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Converting hydration heat to achieve cement mixture with early strength and low hydrating-thermal dissipation

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HIGHLIGHTS

- Energy storage microsphere is developed by coating PCM in PMMA.
- Energy storage microsphere reduces the hydrating thermal dissipation obviously.
- The hydration heat of Aluminate cement is converted to cure Portland cement.
- Cement mixture with early strength and low hydrating thermal dissipation is achieved.

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ABSTRACT

Cement mixture with the properties of early strength and low hydrating thermal dissipation is necessary to cementing the shallow natural gas hydrate formation in deep water area. The research objectives are designed to utilize the energy storage microsphere in cement mixture to achieve early strength and low hydrating thermal dissipation. Considering the strength and hydrating thermal dissipation, the mixture of Class G oil well cement and aluminate cement with the quality ratio of 1:1 is proposed. The polymethyl methacrylate microsphere is used to coat phase change materials to prepare the energy storage microsphere, which can be used in cement mixture directly and stably. The energy storage microsphere could reduce the hydrating thermal dissipation of cement mixture obviously. Because of converting the hydration heat of Aluminate cement to cure Portland cement and PMMA framework, energy storage microsphere has little negative effect on the early strength of cement mixture.

1. Introduction

The oil and natural gas reserves in the South China Sea are about 1.7×10^9 and 5.38×10^{12} m^3 respectively, most of which exist in the deep-water area [1,2], and therefore, the development of oil and gas resources in deep-water area has gradually become one of the main energy strategy in China. The production of oil and gas is achieved via the well connecting the hydrocarbon reservoir and the ground production equipment [3]. Due to the well depth and complex geological conditions, usually the casing is used in well to support the wellbore, and in order to isolate the oil, gas and water layer for guaranteeing the oil and gas safe production, well repair and other well operations, well cementing is conducted in each oil and gas wells. During the process of cementing, first, cement slurry is prepared, and then the slurry is pumped into the annular space between the casing and formation via the inner of casing to form cement sheath [4]. Therefore, the performance of cement materials is one of the key factors affecting the cementing quality [5].

Portland cement has been applied for cementing well for over a hundred years [6]. However, due to the special geological conditions under deep water, the temperature of seabed mud line is very low, which is just about 4 °C [7]. Because of the low temperature, when isolating the shallow formation of which the depth under seabed mud line is less than 1000 m, Portland cement will lose the ability of hydration and hardening to lead isolation failure. Compared with Portland cement, aluminate cement which is one kind of fast-hardening cement can harden quickly at low temperature [8], and even at 4 °C. Therefore, in view of the low temperature, aluminate cement has the potential to be used as well cement for cementing the shallow formation under deep water.

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However, low temperature environment is just one of the harsh conditions needed to be considered for well cementing under the deep water. In the deep water area, due to the special low temperature and high pressure environment, natural gas hydrate can be formed and exist in the shallow formation [9,10]. One of the properties of natural gas hydrate is that when be heated, it will occur thermal decomposition to release a large number of methane gas [11–13], which could induced severe geological disasters, such as landslides, tsunamis, etc. [14]. Due to the early strength property, the hydration process of aluminate cement could release a lot of heat in a short time to cause the around temperature increase obviously. Therefore, aluminate cement is not suitable for cementing the shallow natural gas hydrate formation.

In view of the low temperature and the existence of natural gas hydrate, in order to guarantee the successful development of oil and gas resources under deep water, the well cement mixture with early strength and low hydrating thermal dissipation is necessary. In this paper, first, class G oil well cement is used to decrease the hydrating thermal dissipation of aluminate cement; second, the high-strength and micro-scale energy storage microsphere is developed, and then is applied for converting the hydration heat of aluminate cement to cure Portland cement to achieve cement mixture with low hydrating thermal dissipation. At last, the hydrating thermal dissipation and strength of the cement mixture is tested.

2. Experimental

2.1. Materials

Class G oil well cement and aluminate cement were used in the experiments. The typical chemical composition is given in Table 1. Solid paraffin was choice as the phase change materials (PCM). Fumed silica, Methyl methacrylate (MMA, Chemical Pure), Benzoyl peroxide (BPO, Chemical Pure), divinylbenzene (DVB, Chemical Pure) were used to prepare energy storage microsphere.

Seven cement samples (S1-7) were prepared to research the strength and hydrating thermal dissipation performance of the mixture of aluminate cement and Class G oil well cement, and the mix proportions are shown in Table 2. Furthermore, S8 and S9 as shown in Table 3 were prepared to analyze the effect of energy storage microsphere on the strength and hydrating thermal dissipation of cement mixture.

