



Research paper

Stability, hardening and porosity evolution during hydrothermal solidification of sepiolite clay

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ABSTRACT

Hydrothermal solidification of sepiolite clay was carried out at different curing temperatures (100 °C and 200 °C) with an introduction of calcium hydroxide. The addition of calcium hydroxide greatly affected the stability of sepiolite within sepiolite clay. When Ca/Si molar ratio (C/S) is lower than 0.4, sepiolite sustained well at both curing temperatures even for a long curing time (72 h), and above C/S = 0.4 sepiolite decomposed readily. During early-stage hydrothermal processing (before 12 h), fine-grained particles of calcium silicate hydrate (CSH) gel precipitated and provided an early strength enhancement for the specimens solidified at 100 °C and 200 °C respectively. After that, fibrous CSH(I) that formed after 12 h was responsible for the highest strength and platy tobermorite after 72 h led to a slight decrease in strength at 200 °C, while agglomerated sponge-like CSH gel formed after 72 h contributed to the highest strength at 100 °C. The intercrystalline pores of crystalline CSH, including CSH(I) and tobermorite, formed at 200 °C provided more porosity than the gel pores at 100 °C within solidified specimens.

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1. Introduction

Sepiolite, a hydrous magnesium silicate with a chemical formula of $Mg_8Si_{12}O_{30}(OH)_4 \cdot 6H_2O$ (Perraki and Orfanoudaki, 2008), has a fibrous structure consisting of 2:1 tri-octahedral silicate sheets and pore channels. Over the past decades, sepiolite has been used as catalysts (Shuali et al., 1991), catalyst supports (Lazarevic et al., 2010), adsorbents (Ugurlu, 2009) and molecular sieves (Ruiz-Hitzky, 2001) because of its high surface area and cation exchange capacity.

Sepiolite is widely distributed in Spain, Kenya, Nevada and California (USA), Japan, Russia and China, but there is only limited availability of high-quality sepiolite reserves in the world (Islk et al., 2010). Sepiolite is commonly called 'sepiolite clay' (SC) in China, which has a low grade of sepiolite content, generally around 8% to 20% (Dong, 2001), and poor mechanical performances, e.g. fine-grained appearance with low strength. Besides, sepiolite generally coexists with impurities such as talc, dolomite, calcite and quartz (Karakaya et al., 2004; Perraki and Orfanoudaki, 2008; Singer et al., 1998). Those defects of SC mentioned above greatly degrade its performance.

In order to address those problems, hydrothermal processing was recently adopted to solidify kaolinite (Rios et al., 2009), green tuff (Takagi et al., 2009) and diatomaceous earth (Jing et al., 2007; Maeda et al., 2009). The toughness and porosity of solidified materials were improved through the formation of tobermorite. Tobermorite, which is very rare in

nature but can be readily synthesized under hydrothermal conditions, was shown to have excellent cation exchange capacity (Komarneni and Roy, 1983; Siaucunas et al., 2004). Hydrothermal processing is usually performed at low temperatures (≤ 200 °C) so that the inherent porosity of clay minerals could be sustained during the treatment (Ishida, 2002).

Therefore, hydrothermal processing might be suitable for solidifying SC while retaining its inherent properties, which still has not been reported extensively in literature. The objective of the work discussed in this paper is to improve the mechanical and porous properties of SC with the formation of tobermorite and tobermorite is expected to be hydrothermally produced from the impurities instead of the sepiolite phase within SC. Hydrothermal processing was carried out at a commonly-used curing temperature of 200 °C and a lower one of 100 °C respectively. Hydrothermal processing at 100 °C can avoid using autoclaves, which could largely save energy and reduce the cost of hydrothermal solidification. The stability of sepiolite, hardening mechanism and porosity evolution with duration of hydrothermal processing were investigated. The results are expected to provide practical information on the manufacture of products from SC which could be used as adsorbents, catalysts, carriers and similar application in water treatment.

