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The Synergistic Effect of Nano-Silica with Slag on Frost Resistance of Concrete

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ABSTRACT

The frost resistance of concrete is one of the most important factors for its durability. Supplementary cementitious materials could effectively improve the frost resistance of concrete. On this basis, the synergistic effect of nano-silica (NS) with slag on the frost resistance of concrete is better than the single, which was investigated. Nano-silica and slag were employed as a partial substitute of cement. The effect of these on the related indexes, including the mass loss, relative dynamic elastic modulus and porosity of concrete were measured after specified number of freeze and thaw cycles. Results show that the frost resistance of nano-silica modified concrete was obviously improved. The mass loss of control concrete was 2.5 % after 300 freeze-thaw cycles while that of the nano-silica modified concrete was as low as 1%. Further, the anti-freeze durability factor can reach up to 89.55% for the nano-silica modified concrete. The reasons are that the activity and nucleation effects of nano-silica accelerate the hydration of cement and the filling effect leads to more compact matrix. All of these made concrete better frost resistant. This was also proven by the porosity analysis. When the nano-silica was added, the total porosity of nano-silica modified concrete decreased from 14.57 % to 11.39 % compared with the control concrete. So, the synergistic effect of nano-silica with slag can enhance the frost resistance of concrete and improve its durability.

Keywords: Concrete, Nano-silica, Slag, Frost resistance, Synergistic effect

1.0 INTRODUCTION

Slag is an industrial by-product of blast furnace steelmaking. With the prosperity of the steel industry, the problem of environmental pollution and other issues become more and more serious because of a lot of slag produced. Under the efforts of researchers, the application of slag in the concrete industry achieves great success. The main components of slag are Al_2O_3, SiO_2 and CaO, which provide the possibility of the application of slag in concrete (Markandeya *et al*., 2018). The active components, such as Al_2O_3 and SiO_2, could rehydrate with $Ca(OH)_2$ and generate the C-S-H gel with a better structure. The filling effect of slag could improve the density of concrete structure and reduce the overlap of the initial hydration products, that makes the mechanical properties and durability of concrete improved (Han *et al*., 2017). Many researchers generally believe that the slag, as a lower active mineral admixture, could improve the comprehensive performance of concrete in the late stage (Alkaysi *et al*., 2016; Otieno *et al*., 2014).

However, the application of slag in concrete still has some disadvantages, such as the lower strength at early period and the looser and uncompacted microstructure. Fortunately, the emerging nano-materials, which are superfine particles with very high activity and filling effects of nanometer size (Zhang *et al*., 2017; Liu *et al*., 2016), provide an effective solution. The introduction of nano-materials into concrete, therefore, overcomes the disadvantages of slag-cement concrete system.

The activity effect, filling effect and nucleation effect provided by nano-materials could play significant roles in concrete. The nano-particles could act as nuclei for the cement phases and accelerate the hydration progress (Alireza Naji *et al*., 2010). At the same time, nano-particles could refine the harmful pores, increase the harmless pores, decrease the porosity and improve the pore structure (Du *et al*., 2014). Therefore, nano-materials can enhance the early strength and improve the comprehensive durability of concrete (especially the frost resistance), because of the more compact hardened paste.

Fan (Fan *et al*., 2015) studied the effect of nano-kaolinite clay on the frost resistance of concrete. They found that the samples with 5% nano-kaolinite clay exhibited the best frost resistance. Yanturina (Yanturina, 2017) found that the nano-additives containing graphite significantly improve the frost resistance and thermo-frost resistance. Behfarnia and Salemi (Behfarnia and Salemi, 2013) found that the concrete containing nano-Al_2O_3 has the better frost resistance than that containing the same amount of nano-SiO_2, but the compressive strengths are exactly the opposite. Zhang (Zhang *et al*., 2017) believed that the frost resistance of the concrete can be enhanced by incorporating nano-SiO_2. However, there are no researches about the influences of concrete modified by nano-SiO_2 cooperated with slag. This paper is to study the synergistic effect of nano-SiO_2 with slag on frost resistance of concrete.

