THE INFLUENCE OF HYDRATION ON THE MICROSTRUCTURE DEVELOPMENT OF CEMENT PASTE WITH BLEEDING: AN NMR STUDY

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Abstract

Bleeding can be described as water coming out from fresh cement paste, which not only affects the homogeneity at fresh stage but also decides the hardened state structure. Previous studies have focused on the determination or simulation of the bleeding extent of fresh cement paste and give objective conclusions. However, there are rare researches about the influence of bleeding on the final structure of cement paste. In this study we have monitored the cement paste with various bleeding caused by water cement ratio and slag replacement. The microstructure development of cement paste from top to bottom was measured by using low-field NMR with Hahn spin sequence from 6 h to 72 h. Results showed that within 4.4 mm bleeding thickness the bleeding will decrease the slope of the void ratio as a function of distance which suggests a homogeneous structure is formed. However, when the bleeding water thickness is higher than 4.4 mm, hydration would lead to a heterogeneous structure. Detailed discussions on the connection between the bleeding and the final structure are also presented in this paper.

Keywords: Bleeding, Cement paste, NMR, Hydration, Microstructure

1. INTRODUCTION

Bleeding of cement-based materials is a water-related behavior which can be simply defined as water coming from cement -based materials to their surface. Bleeding has different impacts on cement-based materials in different period of its lifecycle [1-2]. The settlement cracks in early stage of cement-based materials, a weaker layer in construction and deterioration of durability are all considered to be related to the bleeding process. It is also known that bleeding can lead to inhomogeneity of fresh cement paste and instability for commercial application of cement-based products, i.e., self-compacting concrete and grouting materials.

Previous studies [2-4] focused on the prediction of bleeding process by various models and confirmed that the bleeding process is a consolidation process rather than a sedimentation one. However, for the influence of hydration on the microstructure development of cement paste with bleeding, there are rarely reported in literature. In fact, hydration characteristics at different position of cement-based materials with bleeding theoretically directly decides the final performance of the cement-based materials who have bleeding. Therefore further study on hydration characteristics of cement-based materials with bleeding are needed.

As a nondestructive and noninvasive method, NMR can quantitatively study the water distribution and structure of a sample. It can provide important insights into the microstructure development from fresh to hardened state [3, 5]. In our previous study, the Nuclear Magnetic Resonance (NMR) has been used to investigate the microstructure development of cement paste during bleeding [2]. Here in this study, we have monitored the cement paste with various bleeding caused by water cement ratio and slag replacement. The microstructure development of cement paste from top to bottom was measured by using low-field NMR with Hahn spin sequence from 6 h to 72 h. Analysis and discussion about the experimental results are also given in this paper.

2 MATERIALS AND METHODS

2.1 Materials

The cements used in this study (HEIDELBERG Group, ENCI B.V. Netherlands) are Ordinary Portland cement (OPC), which has specific area of 340 m^2/kg. The specific density for the cements is 3.1 g/cm^3. The slag used in this study has a specific area 501 m^2/kg and a specific density 2.93 g/cm^3. In this study various parameters were systematically changed of which an overview of the used mix designs and identification codes are given in Table 1.

Table 1: Mix design and identification codes of the cement paste samples

No.	Water	Cement	Slag	Water reducer/%	Final bleeding[mm]
WC_0.60	0.60	1	-	-	3.1
WC_0.65	0.65	1	-	-	3.6
WC_0.70	0.70	1	-	-	5.5
SL_0 %	0.65	1	-	-	3.6
SL_30 %	0.65	0.7	0.3	-	2.3
SL_60 %	0.65	0.4	0.6	-	5.7

