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Assessment and mechanism study of bleeding process in cement paste by ^{1}H low-field NMR

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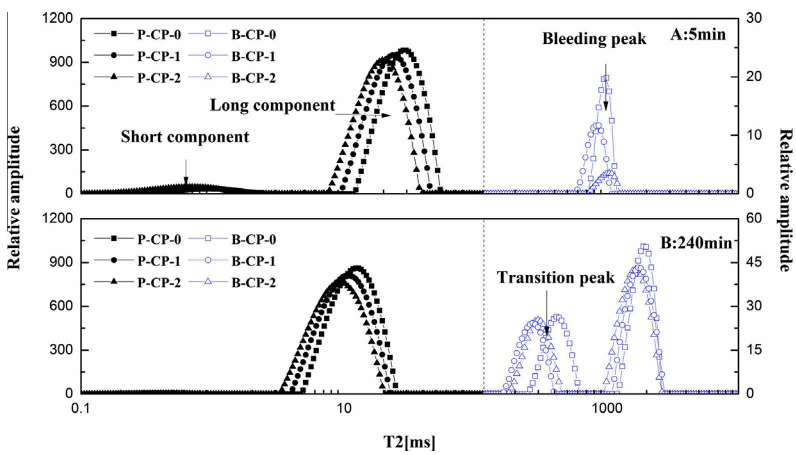
HIGHLIGHTS

- A method based on ^{1}H low-field NMR has been developed for the study of bleeding.
- T_2 peaks correlate with the separated layers of fresh cement paste with bleeding.
- Influence of different parameters on bleeding was investigated by proposed method.
- Results obtained by the proposed method show superior accuracy and repeatability.

GRAPHICAL ABSTRACT



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ABSTRACT

Based on detection technology of ^{1}H low-field nuclear magnetic resonance (NMR), this study developed a novel method for assessment and mechanism study of bleeding. This method is sensitive to bleeding water as well as water in cement paste and diluted grout, gives a vivid scenario of microstructure variation and provides important insights into mechanism of bleeding. In this study, influence of parameters such as cement type, water/cement ratio, chemical additives and environmental temperature on bleeding process was investigated. Results show that bleeding property of cements can be rapidly and precisely evaluated by the proposed method. It is found that peaks of T_2 distribution correlate with separated layers of fresh cement paste with bleeding, and the bleeding process generally consists of a significant growth, a relative stable period and a water-sucking stage. Results also demonstrate that retarder significantly increases bleeding, however, bleeding, to a certain extent, can be reduced by the addition of air-entraining agent. Furthermore, bleeding results of the cement paste under different temperatures (15.5 and 22.5 °C) suggest that higher temperature leads to a smaller T_2 value (around 10 ms) and a lower bleeding rate. The high precision of ^{1}H low-field NMR and linear correlation ($R \geqslant 0.921$) between $R_t(B)$ and bleeding rate both evidenced the superiority and feasibility of the proposed method on study of bleeding.

1. Introduction

Bleeding is a water-related behavior which has different impacts on cement-based materials in different period of its preparation and applications. Excessive bleeding water may cause settlement cracks

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[1] in plastic stage, a thin and weak layer existing in upper sections [2] and decline of durability during service period in engineering structures [3–5]. Bleeding can also result in inhomogeneity of fresh cement paste and instability for commercial application of cement-based products. Bleeding is considered as a phenomenon that free water being forced to the surface as heavier solids in the cement-based material begin to settle [1]. The bleeding extent correlates with composition and properties of the materials, such as water–binder ratio [6], granular packing of binder material [7] and types and quantities of chemical admixtures [6,8,9]. Thus, accurate and convenient evaluation on bleeding is essential to recognize the mechanism of influencing factors on bleeding process, and associating with the scientific instructions of cement-based material design.

Considering fresh cement paste with bleeding water as a distinguishable state including a certain amount of floating water, methods related to volume calibration [1,5,10,11] are widely used to determine the ratio of bleeding. However, both in theory and practice, these methods are unreliable and inefficient due to operating errors. It is also inevitable that a portion of bleeding water is likely to adhere to the inner wall of a vessel caused by surface tension of glassy materials to water molecules. Meanwhile a certain amount of bleeding water may be absorbed on the surface of cement paste, which could not be quantitatively analyzed by visual observations. In addition, in order to probe the mechanism of time-dependent bleeding process in various kinds of cement paste, multiple tests may be conducted on a same fresh cement paste to obtain the results for study of influence factors on bleeding [2,5,9,11] or analysis on permeability of the sedimentation and flocculation [9,12]. However, the samples at early stage are vulnerable and likely to be affected by uncertain factors of test conditions, such as temperature fluctuation, variation of external pressure and external vibration. Bleeding channels formed by the immature pores in fresh cement paste are directly related to the transportation of bleeding water, but characterization of them was not valid and direct enough in previous methods [2,3,8]. Thus, it can be inferred that a nondestructive and precise testing method has been a pressing need for assessment and mechanism study of bleeding in fresh cement paste.

