



# Improvement on microstructure of concrete by polycarboxylate superplasticizer (PCE) and its influence on durability of concrete



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## HIGHLIGHTS

- Influence of PCEs on carbonation, permeability and chloride penetration in concrete was studied.
- Pore structures of mortars with different PCEs were explored by means of MIP.
- Components in cement paste with different PCEs were analyzed by means of TG/DSC.
- Ratio of HD C–S–H to LD C–S–H affected by PCEs was quantified by nano-indentation.

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## ABSTRACT

In this study, the influence of polycarboxylate superplasticizers (PCEs) on durability of concrete was investigated. Carbonation, water impermeability and rapid chloride permeability of concrete with different types of polycarboxylate superplasticizer and polynaphthalene superplasticizer (PNS) were tested. In order to obtain deeper insights into the influence of PCE on concrete durability, microstructure in the concrete was explored by means of mercury intrusion porosimetry (MIP), thermogravimetry (TG) and nano-indentation technique. Smaller carbonation depth, water penetration depth and better resistance to chloride ion penetration show that concretes with PCE have better durability performances than concretes with PNS. MIP results show that the mortars with PCE have lower porosity than that with PNS. The fraction of pores with diameters larger than 100 nm in the mortars with PCE is lower than in the mortar with PNS. According to TG tests, there are more hydration products in the cement pastes with PCE than in the cement pastes with PNS. Nano-indentation tests show a higher ratio of high density C–S–H to low density C–S–H in the cement paste with PCE than in the cement paste with PNS. It can be concluded that PCE leads to denser microstructure in concrete than PNS and, therefore, better durability performances of concrete.

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## 1. Introduction

It is well known that increases in water to cement ratio cause decreases in strength and durability of concrete [1,2]. The use of superplasticizers can reduce water content in concrete mixtures and improve the workability of fresh concrete. Owing to this performance, superplasticizers are necessary chemical admixtures for high performance concretes [3–6] that has already been recognized as an important construction material.

By now, there are various types of superplasticizers available. Conventional superplasticizers, i.e. superplasticizers based on naphthalene (PNS), melamine (PMS) or lignosulfonate (LS) disperse

particles by means of electro steric [7–12]. Differently, polycarboxylate superplasticizers (PCEs) disperse particles by forming a steric obstacle [7–13]. Effects of PCE on reducing water amount and increasing workability of concrete have already attracted many attentions so far [14–17]. It has been reported that PCE has a good performance on improving workability of fresh concrete [14–17]. Meanwhile, it has been demonstrated that PCE can mitigate plastic shrinkage of matrix because of the reduction of the build-up rate of capillary pressure by PCE [18]. Effects of polycarboxylate superplasticizers with different molecular structure on the hydration behavior of cement paste was investigated by Kong et al. [19]. In addition to influence of PCE on hydration of cement, influence of PCE on microstructure of cement paste was reported as well. Zhang et al. [20] studied the influences of PCE on the pore structure of hardened cementitious materials and found that the

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incorporation of superplasticizer obviously reduces the average pore size [20]. It was also reported that the impermeability of hardened cementitious materials was increased by adding PCE [20]. The permeability and compressibility of freshly made cement-based pastes influenced by PCE were investigated as well by Perrot et al. [21]. The authors demonstrated that PCE can reduce the cement paste permeability and does not influence the compressibility of the cement grain network [21]. However, the relationship between microstructure and durability performances, such as resistance to carbonation, water impermeability, resistance to chloride penetration into concrete with PCE is still insufficiently studied.

In this study, influence of PCE on durability of concrete was investigated experimentally. Concretes with the same level of workability and strength were casted with different types of superplasticizer, i.e. polynaphthalene superplasticizers and polycarboxylate superplasticizers synthesized with acrylic acid and maleate. Carbonation of concrete, water impermeability and rapid chloride permeability of concrete were tested. In order to obtain deeper insights into the influence of PCE on concrete durability, microstructure in the concrete was explored. Pore structure of the mortar in the concrete was tested by mercury intrusion porosimetry (MIP). Components in the hardened cement paste with different types of superplasticizer were analyzed by means of thermogravimetry (TG) and differential scanning calorimetry (DSC). Ratio of high density calcium silicate hydrates (C–S–H) to low density C–S–H in hardened cement paste was quantified by using nano-indentation technique.

