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Review Article

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A review on the effect of organic admixtures containing different functional groups on the hydration behaviors of Portland cement

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Abstract: In order to adapt to the complex service environment, the rational application of organic admixtures has become one of the important means of preparing high-performance cementitious materials. The type and functional groups of organic admixtures are crucial to the hydration degree and strength development of Portland cement. Here, the main chemical reactions occurring in different hydration stages and corresponding hydration mechanism of Portland cement were explicated in detail. On this basis, the influence feature and mechanism of organic admixtures containing different functional groups on the overall process and different stages of cement hydration were systematically reviewed. The statistical results show that organic admixtures mainly affect the induction and acceleration periods of cement hydration, and the hydration effect is closely related to the molecular weight, molecular structure, functional groups and charges of organic admixtures. Most of the organic admixtures will prolong the hydration induction period, and the corresponding effect on the hydration acceleration period varies greatly. The mainstream influence mechanisms of organic admixture include complexation and adsorption theories. Some new theories such as “self-assembly of hydration products” are also put forward, but need to be further verified.

Keywords: Portland cement; organic admixtures; functional groups; effects of hydration; hydration mechanism

1 Introduction

Service environment of Portland cement is complex and diverse, and the performance requirements vary greatly in different environments. In order to meet the requirements of different properties of those materials, inorganic/organic admixtures, fiber, and nanomaterials have been widely applied.[1–5] As one of the common cement and concrete admixtures, organic admixtures (Commonly used organic admixtures are shown in Table 1) have the advantages of variety, comprehensive performance and good improvement effect. The organic admixtures with unique molecular structure may have high toughness, elasticity, corrosion resistance, and water resistance and unique properties that are hardly possessed by other types of materials. Organic admixtures introduction can significantly improve the properties of the corresponding cementitious materials such as high brittleness, poor durability and other defects.[6–9] (It is important to note that the effects are the result of the coupling of multiple factors such as the hydration conditions, material ratios, and the type of hydration products, etc.) Eventually, organic-cementitious materials have gradually formed a class of composite materials with novel properties of both organic and inorganic material, which are widely used in the field of building materials.

Organic molecules can change the ionic concentration of the cement paste by electrostatic adsorption and complexation to influence the dissolution-precipitation process of cement.[10–12] The size, structure, electrical properties and functional groups of different types of organic molecules vary greatly, so that there are obvious differences in their effects on cement hydration,[13,14] which also leads to the investigation of the effects of organic admixtures on cement hydration is often difficult. The effects of the electrical properties and functional groups of organic molecules on cement hydration are relatively more obvious, and the results are more abundant at the present stage.[15,16]

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Table 1: Main chemical components, key functions and examples of organic admixture.

Organic admixture	Main components	Key functional groups
Retarder	Acid containing carboxyl groups	-COOH
	Polyol	-OH
	Sugar	
Early strength agent	Alcohol-ammonia	\
Superplasticizer	Naphthalene-based superplasticizer	Naphthalene, $-SO_3Me$
	Sulfamate-based superplasticizer	$-NH_2$, $-SO_3Me$
	Melamine-based superplasticizer	$-SO_3Me$
	Polycarboxylic acid superplasticizer	-COOH, $-SO_3Me$, – COOR, et al.
Air-entraining agent	Rosin thermopolymer	-COOH
	Alkylbenzene sulfonate	Benzenesulfonic acid
Other organic polymers	Polyacrylate	-COOR–COOH
	Ethylene vinyl acetate	-COOH
	Styrene-acrylic emulsion	-COOH

However, researches on the effect of organic admixtures on hydration are mainly concerned with the effect on the overall hydration degree of Portland cement, and there is a certain conflict between the different results. Even if the effects of different functional groups on its hydration have occasionally collated, there is a lack of analysis on the effects of different hydration stages. In contrast, this article not only discusses the effect of organic admixtures containing different functional groups on the early hydration degree, but also explores the effect of functional groups in admixtures on different hydration stages and the influence mechanism (Note that when summarizing and analyzing data from the references, it is necessary to ensure that the cementitious system is consistent. And, also make sure that all other properties of the organic admixture are consistent except for the type or molar amount of the functional group to be analyzed (one of the two). Or the differences are not sufficient to affect cement hydration.), and summarizes a set of more comprehensive theory system for "organic admixtures – Portland cement hydration" relation. It provides a theoretical basis for the rational concrete application of organic admixtures in different scenarios.

2 Hydration mechanism of Portland cement

In-depth understanding of the principle of hydration dynamics of Portland cement helps the development of related technologies, such as the rational application of Portland cement materials and the research and development of cement admixtures.[17–20]

The nature of cement hydration is a dissolution-precipitation process, which is the coupling of a series of chemical actions.[21–23] The specific interactions include dissolution, diffusion, nucleation, growth, precipitation[24–27] and, in most cases, complexation and adsorption among ions and molecules.[28,29] The reactivity of each action process is determined by the properties of the reaction itself and the real-time state of the reaction system.[30,31]

Figure 1 exhibits the hydration heat flow and specific mineral reactions at different hydration stages of Portland cement, containing the following four reaction stages.

2.1 Initial period

The hydration heat at this stage comes mainly from the dissolution and precipitation exotherm of the tricalcium aluminum phase clinker (C_3A, gypsum) and some of the dissolution of the alite phase (C_3S).[32–34] Cement clinker dissolves fast in this phase because the concentration of each substance in the solution is very low, the degree of undersaturation of the solution is very high. Coupled with the exothermic reaction of the C_3A clinker, the final result shows high hydration heat at this stage.

