

## Research Article

# Mechanical Properties and Durability of High-Performance Concretes Blended with Circulating Fluidized Bed Combustion Ash and Slag as Replacement for Ordinary Portland Cement

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This study investigates the mechanical properties and durability of three families of high-performance concrete (HPC), in which the first was blended with fly ash, the second with circulating fluidized bed combustion (CFBC) ash, and the third with CFBC slag. In addition to each of the three mineral additives, silica fume and a superplasticizer were also incorporated into the HPC. Hence, three families of HPC, containing 10%, 20%, and 30% mineral admixtures and 9% silica fume of the binder mass, respectively, were produced. The microstructure and hydration products of the HPC families were examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD) to explore the influence of fly ash, CFBC ash, and CFBC slag on the compressive strength and frost resistance of HPC. The experimental results show that the compressive strength of HPC could reach 60 MPa at 28 d age. When the fly ash content was 30%, the compressive strength of HPC was 70.2 MPa at 28 d age; after the freeze-thaw cycle, the mass loss and strength loss of HPC were 0.63% and 8.9%, respectively. When the CFBC ash content was 20%, the compressive strength of HPC was 75 MPa at 28 d age. After the freeze-thaw cycle, the mass loss and strength loss of HPC were 0.17% and 0.81%, respectively.

## 1. Introduction

Coal-fired power generation in traditional thermal power plants results in the emission of a large amount of sulfur dioxide ( $\text{SO}_2$ ), causing serious environmental pollution [1]. By using the circulating fluidized bed combustion (CFBC) technology, which has a higher combustion and desulfurization efficiency,  $\text{SO}_2$  emission can be greatly reduced. Therefore, this technology has been vigorously promoted in China [2–4]. In this technique, limestone is added as a desulfurizer to the CFBC boiler, so that the boiler discharges a greater amount of ash and slag compared with the pulverized coal boiler [5–7]. Currently, more than 50 million tons of CFBC ash and slag are discharged annually in China [8–10]. As studies on the CFBC ash and CFBC slag are few, CFBC ash and CFBC slag are still not used on a large scale [11–14]. Ash and slag pollute the environment while occupying the land; therefore, governments and power plants

have sought effective methods to dispose them [15–18], especially since the environmental protection tax law was enacted on January 1, 2018.

With the development in the concrete industry, high-performance concrete (HPC), a material with very low porosity, has received great attention due to its excellent mechanical properties and durability [19–21]. To improve the properties of HPC, mineral admixtures with high pozzolanic reactivity, such as silica fume and ground granulated slags, are usually added [22–24]. Mineral admixtures have gradually become a research focus, and fly ash has become one of the main mineral admixtures [25–27].

Fly ash, which is discharged from pulverized coal boilers, has been intensively and widely researched. With the same as fly ash, CFBC ash and CFBC slag also contain some amount of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$ . So, the CFBC ash and CFBC slag have pozzolanic activity too [28]. Abed and Nemes [29] investigated the influence of fly ash on self-compacting HPC and found that the

concrete containing 15% fly ash had better durability performance. Xu et al. [30] researched the effect of fineness and the CFBC ash composition on compressive strength, setting time, and consistency of basic magnesium sulfate cement and observed that with an increase in the fineness of CFBC ash, the consistency of the cement paste increased, the setting time shortened, and the compressive strength slightly improved; this indicates that fine CFBC ash is a good raw material for preparing basic magnesium sulfate cement. Nguyen et al. [31] studied the engineering performance and durability of concrete modified with CFBC ash so that it contained a high volume of low-calcium fly ash. The experiment results showed that the CFBC ash addition did not influence the stability and passing and filling abilities of concrete. However, CFBC ash could significantly improve the compressive strength, bonding property, and durability of concrete.

The CFBC ash and CFBC slag contain some amount of f-CaO and II-CaSO<sub>4</sub>. Excessive f-CaO and II-CaSO<sub>4</sub> will cause concrete damage due to volume expansion in the later stage [32–34]. To eliminate this adverse effect, CFBC ash and CFBC slag should be modified by physical or chemical methods. Studies have shown that physical grinding can decrease the volume expansion of the concrete while increasing the activity of the admixtures [35]. In this study, to prepare HPC, fly ash, CFBC ash, and ground CFBC slag were used as admixtures to replace cement. The influences of different admixtures on the mechanical properties and durability of HPC were also explored. The research results can provide a new basis and reference for the utilization of CFBC ash and slag and the preparation of HPC.

## 2. Materials and Methods

**2.1. Materials.** Grade PO 42.5 Portland cement (PC) from the Zhihai Cement Plant was used in this experiment. Its density was 3.100 g/cm<sup>3</sup>, and its specific surface area was 357 m<sup>2</sup>/kg. Its physical properties are presented in Table 1.

Fly ash (II), which was raw ash from the Taiyuan second thermal power plant, was used in this work. Moreover, CFBC ash and CFBC slag were also used and were obtained from the Pingshuo Coal Gangue Power Plant of Shanxi Province, China. Ground CFBC slag was prepared by grinding the raw CFBC slag for 39 min. The chemical compositions of cement, fly ash, CFBC ash, and CFBC slag are presented in Table 2. Silica fume was also used and was obtained from the Langtian Silica Fume Factory in Sichuan Province, China. The main parameters of the silica fume are listed in Table 3.

Figures 1 and 2 show the scanning electron microscopic (SEM) micrographs and X-ray diffraction (XRD) patterns of fly ash, CFBC ash, and ground CFBC slag, respectively. As can be seen from the SEM micrographs, the CFBC ash particles were irregular, the surface was coarse and porous, and agglomeration was obvious. The ground CFBC slag also featured irregular and coarse and porous lumps, but fly ash particles were regularly spherical, smooth, and dense. The XRD patterns show the presence of quartz, anhydrite, f-CaO, hematite, and calcite in the fly ash, CFBC ash, and CFBC slag. However, fly ash also contained mullite.