## 2. Materials and experiments

### 2.1. Materials

Cement P. I. 52.5, fly ash and slag were used in this study. Their chemical compositions were shown in Table 1. The reference mixtures of concrete (without superplasticizers) were shown in Table 2. Polycarboxylate superplasticizers synthesized with acrylic acid (J1, J3) and maleate (J2, J4, J5) were added into different mixture. The properties of different types of superplasticizer were given in Table 3. For comparison, polynaphthalene superplasticizers (PNS, symbolized as N in Table 4) was studied as well. It should be mentioned that considering the real application concrete tested here were designed to have the same level of workability and compressive strength (see Table 4). The fineness module of sand used was 2.72. The size of coarse aggregates range between 5–16 mm and 16–25 mm.

### 2.2 Experiments

#### 2.2.1. Carbonation tests

Carbonation of concrete was tested according to Chinese national standards GB/T 50082–2009 [22] that is comparable with ASTM C6421997 [23]. Prism specimens of 100 mm × 100 mm × 400 mm were casted. Specimens were cured for 28 days after casting under standard conditions (relative humidity was higher than 95% and the temperature was 20 ± 2 °C). Specimens were then dried under blowing for 48 h before tests. After that, surfaces of the specimens, except the casting surface

**Table 1**  
Chemical compositions of cement, fly ash and slag.

Compositions	Cement	Fly ash	Slag
CaO	64.90	5.09	37.81
Al <sub>2</sub> O <sub>3</sub>	6.23	33.50	16.68
SiO <sub>2</sub>	20.8	48.86	34.07
Fe <sub>2</sub> O <sub>3</sub>	4.88	4.86	0.97
MgO	0.98	1.35	9.61

**Table 2**  
Reference mixtures of concrete without information of superplasticizers (kg/m<sup>3</sup>).

Cement	Fly ash	Slag	Sand	Coarse aggregate	Water
315	90	45	730	1095	157

**Table 3**  
Properties of different types of superplasticizers.

Series	Types	pH	Surface tension (mN/m)	Mass percentage (%)
J1	Acrylic acid-based	5.54	50.8	41.76
J2	Maleate-based	3.53	66.4	42.99
J3	Acrylic acid-based	6.18	64.8	42.07
J4	Maleate-based	7.31	68.4	45.59
J5	Maleate-based	7.27	67.5	39.86
N	Polynaphthalene	7.57	74.5	56.23

**Table 4**  
Workability and compressive strength of concrete with different types of superplasticizers.

Series	Dosage (kg/m <sup>3</sup> )	Slump (mm)	Air content (%)	Compressive strength-7d (MPa)	Compressive strength-28d (MPa)
J1	2.12	215	2.5	50.9	58.3
J2	1.75	200	3.2	42.7	58.9
J3	1.61	212	3.0	45.8	55.5
J4	1.42	213	3.4	40.1	52.6
J5	2.71	205	3.3	42.0	57.3
N	2.96	210	3.1	40.0	54.2

and the one opposite to the casting surface, were sealed by using wax. Specimens were then stored in carbonation curing box where CO<sub>2</sub> concentration ranged between 18% and 22%, relative humidity was 75% and temperature was 20 ± 2 °C.

Specimens after being carbonated were then split into two pieces along the casting surfaces. Carbonation depth in concrete was determined by means of phenolphthalein spray.

#### 2.2.2 Water impermeability tests

Water impermeability tests were performed according to Chinese national standards GB/T 50082–2009 [22] that is comparable with ASTM C6421997 [23]. 6 truncated cone specimens for each series with a bottom surface diameter of 185 mm, a top surface diameter of 175 mm and a height of 150 mm were prepared. Specimens were cured for 28 days after casting under standard conditions (relative humidity was higher than 95% and the temperature was 20 ± 2 °C). Before water impermeability tests, surrounding surfaces of truncated cone specimens were sealed with wax. By using equipment HP-4.0 (Shanghai Le Ao Test Instrument Co., Ltd, China), water was pressed into concrete under a pressure of 1.2 MPa for 24 h. After that, the specimens were split into two pieces along the direction of water penetration. The depth of penetration was measured at 10 locations along the fronts of watermark. 6 parallel measurements were performed at each specimen.

