

# A study on the relationship between porosity of the cement paste with mineral additives and compressive strength of mortar based on this paste

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## Abstract

Mercury intrusion porosimetry study was carried out on ordinary Portland cement (OPC) pastes with 10% to 40% mineral additives, such as steel-making slag, granulated blast furnace slag and fly ash. For all samples, the porosity of paste and compressive strength of mortar based on this paste were determined at 3, 7, 28, 90 and 180 days. Relationship between the porosity and strength was investigated and some equations for the strength–porosity relationship were presented according to Balshin multiplicative model. Results show that mineral additives delayed process that micropore structure of OPC paste developed and strength development of sample with mineral additives was faster than that of OPC sample. Balshin equation fits the results of strength and porosity of all samples and there is a strongly quantitative relationship between strength and porosity. After being mixed with mineral additives, the intrinsic strength  $\sigma_0$  and power  $n$  both increased and the sequence of  $\sigma_0$  and  $n$  for different mineral additives was fly ash>steel-making slag>blast furnace slag.

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**Keywords:** Porosity; Compressive strength; Steel-making slag; Granulated blast furnace slag; Fly ash

## 1. Introduction

These years' various types of by-product and waste materials, such as fly ash and blast furnace slag, are used as mineral additives in the high-performance concrete, in terms of better workability, higher strength or better durability [1,2]. There are many studies on the influence of mineral additives on the porosity and strength of ordinary Portland cement (OPC) paste recently [3,4]. Furthermore, the study on the relationship between porosity and strength of OPC paste without mineral additives has developed for many years [5–7]. However, the study on the relationship between porosity and strength of OPC paste with mineral additives is still seldom reported. Therefore, in this paper, the effect of steel-making slag, blast furnace slag and fly ash on porosity

and compressive strength of OPC paste has been studied and the relationship between compressive strength and porosity has been revealed.

## 2. Raw materials and experimental methods

### 2.1. Materials

Ordinary Portland cement and three mineral additives, namely, steel-making slag, granulated blast furnace slag and fly ash, were collected from different sources in China. After examining their chemical and physical properties (Table 1), the mineral additives were mixed with OPC in 10% to 40% quantity on weight replacement basis. Samples were named as: OPC, control sample without mineral additives; STn, OPC with steel-making slag; SLn, OPC with blast furnace slag; FAn, OPC with fly ash, where  $n=1,2,3$  and 4, respectively, represents 10%, 20%, 30% and 40% ratio of mineral additives replacing OPC.

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Table 1  
Chemical and physical properties of OPC and mineral additives

Contents	OPC	Steel-making slag	Blast furnace slag	Fly ash
SiO <sub>2</sub>	23.03	11.22	33.50	60.53
Al <sub>2</sub> O <sub>3</sub>	5.11	0.94	12.52	21.14
Fe <sub>2</sub> O <sub>3</sub>	3.34	22.45	1.10	7.46
FeO	–	9.84	–	–
MnO	–	0.73	0.31	–
CaO	63.33	43.13	37.90	2.52
MgO	2.06	6.63	9.29	1.91
SO <sub>3</sub>	2.33	0.19	2.51	0.44
K <sub>2</sub> O	–	0.01	–	–
Na <sub>2</sub> O	–	0.09	–	–
P <sub>2</sub> O <sub>5</sub>	–	2.33	–	–
Basic	–	3.18	–	–
module CaO/ (SiO <sub>2</sub> +P <sub>2</sub> O <sub>5</sub> )				
Density	3.14	3.33	2.88	2.67
Specific surface area (Blain) cm <sup>2</sup> /g	3277	3725	3750	4673

## 2.2. Experimental methods

Paste specimens (2×2×2 cm) for porosity measurement were prepared according to Chinese National Standard GB1346-77. Ratio of water to binder was 0.44 in all samples. All samples were cured in water at 20±2 °C and until 3, 7, 28, 90 and 180 days, hydration was stopped by using ethanol. Before porosity tests, samples were subjected to drying in a 105 °C drying oven for 4–5 h to remove the capillary water and ethanol. Porosity measurements were conducted with Micrometer-9420 mercury porosimeter.

