may also be attributed to its enhancing effect in the early-stage bonding strength of cement paste (Kawashima et al., 2014); or the rod-like fibrous morphology of attapulgite improves the crack resistance (An et al., 2008); the activated SiO_2 increases the crosslinking density of cement-based materials, then enhances the splitting-tensile strength (Peng et al., 2009).

The activity of attapulgite is not as good as slag, silica fume, etc., and the increase in flexural strength and compressive strength is not as significant as the splitting tensile strength, but the calcination temperature of attapulgite is much lower than that of cement clinker. Therefore, attapulgite as an auxiliary cementitious material can replace the use of cement, and reduce energy consumption and carbon emissions.

4 Conclusions

The appearance, particle size, mineral composition, and active SiO_2 content of attapulgite before and after calcination were studied. Then the attapulgite calcined at different temperatures is used to replace part of the cement. The influence of calcination temperature on the chemical-bound water content and hydration reaction degree of attapulgite in cement paste is analyzed, and the influence of calcination temperature of attapulgite on the mechanical properties of cement mortar is studied. Analysis of the results yields the following conclusions.

(1) The color of attapulgite changes with the calcination temperature. XRD test results show that the diffraction peak intensity of attapulgite SiO_2 is the highest when the calcination temperature is 500 ℃. At 800 °C, the diffraction peaks of Sekaninaite and Magnetite appeared in the sample, both of which are black minerals, which caused the attapulgite to turn black.

(2) The calcination at 500 °C is most beneficial to the dissolution of SiO_2, and the content of SiO_2 reaches 20.96%. The contents of chemically bonded water in the samples incorporated with calcined attapulgite reduced and that of the samples incorporated with AT500 at 28 days is the same as that of the control group. The reaction degree of AT500 is 78.61% at 28 days.

(3) The test results of the hydration activity indicate that attapulgite calcined at 500 °C has the highest hydration activity, and the durability of cementitious materials mixed with calcined attapulgite clay such as pore structure and resistance to chloride ion penetration is recommended for further study due to the adsorption properties of attapulgite clay.

(4) The mechanical properties of the mortar incorporated with AT500 are the best. Attapulgite calcined at different temperatures can all enhance the splitting-tensile strengths of the cement-based materials.

(5) Compared with cement clinker, attapulgite with lower calcination temperature can replace part of cement cementitious materials and can reduce energy consumption in the cement industry. The evaluation of calcined attapulgite for reducing carbon emissions is worthy of further study.

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Authors' contributions

TS: investigation, data curation, writing—original draft. YL: methodology, data curation, writing—original draft. YZ: conceptualization, writing—review and editing. YL: investigation. QZ: investigation. YZ: supervision. HW: validation, formal analysis. All authors read and approved the final manuscript.

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Availability of data and materials

The datasets used and analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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