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Effects of super absorbent polymer on the early hydration of Portland cement highlighted by thermal analysis

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Abstract The effects of super absorbent polymer (SAP) on the early hydration evolution of Portland cement within 72 h were investigated by isothermal calorimetry, thermal analysis and X-ray diffraction analysis. The results show that the SAP definitely affects the early hydration process of Portland cement, increases the hydration heat evolution rate during the acceleration period and during the main exothermic peak, promotes the earlier appearance of the main exothermic peak, but does not affect the lengths of the initial reaction period and the induction period and the onset of the acceleration period. The SAP can accelerate cement hydration to increase the hydration degree within 72 h. But the dosage variation of SAP has minor influence on the hydration heat evolution and hydration degree. The SAP enhances the formation of $Ca(OH)_2$ after 12 h to keep higher content than that in the reference paste. The SAP does not affect the maximum content of ettringite, but delays the conversion of ettringite to monosulphate to remain ettringite content higher at later hydration time. Besides, no new phases are found to have formed in cement paste with SAP.

Keywords Portland cement · Super absorbent polymer · Early hydration degree · Hydrates · Thermal analysis

Introduction

Due to their quick absorption and slow desorption of water in cement matrix, super absorbent polymers (SAPs) have been used in cement-based materials such as high-performance concrete as internal curing agent to improve the properties. It has been found that SAP can reduce the plastic shrinkage [1, 2], autogenous shrinkage [3–6] and drying shrinkage [5, 7] and increase the sulfate resistance [8] and carbonation resistance [9]. Literature [9–11] reported that SAP may only have a negative effect on the compressive strength at early ages, while literature [12] found that up to one year, the compressive strength of ultra-high-performance concrete with SAP is still lower than that of the reference concrete without SAP. Also, SAP greatly affects the properties of fresh cement matrix. SAP can increase the yield stress and plastic viscosity to influence the rheological behavior of fresh cement matrix [13, 14].

The mechanisms of SAPs on properties of cement matrix have been reported from different aspects. Some literature [15–17] demonstrate that SAPs can successfully improve the microstructure of cement matrix due to internal curing, thereby improving the strength and durability. But due to the great volume reduction in SAP particles as the water is released from swollen SAPs into cement matrix, macro-voids can form in cement matrix with SAPs and additional water to increase the total porosity [5, 18], whereas the total porosity of cement matrix with SAPs and without additional water is lower [18]. It was also reported that the water release continues to improve the hydration of cement so that the porosity is decreased at late ages [19]. Literature [20] reported that cement matrix with SAPs and without additional water shows a slight decrease in porosity in the micro- and meso-

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pore range, and no significant change of porosity in the micro-pore range.

The hydration behavior of cement matrix with SAPs has also been studied by many researchers. Literature [11] reported that the hydration degree of cement paste with SAPs shows a slight decrease compared to that of the reference paste up to 28 days. Literature [14] demonstrated that SAPs can improve the cement hydration to promote the strength and durability. Literature [21] found that the release of water from SAP particles into cement matrix starts by the time of the acceleration period and is finalized one or two days of hydration, depending on the SAP particle size. Literature [22] reported that the hydration degree depends only on the overall amount of water presented in Portland cement matrix with SAP, but did not report in detail on the first few hours of cement hydration. By using isothermal calorimeter, Justs et al. [23] found that SAP can increase the hydration degree at later hydration time in a manner similar to increasing the water-to-binder ratio, but delays the main calorimetric hydration peak, resulting in a slight delay and a diminished extent of cement hydration within the first 30 h, while the cumulative hydration heat and the ultimate hydration degree increase because of the release of water from SAP [23, 24].

SAP can be added to cement-based materials for many different reasons, so it is of essential importance that the basic knowledge of this new compound on the development of cement hydration is well understood. However, the literature presented above shows the contradictions in the effects of SAP on cement hydration. And few studies in the literature have reported the effects of SAP on cement hydrates evolution, especially at the early hydration time. Therefore, the main focus of this paper is to understand the early hydration of Portland cement in the presence of super absorbent polymer (SAP), an important task from the application of SAPs in cement matrix point of view. The mechanism of SAP on the early cement hydration without additional water is discussed from the point of the hydration heat evolution, hydration degree and hydrates evolution. Isothermal calorimetry, thermal analysis (TG-DSC) and X-ray diffraction (XRD) are used in this investigation.

Experimental

Materials

A Portland cement type P.II 52.5R (according to Chinese standard GB 175), deionized water and a commercial super absorbent polymer (SAP) were used. The physical properties, chemical and phase compositions of Portland cement are shown in Tables 1 and 2, respectively. The SAP is a copolymer of acrylamide and sodium acrylate with water absorption capacity of 130 g g^{-1}, bulk density of 700 g cm^{-3} and particle size smaller than 160 μm.

