Abstract: The current work investigates the fluidity and the loss of the flow rate of cement paste and mortar over time, as well as the pore structure and compressive strength of concrete and mortar in the presence of functional polycarboxylic acid high-performance water-reducing agents. The hydration rate, hydration products, and pore structure of the concrete containing different functional polycarboxylic acid superplasticizers were analyzed by means of mercury intrusion test, scanning electron microscopy (SEM), and X-ray diffraction (XRD). The results show that water-reducing agent Z significantly improves the pore structure of concrete and further compacts the structure of concrete and mortar, thereby improving the compressive strength of concrete. Moreover, the shorter side chains and ester functional groups in the structure of water-reducing agent H can slow down cement hydration rate, which lowers the early strength of mortar; nevertheless, at later stages, the pore structure of the concrete and mortar including superplasticizer H is less different from that of the concrete and mortar containing polycarboxylic acid water-reducing agents. Water-reducing agent J performs best but has a weaker effect on the pore structure of concrete and mortar compared to superplasticizer Z; it is also better than naphthalene-based water-reducing agents.

Keywords: functional polycarboxylic acid superplasticizer; high-performance water-reducing agent; cement strength and pore structure; XRD

Highlights

- Functional polycarboxylic acid superplasticizers such as water-reducing superplasticizer, sustained-release superplasticizer, and early-strength superplasticizer delay the initial reaction rate of cement and improve the pore structure of mortar and concrete.
- Superplasticizer Z can promote the hydration reaction of cement and exhibit the characteristics of high early strength.
- Short side chains in the structure of water-reducing agent H and its ester functional groups can slow down the hydration rate of cement and help achieve long-term slump retention.
- Compared with naphthalene water reducer, water-reducing superplasticizer, sustained-release superplasticizer, and early-strength superplasticizer rely on the functional groups in their molecular structure to more easily inhibit mineral phase precipitation.
1. Introduction

Chemical admixtures are the essential materials and core technology for manufacturing modern concrete and key elements in the development of concrete in high-tech fields. Due to their characteristics of low dosage, high water reduction, and lowering slump loss (or improving slump retention), admixture products are a hot topic of research. Water-reducing agents are being developed to offer enhanced performance in terms of a high rate of water reduction, high slump retention ability, high early strength ability, and high durability of concrete. In engineering practices, if the function of the polycarboxylic acid water-reducing agent is only limited to the rate of water reduction and the strength of the concrete, the adaptability and rheological properties of the polycarboxylic acid water-reducing agent and the material in concrete cannot be adjusted, which likely leads to the poor physical workability of the concrete mix and eventually to problems in the stability and durability of the concrete structure, thereby not meeting the service life of the project. Therefore, it is of great significance to study functional superplasticizers based on polycarboxylic acid.

Superplasticizers are widely used to produce flowable, strong, and durable Portland cement concretes and mortars. The hydration behaviors of Portland cement in the presence of superplasticizers have been investigated by a number of researchers [1–3]. Kreppelt et al. [2] studied the effects of different types of polycarboxylic acid superplasticizer on the early hydration of cement using scanning electron microscopy (SEM) analysis and found that the incorporation of polycarboxylic acid superplasticizers inhibited the formation of alumina, ferric oxide, tri-sulfate (AFT), as a hydration product. Roncero et al. [4] employed 29Si MAS NMR and X-ray diffraction (XRD) techniques and discovered that when the cement and water were mixed for 15 min, there was no characteristic peak of AFT in the XRD spectrum of the blank control slurry, but it obviously appeared when polycarboxylic acid water-reducing agent was added to the mixture. The characteristic peak of AFT indicates that the incorporation of polycarboxylic acid water-reducing agent changes the growth rate of AFT. Through differential thermal research, Puertas et al. [5] realized that polycarboxylic acid water reducer decreased the amount of Ca(OH)2 produced in the early hydration products. It was thought that the water-reducing agent suppressed the hydration of the silicate mineral phase and therefore delayed the formation of Ca(OH)2; thus, calcium silicate hydrate (CSH) had no significant effect on the formation of AFT. Ferrari et al. [6] used atomic force microscopy (AFM) to observe the morphology of cement hydration products and obtained the same results as those of Puertas; they believed that the degree of influence depends on the amount of water-reducing agent and the chemical composition of the solution. Water-reducing agents have obvious effects on micro-morphology in cement pastes [7,8] as confirmed by the XRD peaks at different ages [9] and SEM analysis used to study the pore structure of cement pastes [10–15].

