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Pozzolanic reactivity and hydration products of epidote

The pozzolanic reactivity test was carried out on the finely ground powder of epidote. First, 91% of finely ground powder of epidote, 3% of natural gypsum and 6% of calcium hydroxide were mixed together, then during slurrying, 0.3% of PC water reducing agent was added and at last a neat paste test specimen was made at a water-binder ratio of 0.2. XRD, SEM, IR and DSC analysis was carried out on the hydration products of the neat paste specimen. According to the results, the neat paste specimen of finely ground epidote had a compressive strength of 5.50MPa, 6.039MPa and 6.27MPa at the age of 3d, 7d and 28d, respectively, which shows that the finely ground epidote has pozzolanic reactivity. Hydration products mainly include C-S-H gel and ettringite.

Keywords: *Epidote, pozzolanic reactivity, C-S-H gel, ettringite.*

1. Introduction

Tailings are wastes discharged from mineral processing in mines, but they contain a lot of oxides and abundant trace elements. The main chemical components are CaO and SiO_2, similar to those of cement, so reusing tailings as building materials has become an important research direction. This paper takes the mineral tailings containing epidote in a place of Fujian as an example, prepares neat paste specimen with epidote as the main material and studies its pozzolanic reactivity and hydration products to provide important basis for turning skarn-type lead-zinc tailings containing epidote into resources.

2. Test materials and methods

2.1 Test materials

(1) Epidote: supplied by a company in Beijing. The chemical composition is shown in Table 1, from which, it can be seen that epidote contains up to 38.90% of SiO_2 and at the same time involves rich amount of MgO and CaO. Fig.1 is the XRD spectrum of epidote.

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Table 1: Chemical composition of raw materials (mass fraction, %)

Material	Epidote	Gypsum
SiO_2	38.9	3.91
Al_2O_3	0.83	3.61
Fe_2O_3	0.62	0.19
FeO	0.91	0.33
MgO	18.09	8.94
CaO	23.85	30.93
Na_2O	0.44	0.15
K_2O	0.19	0.25
TiO_2	0.11	0.08
P_2O_5	0.013	0.017
MnO	0.052	0.081
Loss	0.23	25.49
S	-	26.28

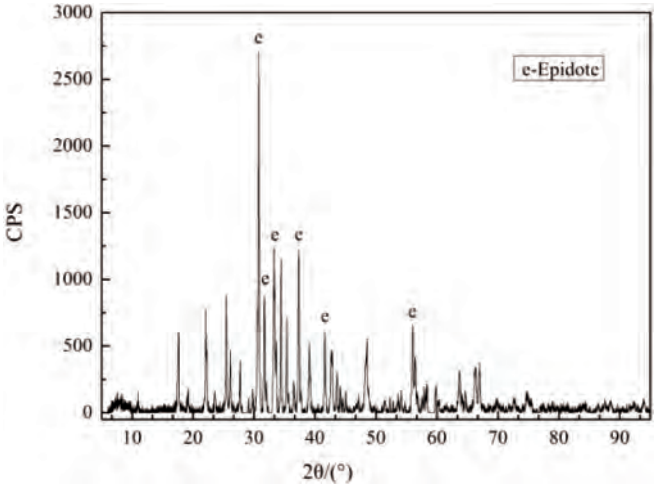


Fig.1 XRD spectrum of epidote

(2) Natural gypsum: supplied by a cement mill in Beijing. The chemical composition is shown in Table 1.

(3) Calcium hydroxide: produced by Sinopharm Chemical Reagent Co., Ltd.

(4) Water reducing agent: efficient polycarboxylate PC water reducing agent, supplied by a company in Beijing.

2.2 Test method

First crush the epidote with a jaw crusher, and then grind it in the sampling machine for 60min to obtain finely ground epidote with a specific surface area of 416.3m^2/kg, whose particle size distribution is shown in Fig.2. Then mix 91% of finely ground epidote, 3% of natural gypsum and 6% of calcium hydroxide together, and during slurrying, add 0.3% of PC water reducing agent and prepare a neat paste specimen with a size of 30mm×30mm×50mm at a water-binder ratio of 0.2, and cure it under standard curing conditions (temperature: (20±1)ºC; humidity: over 95%).