#### 2.2.3. Resistance of concrete to chloride ion penetration

Resistance of concrete to chloride ion penetration was evaluated according to ASTM C1202-97 [24]. Cylinder specimens (100 mm × 200 mm) were casted and cured for 28 days and 56 days under standard conditions (relative humidity was higher than 95% and the temperature was 20 ± 2 °C). Then specimens were sliced into 50 mm thick sections and saturated with water by vacuuming for 24 h before the tests. During the test, a potential difference of 60 V was adopted. The cathode is 3% NaCl solution while anode is NaOH solution of 0.3 mol/L concentration. The amount of charge passing through the specimens, indicating resistance of concrete to chloride ion penetration, was measured during a period of 6 h.

Powder sample for free chloride content analysis were obtained from the specimens that had been used for rapid chloride permeability tests. The free chloride content (by weight of concrete) was determined following ASTM C1218 [25].

#### 2.2.4. Characterization of microstructure in concrete

In order to get deeper insights into the effect of PCE on durability of concrete, microstructure in the concrete was characterized by means of MIP, TG/DSC and nano-indentation.

In order to investigate pore structure in the mortar of concrete by means of MIP, mortars were made according to the mixtures of concretes but without coarse aggregates. After being cured for 28 days under standard conditions, the mortar was immersed in ethanol for 48 h to stop hydration. After that, Poremeter GT-60 was used to test the porosity and analyze pore size distribution in the mortar.

For TG and DSC tests, powder sample was obtained from plain paste with a larger dosage of superplasticizer up to 2.5% of cement (by weight) and w/c ratio of 0.25. During the test, the rising rate of temperature was 10 °C/min. Powder sample

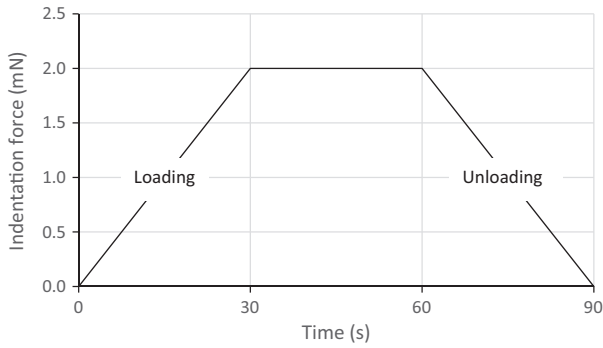


Fig. 1. Loading on the specimen during nano-indentation tests.

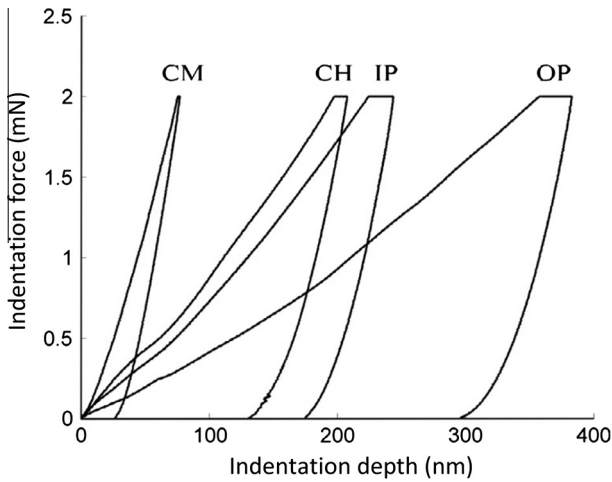


Fig. 2. Characteristic load–depth curve representatives of residual cement clinker (CM), Portlandite (CH), inner product (IP), and outer product (OP) (This figure was reprinted from [25]). In this study, inner products were assumed to be high density C–S–H, outer products to be low density C–S–H.

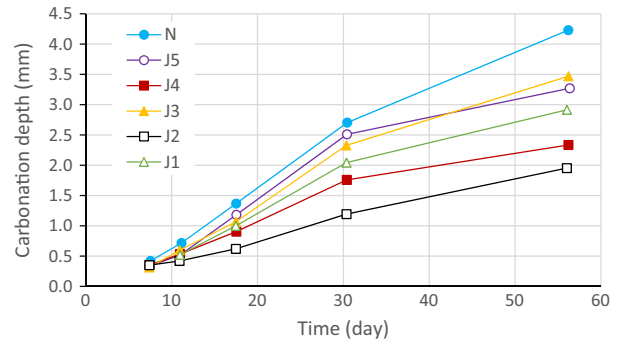
was heated under N<sub>2</sub> atmosphere until the temperature reached 1100 °C. The main components of cement paste with different types of superplasticizer was semi-quantified.