Materials based on hardened cement are generally composed of complex structural systems of hydration products, unhydrated cement mineral phases, and multiscale pores and pore solutions. Multiscale pores affect the mechanical properties of cement-based materials and are of considerable importance for the characterization of the multiscale and complex pore structures of hardened cement pastes [16]. The pore structure reflects the microstructure of the material, and the microstructure-performance relationship is the core of modern material science [17]. Concrete has a heterogeneous and rather complex structure; therefore, its macroscopic performance is also extremely complicated. Thus, studying and mastering the relationship between concrete pore distribution and its macroscopic performance can reflect the effect of water-reducing agents on the structure and performance of concrete. Moreover, it is known that the destruction of the pore structure is the main reason for the failure of concrete.

Therefore, this work focuses on analyzing the influence of different types of polycarboxylic acid superplasticizer on concrete at certain water/cement ratios while using the same admixture and curing conditions. The impact of water-reducing agents on compressive strength, pore structure, and cement hydration process is studied by comparing the differences in pore structure parameters and the changes in XRD peaks at different ages. SEM analysis is also employed to study the pore structure,
which contributes to the macroscopic mechanical properties and illustrates the effect of different functional polycarboxylic acid superplasticizers. The effect of high-performance water-reducing agents based on polycarboxylic acid on hydration process and hardening performance of concrete is also investigated.

2. Experimental

2.1. Materials

Various grades of alkylene alkenyl polyoxyethylene ether (OXAB-702, $M_W = 3000$; OXAB-608, $M_W = 2400$; OXAB-801, $M_W = 4000$) were kindly supplied by Liaoning Oxiranchem, Inc. (Liaoning, China). Sodium methacrylate was purchased from Taicang Xinmao Polyester Chemical Co., Ltd. (Taicang, China), and hydrogen peroxide (analytical pure, 30%) and sodium hydroxide were provided by Tianjin Bodi Chemistry (Tianjin, China). Acrylic acid (AA) was purchased from Wanhua Chemical (Yantai) Petrochemical Co., Ltd. (Yantai, China) and reducing agents (ascorbic acid) were provided by CSPC Holding Group Co., Ltd. (Shijiazhuang, China). Hydroxyethyl acrylate (HEA) was supplied by Beijing Oriental Petrochemical Co., Ltd. (Beijing, China) and mercaptopropionic acid (S) was purchased from Hebei Tongli Chemical Co., Ltd. (Hebei, China). Early-strength polycarboxylic acid superplasticizer (F, 20%) was purchased from Sika (Zurich, Switzerland), and naphthalene-based water-reducing agent (NF) was purchased from Shandong Wanshan Chemical Co., Ltd. (Shandong, China). Ordinary Portland cement PO 42.5 R was purchased from Dalian Onoda Cement Co., Ltd. (Dalian, China) and standard sand was supplied by Xiamen Esi Standard Sand Co., Ltd. (Xiamen, China). River sand with a fineness modulus of 2.7, a mud content of 1.5%, firmness of 2%, and water absorption of 0.5% was provided by Dalian Shiyutong Concrete Co., Ltd. (Dalian, China). Stone with an apparent density of 2680 kg/m$^3$, 5–25 mm continuous grading, a mud content of 0.3%, and a water content of 0.1% was supplied by Dalian Limestone Mine (Dalian, China) and fly ash (FA, second level) was purchased from Dalian Huaneng Power Plant (Dalian, China).

2.2. Preparation of Samples

2.2.1. Synthesis of Water-Reducing Polycarboxylic Acid Superplasticizer J

To a 1 L four-neck flask, 435.6 g of deionized water, 360 g of monomer (OXAB-702), and 5.69 g of sodium methacrylic acid were added, and the flask was heated to 60 °C. Then, a mixture of 3.17 g of hydrogen peroxide and 50 g of deionized water was added to the above four-neck flask, and material A (a mix of 30.24 g of acrylic acid and 80 g of deionized water) and material B (a mix of 1.08 g of ascorbic acid and 11 g of deionized water) were reacted simultaneously. The reaction of materials A and B was completed in 3 and 3.5 h respectively while continuously stirring for 1 h. At the end of the reaction, the reaction polymer was cooled down to below 30 °C, and a mixture of 16.8 g of sodium hydroxide and 39.2 g of deionized water was added to the reaction while stirring. The pH of the reaction was adjusted at 7 to obtain superplasticizer J as a polycarboxylic acid high-performance water-reducing agent.

