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Carbonation property of hardened binder pastes containing super-pulverized blast-furnace slag

Xiong Zhang *, Keru Wu, An Yan

State key lab of concrete materials research, Tongji University, Siping Road 1239, Shanghai 200092, PR China

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Abstract

The carbonation resistant performance of super-pulverized blast-furnace slag is investigated in this study. The mass of hardened binder paste, content of $Ca(OH)_2$, depth of carbonation and pore structure parameters for paste with the super-pulverized BFS (blast-furnace slag) and ordinary BFS are studied by experiments, respectively. The experimental results show that hardened binder paste with the super-pulverized BFS has superior carbonation-resistant performance. In addition, mercury intrusion porosimetry is used to study the mechanism of different carbonation-resistant performance of hardened binder paste with different fineness of BFS. The superior carbonation-resistant performance of super-pulverized BFS is due to the fact that super-pulverized BFS can form compact binder paste structure and prevent binder from forming coarse pore inside the hardened binder paste.

Keywords: Hardened binder paste; Super-pulverized BFS; Carbonation

1. Introduction

The research and development of high-performance concrete or super high-performance is one of the hottest areas of the concrete science and technology in the past 10 years or so [1–3]. The high-performance of concrete is ordinarily achieved by mixing normal Portland cement with superplasticizer and blended additives, including pulverized fly ash PFA, pulverized blast-furnace slag PBS and silica fume SF. The super-pulverized blast-furnace slag (SBFS) is used to mix high-performance concrete due to limited silica fume resources in many countries. In addition, HPC added with SBFS performs better early strength than that with fly ash so that HPC incorporated with SBFS is advantageous for engineering applications.

In the chemical aspect, BFS is composed of a large amount of different glass phase, a small part of crystal phase such as CS and C_2S and other crystals. In the past research work, it is found that BFS has low chemical activities. Thus, many research works have been carried out to study on the methods on how to increase the activities and improve particles gradation of BFS in order to apply BFS more efficient in the areas of construction materials [4–6]. The most widely used method is to increase the fineness and optimize particles gradation of BFS in order to increase the activities for better applying in the civil engineering by pulverizing the original granular slag. However, there is little or no research work on the carbonation of high-performance concrete added with super-pulverized BFS until now. Therefore, this paper makes an attempt to investigate the influence of super-pulverized blast-furnace slag on the carbonation of high-performance concrete. In addition, experiments of pore structure distribution are also studied to understand the carbonation mechanism of super-pulverized BFS.

2. Experimental procedures

2.1. Raw materials and mix proportions

Three kinds of binder materials are listed in Table 1. Pulverized blast-furnace slag and original blast-furnace slag (OBFS) are produced from the same slag-grinding machine. The physical and mechanical properties of 525 normal silicate cement conform to Chinese specification GB175-92 requiring that the strength of cement should be over 52.5 MPa at 28d.

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* Corresponding author. Tel.: +86-21-659-83465; fax: +86-21-659-80530.

E-mail address: tjzxk@sina.com (X. Zhang).

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Table 1
Binder materials

Type of binder	Relative density	Surface area/ $cm^2\,g^{-1}$	Mass percent (%)						
			Loss	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
OPC	3.17	3270	0.6	21.3	5.3	2.6	64.4	2.2	1.9
SBFS	2.89	8380	0.4	33.1	15.4	0.5	41.0	7.5	/
OBFS	2.89	3460	0.4	33.1	15.4	0.5	41.0	7.5	/

Note: where OPC is ordinary Portland cement, SBFS is super-pulverized blast-furnace slag and OBFS is original blast-furnace slag.