Preparation of samples

The mass ratio of water to cement (m_w/m_c) of all cement pastes was kept constant as 0.50. The mass ratios of SAP to cement (m_{sap}/m_c) were 0, 0.2, 0.4, 0.6 and 1.0%. And the cement paste with no SAP was set as the reference paste. No additional water was added in cement pastes with SAP. Specimens to be tested were prepared by mixing SAP particles with cement firstly and then adding water. Specimens for TG-DSC and XRD tests were cured under the conditions of 20 ± 2 °C and 65 ± 5% RH.

To perform TG-DSC and XRD analyses, samples were taken at a depth of more than 1 mm from the surfaces of specimens, broken into pieces, manually ground to powders under 45 μm and then washed with acetone and dried in a vacuum oven under 40 °C to stop further hydration.

Test methods

An isothermal calorimeter (TAM AIR C80, Thermometric, Sweden) was used to measure the hydration heat evolution of cement pastes. The experimental temperature was kept at 20 ± 0.1 °C. All materials were kept at 20 ± 1 °C for 24 h before mixing, and then, water was injected into the reaction vessels and samples were stirred in the calorimeter for several minutes. This procedure allowed monitoring the heat evolution from the very beginning. Data logging continued for 72 h with one datum per minute.

Thermal analyses were performed with a NETZSCH STA 449 C instrument. The TG-DSC curves were recorded in the range of 30–1000 °C, with a heating rate of 10 K min^{-1}, using Pt crucibles, α-Al_2O_3 as reference material, sample mass 25 mg approximately, in nitrogen atmosphere with a flowing rate of 100 mL min^{-1}.

XRD analyses were carried out with a graphite-monochromatized Cu *Ka* radiation generated at 40 kV and 200 mA in a Rigaku D/Max 2550 X-ray diffractometer. The step scanning was conducted with the step length 0.02° and the dwell time 4 s for each step. The integrate areas of ettringite and $Ca(OH)_2$ were calculated using the software of MDI Jade 6.0 with the function of "profile fitting."

Results and discussion

Isothermal calorimetry

The hydration heat evolution rate curves of cement pastes are shown in Fig. 1. The SAP does not change the typical profile of these hydration heat evolution curves since their

Table 1 Physical properties of P.II 52.5R Portland cement

Specific density/g cm^{-3}	Blaine specific surface area/m^2 kg^{-1}	Setting time/min		Compressive strength/MPa		Flexural strength/MPa	
		Initial	Final	3 days	28 days	3 days	28 days
3.20	380	150	210	29.7	59.6	6.0	8.6

Table 2 Chemical compositions and mineralogical constituents of P.II 52.5R Portland cement

Chemical compositions/mass%									Mineralogical constituents/mass%			
SiO_2	CaO	Al_2O_3	Fe_2O_3	SO_3	MgO	K_2O	Na_2O	free-CaO	C_3S	C_2S	C_3A	C_4AF
22.8	65.2	4.99	3.22	2.22	1.14	0.66	0.21	0.20	54.0	24.6	7.8	9.8

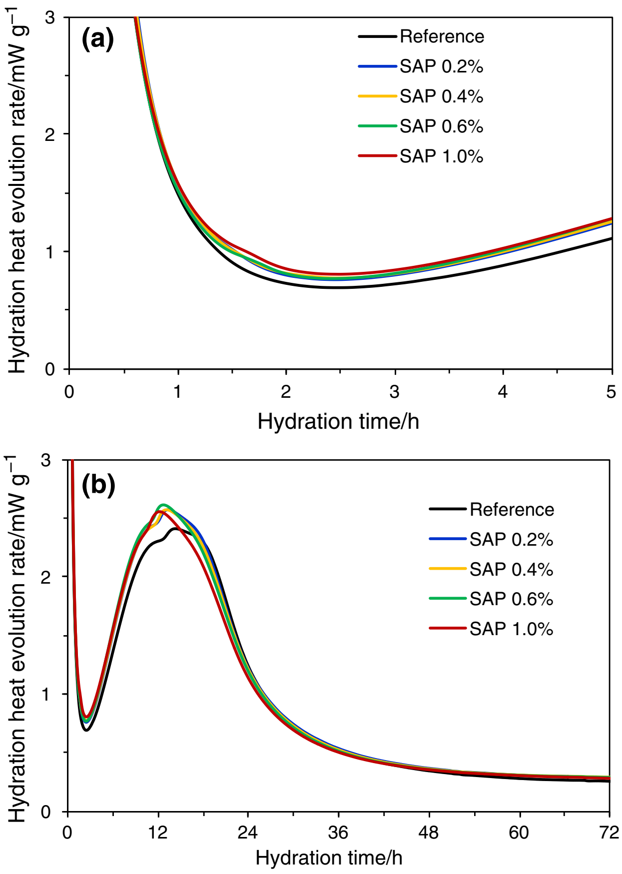

Fig. 1 Hydration heat evolution rate of cement pastes: **a** the first 5 h, **b** 0–72 h

