PAPER • OPEN ACCESS

Effect of Fly Ash Content on the Carbonization Resistance of Cement Paste

To cite this article: Wenhao Gu et al 2018 IOP Conf. Ser.: Earth Environ. Sci. 153 052042

View the article online for updates and enhancements.

You may also like

- Bacterial diversity and community level physiological profiling of terasi (Indonesian shrimp paste) to ensure its food safety
 H Helmi, D I Astuti and P Aditiawati
- <u>Characteristics of flavour paste from bone</u> milkfish (*Chanos chanos*) with additional of tapioca flour
 M Muslimin, A M Sahidu and D Y Pujiastuti
- <u>The Durability of Composite Cement Paste</u> <u>Using Diatomaceous Earth against</u> <u>Sodium Sulfate Attack</u> Nurmasyitah, Muttaqin Hasan and Taufiq Saidi





DISCOVER how sustainability intersects with electrochemistry & solid state science research



This content was downloaded from IP address 3.21.93.168 on 13/05/2024 at 13:47

Effect of Fly Ash Content on the Carbonization Resistance of **Cement Paste**

Wenhao Gu, Feng Xu^{*}, Shuguang Wang, Weiwei Li and Yewen Tan

College of Civil Engineering, Nanjing Tech University, Nanjing 211800, China Corresponding author e-mail: xufeng@njtech.edu.cn

Abstract. Carbonation test was carried out on the cement paste specimens with fly ash content of 0% to70%. The change rules of pore structure of cement paste with different fly ash (FA) content before and after carbonation were studied by means of microscopic test, which included mercury intrusion porosimetry (MIP) test and Brurauer Emmerr Teller (BET) test. It is found that total porosity, harmful holes' prosity (pore diameter>50nm), as well as most probable pore diameter and average pore diameter increase obviously when the content is above 40%, and a certain two order function relationship between the CO_2 gas composite diffusion coefficient and the content of FA is presented.

1. Introduction

Carbonation, as a classic issue of durability, has received intensive attention for more than half a century. Carbonation can reduce the alkalinity of concrete and result in the destruction of oxide film on the surface of steel bar. With the combined effect of air and water, steel bar will be corroded, which leads to the damage even failure of concrete structure. With the wide application of fly ash (FA) concrete in recent years, the research on its durability has become increasingly urgent. The carbonation performance of concrete depends on the change of its complex microstructure characteristics. Therefore, it is of great significance to study the effect of FA content on the pore structure of concrete.

Domestic and foreign scholars had found that CaCO₃ precipitates generated in carbonation reaction block capillary pores and split the original large hole into small pores with the aperture of 2~10nm, which changed the porosity and pore size distribution of cement-based material ^[1-4]. While divergence on the law of FA content on the diffusion coefficient of CO₂ in concrete had been still unsolved. Some research found that the diffusion performance of gas was greatly affected by the water-binder ratio: When the water-binder ratio was 0.25, the gas diffusion coefficient changed little with the FA content of 15%~45% while increased obviously when it was greater than 45%. Whereas, some other research found that FA content can reduce the diffusion coefficient of early-age concrete, and FA had greater influence on reducing gas diffusion with the increase of concrete age ^[5-6]. Actually, as a kind of porous solid medium, concrete had an irregular and discontinuous pore structure with different ratios and aggregates, and certain errorr could not be ignored when concrete was directly taken as the test object. Meanwhile, pore structure was mainly tested through mercury intrusion porosimetry (MIP) test in previous researches, which could only accurately measure pore size of 0.1µm~100µm.

In order to study the pore structure of FA concrete comprehensively and precisely, cement paste specimens was tested, and Brurauer Emmerr Teller (BET) test, which could accurately measure pore size of $2nm \sim 190nm$ ^[12], had been jointly used with MIP test to implement the pore structure test

Content from this work may be used under the terms of the Creative Commons Attribution 3.0 licence. Any further distribution of this work must maintain attribution to the author(s) and the title of the work, journal citation and DOI. Published under licence by IOP Publishing Ltd 1

before and after carbonation. Furthermore, an attempt to reveal the relationship between the FA content and CO_2 composite diffusion coefficient was presented in this paper.

