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Characterization of the absolute volume change of cement pastes in early-age hydration process based on helium pycnometry

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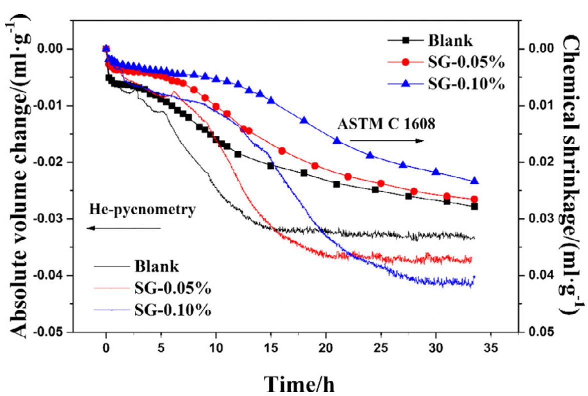
HIGHLIGHTS

- A novel method to study the absolute volume change of cement pastes is proposed.
- Helium pycnometry is proved to be superior than traditional chemical shrinkage test.
- Helium pycnometry is found suitable on studying the hydration process of cement.
- Data of helium pycnometry is accurate, continuous and automatically obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Based on detection technology of helium pycnometry, this study developed a novel approach for characterizing the absolute volume change of cement pastes in early-age hydration process. This method gives an accurate and continuous surveillance on the absolute volume change of cement pastes excluding all the empty pore space even below nm-scale. Traditional methods, such as chemical shrinkage test (based on ASTM C 1608), isothermal calorimetry test and X-ray diffraction (XRD) analysis, are also adopted for comparison and analyzation. It was found that the data obtained by chemical shrinkage test is discontinuous and inaccurate, the data gotten by isothermal calorimetry test is vague and unspecific, and the data gained by XRD analysis is discontinuous and unspecific. Compared with the traditional methods, the results captured by helium pycnometry are continuous, accurate and specific for describing the hydration process, especially the changing details of the absolute volume change. But at the same time, helium pycnometry has a good correspondence with the traditional methods, whose trends are almost the same. Based on the trends of the absolute volume change and heat flow, the absolute volume change of cement pastes in early-age hydration process was then divided into four periods (dissolution period, induction period, fast reaction period and stable period).

1. Introduction

The total absolute volume of cement hydration product is smaller than the combined initial volume of the anhydrous cement and water. This reduction in volume during hydration is known as chemical shrinkage. While chemical shrinkage is determined by the stoichiometry of cement hydration, absolute volume change is a macro-phenomenon of the cement paste, including the dissolution effect and the possible existing inflation caused by temperature rise or some other reasons. Absolute volume change is closely related to the hydration process at the micro and macro level.

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However, it is merely a supplementary study of hydration process generally [1–5], and only few of the authors [3,6] regard the absolute volume change as the main object of their studies. This might result from the limitation of the study methods and the inaccuracy of the testing results.

At present, the absolute volume change of cement pastes mainly refers to chemical shrinkage, and there are two main methods for the study of chemical shrinkage, which are the volumetric method and density method [7–9]. However, human records in a certain time interval is required for the volumetric method, and complex operations are needed for the density method. Thus human errors are inevitable during the measurement process. Moreover, a significant amount of water on top of the specimen is also required for the two methods to keep the cement pastes being saturated [4]. A recent study showed that the quantity and composition of the surface water may have significant impacts on test results [4,6]. Meanwhile, limited by the permeability of water molecules, all the pores in the cement pastes are not filled by water entirely [4,5], which will lead to a smaller value than the actual chemical shrinkage. In this paper, we name this inaccurate "chemical shrinkage" with a quotation mark for differentiation in the following.

Therefore, it can be inferred that an accurate and convenient method for measuring the absolute volume change of the cement pastes has been a pressing need. And helium pycnometry is an ideal choice for this research. Presently, this technique has been widely used in many subject areas, such as chemistry [10], industry [11], oil [12], biomedicine [13] and cement [14–16]. Compared with the traditional methods, helium pycnometry has many advantages, such as its accuracy, continuity and automation. These advantages of helium pycnometry will attract more and more attentions in our field of cement chemistry in the future.