The fine aggregate was natural river sand (S) with a fineness modulus of 2.8 and apparent density of 2.65 g/cm<sup>3</sup>. The coarse aggregate was crushed limestone with a particle size of 5–20 mm and an apparent density of 2.79 g/cm<sup>3</sup>.

Polycarboxylate superplasticizer, produced by the Taiyuan concrete superplasticizer factory, was used as the water-reducing admixture. The water reduction rate was 34%.

**2.2. Methods.** In this study, a total of 9 groups of experiments were designed. Three concrete specimens were fabricated to test the compressive strength and frost resistance of each age. The values in Figures 3 and 4 are the average value of three concrete specimens. The mixture proportions are presented in Table 4. The water-to-binder ratio (W/B) was 0.3. Fly ash, CFBC ash, and ground CFBC slag were used to replace cement, at each of the three dosages of 10%, 20%, and 30%. The amount of silica fume was 9% of the total binder materials. A water-reducing admixture was used to adjust the slump flow. The slump flow values of all the HPCs were controlled within 550–655 mm, which belong to grade SF1.

In this study, the density was tested in accordance with GB/7208-2014 Cement Density Method. The chemical composition was referred to the chemical titration method in GB/T 176 Chemical Analysis Methods of Cement. The calculation method of activity index is carried out in accordance with GB/T 18046 Granulated Blast Furnace Slag Powder Used in Cement and Concrete. The specific surface area shall be determined in accordance with the GB/T 8074 Method for determination of the specific surface area of the cement Blaine method. The adsorption property of silica fume was characterized by the BET nitrogen adsorption method, and its specific surface area was obtained.

The working performance is carried out in accordance with JGJ/T283-2012 Technical Specification for Application of Self-compacting Concrete. According to the filling requirements of the self-compacting index performance, high-performance concrete is carried out with the performance level of SF<sub>1</sub>; that is, it meets the requirement of no reinforcement from the top or a concrete structure with less reinforcement. This test strictly controls the slump expansion range from 550 to 655 mm.

In this study, the specimens were placed in a standard curing box with a temperature of 20 ± 2°C and a relative humidity of more than 95% for curing. After 24 hours, the molds were taken out and demolded. After demoulding, the specimens were placed in 20 ± 3°C water for curing and taken out after the specified age for relevant tests.

The compressive strength tests were performed using a 3000 kN universal compression machine in accordance with the GB/T 50081-2002 Standard Test Method for Mechanical Properties of Ordinary Concrete. In this study, 100 × 100 × 100 mm cubes were tested. The compressive strength of concrete was tested at 3 d, 7 d, and 28 d ages, respectively.

The frost resistance property tests were formed using KDR-V9 concrete rapid freeze-thaw testing machine in

TABLE 1: Physical properties of the portland cement.

Specific surface area (m <sup>2</sup> /kg)	Setting time (min)		Flexural strength (MPa)			Compressive strength (MPa)		
	Initial setting time	Final setting time	3 d	7 d	28 d	3 d	7 d	28 d
357	21	241	5.5	7	8.7	26.1	29.6	50.3

TABLE 2: Chemical compositions of cement, fly ash, CFBC ash, and CFBC slag (wt. %).

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	SO <sub>3</sub>	MgO	K <sub>2</sub> O	LOI (%)
Cement	20.84	4.14	3.35	65.88	2.80	1.89	0.60	—
Fly ash	47.50	30.37	3.97	5.83	0.93	0.48	0.69	3.43
CFBC ash	37.78	32.76	5.42	10.19	4.35	1.93	0.98	6.09
CFBC slag	40.29	32.11	3.77	10.27	3.89	1.43	1.05	6.52

TABLE 3: Main parameters of silica fume (wt. %).

SiO <sub>2</sub>	Cl <sup>-</sup>	Water demand ratio	Specific surface (m <sup>2</sup> /kg)	Activity index	Total alkalinity
95.00	0.012	113	23700	122	0.23

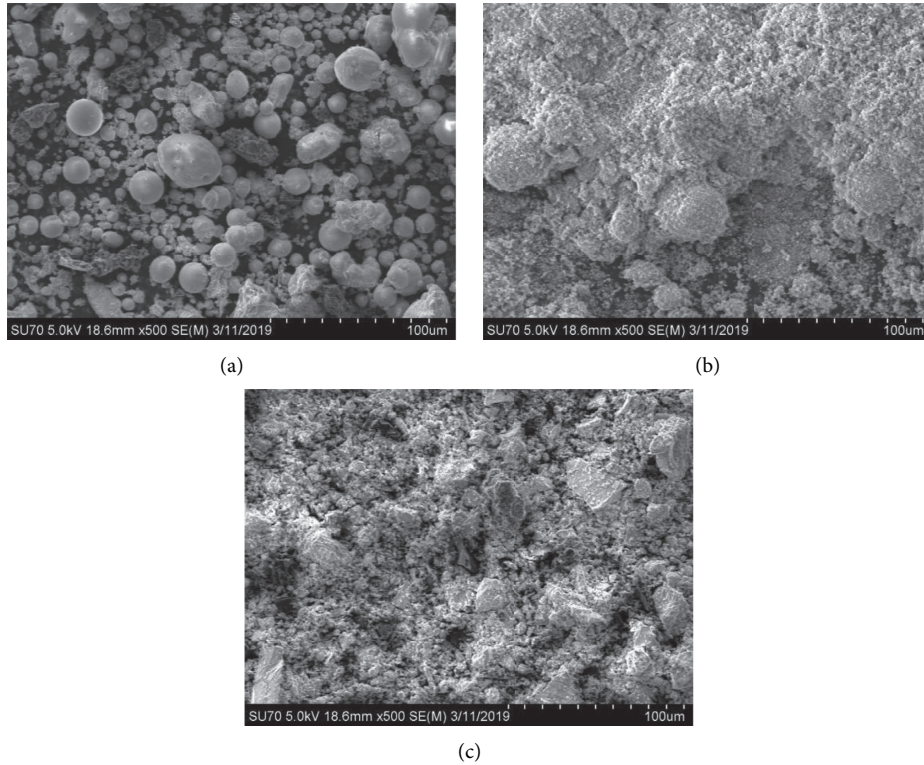


FIGURE 1: SEM micrographs of (a) fly ash, (b) CFBC ash, and (c) CFBC slag.

accordance with GB/T 50082-2009 Standard Test Methods for Long-Term Performance and Durability of Ordinary Concrete. In this study, 100×100×100 mm cubes were tested. In this test, 25 freeze-thaw cycles are used as a group. After each cycle is taken out of the instrument, its mass is weighed. Stop the test when the mass loss rate exceeds 5%, the compressive strength loss rate exceeds 25%, or 50 freeze-thaw cycles are reached.