2.2 Induction period

In this phase, the hydration heat mainly comes from the slow precipitation of ettringite (AFt) and the slow dissolution of C_3S clinker, and the slow formation of calcium silicate hydrate (C–S–H) crystal nuclei.[31,35] The reasons for the emergence of the induction period have been focus reported, and there are numerous and inconclusive theories. The most mainstream theories include metastable barrier hypothesis [36] and slow dissolution step theory.[37–39]

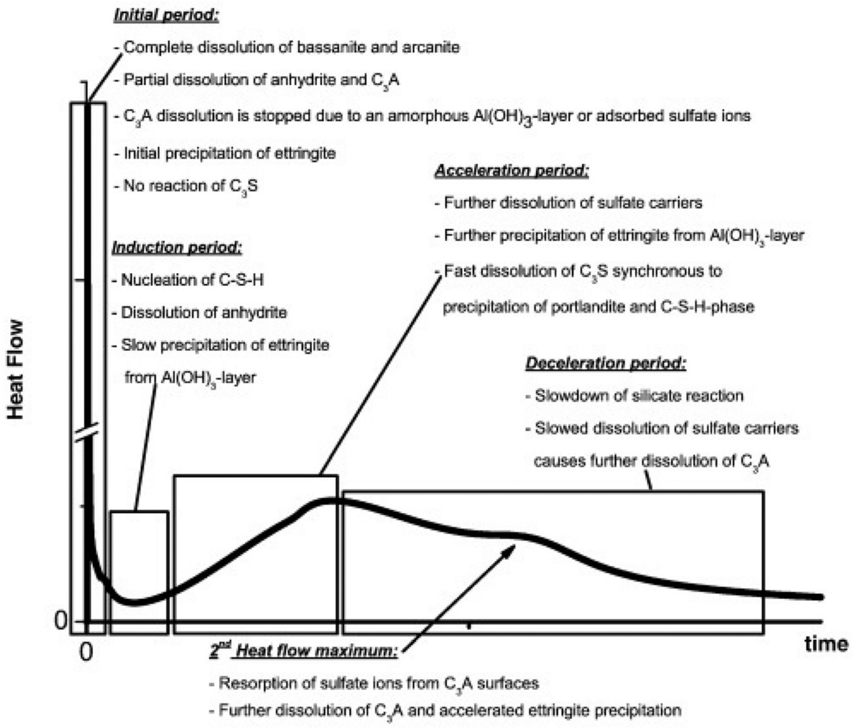

Figure 1: Hydration heat curve and mineral reactions of Portland cement at different stages of hydration.[31]

2.3 Acceleration period

In this period, cement clinker dissolves rapidly, hydration products are generated in large quantities, and the hydration heat rises gradually. Reaching the acceleration period faster is the key to shortening the condensation time and obtaining a higher early strength.[40,41] Currently, the increase in C–S–H nucleation results in accelerated hydration has become dominant.[42,43]

2.4 Deceleration period

The exothermic heat in this period mainly comes from silica-phase hydration. The decreasing of the hydration heat is due to the fact that when the hydration products quantity is enough, it will cover the cement clinker, resulting in the limitation of the solubility of clinker.[44]

3 Effect of organic admixtures containing different functional groups on the Portland cement hydration

At present, scholars mostly analyze the effect of organic admixtures on Portland cement hydration from two perspectives: the type of functional groups and the electrical properties of organic molecules.[45,46] It is worth noting that functional groups of organic admixture can influence or even determine to some extent the structure, electrical properties and complexing ability of molecules.[47–50] They can significantly affect the chemical reactions and physical interactions between the polymer molecules of organic admixture and the ionic or mineral components of the Portland cement system. Currently, the functional groups such as hydroxyl, alcohol-ammonia, carboxyl, sulfonic acid, phosphoric acid, and silane/silanoxy groups are commonly founded in organic admixtures.

3.1 Effect of organic admixtures containing hydroxyl groups on Portland cement hydration

With hydroxyl as the main functional group of organic admixtures mainly include sugar alcohols, and so on. Sugar alcohols are often used as a retarder in the control of rheological properties of cementitious materials. According to the retardation effect can be roughly divided into three categories: the strongest retardation effect for the five-membered ring structure of the non-reducing sugar, including sucrose, cotton seed sugar, etc. Reducing sugar retardation effect is slightly weaker, but can still be used as a good retardant, including glucose, maltose and lactose, etc.

The cement hydration effect is minimized by the non-reducing sugar, including methylglucose, alginate, and so on.[51]

Although some sugar alcohols mainly play the role of retarder in the hydration process, they are not detrimental to the degree of cement hydration. Precisely speaking, most sugar alcohols in the cement hydration process to play a “hydration acceleration delay agent” effect (To extend the hydration induction period, delay the arrival of acceleration period). Cheung et al.[52] found that sugar alcohols on the early cement hydration had a certain effect, but did not significantly reduce the degree of hydration in the middle and late hydration. Although sugar alcohols reduced the degree of early hydration (Figure 2a)), only threitol significantly prolonged the cement setting time, xylitol and sorbitol had less effect on the setting time, and sucrose even significantly shortened the cement setting time (Figure 2b)). Bishop and Barron [53] found that AFt formation was accelerated after sucrose was incorporated into the mixture of C_3A and gypsum, which explained the sucrose accelerated cement setting. Perenchio [54] found that adding sucrose significantly increased the rate of sulfate consumption during early hydration of Portland cement. Consumption of Ca^{2+} by sucrose in solution led to further dissolution of calcium sulfate, which increased the availability of SO_4^{2-} and accelerated AFt production. It could be seen that the effect of “hydration acceleration delay agent” is not significant for clinkers such as C_3A.

C_3S, as the main clinker in cement,[55] is the main receptor for the “hydration acceleration delay agent” effect (Figure 3). The relative ability of sugar alcohols to retard the hydration of C_3S is mainly related to two factors. First, the size of the sugar alcohol molecule (carbon chain length and the number of carbon rings) and the total number of hydroxyl groups. The second is the molecular configuration (the number of threo neighboring hydroxyl groups). In general, the larger is the molecular weight and the higher is the number of hydroxyl groups of the sugar alcohol molecules, the stronger is their relative ability to retard the hydration of C_3S.[56] It should be noted that even at the same molecular size and hydroxyl group amount, the differences in the retardation effect of different sugar alcohols are still very obvious. It is mainly attributed to the number of threo neighboring hydroxyl groups is different (Threo is an isomer whose two identical substituents are on opposite sides in the Fischer projection formula. The erythro is the opposite, as shown in Figure 4(a)). Nalet et al.[56] found that the more is threo neighboring hydroxyl groups in the sugar alcohol molecule, the more obvious is inhibition of C_3S hydration. Moreover, the neighboring arrangement of threo neighboring hydroxyl groups has a stronger inhibitory effect than the crossing arrangement. For example, the three sugar alcohols inhibited C_3S hydration as follows: D-glucitol (threo-threo-erythro) > D-galactitol (threo-erythro-threo) > D-mannitol (thréthro-erythro-erythro), as shown in Figure 4(b).

