

## Resistance to Chloride Ion Permeability of Concrete Mixed with Fly Ash, Slag Powder, and Silica Fume



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### ABSTRACT

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*silica fume, air content, resistance to chloride ion penetration*

This paper attempts to study the resistance to chloride ion permeability of concrete mixed with different admixtures such as fly ash (FA), slag powder (SP), and silica fume (SF). For this, taking the C50 concrete with the 1:1 proportion of FA and SP, the test method for rapid chloride ion migration (RCM) coefficients was used to study the resistance to chloride ion permeability and economic benefits of the concrete under the conditions of different total amount of admixtures, SF content, and air content. The results show that the increase in the total amount of the admixture can improve the concrete resistance to chloride ion penetration, but in a gradually weakening trend; the increase in SF content can increase the concrete resistance to chloride ion penetration, but the enhancement effect is gradually decreased; the SF has more significant effect on improving the 56d concrete resistance to chloride ion penetration; the increase of air content greatly increases the chloride ion migration coefficient of concrete at 28d, and the chloride ion migration coefficient increases linearly at 56d; the air content within 5% has an insignificant effect on the resistance to the chloride ion permeability; the NH40-2 was chosen to be the optimal mix ratio.

## 1. INTRODUCTION

At present, concrete is one of the most widely used building materials. As its service life increases, reinforced concrete (RC) structures are subjected to a series of durability problems, including concrete carbonation, reinforcement bar corrosion, freeze-thaw failure, alkali aggregate reaction, Sulfate erosion, and fatigue damage, etc. [1-5]. Among them, internal corrosion of reinforcement bar caused by chloride penetration can lead to the most serious RC structural damage, which is also the most common in engineering structures [6-11].

Adding an appropriate amount of admixture to concrete can help improve its resistance to the chloride ion penetration [12, 13], and then effectively improve the durability of concrete. In recent years, scholars at home and abroad have conducted many researches on the resistance of concrete to chloride ion penetration. Some scholars studied the effect of FA and SF on the chloride ion permeability and found that the pore structure of concrete and its binding ability with chloride ion are the main influencing factors on the chloride ion permeability [14]; Seleem et al. [15] studied the chloride ion permeability to multi-doped concrete with the SF, ground blast furnace slag, and metakaolin as cementitious materials, indicating the cementing material system composed of cement and SF is the most effective combination to resist the chloride ion penetration. Related research through analysis for the chloride ion permeability of concrete mixed with FA and slag, concluded that the effect of slag on the resistance of self-compact concrete to chloride ion penetration is better than that of FA, and the additive effect of mixtures on this resistance is not obvious [16]; Guo et al. [17] conducted orthogonal experiments and studied the effects of water-binder ratio, FA

content, water consumption, and air entrainer content on the resistance of bridge concrete to the chloride ion penetration, finding that FA has a significant effect on the resistance of concrete to chloride ion penetration, and proper air content can also improve this. Currently, the research on the resistance of concrete to chloride ion penetration mostly focuses on single- or double-mixed concrete [18-20], but little research has been done on concrete with three kinds of admixtures.

FA and SP are common industrial waste materials, which are easy to obtain and low in cost. They can be added to concrete and replace part of the cement for enhancing the compactness of concrete [21-24]. SF is a kind of ultra-active ultrafine siliceous powder material produced in industrial smelting, with an average particle size of less than 0.1 $\mu$ m. It has a good capillary porosity filling effect, significantly improving the microscopic pore structure of concrete [25]. Therefore, by adding FA, SP and SF to C50 concrete, the authors studied the effects of different amount of admixtures, SF content, and air content on the resistance of concrete to the chloride ion penetration, and then concluded the optimal mix ratio of concrete with good chloride ion penetration resistance and low cost. This not only increases the service life of the concrete structure, but also reduces its cost.

## 2. TEST OVERVIEW

### 2.1 Test specimen design

First, fabricate the cylindrical pieces with a diameter of 100mm $\times$ 200mm, and then take out the specimen with a height of 50 $\pm$ 2mm from the center.

Cement: Taihangshan P.O 42.5 ordinary Portland cement.

Fly ash: Class II, from the concrete mixing station of Hebei Construction Group.

Slag powder: S95 grade from the concrete mixing station of Hebei Construction Group.