In this paper, helium pycnometer was used to measure the absolute volume change of cement pastes in early-age hydration process. Based on the trends of the absolute volume change and heat flow, the absolute volume change of cement pastes in early-age hydration process was then divided into four periods (dissolution period, induction period, fast reaction period and stable period). And combined with the traditional methods, such as chemical shrinkage test (based on ASTM C 1608), isothermal calorimetry test and X-ray diffraction analysis, the essential relationship between absolute volume change and cement hydration was discussed in detail.

2. Experiments and methods

2.1. Materials and mix proportion

In this study, Portland cement meeting the requirement of ASTM Type II, sodium gluconate (AR) with an industrial grade level and de-air water were used. Cement pastes retarded by sodium gluconate with a dosage of 0, 0.05% and 0.10% by mass of cement were prepared, and these pastes were noted as Blank, SG-0.05% and SG-0.10%. And the water to cement ratio of the pastes is 0.274, which is the water requirement of normal consistency of the cement.

The chemical and mineral compositions of the cement are shown in Table 1 and Table 2, seperately.

Table 2
Mineral compositions of the cement calculated by Bogue.

C_3S	C_2S	C_3A	C_4AF	f-CaO
64.9	10.39	6.77	9.15	1.00

2.2. Experimental tests

2.2.1. Helium pycnometry

Helium pycnometer was used in this study to measure the absolute volume change of cement pastes in early-age hydration process. It is specifically designed to measure the absolute volume of solid materials by employing Achimedes' principle of fluid (gas) displacement and Boyle's law of gas expansion. Test is available at ambient temperature and atmospheric pressure, and its operating principle is shown briefly in Fig. 1.

In Fig. 1, the shadow areas are the sample chamber and the additional chamber which are both hollow and sealed. Besides, the lines are the pipes and the arrows represent the orientation of gas flow. For the whole process of a test, three stages are involved, which are purge stage, measuring stage and recording stage. Purge stage occurs in the beginning of the test. In this stage, valve 1, valve 2 and valve 3 are all kept open, and helium flows for at least 1 min so as to remove all the other gases especially oxygen and nitrogen in the chambers and pipes which can affect the results of the test. Afterwards, there comes measuring stage with little stop. Measuring stage consists of many circles, and the maximum number of the running circles can be set up before the test. For each circle, valve 1, valve 2 and valve 3 are all open in the beginning, and pressure of the ambient (P) is obtained by the pressure transducer. And Eq. (1) will be workable.

$$PV_A = n_A RT \tag{1}$$

where, P is the pressure of ambient, V_A is the volume of the additional chamber which has already been recorded in the instrument after calibration, n_A is the mole number of helium in the additional chamber, R is universal gas constant, and T is kelvin degree in the sample chamber. Then, valve 2 and valve 3 will close, and valve 1 will open, helium keeps flowing into the sample chamber until a target pressure (19 psi is recommended) is reached, valve 1 will close at once, and pressure in the sample chamber (P_1) will be obtained. And Eq. (2) will be workable at this time.

$$P_1(V_C - V_P) = n_1 RT \tag{2}$$

where, P_1 is the pressure in the sample chamber at this time, V_C is the volume of the sample chamber which has already been recorded in the instrument after calibration, V_P is the absolute volume of sample, and n_1 is the mole number of helium in the sample chamber at this time. Afterwards, valve 2 will open, which will connect sample chamber and additional chamber, and pressure in the sample chamber and additional chamber (P_2) will be obtained. And Eq. (3) will be workable at this time.

$$P_2(V_C - V_P + V_A) = (n_1 + n_A)RT \tag{3}$$

where, P_2 is the pressure in the sample chamber and additional chamber at this time. At last, valve 3 will open and exhaust gas into the ambient, after which a new circle will begin at once. According to Eqs. (1) to (3), Eq. (4) will be gotten.

Table 1
Chemical compositions of the cement wt/%.

SiO_2	CaO	Al_2O_3	Fe_2O_3	MgO	SO_3	K_2O	TiO_2	SrO	MnO	Na_2O	Sum
20.7	65.7	4.48	3.01	0.91	2.39	0.72	0.24	0.03	0.14	0.06	98.38