shapes are very similar for all cement pastes. The initial reaction period and the induction period of all cement pastes last for approximately 1 and 2 h, respectively. And the hydration heat evolution rate of cement paste with SAP is a little higher than that of the reference paste during the induction period (Fig. 1a). Furthermore, the points in time of the minimum rates for all cement pastes are almost the same (at about 2.5 h), indicating the same transition time from the induction period to the acceleration period of cement pastes with and without SAP. Literature [23, 25] reported that SAPs can delay the transition from the induction period to the acceleration period due to the water release, since an increase in the ratio of water to cement (m_w/m_c) is known to delay the transition from the induction period to the acceleration period [26]. Accordingly, it may be concluded that the SAP does not substantially affect the lengths of these two periods and the onset of the acceleration period, and no water is released by the swollen SAP particles at the stage.

During the acceleration period, the hydration heat evolution rate of cement paste with SAP is higher than that of the reference paste, with the minor influence of the SAP dosage variation (Fig. 1b), indicating the improvement of SAP on the hydration heat evolution rate during the acceleration period, which is in agreement with the results in the literature [23]. As it known that a decrease of m_w/m_c leads to the increase in the hydration heat evolution rate during the acceleration period due to higher concentration of alkalis in the pore solution [23, 26–28]. The soluble alkalis in cement paste can lead to a rapid pH rise that is known to accelerate cement hydration. This acceleration is directly dependent on the alkali concentration, which is dependent on m_w/m_c. In this study, the total m_w/m_c of cement pastes are kept constant as 0.50, while with excellent water absorption ability, the SAP particles absorb some water to decrease the actually effective m_w/m_c in cement pastes. Accordingly, by decreasing the effective m_w/m_c the initial pore solution becomes thick with respect to alkali and hydroxide ions, and this subsequently provides more acceleration of cement hydration during the acceleration period of cement pastes with SAP. Therefore, it can be concluded that the SAP still does not release the stored water into cement paste during the acceleration period.

Compared to that of the reference paste, the main exothermic peaks of cement pastes with SAP appear earlier and higher. And the main exothermic peaks appear earlier with the SAP dosage increasing from 0 to 1.0% (Fig. 1b). The SAP increases the main exothermic peak value, but its dosage variation does not substantially affect it. Literature [12, 23] demonstrated that compared to the reference paste, the main exothermic peaks of cement pastes with SAP also occur earlier at low m_w/m_c, but the heights of the main peaks are lower. While Schroefl et al. [25] believed no pronounced effect of SAPs on the appearance of the main exothermic peak. In general, the height of the main exothermic peak increases with m_w/m_c. And the water release by SAP particles can keep a high internal relative humidity in cement paste to promote the hydration of cement [29, 30]. So it can be concluded that the SAP just has begun to release stored water to cement paste at the end of the acceleration period to improve the cement hydration, and accordingly to increase the height of the main exothermic peak. For cement pastes with low m_w/m_c of 0.25–0.42, the water will be released from SAPs by the start of the acceleration period and even earlier in the middle of the induction period [21, 23, 25]. Instead, in this study the SAP releases water into cement paste later up to the end of the acceleration period at a higher m_w/m_c of 0.50. One possible reason is that the higher m_w/m_c hinders the release of stored water from SAP particles. Another possible reason is that the SAP used in this study has much better water absorption and retention ability to store water in its swollen particles.

The SAP also affects the hydration heat evolution rate of the deceleration period. During the early deceleration period from about 17–25 h, the heat evolution rates of cement pastes with SAP are slightly lower than that of the reference paste and decrease with the SAP dosage increasing (Fig. 1b), while during the later deceleration period and the stable period the heat evolution rate nearly equals to that of the reference paste (Fig. 1b), which is similar to the conclusions of literature [12, 23, 25]. The SAP slightly decreases the heat evolution rate during the early deceleration period, but has negligible influence on the heat evolution rates during the later deceleration period and the stable period. According to cement hydration theories [26, 31, 32], during the deceleration and stable periods, the cement hydration is controlled by ions diffusion rate, which increases with the dissipation of liquid phases in cement paste, and ettringites also tend to transform to monosulfates. So the decrease in heat evolution rate of cement paste with SAP during the early deceleration period may be attributed to the decrease in ions diffusion rates with the increase in liquid phases due to the water release by SAP. And the water release fades with hydration time prolongation.

The cumulative hydration heat amounts of cement pastes are shown in Fig. 2. The hydration degrees, calculated as the ratios of the cumulative hydration heat to the theoretic hydration heat of the completely hydrated Portland cement, are shown in Fig. 3. The theoretic hydration heat of the completely hydrated Portland cement is calculated as 468.5 J g^{-1} according to literature [33].

