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Quantitative analysis of fly ash in hardened cement paste

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HIGHLIGHTS

- Selectively dissolution combine with thermogravimetric method are used to analyze the FAs in hardened pastes.
- Accurately analyzed the content of unburned carbon in fly ash and hardened cement-FA paste.
- According to the unburned carbon to compute the content of FA in hardened paste.

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ABSTRACT

Fly ash (FA) is one of the common supplementary cementitious materials used in cement and concrete. Because of the complexity of morphology, component, hydration and other factors of FA, it is very difficult to measure the content of FA in hardened concrete. According to the characteristic of the unburned carbon in FA neither dissolving in concrete nor participating in the chemical reaction, three different kinds of FA were used to prepare FA-cement pastes with different volumes. Then selective dissolution method and thermal analysis were used to quantitatively analyze the content of FA in hardened paste. The results indicated that the differences of testing data were less than 1.5%, compared with the theoretical values by the method of selective dissolution combined with thermal analysis. Therefore, it is concluded that the method of selective dissolution combined with the thermal analysis can measure the content of FA in hardened FA-cement system more accurately.

1. Introduction

Fly ash (FA), as one of the common supplementary cementitious materials in cement paste, has been widely used in modern concrete due to several well-known advantages. For instance, FA was capable of improving the workability of concrete [1]. In addition, it can also reduce the total heat generation [2] and enhance the durability of concrete [3]. However, because of the diversity of particle morphology, differences of compositions, effect of hydration products and other influences [4–7], it was very difficult to conduct the quantitative measurement of FA in hardened FA-cement system.

Different methods have been used to analyze the content of FA in hardened FA-cement system. Yue Li [8] utilized the backscattering imaging method to analyze the FA content in the cement paste. It was found that the grey value of the backscattering image of the FA was close to the hydration product, which can only be distinguished by circular shape of the FA. However, it was difficult to identify the FA morphology due to the surface hydration, leading to relative large differences. The standard of ENV1946-4 [9] proposed a method of selective dissolution, exploiting the characteristic that FA did not dissolve in hydrochloric acid while the cement and slag can be dissolved, to determine the content of FA in hardened FA-cement system. S. Ohsawa [10] used the selective dissolution of picric acid to analyze the content of FA in the hydrated fly ash-$CaSO_4 \cdot 2H_2O$-$Ca(OH)_2$ system and found that this method was suitable for measuring the FA with low content of calcium oxide. Furthermore, it can be used in FA-cement system if amended. Some other selective dissolution solvents, such as the compound of EDTA with TEA [11] and EDTA with NaOH [12], had also been utilized to quantitative determination of fly ash in hardened cement paste, but the result was not ideal. M. Ben Haha [13] studied the fly ash reaction in the cement paste using selective dissolution. The testing results pointed out that the different assumptions led to large differences on the estimate of FA reaction.

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In this paper, in view of the unburned carbon in fly ash neither participating in hydration reaction nor dissolving in acid, hydrochloric acid was chosen as the selective dissolution solvent to dissolve the FA and hardened fly ash-cement paste. Then, the residues of the FA and FA-cement were analyzed by TG-DSC to calculate the unburned carbon content of the FA and the hardened FA-cement paste thereby computing the FA content of the hardened cement paste.

2. Experiments

2.1. Materials

The chemical compositions and XRD analysis of the FA samples are shown in Table 1 and Fig. 1. The cement is Portland cement without any admixture, and the chemical compositions are listed in Table 2. The hydrochloric acid and alcohol used in the tests were analytically pure with a concentration of 33%-36% and 99%.

Table 1 shows the chemical compositions of three types of FA. It can be found that the content of SiO_2 and Al_2O_3 are higher compared to the content of CaO and SO_3. The XRD patterns of the FA samples are shown in Fig. 1. The $CaCO_3$, $CaSO_4$ and $3Al_2O_3{\cdot}2SiO_2$ of the minerals were detected from the FA. The decomposition temperature of the main minerals and the oxidation temperature of unburned carbon are shown in Table 3.

2.2. Methods

2.2.1. X-ray diffraction analysis

XRD patterns of the FA samples were obtained by a Standard laboratory-based bulk powder X-ray diffractometer with Cu-Ka radiation (wavelength $\lambda = 0.154$ nm). The X-ray tube was operated at 40 kV and 40 mA. The measurements were implemented using aθ-θ reflection geometry. The test data were collected from the diffraction angle of 10° to 60° on the continuous mode, analyzed by the software of JADE.

