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A study on anticorrosion effect in high-performance concrete by the pozzolanic reaction of slag

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Abstract

The study examines the pozzolanic reaction brought by the addition of slag to the cement paste using the synchrotron radiation accelerator (SRA), the mercury intrusion porosimetry (MIP), and scanning electron microstructural analysis. The anticorrosion effect in high-performance concrete with and without slag added is also assessed by its electrical resistivity and permeability. Results show that pozzolanic reaction due to the addition of slag can decrease the amount of calcium hydroxide, reduce the volume of capillary pores (Pc), and lower its permeability, thus making the concrete more compact and durable. As evidenced by the enhanced electrical resistivity and reduced permeability, the addition of slag to high-performance concrete can indeed strength the anticorrosion effect.

Keywords: Pozzolanic reaction; High-performance concrete; Synchrotron radiation accelerator; Electrical resistivity; Electrical permeability

1. Introduction

The five major elements involved in the corrosion mechanism of steel in reinforced concrete are cathode, anode, conducting path, corrosion current, and electrolyte [1,2]. In general, the coating alkalinity derived from cement hydration provides excellent protection for steel reinforcement in the concrete. The protective ferric oxidized covering (γ-Fe_2O_3) around the steel prevents corrosive reaction. According to the pourbaix diagram of electrochemical potential versus pH value, corrosion will occur only at a pH value of lower than 9 or higher than 14. In actual practice, the former is more probable while the latter is rare [1–6]. Cracks are produced in concrete because of a number of artificial and natural factors such as specifications, engineering designs, material preparation, construction, curing tasks, and so on. Concrete with cracks is subject to direct corrosion. Even high-quality concrete is no exception. On the other hand, for concrete without cracks, its corrosion rate is controlled by its permeability. Bleeding and segregation not only increase the permeability of concrete, but also forms a weak interface along the lower edge of the aggregate and the reinforcing steel [7].

Power [8] classified pores into capillary pores (Pc) and gel pores (Pg). Pc have a diameter greater than 100 Å, that is 10 nm (10×10^{-9}). Pg are the original pores of the bond water existing between the C-S-H gel layers. They have a diameter smaller than 100 Å and their content is steady. There exists a close relationship between permeability and Pc. Water molecules of 2.54×10^{-10} m in size can permeate almost any pores. $Ca(OH)_2$, a hydration product from concrete, can be easily dissolved in water and produces efflorescence [6–8]. Capillary action brings the dissolved $Ca(OH)_2$ to the surface of the concrete, forming pores. Carbonation occurs when $Ca(OH)_2$ reacts with carbon dioxide in the air or water. The calcium carbonate thus produced lowers the pH. High temperature and carbon dioxide in high concentration fosters carbonation, lowering the pH to 6–7. This reduces the protection of the passive layer on the surface of the steel and enhances the corrosion of the steel. For concrete of poor quality or with too many pores, SO_4^{2-} will permeate the concrete along with water and react with the Ca^{2+} and OH^- derived from the $Ca(OH)_2$ to form gypsum. This causes the AFm ($C_3A \cdot CS \cdot H_{12}$) in the concrete to expand in the presence of water. The AFt($C_3A \cdot 3CS \cdot 32H$) thus formed damages the concrete and accelerates corrosion [6–8].

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Alkali-aggregate reaction (AAR) occurs when the alkali present in the concrete reacts with the aggregate containing activated silicate and yields expanded gel such as N/K-S-H. This results in internal stress and formation of cracks, which favors corrosion. Chloride (Cl^-) ions present in the concrete or originated from the external environment can cause destruction to the passive oxide film. Chloride ions are mainly found in materials like cement, admixture, water, and aggregate, or in the environment under exposure to seawater vapor. Iron in the concrete will react with the chloride ions to form $FeCl_2$. When the iron dissolves and changes to Fe^{2+}, it reacts with the oxygen or the hydroxyl ions, forming compounds such as yellow $FeCl_2 \cdot nH_2O$ and black $Fe(OH)_3$ $FeCl_2$ [7–9]. These compounds may cause the volume of steel to expand to 2–14 times its usual size, causing structural damage.

A thorough understanding of the corrosive mechanism would shed light on how to enhance the structure's durability and safety, thus avoiding the waste of resources [6–9]. Previous studies [10–16] have proved that superior properties such as high strength, good workability, long durability, excellent waterproofing, high wear resistance, low shrinkage, and minimum creeping can be achieved by lowering the water-to-binder (W/B) ratios, improving the densified mixture proportion, the use of superplasticizer, and the addition of pozzolanic materials. The study focuses on examining the anticorrosion effect of high-performance concrete brought by the pozzolanic reaction through the addition of slag.