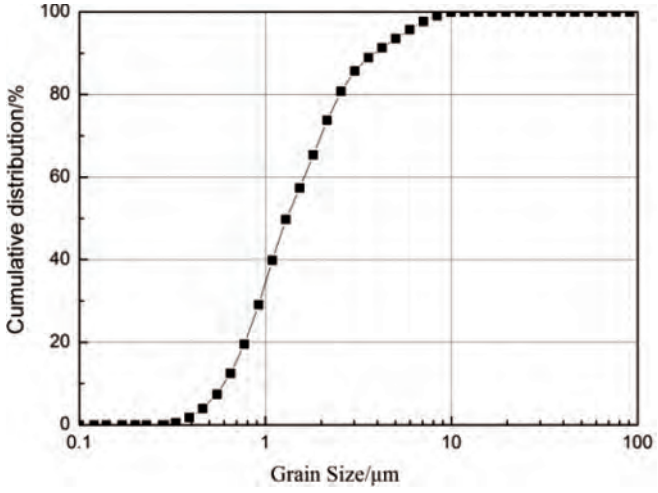


Fig.2. Particle size distribution of finely ground epidote

XRD, SEM, DSC and IR analysis was carried out. The XRD analysis used Rigaku D/MAX-RC 12kW rotating anode diffractometer, with a Cu target, a wavelength of 1.5406Aº, an operating voltage of 40kV, an operating current of 150mA and a scanned area of 5º<2θ<90º. The SEM analysis used the Cambridge S250 scanning electron microscope, with an accelerating voltage of 20kV. Differential scanning calorimetry analysis used Netzsch STA 449C, with a temperature rise rate of 10K/min, a temperature range of 20~1000ºC and the air as the medium. The infrared spectroscopy used the NEXUS70 fourier infrared spectrometer (350~7000cm-1) with a resolution of 3cm-1.

3. Result analysis and discussion

3.1 Compressive strength of the neat paste specimen of epidote

Table 2 shows the compressive strength test results of the neat paste specimen of epidote at different ages. It can be seen that the compressive strength of the neat paste specimen of epidote increased from 5.50MPa at the age of 3d to 6.27MPa at the age of 28d, indicating that the finely ground epidote has pozzolanic reactivity.

Table 2: Compressive strengths of the neat paste specimen of epidote at different ages

Curing age	3d	7d	28d
Compressive strength/MPa	5.50d	6.03d	6.27d

3.2 XRD analysis on the neat paste specimen of epidote

Fig.3 shows the XRD test results of the dry mixed powder and the neat paste specimen of epidote at different ages. It can be seen that, the characteristic peak of calcium hydroxide (2θ ≈ 18.04°, 28.67°, 34.04°, 47.11°, 50.81°, 54.35°, 62.63°, 64.23°) gradually becomes weak with the age[1], and that part of the peak almost vanishes at the age of 28d, indicating that, with the reaction going on, calcium hydroxide is being continuously consumed and almost exhausted at the age of 28d. The characteristic peak of gypsum (2θ 11.63°, 20.72°, 29.11°) vanishes at the age of 3d, indicating that the vast majority of gypsum is consumed at the age of 3d. The characteristic peak of ettringite appears at the age of 3d (2θ 9.16°, 15.68°, 23.03°) and gradually increased with the age, indicating that ettringite is generated in the reaction. In the 2θ angle range (26°-34°) where typically C-S-H gel [2] can easily lead to convexes in the XRD chart, background values increased and convex hulls appears along with the curing period in the XRD charts of the specimen in this experiment, indicating that the C-S-H gel in the specimen is on a growing trend with the age. The generation of ettringite and C-S-H gel well explain the sources for the compressive strength of the neat paste specimen in 2.1.

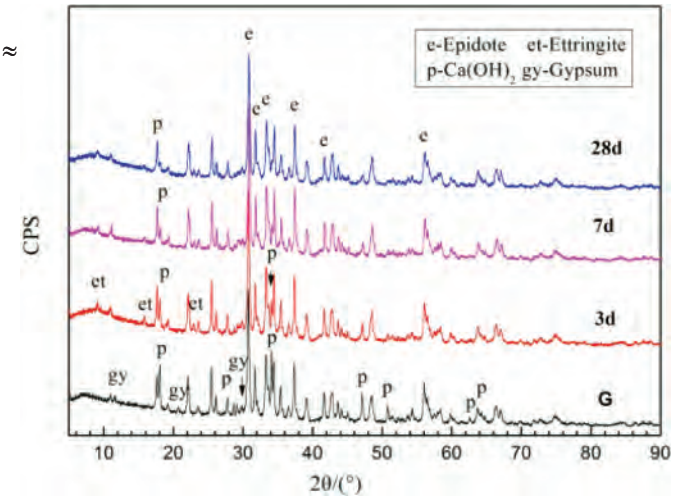


Fig.3 XRD spectrums of the dry mixed power and the neat paste specimen at different ages