In the present study, a novel method based on ^1H low-field NMR was developed to study and assess bleeding in various kinds of cement paste and the results were then compared with the ones obtained by conventional method. The method proposed in this paper, which can be performed at room temperature and normal pressure, is sensitive to bleeding water, pore water and water in diluted grouts with high accuracy. Previous studies [13,14] have already shown the relevance of T_2 (transverse relaxation time) distribution to the properties of fresh cement paste, and evidenced that the peaks of T_2 distribution correlate with the microstructure of the fresh cement paste. In this research, under identical fluidity, bleeding property of three different types of cement was evaluated by the proposed method. In addition, by analyzing the peaks in T_2 distribution, the influence of water/cement ratio, cement retarder, air-entraining agent and temperature on the bleeding process and microstructure in fresh cement paste were investigated. Moreover, the correlation between the conventional method and proposed method was also discussed in this paper.

2. Materials and methods

2.1. Materials

Cement with a ferric content of 0.27%, manufactured by Onoda, was mainly used. In this study, two other types of commercial cement were also used for comparison analysis. The detail chemical composition and physical properties of these three kinds of cement are shown in Table 1. The particle size distributions of the cements measured in ethanol by using particle size analyzer are given in Fig. 1. In addition, sodium dodecyl benzene sulfonate (SDBS) as air entraining agent and sodium gluconate (SGE) as retarder were also used in this study.

Table 1
Chemical composition/wt% and physical properties of cement.

	Cem-0	Cem-1	Cem-2
SiO_2	20.93%	22.70%	24.55%
Al_2O_3	2.53%	2.96%	3.39%
Fe_2O_3	0.27%	0.44%	0.62%
CaO	64.20%	64.20%	64.23%
MgO	0.02%	0.03%	0.04%
SO_3	2.87%	2.88%	2.89%
K_2O	0.25%	0.29%	0.33%
Blaine [m^2/kg]	396	416	442
Initial setting time/min	105	97	95
Specific weight [g/cm^3]	3.08	2.96	2.79

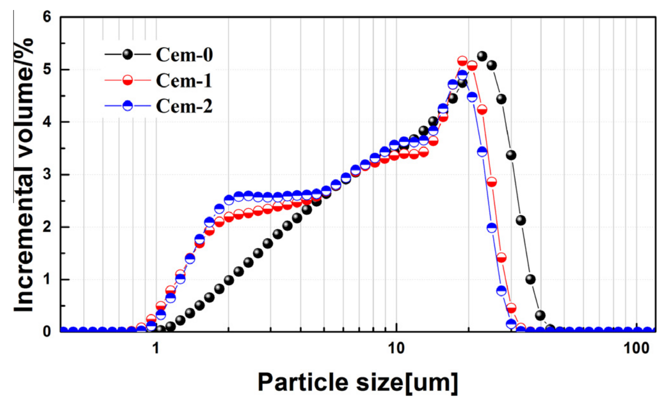

Fig. 1. Particle size distribution of the cements.

The fluidity test of cement paste was applied to determine the amount of water for the cements. In order to keep the similar fluidity (200 ± 5 mm), the w/c ratio for Cem-0, Cem-1 and Cem-2 is adjusted to 0.53, 0.48 and 0.55 respectively. CP-0, CP-1 and CP-2 represent these three kinds of cement paste respectively. In addition, WB50, WB60, WB70 and WB80 respectively represent the samples in which w/c ratios of 0.50, 0.60, 0.70 and 0.80 were selected. In the case of cement paste with retarder and air entraining agent, w/c ratio of 0.60 was kept, and certain quantity of additives was mixed with water and then mixed with cement. This study also set up two different temperatures, TP-0 (15.5 °C) and TP-1 (22.5 °C), by regulating the air-conditioner for investigating the influence of environmental temperature on bleeding. Besides, unless otherwise noted, the cement used for preparing samples was all referred to the Cem-0. The detailed mix designs are given in Table 2.

2.2. NMR experiments

The instrument (MICRO-MR20; Niumag Electric Corporation, Shanghai, China) with a constant magnetic field of 0.5 T and a 25 mm magnet coil, operating at 21 MHz, was used for the low-field NMR experiments in this study. The transverse relaxation curve was fitted to a multi-exponential curve with the Multi-Exp Inv Analysis software (Niumag Electric Corporation, Shanghai, China), which uses the inverse Laplace transform algorithm. In order to obtain full information of the samples, exponential curves with completely decay are required. In addition, bleeding water is freer than the water confined in fresh cement paste that we focused on in previous studies [13,14]. The vulnerable cement paste may also be affected by environmental factors such as temperature difference between inside and outside the NMR instrument and vibration caused by movement of samples. Therefore, that favorably reducing testing time and unnecessary movement is also recommended. By trial and error method, parameter setting of the NMR equipment was adjusted according to initial experiment results including repeated sampling waiting time (TW), sampling points (TD), echo number(NECH), echo time(TE), number of scans (NS) and pre-amp gain (PRG). The optimized results are shown in Table 3.

After instrument debugging, the prepared cement paste was poured into an NMR tube with a height between 17 mm to 20 mm and then sealed by a PTFE film. Besides, each sample was tested at a preset interval. Through the built-in computing method, the sampling data was inversed as T_2 distribution. Then, weighted T_2 was calculated with weight of relative amplitude.

In theory, it has been confirmed that transverse relaxation of ^1H protons in porous media consists of free fluid relaxation, diffusion relaxation and surface relaxation [15]. On the premise of not considering the contribution of bulk fluid relaxation rate, the fitness of the fast exchange model [16] on pore microstructure is generally influenced by diffusion relaxation of samples caused by uniformity of