2.2 Method

In an NMR experiment, the signal intensity *S* of a Hahn spin-echo sequence [5] is proportional to the amount of hydrogens and can be described by [5, 6]:

$$S(t_E) = \rho \exp\left(-\frac{t_E}{T_2}\right)\left(1 - \exp\left(-\frac{t_R}{T_1}\right)\right) \quad (1)$$

where ρ is the density of the hydrogen nuclei, T_1 is the spin-lattice relaxation time, T_2 is the spin-spin relaxation time and t_R is the repetition time and t_E is the echo time. Assuming the pores are saturated, the signal intensity $S(t_E)$ will be proportional to the porosity, i.e., it will give us a direct indication of the void ratio (e). It has been well established [2, 5] that the relaxation rate can be correlated with the pore size. In the so-called fast diffusion regime, both T_1 and T_2 are related to the surface-to-volume ratio of pores as:

$$\frac{1}{T_{1,2}} = \frac{1}{T_{bulk}} + \rho_{1,2}\frac{S}{V} \quad (2)$$

where $\rho_{1,2}$ is the surface relaxivity for T_1 and T_2 relaxation respectively, which reflects a sink at the surface of the pores. As T_{bulk} for water at room temperature is in the order 3 seconds the first term for many porous building material with sufficient small pore can be neglected [2,3]. For measuring a complete profile using Hahn spin-echo sequence during hydration (6-72 h), approximately 92 seconds are needed. In all the NMR experiment, the sampling parameters such as the echo time (280µs) and repetition time (500 ms) were kept constant.

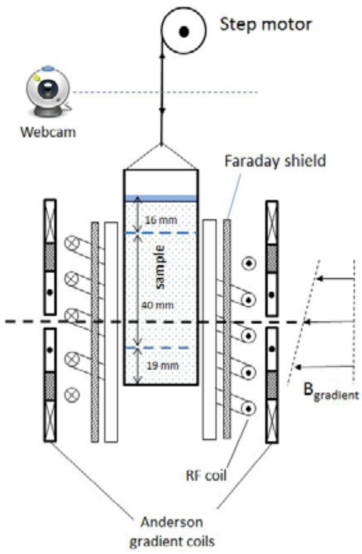
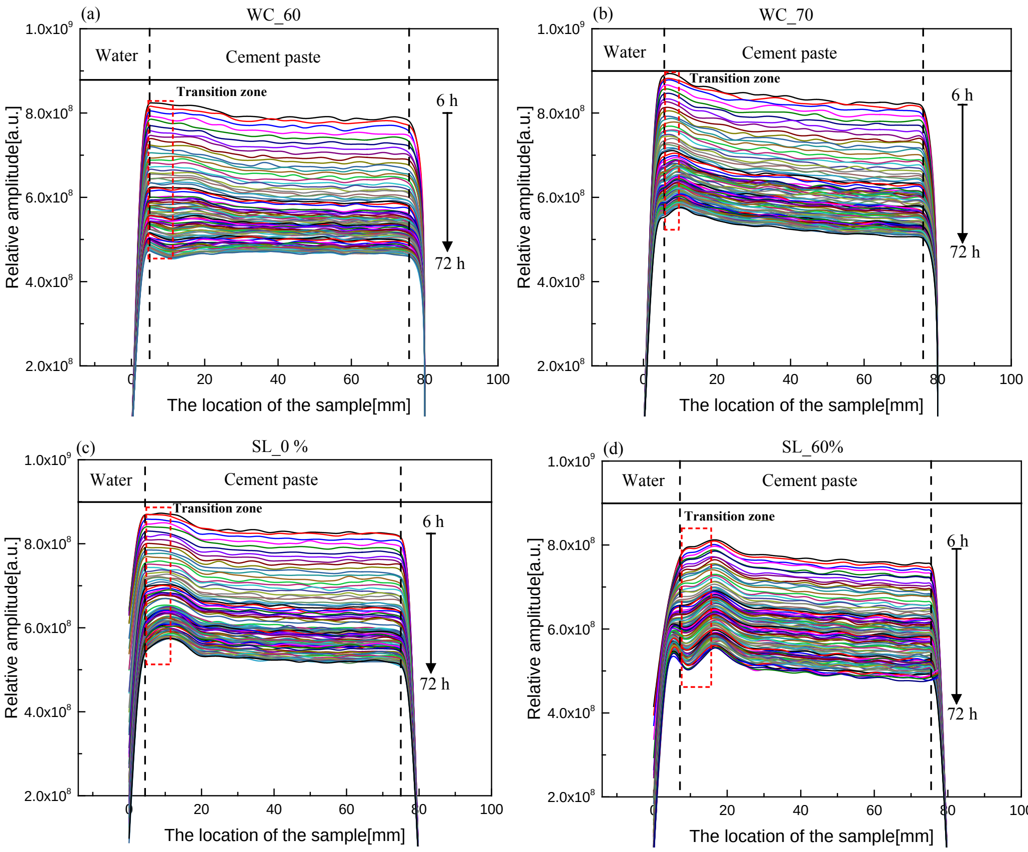