The XRD patterns were detected using the D/max-RB XRD system (Japan Rigaku Corporation, Tokyo, Japan). The

microstructures were detected using SEM (Hitachi S 4800 and SU-70; Hitachi, Ltd., Tokyo, Japan).

### 3. Results and Discussion

**3.1. Mechanical Properties of HPC.** The compressive strength of HPC specimens is illustrated in Figure 3. For all of the specimens, the compressive strength at 3 d ages reached 40 MPa, indicating early strength characteristics. The compressive strength of S4–S8 reached 80 MPa at 90 d ages.

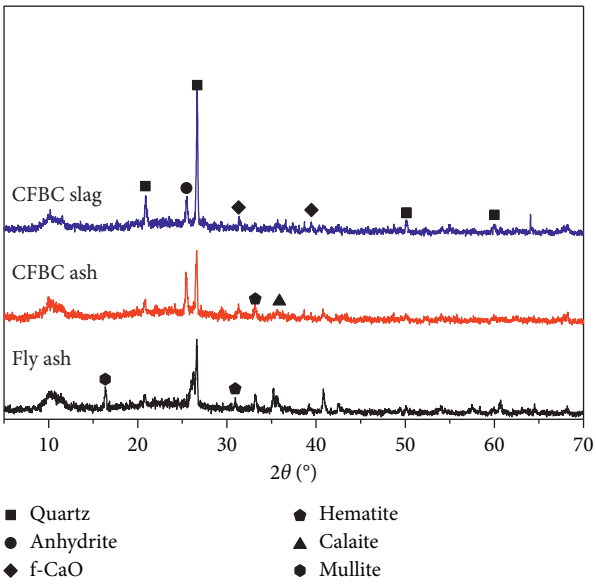


FIGURE 2: XRD patterns of fly ash, CFBC ash, and CFBC slag.

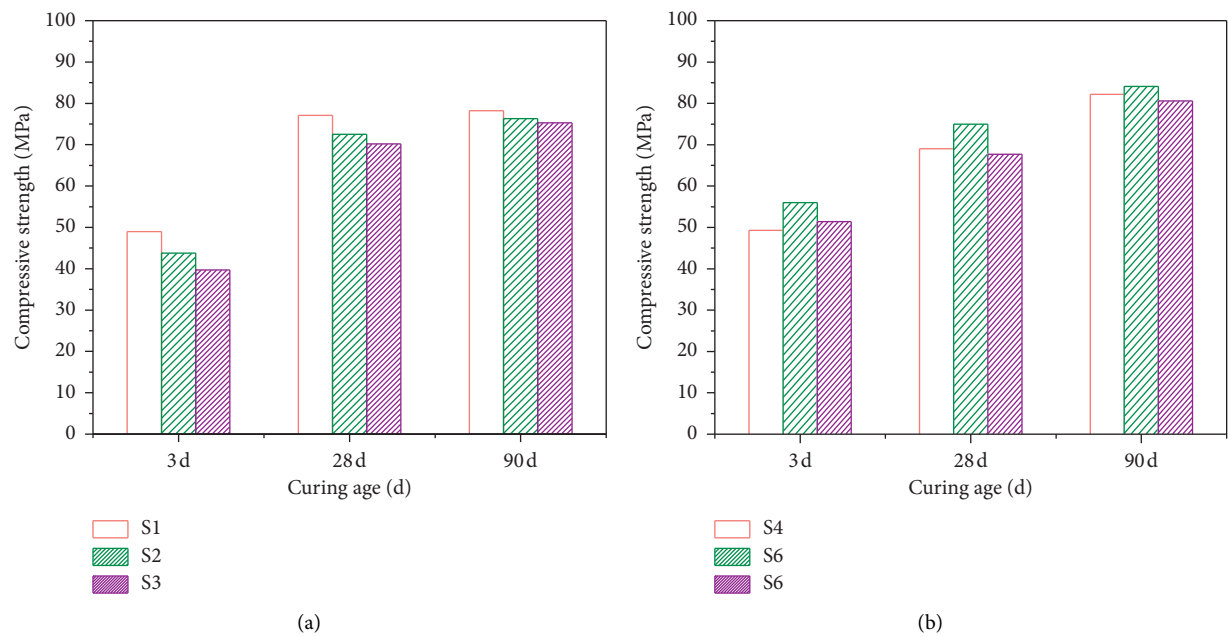


FIGURE 3: Continued.

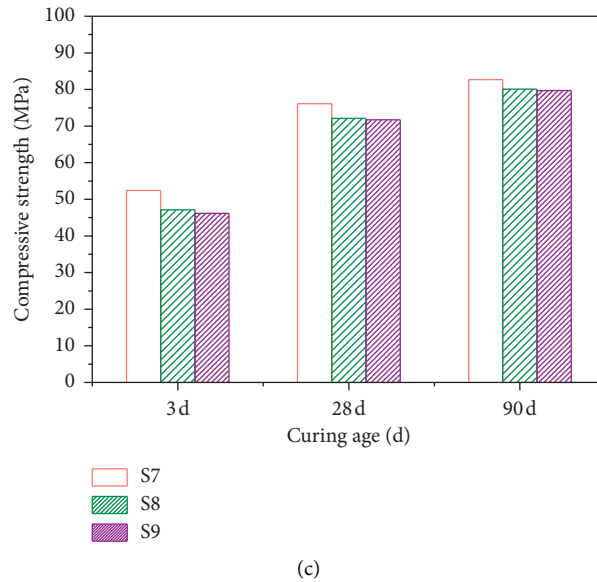


FIGURE 3: Compressive strength of HPC with different mineral admixtures. (a) Fly ash; (b) CFBC ash; (c) CFBC slag.