Strength measurement was conducted according to Chinese National Standard GB177-85. Ratio of binder/sand/water was 1:3:0.44 in all samples. All samples (4×4×16 cm) were cured in water at 20±2 °C and until 3, 7, 28, 90 and 180 days, strength tests were carried out. The surface of the sand could influence the porosity of the mortar, but these circumstances could be negligible by using Chinese standard sand (GB178-77) in this study.

## 3. Results and discussion

### 3.1. Porosity and strength of OPC sample with mineral additives

The porosity of the OPC paste with mineral additives and compressive strength of mortar based on this paste were listed in the Table 2. There was a decrease in the porosity of all samples with advancement of hydration period, due to the gradual filling of large pore by hydration products of cementitious materials [3,8,9]. Porosity of OPC paste had little change after 28 days, while that of OPC pastes with different mineral additives still had an obvious decrease at 90 days, which means that mineral additives delayed the process that the micropore structure of the OPC paste developed.

It was observed that porosity of paste increased with the amount of steel-making slag and fly ash replacing OPC at a respective age, while porosity of paste has a minimal value when ratio of blast furnace slag replacing OPC was 20 wt.% at respective ages, and after 28 days, porosity of samples with blast furnace slag was lower than that of the OPC sample. The authors think that it is not an experimental error because the porosity of both the SL2 and SL3 samples are relatively low in comparison to SL1 and SL4 in different ages. Maybe cement paste with 20–30% BFS can form a denser accumulate due to their optimal proportion match and particle size match. On the other hand, the authors also think that it is reasonable that porosities of samples with BFS (SL1 to SL4) are distinctly lower than those with the other two mineral additives. Blast furnace slag has higher reactivity than fly ash and steel-making slag and it also improves workability of cement paste, so the paste with BFS can form denser microstructure at different ages.

Comparing the three kinds of different mineral additives, the sequence of their capacity of filling large pore was blast furnace slag>steel-making slag>fly ash.

The compressive strength of all samples increased with the advancement of hydration age, while there was a greater

Table 2  
Porosity and compressive strength of cement paste with mineral additives

No.	Total porosity (%)					Compressive strength (MPa)				
	3 days	7 days	28 days	90 days	180 days	3 days	7 days	28 days	90 days	180 days
OPC	38.11	31.85	21.76	20.64	20.81	35.8	45.4	54.4	55.2	57.6
ST1	37.07	32.57	23.54	20.51	21.37	33.3	43.2	54.4	60.0	63.6
ST2	40.53	35.89	26.38	24.22	22.86	29.6	42.7	50.0	60.0	60.1
ST3	41.77	37.03	29.67	26.36	25.82	23.5	38.1	47.1	57.6	58.8
ST4	44.95	40.16	32.82	29.55	29.63	18.1	32.1	44.1	54.2	57.9
SL1	39.67	30.89	21.36	18.98	18.18	36.3	46.6	60.3	60.4	59.7
SL2	32.80	24.46	15.59	12.96	12.04	29.1	41.8	56.4	61.8	61.8
SL3	35.77	32.70	20.01	17.05	17.05	23.3	37.5	54.2	68.1	68.8
SL4	42.74	34.36	21.35	18.62	18.36	19.7	34.8	52.0	69.0	69.8
FA1	38.86	32.08	23.34	21.48	20.32	31.0	40.0	47.6	64.7	66.4
FA2	39.83	33.44	26.72	24.03	23.99	24.4	32.4	45.8	63.3	71.6
FA3	41.12	36.10	29.30	26.95	26.81	20.5	28.8	41.6	59.2	70.3
FA4	42.93	38.19	33.03	31.13	31.19	12.9	20.8	33.3	46.1	55.7

increase for samples mixed with mineral additives. These results showed that strength development of mortar with mineral additives was faster than that of OPC mortar, which was similar with results of Pandey and Sharma [3].

At 28 days, strength of samples with steel-making slag and fly ash was less than that of OPC, while strength of samples with blast furnace approached to or exceeded that of OPC. After 90 days, strength of samples with 10% to 30% different mineral additives exceeded that of OPC sample.