Silica fume: off-white powder, apparent density: 2200kg/m<sup>3</sup>, SiO<sub>2</sub> content: 95.6%.

Fine aggregate: river sand, with fineness modulus 2.71, medium sand; apparent density 2655kg/m<sup>3</sup>, clay content 1.3%, and clay lump content 0.

Coarse aggregate: 5 to 20mm continuous grading crushed stone, with apparent density: 2715kg/m<sup>3</sup>, crushing index 7%, total content of needle-like particles 3.6%, clay content 0.8%, and clay lump content 0.

Water reducer: polycarboxylic acid-based high-efficiency superplasticizer with the solid content of 40%, from Baoding

Muhu Hengyuan New Building Material Co., Ltd.

Air-entrainer: AE-P air-entraining agent produced by a Japanese company.

The water-binder ratio was adjusted to ensure that the concrete can meet the requirements of C50 strength grade; the proportion of FA and SP was fixed to 1: 1, and the same amount of mineral admixture replaced 30%, 40% and 50% of cement, of which the SF content was 5%; with the total amount of mineral admixture for 40% of cement, the SF content was 0%, 2.5%, and 5%; with the total amount of mineral admixture for 40% and the content of SF for 5%, the air content was 3%, 4% and 5% respectively. The amount of polycarboxylic acid superplasticizer was also adjusted to meet the requirements of large fluidity in concrete mixture. The mix ratio of C50 concrete is shown in Table 1.

**Table 1.** Concrete mix ratio

No	Water-binder ratio	Amount of materials /kg/m <sup>3</sup>						Water content / (%)	Sand ratio	Slumps / (mm)	Compressive strength / (MPa)	
		Fly ash	Slag powder	Silica fume	SanfStone	Water	Water reducer					
HN30-1	0.40	53	53	21	756	1044	170	2.1	-	42%	203	64.58
HN40-1	0.38	80	80	23	733	1012	175	2.3	-	42%	215	62.25
HN40-2	0.34	92	92	12	731	1009	165	2.7	-	42%	212	66.53
HN40-3	0.33	100	100	0	728	1005	165	2.5	-	42%	228	62.13
HY40-1	0.38	80	80	23	733	1012	175	2.3	3	42%	218	60.29
HY40-2	0.38	80	80	23	733	1012	175	2.3	4	42%	220	62.89
HY40-3	0.38	80	80	23	733	1012	175	2.3	5	42%	225	62.03
HN50-1	0.37	104	104	23	732	1011	170	2.0	-	42%	213	63.12

Note: HN<sup>xx</sup> means no air-entraining agent, HY<sup>xx</sup> means air-entraining agent added, and 30, 40, 50 means that the total amount of admixtures is 30%, 40% and 50% respectively.

## 2.2 Test method

According to the *Standard for Test Method of Long-term Performance and Durability of Ordinary Concrete* (GB/T50082-2009) [26], test method for rapid chloride ion migration coefficient (RCM) was used to measure the chloride ion permeability coefficients of concrete in the age of 28d and 56d. The ordinary concrete at 28d can reach the design value of compressive strength. Because the strength of concrete mixed with mineral admixture increases slowly, 56d was taken as the detection age. After the test specimens reached the age, they were taken out of the curing tank, and measured in terms of their diameter and height. Then, the test specimens were placed in a concrete vacuum saturated machine (Figure 1) and treated with a saturated calcium hydroxide solution in distilled water. After the vacuum treatment, the specimen was placed in the bottom of the rubber sleeve, and the outer side of the rubber sleeve was tightly covered with a stainless steel hoop, to ensure the side of the specimen in a sealed state. Next, install the RCM device (Figure 2), inject 300L of 0.3mol/L NaOH solution into the rubber sleeve and immerse the anode plate and the specimen, and then inject 12L of 10% NaCl solution into the cathode test tank. Thus, the test started. After the test, the specimens were cut along the axis, and the split surface was sprayed with the discolored indicator of AgNO<sub>3</sub> solution with a concentration of 0.1mol/L. The discolored surface was divided into 10 equal sections, and the distance of color boundary from the bottom of the specimen is the depth of chloride ion penetration (Figure 3).