For ordinary concrete (without adding fly ash, CFBC ash, and CFBC slag), W/B is 0.3, silica fume content is 9%, and its 28 d ages compressive strength exceeds 70 MPa [36]. When the W/B is 0.3 and the silica fume content is 10%, the compressive strength at 28 d ages exceeds 80 MPa [37, 38]. Compared with ordinary concrete, the 28 d ages compressive strength of concrete mixed with fly ash, CFBC ash and CFBC slag is slightly lower. But the compressive strength of S1–S9 specimens at 28 d ages could reach 60 MPa, which belongs to high-strength concrete. As shown in Figure 3(a), with the increase in the amount of fly ash, the compressive strength of HPC decreased continuously. It can be seen from Figure 3(b) that with the increase of the CFBC ash amount, the compressive strength of HPC first increased and then decreased. According to Figure 3(c), with the increase of the amount of CFBC slag, the compressive strength of HPC decreased continuously. From Figure 3, the effect of mineral admixtures on the compressive strength of concrete is more obvious. The  $D$ -value between the maximum and minimum of the 3 d ages compressive strength of fly ash, CFBC ash, and CFBC slag is greater than 10%. But in the later curing age, the effect on strength is not obvious.

It can be seen from Figure 4(a) that when the admixture amount was 10%, the compressive strength of HPC with CFBC slag was higher than that of the other HPCs at 3 d and 90 d ages. Figure 4(b) shows that when the admixture amount was 20%, the compressive strength of the HPC with CFBC ash was higher than that of the other HPC at all ages. According to Figure 4(c), when the amount was 30%, the compressive strength of the HPC with CFBC ash was the highest at the 3 d and 90 d ages. And when the amount was 30%, the compressive strength of the HPC with CFBC slag was the highest at the 28 d ages. These indicate that the medium-term strength developed slowly when the amount of CFBC ash was 30%.

The XRD patterns of HPCs with different mineral admixtures are shown in Figure 5. As can be seen from the figure, the hydration products of HPC mainly included hydrated calcium silicate gel, gypsum, calcium hydroxide, and ettringite. Calcite appears in Figure 5 for two reasons: on the one hand, it comes from the coarse aggregate. On the other hand, it comes from the unreacted limestone residue in the CFBC ash and CFBC slag; that is, the limestone that is not completely thermally decomposed during the CFBC. It can be seen that as the age increases, the XRD peak intensity of  $\text{Ca}(\text{OH})_2$  decreases, whereas the XRD peak intensity of gypsum increases. The main reaction of calcium hydroxide was to produce a C-S-H gel and react with gypsum to form ettringite, whereby C-S-H gel and ettringite are the main materials to form the strength of the cementitious system [39, 40]. In addition, the ground CFBC slag is conducive to maximize the activities of various substances [41, 42]. As shown in Figure 6, large amounts of gypsum and C-S-H gel were found.

**3.2. Frost Resistance of HPC.** Figure 7 illustrates that as the amount of admixture increases, the compressive strength and mass loss rate of HPC first decreased and then increased. When the amount was 20%, the strength and mass loss rate of HPC were the minimum, and the frost resistance was the highest. For the HPC with fly ash, fly ash particles can evenly fill internal pores at the early age to block water channels, and hydration products generated by the secondary hydration reaction in the later age can improve the pore structure while filling pores, thereby improving the frost resistance of HPC. However, when the fly ash amount is too high, the proportion of cement decreases, resulting in a large reduction in gel, ettringite, and so on, and therefore, the internal pores