2.2.2. Synthesis of Sustained-Release Polycarboxylic Acid Superplasticizer H

We added 461.4 g of deionized water and 360 g of monomer (OXAB-608) to a 1 L four-neck flask and raised the temperature to 40 °C. Then, a mixture of 3.31 g of hydrogen peroxide and 50 g of deionized water was then added to the above four-neck flask, and material A (a mix of 25.92 g of acrylic acid, 27.87 g of hydroxyethyl acrylate, and 84 g of deionized water) and material B (a mix of 1.66 g of ascorbic acid, 0.80 g of mercaptopropionic acid, and 10 g of deionized water) were reacted simultaneously. The reaction of materials A and B was completed in 3 and 3.5 h respectively while continuously stirring for 1 h. At the end of the reaction, the obtained polymer was cooled down to below 30 °C, and a mixture of 14.4 g of sodium hydroxide and 33.6 g of deionized water was
added while stirring. The pH of the reaction was adjusted at 7 to obtain superplasticizer H as a sustained-release polycarboxylic acid water-reducing agent.

2.2.3. Synthesis of Early-Strength Polycarboxylic Acid Superplasticizer Z

To a 1 L four-neck flask, 457.46 g of deionized water and 360 g of monomer (OXAB-801) were added and heated to 40 °C. Then, a mixture of 3.22 g of hydrogen peroxide and 50 g of deionized water was added to the above four-neck flask, and material A (a mix of 25.92 g of acrylic acid, 12.79 g of acrylamide, and 71.29 g of deionized water) and material B (a mix of 1.61 g of ascorbic acid, 0.48 g of mercaptopropionic acid, and 10.5 g of deionized water) were titrated simultaneously. The titration of materials A and B was completed in 3 and 3.5 h respectively while continuously stirring for 1 h. At the end of the reaction, the reaction polymer was cooled down to below 30 °C, and a mixture of 14.4 g of sodium hydroxide and 33.6 g of deionized water was added to the action while stirring. The pH of the reaction was adjusted at 7 to obtain superplasticizer Z as an early-strength polycarboxylic acid water-reducing agent.

2.2.4. Properties of Functional Polycarboxylic Acid Superplasticizers

Table 1 tabulates the physical properties of the synthesized functional polycarboxylic acid high-performance water-reducing agents.

| Sample ID | Solid Content (%) | Water Reduction Rate of Concrete (%) |
|-----------|-------------------|--------------------------------------|
| J         | 40                | 30                                   |
| H         | 40                | 18                                   |
| Z         | 40                | 25                                   |

2.2.5. Concrete Composition

The composition of the various concrete samples prepared is summarized in Table 2.

| Sample ID | Water/Cement Ratio | Sand Rate | Concrete Mix Ratio (kg m⁻³) | Amount of Water-Reducing Agent (%) |
|-----------|--------------------|-----------|-----------------------------|-----------------------------------|
|           |                    |           | Water | Cement | Fly Ash | Sand | Stone |                     |
| C40       | 0.42               | 0.39      | 210  | 425    | 75   | 704  | 1100  | 0                    |
| J         | 0.27               | 0.39      | 137  | 425    | 75   | 704  | 1100  | 1.0                  |
| Z         | 0.27               | 0.39      | 137  | 425    | 75   | 704  | 1100  | 1.0                  |
| H         | 0.27               | 0.39      | 137  | 425    | 75   | 704  | 1100  | 1.0                  |
| F         | 0.32               | 0.39      | 160  | 425    | 75   | 704  | 1100  | 2.0                  |
| NF        | 0.34               | 0.39      | 170  | 425    | 75   | 704  | 1100  | 2.0                  |

Note: the slump of the concrete is controlled to be 20 ± 2 cm.