2.0 MATERIAL AND SPROCEDURES

2.1 Materials

This research used the 42.5 type Ordinary Portland cement (OPC) and the granulated blast-furnace slag, complying with the Chinese National Standard GB175-2007 and GBT203-2008. The particle size distribution of cement (Fig. 1) shows that the average particle size (Xav) is 14.29 μm and the median particle size (X50) is 10.21 μm. And the particle size distribution of slag (Fig. 2) shows that the average particle size (Xav) is 12.15 μm and the median particle size (X50) is 8.41 μm. The nano-silica (Hydrophilic type, gas phase NS, Hydrophilic -300) was purchased from Shanghai Aladdin industrial company. Physical properties and chemical composition of cement, slag and nano-silica are presented in Table 1.

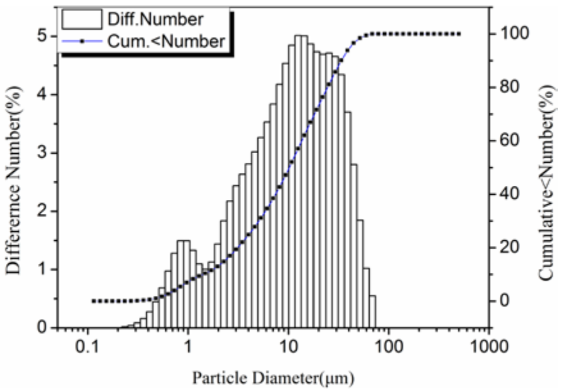

Fig. 1. The particle size distribution of cement

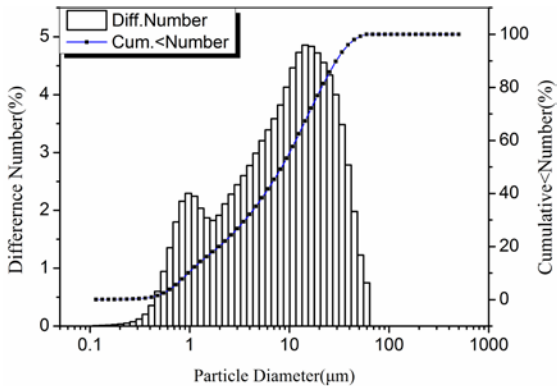

Fig. 2. The particle size distribution of slag

The granite aggregates smaller than 20mm were used as coarse aggregates. And the fine aggregates were siliceous sand. In order to avoid the influence of the impurities on the aggregates, wash them for 20 minutes and dry. The basic properties of the coarse aggregates and the fine aggregates were measured in accordance with the Chinese Standard GB/T 14685-2001 and GB 14684-2011, respectively. Table 2 shows the physical properties of them. The naphthalene superplasticizer was used as a surfactant to improve the workability of fresh concrete.

Table 1. Chemical composition and physical properties of cementitious materials

		Portland cement	Slag	Nano-silica
Chemical Compositions (%)	CaO	59.1	34.47	-
	SiO_2	20.26	33.31	>99.8
	Al_2O_3	5.17	16.42	-
	MgO	4.35	11.01	-
	Fe_2O_3	3.59	0.29	-
	SO_3	2.97	2.54	-
	LOI	4.56	2.16	-
Physical properties	Surface Area(m^2/kg	311	480	300000[a]

[a] as obtained from the manufacture's specifications

Table 2. The physical properties of the coarse and fine aggregates

Property	Granite (aggregates)	Siliceous sand
Specific weight (t/m^3)	2.62	2.62
Bluk density (t/m^3)	1.59	1.50
Void ratio (%)	39%	43%
Water absorption (%)	0.6%	-
Crushing value (%)	9.1%	-
Silt content (%)	0.25%	1.0
Fineness modulus	-	2.89

2.2 Preparation of Specimens

Two kinds of mixture of concrete have been manufactured with different dosages of nano-silica in order to compare the performance of nano-silica added to concrete with slag. The water-binder ratios (w/b) were equal to 0.28 and 0.39 for two different mixes. Table 3 lists the mix proportion of concrete with different dosages of nano-silica. For group A, the weights of sand and Granite are 624 kg and 975 kg, respectively. And for group B, the weights of sand and Granite are 703 kg and 1100 kg, respectively.