Besides sugar alcohols, common hydroxyl-containing organic admixtures include ethanol, ethylene glycol and propylene glycol, etc. Most of the above materials are small organic molecules containing hydroxyl groups. Studies have shown that most of these have little effect on cement hydration and basically do not affect the induction period and the maximum hydration rate. It is worth noting that propylene glycol and propanetriol can promote the secondary hydration of aluminum-phase clinkers, which increases the peak hydration rate at the end of the acceleration period of cement hydration to a certain extent.[43]

3.2 The effect of alcohol-ammonia organic admixtures on Portland cement hydration

Alcohol-ammonia admixtures are usually used as grinding aids or early-strengthening agents for cementitious materials. Commonly used ones include triethanolamine (TEA),

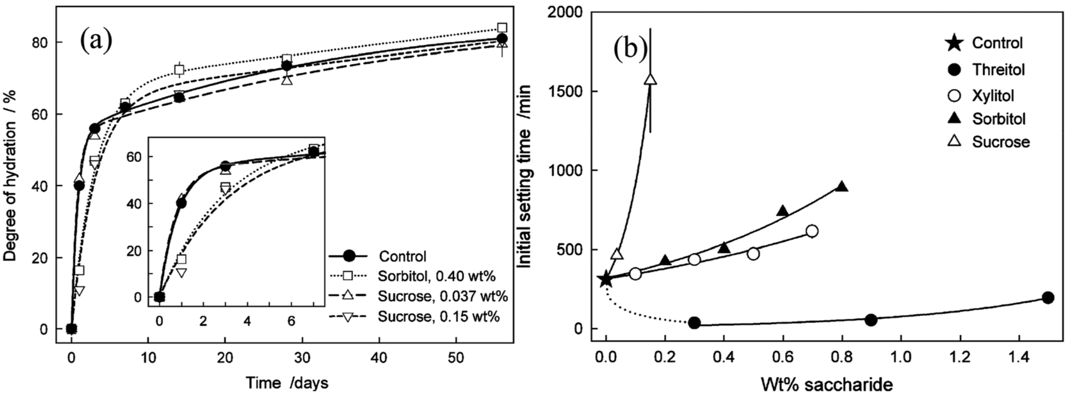

Figure 2: Effect of different sugar alcohols on the degree of hydration and setting time:[52] a) Degree of hydration; b) setting time.

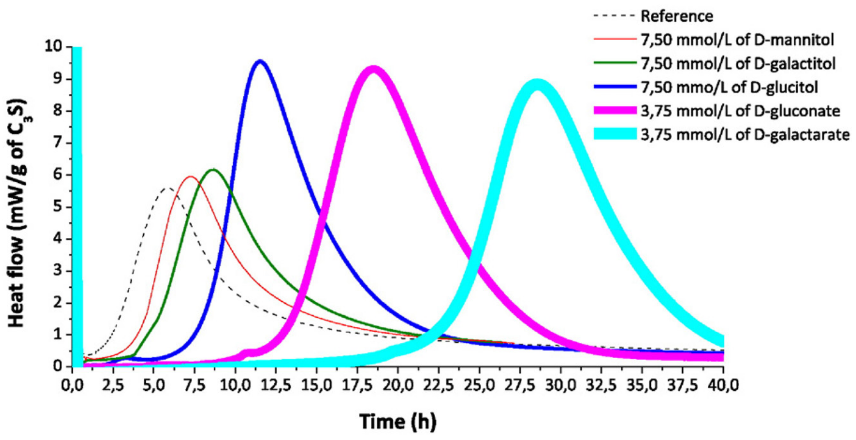

Figure 3: Effect of different sugar alcohols on the exothermic process of C_3S hydration.[56]

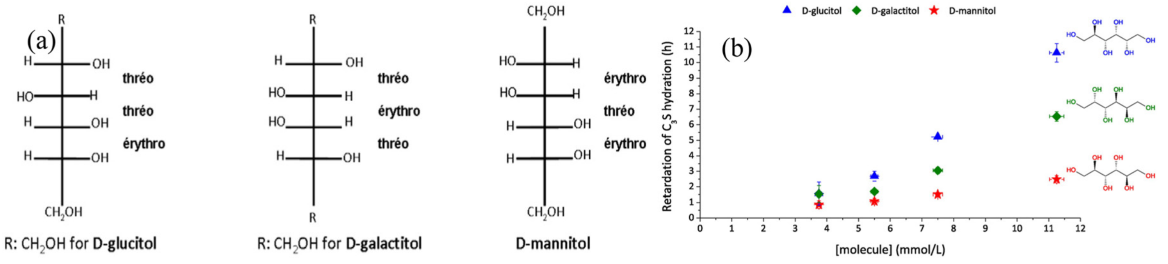

Figure 4: Fisher's projections of three different molecular configurations of sugar alcohol molecules and their effect on the hydration degree of C_3S:[56] a) Fisher's projections; b) effect on the hydration degree of C_3S.

triisopropanolamine (TIPA), methyldiethanolamine (MDEA), diisopropanolamine (DIPA), and other kinds of alkanolamines. Wu et al.[57] found that TEA could promote the C_3A hydration to produce AFt, which improved the early hardening strength of cement. However, it would prolong the induction period of C_3S to a certain extent, but even so, TEA still led to an overall increase in the early strength of hardened cement, and TIPA was able to complex with Fe^{3+}, which in turn promoted the C_4AF hydration and improved the late strength. Lu et al.[43] studied the effect of different alcohol-ammonia admixtures on cement hydration. From Figure 5(a), it could be seen that alcohol-ammonia caused a bimodal distribution of the peak hydration rate in the accelerated period of hydration (only TEA had a weaker effect). It was because alcohol-ammonia effectively promotes aluminum-phase secondary dissolution and AFt precipitation, but did not do so for the silica-phase. Moreover, the hydration induction period was prolonged after the addition of alcohol-ammonia. However, at the same time, Figure 5(b) showed that the total hydration exotherm did not decrease and even increased, indicating that alcohol-ammonia could improve the hydration degree to some extent. And, with the increase of the amount of methyl in the alcohol-ammonia molecule, the appearance of the second shoulder of the bimodal peaks was delayed. It indicated that the methyl delayed the secondary dissolution of C_3A and the precipitation of AFt.