3.3 SEM analysis on the neat paste specimen of epidote

Figs.4-6 show the SEM charts of the neat paste specimen of epidote at different magnifications at different ages. Figs.4(a) and (b) are the charts of the neat paste specimen of epidote magnified by 20k and 100k times at the age of 3d from the same field of vision. From Fig.4(a), it can be seen that a certain amount of C-S-H gel is already generated at the age of 3d. Fig.4(b) shows the typical C-S-H gel structure, which contains some particles with a size of less than 100nm. Finely ground epidote cannot possibly contain particles of such size, so it can

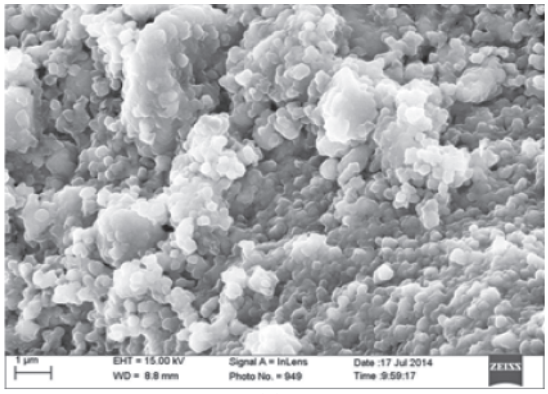
be deduced that these particles are C-S-H gel [3]. Fig.4(d) is an enlarged image of the portion in the box in Fig.4(c), and it can be seen that there are some needle-like substances, which may be ettringite judging from its appearance.

Figs.5 (a) (b) (c) are the charts of the neat paste specimen of epidote magnified by 20k, 100k times at the age of 7d respectively from different fields of vision and the same field of vision. In Fig.5(a), the system structure becomes more compact and the gaps between epidote particles are gradually reduced. Fig.5(b) shows that, at the age of 7d, the C-S-H gel particles become thicker and are incorporated into tablets. It can be seen from Fig.5(c) that ettringite and C-S-H gel are intertwined and tightly bonded to make the system firmer.

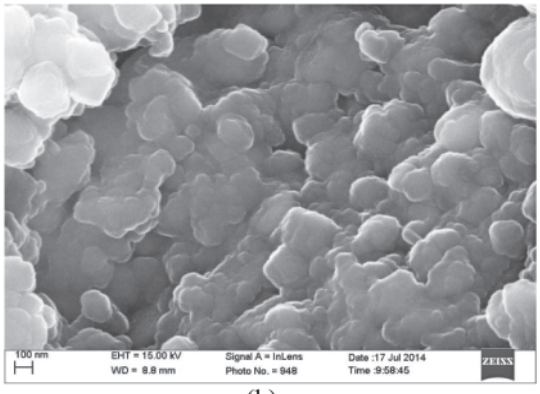
Fig.6(a) and (b) are charts of the neat paste specimen of epidote magnified by 20k and 100k at the age of 28d from the same field of vision. It can be seen from Fig.6(a) that, at the age of 28d, the system structure is very compact. Fig.6(b) show that ettringite is well bonded with C-S-H gel, and that the needle-shaped ettringite is tightly wrapped by the C-S-H gel, so it can be concluded that the C-S-H gel is very thick.