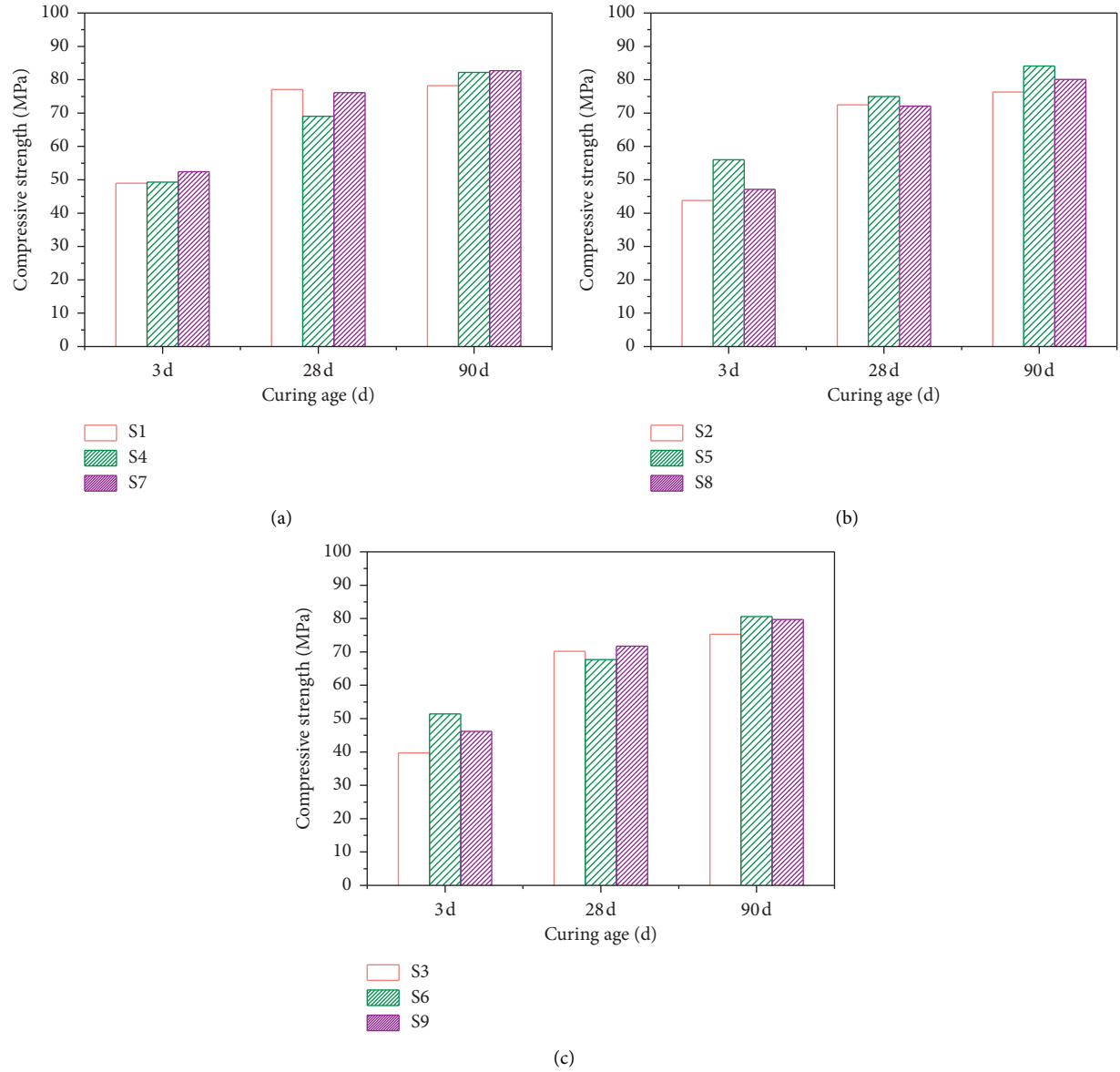


FIGURE 4: Compressive strength of HPC with different amounts of mineral admixtures. (a) 10%; (b) 20%; (c) 30%.

TABLE 4: Mixture proportions of HPC ( $\text{kg/m}^3$ ).

Mixture	W/B	Fine aggregate	Coarse aggregate	Fly ash	CFBC ash	CFBC slag	Silica fume	Cement	Water-reducing admixture
S1	0.3	790	890	56	—	—	50.4	453.6	6.16
S2	0.3	790	890	112	—	—	50.4	397.6	6.72
S3	0.3	790	890	168	—	—	50.4	341.6	7.84
S4	0.3	790	890	—	56	—	50.4	453.6	5.6
S5	0.3	790	890	—	112	—	50.4	397.6	7.28
S6	0.3	790	890	—	168	—	50.4	341.6	8.4
S7	0.3	790	890	—	—	56	50.4	453.6	5.6
S8	0.3	790	890	—	—	112	50.4	397.6	6.72
S9	0.3	790	890	—	—	168	50.4	341.6	10.08