2. Experimental

2.1. Materials

SC used in this study without any pretreatment was obtained from Hongyan Sepiolite Co., Ltd. (Hunan Province, China). The main chemical composition, measured by X-ray fluorescence (XRF), was 55.9% of SiO_2 ,

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15.5% of MgO, 6.29% of CaO, 4.61% of Al₂O₃, 1.66% of Fe₂O₃, 0.35% of K₂O, 0.17% of TiO₂ and 15.42% of ignition loss. The mineral composition measured by X-ray diffraction (XRD) was sepiolite (Mg₈Si₁₂O₃₀(OH)₄·6H₂O), quartz (SiO₂), talc (Mg₃Si₄O₁₀(OH)₂) and calcite (CaCO₃). The content of sepiolite within SC measured by a thermal gravimetric analysis (TG) according to the method depicted by Yener et al. (2007) was about 30%. Reagent-grade calcium hydroxide (Ca(OH)₂, Sinopharm Chemical Reagent Co., Ltd.) was served as an additive.

2.2. Hydrothermal processing

SC mixed with calcium hydroxide at different Ca/Si molar ratios (C/S) from 0.12 (raw SC) to 1.0 respectively was used as starting materials. The starting material was mixed manually in a mortar with 15 mass% of distilled water, and then the mixture was compacted in a rectangular-shaped mold (5 × 40 × 45 mm³) at a pressure of 30 MPa. The green specimens removed from the mold were first autoclaved under saturated steam pressure at 200 °C for 12 h to investigate the effect of calcium hydroxide addition on the stability of sepiolite and the strength of specimens solidified after hydrothermal processing. The optimum C/S of 0.4 was then used for following experiments to study the stability of sepiolite, hardening mechanism and porosity evolution of solidified specimens for different curing times (up to 72 h) at 100 °C and 200 °C respectively. The Teflon-lined stainless steel apparatus used for autoclaving in this experiment was described in detail in our previous work (Jing et al., 2007). After autoclaving, all the solidified specimens were dried at 80 °C for 24 h.

2.3. Characterization

The XRF data of SC were collected on a Bruker SRS3400 WDS spectrometer with a rhodium tube. The sample was prepared as a bead by fusing a mixture of 0.8 g SC and 8 g Li-Tetraborate (Li₂B₄O₇). The mineral composition was characterized by X-ray powder diffraction method (XRD, RINT 2200VL, Rigaku) using CuKα radiation (λ = 1.5406) between 5° and 70° 2θ at a scan speed of 5° 2θ/min with a 2θ step of 0.02°.

All solidified specimens (15 × 40 × 7 mm³) were first used to measure three-point flexural strength, and the measurements were conducted in triplicate on a strength testing machine (XQ-106A, Xie Qiang Instrument Technology) at a loading rate of 0.5 mm/min, and all strength values were the averages of three measurements on three different specimens. Then the crushed specimens were investigated using several techniques. XRD analysis was used to characterize the evolution of crystalline phases. Fourier-transform infrared (FTIR) spectra were recorded on a Bruker Tensor37 spectrometer using a pressed-disk technique that prepared samples by compressing the mixture of 2 mg specimen and 200 mg KBr. Thermo-gravimetric analysis and differential scanning calorimetry (TG-DSC) was performed using a NETZSCH STA449F3 Jupiter simultaneous thermal analyzer in the temperature range from 25 °C to 1000 °C with a heating rate of 10 °C/min. The morphology of the fracture surface coated with Au under argon atmosphere was observed by scanning electron microscopy (SEM, S-4100, Hitachi) using an acceleration voltage of 5 kV. The pore size distribution was obtained by mercury intrusion porosimetry (MIP, Poremaster 33, Quantachrome). – 196 °C N₂ gas adsorption between 0.05 and 0.95 in relative pressure was conducted on a surface area and pore size analyzer (Autosorb-1, Quantachrome) before the samples were outgassed for 24 h at 80 °C to remove adsorbed water. The specific surface area (SSA) was calculated according to the Brunauer Emmett and Teller method (BET) and the pore volume (PV) was derived from the following formula:

$$V = 1.55 \times 10^{-3} V_a$$

where V_a denotes the adsorbed volume of N₂ under a relative pressure of 0.95.