2.3. Characterization

2.3.1. Compressive Strength Analysis

Procedure for Compressive Strength Test of Cement Slurry

Small cubic samples (20 mm × 20 mm × 20 mm) were prepared to minimize the cement pastes used in the analysis of the compressive strength tests. A group of test pieces consists of six test pieces. The clinker samples with or without gypsum addition were incorporated using deionized water and a water-to-cement ratio of 0.4. In the molding process, only simple ramming was performed, and the mold did not use the vibration table because the water-to-cement ratio is a typical ratio used in general
projects and sufficient to form workable pastes. When the pastes were poured into molds, every mold surface was covered with plastic film, and they were then placed in a standard curing box. After one day of curing, the mold was removed, and the cubic samples were put into deionized water at a constant temperature of 20 °C and cured for a certain age of 1, 7, and 28 days. The test specimens were taken out at the proper age and dried, and the sides of the samples were used as the upper and lower compression surface when molding to conduct the compressive strength test. The loading speed during the compressive strength test was 1.0–1.5 kN/s; when the specimen is near failure and starts to deform, the adjusting throttle of the testing machine should be stopped until the specimen is destroyed, and the ultimate damage load is recorded. The compressive strength is the average of the values obtained for a group of test pieces. When the maximum or minimum value of the compressive strength in a group of samples differs from the average value by more than 20%, the average value of the strength of the four test pieces in the middle should be considered. After testing the compressive strength of the samples, the center of the block was extracted as the sample pastes for characterization.

Concrete Compressive Strength Test Process

A concrete test piece with the dimensions 150 mm × 150 mm × 150 mm was formed. A group of test pieces consists of three test pieces, which were cured to a specified age under standard curing conditions. The test piece was taken out and dried during the test, and the sides were used as the upper and lower pressure surface when forming. The test piece was placed on the ball seat that was placed in the center of the press; the load was applied at a speed of 0.5 to 0.8 MPa/s. When the test specimen approaches deformation and begins to deform, the adjusting throttle of the test machine is stopped until the test specimen is destroyed, and the ultimate damage load is recorded.

2.3.2. Procedure for Measuring Fluidity of Cement Slurry

The glass plate was placed in a horizontal position, and the glass plate and the truncated cone mold were wiped evenly with a damp cloth to make the surface wet without water stains. The truncated cone mold was then placed in the center of the glass plate and covered with a damp cloth for use. The pure slurry was quickly mixed into the truncated cone mold and scraped with a spatula; the truncated cone mold was put in the vertical direction. We then let the cement paste flow on the glass plate for 30 s and used a ruler to measure the maximum diameter of the flowing part in two directions perpendicular to each other. The average value was regarded as the cement paste fluidity.

2.3.3. XRD Analysis

The XRD analyses were conducted on different clinker and hydrated samples. To this end, the cured sample pastes were stored in water at a constant temperature of 20 °C until it was time to stop the hydration, and then the crushed hydrated pastes were immersed in ethyl alcohol. Afterward, the immersed pastes were stored in a desiccator at room temperature for 24 h over a silica gel to remove the solvent and/or water and prevent moisturization. Next, the cured samples were dried in a vacuum drying oven at 35 °C for 24 h. The clinker samples and the cured samples were all ground and sieved on a 45-lm standard sieve. A Bruker D8 Advance Davinci design X-ray diffractometer was used with CuKa1,2 radiation ($k_1 = 0.15406$ nm, $k_2 = 0.15444$ nm) at 40 kV and 40 mA for conducting the XRD analyses on the powder. The overall measurement time for every sample was about 31 min per individual pattern to obtain a favorable signal-to-noise ratio in the angular range of 5–80° (2θ) with a step size of 0.02. Finally, the XRD patterns were analyzed utilizing an evaluation (EVA) software package to determine the crystalline phases of the samples.

2.3.4. FTIR Spectroscopy

FTIR spectroscopy was conducted using a Thermo Fisher Nicolet iS5, which included an ATR iD5 attenuated total reflection attachment to analyze the vibration and deflection of the molecular bonds of
the samples. The analysis was performed in a wavenumber range of 4000–400 cm$^{-1}$ and at a spectral resolution lower than 4 cm$^{-1}$ using a sample quantity of 5 ± 1 mg.