2.2. Method

2.2.1. Manufacturing process

Cement slurry was mixed according to API 10B-2-2013 [15]. After being prepared, cement slurry was placed into a thermal insulation container to test the hydrating thermal dissipation and compressive-strength moulds (5 cm × 5 cm × 5 cm).

2.2.2. The testing of hydrating thermal dissipation

The hydrating thermal dissipation was characterized by evaluating the temperature change of cement mixture. The temperature of cement mixture was tested by calorimeter, and the testing device was designed as shown in Fig. 1. During the testing process, the calorimeter was kept in a constant temperature environment, and the cement mixture was kept in a thermal insulation container. In this research, the constant temperature environment was realized by water bath with 20 °C. With the time extending, the temperature of cement mixture can be outputted directly by the data acquisition system and displayed as curve on the screen of the computer in real time. The heat dissipation constant of this device is K = 120.84 J/(h °C) which is less than the value of international standard (167 J/(h °C)), and therefore, this testing method can be applied for testing the hydrating thermal dissipation of cement mixture.

2.2.3. Compressive strength

The device and moulds were put into curing chamber with water. Considering the low temperature circumstance under deep water, cement slurries were cured for 24 h at 4 °C, 10 °C and 20 °C, which was choice to simulate the downhole temperature. The curing pressure was 0.1 MPa. After curing, the hardened cement cubes were removed from the moulds, and placed in hydraulic compression test equipment, and loaded to failure. The compressive strength is recorded as the maximum compressive stress.

2.2.4. The preparation of energy storage microsphere

The energy storage microsphere was prepared by suspension polymerization in the laboratory. A procedure and selected experimental conditions were given as follows. Fumed silica which was used as dispersant was dispersed into 200 ml distilled water by stirring at the speed of 650r/min for 15 min to prepare the continuous medium. And then the medium was carried out in a 500 ml three-necked flask equipped with a stirrer at the speed of 350 r/min. MMA (13 g), BPO (0.36 g), DVB (0.063 g) and paraffin which was prepared by melting the solid paraffin were mixed to obtain the oil phase solution. And then the oil phase solution was added to continuous medium with stirring in a water bath of 85 °C. After the polymerization proceeded for 2 h, the energy storage microspheres were obtained. After being dried in vacuum at 50 °C, The microsphere was used in cement mixture directly.

2.2.5. SEM

Scanning Electronic Microscope (SEM) analyses were conducted in the State Key Laboratory of Heavy Oil Research to observe the appearance of microsphere by using scanning electronic microscope in secondary electron mode. The surface of energy storage microsphere is coated by gold/palladium.

2.2.6. DSC

Differential Scanning Calorimeter (DSC) was choice to test the phase transition temperature and phase transition enthalpy of energy storage microsphere. The testing temperature scope is from 0 to 100 °C, the temperature changing rate is 10 °C/min and the displacement of N_2 was set as 70 mL/min.

2.2.7. TGA

Thermal Gravimetric Analyzer was used to evaluate the thermal stability of energy storage microsphere. The displacement of N_2 was set as 20 mL/min. The sample was heated from room temperature to 600 °C at the rate of 10 °C/min. Ceramic sample pot was used as reference material.

2.2.8. Encapsulation efficiency

Energy storage microsphere comprises solid paraffin (PCM) and monomer polymer. The encapsulation efficiency of PCM in energy storage microsphere is related to the phase transition enthalpy of PCM and energy storage microsphere and the mass ratio of PCM to monomer polymer. The encapsulation efficiency was calculated from Eq. (1).

$$\eta = \frac{Hm}{\left(\frac{Wpc/Wm}{Wpc/Wm+1}\right) \cdot \Delta Hp} \times 100\% \quad (1)$$

where η is the encapsulation efficiency, %; ΔHm is the phase transition enthalpy of energy storage microsphere, J/g; ΔHp is the phase transition enthalpy of PCM, J/g; Wpc/Wm is the mass ratio of PCM to monomer polymer.

3. Results and discussion

3.1. The mixture of Class G oil well cement and aluminate cement

Because of the low temperature under deep water, Portland cement will lose the ability of hydration and hardening. Considering the existing of natural gas hydrate, due to hydration heat releasing, the aluminate cement with the early strength property also cannot be applied for cementing the shallow formation under deep water directly. In order to decrease the hydrating thermal dissipation of cement mixture, the Class G oil well cement of which the hydration rate is very slow at low temperature is used to mix with aluminate cement in our research. However, the oil well

Table 1
Chemical composition of Class G oil well cement and aluminate cement.

Chemical component (wt%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	MgO	TiO_2
Class G oil well cement	22.7	3.39	4.81	65.6	0.90	1.21	0.90	–
Aluminate cement	6.74	52.0	2.23	34.8	0.81	–	–	0.37