2. Experimental design

2.1. Test materials

The following test materials were employed in this study.

1. Type I cements, produced by Taiwan Cement Corporation.
2. Slag, produced by China Steel Corporation.
3. Type G superplasticizer.

The physical and chemical properties of the test materials are shown in Table 1, and the mixture proportion of the high-performance concrete is displayed in Table 2.

2.2. W/B ratio and age

The W/B ratios of concrete are 0.28, 0.34, and 0.40, and the curing ages are 1, 7, 28, 56, and 90 days.

2.3. Experimental procedures

2.3.1. Compressive strength

Compressive strength tests are performed according to ASTM 39 or CNS 1232, the Test Method of the Compressive Strength of Round-Columned Concrete Specimens. The dimensions of the specimens used in this study are $\psi 10 \times 20$ cm.

Table 1
Properties of pozzolanic cements and slag

Test program			Cement (Type I)		Slag
			CNS61	Taiwan Cement Corporation	China Steel Corporation
Chemical properties (%)	SiO_2(S)		–	22.01	34.86
	Al_2O_3		–	5.57	13.52
	Fe_2O_3(F)		–	3.44	0.25
	S + A + F		–	31.02	48.63
	CaO		–	62.8	41.77
	MgO		Max: 6.0	2.59	7.18
	SO_3		Max: 3.0	2.08	1.74
	f-CaO		–	1.05	–
	TiO_2		–	0.52	–
	Na_2O		–	0.40	–
	K_2O		–	0.78	–
	V_2O_5		–	0.05	–
	Ignition loss		Max: 3.0	0.51	0.31
	Insoluble Residue		Max: 0.75	0.08	–
	Potential clinker	C_3S	–	40.10	–
		C_2S	–	32.08	–
		C_3A	–	8.90	–
		C_4AF	–	10.50	–
Physical properties	Fineness		Min: 2800	2970	4350
	Specific gravity		–	3.15	2.88
	Initial setting (min/s)		45	04:37 (W/C = 0.47)	–
	Final setting (min/s)		06:15	08:22	–

2.3.2. SRA observation

High-performance slag concrete paste of 200 g with different W/B ratios were observed under the synchrotron radiation accelerator (SRA). Using the wavelength λ and d-spacing, we can figure out the Bragg angle, that is, the diffraction angle. The spectrogram can then be obtained as the x-axis from the fixed crystals angle of the hydration products or the parallel spacing, d-spacing, while the radiation strength is taken as the y-axis. The integration of the area under the curve of different time gives the values of the radiation strength. These values represent the different sizes of the hydration products with varying ages and W/B ratios.

2.3.3. SEM tests

Hydrated specimens were fixed on the test base. Then the specimens are subjected to vacuity and gilded, placed into the column of the electron microscope, and vacuity again. Projecting the electron beam, the specimens will be scanned in order to get photograph.

2.3.4. Mercury intrusion porosimetry (MIP) tests

Mercury intrusion porosity was examined by injecting Hg into the dried specimens under high pressure. The

Table 2
The mixture proportion of HPC

Mixture proportion	No.					
	1	2	3	4	5	6
W/B	0.28	0.34	0.40	0.28	0.34	0.40
Slag	0	0	0	15	15	15

amount of Hg in the specimen under the pressure is measured, and after the transformation according to the formula, such data like pore volumes, distributions, and the types of pores can be gathered.

2.3.5. Permeability tests

Permeability tests were performed on specimens made according to PCA Bulletin J ISA A6101 after curing in saturated lime for 90 days and then subject to compression of 15 kg/cm^2 for 3 days.

2.3.6. Electrical resistance tests

Electrical resistance of the concrete was measured using a Concrete Resistance Meter (C.N.S. Electronics). The measurements obtained serve as the basis for determining the degree of densification and corrosion.

2.3.7. Electrical permeability tests

The relative ease and magnitude for chloride ions to penetrate the concrete were estimated according to ASTM C1202.

3. Results and discussion

3.1. SRA observation

With water added to cement, calcium hydroxide (CH), with striped framework and well-formed crystal structure, is produced from the calcium silicate hydrates. If bleeding and segregation occur in concrete, these hydrates often accumulate on the interface of the aggregate. Water permeating into concrete will lead to hydroxylation, generating efflorescence. This has a detrimental effect on the concrete. Fig. 1 shows the relationship between radiation strength and ages of cement pastes with different W/B ratios and slag contents. As can be seen, at high W/B ratios and moisture content, radiation strength of CH increases with longer curing age, thus producing more CH. With the same W/B ratios, adding 15% more slag will reduce the radiation strength of CH of all specimens as compared with that without slag added. The addition of slag to concrete serves to foster the formation of C-S-H and C-S-A gel through pozzolanic reaction, thereby reducing the CH content and enhancing the quality of concrete. This effect is most obvious between curing age of 28 and 90 days, which is the hydration period.