2. Experimental Investigation

2.1 Raw Materials

Specimens was prepared with ordinary portland cement (OPC) and FA. Local commercial Type I Portland cement conforming to ASTM C150 had a standard compressive strength of 52.5N/mm² (Class 52.5). FA sample for this study was collected from Chongqing Power Plant in China. The chemical compositions of the FA sample and cement are presented in Table 1. FA is added to cement by replacing it with equal quantity and the proportions are 0%, 10%, 20%, 30%, 40%, 50%, 60%, 70%. The details of the mix design and designation of cement paste specimens are presented in Table 2.

2.2 Carbonation Test

Specimens of $40 \times 40 \times 160$ mm were cast and cured in a standard curing room (95%±5% relative humidity and $20\pm2^{\circ}$ C) for 90 days. Later, these specimens were transferred to an accelerated carbonation chamber that maintained (20±3) % concentration of CO₂, temperature of (20±5) °C, and relative humidity of (75±5) % for 28 days. To distinguish the carbonized section and the uncarbonized section, 1% phenolphthalein was sprayed on the surface of the specimens, and phenolphthalein changed from red to colorless was the carbonized section. Then the uncarbonized and carbonized cement paste specimens with different content of FA were cut into cubes of 3~5mm, 0.5~1mm. After that, absolute ethyl alcohol was added to prevent these cubes from hydration. Finally, cubes were dried in a vacuum drying oven at 50°C for 7 days in order to remove the ethanol before pore structure test.

Table 1. Chemical composition of cement and fly ash / (wt%).

Oxide	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	K ₂ O+ Na ₂ O	TiO ₂	MnO	SO ₃	P ₂ O ₅	Others	LOI
Cement	62.72	21.35	4.29	2.71	0.69	0.84	0.20	0.11	4.06	0.07	0.19	2.73
Fly Ash	10.03	46.41	23.29	8.71	2.47	3.85	0	0	1.68	0	0	1.52

Table 2. Mix proportion design of cement paste with different fly ash content.									
Sample ID	Volume of fly	W//D	Unit content (kg/m ³)						
Sample ID	ash	W/D	Cement	Fly ash	Water				
FA0	0%	0.53	1179.99	0	625.39				
FA10	10%	0.53	1061.99	118.00	625.39				
FA20	20%	0.53	943.99	236.00	625.39				
FA30	30%	0.53	825.99	354.00	625.39				
FA40	40%	0.53	707.99	472.00	625.39				
FA50	50%	0.53	589.99	590.00	625.39				
FA60	60%	0.53	472.00	707.99	625.39				
FA70	70%	0.53	354.00	825.99	625.39				

3. Results and Discussion

3.1 Analysis of MIP Tset Result

The porosity and pore size distribution curves before carbonization (NC) and after carbonization (C) of cement paste specimens with different FA content obtained through MIP test are shown in Figure1~Figure4. According to the results, the evolution law of pore structure is shown in Table 3.



Figure 3. Pore size distribution before carbonation

Figure 4. Pore size distribution after carbonation

Sample		Median poreAverage porewidth(nm)width(nm)		Most probable pore width(nm)	Porosity (%)	Critical pore width(nm)
FA0	NC	20.97	25.23	17.36	17.8	38.07
	С	34.89	21.11	7.09	21.29	118.2
FA10	NC	29.54	23.14	24.95	17.49	74.22
	С	30.72	21.96	7.81	20.88	166.80
FA20	NC	23.54	22.72	19.76	16.14	65.94
	С	21.24	15.09	4.95	21.98	181
FA30	NC	28.17	25.27	24.93	17.73	69.96
	С	32.94	24.47	7.11	23.66	591.3
EA 40	NC	42.04	34.49	39.95	21.88	97.29
FA40	С	49.28	28.38	7.11	25.17	1635
FA50	NC	46.05	36.44	44.90	22.41	105.2
	С	117.9	34.98	7.12	30.71	1387
FA60	NC	80.8	50.42	27.90	31.95	820
	С	132.4	42.06	7.12	33.1	1281
FA70	NC	356.8	100.8	47.25	32.88	1155
	С	381.40	58.62	7.08	38.37	2366

Table 3. Pore structure before and after carbonation (MIP).