3.3 Effect of organic admixtures containing carboxyl groups on the Portland cement hydration

There is a wide variety of compounds containing carboxyl groups that can be used in cementitious materials, such as carboxylic acid organic small molecules, water-soluble polymers and polymer emulsions with carboxyl groups. The carboxyl groups can greatly influence the hydration of cement based on their electrical properties and their complexation with ions in the cementitious system.[58–60]

Organic small molecules, as polymerization monomers of polymeric materials, determine the properties of polymers to a large extent. However, organic small molecules containing carboxyl groups are rarely used in cementitious materials, due to their weak influence on cement hydration. Chaudhari et al.[61] compared the effect of acetic acid and glycolic acid on cement hydration by means of experiments and molecular dynamics simulations. Acetic acid had essentially no effect on cement hydration, whereas glycolic acid significantly retarded cement hydration, which was

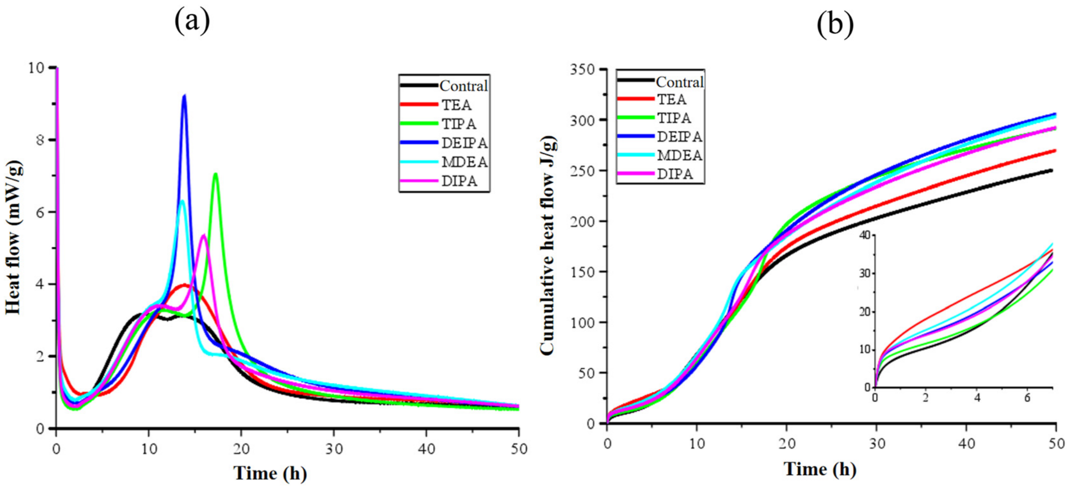

Figure 5: Effect of different alcohol-ammonia on hydration exothermic rate and exothermic amount of cement:[43] a) Exothermic rate; b) exothermic amount.

suggested to be related to the complexation of both with Ca^{2+}. Calcium glycolate's adsorption on the surface of C_3S and CH was stronger, which would hinder the dissolution of C_3S and the precipitation of CH. Actually, the commonly used organic small molecules containing carboxyl groups tend to prolong the induction period and also reduce the peak hydration rate of cement to a small extent.[62] In general, the higher is the amount of carboxyl groups, the more pronounced is the inhibition of hydration. Besides, the molecular structure is also one of the important reasons for the inhibition effect. Lu et al.[43] tested the effect of glycolic acid, propanedioic acid, succinic acid and itaconic acid on the exothermic rate of cement hydration under the same carboxyl group molar mass. The results showed that except for malonic acid, the effect of prolonging the induction period with increasing molecular chain length was stronger, and the peak exothermic rate and total exothermic amount decreased more. It was also worth noting that the larger is the spacing between carboxyl groups, the stronger is the inhibition of hydration under the same molecular chain length. It was speculated that this might be related to the adsorption between small molecules with different structures and cement particles.

Polycarboxylic acid (PCA) water-soluble macromolecules are the most commonly used organic admixtures for cementitious materials. They play irreplaceable roles in improving the compatibility of cementitious materials and preparing high strength and performance concrete materials. Jansen et al.[63] tested the effect of PCA superplasticizers on the hydration of C_3A phase by *in situ* XRD. As shown in Figure 6, the PCA superplasticizers prolonged the initial dissolution time of anhydrous gypsum to 12.5 h, with a delay of 5.9 h, and prolonged the rapid dissolution time of C_3A to 16.3, with a delay of 3.8 h. It was suggested that this was a result of the carboxyl groups complexing a large amount of Ca^{2+}, which in turn led to the impeded AFt precipitation. PCA superplasticizers not only inhibited the hydration of aluminum phase significantly, but also weakened the C_3S hydration to a certain extent, as proved by Zhang et al.[64] Different types of PCA superplasticizers could prolong the induction period and reduce the peak rate of C_3S hydration to different degrees. The retardation effect was closely related to the adsorption caused by the charge of the PCA molecules and the strength of the complexation between carboxyl groups and Ca^{2+}.

It is well known that the water reducing effect of PCA superplasticizer depends on its molecular structure. In fact, the molecular structure is also the key factor affecting the cement hydration without considering the existence of complex functional groups.[65] The molecular structure of PCA superplasticizers mainly consists of carboxyl group-containing main chains and long side chains. Among them, the carboxyl groups can play the roles of anchoring and adsorbing on the surface of cement particles, and the long side chains will extend to the pore solution and play the steric effects to disperse the cement particles.[66] Zhu et al.[67] found that the longer is the carbon chain and the more complex is the branched chain of PCA superplasticizer molecules, the stronger is its effect on C_3A to retard hydration. It's also proved that the molecular side chains have a significant effect on the hydration rate and the morphology of hydration products. With the increase of molecular weight of long side chains, the C_3A hydration was further slowed down, and the generation rate of $Al(OH)_3$ and C_2AH_8

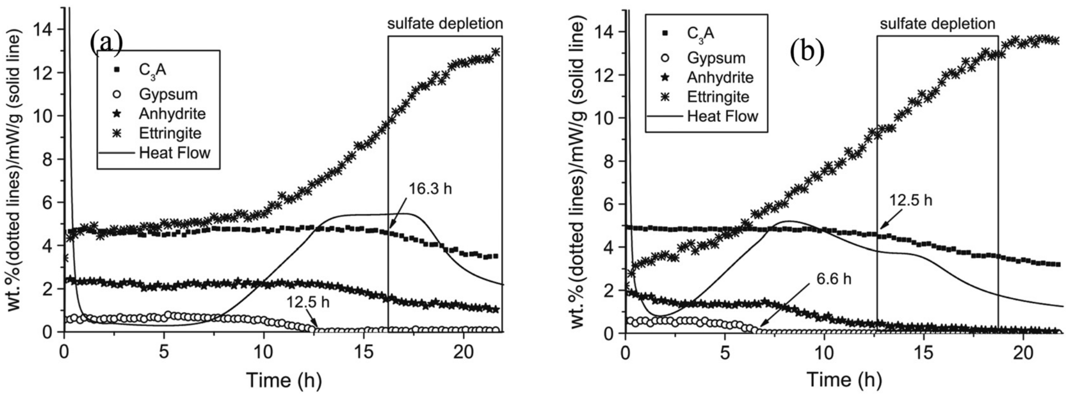

Figure 6: Hydration curves of aluminum phase clinker in cement:[63] a) Without superplasticizers; b) with superplasticizers.