2.3.5. Mercury Intrusion Porosimetry

Mercury intrusion porosimetry (MIP) was conducted using an AUTOPORE IV 9500 (a maximum pressure of 33,000 psi) series made by Micromeritics Instrument Corp. (Atlanta, GA, USA) to characterize the pore size distribution of the samples. To this end, some pieces of block samples of about 1.5–2.5 g were used for the analysis, and the samples were dried in a vacuum drying oven at 35 °C for 24 h to remove the water from the porous structure of the samples.

2.3.6. SEM

SEM images were employed to analyze the microstructure of the samples, to find cracks in the interfacial transition zone (ITZ), and to study the porosity of different samples.

3. Results and Discussion

3.1. FTIR Spectra

The FTIR spectrum of superplasticizer J is delineated in Figure 1. The asymmetric absorption peak in the range of 3115 to 3655 cm$^{-1}$ is ascribed to –OH group, indicating that the peak at 3481 cm$^{-1}$ may be the stretching vibration of carboxyl (–COOH) and hydroxyl (–OH) groups in superplasticizer J. The peaks at 2876, 1452, and 1356 cm$^{-1}$ denote the characteristic absorption of methyl and methylene groups, and the peak at 1729 cm$^{-1}$ represents the stretching vibration of –C=O– in the ester group. The characteristic absorption peak at 1107 cm$^{-1}$ is attributed to the polyether –C–O–C– stretching vibration in superplasticizer J [18].

![Figure 1. FTIR spectrum of superplasticizer J.](image1)

Figure 2 depicts the FTIR spectrum of superplasticizer H. The asymmetric peak of hydroxyl (–OH) stretching vibration lies in the range of 3115–3655 cm$^{-1}$, indicating that the absorption peak at 3448 cm$^{-1}$ may be related to carboxyl (–COOH) and hydroxyl (–OH) groups. The peaks at 2880, 1456, and 1352 cm$^{-1}$ denote the characteristic absorption of methyl and methylene groups, and the peak at 1729 cm$^{-1}$ represents the stretching vibration of –C=O– in the ester group. The characteristic absorption peak at 1107 cm$^{-1}$ is also ascribed to the polyether –C–O–C– stretching vibration in superplasticizer H.
According to the FTIR spectrum of superplasticizer Z (Figure 3), the asymmetric stretching vibration peaks in the range of 3115 to 3655 cm\(^{-1}\) are related to hydroxyl groups (–OH), which indicates that the peak at 3436 cm\(^{-1}\) may be related to the absorption of carboxyl (–COOH) and hydroxyl (–OH) groups. The peaks at 2880, 1456, and 1350 cm\(^{-1}\) denote the characteristic absorption of methyl and methylene groups, and the peak at 1729 cm\(^{-1}\) represents the stretching vibration of –C=O– in the ester group. The characteristic absorption peak at 1107 cm\(^{-1}\) is attributed to the polyether –C–O–C– stretching vibration in superplasticizer Z [19].

3.2. Compressive Strength

The fluidity of cement paste mixed with functional polycarboxylic acid water-reducing agents was measured as a function of time, as illustrated in Figure 4. The compressive strength of cement paste, mortar, and concrete was measured as a function of time (at the age of 1, 7, and 28 days), as respectively displayed in Figures 5–7.
3.3. XRD

Concrete, thereby further reflecting the characteristics of the early-strength functional polycarboxylic hydration reaction at the early stage and improves the early strength of cement, mortar, and/or the other superplasticizers. Therefore, it can be concluded that superplasticizer Z promotes the development faster over time, which demonstrates its superiority to other superplasticizers in a time range of zero (fresh cement) to one hour, which indicates that the slope of the fluidity curve of superplasticizer Z is larger than the slope of the fluidity curves of the other superplasticizers. Whether in the state of cement, mortar, or concrete, the main hydration reaction of cement is quicker, and the network structure of cement is formed faster in the presence of superplasticizer Z. Whether in the state of cement, mortar, or concrete, the main hydration reaction of cement is quicker, and the network structure of cement is formed faster in the presence of superplasticizer Z. Whether in the state of cement, mortar, or concrete, the main hydration reaction of cement is quicker, and the network structure of cement is formed faster in the presence of superplasticizer Z. Whether in the state of cement, mortar, or concrete, the main hydration reaction of cement is quicker, and the network structure of cement is formed faster in the presence of superplasticizer Z.