3.2. SEM observation

The hydration product comprises mainly C-S-H gel, CH crystal, and calcium sulfoaluminate. The microstructure of concrete varies mainly with ages, degree of hydration, and addition of pozzolanic materials. Fig. 2 displays the SEM structure of the specimen without slag after 1 day of curing. Because of bleeding, a great deal of CH is accumulated. There is also calcium sulfoaluminate resulted from the rapid hydration of C_3A, along with a little C-S-H gel. Fig. 3 demonstrates the microstructure of the specimen with slag added after 1 day of curing. The amount of cement is relatively less because slag has replaced 15% of it. As can be seen, the hydration structure after 1 day is looser and less dense. Weak areas can be easily formed, thus diminishing the strength. Fig. 4 shows the microstructure of cement with ACI mixture proportion after 90 days of curing. Without the addition of pozzolanic materials, a large number of slat-shaped CH crystals with C-S-H gel are formed. Moreover, ettringite (AFt) and a small amount of monosulfoaluminate are also produced. On the other hand, with the addition of slag to the concrete, both the CH solution released from the hydration of concrete and the CH•NH or CS provided by the external environment will cause the slag to release CA^{2+}. This, in turn, will destroy the acidic surface film due to the erosion of alkali. As a result, hydration continues with the slag particles reacting with CH through pozzolanic reaction. The hydration products formed in this process are generally classified as follows: (1) ettringite, (2) needle-shaped C-S-H crystals produced from tobermolite, (3) C-(N/K)-S-H gel, (4) C_4AH or derivatives from monosulfoaluminate hydrates, and (5) CH in greatly reduced quantity. Fig. 5 illustrates the microstructure of the specimen with 15% slag added after 90 days of curing. As can be seen, pozzolanic reaction can transform CH of higher density into C-S-H and the considerably large pores into smaller ones, thus diminishing the problem of interface and enhancing the densification of concrete.

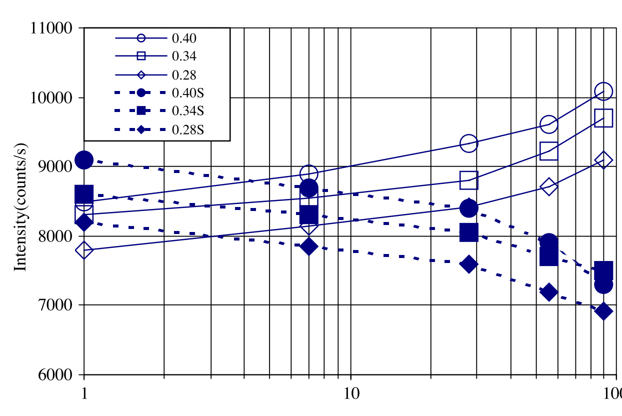

Fig. 1. The relationship between radiation strength and age of cement pastes with different W/B ratios and different slag contents.