was reduced. With the increase of molecular proportion of long side chains, the generation rate of $Al(OH)_3$ and C_2AH_6 was also reduced, but it was easier to observe C_2AH_8 in the hydration products. Moreover, the more carboxyl groups in the PCA molecules, it was easy to produce more flake-like C_2AH_6. Carboxylic acid polymer molecular structure is not only able to change the hydration process of the aluminum phase clinker, but also has a significant effect on the silica phase and even the overall cement hydration. Kong et al.[68] deeply investigated the effects of carboxyl group density, molecular weight and side chain structure of PCA superplasticizer molecules on the hydration process of cement. Firstly, the higher is the molecular carboxyl group density, the more significant is the hydration inhibition effect of initial and induction period hydration. It was due to the fact that the increase in carboxyl group density made the molecules be easier to adsorb on the positively charged C_3A and C_4AF surfaces, and the increase in carboxyl groups would promote Ca^{2+} complexation, both of which were detrimental to the early hydration of cement particles. However, it was important to note that before the carboxyl group density reached the critical threshold, the negative effect of the superplasticizer molecules on the hydration degree in the middle and late stages of hydration gradually weakened with the increase of the carboxyl group density. It was attributed to the fact that the tightly adsorbed superplasticizer molecules could better disperse the cement particles (Figure 7(a)), which was favorable to the later hydration. However, when the density of carboxyl groups was too high, the superplasticizer molecules were prone to further copolymerization, resulting in excessively long molecular main chains. Instead, it would cause agglomeration of adsorbed particles, which was not conducive to the hydration of cement. Secondly, the larger is the molecular weight, the stronger is the adsorption capacity and the stronger is the retardation effect. According to its research results, it was presumed that the main retardation mechanism of superplasticizer molecules with high molecular chain was that a single molecule adsorbed multiple cement particles at the same time leading to their agglomeration and hindering hydration, as shown in Figure 7(b). Thirdly, the shorter is the molecular side chains, the stronger is the retarding effect and the lower is the degree of hydration. Long side chains made it be difficult to approach the anionic sites. And with the increase of the proportion of long side chains, the adsorption of the superplasticizer molecules on the cement particles decreased, and then the hydration inhibition effect was weakened.

Besides water-soluble polymers, polymer emulsions containing carboxyl groups are also widely used in cementitious materials. Commonly used ones include ethylene vinyl acetate emulsions (EVA), styrene-acrylic emulsions (SA) and highly carboxylated polymer emulsions.[28,69,70] These polymers are characterized by often containing a larger variety of major functional groups and more complex effects on cement hydration. By studying the mechanism of SA and EVA on cement hydration, Wang et al.[71] found that both types of emulsions are hydrolyzed under alkaline conditions to produce the corresponding PCA or acetic acid. The carboxyl groups in the acid complexed with Ca^{2+}, which in turn affected the cement hydration process. Lu et al.[72] found that highly carboxylated polystyrene emulsions had a significant inhibitory effect on cement hydration. But they believed that this effect mainly originated from the adsorption of carboxyl groups on cement clinkers, which inhibited the nucleation sites, rather than the complexation of the molecules with Ca^{2+}.

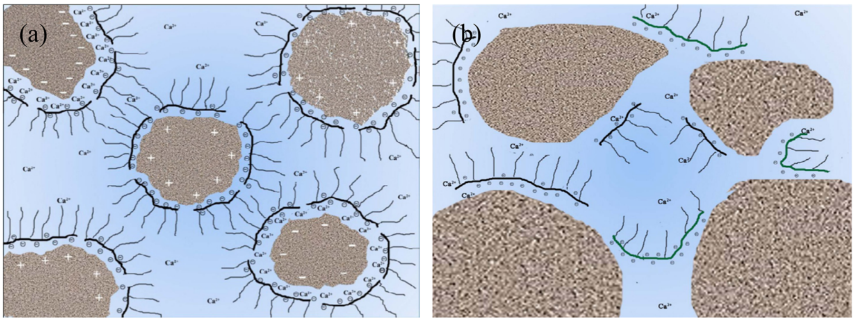

Figure 7: Schematic diagram of PCA superplasticizer molecules adsorbed on the surfaces of cement particles:[65] a) PCA molecules dispersing cement particles; b) molecules with longer main chains adsorbed on the multiple particle surfaces.

3.4 Effect of organic admixtures containing sulfonic groups on the Portland cement hydration

The sulfonic group is similar to the carboxyl group and is often used as a reactive group in admixtures for cementitious materials. Sulfonic groups dissociate in alkaline solutions to form anionic groups with negative charges and strong adsorption property.

He et al.[73] investigated the effect of PCA superplasticizer admixtures with some of the carboxyl groups replaced by ester groups (PEG_1-$AA_{3.5}$-$ES_{0.5}$), amide groups (PEG_1-$AA_{3.4}$-$AM_{0.6}$), and sulfonic groups (PEG_1-$AA_{3.8}$-$SA_{0.2}$) on the hydration of the cement, respectively (Figure 8). The results showed that all organic admixtures containing different functional groups prolonged the induction period. The effect was enhanced by the substitution of some carboxyl groups by ester and amide groups, but the delaying effect was weakened by the introduction of sulfonic groups. And the peak hydration rate at the end of the accelerated period was also slightly increased (Figure 8(a)). From the figure of total heat release after 48 h of hydration (Figure 8(b)), it could be seen that, except for the superplasticizer molecules with sulfonic groups replacing part of the carboxyl groups which could increase the degree of hydration by a very small amount, all the other admixtures would reduce the degree of hydration to some extent, and the magnitude of the reduction would be small. It was suggested that the sulfonic group retarded the nucleation of hydration products more weakly than the carboxyl group because of the difference in complexation between the two and Ca^{2+}, but no clear explanation was given. It was worth mentioning that He et al. found that the adsorption properties of superplasticizer molecules were enhanced after the introduction of sulfonic groups. It was due to the presence of double negative charge groups of carboxyl and sulfonic groups, which provided the molecules with stronger electrostatic adsorption, and increased electrostatic attraction to the aluminum phase. It conflicted with the results of Zhang et al.[64] who studied the adsorption and effect on cement hydration of PCA and polysulfonic acid homopolymers polymerized from acrylic acid and sodium styrenesulfonate monomers, respectively. The results showed that both PCA and polysulfonic acid homopolymer had strong adsorption on the surface of cement particles, but the PCA homopolymer was stronger. It was due to the strong complexation of carboxyl groups with Ca^{2+}, and the negatively charged silica phase clinker surfaces enriched with Ca^{2+} was able to complex many PCA molecules (Figure 9). In fact, the adsorption of molecules on the cement particle surfaces was not the result of pure electrostatic adsorption, but the molecular structure, intermolecular forces and entropy effects also had a significant influence on the adsorption.[74] The study of the exothermic hydration process revealed that both homopolymers prolonged the induction period and reduced the peak hydration rate, which was not conducive to early hydration. Zhang et al. suggested that the effect was related to molecular adsorption and complexation. The PCA molecules with stronger adsorption capacity could hinder the ionic diffusion of the cement minerals into the liquid phase, which had a stronger hydration inhibition effect.