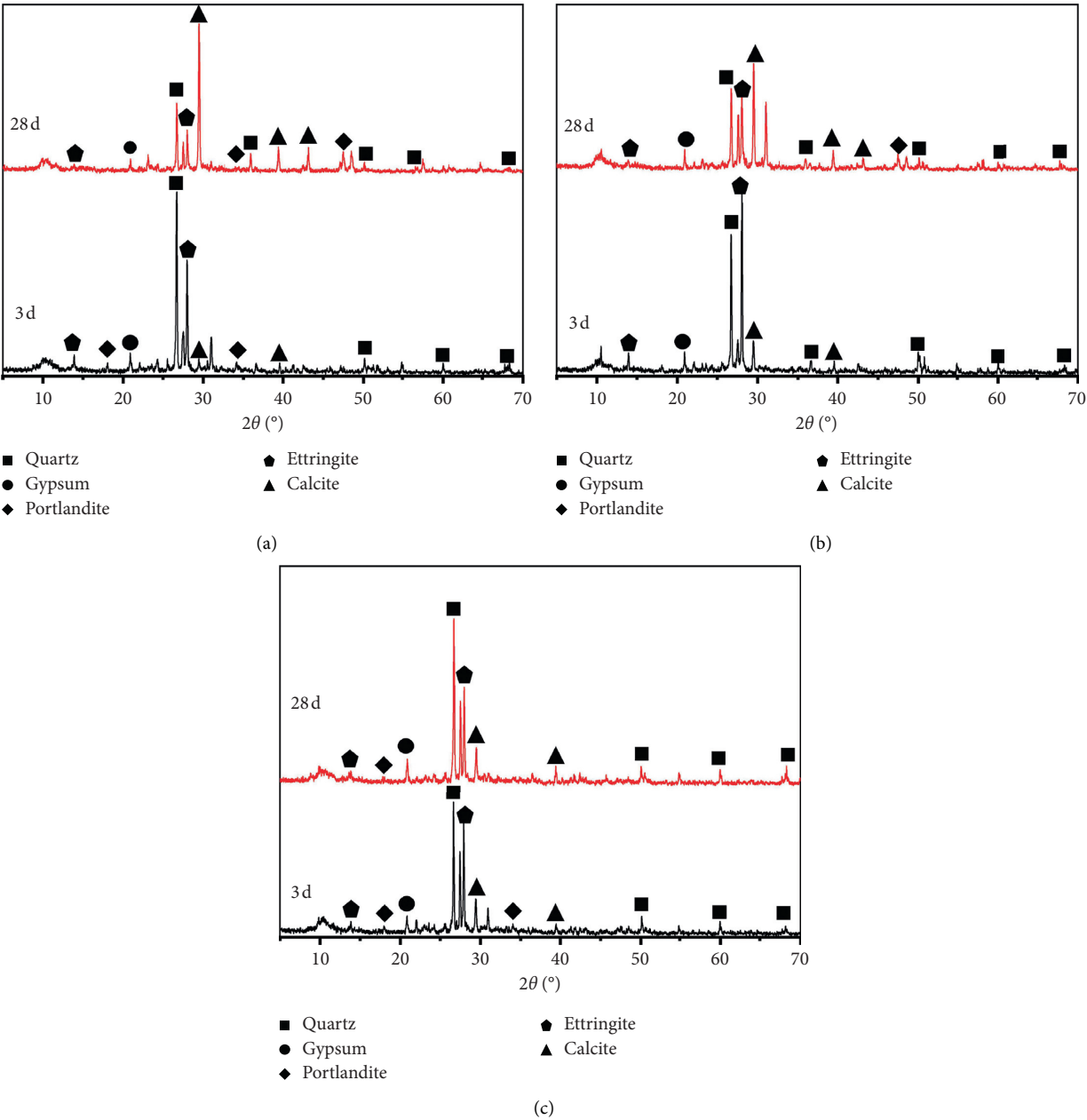


FIGURE 5: XRD pattern of HPC with different mineral admixtures. (a) Fly ash; (b) CFBC ash; (c) CFBC slag.

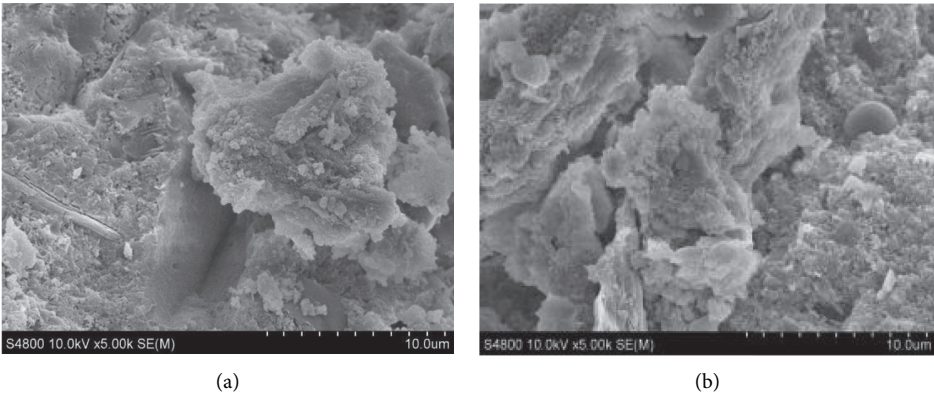
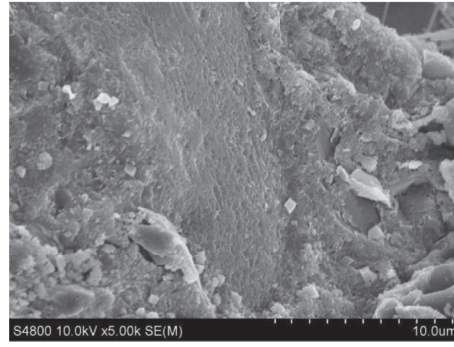


FIGURE 6: Continued.



(c)

FIGURE 6: SEM of HPC with different mineral admixtures. (a) Fly ash; (b) CFBC ash; (c) CFBC slag.

