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Controlling the heat evaluation of cement slurry system used in natural gas hydrate layer by micro-encapsulated phase change materials

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ABSTRACT

Based on the low hydration heat requirement of cement slurry system used in natural gas hydrate layer and the shortcoming of traditional methods, a novel material, namely, micro-encapsulated phase change material (MPCM-1) was synthesized and used to regulate the temperature profiles and hydration heat of the cement slurry system by a physical method. During this study, the hydration heat was absorbed by MPCM-1 when the temperature of cement slurry system beyond the melting point of the phase change material (PCM), and then the hydration heat was released by the MPCM-1 when the temperature of cement slurry system drops below the crystallization point of PCM. The MPCM-1 containing low melting paraffin wax with urea formaldehyde resin shell was prepared by the method of in situ polymerization. At first, the structure of MPCM-1 was obtained by infrared spectrum analysis (FT-IR). Secondly, the phase change properties of MPCM-1 were measured by using a differential scanning calorimeter (DSC). As a result, it was shown that the melting point and heat of fusion of MPCM-1 is 23.09 °C and −97.49 J/g, respectively. Moreover, the thermal stability of MPCM-1 was obtained by using a synchronous thermal analyzer. Simultaneously, the surface morphology, particle size and distribution of MPCM-1 were also measured by using a scanning electronic microscope (SEM) and Laser particle size analyzer. Then, the MPCM-1 was introduced into the ordinary Portland cement slurry system to prepare a low hydration heat cement slurry system, the heat evaluation of cement slurry system were investigated by using a developed semi-adiabatic test equipment. The controlling effects of MPCM-1 on the heat evaluation of cement slurry system were investigated by the temperature profiles and hydration heat. Particularly, the temperature profiles were characterized by the initial temperature (T_{in}), temperature rise (T_r), maximum temperature (T_{max}), and the hydration time (t_{max}) corresponding to the maximum temperature (T_{max}), respectively. Besides, the effects of MPCM-1 on the mechanical strength of cement slurry system were also studied. As a result, it was shown that the use of the synthesized MPCM-1 reduced the T_r and T_{max} of cement slurry system, it was also confirmed that the cement slurry system prepared by the synthesized MPCM-1 presented excellent mechanical properties.

1. Introduction

Natural gas hydrates are made up of guest gas molecules and main water molecules (Lee et al., 2011; Safronov et al., 2010), and the amount of natural gases trapped in hydrate-bearing sand layers to be 10^{13} m^3 STP–10^{15} m^3 STP (Zhao et al., 2015; Chen et al., 2015). The larger amount of reserves indicate the great potential of natural gas hydrates as a new energy resource if reasonable and economical exploration method was developed (Lee et al., 2011). But, in the deep-water cementing operations, a large number of natural gas hydrates exist in many deep water areas (Xu et al., 2017; Vogt and Jung, 2002; Babu et al., 2014), which poses a great challenge to deep-water cementing, such as low temperature, shallow water and air flow. However, the stability of hydrate formation is the biggest challenge in cementing (Chen, 2011).

It is well know that there are many circumstances in which it is very crucial to control the hydration heat and temperature profiles of the developed cement slurry system, especially during the early hydration periods of cement slurry system, because the early hydration of cement slurry system would produce a significant amount of hydration heat (Wilińska and Pacewska, 2014; Wang and Yan, 2006). Especially for the cementing through the natural gas hydrate layer requires the cement slurry system to quickly set and harden at lower temperature without results in high hydration heat release rate and temperature rise. Because the natural gas hydrate is a meta-stable substance, there are a great influences of temperature and pressure on the stability of gas hydrate, namely, the changes of temperature and pressure can easily lead to the decomposition of gas hydrate (Vasil'ev et al., 2006;

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Khasanov and Shagapov, 2016). Generally, the hydration heat of cement based materials was traditionally regulated by reducing the heat of the hydration of the composite, and the temperature profiles of cement slurry system were traditionally regulated by reducing the hydration heat of cement based materials. For example, generally, the temperature profiles of cement slurry system could be reduced by fly ash, slag, aluminum silicate and silica through chemical means (Osmanlioglu, 2014; Romano et al., 2017; Boncan et al., 2000). But the total amount of heat generated by a cement slurry system is primarily determined by the hydration extent of the cement that has a strong correlation with the strength development. Thus, the strength development of cement slurry system was weakened by reducing the hydration heat through chemical means, especially during the early hydration periods of cement slurry system (Pang et al., 2016). Moreover, the hydration heat of cement slurry system could be also reduced by using phase change materials (PCMs), but the strength development of cement slurry system was limited attribute to the melting effect of PCMs (Sakulich and Bentz, 2012).

Therefore, based on the low hydration heat requirement of cement slurry system used in natural gas hydrate layer and the shortcoming of traditional methods, a novel material, micro-encapsulated phase change materials (MPCM-1) was synthesized, and then used to regulate the temperature profiles of cement slurry system through physical means. Because the solid polymer shell that encapsulates the PCM prevents the melted material from chemically interacting with the cement slurry system. Thus, the early strength development of cement slurry system was largely unaffected. Moreover, the influences of the melting effect of phase change materials on the strength development of cement slurry system was also avoided. At first, the MPCM-1 containing low melting paraffin wax with urea formaldehyde resin shell was synthesized by the method of in situ polymerization, and the structure of MPCM-1 was confirmed by FT-IR. Secondly, the phase change properties and thermal stability were investigated by DSC and synchronous thermal analyzer, respectively. Simultaneously, the surface morphology, particles size and distribution of MPCM-1 were measured by SEM and Laser particle size analyzer, respectively. Then, the MPCM-1 was introduced into the ordinary Portland cement slurry system to prepare a low hydration heat cement slurry system. Currently, the semi-adiabatic test apparatus was developed and used to test the temperature profiles and hydration heat of the developed cement slurry system in early hydration stage (48 h). Besides, the influences of MPCM-1 on the mechanical performances of cement slurry system were also investigated.

