Early age shrinkage and heat of hydration of cement-fly ash-slag ternary blends

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HIGHLIGHTS

- Autogenous shrinkage of cement mortars after mixing is investigated.
- The total hydration heat of cement paste is more controlled by cement content.
- Air voids within samples are tested and being transformed to chemical shrinkage.
- The calculated chemical shrinkage shows good relation to hydration heat of samples.

ARTICLE INFO

ABSTRACT

This study investigated the early age autogenous and chemical shrinkage of mortars with slag and fly ash obtained by sieving the freshly mixed concrete after mixing. The hydration heat and contents of air voids formed within mortars during cement hydration were also tested using isothermal calorimetry and ^{1}H NMR. The results showed that the decrease of w/b ratio significantly increased the autogenous shrinkage of mortars, which was more significant for the mortars containing fly ash and slag. With the increase of slag and fly ash replacement level, the autogenous shrinkage of cement mortars decreased linearly. At the same w/b ratio the cumulative heat of hydration and autogenous shrinkage of cement pastes have a good linear correlation. The fraction of voids formed during hydration increased significantly with increasing w/b ratio. For samples with high w/b ratio (e.g. 0.4), the volume of air voids was higher than that of autogenous shrinkage, which was lower for sample with w/b ratio 0.3. The chemical shrinkage calculated from air voids and measured autogenous shrinkage can be well correlated to the hydration heat.

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1. Introduction

Due to the increased application of high strength and high performance concrete, researches and practical application of lower water-to-binder (w/b) ratio and higher cementitious materials used concrete have been more and more developed. This has resulted in a dramatic increase of early shrinkage of cement-based materials [1–3]. Early age shrinkage of cement-based materials is the result of a physico-chemical process related to hydration and the hardening [1]. As a result of the relatively lower early tensile strength, concrete is more susceptible to crack during this period from early shrinkage. The importance of studies on chemical and autogenous shrinkage is strikingly pronounced, since

the growth of cracking will aggravate the mechanical and durability performance of concrete.

When moisture exchange between cement-based materials and the environment is blocked, the hydration reaction of cementitious materials will be the single reason for the initiation of shrinkage. Among these shrinkages, chemical and autogenous shrinkage received most attention in previous studies [4–7]. Hydration of cementitious materials is a process with the reduction in total volume, which is referred to as chemical shrinkage. While the reduction of macroscopic volume due to the self-desiccation from the unsaturation of inner pore is known as autogenous shrinkage. The definition of chemical shrinkage from Tazawa [4] lied the relation and differences between chemical and autogenous shrinkage in the air voids formed within concrete during the hydration process.

Many studies have been conducted on how various factors influenced chemical and autogenous shrinkage of cementitious

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materials [5]. The presence of limestone filler [6] or metakaolin [7] was considered to cause an acceleration of the hydration of cement-based materials and chemical shrinkage. While the replacement of cement by supplementary cementing materials (SCMs) like slag and fly ash decreased the autogenous shrinkage of cement concrete at different levels with the different fineness and replacement levels [8,9]. The results of Tazawa [10] showed that the incorporation of slag with fineness higher than 400 m²/ kg can increase the autogenous shrinkage of concrete with the increase of replacement level to 75%. Tazawa [12] also reported that the addition of slag can decrease the autogenous shrinkage at early age and then increase in a long term. However, due to the different measurement techniques on chemical and autogenous shrinkage, limited studies on comparison of chemical and autogenous shrinkage of cement-based materials were conducted [11].

In 1995, Tazawa et al. [12] calculated the chemical shrinkage of cement pastes from chemical equation of hydration and the results were compared to the measured autogenous shrinkage. Different correlation between chemical and autogenous shrinkage for different types of cement were obtained and the internal air voids formed within hardened cement pastes were considered as the reason lead to these differences. Holt [13] measured the chemical shrinkage of paste and mortar by measuring the amount of the consumed water and correlated to the autogenous shrinkage based on correlation studies described elsewhere [14]. In these studies, the measurements of chemical shrinkage were done with the assumption that the water was absorbed into all of the formed pores or with existing information on hydration degree, which is mostly not practical. It's of importance and significance to investigate the influences of different mineral admixtures on autogenous and chemical shrinkage and correlate the value of chemical and autogenous shrinkage for the same sample.

In this paper, the autogenous shrinkage of cement mortars from a concrete mixing and hydration heat of the corresponding pastes have been measured. Factorial design method was applied to study the autogenous shrinkage and hydration process of cement-fly ash-slag ternary cementitious components. After that, ¹H NMR relaxometry measurements were applied to test the air voids formed within samples during autogenous shrinkage measurement. Based on the measured air voids content formed along with autogenous shrinkage test, the chemical shrinkage was calculated from the results of autogenous shrinkage and correlated to hydration heat of cement mortars.