3.4 FT-IR analysis on the neat paste specimen of epidote

Fig.7 shows the FT-IR spectrums of the dry mixed powder and the neat paste specimen of epidote at different ages. The absorption peak in the range of 3800cm^{-1} to 3000cm^{-1} is the stretching vibration band of the O-H bond in the system. The prominent absorption peak near 3641cm^{-1} is the asymmetric stretching vibration absorption peak of the O-H bond in calcium hydroxide [4-7], which gradually weakens with the age, indicating that with the hydration reaction going on, calcium hydroxide is being constantly consumed. The less prominent absorption peak near 3533cm^{-1} is the vibration peak of the O-H bond of the crystal water in the gypsum, which totally vanishes at the age of 3d, indicating that with the hydration reaction going on, the gypsum is almost completely consumed at the age of 3d. The absorption peak at 3370cm^{-1} in the FT-IR spectrum of the dry mixed powder is the asymmetric stretching vibration peak of the O-H bond connecting silicon dioxide [8]. The surfaces of the fine particles of silicate minerals would all form such bonds with the water molecules in the air. The surfaces of the finely ground epidote are hydroxylated when in contact with the air, which will also contribute to the peak at 3370cm^{-1}. The absorption peaks at 3369cm^{-1}, 3370cm-1 and 3370cm^{-1} in the FT-IR spectra at the age of 3d, 7d and 28d are formed by the superimposition of the O-H bond connecting silicon dioxide and ettringite and the O-H bond in the C-S-H gel. From the dry mixed powder sample to the specimen at the age of 3d, 7d and 28d, the area of this peak increases, indicating that the total amount of ettringite and C-S-H gel is increasing. On the other hand, the absorption band between 3800cm^{-1} and 3000cm^{-1} is increasing, indicating that the hydration reaction is constantly going on with the age, which is consistent with the results obtained by XRD and SEM analysis.



(a)



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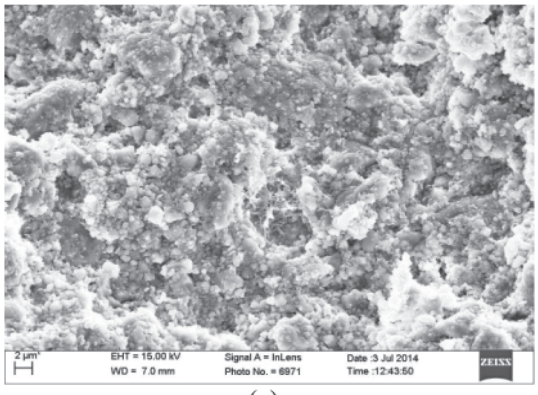

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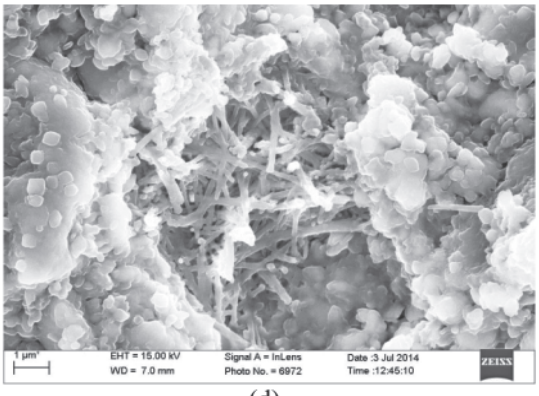
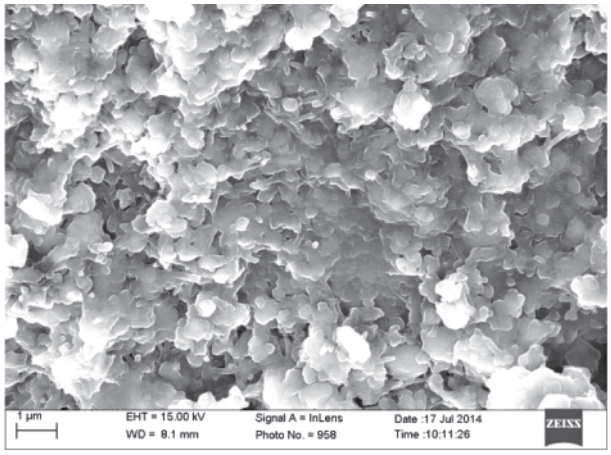
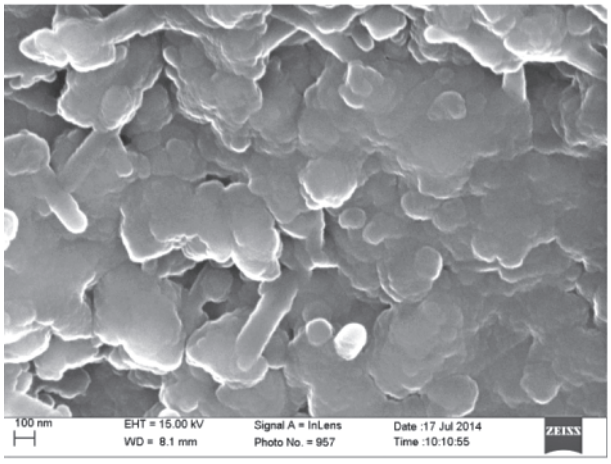