Nano-indentation tests were performed in order to quantify amount of high density C–S–H and low density C–S–H. Plain paste with a larger dosage of superplasticizer up to 2.5% of cement (by weight) and w/c ratio of 0.25 was made. After stopping hydration at the age of 28 days, plain cement paste was ground and then polished by following the steps in [26]. The loading on the specimen during the test was shown in Fig. 1. According to the load–depth curves for different components (see Fig. 2 reprinted from [27]), high density C–S–H can be distinguished from low density C–S–H and the ratio between them can be determine.

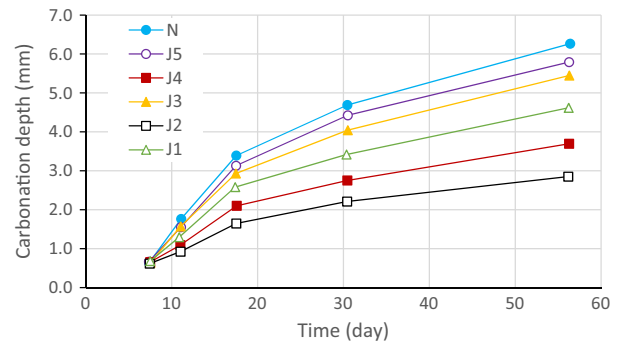
### 3. Experimental results

#### 3.1. Carbonation of concrete

Fig. 3 shows carbonation depths of concrete and mortar with different types of superplasticizer. It can be seen that carbonation depth in concrete (in Fig. 3(a)) is smaller than in mortar (in Fig. 3 (b)). Concrete and mortar with J2 have best a performance of carbonation resistance, compared to concretes and mortars with other PCE. It is worth noting that the carbonation depth in concrete with J2 is less than one half of the carbonation depth in concrete with PNS after carbonated for 56 days. Both concrete and mortar with PCE have a smaller carbonation depth than that with PNS. Therefore, PCE make concrete have a better performance of carbonation resistance than PNS.



(a)



(b)

Fig. 3. Carbonation depth in concrete (a) and mortars (b) with different types of superplasticizers.

#### 3.2. Water impermeability

As described in Section 2.2.1, in order to evaluate water impermeability of concrete, height of water penetrating into concrete with different types of superplasticizer was determined. According to the data in Fig. 4, the mean water penetration height in concrete with acrylic PCE (J1, J3) was 20.5 mm, while 18.99 mm in concrete with maleate PCE (J2, J4, J5). The difference between them (20.5/18.99 = 1.1) is slightly smaller than that of carbonation test results shown in Fig. 3(a), where the mean carbonation depth in concrete with acrylic PCE (J1, J3) is almost 1.2 times of that with J2.

By comparing water penetration in specimens of PCE with specimens of PNS, it is found that water penetration height in concrete with PCE is smaller than that of concrete with PNS, indicating that concrete with PCE has better performance of water impermeability than concrete with PNS.

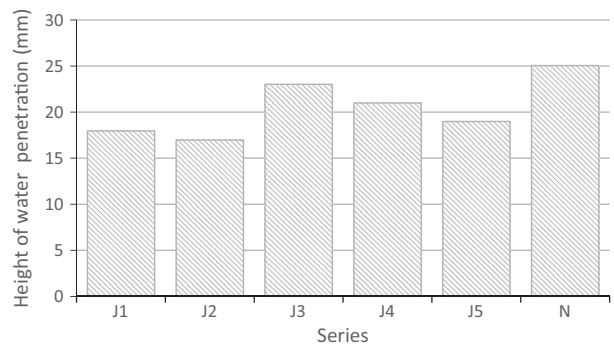


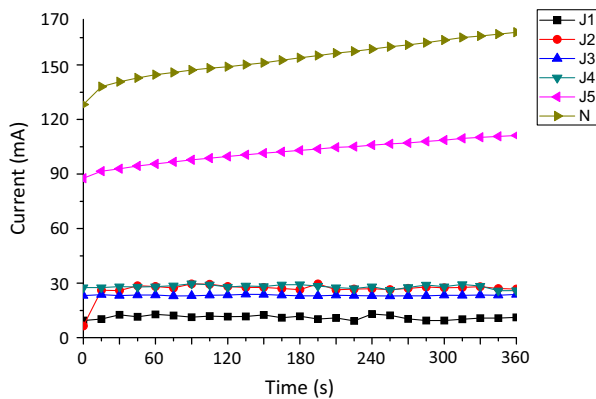
Fig. 4. Height of water penetration in concretes with different superplasticizers during water impermeability tests.