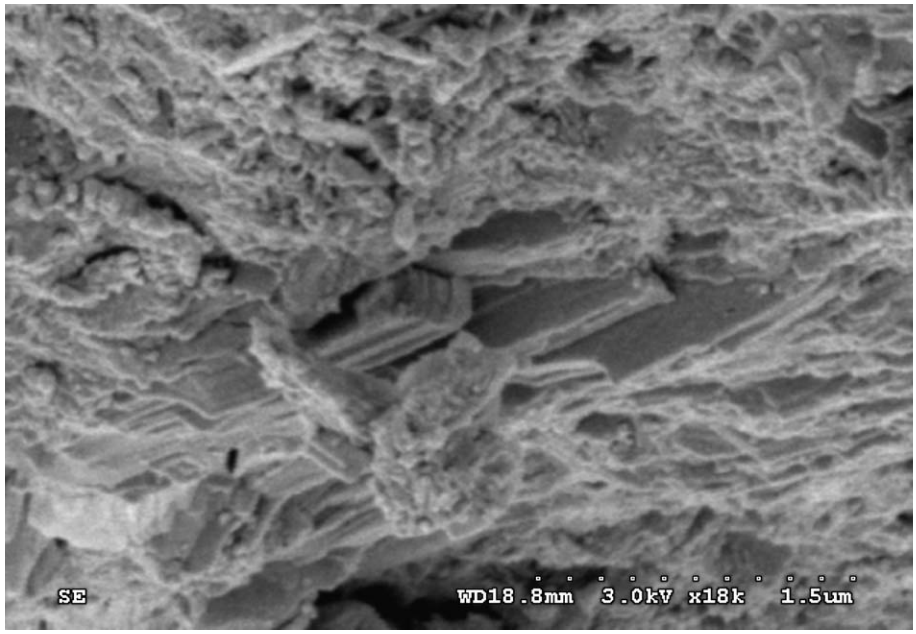

Fig. 2. The early phase microstructure of HPC of ACI mixture proportion.

3.3. MIP tests

As mentioned above, Powers [8] classified pores into Pc and Pg. Pc have a diameter of greater than 100 Å and are mostly filled with hydration water of the cement paste. The volume of Pc is chiefly controlled by the W/B ratios. They take up a volume of about 15% and are closely related to the permeability of concrete. Pg are primitive-generated pores with a diameter smaller than 100 Å. They are filled with the combined water of C-S-H. Unlike that of Pc, the volume of Pg is not influenced by the W/B ratio. The total volume of pores (Pt), shown in Table 3, equals the sum of Pc and Pg. Table 4 displays the volume of Pc. Comparing between the HPC specimens with or without slag, we can see that with the same curing age, the smaller the W/B ratios, the smaller the volume of Pc will be. With increasing age, the degree of hydration will be more complete, thus reducing the volume of Pc present in the HPC. On the contrary, the volume of Pg increases with longer curing age. The pozzolanic reaction due to the addition of slag fills up the pores originally

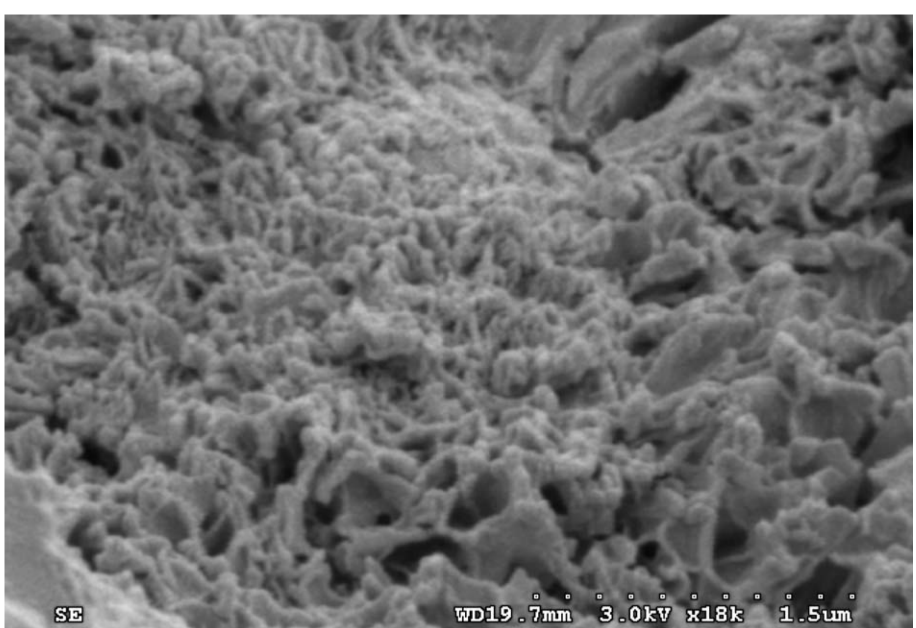

Fig. 3. The early phase microstructure of HPC with 15% of slag added.