(d)

Fig.4 SEM charts of the neat paste specimen of epidote at the age of 3d



(a)



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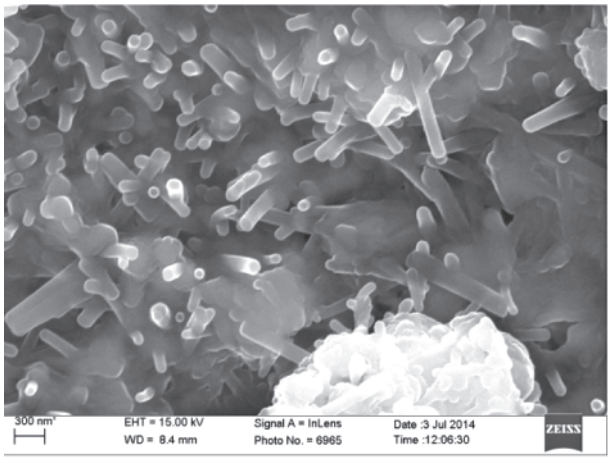
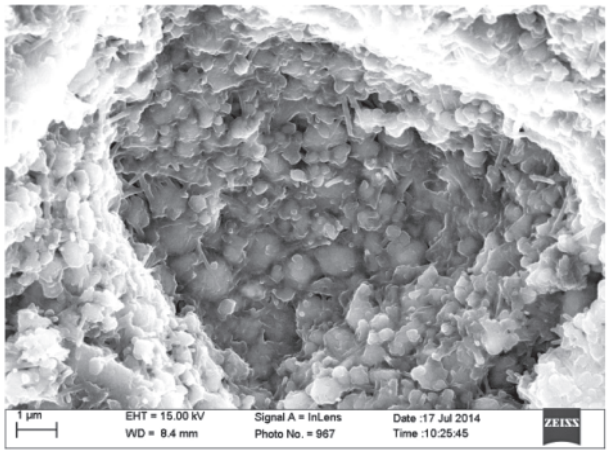


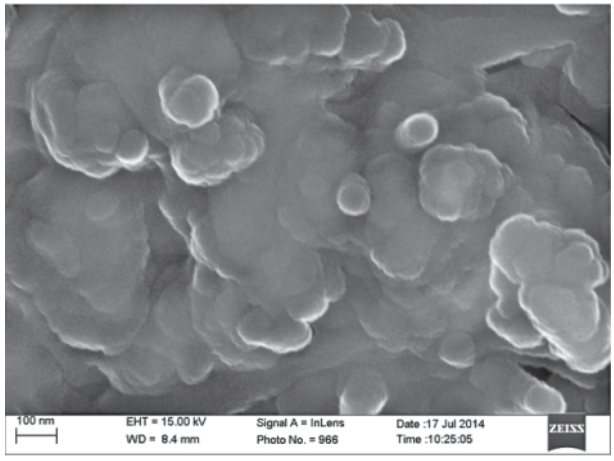
(c)

Fig.5 SEM charts of the neat paste specimen of epidote at the age of 7d

The absorption peak at 1621cm^{-1} in the FT-IR spectrum of the dry mixed powder is the bending vibration peak of the O-H bond in the hydroxyl structure water or the crystal water [9]. In this system, the natural gypsum in the dry mixed powder specimen contributes to this peak. Similar absorption peaks also



(a)



(b)

Fig.6 SEM charts of the neat paste specimen of epidote at the age of 28d

appear at 1610cm^{-1}, 1621cm^{-1} and 1623cm^{-1} in the spectra at the age of 3d, 7d and 28d, respectively. It can be seen that the wave numbers of the absorption peaks are increasing with the age, showing that the amount of C-S-H gel is increasing.