3.3. Resistance of concrete to chloride ion penetration

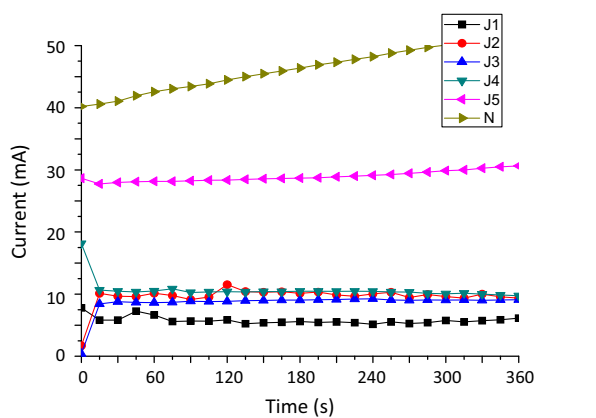
Fig. 5 presents the current through concretes with different types of superplasticizer during rapid chloride ion penetration tests. The amounts of charge passing through the specimens, indicating resistance of concrete to chloride ion penetration, were shown in Fig. 6. Both concretes at the age of 28 days and 56 days were tested. It is conceivable that the resistance to chloride ion penetration in 56-day-old concrete is better than that of 28-day-old concrete, in particular for concretes with polycarboxylate superplasticizer J5 and PNS of which the amounts of charge decrease by more than 60% (see Fig. 6).

As shown in Fig. 6, the resistance to chloride ion penetration in concretes with J1, J2, J3, J4, respectively, is close to each other. However, the chloride permeability of concrete with J5 is much larger than that of concretes with other polycarboxylate superplasticizer, i.e. J1, J2, J3, J4. This is not consistent with the results of water impermeability tests in Fig. 4, which shows that water impermeability of concretes with PCE is close to each other.

It is interesting to note that the resistance to chloride ion penetration in concrete with PNS is worse than that in concrete with polycarboxylate superplasticizer J5 (see Fig. 6). The amount of charge passing through 28-day-old concrete with PNS is about 1.5 times the amount of charge through concrete with J5 and even 5 times the amount of charge through concretes with other PCE. Therefore, compared to concrete with PNS, concrete with PCE shows a better performance on resistance of chloride ion penetra-



(a) 28 days



(b) 56 days

Fig. 5. Current through concretes with different types of superplasticizer during rapid chloride permeability tests: (a) the age of concrete is 28 days; (b) the age of concrete is 56 days.

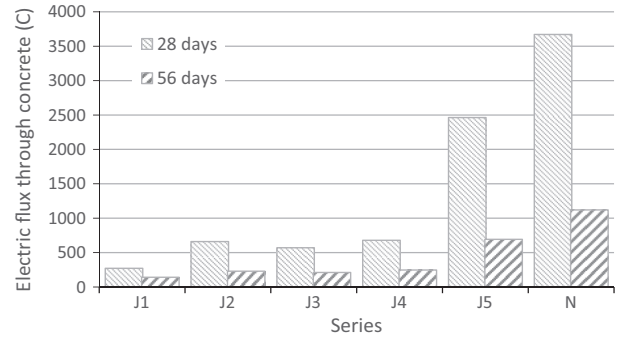


Fig. 6. Amount of charges through concretes during rapid chloride permeability tests.

Table 5

Free chloride contents in concretes with different types of superplasticizers after rapid chloride permeability tests.

Series	J1	J2	J3	J4	J5	N
Free chloride content (% by weight of concrete)	0.0172	0.0184	0.0182	0.0187	0.0192	0.0196

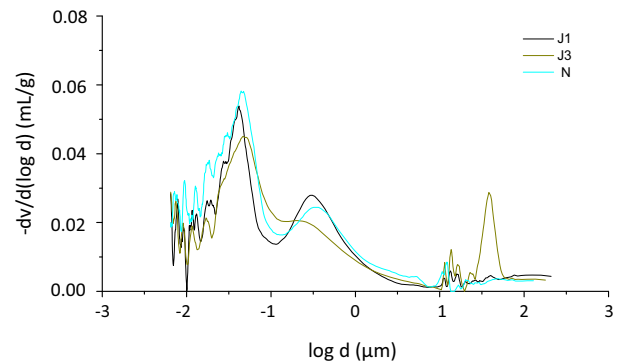


Fig. 7. Pore size distribution in mortars with different superplasticizers determined by means of MIP.