Within 6 h of hydration, the hydration heat and hydration degree of cement pastes are similar, indicating the negligible influence of SAP on the very early hydration. From 6 to 72 h of hydration, the hydration heat and hydration degree of cement pastes with different SAP dosages are similar but are higher than that of the reference paste, indicating the promotion of the SAP on cement hydration after 6 h, with negligible influence of its dosage variation. Therefore, it can be concluded that the SAP can accelerate the cement hydration and increase the hydration degree of cement paste within 72 h of hydration, but its dosage variation has minor effect. Higher hydration degree can partially help compensating for the initial porosity and the strength loss at later ages. Instead, Literature [12, 23] demonstrated that at low m_w/m_c of 0.18–0.30, the hydration degrees are about the same for all cement pastes with and without SAP after 24 h of hydration.

Thermal analysis

The DSC curves of cement pastes at different hydration time are presented in Fig. 4. The calculated contents of $Ca(OH)_2$ in cement pastes are presented in Fig. 5. At 3 and 6 h of hydration, there are four endothermic reactions appearing on the DSC curves of the reference paste and cement paste with 0.4% SAP. The endothermic reactions at about 80 and 120 °C correspond to the free water and the water removal from CSH gels [34], from gypsum, from calcium alumino silicate hydrates [35], and from calcium alumino hydrates, ettringite and sulphoaluminates [36]. The small endothermic reaction at 390–440 °C corresponds

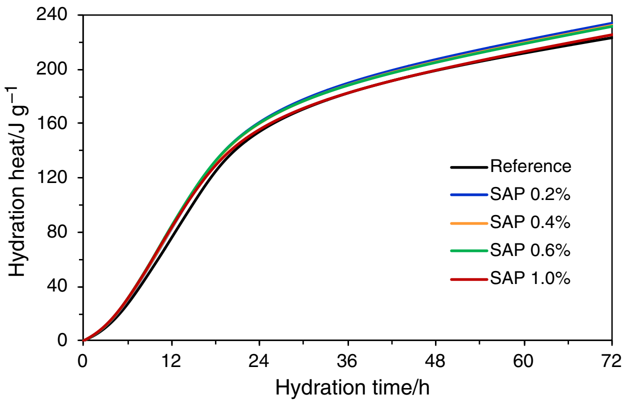

Fig. 2 Cumulative hydration heat of cement pastes

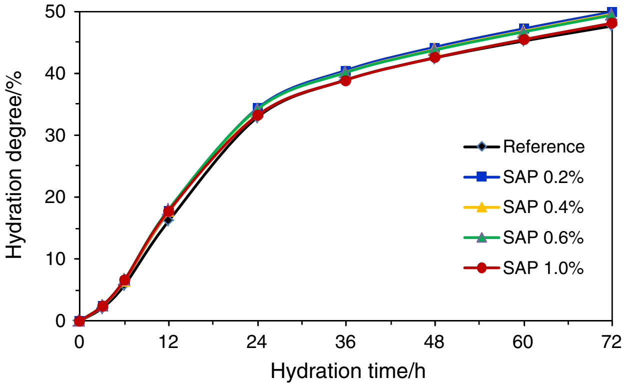

Fig. 3 Hydration degrees of cement pastes

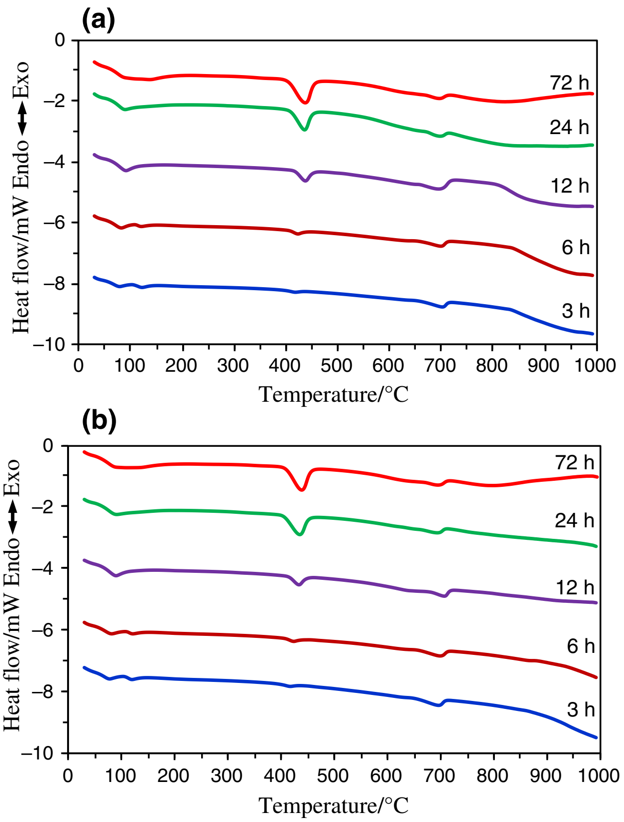

Fig. 4 DSC curves of cement pastes at different hydration time: **a** the reference paste, **b** cement paste with 0.4% SAP