To get better workability of this concrete, nano-silica must be dispersed by special method, viz. the ultrasound dispersion. Then, prepare fresh concrete according to Table 3 and get homogeneous concrete paste. The specimens of 100×100×400 mm in dimensions were produced from these fresh mixes. In addition, cubes with each length of 100 mm were produced from the same mixes. And the specimens were cured with a controlled temperature of 20 ± 2°C and 90% relative humidity. When the specimens had reached an age of 24 days they were placed in water at a temperature of 20°C for another 4 days. After that, freeze-thaw tests were carried out.

Table 3. Mix proportions of concrete with nano-silica

Mix ID	Cement (kg)	Nano-silica (kg)	water reducer (kg)	Slag (kg)	w/b (%)
A1	437	0	12.5	188	0.28
A2	434.5	2.5	-	-	-
A3	432	5	-	-	-
A4	429.5	7.5	-	-	-
B1	300	0	8.57	128	0.39
B2	297.86	2.14	-	-	-
B3	295.72	4.28	-	-	-
B4	293.58	6.42	-	-	-
B5	291.44	8.56	-	-	-

2.3 Freeze-Thaw Tests

At present, the evaluation of frost resistance of concrete is mainly measured by two aspects: one is the appearance damage caused by the freeze-thaw cycles, the other is the internal structural damage. The latter is the most main reason. In this experiment, the fast freezing and thawing method was used to measure the frost resistance of concrete. These tests were run according to the Chinese standard GB/T 50082–2009. When the concrete specimens have reached an age of 28 days, take them out and wipe off the surface water with a damp cloth. Then, observe the appearance, weigh the initial mass of the specimens and measure the initial value of the transverse fundamental frequency. After that, they were exposed to the freeze-thaw cycles in the appropriate chamber. In this case one cycle of freezing and thawing lasts about 2 ~ 4 hours. The temperature of the cooling box varies between 20 ± 2°C and −20 ± 2°C. The temperature in the center of the concrete specimens varies under the given conditions between 5 ± 2°C and −18 ± 2°C. The mass and transverse fundamental frequency were measured after 50, 100, 150, 200, 250 and 300 freeze-thaw cycles. The influence of freeze-thaw cycles on porosity and pore size distribution was determined by mercury intrusion porosimetry (MIP).

2.4 Porosity and Pore Size Distribution Tests

Mercury intrusion porosimetry (MIP) was used to determine the porosity and pore size distribution of the concrete cured for 28 days. The tests were performed using the Quantachrome Instruments Poremaster-60 mercury porosimeter with a maximum pressure of 60000pisa. Approximately 1.0 gram of the hardened cement paste sample (3–5 mm in size) were used for each test.

3.0 RESULTS AND DISCUSSIONS

3.1 Mass Change of Concrete

Figures 3 and 4 show the mass loss of concrete after specific freeze-thaw cycles for group A and B, respectively. In general, the mass loss of concrete less than 5% is believed as basically no damage. As for group A, the mass losses of all mixtures are less than 5% after 300 freeze-thaw cycles. This is because the lower w/b (0.28) makes the pastes more compact. The lowest mass loss of concrete is when the content of NS is 0.8% (A3), which is almost no damage at the surface. When the content of NS is 0.4% or 1.2%, the mass losses are lower than the control group (A1) but larger than A3. That is to say, as for the mass loss of concrete, the best content of NS is 0.8%, which is good for frost resistance.