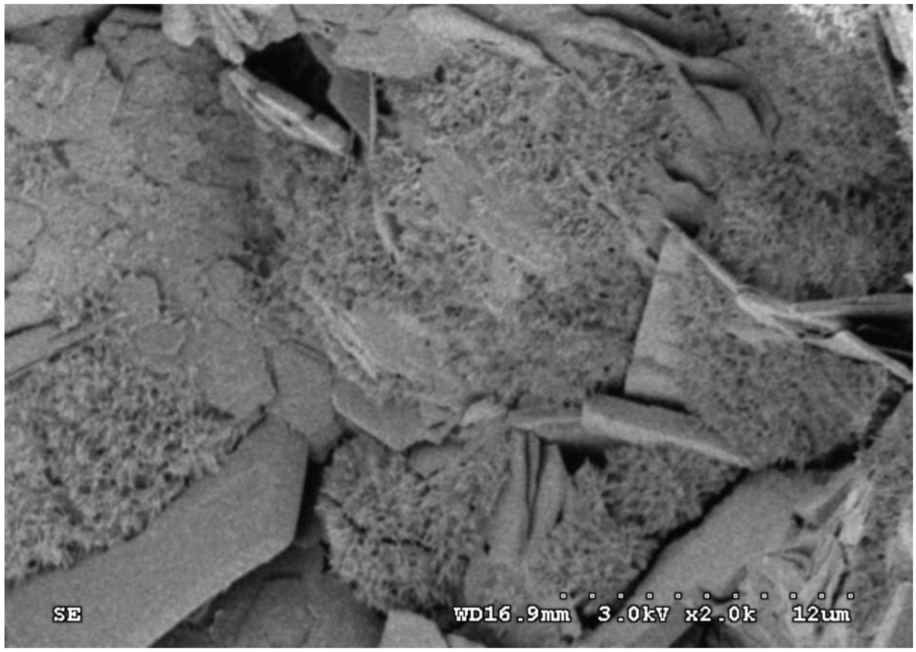

Fig. 4. The 90th-day microstructure of HPC of ACI mixture proportion.

existing in the cement hydrates, making the microstructure denser and reducing the volume of Pc. The more compact concrete has greater compressive strength and can lower the permeability of chloride ions. All these benefit greatly the corrosion resistance of steel in concrete.

3.4. Compressive strength

Compressive strength is usually considered as one of the most important properties of concrete and a major indicator of general quality control. Factors influencing the strength of concrete include the types and quality of materials, the mixture proportion, the construction method, the curing condition, and the test method. From the microscopic point of view, both the degree of hydration and the porosity play important roles. The greater the volume of the pores, the lower the strength of the concrete will be. In addition, with decreasing binder/space ratio (defined as the ratio of the content of C-S-H gel to the original volume of space), the strength will become greater. This is evident in Fig. 6, which

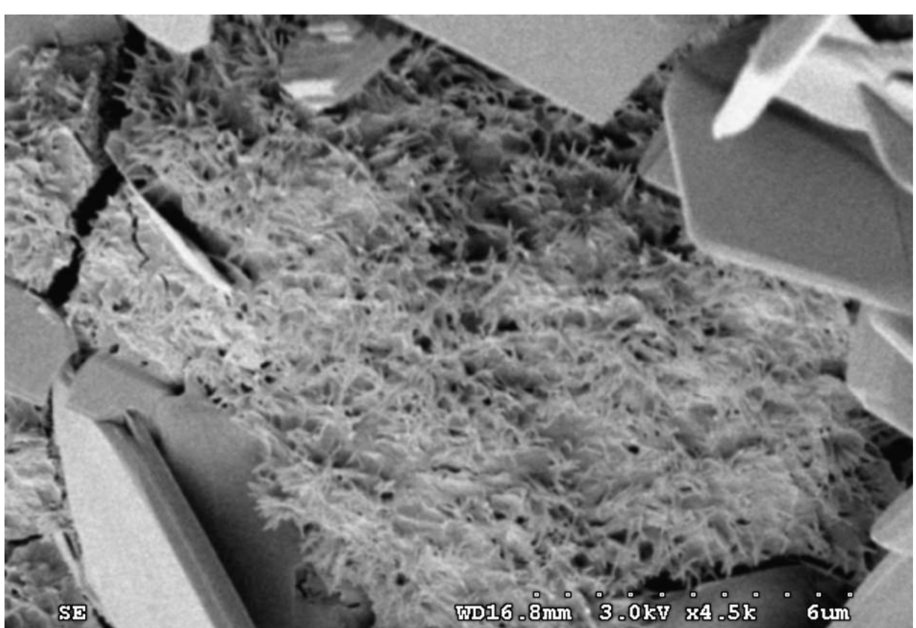

Fig. 5. The 90th-day microstructure of HPC with 15% of slag added.

Table 3
The total volume of pores (cc/g)

Age (days)	W/B ratios					
	0.28	0.34	0.40	0.28	0.34	0.40
	Slag (%)					
		0	0	15	15	15
1	0.163	0.243	0.275	0.165	0.245	0.281
7	0.117	0.210	0.266	0.119	0.212	0.273
28	0.093	0.164	0.220	0.095	0.160	0.221
56	0.083	0.119	0.193	0.082	0.117	0.190
90	0.080	0.110	0.187	0.083	0.112	0.187

shows the relationship between curing age and compressive strength of concrete at various W/B ratios and ages. In the early phase, the addition of slag reduces the amount of cement by 15%, the volume of Pc then increases, accumulating CH on the interface. As a result, the structure is less compact, causing the strength to be lower than that of the specimen without slag added. After 28 days, pozzolanic reaction starts to proceed, decreasing the amount of CH and improving the densification. Consequently, the compressive strength is enhanced in the later phase.

