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Comparative study of reaction degree of mineral admixture by selective dissolution and image analysis

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HIGHLIGHTS

- Reaction degrees are obtained by selective dissolution and BSE image analysis.
- Reaction degree is overestimated at early age by selective dissolution.
- Reaction degree is underestimated at later age by selective dissolution.
- Deviation of result obtained from image at different magnifications is within 5%.
- Image analysis gives more reliable results than selective dissolution.

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ABSTRACT

The reaction degrees of slag and fly ash in composite binder pastes were comparatively studied by selective dissolution and BSE image analysis. The reaction degree of slag or fly ash determined by selective dissolution is higher than that by image analysis at early age, but the inverse regularity is observed at later age. When the selective dissolution method is used, the reaction degrees of slag and fly ash may be overestimated at early age due to the loss of the superfine particles through the filtration and the partial dissolution of slag or fly ash, and underestimated at later age owing to the presence of cement and hydration products. The narrow reacted slag rims formed at early age cannot be accurately identified during image analysis procedure, which leads to an underestimation of the reaction degree of slag. Due to the destruction of fly ash particles during grinding or polishing process, the reaction degree of fly ash obtained by image analysis is overestimated. At later age, the small particles cannot be fully counted at low magnification and the outer part of particles cannot be calculated at high magnification, and thus high reaction degree may be obtained. BSE image analysis could give more reliable results with acceptable error than selective dissolution.

1. Introduction

Mineral admixtures are commonly used in modern concrete either as a partial substitution of clinker in cement or as a partial substitution of cement in concrete. The increasing use of such materials leads to lower cost and lower environmental impact as well as better properties of concrete [1,2]. Ground granulated blast furnace slag and fly ash are commonly used mineral admixtures in concrete and their effects on the mechanical property and microstructure of concrete are widely investigated. The blending mineral admixture with Portland cement results in a complicate system. Apart from the different clinker phases hydrating at various rates [3,4], the slag and fly ash particles will be dissolved due to the high alkalinity of pore solution and will react with $Ca(OH)_2$ produced by cement hydration to form hydration products similar to the ones formed by Portland cement [5]. Thereby the hydration of Portland cement and the pozzolanic reaction of mineral admixture occur simultaneously and affect the reaction activity of each other [6]. In order to better understand the effect of mineral admixture on the hydration of Portland cement and on the strength and microstructure development of concrete, it is essential to determine quantitatively the reaction degree of mineral admixture in the composite binder.

The reaction degree of Portland cement could be obtained by quantitative X-ray diffraction (QXRD) coupled with Rietveld analysis [7–10]. However, due to the large amount of amorphous phases existing in mineral admixtures, it is difficult to quantify the

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unreacted mineral admixture by QXRD. The content of $Ca(OH)_2$ is used to measure the reaction degree of mineral admixture due to the consumption of $Ca(OH)_2$ by its pozzolanic reaction. But the reaction of mineral admixture further promotes the hydration of Portland cement that increases the content of $Ca(OH)_2$. Methods reported in literatures to determine the reaction degree of mineral admixture also include selective dissolution and backscattered electron image analysis.

The selective dissolution method is aimed at dissolving the hydration products and unhydrated cement and leaving the unreacted slag or fly ash. It could directly obtain the amount of unreacted mineral admixture and further obtain its reaction degree. Lumley et al. [11] reported that the reaction degree of slag was 30–50% at 28 days and 45–75% at 1–2 years in the case of water to binder ratio of 0.4–0.6 and 20 °C. Escalante et al. [12] found that the reaction degree of slag increased with rising temperature, increasing water to binder ratio and decreasing the replacement ratio of slag. Han et al. [13] found that the reaction degree of fly ash increased with increase of its fineness, but water to binder ratio had little influence on its reaction degree. Termkhajornkit et al. [14] also found that change of water to binder ratio from 1.0 to 0.8 by volume had little effect on the hydration degree of fly ash. Zeng et al. [15] reported that the reaction degree of fly ash determined by the selective dissolution procedure using picric acid was about 10% at 7 days and 20 ~ 40% at 90 days. Brunet et al. [16] used the selective dissolution method that derived from the procedure described by Luke and Glasser [17] to study the reaction degree of slag. The reaction degrees of slag in paste containing 22% of slag at the age of 28 days, 1 year and 10 years were 33%, 35% and 42%, respectively, with water to binder ratio of 0.3. Increasing water to binder ratio to 0.4, the reaction degrees of slag became 45%, 48% and 58%, respectively. However, some researchers found that the reaction degree of mineral admixture obtained by selective dissolution was unreliable due to incompleted dissolution [18–20].