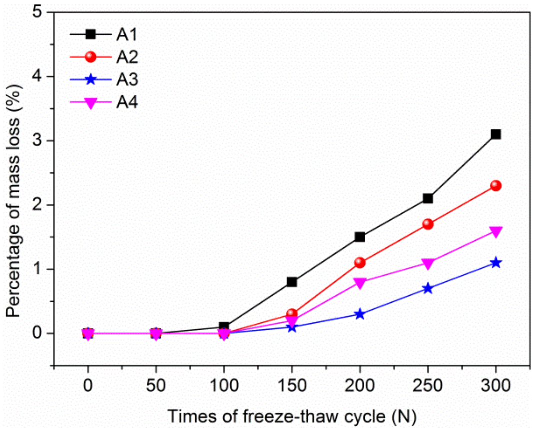

Fig. 3. Mass loss of concrete after freeze-thaw cycles for group A

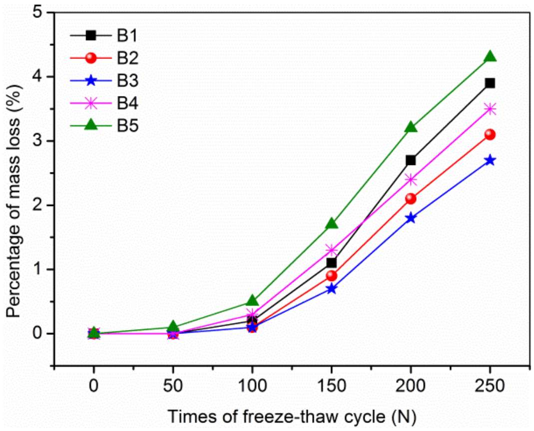

Fig. 4. Mass loss of concrete after freeze-thaw cycles for group B

When the w/b equal to 0.39 (group B), concrete specimens were severely damaged after 300 freeze-thaw cycles. It should be noted that all the mass loss values are small and well below acceptable mass loss limits. In other words, there are poor frost resistance for group B even though there is NS addition. As for group B, the best content of NS is 1% which has the lowest mass loss after 250 cycles. Especially, there is the more mass loss than the control group when the content of NS is 2%. This is because, perhaps, larger content of NS deteriorates the workability of concrete and introduces more defects.

3.2 Dynamic Elastic Modulus

The elastic modulus of concrete is an important parameter for determining the deformation of structural members(Saxena and Tembhurkar, 2018). The relative dynamic elastic modulus of concrete specimens is calculated as:

$$P_{ni} = (f_{ni}^2/f_{0i}^2) \times 100\% \quad (1)$$

where: P_{ni} is the i test sample's relative dynamic elastic modulus after N cycles of freezing and thawing; f_{ni} is the i test sample's natural frequency after N cycles of freezing and thawing; f_{0i} is the i test sample's initial natural frequency.

Figures 5 and 6 represent the relative dynamic elastic modulus of concrete for group A and group B, respectively. The same trend as the mass loss, group A has the better influence than group B. From Fig. 5, the best content of NS is also 0.8%, which has the biggest relative dynamic elastic modulus about 89.55% compared with the control group (A1) about 75.67 after 300 freeze-thaw cycles. Not the amount of NS as much as possible, such as the 1.2% of NS.

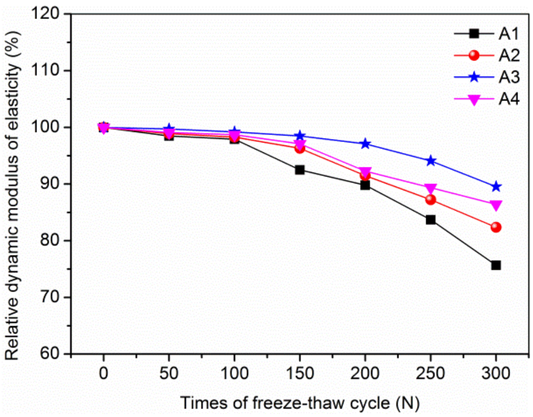

Fig. 5. Relative dynamic elastic modulus of concrete for group A

Figure 6 shows that group B (w/b is 0.39) has the worse frost resistance than group A because of the lower relative dynamic elastic modulus. After 250 freeze-thaw cycles, the relative dynamic elastic modules of mixtures are lower than 60%. When the content of NS is 1%, the biggest is 57.1% after 250 freeze-thaw cycles. While the content of NS is 2%, the smallest is 35.1%, which is lower than control group (B1) about 44.2%.