Figure 4. Fluidity of cement paste.

Figure 5. Comparison of the strength of cement paste as a function of time (after 1, 7, and 28 days).

Figure 6. Comparison of the strength of mortar as a function of time (after 1, 7, and 28 days).
Figure 7. Comparison of the strength of concrete as a function of time (after 1, 7, and 28 days).

Figure 4 displays the flow rate of cement paste as a function of time, and the slope of the curves represents the loss of the flow rate of cement paste over time. It is clear that the absolute value of the slope of the fluidity curve of superplasticizer Z is larger than the slope of the fluidity curves of the other superplasticizers in a time range of zero (fresh cement) to one hour, which indicates that the hydration reaction of cement is quicker, and the network structure of cement is formed faster in the presence of superplasticizer Z. Whether in the state of cement, mortar, or concrete, the main component participating in the hydration reaction is cement, hence cement paste can contribute to the fluidity and the loss of flow rate of mortar and concrete to a certain extent.

It can be inferred intuitively from Figures 5–7 that the early strength of the group containing superplasticizer Z is higher than that of the other groups, and superplasticizer Z helps the strength of cement, mortar, and/or concrete to develop faster over time, which demonstrates its superiority to the other superplasticizers. Therefore, it can be concluded that superplasticizer Z promotes the hydration reaction at the early stage and improves the early strength of cement, mortar, and/or concrete, thereby further reflecting the characteristics of the early-strength functional polycarboxylic acid superplasticizer.

3.3. XRD

Figures 8–10 compare the hydration products of the cement mixed with different functional polycarboxylic acid high-performance water-reducing agents. The fresh cement mixed with superplasticizer Z shows the weakest peaks of gypsum, gypsum with aluminates, and aluminum. The formation of Ettringite due to the reaction of acidic minerals can also prove that the early strength is increased while the hydration of the cement is delayed. The ultra-long side chains in the structure of superplasticizer Z have a strong steric hindrance effect and properly improve cement dispersion. In fact, the particles are better dispersed since they have a higher contact area with water; moreover, the ultra-long side chains have a less shielding effect on hydration, which promotes cement hydration and is beneficial to the formation of the cement or concrete structure. Therefore, the characteristics of the early strength of the cement are also revealed [20].
Hence, the degree of hydration is better and the structure is more compact, which is conducive to the development of higher early strength. The compactness of the structure of the other samples. Figure 14 compares the SEM images of the samples containing water-reducing agents Z and F at a magnification of 1000, 2000, and 5000 times. The compactness of the structure of superplasticizer Z is similar to that of superplasticizer F, and the total pore volume, total pore area, and porosity of the sample containing water-reducing agent Z are all smaller than those of the other samples. Figure 15 presents the SEM images of the samples containing superplasticizers Z and F for a magnification of 5000 times, and the SEM images of the samples containing superplasticizers Z and F are presented in Figures 11 and 12 and Tables 3 and 4. At the age of 28 days, the pore volume of the samples containing superplasticizers Z and F is relatively uniform and much higher than that of the other samples. Figure 16 compares the SEM images of the samples containing water-reducing agents Z and F for a magnification of 5000 times. The ultra-long side chains in the structure of superplasticizer Z have a strong steric hindrance effect and properly improve cement strength is increased while the hydration of the cement is delayed. The ultra-long side chains in the formation of Ettringite due to the reaction of acidic minerals can also prove that the early characteristics of the early strength of the cement are also revealed.

Further, when the SEM image in Figure 13 is magnified 100 times, it can be seen that the density dispersion. In fact, the particles are better dispersed since they have a higher contact area with water; the characteristics of the cement or concrete structure. Therefore, the degree of hydration is better and the structure is more compact, which is conducive to the development of higher early strength.
3.4. Mercury Intrusion Porosimetry

The mercury pressure experimental data obtained from mercury intrusion porosimetry analysis are presented in Figures 11 and 12 and Tables 3 and 4. At the age of 28 days, the pore volume of superplasticizer Z is similar to that of superplasticizer F, and the total pore volume, total pore area, and porosity of the sample containing water-reducing agent Z are all smaller than those of the other groups at a similar average pore diameter. It should be noted that superplasticizer F is a commercial early-strength polycarboxylic acid water-reducing agent used as a reference point to evaluate the performance of early-strength polycarboxylic acid water-reducing agent Z synthesized in the current work.