The absorption peak at 1419cm^{-1} in the FT-IR spectrum of the dry mixed powder is the stretching vibration peak of CO_3^{2-}, which is caused by the carbonization of the components in the dry mixed powder sample with the CO_2 in the air. Similar absorption peaks also appear at 1428cm^{-1}, 1438cm^{-1} and 1424cm^{-1} in the spectra at the age of 3d, 7d and 28d. The absorption peak area increases, indicating that during the preparation, the sample would react with CO_2 in the air.

3.5 DSC ANALYSIS ON THE NEAT PASTE SPECIMEN OF EPIDOTE

Fig.8 shows the DSC curves of the neat paste specimen of epidote at different ages. Most endothermic peaks at around 719.0°C are due to the decomposition and decarburization of $CaCO_3$ produced through the carbonization of $Ca(OH)_2$ in the specimen[10]. The absorption peaks at about 452.5°C are caused by the decomposition of $Ca(OH)_2$. Such peaks are present in the specimen at three different ages, indicating that

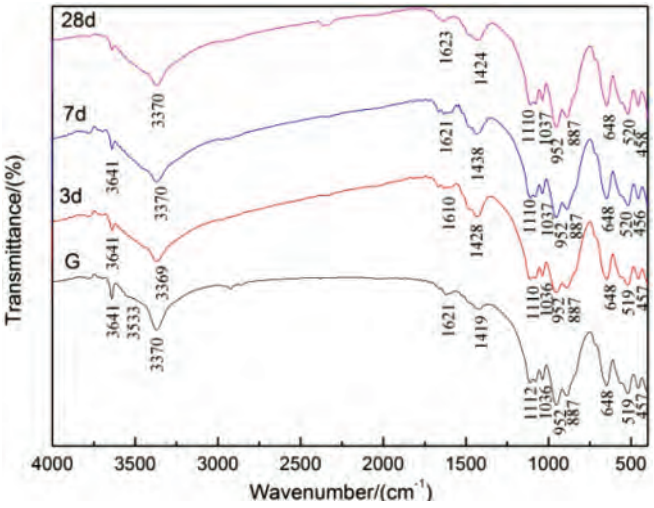


Fig.7 FT-IR spectrums of the dry mixed powder and neat paste specimen of epidote at different ages

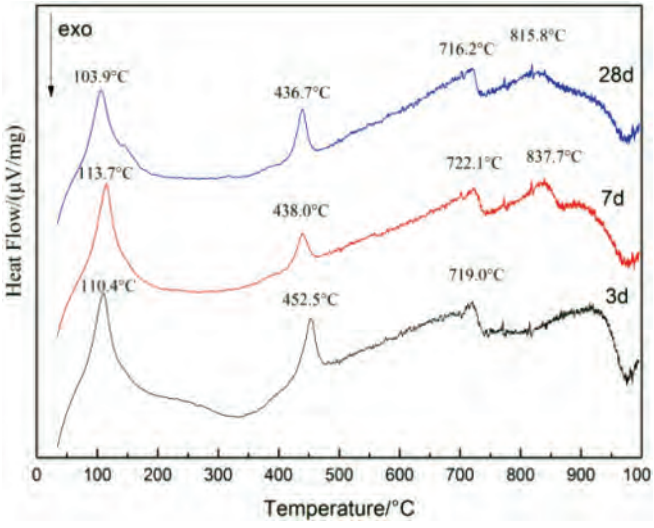


Fig.8 DSC curves of the neat paste specimen of epidote at different ages

$Ca(OH)_2$ exists in the whole system during the hydration process. This is consistent with the XRD and FT-IR analysis shown in sections 2.2 and 2.4. The absorption peaks at 110.4°C, 113.7°C and 103.9°C are due to the dehydration of ettringite and C-S-H gel [11-14]. These three absorption peaks are sharp and high, indicating that at the age of 3d, a considerable amount of ettringite and C-S-H gel is already generated in the system, which is consistent with the XRD, SEM and FT-IR analysis results in sections 2.2-2.4.

4. Conclusions

(1) The neat paste specimen mainly made of epidote had a compressive strength of 5.50 MPa, 6.039 MPa and 6.27 MPa at the age of 3d,d and 28d, respectively indicating that finely ground epidote has pozzolanic reactivity.

(2) Through XRD, SEM, FT-IR and DSC analysis, it is found that the main hydration products of the finely ground epidote are C-S-H gel and ettringite. C-S-H gel can closely combine and grow with mineral particle surfaces.

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