3.5 Effect of organic admixtures containing phosphate groups on the Portland cement hydration

The introduction of phosphate groups in the synthesis process of PCA superplasticizer forms a new type of superplasticizer containing phosphate group, which can be called polyphosphate superplasticizer. Monophosphate group has stronger adsorption compared with monocarboxyl group,[75] so polyphosphate superplasticizer can disperse cement particles, improve the fluidity of cementitious materials and reduce viscosity more effectively.[76,77] At the same time, the introduction of phosphate groups will also have a non-negligible effect on cement hydration.

Stecher et al.[78] synthesized a polyphosphate superplasticizer using 2-(methacryloxy) ethyl phosphate and ethylene glycol methacrylate macromolecules and investigated

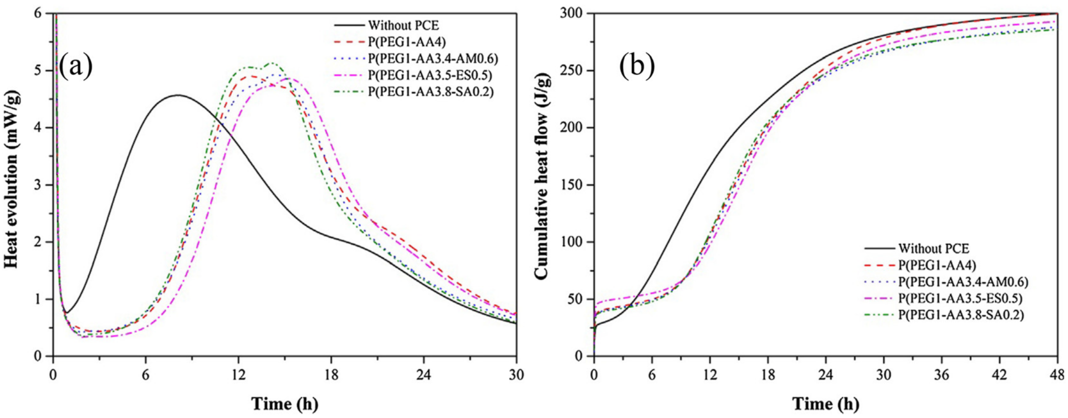

Figure 8: Effects of different types of superplasticizers on cement hydration:[70] a) Heat evolution; b) cumulative heat flow.

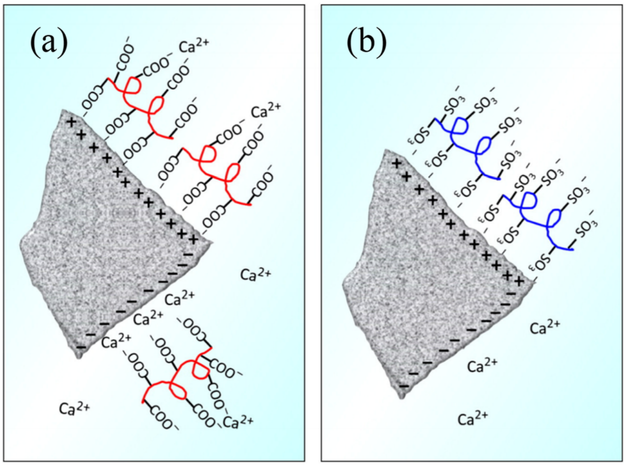

Figure 9: Mechanism of two polymers adsorbed on the surfaces of cement clinkers:[64] a) Admixtures containing carboxyl groups; b) admixtures containing sulfonic groups.

the differences in performance between them and PCA superplasticizers. The results showed that both polymers retarded cement hydration without reducing the peak hydration rate. While the polyphosphate superplasticizer had a relatively weak retarding effect. It was also noted that the same number of phosphate groups had twice the charge of carboxyl groups in the liquid phase, so that the phosphate groups had a significantly stronger complexation with Ca^{2+} than the carboxyl groups. In fact, Stecher realized that there was a certain contradiction in his conclusion. They thought the effect of organic molecules on hydration inhibition was related to the ability to adsorb and complex Ca^{2+} (The stronger the adsorption and complexation, the stronger the inhibition of hydration), but his findings did not follow this pattern. The test results of Qian et al.[79] were slightly different from the above. The retardation effect of polyphosphate superplasticizer was found slightly weaker than that of PCA superplasticizer. It might be due to the difference in the molecular structure of the polyphosphate superplasticizer (The present polyphosphate superplasticizer was produced by the polymerization of isopropylenephosphoric acid and isopentenol polyoxyethylene-polyoxypropylene ether). In terms of adsorption, the results were similar to those of Stecher, but with a different explanatory mechanism. Qian attributed the greater adsorption of the polyphosphate molecule to the difference in the hydrodynamic radii of the molecules. Compared with PCA molecules, polyphosphate superplasticizer molecules had smaller hydrodynamic radii and higher degrees of freedom in the cement pore solution, which enabled them to be rapidly dispersed and adsorbed on the surfaces of cement particles. The results differentiation also reflected that although there were differences in the effects of phosphate and carboxyl groups on hydration, they were not the decisive factors.