2.2.2. Selective dissolution

The principle of selective dissolution is that the cement and its products can be well dissolved in hydrochloric acid, whereas the unreacted portion of FA is almost insoluble in hydrochloric acid except some alkaline minerals. Hence, the method of the selective dissolution can be utilized to decrease the influence of carbonate minerals on the analysis of unburned carbon content in FA during the heating process. In this study, the selective dissolution method was conducted according to JC/T729-2005. The specific operations are as follows. 100 ml deionized water was measured accurately and added in a beaker. Then 0.5 g FA sample was added into the beaker. After that, the sample was placed in a magnetic stirrer, stirred for 5 min. When the sample spread out, 50 ml hydrochloric acid was added to the beaker, stirred for 25 min. Subsequently, the sample was suction-filtered by the filter membrane dried to constant weight. The residue of the dissolved sample was washed by deionized water for 8 times, transferred to a funnel and washed 3 times with alcohol. The membrane with residue was placed in an oven, dried for 1 h with temperature of 65 °C, placed in a drier until the temperature cooling down to room temperature. The heating and cooling procedure was repeated till the weight of the sample was constant.

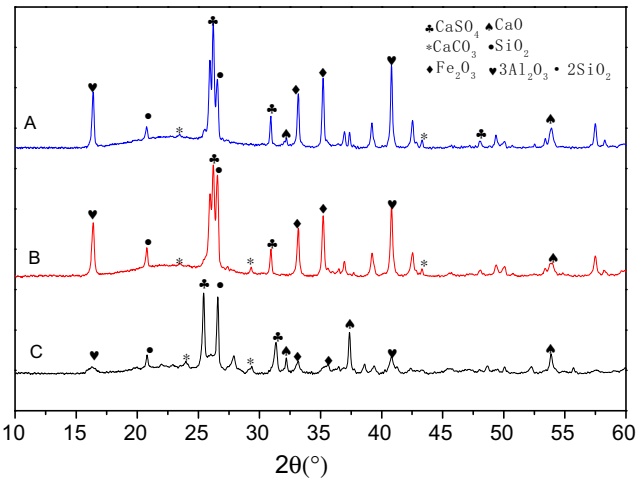

Fig. 1. The XRD patterns of FA samples.

2.2.3. Measurement of loss on ignition

The loss on ignition of FA was measured according to GB/T176-2008, methods for chemical analysis of cement. The 1.000 g FA sample dried to constant weight in a drying cabinet with a temperature of 65 °C was placed into a heated alumina crucible with constant weight, laid in a muffle furnace and heated up to 925 ± 25 °C. Then the sample was temperature-insulated for 25 min, cooling down to room temperature and weighed. The heating-weighing procedure was repeated until the weight of the FA sample remained constant.

2.2.4. Differential scanning calorimetry-thermogravimetric analysis

Thermal analysis was performed on a NETZSCH STA 449F3 instrument with a combined TG and DSC system. Considering the decomposition and oxidation temperature of carbonates and unburned carbon, and the purpose to avoid the impact of other minerals on the test results, the samples processed in section 2.2.3 were heated from 30 °C to 1000 °C at a heating rate of 10 °C/min under N_2 and air atmosphere, respectively. The amounts of carbonate were deduced from the weight loss between 600 °C and 900 °C. Besides, the amounts of unburned carbon were deduced from the weight loss between 500 °C and 700 °C. The content of the unburned carbon in the sample was calculated by the characteristic of endothermic unburned carbon when oxidized.

2.3. Paste experiments

Paste experiments were conducted to investigate the content of the FA in the hardened FA-cement system. The proportions of the cement paste with FA samples are shown in Table 4.

Table 1
Chemical compositions of FA.

Sample	Chemical composition (%)								
	SiO_2	Al_2O_3	CaO	SO_3	Fe_2O_3	TiO_2	MgO	K_2O	P_2O_5
A	43.2	35.8	10.6	4.1	2.3	1.7	0.6	0.5	0.3
B	50.9	34.9	4.4	0.8	4.5	1.8	0.5	1.0	0.4
C	48.4	36.0	5.3	0.6	4.5	1.7	0.6	1.0	0.5