2. Experimental

2.1. Materials

Portland cement (P.I. 52.5) with a specific surface area of 336 m²/kg was used in this study. Class F Fly ash and S95 slag (or grade 100 for ASTM C989) in accordance with the standard GB/T18046-2000 were employed. The chemical compositions of the Portland cement, fly ash and slag are shown in Table 1. In accordance with ASTM C618, residue fly ash on sieve with 45 μm square hole is 6.2%. The density and specific area of slag is 2900 kg/m³ and 446 m²/kg, respectively. The aggregates used in this study were river sand with a fineness modulus of 2.8 and gravel with a continuous gradation from 5 mm to 25 mm. In order to improve the rheology and control the flow of the freshly mixed concretes, a polycarboxylate based superplasticizer was also introduced, which has a solid content of 18.24 wt%, water-reducing rate of 30.6 wt%, air content of 4.5 vol% and pH value of 6.03.

2.2. Mix design

The ternary binder materials comprised of Portland cement, fly ash and slag were designed using a factorial design method as previously used in [15]. The mix proportions of the binder materials are shown in Table 2 and projected in a ternary diagram as shown in Fig. 1. Concrete mixtures with three different w/b ratios were prepared, which are shown in Table 3.

2.3. Measurements

2.3.1. Autogenous shrinkage

The autogenous shrinkage in this study was measured on mortar samples prepared by sieving (using a sieve with square mesh of 5 mm) the coarse aggregates from freshly mixed concrete after the mixing process. The measurements of the autogenous shrinkage on resulting mortar samples were carried out according to the approach described in [16]. The principle of this approach can be described as: the volumetric change of a sample in a water-filled glass container will result in changes in the liquid level in a glass tube connected to the container. Therefore the shrinkage of the samples under investigation can be obtained from the liquid level in glass tube. The smaller the diameter of tube and the larger of the sample volume is, the higher the testing precision will be. To measure the autogenous shrinkage of the mortar samples, 200 ± 20 cm³ of the sieved mortar samples were added in a balloon. It's flexible enough to shrink along with the samples and the penetration of water across the balloons can be ignored. The air bubbles were removed by shaking the samples and the balloon was fastened and sealed. After that, the samples were placed into a glass container filled with cold boiled water. A tight lid with a graduated glass tube was used and the neck of container was sealed with paraffin. An illustration of the experimental setup is shown in Fig. 2. The experiment was performed at constant temperature (20 ± 1 °C) and relative humidity (RH = 99%) and the changing of liquid level in glass tube was recorded every 2 h and transferred into the volumetric change of testing samples. The test started just after the coarse aggregates were sieved out and continued up to 3 days, which means the results obtained in this study contain the macroscopic volumetric decrease of samples from chemical shrinkage within the first 3 days after mixing, named autogenous shrinkage or just early age shrinkage in this study.

2.3.2. Isothermal calorimetry

The heat flow of the hydration was determined on paste samples directly mixed in the testing vessels (4 g nearest to 0.0001 g) placed in an isothermal calorimetry instrument (TAM Air 8 Channel isothermal micro calorimeter). Superplasticizer was pre-dissolved in the mixing water and injected into the vessel after the temperature reached a stable state (25 °C). The test was continued for 90 h. The testing pastes were prepared according to the binder proportions, w/b ratios and dosages of superplasticizer as described in Table 3.

2.3.3. ¹H NMR relaxometry

At the end of the autogenous shrinkage measurement, two cylinder specimens of ϕ25mm∗25mm were drilled from the center of the mortar. One of the specimens was kept sealed before testing, another one was vacuum saturated with bath water (the samples were placed in a vacuumed container for half an hour without and with water relatively and kept at ambient pressure for 5 h with water). After that, ¹H NMR test was conducted for these two samples. MicroMR12-025 produced by Niumag corporation (Shanghai, China) was used for NMR relaxometry measurement. The resonance frequency was 11.845 MHz and the transversal relaxation time T_2 was measured at 20.00 °C. Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence [17] was employed to measure NMR transverse relaxation time and the NMR results were transferred into pore size distribution according to the following equation proposed in reference [18]:

$$\frac{1}{T_2} \approx \frac{1}{T_{2,surf}} = \rho_2 \left(\frac{S}{V}\right)_{pore} = F_s \times \frac{\rho_2}{r} \tag{1}$$

where T_2 is the transversal relaxation time of water; $T_{2,surf}$ is transversal relaxation time due to surface relaxation; $(S/V)_{pore}$ is specific surface area of pore; F_s is geometrical factor, $F_s = 2.0$ for cylinder pore; ρ_2 is surface relaxivity, here assumed 50 μm/s for cement mortars. Normally, the surface relaxivity rests with the "thickness" of surface layer, and average value of ρ was adopted in literatures [17,19]. In this study, it is assumed that the average surface relaxivity of the testing samples are identical, and an approximate value is decided just to qualitatively study the differences of pore size distribution between different samples.

Table 1
Chemical composition of Portland cement (wt.%).

	SiO₂	Al₂O₃	Fe₂O₃	CaO	MgO	K₂O	Na₂O	SO₃
Cement	21.91	5.30	3.67	65.10	1.51	0.62	0.19	0.44
Fly Ash	54.29	22.55	5.53	1.34	2.56	0.71	0.19	0.44
Slag	33.00	13.91	0.82	39.11	10.04	1.91	–	0.16