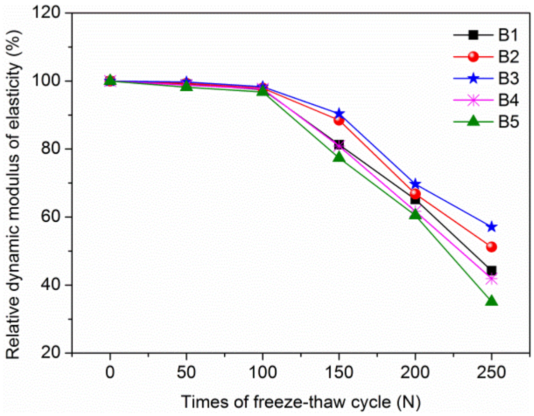

Fig. 6. Relative dynamic elastic modulus of concrete for group B

3.3 Durability Factor

The durability factor (DF) of concrete was also used to evaluate its frost resistance. DF is calculated as:

$$DF = (E_N/E_0) \times (N/300) \times 100\% \quad (2)$$

where: DF is the concrete durability factor (%); E_N is the dynamic elastic modulus of concrete specimens after N cycles of freezing and thawing (MPa); E_0 is the initial dynamic elastic modulus of the specimens before freezing and thawing cycles (MPa); N is the cycles of freezing and thawing when the mass loss rate of specimens more than 5% or relative dynamic elastic modulus lower than 60%.

In general, concrete is considered durable when the DF higher than 60%. On the contrary, DF less than 60% is shown that the concrete is easily damaged by freezing and thawing(Chung *et al*., 2010). The results of DF for this research are given in Figs. 7 and 8. When the w/b is 0.39 (group B), the DF values of all mixtures are lower than 60%. This is shown that the concrete with or without NS has poor ability about frost resistance for this w/b equal to 0.39. Nevertheless, appropriate amount of NS can also improve its frost resistance. When the content of NS is 1%, the value of DF increases from 39.35% to 46.47%. As dosage of NS increase more, DF decreased, even lower than that of control group (B1). This may be caused by the internal defects which due to more NS makes the worse workability of fresh concrete.

When the w/b is 0.28 (group A), the DF of concrete is higher than 60%. Especially when the dosage of NS is 0.8%, the value of DF increased from 75.67% to 89.55% compared with the control group (A1). Similarly, the more NS, the smaller value of DF such as A4.