Table 2
Mix proportion

Specimens	Mass percent (%)		
	OPC	SBFS	OBFS
S_1	50	50	/
S_2	50	/	50

Table 3
Mass increment of specimen

Specimens	Mass increment of specimen ($g\,g^{-1}$)			
	3d	7d	14d	28d
S_1	0.001	0.003	0.005	0.009
S_2	0.076	0.105	0.105	0.108

The mix proportion of specimens S_1 and S_2 are shown in Table 2. The water binder ratio is 0.4 for both S_1 and S_2 and the size of all specimens is 80 mm × 20 mm × 20 mm. The specimens are cured in the curing room at relative humidity (RH) of 100% of N_2 for 1day after casting and then sawed into the specimens with size of 80 mm × 20 mm × 3 mm. Later the specimens were submerged in the water at 20 ± 2 °C for further 27 days and then were cured in a saturated NaBr solution for another 5 days in order to obtain the appropriate RH of 55%.

2.2. Experimental procedures

Carbonation apparatus is a special integral device, which are composed of carbonation chamber for samples and computer data process system. The RH, temperature and CO_2 concentration can be controlled in the chamber and samples' mass and absorbed CO_2 mass can be measured continuously. In the chamber, RH was 55%, concentration of CO_2 was 20% and temperature was 20 °C. During the course of carbonation, for specimens S_1 and S_2, mass data of samples and absorbed CO_2 were grabbed continually and depth of carbonation was determined by phenolphthalein solution.

Mercury intrusion porosimetry was used to determine porosity parameters before and after carbonation. During the course of carbonation, $Ca(OH)_2$ mass in the hardened cement paste was determined quantitatively by DSC made in Japan.

3. Experimental results and discussions

3.1. Mass of hardened binder paste and absorbed mass of CO_2

During the course of carbonation, the mass increment of specimens was listed in Table 3. The experimental results of carbonation indicate that the increase of mass for specimen S_1 is almost zero from 3d to 28d, while that of mass for specimens S_2 reaches 0.076 $g\,g^{-1}$ at 3d. The increase of mass for S_2 increases gradually with the increase of age, which is 0.105 $g\,g^{-1}$ at 7d and 0.108 $g\,g^{-1}$ at 28d. As shown in Fig. 1, the mass of absorbed CO_2 of hardened binder paste increases with the increase of curing age. Specimens S_1 and S_2 have the same tendency, while the increment of absorbed mass of S_1 is lower than that of S_2. The absorbed mass of S_1 and S_2 at 3d is 0.045 $g\,g^{-1}$ and 0.180 $g\,g^{-1}$, respectively, and the absorbed mass of S_1 and S_2 at 28d becomes 0.132 $g\,g^{-1}$ and 0.260 $g\,g^{-1}$, respectively. Thus, the absorbed mass of S_1 at 28d is lower than that of S_2 at 3d. According to the above results, it can be drawn a conclusion that the carbonation degree of S_1 is not as high as that of S_2.

3.2. Depth of carbonation and content of $Ca(OH)_2$

In Fig. 2, for specimens S_1 and S_2, the carbonation depth is plotted versus the age. From Fig. 2, it is found

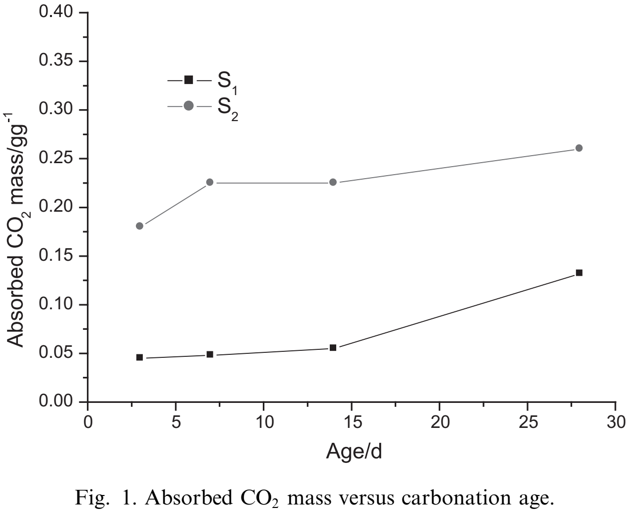

Fig. 1. Absorbed CO_2 mass versus carbonation age.