Backscattered electron image analysis can determine the reaction degree of Portland cement [21–23], and is further developed to tackle composite binder. The phases could be identified according to their brightness that depends on their average atomic number. The higher the average atomic number, the brighter it is in the BSE images. The volume fraction of unreacted mineral admixture could be obtained based on the grey level of BSE image. Kocaba et al. [18] compared methods for determining the reaction degree of slag in composite binder containing 40% of slag with water to binder ratio of 0.4, including selective dissolution, differential scanning calorimetry, BSE image analysis, isothermal calorimetry and chemical shrinkage. The most precise method was suggested to be BSE image analysis, while selective dissolution overestimated the reaction degree of slag at early ages. Feng et al. [24] estimated the reaction degree of mineral admixture by SEM point-counting procedure and reported that the results were comparable to the results from selective dissolution methods as performed by other researches. Yio et al. [25] also used this method to determine the reaction degree of slag and pointed out that the reaction degree of slag at 28 days and 1 year increased with increasing water to binder ratio. Moreover, the reaction degree of slag decreased with increasing slag to binder ratio for constant water to binder ratio. Durdziński et al. [26] assessed fly ash composition and studied the reaction of its individual components based on SEM-EDS. Fly ash was composed of 70% volume of aluminosilicates and calcium-silicates and reached 60% reaction at 90 days.

Based on the view of current literatures, it is evident that selective dissolution and BSE image analysis are still the most commonly used method for quantification of the reaction degree of mineral admixture. However, there is little information regarding the cause of differences in the reaction degree of mineral admixture between that obtained by selective dissolution and that by BSE image analysis. Moreover, lack of detailed analysis of the advantages and shortcomings of the two methods for determination of the reaction degree. In the present studies, the reaction degree of mineral admixture is often determined in composite binder paste cured under standard condition (20 °C, 95% RH). The effect of temperature on the reaction degree of mineral admixture is rarely considered, especially for the reaction degree obtained by BSE image analysis.

Therefore, in this paper, the reaction degrees of slag and fly ash in composite binder pastes were determined by selective dissolution and BSE image analysis, taking into account of the curing temperature and replacement ratio of slag or fly ash. Furthermore, the results determined by the two methods were comparatively analyzed. The reasons for the difference between the reaction degrees of mineral admixtures obtained by the two methods were also given.

2. Experimental

2.1. Materials and mix proportions

P.I 42.5 Portland cement, S95 ground granulated blast furnace slag and Class I fly ash conforming to Chinese National Standards GB175-2007, GB/T18046-2008 and GB/T1596-2005, respectively, were used in this paper. The specific information of related Chinese National Standards was given in literature [27]. The chemical compositions of cement and mineral admixtures are shown in Table 1.

The true densities of cement, slag and fly ash are 3.12 g/cm^3, 2.93 g/cm^3 and 2.24 g/cm^3, respectively. The cumulative particle size distributions of cement and mineral admixtures are presented in Fig. 1. It is evident that the particle sizes of mineral admixtures are finer than that of cement. The mix proportions of composite binder pastes are shown in Table 2.

2.2. Test methods

The composite binder pastes were prepared according to the mix proportions shown in Table 2. After stirring evenly, the pastes were cast into plastic tubes of 15 mm diameter and 80 mm length, and then sealed. All the pastes were divided into two groups, which were cured at 20 °C and 60 °C, respectively. After cured for 7 days, all the samples were placed in an environmental chamber of 20 ± 1 °C, 95% RH until testing ages. At the age of 3, 28, 90 and 365 days, same fragments of hardened pastes were cut from the center of cylinder. For determination of reaction degree of mineral admixture by BSE image analysis, the fragments were directly put into acetone to cease further hydration. For determination of reaction degree of mineral admixture by selective dissolution, the fragments were crushed to small pieces and put into acetone.

2.2.1. Selective dissolution

The reaction degree of mineral admixture was determined conforming to Chinese National Standard GB/T 12960-2007. The reaction degrees of slag and fly ash were obtained by selective dissolution procedure based on EDTA and hydrochloric acid (HCl), respectively.

In the procedure of determination of reaction degree of slag, EDTA solution was prepared with 0.15 M EDTA and 0.25 M NaOH. 50 mL EDTA solution, 10 mL triethanolamine solution prepared by mixing triethanolamine with deionized water at the ratio of 1:2 (by volume) and 80 mL deionized water were added to a glass beaker. The pH of the solution was then adjusted at 11.60 ± 0.05 with 1.25 M NaOH solution. 0.3 g of paste powder ground to pass 75 μm sieve was added into the solution and stirred on a magnetic stirrer for 30 min.

In the procedure of determining the reaction degree of fly ash, 80 mL deionized water, 40 mL HCl solution by mixing concentrated hydrochloric acid with deionized water at the ratio of 1:2 (by volume) were added to glass beaker. 0.5 g of ground and sieved paste powder was added into the solution, and then stirred for 30 min.

The residue was filtered under vacuum. All the residual material was washed 8 times with deionized water, and then 2 times with ethanol. Finally, the residue was dried in an oven at 105 °C until a constant weight was achieved. The reaction degree of mineral admixture, α_M, was calculated by Eq. (1).

$$\alpha_M = \frac{\frac{w}{1-w_{ne}} - f_C w_{C,E}}{f_M w_{M,E}} \tag{1}$$

where w, $w_{C,E}$ and $w_{M,E}$ were the dissolution residue percentages of composite binder paste, pure cement and mineral admixture, respectively. w_{ne} was the non-evaporable water content of composite binder paste. f_C and f_M were the mass percentages of cement and mineral admixture in the composite binder, respectively.