**Figure 1.** Concrete vacuum saturated machine



**Figure 2.** RCM device



**Figure 3.** Discolored specimens

According to the recorded data, the unsteady chloride ion migration coefficient of concrete is calculated as:

$$D_{RCM} = \frac{0.0239 \times (273 + T)L}{(U - 2)t} (X_d - 0.0238 \sqrt{\frac{(273 + T)LX_d}{U - 2}}) \quad (1)$$

where:

$D_{RCM}$ : Unsteady chloride ion migration coefficient of concrete, with the accuracy of  $0.1 \times 10^{-12} \text{m}^2/\text{s}$ ;

$U$ : The absolute value of the voltage (V);

$T$ : The average value of the initial temperature and the end temperature of the anode solution ( $^{\circ}\text{C}$ );

$L$ : Thickness of test piece (mm), with the accuracy of 0.1mm;

$X_d$ : The average value of chloride ion penetration depth (mm), accurate to 0.1mm;

$t$ : Test hours (h).

### 3. TEST RESULTS AND ANALYSIS

#### 3.1 Effects of total amount of admixture on resistance to chloride ion penetration of C50 concrete

Under the conditions of the C50 strength grade, the 1:1 proportion of FA and SP, and 5% SF content, the chloride ion migration coefficients at 28d and 56d of HN30-1, HN40-1, and HN50-1 are shown in Table 2 and Figure 4.

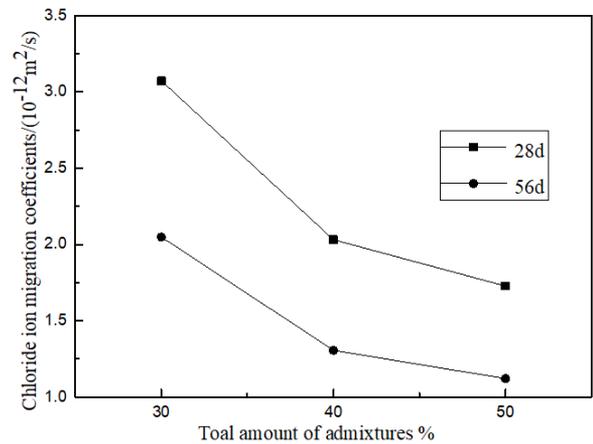
It can be seen from Figure 4 that for concrete of the same strength, as the total amount of admixture increased, the FA and SP also increased relatively and the resistance to chloride ion migration coefficients of concrete at 28d and 56d continued to decrease. Compared with HN30-1, the chloride ion migration coefficients of HN40-1 at 28d and 56d decreased by 33.9% and 36.3%, respectively; compared with HN40-1, the chloride ion migration coefficients of HN50-1 at 28d and 56d decreased by 15.0% and 14.2%. Compared with existing research results, this can more clearly indicate that the chloride ion migration coefficient of concrete decreased more slowly when the total amount of the admixture increased from 40% to 50% than from 30% to 40%.

This indicates that with the same concrete strength grade, certain SF content, and the same proportion of FA and SP, the concrete with 50% total admixture has better resistance to chloride ion penetration than 30% and 40%. The increase of the total amount of admixture can improve the resistance to chloride ion penetration, but at a gradually weakening rate. This is mainly because the increase in the total amount of admixtures for the same strength grade of concrete will lead to three phenomena: a decrease in the water-to-binder ratio to

varying degrees, an improvement in the micro-aggregate filling effect of admixtures, and a decline in the secondary hydration micro-filling effect of the admixture; the former two decreased the chloride ion migration coefficient of the concrete, while the last one increased this coefficient. Therefore, with the increase of the total admixture, the effects of the former two factors on reducing the concrete resistance to chloride ion migration coefficients are far greater than that of third factor, so the combined effects of various factors can greatly enhance the resistance of concrete to chloride ions; also, when the total admixture continues to increase, the effect of the third factor on increasing the chloride ion migration coefficient will gradually increase, so the combined effect of various factors will slow down the increase in the resistance of concrete to chloride ion.