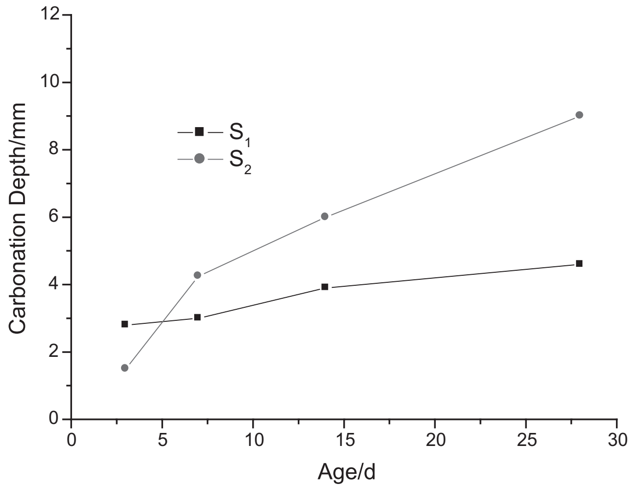

Fig. 2. Carbonation depth versus carbonation age.

that the carbonation depth of S_1 and S_2 at 3d is 2.8 and 1.5 mm, respectively and that the carbonation depth of both S_1 and S_2 increases as the age increases. But the increase of S_2 is greater than that of S_1. The carbonation depth of S_2 at 7d, 14d and 28d is higher than that of S_1. And at 28d the carbonation depth of S_2 is 9.0 mm, nearly two times of that for S_1. The DSC is employed to determine the content of $Ca(OH)_2$ quantitatively (Fig. 3). Before carbonation testing, content of $Ca(OH)_2$ mass for S_1 and S_2 is 4.0% and 6.5%, respectively. The content of $Ca(OH)_2$ for both S_1 and S_2 decreases gradually with the increase of carbonation age and that of S_2 is greater than that of S_1. The decrease of S_1 becomes less and less after 3d, while the content of $Ca(OH)_2$ for S_2 decreases from 6.5% to 2.8% for 0d and 3d and there still exists the decrease tendency of $Ca(OH)_2$ after 3d. At 28d, the residual mass of $Ca(OH)_2$ for S_2 is 0.05%, while that for S_1 is 2.5%. The carbonation depth and content of $Ca(OH)_2$ reflect the carbonation characteristic of binder paste simultaneously, which indicates that hardened binder paste added with super-pulverized blast-furnace slag has better carbonation-resistant property than OBFS (Fig. 3).

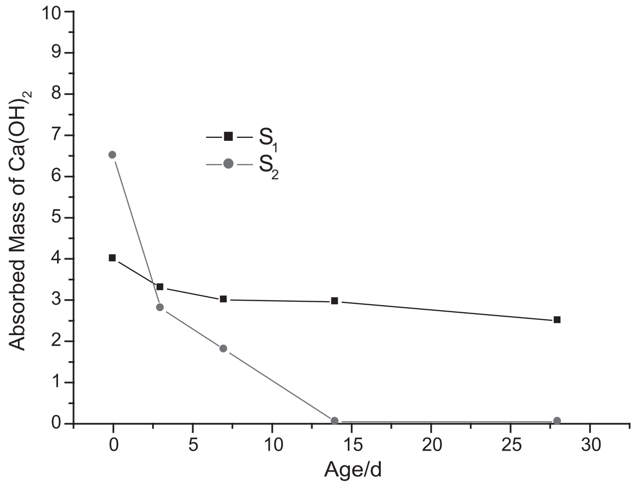

Fig. 3. Absorbed $Ca(OH)_2$ mass versus carbonation age.