Table 6

Information of pores in mortars with different superplasticizers determined by means of MIP.

Series	Porosity (%)	Fraction of pores with different diameters			Critical pore diameter (nm)
		<10 nm (%)	10–100 nm (%)	>100 nm (%)	
J1	12.54	17.84	40.57	41.59	41.78
J3	13.30	15.74	40.04	44.22	46.57
N	14.53	20.55	31.91	47.54	47.20

tion, which is consistent with the results of carbonation tests and water impermeability tests.

Free chloride content in concrete after chloride penetration tests were determined. By comparing data in Table 5 with that in Fig. 6, it was found that free chloride content in concrete increases with the amount of charge passing through concrete, indicating the validity of rapid chloride ion penetration tests.

3.4. Microstructure of concrete with PCE and PNS

Pore structures in mortar with polycarboxylate superplasticizer J1, J3 and PNS were investigated by means of MIP. Fig. 7 presents

pore size distribution profiles of mortars with different types of superplasticizer. Total porosity and fractions of pores with diameters less than 10 nm, between 10 and 100 nm and larger than 100 nm are listed in Table 6, respectively. Critical pore sizes of pore structures in the mortars with PCE and PNS were given in Table 6 as well. From Table 6, it was found that the mortars with PCE have lower porosity than that with PNS. Moreover, the fraction of pores with diameters between 10 nm and 100 nm in the mortars with PCE is higher than in the mortar with PNS. The fraction of pores with diameters larger than 100 nm in the mortars with PCE is

lower than in the mortar with PNS. The mean critical pore size of pore structures in the mortars with PCE is 44.12, smaller than that in the mortar with PNS. Regarding PCE, the fraction of pores with diameters larger than 100 nm in mortars with J1 is lower than in mortar with J3. Critical pore sizes of pore structures in mortars with J1 are smaller than that in mortar with J3 as well.

In addition to pore structure, the components of cement paste with different types of superplasticizer were analyzed by means of TG and DSC. Fig. 8 shows TG and DSC profiles of cement paste with PCE and PNS. In each DSC profile, peaks at different ranges

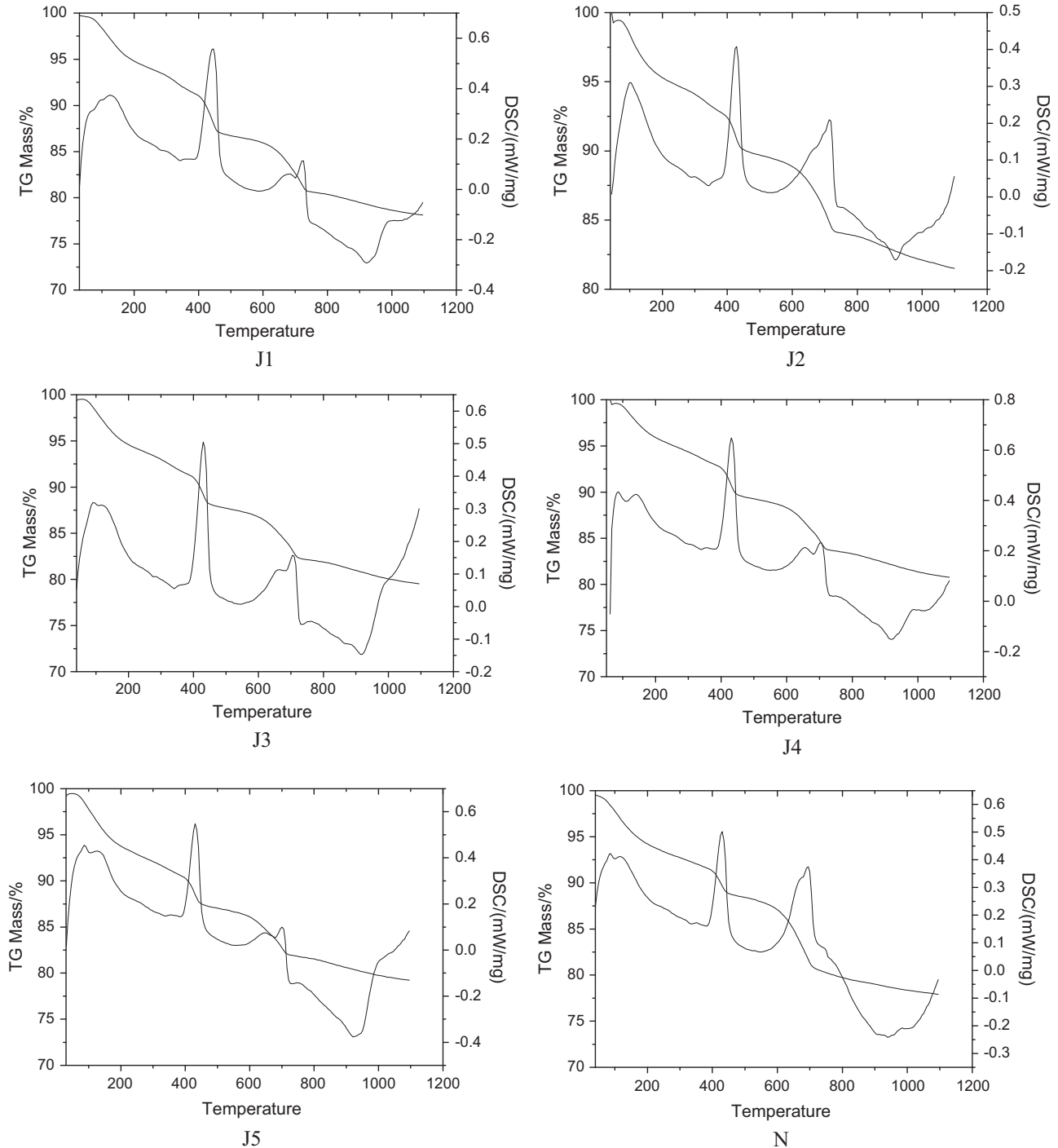
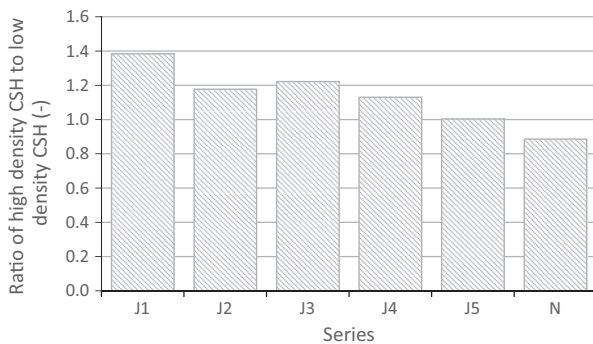