**Table 2.** The chloride ion migration coefficients of concrete  $D_{RCM} \cdot 10^{-12} \text{m}^2/\text{s}$

No.	HN30-1	HN40-1	HN50-1
28d	3.073	2.031	1.727
56d	2.049	1.306	1.121



**Figure 4.** Effects of total amount of admixtures on chloride ion migration coefficients

#### 3.2 Effect of silica fume content on resistance to chloride ion penetration of C50 concrete

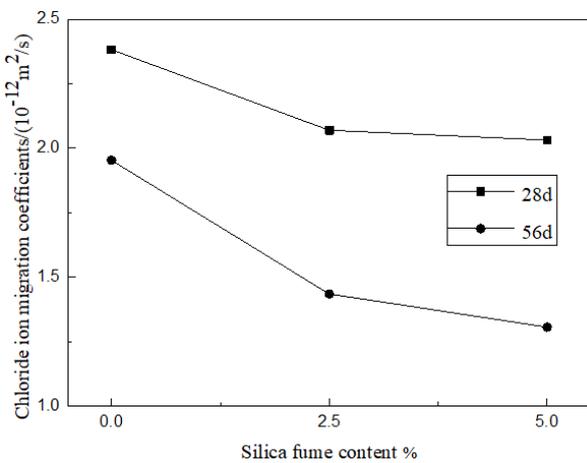
Under the conditions of the C50 strength grade, the 1:1 proportion of FA and SP, and 0%, 2.5%, and 5% SF content, the chloride ion migration coefficients at 28d and 56d of HN40-1, HN40-2, and HN40-3 are shown in Table 3 and Figure 5.

It can be seen from Figure 5 that the addition of SF has a significant effect on the chloride ion migration coefficient of C50 concrete. When the total amount of the admixture was 40%, with the increase of the SF content, the admixture amount of FA and SP relatively decreased, the chloride ion migration coefficients of C50 concrete on 28d and 56d decreased, and the resistance of concrete to chloride ion penetration gradually increased.

With the addition of SF, the chloride ion migration coefficient on 56d of the Hd40-1 with 5% SF decreased by 14.7%, and the coefficient on 56d decreased by 33.1%, compared to HN40-3 without SF. This shows that the addition of SF below 5% can improve the resistance to chloride ion penetration of concrete at 56d more significantly than that at 28d. When the SF content in concrete increased from no SF in

HN40-3 to 2.5% in HN40-2 and then to 5% in HN40-1, the 28d chloride ion migration coefficient of concrete decreased from 13.1% to 1.8%; the 56d coefficients decreased from 26.6% to 8.9%. The results clearly indicate that when the SF content is below 5%, the effect of SF on the chloride ion migration coefficient gradually decreases, while the effect on enhancing the resistance of concrete to chloride ion penetration gradually weakens.

This is because of the small particle size of SF, 100 times smaller than that of cement. The particle filling effect of SF is conducive to filling the pores of relatively large particles in cementitious material and reduce the volume of capillary pores in concrete, thereby making concrete more compact; the nucleation effect of SF is wrapped around the particles of other cementitious materials, which causes the cement to undergo hydration reaction and produce smaller CH crystals; also, the fibrous CSH glue caused by the pozzolanic activity effect of SF makes the micro-pore structure of concrete compact and dense.



**Figure 5.** Effects of silica fume content on chloride ion penetration coefficients

**Table 3.** Concrete chloride ion penetration coefficients  $D_{RCM}$   $10^{-12}m^2/s$

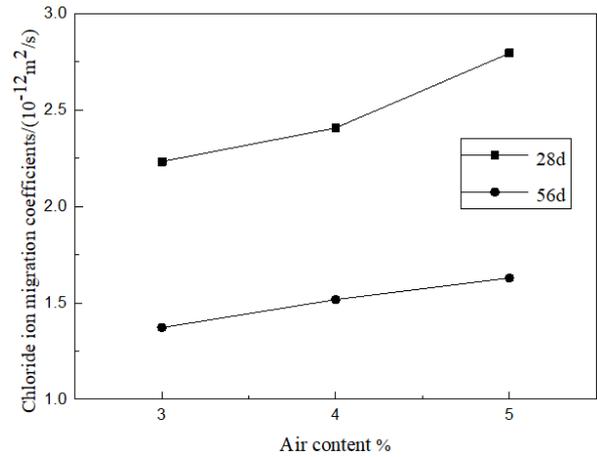
No.	HN40-1	HN40-2	HN40-3
28d	2.031	2.069	2.382
56d	1.306	1.434	1.953

### 3.3 Effects of air content on resistance to chloride ion penetration of C50 concrete

Under the conditions of the C50 strength grade, the 1:1 proportion of FA and SP, 5% SF content, and the air content of 3%, 4%, and 5%, the chloride ion migration coefficients at 28d and 56d of HY40-1, HY40-2, and HY40-3 are shown in Table 4 and Figure 6.

