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Research Paper

Investigation of the hydration kinetics and microstructure formation mechanism of fresh fly ash cemented filling materials based on hydration heat and volume resistivity characteristics

Bo Yin[a,b], Tianhe Kang[a,*], Jianting Kang[a], Yuejuan Chen[a,b], Linlin Wu[a], Mingze Du[a]

[a] Institute of Mining Technology, Taiyuan University of Technology, Taiyuan 030024, China
[b] School of Mining and Technology, Inner Mongolia University of Technology, Hohhot 010051, China

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ABSTRACT

Fly ash cemented filling materials (FCFM) have received a great deal of attention in recent years as more sustainable solutions to the large-scale utilization problems of fly ash and coal gangue. Based on the hydration heat and the volume resistivity characteristics, this study examined the changes in the fresh FCFM properties from the thermodynamic and electrical perspectives, which reflected the characteristics of the hydration kinetics and microstructure formation mechanism of the FCFM. The results showed that the hydration exothermic process of the FCFM exhibited a rapid reaction stage, an induction stage, an acceleration stage, a deceleration stage and a stable stage. Compared with cement, the mixture of fly ash and coal gangue resulted in a substantially lower hydration heat. The volume resistivity of the FCFM changed over time, initially increasing, then decreasing, then increasing again. The hydration kinetics of the FCFM could be described by three processes: nucleation and crystal growth (NG), interactions at the phase boundaries (I) and diffusion (D). The NG process dominated in the early stage of hydration, and the I and D processes gradually became dominant as the hydration degree increased. Compared with cement, changing the hydration kinetics required a higher degree of hydration in the mixture of fly ash and coal gangue. The improvement in the hydration reaction rate of FCFM due to additives was primarily reflected in the early hydration stage. The calculated data on the C-S-H gel content of the FCFM paste agreed well with the changes in the uniaxial compressive strength (UCS) and plane porosity over time. Remarkable negative correlations between the plane porosity and the UCS and between the plane porosity and the C-S-H gel content were found, along with a significant positive correlation between the C-S-H gel content and UCS. A microstructure formation mechanism model of the FCFM was constructed, and the hydration process of the filling material was divided into a dissolution period, a hydration period and a flocculated-structure formation and growth period. These findings provide new insights into the hydration kinetics and microstructure formation mechanism of fresh FCFM.

1. Introduction

Coal is China's most important energy resource and plays an enormous role in promoting China's economic development and social progress. However, because of the large-scale exploitation of coal, China has also paid a heavy price in terms of environmental degradation and security (Tian et al., 2010; Xie et al., 2006; Zhang et al., 2018). The longwall caving method has been mostly used for coal mining in China. This mining mode has caused surface subsidence, which triggers ecological environmental destruction and poses geological hazards (Chen et al., 2018; Hu and Lian, 2015; Li et al., 2016). In addition, fly ash is an industrial by-product of coal fired in thermal power plants. Coal gangue is solid waste generated in coal mining and washing processes, and it consists primarily of clay rocks. In recent years, the amount of fly ash and coal gangue generated has rapidly increased. A large amount of emissions and low utilization of fly ash and coal gangue can cause a number of serious problems, such as water and soil pollution, disruption of ecological cycles, and various environmental hazards (Blissett and Rowson, 2012; Li et al., 2017a; Priyadharshini et al., 2017; Yao et al., 2015; Zhou et al., 2014).

In recent decades, the use of backfill mining technology with fly ash cemented filling materials (FCFM) has attracted increasing attention in China (Huang et al., 2011; Zhang et al., 2015). The FCFM has obvious advantages, such as reductions in engineering costs and pumping power

* Corresponding author.
E-mail address: kangtianhe@163.com (T. Kang).

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requirements. Thus, fly ash and coal gangue are used in backfill mining, providing a green solution for the large-scale use of fly ash and coal gangue while avoiding the adverse environmental and ecological effects of these waste materials. Regarding the FCFM characteristics, previous studies have primarily focused on raw material composition, material proportions, rheological behavior, and backfilling technology (Huang and Sun, 2004; Peyronnard and Benzaazoua, 2012; Rani and Jain, 2017; Wu et al., 2013). Nevertheless, the performance of the filling material still does not meet the requirements of coal enterprises, and some shortcomings remain, such as low early strength, large deformation and severe bleeding (Du et al., 2016; Yin et al., 2018). The FCFM, composed of fly ash, coal gangue, cement, additives and water, is a multicomponent mixed material, in which the differences in physical and chemical properties of the different components directly affect the hydration process of the filling material. Accurately understanding the changing rules of the hydration kinetics process and the microstructure formation mechanism of the FCFM will facilitate analysis of the reasons for the above shortcomings and then control of the formation process of the filling material structure, as well as provide reasonable process parameters. To date, few reports exist on the hydration kinetics of FCFM, the FCFM and water contact's influence on the hydration reaction, plastomer formation and till hardening; in addition, the entire development process of the microstructure and its formation mechanisms are not well understood.

