



Preparation, characterization and investigation of low hydration heat cement slurry system used in natural gas hydrate formation



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ABSTRACT

Based on the low hydration heat requirement of cement slurry system used in natural gas hydrate formation and the effective utilization of industrial waste materials, the fly ash and slag were introduced into ordinary Portland cement to prepare a low hydration heat cement slurry system. During this study, the influences of fly ash and slag on the heat evaluation of cement slurry system were investigated by temperature profiles and hydration heat, which were tested by using a developed semi-adiabatic test equipment. Currently, the temperature profiles of cement slurry system were studied by the initial temperature (T_i), temperature rise (T_r), maximum temperature (T_m), and the hydration time (t_m) corresponding to the maximum temperature, respectively. Moreover, the investigations of the influences of fly ash and slag on the strength property of cement stone were investigated. Then, a novel low hydration heat cement slurry system CFS₁₋₁ used in natural gas hydrate formation was developed by the mass ratio of 2:1:1 (cement: fly ash: slag). Simultaneously, the initial hydration process of CFS₁₋₁ was investigated by low field NMR, the rheological and thickening properties of CFS₁₋₁ were also studied. Besides, some other application performances, such as density, fluidity, stability and consistency, were also studied. As a result, it was found that the application performances of CFS₁₋₁ meet the cementing requirement of hydrate formation. In addition, the effective and reasonable utilization of industrial waste materials were also realized during this study.

1. Introduction

There are a large output of fly ash and slag in China, and about 500 million tons of fly ash has been produced by power plant, simultaneously, the production of slag has also increased year by year (Chen et al., 2010; Itoh, 2004). As a result, the efficient utilization of slag and fly ash has caused great concern in the worldwide (Yao et al., 2011). Fly ash and slag have been extensively used as supplementary cement based materials in the architecture field, the main reason is that the application performances of concrete was improved by using fly ash and slag (Han et al., 2016). Currently, the main researches are focused on the study of the influences of fly ash and slag on the durability and mechanical properties of concrete specimen (Yao et al., 2011; Eren, 2002; Wang et al., 2014). Simultaneously, the influences of industrial waster materials on the hydration reaction of concrete cement paste have been also studied by using calorimetric and thermal analysis (Wang et al., 2011, 2014; Wilińska and Pacewska, 2014). However, the researches on the application of slag and fly ash in oil well cement are short. As early as the 90s of the last century, many researches have

investigated the preparation of drilling fluids solidified with blast furnace slag (MTC) (Cowan et al., 1992; Bengé and Webster, 1994), but the field application shows that the MTC solidified body was liable to serious embrittlement, and the MTC method can only be used in the cementing of surface and intermediate casing. Thus, the application of fly ash and slag in cementing was limited. At present, the fly ash and slag were used to prepare low-density cement slurry system (Chen et al., 2012; Liu et al., 2015).

Natural gas hydrate is considered as a new type of energy with great potential for development, and the most widely cited estimate of natural gas in global hydrates is $21 \times 10^{15} \text{ m}^3$ of methane at STP (corresponding to about 10 Tt of methane carbon) (Seol and Lee, 2013; Sun et al., 2014). Hydrates have attracted considerable attention all over the world attribute to their potential as a future energy resource, besides, the possible threat they pose to seafloor stability and global climate was also included (Sun et al., 2014). Additionally, deep-water oil and gas resources are considered a preface to today's oil industry. Thus, the study of deep water cementing is of great significance (Khain and Polyakova, 2004). However, because hydrate is a meta-stable substance

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and easily decomposed attribute to the changes of temperature and pressure (Lee et al., 2011), moreover, the low temperature and low formation fracture pressure of deep water shallow have caused great difficulties (Khain and Polyakova, 2004). Therefore, there are still many challenges that need to be overcome in deep water cementing (Max and Johnson, 2016; Liu et al., 2017).

Investigations of the influences of fly ash and slag on the hydration process of composite binder in the early stage were studied by a large number of researchers (Yao et al., 2011; Wilińska and Pacewska, 2014). As a result, it was shown that the use of fly ash and slag reduced the hydration heat of cement slurry system and the early mechanical strength of cement stones. Besides, a retarding effect of fly ash and slag on the hydration of composite binders was also observed, moreover, it was found that the later mechanical strength and durability of composite binders are increased (Han et al., 2016; Liu et al., 2014). Therefore, during this study, the industrial waster materials, such as fly ash and slag, were introduced into ordinary Portland cement to prepare a low hydration heat cement slurry system, the hydration heat evaluation of cement slurry system was measured by a developed semi-adiabatic test equipment. It was worth mentioning that the main function of fly ash and slag is to control the hydration heat of cement slurry system. Besides, the slag was used to accelerate the initial hydration rate of cement slurry system attribute to filling effect and nucleation, and the fly ash was used to improve the durability of cement stone in later hydration stage. Here, the controlling effects of fly ash and slag on heat evaluation of cement slurry system were characterized by temperature profiles and hydration heat. Besides, the investigations of the influences of fly ash and slag on the early hydration reaction of cement slurry system were produced by low field NMR. A new attempt about cementing of natural gas hydrate formation has been done in our current study. Of course, the effective and reasonable utilization of fly ash and slag were also included.