Figure 1: A schematic representation of the NMR set up for measuring the microstructure changing of fresh cement paste. The sample holder is a Perspex cylindrical tube with a diameter of 27 mm, which with the help of a step motor is moved through the NMR. A webcam has been added as to measure free moisture content on top to the sample, i.e., the bleeding. After 6 hours the complete profile is measured

3 RESULTS AND DISCUSSION

3.1 Profiles of the cement paste with bleeding



Fgure 2: The NMR profiles of typical cement pastes with bleeding water measured during hydration 6-72 h (a: WC_60, b: WC_70). The vertical dash line was placed to differentiate the bleeding water and cement paste

In Fig. 2, the measured profiles during hydration (6 h-72h) are given for typical cement paste with bleeding. It can be seen that bleeding water has different relative amplitude which has a range altering from 8×10^{-9} to 9×10^{-9}. Here special attention has to be paid to NMR profiles of cement paste part below the bleeding water. The presence of bleeding water ensures that the pore in cement paste is saturated during the whole NMR method. Thus the water amount expressed as relative amplitude (Hahn spin) linearly correlated with the porosity at different locations in theory [6].

As expected, the moisture profile generally decrease as function of hydration time from 6 h to 72 h, and during the whole hydration process the moisture exhibit different values with the distance from the bleeding surface. To be specific, the part close to the bleeding surface (named as transition zone) has shown an opposite trend (increasing relative amplitude with distance) compared to the rest of the cement paste sample. One possible reason for the existence of transition zone may correlate with uneven distributed gypsum during the sediment process. The large distance between particles during sediment process allows more gypsum particles stay in utter section of a cement paste because they have a comparably lower density and smaller particle size [7]. This would therefore lead to more SO_4^{2-} existing in this part and may facilitate the formation of hydration products such as ettringite (Aft) and calcium hydroxide (CH). The transition zone of a cement paste with bleeding has more crystalline products and can weaken the surface integrity and mechanical property in practical engineering, and it needs more systematic to investigate this point. In addition, the majority of the sample showed that the moisture signals decrease with the distance from surface.

3.2 The microstructural homogeneity during hydration

In this study, the slope of the relative amplitude versus depth(the transition zone are not taken into consideration) was used to evaluate the influence of sediment and consolidation on the heterogeneous property during hydration. Using the Eq. 3, the slope was calculated and the results are shown in Fig. 3.

$$K = (\frac{N\Sigma LA - \Sigma L \Sigma A)}{N\Sigma L^2 - (\Sigma L)^2} \quad (3)$$

where N is the number of the data, L is the distance from the transition zone boundary to bottom and A is the relative amplitude. Results in the Fig. 3 indicated that the hydration have different influence on the heterogeneous cement paste with bleeding in the control factors of water cement ratio, slag powder replacement and PCEs dosage.