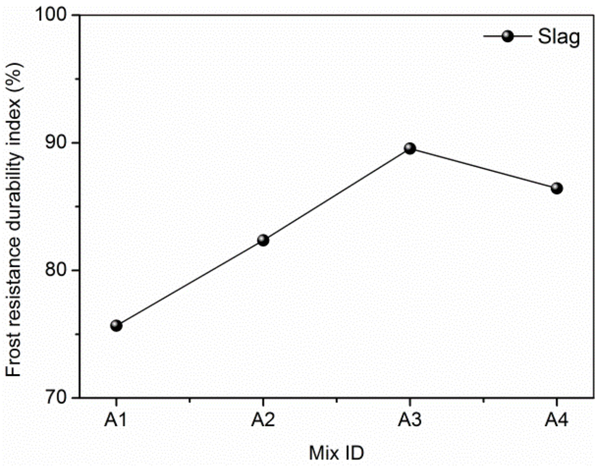

Fig. 7. Frost resistance durability factor of concrete for group A

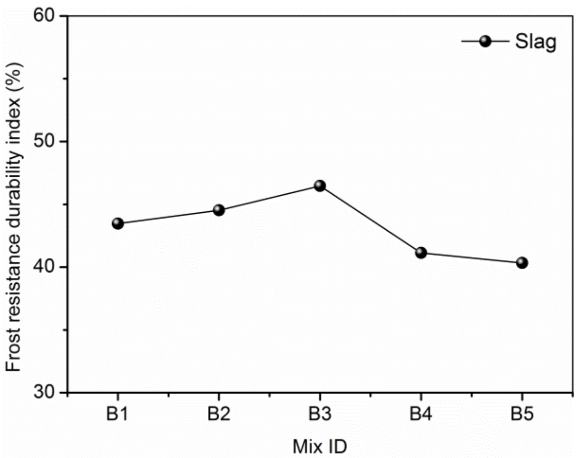

Fig. 8. Frost resistance durability factor of concrete for group B

These two figures reveal that there is less microcracking occurred in the concrete specimens when the content of NS is appropriate than that of control group. But the excess dosage of NS makes more internal defects that results in the decline of the anti-frost property.

3.4 Porosity and Pore Size Distribution

Freeze-thaw cycles could make the pore size increase and the closed pores connect with each other(Qin *et al*., 2016). Slag has the potential of hydration reaction and could form cementitious products, which leads to refinement of the concrete pore structure (Otieno *et al*., 2014). Many researchers investigated that the ability of frost resistance of the concrete was improved by incorporating NS particles because of the number of impervious holes in hardened concrete increased (Zhang *et al*., 2017, Zhao *et al*., 2012). Figures 9 and 10 show the pore size distribution of concrete for group A and group B, respectively. From these two figures, NS made the total porosity decreased. For Group A, the 0.8% dosage of NS reduced the total porosity from 14.57% of the control group to 11.39%.

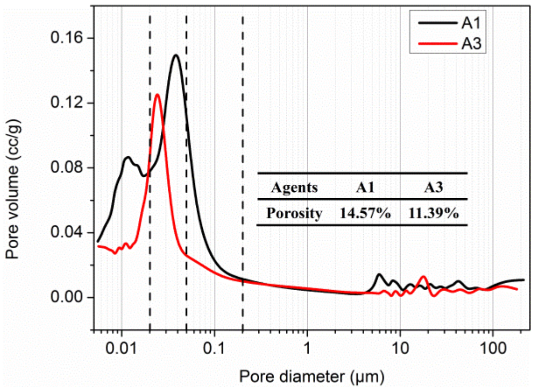

Fig. 9. Pore size distribution of concrete for group A

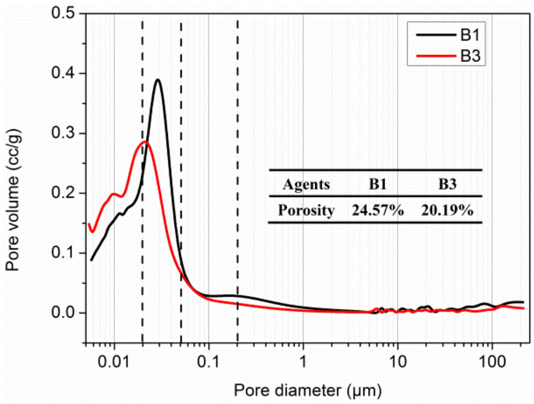

Fig. 10. Pore size distribution of concrete for group B

For group B, when the optimum dosage of NS was 1%, the total porosity decreased from 24.57% of the control group to 20.19%. At the same time, NS could reduce and refine the harmful pores. In short, the pore volume decreased and the critical pore diameters were refined as hydration progressed.

4.0 CONCLUSIONS

The destruction of concrete structure by freeze-thaw cycles is not only affected by the environment of concrete working but also depends on its own microstructure, especially the influence of porosity and pore structure. The synergetic effect of nano-SiO_2 and slag can effectively improve the pore structure of concrete and reduce the porosity, which stops water penetration and reduces the effects of freeze-thaw damage. This is mainly reflected in the smaller mass losses, higher dynamic modules and durability factors of these modified concretes.

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