(1) For uncarbonated specimens, when FA content ranges from 0% to 30%, the total porosity decreases compared with pure cement paste specimen, the proportion of harmful pore (pore size>50 nm) decreases, while proportion of harmless and less harmful pore (pore size<50 nm) increases. When the content is more than 40%, the porosity continuously increases and the total porosity increases significantly in the case that the content is higher than 60%. Product generated in the microaggregate effect of FA and the secondory hydration reaction between active substance and cement hydration product $Ca(OH)_2$ fill the pores, which not only decrease the porosity of concrete materials and increase the compactness of materials, but also refine the pore and reduce the porosity. Moreover, with the increase of FA content, the cement content and the total hydrate in specimen decrease, and the secondary hydration reaction of fly ash is slow. Combined with the above two reasons, the beneficial distribution of pore structure reaches an extreme value when the FA content is 40%.

(2) Combined with the change law of porosity before and after carbonization, it can be found that: (1) the proportion of harmless pores (pore size<20nm) obviously increases. According to the carbonation mechanism, CaCO₃ generated from carbonation reaction block the pores and cut the large pores into small pores, which increases the proportion of harmless pores. This conclusion is consistent with previous studies ^[7]. (2) The proportion of more harmful pores (pore size>200nm) of all specimens after carbonization (28d) is much higher than that before carbonization. FA mixed in cement paste will react with cement hydration product Ca(OH)₂ to form hydrated calcium silicate gel ^[8-9]. During the reaction of carbonation, the hydrated calcium silicate (CSH) gel is decomposed into silica gel, which affects the pore structure distribution of the material and moves towards the large pore direction. As a result, the proportion of more harmful pores increases (pore siz >200 nm). (3) The porosity of all specimens increases after carbonization.

(3) Carbonation reaction significantly influences the average pore size and the most probable pore size of the specimens, the values of which are obviously smaller than those before carbonization. Meanwhile, the critical pore size of the specimen after carbonation is obviously larger than that before carbonization. Critical pore size refers to the maximum level of pores that can connect larger pores. It represents the connectivity between the pores and reflects the curvature of the permeability path. The change of its value influences the medium transport in cement based materials. The critical pore size of the carbonized specimen increases obviously, which indicates that the connectivity decreases and the curvature degree increases after carbonization. Also, the transmission coefficient of carbon dioxide in the specimen become smaller.

3.2 Analysis of BET Tset Result

The cumulative pore volume and differential pore size distribution curves of cement paste cpecimens with different FA content before and after carbonization obtained through BET testare are shown in Figure 6~Figure 9.





after carbonation

2018 2nd International Workshop on Renewable Energy and Development (IWRED 2018)IOP PublishingIOP Conf. Series: Earth and Environmental Science 153 (2018) 052042doi:10.1088/1755-1315/153/5/052042



Figure 8. Pore size distribution before carbonation Figure 9. Pore size distribution after carbonation

Table 4. Pore structure before and after carbonation (BET).								
Sample		BET specific surface area (m ² /g)	Average pore width (nm)	Cumulative pore volume (cm ³ /g)	Most probable pore width (nm)			
FA0	NC	51.649	9.329	0.117	3.29			
	С	41.297	10.190	0.104	3.29			
EA 10	NC	51.656	10.489	0.132	3.29			
FAIO	С	31.376	11.095	0.085	3.29			
EA 20	NC	43.941	10.829	0.116	3.72			
FA20	С	39.178	10.49	0.099	7.05			
EA 20	NC	33.247	11.053	0.110	3.72			
FA30	С	54.981	8.608	0.090	3.72			
EA 40	NC	39.088	13.967	0.134	4.28			
FA40	С	47.962	9.167	0.119	3.72			
E 4 5 0	NC	30.585	13.72	0.103	4.21			
FA30	С	40.319	9.958	0.095	3.72			
FA60	NC	38.874	10.614	0.100	3.29			
	С	35.518	11.07	0.094	12.11			
E A 70	NC	25.361	11.216	0.069	3.29			
FA/0	С	29.043	10.78	0.075	12.11			