to the $Ca(OH)_2$ decomposition (Fig. 4), indicating the formation of $Ca(OH)_2$ in the reference paste and in cement paste with 0.4% SAP. And the content of $Ca(OH)_2$ in the reference paste is almost equal to that in cement paste with 0.4% SAP (Fig. 5). The SAP does not affect the formation of $Ca(OH)_2$ within 6 h of hydration. The endothermic reaction at 660–720 °C corresponds to the calcium carbonate decomposition, but the reaction peak is not significantly influenced by SAP at different hydration time from 3 to 72 h.

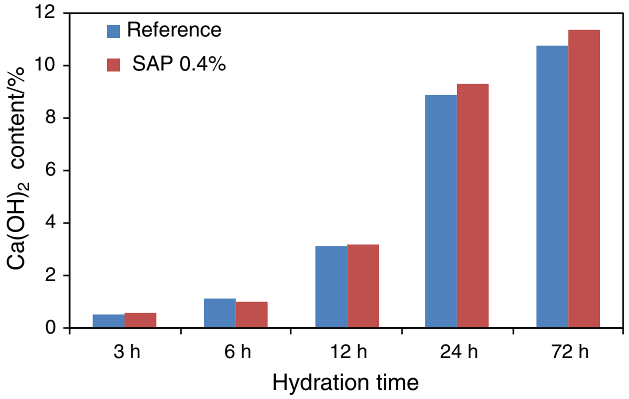

Fig. 5 $Ca(OH)_2$ content of cement pastes at different hydration time

After 12 h of hydration, in cement pastes with and without SAP, these two endothermic reaction peaks at about 80 and 120 °C gradually weaken and a broader endothermic reaction peak appears at 70–150 °C, which is also assigned to the water removal from cement hydrates [34–36]. And the endothermic reaction assigned to $Ca(OH)_2$ gradually enhances and the decomposition temperature of $Ca(OH)_2$ gradually ascends over hydration time (Fig. 4), indicating that more and more $Ca(OH)_2$ have gradually formed in the reference paste and in cement paste with 0.4% SAP. At 12 h of hydration, the content of $Ca(OH)_2$ in cement paste with 0.4% SAP still equals to that in the reference paste. But at 24 and 72 h of hydration, the contents of $Ca(OH)_2$ in cement paste with 0.4% SAP are a little higher than that in the reference paste (Fig. 5). So the SAP enhances the cement hydration to increase the formation of $Ca(OH)_2$ after 12 h of hydration. It is also reported that SAP can increase the content of $Ca(OH)_2$ at 3 and 28 days [37]. But no previous reports in the literature have described the formation evolution of $Ca(OH)_2$ in cement paste with SAP at early hydration time within 72 h.

With the prolongation of hydration time, the decomposition temperature of $Ca(OH)_2$ gradually increases. And at the same hydration time, the decomposition temperature of $Ca(OH)_2$ in cement paste with 0.4% SAP is nearly the same to that of the reference paste (Fig. 4). As is known that the decomposition temperature of $Ca(OH)_2$ mainly depends on the crystallization degree and the crystal size of $Ca(OH)_2$ [34, 35, 38], but is hardly affected by the content variation of $Ca(OH)_2$ [39]. So it may be concluded that the crystallization degree and crystal size of $Ca(OH)_2$ gradually increase over hydration time, but the SAP has negligible effect on them.

X-ray diffraction analysis

The XRD patterns of cement pastes at different hydration time are shown in Fig. 6. The integrated areas of ettringite