3.5. Permeability tests

The invasion of harmful substances into concrete or the permeating and/or flowing of matters are all related to the flows of water. Such that is governed by Darcy's law. The permeability (Kp) of water is closely related to the size of the pores. The larger the pores, the greater the permeability will be. Upon hydration of cement, the hydration products along with aggregates and the air trapped form the principal part of the concrete. Therefore, concrete is in essence a multipore structure. As reported by Power [8] and Mehta and Monteiro [4], if the water-to-cement (W/C) ratio is under 0.32 and hydration is complete, there will be no Pc produced. As seen in Fig. 7, at a curing age of 90 days, the lower the W/B ratio, the lower the permeability of concrete is. As for the HPC with slag added, the Pc are transformed into the Pg due to the pozzolanic reaction, improving the densification of concrete; thus, the permeability is smaller that that without slag added. This illustrates the important role played by pozzolanic materials. With lower permeability, it is hard for water to permeate into concrete. As a result, corrosion of steel is less likely to occur. In other words, the addition of pozzolanic materials can enhance the corrosion resistance of concrete.

Table 4
The volume of Pc (cc/g)

Age (days)	W/B ratios					
	0.28	0.34	0.40	0.28	0.34	0.40
	Slag (%)					
	0	0	0	15	15	15
1	0.101	0.169	0.216	0.117	0.183	0.219
7	0.054	0.133	0.198	0.105	0.154	0.210
28	0.040	0.089	0.150	0.037	0.085	0.148
56	0.031	0.044	0.120	0.021	0.036	0.090
90	0.026	0.035	0.055	0.010	0.023	0.041

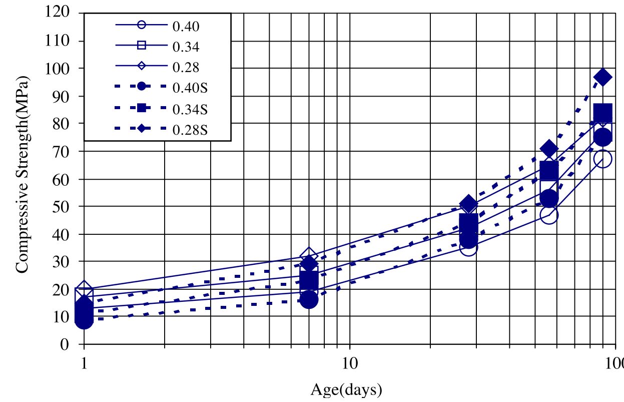

Fig. 6. The relationship between strength and age of HPC.

3.6. Electrical resistance tests

The conduction of ions of the hydration solution in the pores causes corrosion. With denser concrete and lower W/B ratio, the electrical resistance will increase. According to Brian and Alan [16], the minimum value beyond which corrosion cannot occur is 8.5 KΩ/cm, while Vassic's recommended value is 12 KΩ/cm and Woodrow's is 20 KΩ/cm, which corresponds to the special specification of HPC. As seen in Fig. 8, for HPC specimens of denser mixture proportion and lower W/B ratios, the electrical resistivity of concrete measured after 28 days of curing are all higher than the suggested 20 KΩ/cm. In other words, the higher the electrical resistance, the greater the corrosion endurance will be. In this study, the pozzolanic reaction due to the addition of slag reduces the volume of Pc and enhances the impermeability of concrete. As seen in Fig. 8, after 28 days, the electrical resistance of the HPC with slag added rises sharply. Particularly obvious is that of the specimens with

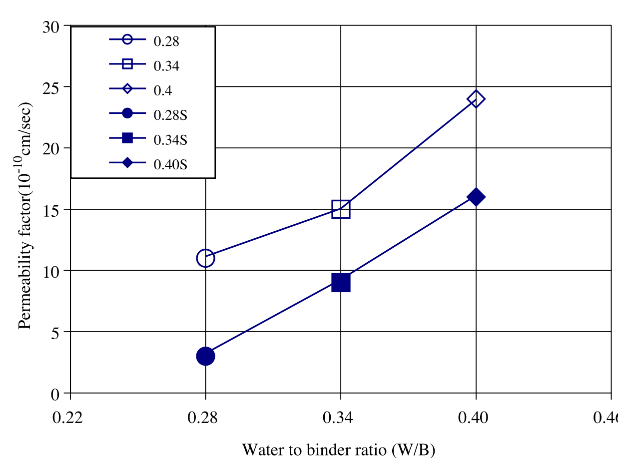

Fig. 7. The permeability of HPC at different W/B ratios.