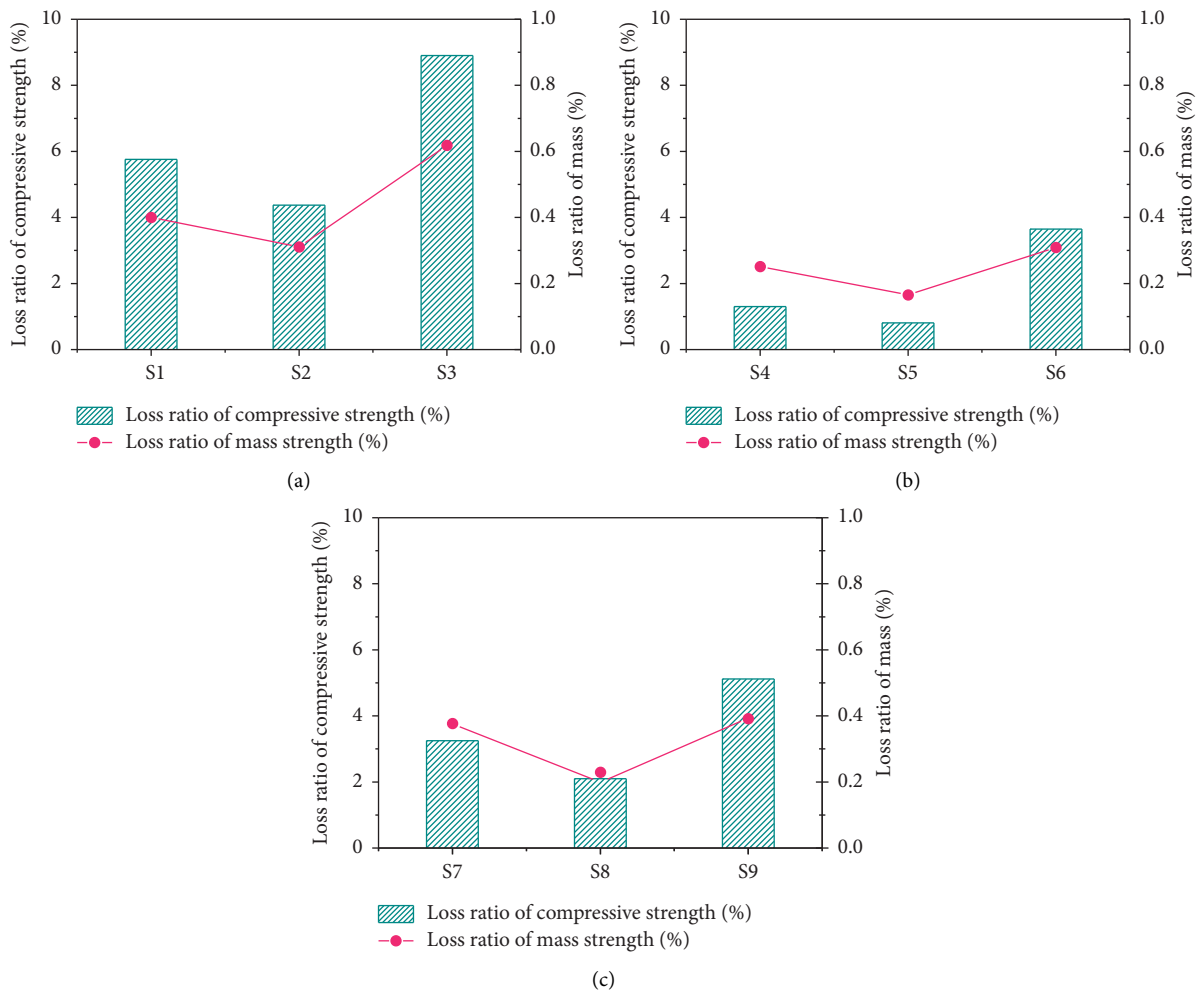


FIGURE 7: Compressive strength and mass loss rate of HPC with different mineral admixtures. (a) Fly ash; (b) CFBC ash; (c) CFBC slag.

cannot be filled. The amount of  $\text{Ca}(\text{OH})_2$  produced is not enough to support the secondary hydration reaction of fly ash, resulting in a reduction in the strength and frost resistance of HPC [43].

The CFBC ash and CFBC slag all contain f-CaO and II- $\text{CaSO}_4$ , which can react to form hydration products and

chemically react with other mineral components to form C-S-H gel and ettringite. And this will cause the strength of the concrete to increase rapidly and the expansion will develop inward [35], thus greatly improving the compactness of the HPC by blocking the interior water passages. Therefore, the frost resistance of the HPC improved.



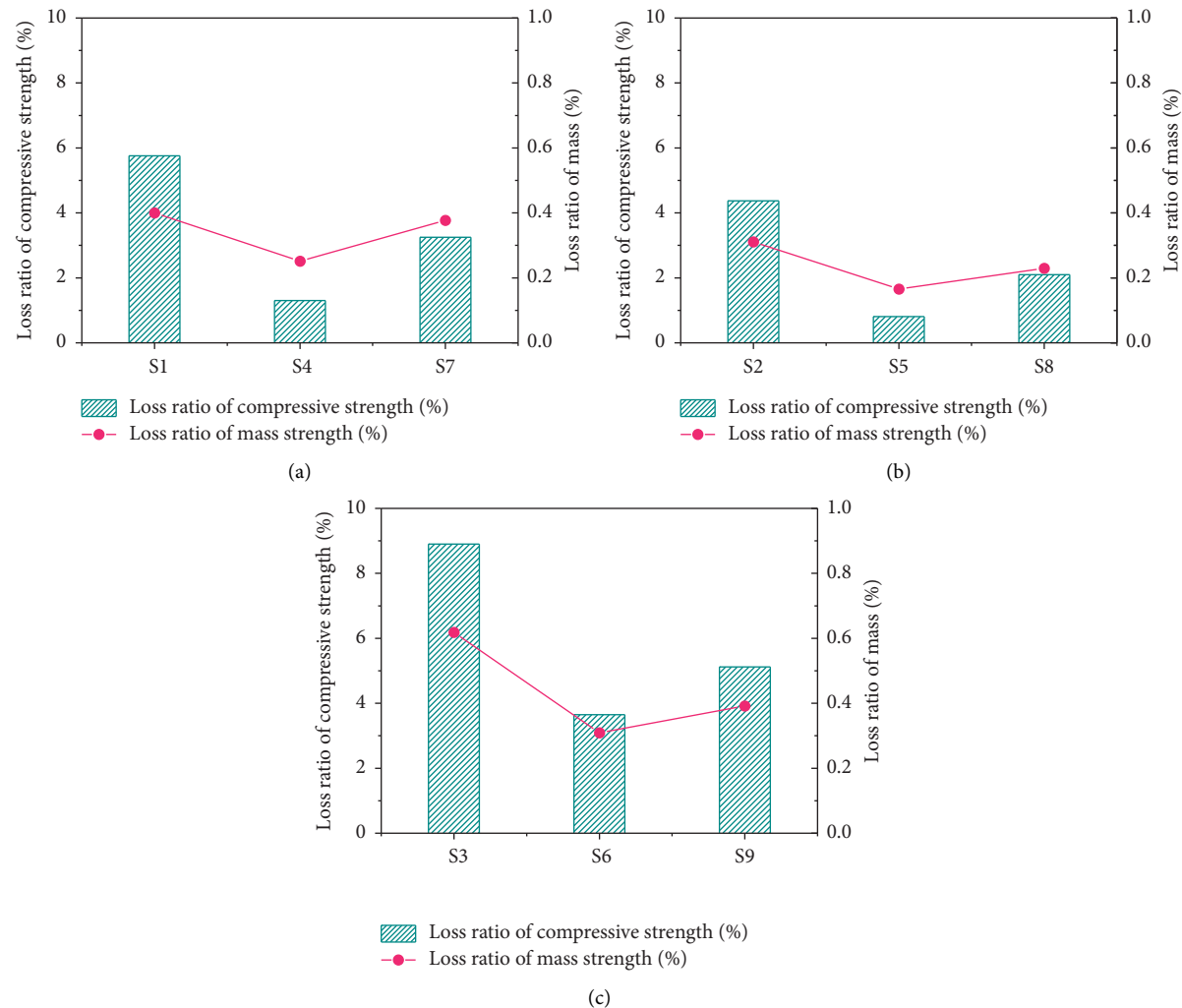


FIGURE 8: Compressive strength and mass loss rate of HPC different amounts of mineral admixtures. (a) 10%, (b) 20%, (c) 30%.