Figure 11. Effect of water-reducing agents on the pore structure of concrete.

Figure 12. Effect of water-reducing agents on the pore structure of mortar.

Table 3. Parameters describing the structure of concrete.

| Water-Reducing Agent | Total Pore Volume (mL/g) | Total Hole Area (m²/g) | Porosity (%) | Average Pore Size (nm) |
|----------------------|--------------------------|------------------------|--------------|------------------------|
| Standard C40         | 0.0651                   | 7.164                  | 11.9276      | 36.4                   |
| J                    | 0.0233                   | 2.813                  | 5.4088       | 33.2                   |
| Z                    | 0.0159                   | 1.835                  | 3.7872       | 34.7                   |
| F                    | 0.0229                   | 2.779                  | 5.3845       | 32.9                   |
| NF                   | 0.0603                   | 6.137                  | 12.6345      | 39.3                   |
Table 4. Parameters describing the structure of the mortar.

| Water-Reducing Agent | Total Pore Volume (mL/g) | Total Pore Area (m²/g) | Porosity (%) | Average Pore Size (nm) |
|----------------------|--------------------------|------------------------|--------------|------------------------|
| J                    | 0.1239                   | 3.798                  | 24.1222      | 130.5                  |
| Z                    | 0.0598                   | 2.799                  | 13.3953      | 85.4                   |
| H                    | 0.0915                   | 4.036                  | 19.1709      | 90.7                   |
| F                    | 0.0593                   | 3.428                  | 13.2647      | 69.2                   |

Further, when the SEM image in Figure 13 is magnified 100 times, it can be seen that the density of the samples containing superplasticizers Z and F is relatively uniform and much higher than that of the other samples. Figure 14 compares the SEM images of the samples containing water-reducing agents Z and F at a magnification of 1000, 2000, and 5000 times. The compactness of the structure of samples Z and F is similar, but sample Z has a more uniform structure. The cement paste can be approximately cemented into a hole, and no water is observed on the surface of the particles. When magnified 5000 times, the SEM images demonstrate that the lamellar crystals of Ca(OH)₂ are intertwined, and the C-S-H hydrated gel accompanies the surrounding and tightly wraps it to form a dense whole. Hence, the degree of hydration is better, and the structure is more compact, which is conducive to the development of higher early strength.

![Figure 13. SEM images of the concrete at a magnification of 100x.](image1)

![Figure 14. SEM images of the concrete mixed with water-reducing agents Z and F.](image2)
3.5. SEM

The strength of the cement mixed with water-reducing agent H is low after one day, but it increases rapidly in 7 days and demonstrates the same characteristics in concrete, mortar, and cement. According to Figure 4, the flowability of sample H gradually increases with time, which is in line with the performance trend of the other groups. The fluidity of the cement slurry increases over time, and it plays a role of slow-releasing because water-reducing agent H has a small molecular structure with polyoxyethylene and ester functional groups and the branched chains penetrating into the liquid phase to disperse particles. The formation of the water film increases the stability of the hydration layer, delays/inhibits the cement hydration, and prevents the formation of the cement structure to a certain extent; thus, the cement slurry remains plastic for a certain period of time, which leads to the low early strength of the cement. The water reduction rate of water-reducing agent H is lower than that of superplasticizers J and Z; therefore, because of its property of delaying hydration, the hydration of superplasticizer H is not as good as that of water-reducing agents Z and F after the same age of 28 days (compare Figure 15 with Figure 14).