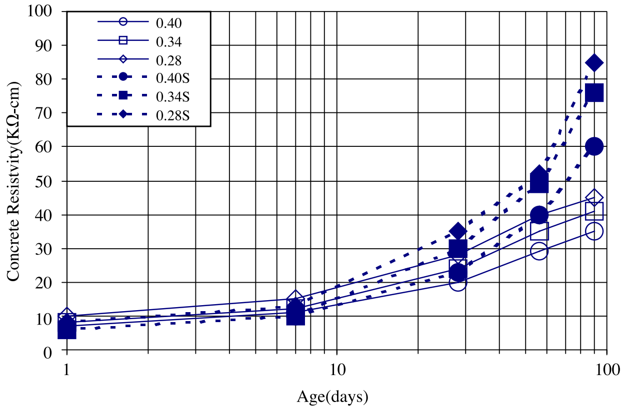

Fig. 8. The development of electrical resistance of HPC with age.

lower W/B ratios. This indicates the effects of solidification brought by pozzolanic reaction can indeed increase the electrical resistance of concrete.

3.7. Electrical permeability tests

The presence of chloride ions is an important factor accounting for the corrosion of steel. To enhance the durability of structure, the content of harmful chloride ions must be limited. According to the specifications of AASHTO, if the current is lower than 100 coulombs, the permeability of Cl^- can be neglected. On the other hand, if the current is higher than 4000 coulombs, Cl^- can easily permeate. Fig. 9 shows that electrical permeability declines with decrease in W/B ratios and increase in curing age. In addition, the more compact the concrete, the lower the electrical permeability will be. As seen in Fig. 9, after curing for 90 days, the electrical permeability of specimens with various mixture proportions all fall under 2000 coulombs. Moreover, the HPC with slag added has an extremely low electrical permeability of Cl^-. It is because pozzolanic reaction due to addition of slag makes the microstructure of concrete more compact.

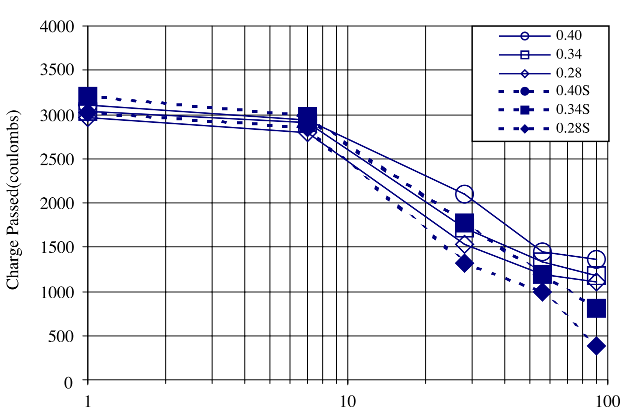

Fig. 9. The relationship between electrical permeability and age of HPC.

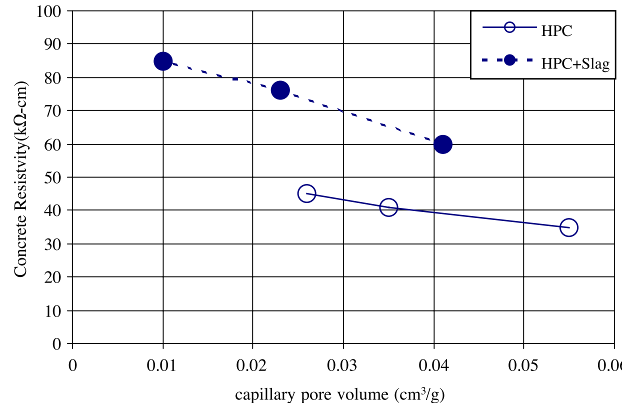

Fig. 10. The relationship between volume of Pc and electrical resistance (age: 90 days).