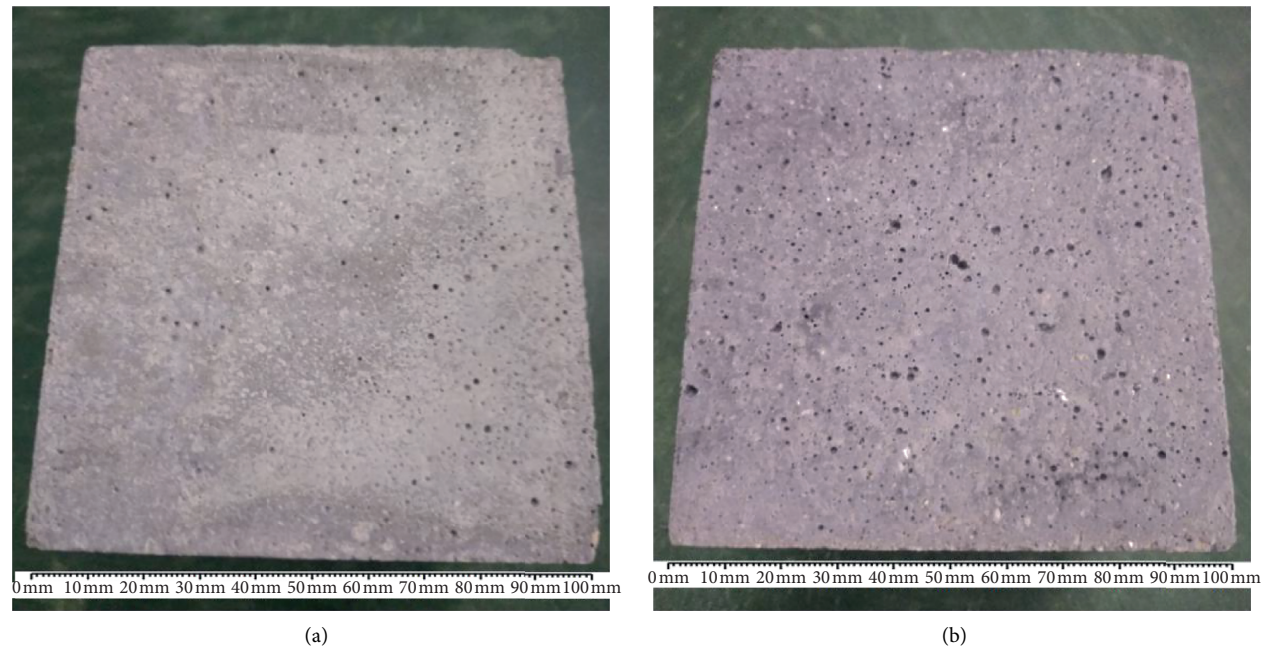


FIGURE 9: HPC surface after 50 times freeze-thaw cycles. (a) Before; (b) after.

Further, due to the relatively coarse and porous structure of CFBC ash and CFBC slag and the large number of internal pores, both played the role of air-entraining agents; thus, the frost resistance of the HPC was improved. However, when the CFBC ash and CFBC slag amount are too high, the proportion of cement decreases. Moreover, the amount of gel produced is reduced, the working performance of the HPC declines, and the internal compactness is insufficient. In the case of insufficient alkalinity in the later age, the internal components are easy to decompose; as a result, the pore structure changes and the frost resistance decreases.

Uysal et al. research shows that concrete mixed with fly ash can effectively improve the frost resistance of concrete [44, 45]. As shown in Figure 8, the strength and mass loss rate of the HPC with fly ash were much higher than those of the other HPCs. It can be seen that, for all additive amounts, the HPC with CFBC ash had the best frost resistance compared with the other HPCs. Compared with the CFBC ash and CFBC slag, the early activity of fly ash was inadequate, and the expansion performances of CFBC ash and CFBC slag were mainly concentrated at the early age. A large number of expansion materials are formed, and they fill the internal pores of HPC, improving the pore structure and making the interior of HPC more compact and frost resistant. The physical appearances of HPC after 50 times freeze-thaw cycles are shown in Figure 9. After 50 times the freeze-thaw cycle, many pores appeared on the HPC surface, and the previously existing pores became larger, which was the main reason for the decrease in mass and strength.

#### 4. Conclusions

- (1) It is feasible to prepare high-performance concrete using fly ash, CFBC ash, and CFBC slag as mineral admixtures. The high-performance concretes can be prepared by mixing fly ash, CFBC ash, CFBC slag, and 9% silica fume with the amount of 10%, 20%, and 30%. The compressive strength can reach more than 60 MPa at 28 d ages. After 50 times freeze-thaw cycles, the mass loss and strength loss are low, no more than 0.7% and 0.9%.
- (2) The varieties and amounts of mineral admixtures have obvious effects on the early compressive strength of high-performance concrete but have little effect in the later period of curing. The law of the fly ash and CFBC slag's amount on the HPCs' compressive strength is the same. While the amounts of the fly ash and CFBC slag increase, the HPCs' compressive strength decreases at each age. When the content of fly ash and CFBC slag is 10%, the compressive strength reaches the maximum at each age. While the amount of CFBC ash increases, the compressive strength of the HPC first increases and then decreases at each age. When the amount is 20% of CFBC ash, the compressive strength reaches the maximum at each age.
- (3) There are same laws for the frost resistance of HPCs with fly ash, CFBC ash, and CFBC slag. When the

amount is 20%, the frost resistance is the best. Among all three admixtures, HPC with CFBC ash has the best frost resistance.

#### Data Availability

The data used to support the findings of this study are included within the article and the supplementary information file.

#### Conflicts of Interest

The authors declare that they have no conflicts of interest.

#### Acknowledgments

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#### Supplementary Materials

Figure S1: the images of CFBC ash, CFBC slag, and fly ash. Figure S2: the photos of freeze-thaw cycle test. Tables S1–S4: the data of the compressive strength of HPC. Tables S5–S7: the data of the compressive strength and mass loss of HPC after the freezing-thawing cycle in 28 d ages. (*Supplementary Materials*)

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