The compressive strength of the FA4 sample was quite low and its porosity was very high. Hydration of fly ash needs more CH than that of blast furnace slag and steel-making slag according to their chemical constitution; thus, when the volume of mineral additives replacing OPC was 40% in the paste, maybe OPC cannot enough activate fly ash. Therefore, at 90 days, the strength of FA4 was very low and porosity of F4 was extremely high.

### 3.2. Relationship between porosity and strength of OPC sample with mineral additives

From the results above, it can be found that porosities of samples with steel-making slag and fly ash were more than those of OPC sample at respective ages; however, their compressive strength exceeded that of OPC sample after 90 days. It seems unreasonable because steel-making slag and fly ash could not make OPC sample denser but improved compressive strength of the OPC sample at later age. In fact, these results indicated mineral additives not only influenced porosity and strength, but also probably changed quantitative relationship between porosity and strength of the OPC sample.

Robler and Odler [5] used four expressions that had been derived by other works to express the relationship between porosity and compressive strength of porous solids; furthermore, they concluded that the linear relation (Hasselman model) fits their results best. While concerning development of compressive strength and porosity in 1

Table 3

Equation for the strength–porosity relationship of cement paste with mineral additives

No.	Balshin equation	$\sigma_0$	$n$	Regression coefficient
OPC	$\sigma_c = 83.5 \times (1-P)^{1.7084}$	83.5	1.71	0.98
ST1	$\sigma_c = 104.3 \times (1-P)^{2.3813}$	104.3	2.38	0.99
ST2	$\sigma_c = 116.3 \times (1-P)^{2.5034}$	116.3	2.50	0.95
ST3	$\sigma_c = 170.4 \times (1-P)^{3.5226}$	170.4	3.52	0.97
ST4	$\sigma_c = 241.0 \times (1-P)^{4.1952}$	241.0	4.20	0.98
SL1	$\sigma_c = 90.425 \times (1-P)^{1.799}$	90.4	1.80	1.00
SL2	$\sigma_c = 92.492 \times (1-P)^{2.8886}$	92.5	2.89	1.00
SL3	$\sigma_c = 128.84 \times (1-P)^{3.561}$	128.8	3.52	0.96
SL4	$\sigma_c = 118.65 \times (1-P)^{3.1354}$	118.7	3.14	0.99
FA1	$\sigma_c = 100.68 \times (1-P)^{2.4201}$	100.7	2.42	0.97
FA2	$\sigma_c = 165.76 \times (1-P)^{3.8628}$	165.8	3.86	0.98
FA3	$\sigma_c = 226.64 \times (1-P)^{4.5795}$	226.6	4.58	0.98
FA4	$\sigma_c = 490.69 \times (1-P)^{6.5284}$	490.7	6.53	0.99

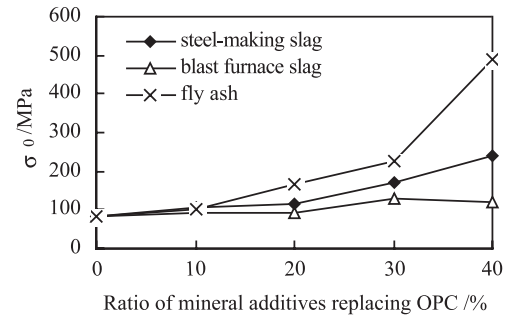


Fig. 1. The effect of different mineral additives on  $\sigma_0$ .

year, Kearsley and Wainwright [10] found that the multiplicative model derived by Bashin was best fit to the results of compressive strength and porosity. In this study, the Bashin equation was carried out on the relationship between porosity and strength of all samples with mineral additives (Eq. (1)).

$$\sigma_c = \sigma_0(1 - P)^n \quad (1)$$

where  $\sigma_c$ =compressive strength of sample with porosity  $p$ ;  $\sigma_0$ =an intrinsic strength, namely, compressive strength at zero porosity;  $p$ =porosity;  $n$ =a power coefficient.