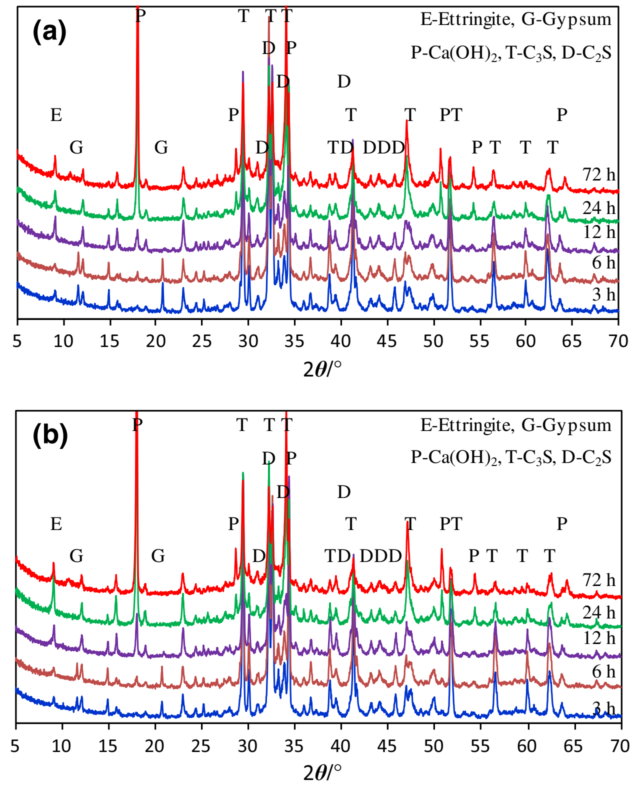

Fig. 6 XRD patterns of cement pastes at different hydration time: **a** the reference paste, **b** cement paste with 0.4% SAP

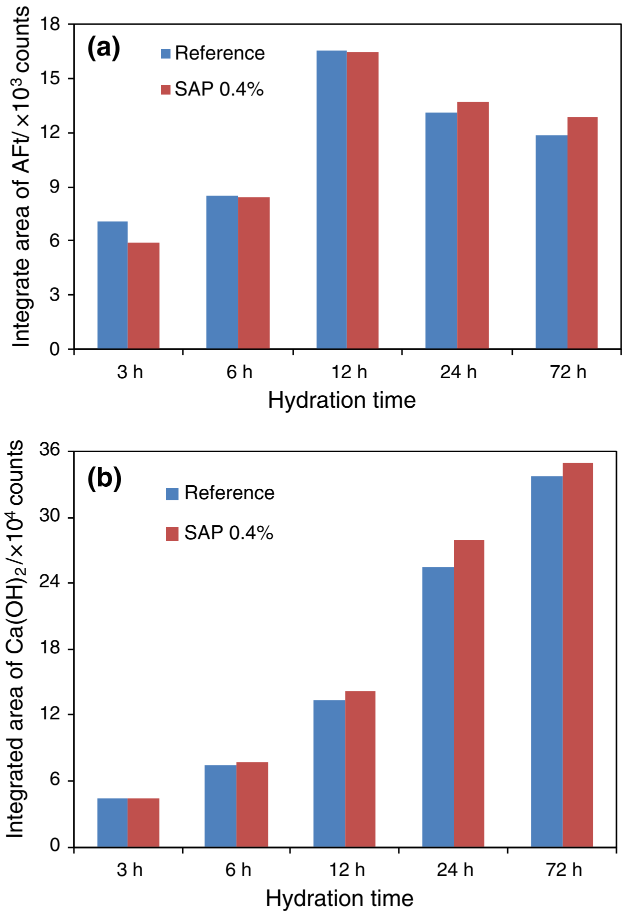

Fig. 7 Integrated area of hydrates in XRD patterns of cement pastes: **a** Ettringite, **b** Ca(OH)$_2$

and Ca(OH)$_2$ calculated from XRD patterns are shown in Fig. 7. At 3 h of hydration, a small peak for ettringite at 2θ of 9.1° appears both in the reference paste and in cement paste with 0.4% SAP (Fig. 6); some ettringite crystals have formed, with lower content in cement paste with 0.4% SAP (Fig. 7a), indicating the slight retardation of SAP on the formation of ettringite at 3 h. At 6 h of hydration, more ettringite crystals have formed, and the contents are equal in these two pastes (Figs. 6, 7a). At 12 h of hydration, the peaks for ettringite further increase and the peak for gypsum disappears, more ettringite crystals have formed, and the contents of ettringite reach the maximum value and are nearly equal in cement pastes with and without SAP (Figs. 6, 7a). It can be concluded that the SAP does not affect the formation of ettringite during the hydration time from 6 to 12 h and the maximum content of ettringite.

At 24 and 72 h of hydration, the peaks and the contents of ettringite gradually decrease (Figs. 6, 7a), due to the conversion of ettringite to monosulphate [40]. But the content of ettringite in cement paste with 0.4% SAP keeps higher than that in the reference paste (Fig. 7a). It is obvious that the SAP delays the conversion of ettringite to monosulphate. The evolution of calcium aluminate hydrates, such as ettringite and monosulphate, is closely related to the shrinkage of cement mortar [41]. Accordingly, the decrease in the drying shrinkage and autogenous shrinkage of cement matrix [3–6] may be attributed to the influence of SAP on the formation and evolution of ettringite.

With hydration time prolongation, the peaks and the contents of Ca(OH)$_2$ gradually increase both in the reference paste and in cement paste with 0.4% SAP (Figs. 6, 7b), which is consistent with the results from thermal analyses presented above. Moreover, at the same hydration time, compared to that of the reference paste, no new peaks appear in the XRD pattern of cement paste with 0.4% SAP, indicating that no new hydrates have formed in cement paste with SAP within 72 h of hydration. While literature [37] reported that the introduction of SAP into cement paste may result in substantial "new" hydration products, but did not demonstrate what the new hydrate is. And no more literature has confirmed the formation of new hydrates in cement paste with SAPs.