**Table 4.** Concrete chloride ion migration coefficients  $D_{RCM}$   $10^{-12}m^2/s$

No.	HY40-1	HY40-2	HY40-3
28d	2.233	2.408	2.795
56d	1.372	1.517	1.629



**Figure 6.** Effects of air content on chloride ion migration coefficients

It can be seen from Figure 6 that under the same conditions above, 28d and 56d chloride ion migration coefficients of C50 concrete increased with the increase of air content. Compared with HY40-1 with 3% air content, the 28d chloride ion migration coefficient of HY40-2 with 4% air content increased by 7.8%, while compared to HY40-2, that of the HY40-3 with 5% air content increased by 16.1%. With the increase of air content, the 28d chloride ion migration coefficient of concrete doubled, and the 56d coefficient continued to increase linearly.

Compared to HN40-1 without air entrainer, the chloride ion diffusion coefficients on 28d and 56d of HY40-1 with 3% air content, HY40-2 with 4% and HY40-3 with 5% all increased below  $0.7 \times 10^{-12}m^2/s$ , meeting the current requirements of RCM-IV about resistance to chloride ion penetration of ready-mixed concrete. Compared with the existing research results, it shows more specifically that the air content below 5% has no significant effect on the concrete resistance to chloride ion penetration. This is because the increase in air content changes the microscopic pore structure of the concrete, so that the capillary porosity and the capillary pore volume increases, and the concrete resistance to chloride ion penetration decreases.

### 4. ECONOMIC BENEFITS

The unit prices of concrete raw materials were from the market inquiry in 2019. Table 5 lists the amount and cost per cubic meter of concrete raw materials.

**Table 5.** Concrete cost per cubic meter

No.	Use of concrete raw materials (kg/m <sup>3</sup> )					Unit price of concrete raw material (Yuan/on)					Cost per cubic meters
	Cement	Fly ash	Slay powder	Silicon fume	Sand Stone	Cement	Fly ash	Slay powder	Silicon fume	Sand Stone	
HN30-1	296	53	53	21	756 1044	400	120	320	2000	113 87	360.32
HN40-1	274	80	80	23	733 1012	400	120	320	2000	113 87	361.10
HN40-2	295	92	92	12	731 1009	400	120	320	2000	113 87	353.55
HN40-3	300	100	100	0	728 1005	400	120	320	2000	113 87	333.64
HN50-1	231	104	104	23	732 1011	400	120	320	2000	113 87	354.96

Table 5 shows that with no SF in NH40-3 and the highest SF content in NH40-1, NH40-2 had the lowest cost, NH40-1 had the highest, and NH40-2 was 1.41 yuan lower than the NH50-1. Meanwhile, the 56d chloride ion migration coefficients of NH40-1, NH40-2 and NH50-1 all meet the RCM-V requirements. Considering the concrete's resistance to chloride ion penetration, the NH40-2 was chosen as the optimal mix ratio.

## 5. CONCLUSIONS

(1) With the same strength grade of C50, and the same proportion of FA and SP, the resistance to chloride ion penetration of concrete with total admixtures of 50% is better than 30% and 40%; the increase in the total amount of the admixture can improve the resistance to chloride ion penetration, but at a gradually decreasing rate.

(2) For concrete of the same strength grade, the same amount of admixture, and fixed proportion of FA and SP, an increase in the SF content can improve the concrete resistance to chloride ion penetration; when the SF content is within 5%, the effect of SF on strengthening the concrete resistance to chloride ion penetration gradually weakens with the increase of the SF; the SF doped below 5% can improve the chloride ion penetration resistance of concrete at 56d more significantly than that at 28d.

(3) Under the conditions of the same admixture content, 1:1 proportion of FA and SP, and SF content of 5%, the 28d chloride ion migration coefficient of concrete of the same strength grade increases with the air content, ranging 7.8% to 16.1%, and the 56d chloride ion migration coefficient increases linearly; the chloride ion migration coefficient of concrete with an air content below 5% increases within  $0.7 \times 10^{-12} \text{m}^2/\text{s}$ , which has no significant effect on concrete resistance to chloride ion penetration.

(4) Taking the concrete's resistance to chloride ion penetration and economic benefits into comprehensive consideration, the NH40-2 was chosen as the optimal mix ratio design.

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