If compressive strength and porosity of the OPC sample with mineral additives could meet the Balshin equation,  $\sigma_0$  and  $n$  can be determined by the results of compressive strength and porosity in Table 2. Balshin equations and regression coefficient of Balshin equations were calculated and listed in Table 3.

From Table 3, it can be found that regression coefficients of all Balshin equations are more than 0.95, which means that there is a relatively strongly quantitative relationship between compressive strength and porosity of all samples with mineral additives. After the OPC sample was mixed with different mineral additives, expression of the Balshin equation of different samples were obviously different; however, compressive strength and porosity of all samples still meet the Balshin equation.

The expression of the Balshin equation was determined by  $\sigma_0$  and  $n$ . From Figs. 1 and 2, it can be found that  $\sigma_0$  and  $n$  both increased with ratio of mineral additives replacing OPC. After being mixed with mineral additives, the intrinsic strength of OPC sample,  $\sigma_0$ , increased, which

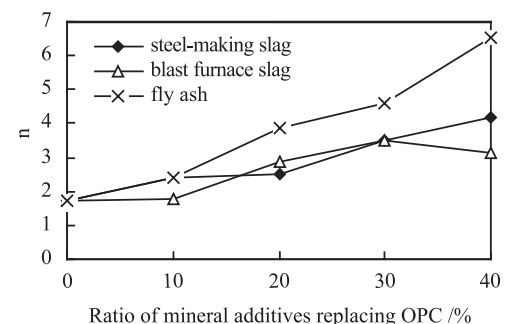


Fig. 2. The effect of different mineral additives on power  $n$ .

just explained why later-age strength of the OPC sample with mineral additives exceeded that of the OPC sample. On the other hand, the rate of strength development with porosity depended on the value of power  $n$  in the Balshin equation; thus, an increase of  $n$  means that the extent of strength development improved, which confirmed that strength development of the sample with mineral additives was faster than that of the sample without mineral additives.

Comparing values of  $\sigma_0$  and  $n$  for different mineral additives, it was observed that the sequence of  $\sigma_0$  and  $n$  was fly ash>steel-making slag>blast furnace slag, which was the reverse sequence of capacity of filling the big pore of mineral additives. It can be seen that fly ash and steel-making slag could not fill the big pore very efficiently, but samples containing them had higher  $\sigma_0$  and  $n$ ; hence, later-age strength of the OPC sample with them still could exceed that of the OPC sample. These results just explained seeming unreasonable results that steel-making slag and fly ash could not make the OPC sample denser but improved the compressive strength of the OPC sample at later age.

In a word, after being mixed with mineral additives, the intrinsic strength of the OPC sample,  $\sigma_0$ , and power  $n$  both increased and sequence of  $\sigma_0$  and  $n$  for different mineral additives was fly ash>steel-making slag>blast furnace slag. Moreover,  $\sigma_0$  and  $n$  can confirm development of compressive strength and porosity of the OPC sample with mineral additives.

#### 4. Conclusions

- (1) Mineral additives delayed the process that the micro-pore structure of the OPC paste developed. Fly ash and steel-making slag increased porosity of the OPC paste at a respective age, while blast furnace slag decreased porosity of the OPC paste after 28 days. Furthermore, the sequence of capacity of filling the large pore was blast furnace slag>steel-making slag>fly ash.
- (2) Strength development of the sample with mineral additives is faster than that of the OPC sample. At 28 days, the compressive strength of the samples with steel-making slag and fly ash was less than that of the OPC sample, while the compressive strength of the

samples with blast furnace approached to, or exceeded, that of the OPC sample. After 90 days, strength of samples with 10% to 30% different mineral additives exceeded that of OPC.

- (3) The Balshin equation fits the results of strength and porosity of all samples and there is a relatively strong quantitative relationship between compressive strength and porosity of all OPC samples with mineral additives.
- (4) After being mixed with mineral additives, the intrinsic strength of OPC,  $\sigma_0$ , and power  $n$  both increased and the sequence of  $\sigma_0$  and  $n$  for different mineral additives was fly ash>steel-making slag>blast furnace slag. Moreover,  $\sigma_0$  and  $n$  can confirm development of compressive strength and porosity of the OPC sample with mineral additives.

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