Conclusions

The SAP has significant effects on the early hydration process of Portland cement. The SAP does not affect the lengths of the initial reaction period and the induction period and the onset of the acceleration period, but increases the hydration heat evolution rate during the acceleration period and the main exothermic peak value. Compared to the reference paste, the main exothermic peak appears earlier in cement pastes with SAP. Besides, the SAP has slight influence on the heat evolution rate during the deceleration period and the stable period. The SAP can accelerate the cement hydration and increase the hydration degree of cement paste within 72 h of hydration, with negligible influence on the very early hydration of cement within 6 h. And the dosage variation of SAP has minor influence on the heat evolution and hydration degree.

Additionally, the SAP has great influences on cement hydrates evolution according to the results obtained with DSC and XRD analyses. The SAP does not affect the formation of $Ca(OH)_2$ within 12 h of hydration, but enhances the formation of $Ca(OH)_2$ after 12 h to keep slightly higher content than that in the reference paste, with no influence on the crystallization degree and crystal size of $Ca(OH)_2$. The SAP does not affect the maximum content of ettringite, but may have slight retardation on the formation of ettringite at very early hydration time, and delays the conversion of ettringite to monosulphate to remain ettringite content higher than that in the reference paste after 12 h of hydration. In addition, no new phases are found to have formed in cement paste with SAP.

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References

1. Pang LF, Ruan SY, Cai YT. Effects of internal curing by super absorbent polymer on shrinkage of concrete. Key Eng Mater. 2011;477:200–4.
2. Chen DP, Qian CX, Gao GB, et al. Mechanism and effect of SAP for reducing shrinkage and cracking of concrete. J Funct Mater. 2011;38(3):475–8.
3. Wang F, Zhou Y, Peng B, et al. Autogenous shrinkage of concrete with super-absorbent polymer. ACI Mater J. 2009;106: 123–7.
4. Schröfl C, Mechtcherine V, Gorges M. Relation between the molecular structure and the efficiency of superabsorbent polymers (SAP) as concrete admixtures to mitigate autogenous shrinkage. Cem Concr Res. 2012;42(6):865–73.
5. Kong X, Zhang Z, Lu Z. Effect of pre-soaked superabsorbent polymer on shrinkage of high-strength concrete. Mater Struct. 2014;48(9):1–18.
6. Snoeck D, Jensen OM, De Belie N. The influence of superabsorbent polymers on the autogenous shrinkage properties of cement pastes with supplementary cementitious materials. Cem Concr Res. 2015;74(4):59–67.
7. Lee HXD, Wong HS, Buenfeld NR. Potential of superabsorbent polymer for self sealing cracks in concrete. Adv Appl Ceram. 2010;109(5):296–302.
8. Song XF, Wei JF, He TSH. A novel method to improve sulfate resistance of concrete by surface treatment with superabsorbent resin synthesised in situ. Mag Concr Res. 2008;60(1):49–55.
9. Beushausen H, Gillmer M, Alexander M. The influence of superabsorbent polymers on strength and durability properties of blended cement mortars. Cem Concr Compos. 2014;52(4):73–80.
10. Craeye B, Geirnaert M, Schutter GD. Super absorbing polymers as an internal curing agent for mitigation of early-age cracking of high-performance concrete bridge decks. Constr Build Mater. 2011;25(1):1–13.
11. Farzanian K, Pimenta Teixeira K, Perdigão Rocha I, et al. The mechanical strength, degree of hydration, and electrical resistivity of cement pastes modified with superabsorbent polymers. Constr Build Mater. 2016;109(2):156–65.
12. Justs J, Wyrzykowski M, Bajare D, et al. Internal curing by superabsorbent polymers in ultra-high performance concrete. Cem Concr Res. 2015;76(5):82–90.
13. Paiva H, Esteves LP, Cachim PB, Ferreira VM. Rheology and hardened properties of single-coat render mortars with different types of water retaining agents. Constr Build Mater. 2009;23(2): 1141–6.
14. Mechtcherine V, Secrieru E, Schröfl C. Effect of superabsorbent polymers (SAPs) on rheological properties of fresh cement-based mortars—development of yield stress and plastic viscosity over time. Cem Concr Res. 2015;67(1):52–65.
15. Hasholt MT, Jensen OM. Chloride migration in concrete with superabsorbent polymers. Cem Concr Compos. 2015;55(1):290–7.
16. Snoeck D, Schaubroeck D, Dubruel P, De BN. Effect of high amounts of superabsorbent polymers and additional water on the workability, microstructure and strength of mortars with a water-to-cement ratio of 0.50. Constr Build Mater. 2014;72(12):148–57.
17. Sikora KS, Klemm AJ. Effect of superabsorbent polymers on workability and hydration process in fly ash cementitious composites. J Mater Civ Eng. 2015;27(5):1–13.
18. Mönnig S, Lura P. Superabsorbent polymers—an additive to increase the freeze thaw resistance of high strength concrete. Advances in construction materials. Berlin : Springer; 2007. p. 351–8.
19. Igarashi S, Watanabe A. Experimental study on prevention of autogenous deformation by internal curing using super-absorbent polymer particles. In: Int. RILEM conference on volume Changes of hardening concrete: testing and mitigation, RILEM proceedings PRO 52, RILEM publications S. A. R. L; 2006, 77–86.
20. Snoeck D, Velasco LF, Mignon A, et al. The effects of superabsorbent polymers on the microstructure of cementitious materials studied by means of sorption experiments. Cem Concr Res. 2015;77(7):26–35.
21. Nestle N, Kühn A, Friedemann K, et al. Water balance and pore structure development in cementitious materials in internal curing with modified superabsorbent polymers studied by NMR. Microporous Mesoporous Mater. 2009;125(1–2):51–7.
22. Reinhardt HW, Assmann A. Time dependent behavior of SAP modified concrete. In: Application of superabsorbent polymers and other new admixtures in concrete construction, RILEM proceedings PRO 95, RILEM publications S.A.R.L., Bagneux; 2014, 235–43.