Over the past several decades, numerous authors (Chaube et al., 2005; Knudsen, 1980; Krstulović and Dabić, 2000; Navi and Pignat, 1996; Tomosawa, 1997) have proposed several hydration kinetic models based on the cement hydration kinetics law. These works laid a good foundation for further research on the cement hydration mechanism. With the development and deepening of research, it was revealed that, compared with cement, the hydration of cement that incorporates mineral admixture materials is much more complex because of the coexistence of cement hydration and reactions of the mineral admixtures. Thus, some authors (Han et al., 2015; Merzouki et al., 2013; Tydlitát et al., 2014; Wang et al., 2010; Zhang et al., 2016) have also examined the hydration kinetics of cement-slag, cement-red mud, cement-fly ash, and other cement-based materials. Currently, the most commonly used method to study the hydration kinetics of cement-based materials is to determine the isothermal hydration heat emission curve of the material. According to the hydration heat characteristics of the cement-based materials, the hydration kinetics of the hydration process were analyzed. The rate of hydration and the degree of hydration could be clearly described by the change in the characteristics of the hydration kinetics. Furthermore, the resistivity method has been widely used over the past few years to study the cement hydration process (Li et al., 2017b; Lu et al., 2018; Muazu et al., 2016; Pei et al., 2017; Wei, 2004; Wei et al., 2008; Xiao and Li, 2009; Zhang et al., 2009). The resistivity method is a nondestructive testing method, and the resistivity versus time curve reflects the changes in the macroscopic and microscopic properties of fresh cement-based materials during setting and hardening.

In this paper, based on the hydration heat and the volume resistivity methods, the changes in fresh FCFM properties were observed from thermodynamic and electrical perspectives, which reflected the characteristics of the hydration kinetics and hydration process of the FCFM. In addition, the water adsorption method was used to estimate the C-S-H gel content in the FCFM with different curing times, allowing a comparative study of the relationships between the C-S-H gel content and strength and between the C-S-H gel content and porosity. These analyses represent a suitable way to explain the microstructure formation mechanism of the FCFM.

2. Materials and properties

2.1. Raw material composition and mix design

The FCFM primarily consisted of fly ash, coal gangue, cement, and compound additive. The fly ash samples were collected from the Xingneng Power Plant (Shanxi Province, China). The coal gangue samples were collected from the Zhenchengdi mine of the XiShan Coal Electricity Group Co., Ltd. (Shanxi Province, China). Ordinary Portland cement (OPC) P·O 42.5 was supplied from the Xishan Cement Factory (Shanxi Province, China). The compound additive (M) was primarily composed of an early strength water-reduced agent (Taiyuan JKT Engineering Materials Company), an accelerating agent (Taiyuan JKT Engineering Materials Company) and an expansive agent (Taiyuan JKT Engineering Materials Company). Tap water was used.

Prior to this study, the authors of this paper conducted numerous mixture proportion tests of the raw materials (Wu et al., 2015; Yin et al., 2018). The optimal proportion of the FCFM for the mass ratios of OPC to fly ash to coal gangue was determined to be 1:3:5, and the optimal water-to-binder (W/B) ratio was determined to be 0.63. The compound additive (M) total dosage was 3% of the fly ash mass, in which the early strength water-reduced agent, the accelerating agent and the expansive agent dosages were 0.4%, 0.85% and 1.75% of the fly ash mass, respectively.

2.2. Raw material properties

The particle size distribution of the fly ash and OPC samples was analyzed using a Mastersizer 2000 laser particle size analyzer (Malvern Instruments Ltd., UK). The particle size distribution of the fly ash and OPC samples is illustrated in Fig. 1.

The mineral composition of the fly ash and coal gangue samples was obtained from X-ray diffraction (XRD) analysis using a Rigaku D/Max2500 at 40 kV and 200 mA, with nickel-filtered CuKα radiation (λ = 0.154056 nm). The scanned angle (2θ) ranged from 10° to 60° with a step size of 0.05°. The XRD patterns of the fly ash and coal gangue samples are illustrated in Fig. 2. The major mineralogical compositions of the fly ash samples were quartz, mullite, and amorphous constituent phases. The major mineralogical compositions of the coal gangue samples were quartz, muscovite and kaolinite.

The chemical components of the fly ash, coal gangue and OPC were determined by X-ray fluorescence spectrometry (XRF) using a Bruker S8 TIGER (Germany) under 50 kV and 50 mA tube-operating conditions with an Rh tube. The detector was a gas-flow proportional counter, a scintillation detector or a combination of the two. The gas-flow proportional counter used P10 gas, which is a mixture of 90% argon and 10% methane. The results are shown in Table 1.

In addition, the strength activity index values of fly ash and coal gangue were determined based on the ASTM C311 (2005) specification. The test results showed that the strength activity index values of fly ash and coal gangue for 28 days were 78% and 65%, respectively. The fly ash samples were classified as Class F according to the definition in standard ASTM C618 (2010). The specific surface areas of fly ash and

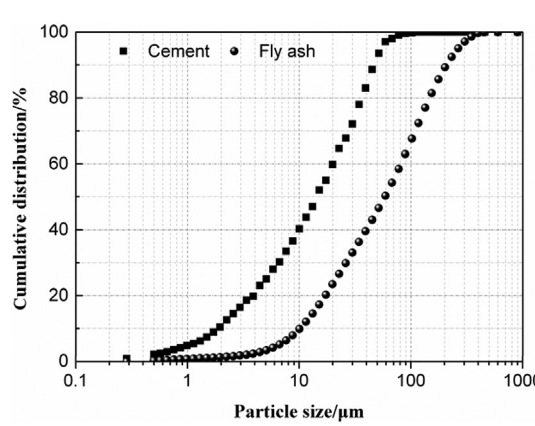

Fig. 1. Particle size distribution of (a) raw fly ash and (b) cement.