2. Experiment

2.1. Materials

Low melting paraffin wax (Industrial products, phase transition temperature T_m is 20 °C) was purchased from Zhenjiang Runzhou zezone special wax factory. Acetic acid (AR, ≧99.5%), triethanolamine (AR, ≧99.0%), urea (AR, ≧99.0%), sodium hydroxide (AR, ≧98.0%), formaldehyde (AR, 37.0% ~ 40.0%), ammonium chloride (AR, ≧99.5%), emulsifier OP-10 (AR, ≧99.0%), all the reagents are purchased from Chengdu Kelong Chemical Co., Ltd (Chengdu, China). SMA Scripset 520 was a product of Xinxiang Xinli Industry, the anionic emulsifiers SMA Scripset 520 is a copolymer of styrene and maleic anhydride, and the molecular weight of SMA Scripset 520 is about 7×10^4–8×10^4 g/mol. Fresh and deionized water were prepared in our own laboratory, and the specific conductivity of deionized water is 1.45 μS when the ambient temperature is 25 °C.

The G grade oil well cement was purchased from Jiahua Co. Ltd. with No. P·II 52.5 Portland. The chemical compositions of cement, fly ash and slag are given in Table 1, and the physical properties are presented in Table 2. Besides, the particle size and distribution was measured by using a laser particle size analyzer (Master sizer 2000, Malvin instruments), which as shown in Fig. 1. As a result, it was shown that the medium particle diameters of cement, fly ash and slag (i.e., D_{50}) are 13.1 μm, 3.53 μm and 6.99 μm, respectively.

2.2. Synthesis of MPCM-1

(1) **Emulsion preparation:** At first, the dispersion of styrene-maleic anhydride copolymer was prepared with 1.60 g Scripset SMA 520, 0.20 g sodium hydroxide and 80 g deionized water. Secondly, 23.0 g low melting paraffin wax and 0.44 g emulsifier OP-10 were added into above emulsion system, then, the above emulsion system was mixed by using a digital high-speed stirring apparatus (ZNJ-2, Qingdao Tongchun Oil Instrument CO.,China.) at 8000 r/min for 30 min. Besides, the pH value of the above emulsion was adjusted to 5.0 with a certain amount of acetic acid.

(2) **Prepolymer synthesis:** 20 mL deionized water, 6.0 g urea and 14.6 mL formaldehyde were mixed and used to synthesize the urea formaldehyde resin prepolymer. The pH value of the solution system was adjusted to 8.0–8.5 by triethanolamine. Then, the above solution system was stirred at 60 °C about 2 h, and the prepolymer was obtained by adding the same volume of deionized water into above solution.

(3) **Preparation of MPCM-1:** Firstly, the prepolymer was added into the emulsion by using a constant pressure drop funnel within 30 min, and the emulsion was stirred by using a electric blender (JJ-1, Shanghai Shuang Jie Experimental Equipment Co., Ltd.) at a rate of 300 r/min. Secondly, the above mixtures were continued to stir for 30 min, and the temperature of the reaction system was raised to 65 °C. Then, an appropriate amount of ammonium chloride solution (10 wt%) was added into the mixtures in droplets within 2 min. Finally, the pH value of the mixtures was adjusted to 9.0 by 10 wt% NaOH solution, with this, the polymerization was terminated. Fig. 2 shows the schematic diagram for the synthesize of MPCM-1. Moreover, the mixtures was cooled to room temperature and filtered. Then, the MPCM-1 was washed twice by distilled water, and the wet MPCM-1 was then dried by using a freezing dryer (FD-1A-50, Beijing boyikang laboratory equipment Co., Ltd.).

Additionally, the core content of MPCM-1 was measured by the DSC heating curve according to the following formula (1). The result shows that the core content of MPCM-1 is 66.89%.

$$w = \frac{\Delta H_{MPCM-1}}{\Delta H_{paraffin}} \times 100\% \quad (1)$$

where ΔH_{MPCM-1} is the melting enthalpy of MPCM-1, $J \cdot g^{-1}$, and the $\Delta H_{paraffin}$ is the melting enthalpy of low melting paraffin wax, $J \cdot g^{-1}$.

2.3. Characterization of MPCM-1

2.3.1. Infrared spectrum analysis

The Fourier transform infrared spectroscopy (FT-IR) of low melting paraffin wax, urea formaldehyde resin prepolymer and MPCM-1 were obtained by Perkin Elmer RX-1 spectrophotometer (Beijing Reili Analytical Instrument) in the optical range of 440–4400 cm^{-1}. The scanning number was 32, the resolution was 4 cm^{-1}. Besides, the known weight (about 1.0 mg) of the synthesized MPCM-1 was mixed with a appropriate amount of KBr, then, the KBr pellet was prepared. For the low melting paraffin wax and prepolymer, the pure KBr pellets were prepared firstly, then, the moderate amount of low melting paraffin wax and prepolymer were dropped onto the KBr pellets, the KBr pellets were used to test.

2.3.2. Thermal analysis

The phase change properties of the dried MPCM-1 were investigated by using a differential scanning calorimeter (American TA, DSCQ20).