Figure 10. Porosity evolution of cement paste with different FA content

before and after carbonation

When FA content ranges from 0 to 50%, the cumulative pore volume of the carbonized sample is smaller than that before carbonization. The larger the content of FA, the smaller the reduction of cumulative pore volume. Meanwhile, the average pore size of most specimens is reduced after carbonization. By analyzing the change law of cumulative pore volume and average pore size, it can be concluded that the CaCO₃ generated from carbonation reaction will block the pore, and the large pores will be divided into small pores. As a result, the accumulative pore volume and the average pore size are reduced, and the pore size is refined. When the content of FA is greater than or equal to 60%, the cumulative pore volume curves before and after carbonization almost overlap. The cumulative pore volume of the specimen with 70% FA content after carbonization is larger than that before carbonization because the proportion of cement replaced by FA is high. The cement content in the specimen is greatly reduced, which results in a sharp decrease in the content of Ca(OH)₂ generated from hydration. After the secondary hydration reaction with FA, the content of Ca(OH)₂ is quite small, and the materials in the specimen are mainly the residual FA and calcium silicate hydrated gel. FA content is higher, Ca(OH)₂ content is lower in the specimen when the mixing proportion is 60% ~70%.

4. Research on Diffusion Ability of CO₂ in FA Cement Paste

The determining condition for the transport and diffusion of gas CO_2 in cement-based materials is the relative size relationship between the average free path and pore size of gas molecule. According to the different diffusion modes, it can be divided into Fick diffusion, Transition diffusion and Knudsen diffusion. Owing to the complex change of the pore size, the gas transport distance is much greater than the vertical depth, so it is exparte to describe the transmission of CO_2 in the carbonization of cement-based materials only through Fick diffusion, another two modes should also be considered. Moreover, data tested by MIP should be replaced by BET when pore size is less than 50nm. Here is the formula as below ^[10].

$$D_0 = \varepsilon \alpha D_{Fick} + \varepsilon \beta D_{Transition} + \varepsilon \varphi D_{Knudsen} \tag{1}$$

Where D_0 is the composite diffusion coefficient, α , β , φ is the porosity corresponding to three modes of diffusion, ε is the total porosity. With formula (1), the composite diffusion coefficient of CO₂ in cement paste with FA content of 0%~70% can be obtained, as shown in Table 5. Table 5. Composite diffusion coefficient of CO₂ gas in fly ash cement paste

Tuble 5. Composite unfusion coefficient of CO2 gas in my ash cement paste.									
Sample ID	α(%)	β (%)	φ(%)	E (%)	D_{Fick} (10 ⁻⁶ m ² /s)	$D_{Transition}$ (10 ⁻⁶ m ² /s)	$D_{Knudsen}$ (10 ⁻⁶ m ² /s)	D_0 (10 ⁻⁶ m ² /s)	
FA0	2.252	0.038	14.696	17.80	5.66	1.758	2.549	2.824	
FA10	1.531	2.404	12.848	17.49	5.66	1.795	2.629	2.673	
FA20	0.653	1.847	13.220	16.14	5.66	1.801	2.641	2.598	
FA30	0.692	2.262	13.974	17.73	5.66	1.814	2.670	2.557	
FA40	1.688	8.200	11.625	21.88	5.66	1.818	2.679	2.541	
FA50	2.360	10.139	9.394	22.41	5.66	1.814	2.670	2.536	
FA60	5.458	16.886	8.92	31.95	5.66	1.838	2.722	2.698	
FA70	14.171	15.103	3.269	32.88	5.66	1.816	2.672	3.539	