Fig. 8. TG and DSC profiles of cement pastes with different superplasticizers.



**Table 7**  
Weight loss (%) of cement paste with different superplasticizers at different temperatures during TG tests.

Series	Temperature range		
	145–420 °C (C–S–H dehydrated)	420–530 °C (Ca(OH) <sub>2</sub> decomposition)	600–1000 °C (CaCO <sub>3</sub> decomposition)
J1	6.21	3.44	8.06
J2	5.01	1.82	7.57
J3	6.16	2.30	7.64
J4	5.90	2.27	7.88
J5	6.18	2.27	7.26
N	5.38	1.94	10.04



**Fig. 9.** Ratio of high density C–S–H to low density C–S–H in cement pastes with different types of superplasticizers.

of temperatures are noticeable, representing decompositions of different components in cement paste. The main components of cement paste with different types of superplasticizer was semi-quantified based on the data from TG tests. It was assumed that (1) weight loss of cement paste on the temperatures between 145 and 420 °C was mainly caused by dehydration of C–S–H; (2) weight loss of cement paste on the temperatures between 420 and 530 °C was mainly due to decomposition of Ca(OH)<sub>2</sub> (CH); (3) weight loss of cement paste on the temperatures between 600 and 1000 °C was mainly due to decomposition of CaCO<sub>3</sub>. From Table 7, it can be seen that the cement pastes with PCE (except J2) have larger percentages of C–S–H and CH. It reveals that there are more hydration products in the cement pastes with PCE and, therefore, denser microstructures. This is consistent with the MIP results discussed above. Presence of CaCO<sub>3</sub> indicates that carbonation of hydrates products took place during the preparation of powder samples. We can see that under the same conditions, carbonation of cement paste with PNS is more serious than that with PCE, which is in a good agreement with results of carbonation tests in Section 3.1.