2. Experiment section

2.1. Materials

Class G oil well cement was provided by Jiahua Co. Ltd. with No. P-II 52.5 Portland. The chemical compositions of cement, fly ash and slag are given in Table 1.

The particle size and distribution of cement, fly ash and slag were tested by using a laser particle size analyzer (Master sizer 2000, Malvin instruments), and the results were presented in Fig. 1. It was confirmed that the fly ash and slag are finer than cement, the medium particle diameters (D_{50}) of cement, fly ash and slag are 13.1, 3.53 and 6.99 μm , respectively.

2.2. Preparation of cement slurry system

During this study, the cement slurry, which as shown in Table 2, were prepared and investigated. The preparation and measurement were accomplished according to the API recommended practice 10 B (19). Additionally, because the hydration heat of cement slurry system are mainly depends on the content of cement based materials, therefore, the content of cement based materials is approximately consistent in each cement slurry systems.

Table 1

Chemical compositions of cement, fly ash and slag/%.

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	Na ₂ Oeq	SO ₃	LOI
Cement	22.8	4.55	2.82	65.3	2.74	–	–	0.55	2.92	3.9
Fly ash	60.1	23.4	4.14	3.52	0.80	0.42	2.13	–	0.46	5.34
Slag	34.7	11.6	–	35.9	10.7	0.80	0.60	–	5.70	1.27

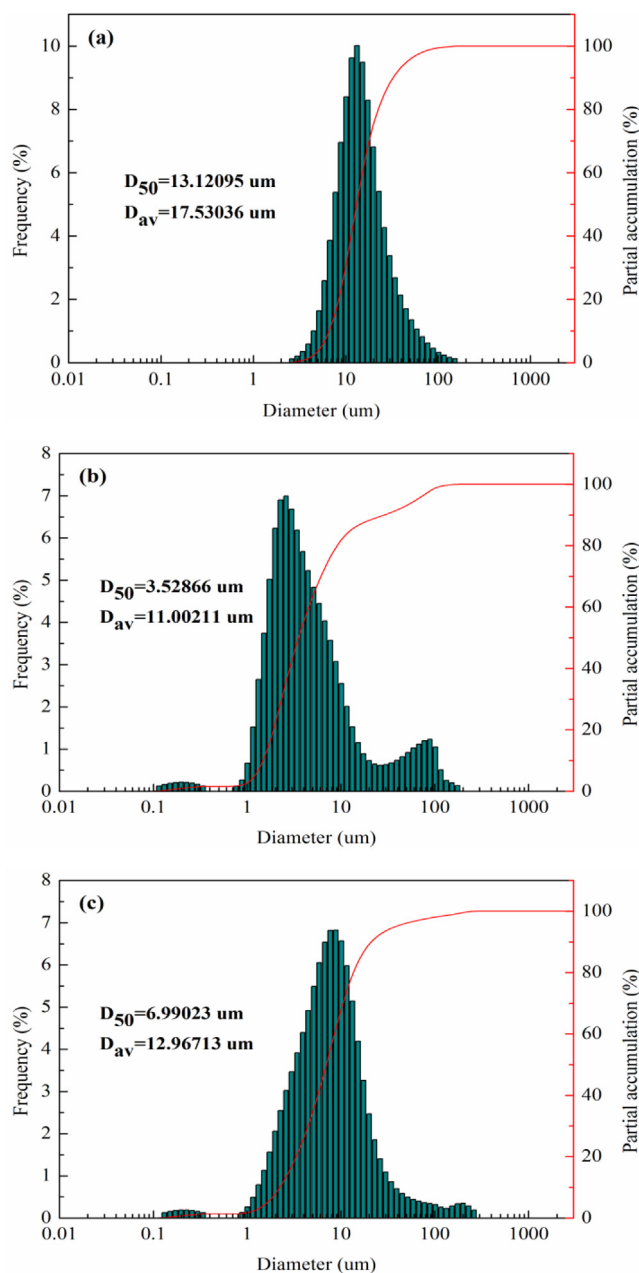


Fig. 1. The particle size distribution curve of cement (a), fly ash (b) and slag (c).

2.3. Heat evaluation of cement slurry system

During this study, the heat evaluation of cement slurry system was investigated by temperature profiles and hydration heat. Particularly, the temperature profiles of were characterized by the parameter of T_i , T_r , T_m and t_m , respectively. Semi-adiabatic test apparatus was developed and used to measure the temperature profiles of cement slurry system, and then the hydration heat of cement slurry was calculated according to the international standard GB/T 12959-2008. The developed semi-

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