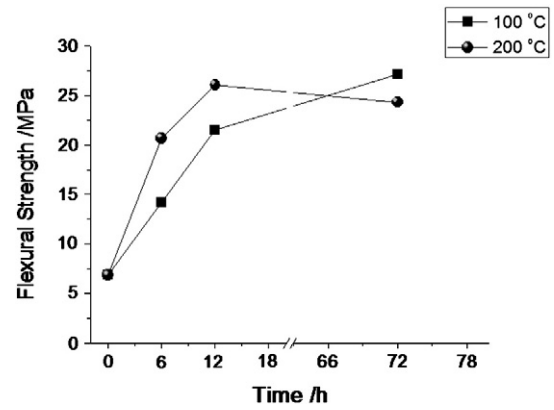


Fig. 1. The effect of calcium hydrate addition on the strength development of the specimens solidified with Ca/Si molar ratio of 0.4 at different curing temperatures of 200 °C (●) and 100 °C (■) for up to 72 h.

3. Results

3.1. Flexural strength

For the specimens solidified with different C/S at 200 °C for 12 h, the highest flexural strength (>25 MPa) was obtained with C/S = 0.4 (not shown as figures). The strength development of the specimens solidified with C/S = 0.4 at different curing temperatures (200 °C and 100 °C) is shown in Fig. 1. For the curing temperature of 200 °C, the solidified specimens increased in flexural strength at an early stage, and then decreased after a longer curing time. However, the flexural strength obtained at 100 °C kept increasing for up to 72 h.

3.2. X-ray diffraction analysis

The mineral phase evolution of the specimens solidified with different C/S at 200 °C for 12 h is shown in Fig. 2. With the addition of calcium hydroxide, the characteristic reflection peaks of sepiolite (at 2θ of 7.3° and 16.7°) remained unchanged until C/S = 0.4, and at the same time a trace of shoulder reflection (at 2θ of 7.7°) corresponding to the (020) plane of 1.1 nm tobermorite tended to form. Over C/S = 0.8, however, both sepiolite and tobermorite phases were no longer observed. The XRD patterns of the specimens solidified with C/S = 0.4 at 200 and 100 °C respectively for up to 72 h are displayed in Figs. 3 and 4. The formation of tobermorite was confirmed during hydrothermal processing at 200 °C, while it was not observed at 100 °C.

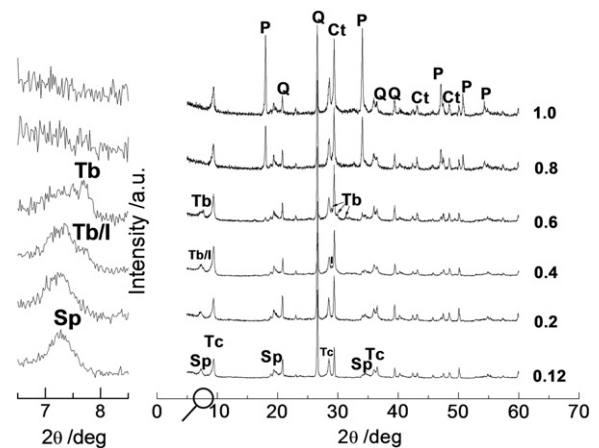


Fig. 2. XRD patterns and assignments of the specimens solidified with different Ca/Si molar ratios at 200 °C for 12 h. The 2° region between 6.5 and 8 is magnified. The reflections are labeled Sp (Sepiolite), Tb (Tobermorite), I (CSH(I)), Tc (Talc), P (Portlandite), Q (Quartz) and Ct (Calcite).

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