3.3. Pore structure analysis of hardened binder paste

The curves of pore size distribution are obtained by using mercury intrusion porosimetry. As shown in Fig. 4, before carbonation the pore volume of S_1 and S_2 with the size ranging from 7.5 to 7500 nm is 0.067 $cm^3\,g^{-1}$ and 0.144 $cm^3\,g^{-1}$, respectively. It means that structure of hardened binder paste of S_1 is denser than that of S_2. At 3d of carbonation, the pore volume of S_1 is almost the same as that of S_1 before carbonation and compared with that before carbonation, there is little change of pore size distribution of S_1 at 3d. It indicates that carbonation of hardened binder paste has little effect on the pore structure of S_1. The fine pore volume of S_2 at 3d reduces to 0.101 $cm^3\,g^{-1}$, while coarse pore volume increases greatly or the curve of pore size distribution moves towards the right of original curve. The pore radius of maximum probability for S_2 is 0.07 μm before carbonation and it reaches 0.1 μm at 3d after carbonation, which indicates that pore size of S_2 becomes coarser due to carbonation reaction.

3.4. Mechanism analysis of the effect of SBFS on the carbonation-resistant property of hardened binder paste

In general, the carbonation-resistant property of hardened binder paste can be improved by adding SBFS. The mechanisms are listed as follows.

(1) The surface area of SBFS in this study is 8380 $cm^3\,g^{-1}$, which means that SBFS particles are much smaller than OPC or OBFS particles. The different size of SBFS particles is mixed together to form a compacted optimizing group so that pore volume of hardened binder paste is small, which is

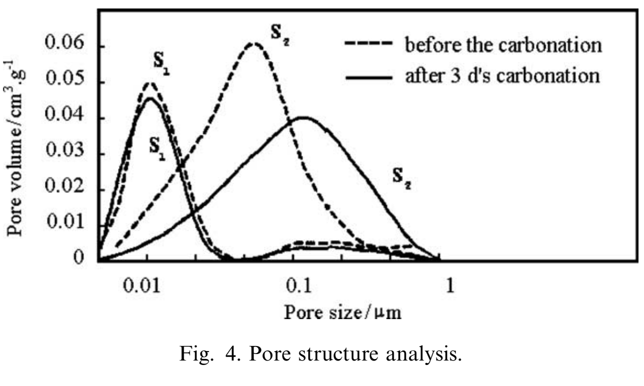

Fig. 4. Pore structure analysis.

substantiated from the analysis of pore structure determined by MIP. Not only the surface area of SBFS is large, but also reactivity of SBFS binder is enhanced greatly so that velocity of hydraulic reaction increases and more products of reaction are formed. In the other hand, SBFS particles has the effect of microcrystals which accelerate the hydraulic reaction and improve the topography and size distribution of hydraulic products to make the hardened binder paste more compacted.

(2) The experimental results from quantitative DSC analysis show that the content of $Ca(OH)_2$ of paste with super-pulverized BFS is lower than that of ordinary BFS. More $Ca(OH)_2$ is absorbed to form C–S–H gel with low mass ratio of CaO/SiO_2 because the reactivity of SBFS is high to form more hydraulic reaction products. Carbonation reaction is accompanied with shrinkage of solid phase and theoretical analysis results show that carbonation shrinkage of $Ca(OH)_2$ crystal is greater than that of C–S–H gel. Hardened binder paste of SBFS with low content of $Ca(OH)_2$ has advantageous and disadvantageous effects on carbonation-resistant properties, low content of $Ca(OH)_2$ causes low carbonation resistance, while low content of $Ca(OH)_2$ results in low shrinkage preventing the formation of coarse hardened binder paste. And it can be proved from pore size distribution.

In general, there are two aspects that causes better carbonation resistance of SBFS, the effect of dense structure of hardened binder paste inhibiting absorbed CO_2 and the effect of decrease of pore size causing the carbonation reaction happens almost near the surface of prevention layer. Therefore, during the course of carbonation, the mass of hardened binder paste is almost constant and absorbed mass of CO_2 is quite low.

4. Conclusions

Based on the findings in this study, the following conclusions can be drawn.

(1) Carbonation-resistance properties of hardened binder paste with super-pulverized BFS are superior to that of original BFS.
(2) The improved carbonation-resistant properties can be attributed to two aspects, one is that addition of super-pulverized BFS can help to form dense structure of paste and the other is that lower $Ca(OH)_2$ is produced in the SBFS sample. The two aspects inhibit the diffusion of CO_2 into hardened binder paste.

Acknowledgements

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