23. Justs J, Wyrzykowski M, Winnefeld F, et al. Influence of superabsorbent polymers on hydration of cement pastes with low water-to-binder ratios. J Therm Anal Calorim. 2014;115(1): 425–32.
24. Zhutovsky S, Kovler K. Hydration kinetics of high-performance cementitious systems under different curing conditions. Mater Struct. 2013;46(10):1599–611.
25. Schroefl C, Mechtcherine V, Vontobel P, et al. Sorption kinetics of superabsorbent polymers (SAPs) in fresh Portland cement-based pastes visualized and quantified by neutron radiography and correlated to the progress of cement hydration. Cem Concr Res. 2015;75(5):1–13.
26. Bullard JW, Jennings HM, Livingston RA, et al. Mechanisms of cement hydration. Cem Concr Res. 2011;41(12):1208–23.
27. Langan BW, Weng K, Ward MA. Effect of silica fume and fly ash on heat of hydration of Portland cement. Cem Concr Res. 2002;32(7):1045–51.
28. Danielson U. Heat of hydration of cement as affected by water/cement ratio. In: Fourth international symposium of the chemistry of cement. Washington DC; 1960.
29. Jensen OM, Hansen PF. Water-entrained cement-based materials II. Experimental observations. Cem Concr Res. 2002;32(6):973–8.
30. Wyrzykowski M, Lura P, Pesavento F, Gawin D. Modeling of internal curing in maturing mortar. Cem Concr Res. 2011;41(12): 1349–56.
31. Thomas JJ, Biernacki JJ, Bullard JW, et al. Modeling and simulation of cement hydration kinetics and microstructure development. Cem Concr Res. 2011;41(12):1257–78.
32. Gallucci E, Mathur P, Scrivener KL. Microstructural development of early age hydration shells around cement grains. Cem Concr Res. 2010;40(1):4–13.
33. Schindler AK, Folliard KJ. Heat of hydration models for cementitious materials. ACI Mater J. 2005;102(1):24–33.
34. Kontori E, Perraki T, Tsivilis S, et al. Zeolite blended cements: evaluation of their hydration rate by means of thermal analysis. J Therm Anal Calorim. 2009;96(3):993–8.
35. Chaipanich A, Nochaiya T. Thermal analysis and microstructure of Portland cement-fly ash-silica fume pastes. J Therm Anal Calorim. 2010;99(2):487–93.
36. Pacewska B, Blonkowski G, Wilinska I. Investigations of the influence of different fly ashes on cement hydration. J Therm Anal Calorim. 2006;86(1):179–86.
37. Esteves LP, Lukošiūtė I, Čėsnienė J. Hydration of cement with superabsorbent polymers. J Therm Anal Calorim. 2014;118:1385–93.
38. Menendez E, Andrade C, Vega L. Study of dehydration and rehydration processes of portlandite in mature and young cement pastes. J Therm Anal Calorim. 2012;110(1):443–50.
39. Ray I, Guptab AP, Biswas M. Physicochemical studies on single and combined effects of latex and superplasticiser on portland cement mortar. Cem Concr Compos. 1996;18(5):343–55.
40. Taylor HFW. Cement chemistry. 2nd ed. London: Thomas Telford Publishing; 1997.
41. Bensted J, Barnes P. Structure and performance of cements. 2nd ed. New York: Spon Press; 2008.