Figure 11. Composite diffusion coefficient of CO₂ gas in fly ash cement paste

According to Table 5 and Figure 11, for cement past with water-binder ratio of 0.53, when the FA content ranges from 0% to 50%, the CO_2 gas composite diffusion coefficient of the sample will not increase by the mixing of FA.Through the regression analysis of data, the prediction model of CO_2 gas composite diffusion coefficient related to the content of FA can be obtained as shown in formula (2).

$$D_0 = f(m_f) = (0.1403m_f^2 - 0.002969m_f + 2.534) \times 10^{-6}$$
(2)

Where m_f is the FA content (%), R² is 0.951.

5. Conclusion

(1) The proportion of harmless pores (pore size<20nm) increases obviously after carbonation results from the CaCO₃ generated in carbonation reaction precipitated in the pore, which divides the large pores into small ones. Meanwhile, the reaction between FA and Ca(OH)₂ results in the decomposition of CSH gel into silica gel during carbonization reaction, which increases the ratio of more harmful pores (pore size>200nmm).

(2) The critical pore size of the carbonized specimen increases largely, which demonstrates that the connectivity of the specimen, combined with the transmission coefficient of CO_2 decreases after carbonization.

(3) Based on the data of MIP test and BET test, the corresponding values of Fick diffusion, Transition diffusion and Knudsen diffusion, along with porosity α , β and φ are obtained. It can be found that the content of FA has little influence on the ratio of fraction porosity to total porosity (α/ϵ , β/ϵ and φ/ϵ). In the meantime, a quadratic function relationship between the diffusion coefficient of CO₂ and the content of FA in the cement paste specimens is presented.

Acknowledgments

The financial supports from the National Key Research and Development Program of China with Grant No. 2016YFC0701406, the National Basic Research Program of China (973 Program) with Grant No. 2011CB013801 and the National Natural Science Foundation of China with Grant No. 51308285 are greatly acknowledged.

References

- Morales-Florez V, Findling N, Brunet F. Changes on the nanostructure of cementitius calcium silicate hydrates (C–S–H) induced by aqueous carbonation[J]. Journal of Materials Science, 2012, 47(2):764-771.W. Strunk Jr., E.B. White, The Elements of Style, third edition, Macmillan, New York, 1979.
- [2] Borges P H R, Costa J O, Milestone N B, et al. Carbonation of CH and C-S-H in composite cement pastes containing high amounts of BFS[J]. Cement & Concrete Research, 2010, 40(2):284-292.

- [3] Dewaele P J, Reardon E J, Dayal R. Permeability and porosity changes associated with cement grout carbonation[J]. Cement & Concrete Research, 1991, 21(4):441-454.
- [4] Johannesson B, Utgenannt P. Microstructural changes caused by carbonation of cement mortar[J]. Cement & Concrete Research, 2001, 31(6):925-931.
- [5] Shi Hui-sheng , Xu Bi-wan. Study on gas permeability of high performance concrete with fly ash[J] . Journal of Tongji University :Natural Science , 2007, 35(9):1230-1234.
- [6] Hassan K E, Cabrera J G, Maliehe R S. The effect of mineral admixtures on the properties of high-performance concrete[J]. Cement and Concrete Composites, 2000, 22(4):267-271.
- [7] Claisse P A, Elsayad H I, Shaaban I G. Permeability and pore volume of carbonated concrete[J]. Aci Materials Journal, 1999, 96(3):378-381.
- [8] Ohga H, Nagataki S. Prediction and evaluation of the depth of carbonation of concrete by accelerated test[J]. 1988, 8(390):225-233.
- [9] Asaga K, Ito S, Suzuki Y, et al. Changes in pore structure of hardened body with large water cement ratio by a carbonation process[J]. Journal of the Chinese Ceramic Society, 2010.
- [10] Housta Y F, Wittmannb F H. Influence of porosity and water content on the diffusivity of CO₂ and O₂ through hydrated cement paste[J]. Cement & Concrete Research, 1994, 24(6):1165-1176.