![Figure 15. SEM images of the concrete mixed with water-reducing agent H.](image_url)

When the SEM image is magnified 5000 times, you can see that some fibrous CSH gel and some irregular needle/rod AFt are staggered on the CSH gel, which means that the structure is not dense and contains some pores at this time. Therefore, the porosity, total pore area, and pore volume of the concrete mixed with the sample H water-reducing agent are higher than the concrete mixed with the samples Z and F (as shown in Table 4). According to the XRD images shown in Figures 8–10, the AFt and CH peaks of the cement slurry mixed with the superplasticizer H are the weakest, indicating that the CH crystal form of the cement slurry mixed with the sample H is not as good as that of the J and Z superplasticizers. The CH crystal form of the cement slurry is good, which is mainly due to the short molecular side chain of the H superplasticizer, which can extend the setting time of the cement. In addition, the ester group in the H superplasticizer is slow under the alkaline environment of the cement system. Hydrolysis into carboxyl water-reducing functional groups can further delay the hydration of cement. Therefore, compared to J and Z superplasticizers, H superplasticizers can delay cement hydration. More unhydrated cement particles lead to a slower rate of strength development. It can be seen from Figures 5–7 that the early strength and the later strength of cement mortar, and cement mortar and concrete mixed with H water reducer are relatively lower than those of superplasticizer J and Z.

Compared to superplasticizer H, the structure of water-reducing agent J includes longer side chains; nonetheless, its side chains are shorter than those of superplasticizer Z. It can be inferred from the flow rate of the cement (see Figure 4) that, under similar water consumption, superplasticizer J initially has high fluidity and the lowest rate of fluidity loss over time in each group, indicating that water-reducing agent J can adsorb the water on the surface of cement particles. Thus, the water molecules are released to the maximum extent, providing high fluidity and enhancing water retention. In terms of compressive strength, the cement mixed with superplasticizer J is stronger than the one mixed with the standard C40 group. In fact, the proper dispersion of the cement can greatly enhance the reaction between cement and water. It can be seen in Figure 16 that the cement mixed with standard C40 can have many tiny pores and can form a nonuniform structure containing both dense
and loose/porous areas. The pore structure of sample NF is denser than that of the standard C40 sample but far looser than that of sample J.

![Figure 16. Comparison of the SEM images of the cement mixed with standard superplasticizers C40, J, and NF.](image)

Furthermore, it should be noted that although there are fewer pores in sample NF, more particles are exposed at the interface between the cement and fly ash. In fact, the cement structure suffers from a weak interface between the fly ash particles and cement. When the fly ash particles are damaged in the early stage, they separate from cement, therefore they do not participate in bearing external forces and make little contribution to the strength of concrete [12]. Compared with the standard C40 sample, sample J has plenty of large holes and many uniform small holes. On the other hand, the structure of the CSH gel is dense, which fills the pores of the cement stone and increases its compactness. Observing the SEM images at a magnification of 5000 times reveals that there are more flocculent hydrated gels, but no visible fly ash particles and/or AFt crystals are noticed, which may be attributed to the fact that water-reducing agent J is formed into the original gypsum through the adsorption of $\text{SO}_4^{2-}$ tricalcium aluminate hydrate. This process reduces competition effects and thus inhibits the production of AFt [21]. Although the overall structure of sample J is still not dense, it is significantly better than the structure of the standard C40 sample, indicating that water-reducing agent J played a more significant role in improving the microstructure of cement.

4. Conclusions

Functional polycarboxylic acid superplasticizers, named Z, J, and H, do not participate in the cement hydration reaction but rather slow down the rate of the initial reaction of the cement. Superplasticizer Z has a strong steric hindrance effect, due to the ultra-long side chains in its structure, which can increase the contact area between cement particles and water, accelerate cement hydration, promote the generation of CH and AFt, and be closely combined with CSH. It can be seen from the SEM results that the Z water-reducing agent can form a dense structure of cement stone; thus, it presents higher early-strength characteristics to cement. On the other hand, superplasticizer H with shorter side chains in its structure and its ester functional groups can slow down the cement hydration rate,
thereby helping achieve long-term slump retention performance. However, it can be seen from the SEM results that compared with the Z water reducer and the J water reducer, the H water reducer makes the overall cement stone structure less dense. Superplasticizer J can ensure the homogeneity and high fluidity of concrete while satisfying a high rate of water reduction and improving the pore structure and strength of concrete. Compared with water-reducing agent NF, functional polycarboxylic acid superplasticizers (i.e., Z, J, and H) mainly rely on functional groups such as hydroxyl, carboxyl, sulfonic acid, and polyoxyethylene, in their molecular structure to more easily inhibit the precipitation of the initial phase of the minerals.

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