3.6 Influence of organic admixtures containing silaneoxy groups on the Portland cement hydration

Silaneoxy groups can be hydrolyzed to obtain highly reactive silicone hydroxyls, which can be dehydrated and condensed with other hydroxyls to form Si–O-X. The bonding is a strong chemical interaction, which is significantly stronger than that of electrostatic adsorption. Therefore, in general the admixtures containing silaneoxy can realize the close adsorption or bonding of organic-inorganic and organic-organic interfaces. However, it should be noted that when the content of silaneoxy group is too large, the silanes are prone to polycondensation between each other, forming polymers, and which is not conducive to the bonding behavior of silanes.[80] The main admixtures containing silaneoxy commonly used in cementitious materials are silaneoxy superplasticizer, hydrophobic agent and viscosity increasing agent.[81–83]

Chen et al.[84] divided the hydration process of silane coupling agent modified cement into five stages (I) the dissolution stage (II) the dynamic balance stage (III) the setting stage (IV) the hardening stage and (V) the steady hardening stage. In the dissolution stage, part of the surfaces of the cement particles are covered with silane coupling agent, which prevents the cement minerals dissolving. In the dynamic balance stage, the degree of silane hydrolysis is high and it will gradually condense. The intermediates formed after hydrolysis and condensation will form hydrogen bonds with the C–S–H gels and C–H crystals generated from the early hydration, which will combine with them and prevent nucleation and growth. At this stage, the higher the degree of silane hydrolysis, the more significant its inhibition of cement hydration. At the stage of setting and hardening, silane hydrolysis and condensation to form substances similar to the structure of SiO_2. They can react with C–H crystals to form C–S–H gels, which can improve the degree of hydration in the later stage to a certain extent. In addition, the silaneoxy groups are often introduced into the PCA superplasticizer molecules as adsorption functional groups, and their influence on the cement hydration process differs significantly from that of the carboxyl groups. He et al.[85] found that the retardation effect of superplasticizers on the induction period was more obvious after silaneoxy groups were introduced into the PCA molecules, and the retardation effect was positively correlated with the amount of silaneoxy group. It corresponded to the conclusion of the difficulty in dissolving cement minerals due to the strong adsorption of silanoxy groups in the dissolution stage mentioned by Chen et al. Moreover, the promotion effect on the later hydration stage was also significantly weakened compared with that of ordinary PCA superplasticizers. It might be due to the fact that the excessive silaneoxy group content caused mutual condensation between the superplasticizer molecules, which in turn reduced the dispersibility of the cement particles. Finally, it led to the difficulty of later cement hydration. Kong et al.[86] investigated the effects of three types of silanoxy compounds (tetraethoxysilane (TEOS), 2-aminopropyltriethoxysilane (APTES) and *N*-2-aminoethyl-3-aminopropyltrimethoxysilane (AEAPTMS)) on the adsorption and dispersibility and the hydration process of cement particles. The results showed that the longer is the alkyl chain length among the three types of molecules, the weaker is the adsorption performance. However, the longer alkyl chains provided better dispersibility. It was because the long alkyl chains could provide stronger steric effect. The hydrolysis condensation by-products of the three compounds had little effect on hydration (Methanol from the hydrolysis of AEAPTMS, and ethanol from the hydrolysis of TEOS and APTES), and none of them prolonged the induction period, but decreased the peak hydration rate, as shown in Figure 10(a). Combined with Figure 10(b and c), it could be hypothesized that the difference in the effect on the hydration process of the three may be related to both adsorption effect and main chain structure, and not determined by silaneoxy group alone.

3.7 Discussion and analysis

§3.1-§3.6 generally introduces the effects of organic admixtures containing different functional groups on the Portland cement hydration performance. It is not difficult to find that organic admixtures mainly affect the induction and acceleration periods, and the research on the effects of other periods is relatively small and poor regularity. By summarizing and analyzing the above research results, the major periods of organic admixtures containing different functional groups on the cement hydration and effect are obtained, as shown in Table 2.

In order to show intuitively the influence of different kinds of admixtures on the cement hydration exothermic process, we have counted the key parameters of the hydration exothermic process in the existing results, as shown in Table 3. The parameters can quantify to a certain extent the influence of different organic admixtures on the various cement hydration periods. Δt_A can represent the change of the induction period after the incorporation of the organic admixtures, and the bigger the value indicates that the extension time is longer. $\Delta K_{A\text{-}B}$ reacts to the influence of the organic admixtures on the nucleation rate of hydration products, and the bigger the value indicates that the growth of the nucleation rate is more obvious. $\Delta(dQ/dt)_C$ reacts to the change of the maximum nucleation quantity of hydration products, the larger is the value, the greater is the increase in the nucleation quantity. $\Delta Q_{A\text{-}C}$ reacts to the change of the total exothermic amount of the cement minerals dissolved and the hydration products deposited in the acceleration period, the larger is the value, the larger is the exothermic increment (A, B and C in the symbols of each parameter represent different nodes in the exothermic curve of hydration, Figure 11).

Figure 12 shows the data change distribution of different organic admixtures. It can be seen that the Δt_A of sugar alcohols, alcohol-ammonia, small molecules containing carboxyl groups, PCA macromolecules, polymer emulsions containing carboxyl groups, organic admixtures containing sulfonic groups, phosphate groups, and silanes, respectively, were concentrated in the ranges of 0–5 h, 0–1 h, 0–1.5 h,

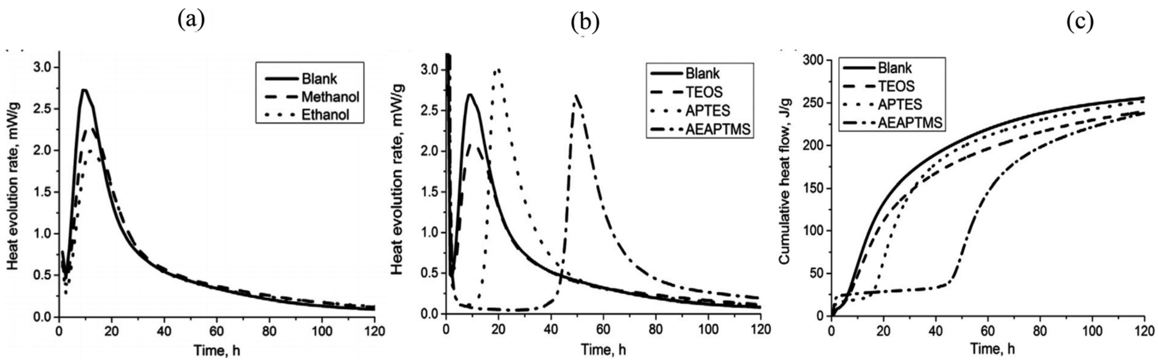

Figure 10: Effect of different silanes and their by-products on cement hydration: a) Effect of by-products on the hydration exothermic process; b) effect of silanes on the hydration exothermic process; c) effect of silanes on the cumulative hydration exothermic amount.