Nano-indentation tests were also performed to investigate microstructure of cement paste, particularly the main hydration product C–S–H. As described in Section 2.2.4, high density of C–S–H can be distinguished from low density C–S–H according to the load–depth curve obtained during the nano-indentation tests. The ratio of high density C–S–H to low density C–S–H can be determined as well. Fig. 9 shows the ratio of high density C–S–H to low density C–S–H in cement paste with different types of superplasticizer. It is worth noting that the ratio of high density C–S–H to low density C–S–H in the cement paste with PNS is about 0.89. In comparison, the ratios of high density C–S–H to low density C–S–H in the cement pastes with PCE are all higher than 1.00. In particular, the ratio of high density C–S–H to low density C–S–H in cement paste with polycarboxylate superplasticizer J1 is 1.38, more than

1.5 times the value for cement paste with PNS. Higher ratio of high density C–S–H to low density C–S–H can lead to a denser microstructure and better mechanical properties of the material.

#### 4. Discussions

Carbonation tests, water impermeability tests and rapid chloride permeability tests can reflect information of pore structure of concrete. Smaller carbonation depth, water penetration depth and chloride permeability of concrete with PCE show that mass transport through concrete with PCE is more difficult than through concrete with PNS. This is consistent with the results from microstructure characterizations. Compared to concrete with PNS, the distribution of C–S–H in concrete with PCE is more homogenous. The retard of C–S–H at the surfaces of cement grains on cement hydration becomes weaker. As a result, a higher degree of cement hydration in concrete with PCE is obtained. Therefore, more hydration products (in particular more high density C–S–H) and lower porosity was detected in concrete with PCE. It is conceivable that transport of water and ions in a concrete with a low porosity is more difficult than in concrete with a high porosity. Moreover, the fraction of pores with diameters larger than 100 nm in the mortars with PCE is lower than in the mortar with PNS. Critical pore sizes of pore structures in the mortars with PCE are smaller than that in the mortar with PNS. It was reported that mass mainly transports through the pores with large diameters (i.e. larger than 100 nm) in concrete [28,29] and the larger the critical pore size, the more permeable the concrete [30]. From this study, it was found that the addition of PCE makes concrete denser than that with PNS and optimizes pore structure of concrete. Therefore, PCE leads to better durability performances than the concrete with PNS.

By comparing Fig. 3 with Fig. 4, it is noticed that carbonation depths in concretes with polycarboxylate superplasticizers are quite different from each other while water penetration depth concretes with polycarboxylate superplasticizers are close to each other. It is known that diffusion of CO<sub>2</sub> into concrete matrix not only depends on the pore structure of concrete, but also the saturation degree of pores [31]. When the saturation degree of pores is very high, most of pores are filled with water and the pathways for CO<sub>2</sub> penetration are blocked [32,33]. As a result, carbonation hardly takes place inside the concrete matrix [34]. If the saturation degree of pores in concrete is very low, although CO<sub>2</sub> penetrates into concrete easily, carbonation still hardly takes place because of the lack of water as a medium for carbonation reaction [34]. There is a critical degree of water saturation, at which the pores filled with water are not connected any more. The detailed information on critical saturation degree of cement-based materials can be found in [32,33]. Therefore, carbonation of concrete is not only related to pore structure of concrete, but also internal relative humidity of concrete. The complexity of carbonation of concrete may leads to difference between results of carbonation tests and water impermeability tests.

#### 5. Conclusions

In this study, influence of polycarboxylate superplasticizers (PCEs) on durability of concrete was investigated by performing carbonation tests, water impermeability tests and rapid chloride permeability tests. In order to obtain deeper insights into the influence of PCE on concrete durability, microstructure in the concrete was characterized by means of MIP, TG/DSC. Ratio of high density calcium silicate hydrates (C–S–H) to low density C–S–H was quantified as well by using nano-indentation technique. Based on the experimental results, the following conclusions can be drawn:

- Smaller carbonation depth, water penetration depth and chloride permeability of concretes with PCE show that concretes with PCE have better durability performances than concretes with PNS.
- Mortars with PCE have lower porosity and smaller critical pore diameters than that with PNS. The fraction of pores with diameters larger than 100 nm in the mortars with PCE is lower than in the mortar with PNS. Therefore, compared to PNS, PCE optimizes pore structure of concrete.
- Cement pastes with PCE have more hydration products, i.e. C–S–H and CH than in the cement pastes with PNS and, therefore, denser microstructures.
- The ratio of high density C–S–H to low density C–S–H in cement paste with PCE are much higher than that in the cement paste with PNS, leading to a denser microstructure and better mechanical properties of the material.
- Experimental results show that compared to PNS, PCE can improve microstructure of concrete and, therefore, enhance durability of concrete.

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