As expected, higher water cement ratio will lead to an uneven pore structure from the top to bottom and the hydrations in 72 hours will aggravate the heterogeneous property because an even larger slopes were found for the sample WC_65 and WC_70. For the sample WC_60, the slope kept on increasing after a short time decreasing, during the hydration may due to the water supplied from the surface have curing effect on the system which then in turn reduce the heterogeneous property. In Fig.3 b, compared with the reference sample, the 60% slag replacement sample has a trend that absolute slope value will continue to increase. The slope curve for the SL_30% has a same pattern which first decrease then increase during hydration. This suggest the high slag replacement mixing sample will form an even more heterogeneous structure after the hydration. Reason for this may be due to the that the lower density particles (slag) may pass through the space between the particle during sediment process, then lead to more slag powder existing in the top section of a paste. The slag powders are poor activity materials [8]. High amount of slag means less products are formed in the pore structure, thus it would increase the inhomogeneity during the hydration.

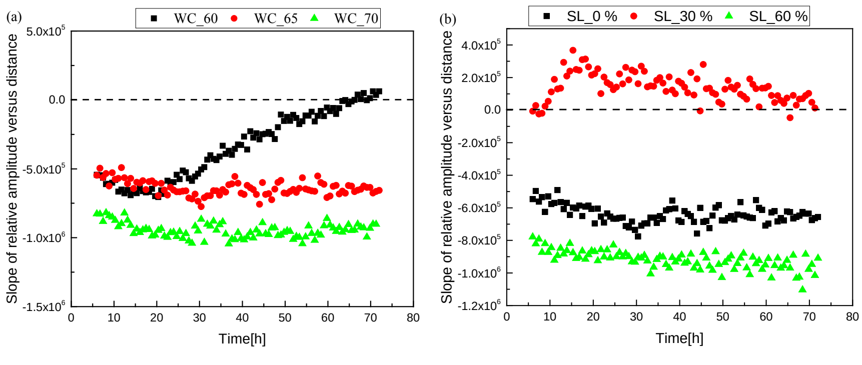


Figure 3: The slope of the relative amplitude versus depth derived from the cement paste sample with bleeding (a: Water cement ratio, b: Slag powder replacement)

3.3 The impacts of bleeding extent on microstructural homogeneity

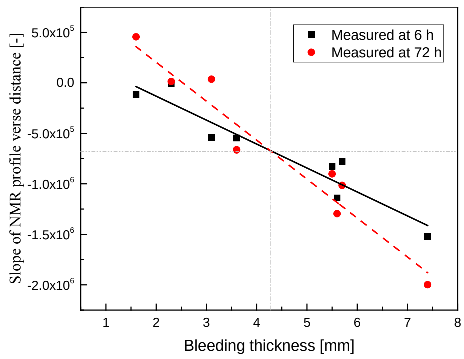


Figure 4: Relationship between the bleeding thickness and the slope of the NMR with distance at 6 h and 72 h

In Fig.4, the relationship between the bleeding thickness and the slope of the NMR with distance at 6 h and 72 h is shown. It was found that the bleeding thickness decrease with the slope of the NMR with distance, and the bleeding thickness is linearly correlated to the slope. In addition, compare the results at 6 h and 72 h, it can be seen that the within 4.4 mm bleeding thickness the hydration will decrease the slope of the void ratio as a function of distance which suggests a homogeneous structure is formed. However, when the bleeding water thickness is higher than 4.4 mm, hydration would lead to a heterogeneous structure.

4 CONCLUSIONS

The microstructure development of cement paste from top to bottom as well as a transition zone of the cement paste can be measured by using low-field NMR with Hahn spin sequence. The majority of the sample showed that the moisture signals decrease with the distance from surface. It was found the bleeding thickness decrease with the slope of the NMR with distance, and the bleeding thickness is linearly correlated to the slope. Within 4.4 mm bleeding thickness the bleeding will decrease the slope of the void ratio as a function of distance which suggests a homogeneous structure is formed. However, when the bleeding water thickness is higher than 4.4 mm, hydration would lead to a heterogeneous structure.

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