3.8. Relationship among capillary pore volume, electrical resistance, permeability, and comprehensive strength

Fig. 10 displays the relationship between Pc volume and electrical resistance. A higher W/B ratio implies a greater amount of water present in the cement paste. Under this situation, the volume of Pc will be bigger and the electrical resistance will be reduced. With the addition of pozzolanic materials, the pores will get smaller and fewer, thereby increasing the electrical resistance. Water molecules of fixed size can only pass through pore of larger diameters. As seen in Fig. 11, the greater the volume of Pc, the higher the permeability of concrete will be. Comparatively, the volume of pores in concrete is much larger than that in cement. Therefore, besides the W/B ratio and hydration duration, the volume of pores should not be neglected. The addition of pozzolanic materials can help reduce the formation of weak areas. As seen in Fig. 12, the greater the volume of Pc, the lower the compressive strength will be. If the pores can be eliminated completely, the very natural strength of cement paste can be achieved. In other words, lowering W/B ratio and adding pozzolanic materials will both help decrease

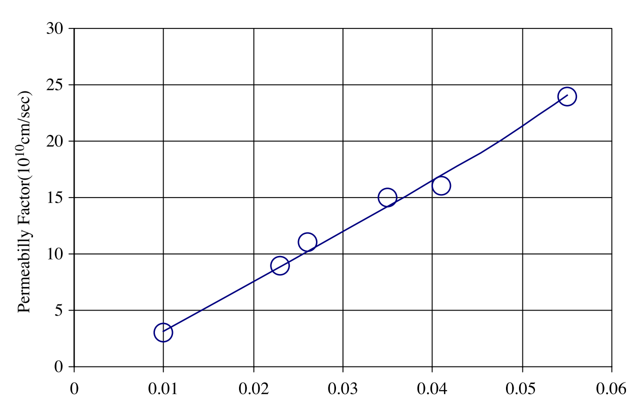

Fig. 11. The relationship between volume of Pc and permeability (age: 90 days).

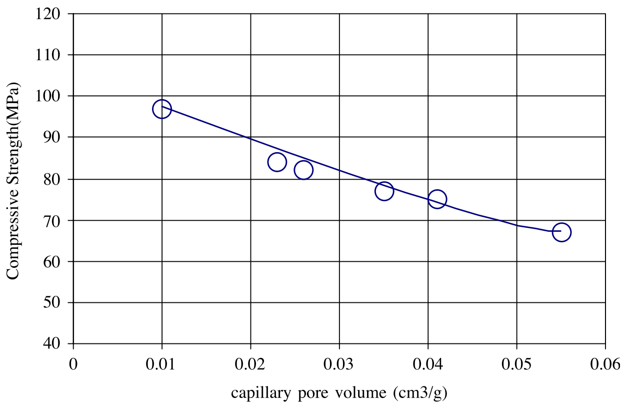

Fig. 12. The relationship between volume of Pc and compressive strength (age: 90 days).

significantly the volume of Pc and enhance electrical resistance several folds.

4. Conclusions

1. SRA analyses show that the content of CH increases with increasing W/B ratio and longer curing age. The addition of slag in the later phase of the reaction will consume CH and the effect of pozzolanic reaction becomes more evident.
2. The SEM microstructure indicates that without slag added, the HPC interface is full of slat-shaped CH crystals. On the other hand, with slag added to the reaction, the pozzolanic reaction in the later phase will produce more pin-shaped crisscrossed C-S-H gel.
3. When the W/B ratio increases, the Pc become bigger and greater in number. With longer curing age, the hydration is more complete, thus reducing the volume of Pc. The pozzolanic reaction due to the addition of slag transforms the Pc into gel ones thereby also decreasing the volume of Pc. The lower the W/B ratio, the smaller the volume of Pc and the lower the permeability of concrete will be. In other words, HPC with slag added has a low permeability.
4. Compressive strength is greatly enhanced with lower W/B ratio and longer curing age. When 15% of cement is replaced by slag, the compressive strength in the early phase is lower than that in the later phase. It is due to the pozzolanic reaction that occurs after 28 days, thus enhancing its strength in the later phase.
5. After 90 days of curing, the electrical resistance of all HPC specimens become higher than 20 KΩ/cm, which is consistent with the value recommended by Woodrow. Similarly, for all HPC specimens, the electrical permeability of Cl^- are all below 2000 coulombs after 90 days of curing, which also corresponds to the specifications of AASHTO. In other words, HPC with slag added has extraordinary resistance and extremely low electrical permeability of Cl^-, showing a great capacity for corrosion resistance. If both the volume of Pc and the amount of pores increase, the electrical resistance will decrease but permeability will increase, thus diminishing the compressive strength.

5. Suggestions

1. It is proved that the addition of slag to HPC can improve the densification of concrete and enhance the corrosion resistance, but the optimum amount to be added that will lead to the best performance merit further exploration.
2. The effects of pozzolanic materials other than slag on improving the corrosion resistance of concrete are worth further study.

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