Table 2: Major periods of cement hydration affected by organic admixtures containing different functional groups.

Admixtures	The period of major impacts	Trends in impact	Specific effects
Sugar alcohols	Induction period Peak hydration rate	Prolong induction period Increase peak hydration rate	The larger the molecular weight, the higher the number of hydroxyl groups, and the more the number of threo neighboring hydroxyl groups, the more pronounced the prolongation of the induction period.
Alcohol-ammonia	Initial period	Increase exothermic energy	Significantly accelerates the aluminum phase clinker reaction to produce AFt,.
	Induction period	Prolong induction period	TEA and DEIPA impede C_3S hydration significantly.
	Peak hydration rate	Generate strongly hydrated bimodal peaks	(1) Effectively promote aluminum phase secondary dissolution and AFt precipitation. (2) the amount of methyl groups in the alcohol-ammonia molecule increases, and the second shoulder of the bimodal peak is delayed.
Organic admixtures containing carboxyl groups	Induction period	Prolong induction period	In general, the larger the molecular weight and the more carboxyl groups, the more serious the delayed hydration.
	Peak hydration rate	Increase peak hydration rate	(1) Near the thresholds of carboxyl group density and molecular weight will increase the peak rate of cement hydration. (2) with the increasing of long side chains, the peak hydration rate will first decrease and then increase.
		Reduce peak hydration rate	When the doping exceeds critical thresholds, the peak hydration rate decreases with carboxylate density and molecular weight increasing.
Organic admixtures containing sulfonate groups	Induction period	Prolonged induction period	The sulfonate group can significantly prolong the induction period, with a weaker prolongation effect compared to the carboxyl group.
	Peak hydration rate	Increase or reduce peak hydration rate	Compared to the carboxyl group, the effect of the same amount of sulfonate group in reducing the peak hydration rate is weaker.
Organic admixtures containing phosphate groups	Induction period	Prolonged induction period	It has strong adsorption and complexation, but the effect of admixtures containing phosphate group to prolong the induction period is not necessarily stronger than that of the carboxyl group.
Organic admixtures containing silaneoxy groups	Induction period	Prolonged induction period	The prolongation time is proportional to the amount of silaneoxy groups and the degree of silane hydroxyl hydrolysis
	Peak hydration rate	Increase or reduce peak hydration rate	The stronger the adsorption and the higher the hydrolysis degree, the lower the peak hydration rate. But, they are not the determining factors.

2–6 h, 0–3 h, 0.9–1.5 h (organic small molecules containing sulfonic groups were about 0–0.3 h), 1–1.5 h, and 0–10 h; $\Delta K_{\text{A-B}}$ was respectively concentrated in the ranges of −0.2–0.05 mW/(g·h), −0.08–−0.02 mW/(g·h), −0.1–0.05 mW/(g·h), −0.2–−0.03 mW/(g·h), −0.25–−0.45 mW/(g·h), −0.3–−0.25 mW/(g·h) (−0.001 mW/(g·h) for SSS, −0.067 mW/(g·h) for PSSS), −0.07–0.2-mW/(g·h), and −0.5–−0.1 mW/(g·h); $\Delta(dQ/dt)_{\text{C}}$ was concentrated in the ranges of −1–4 mW/g, −0.8–0.2 mW/g, −0.5–0.1 mW/g, −3–4 mW/g, −2–−1 mW/g, 0.2–0.4 mW/g (−0.04 mW/g for SSS and −0.2 mW/g for PSSS), 0–3 mW/g, and −0.8–0 mW/g.

Table 3: Change of exothermic, rate and total exothermic amount that cement modified with organic additives.

Type of substance (functional group)	Admixtures	Dosage①	Base material	Changes in the parameters of exothermic hydration process compared to the cement without admixtures						
				Δt_A/h	$\Delta(dQ/dt)_A$/mW/g	ΔQ_A/J/g	$\Delta K_{A\text{-}B}$/mW/(g·h)	$\Delta(dQ/dt)_C$/mW/g	Δt_C/h	$\Delta Q_{A\text{-}C}$/J/g
Sugars and alcohols[43,56]	D-mannitol	18 μmol/g	C_3S	0.9	−0.23	–	−0.131	0.281	1.2	–
	D-galactitol	18 μmol/g		2.5	−0.24	–	−0.182	0.552	2.9	–
	D-glucitol	18 μmol/g		3.8	−0.25	–	0.045	3.975	5.6	–
	D-gluconate	7.5 μmol/g		8.8	−0.29	–	−0.173	3.61	12.5	–
	D-galactarate	6 μmol/g		16.5	−0.35	–	−0.362	3.18	22.8	–
	Ethyl alcohol	20 μmol/g	P·I 42.5	0.1	−0.14	−1.28	−0.077	−0.09	0.76	−2.87
	Ethylene glycol			0.1	−0.04	−0.19	−0.059	−0.03	0.32	−1.47
	Glycerol			0.2	0.11	2.68	0.032	0.00	−0.04	−1.23
Alcohol-ammonia[43,57]	Trolamine (TEA)	0.1 wt%		2.8	0.35	16.15	−0.061	−0.46	0.4	−19.66
	Triisopropanolamine (TIPA)	0.1 wt%		0.2	−0.05	1.82	−0.024	0.09	2.0	7.89
	N,N-Bis(2-Hydroxyethyl)Isopropanolamine (DEIPA)	0.1 wt%		0.5	0.13	5.21	−0.072	−0.71	1.2	−4.72
	N-MethyldiethanolaMine (MDEA)	0.1 wt%		0.3	0.20	5.59	−0.061	0.18	0.6	0.88
	Diisopropanolamine (DIPA)	0.1 wt%		0.3	0.05	4.03	−0.026	0.21	1.6	8.27
Small molecules and homopolymers containing carboxyl groups[43,61,64]	Acetic acid	0.226 wt%	Ordinary type I/II low-alkali cement	2.6	−0.34	–	−0.009	−0.29	5.2	–
	Glycolic acid	0.286 wt%		2.4	−0.30	–	−0.018	−0.47	5.4	–
	Acrylic acid (AA)	20 μmol/g	P·I 42.5	0.6	0.03	1.35	−0.051	−0.11	0.7	−2.41
	Oxalic acid			0.3	0.02	2.30	−0.036	−0.06	0.3	−3.17
	Propanedioic acid			0.9	−0.04	3.11	−0.015	0.04	1.4	0.06
	Succinic acid			0.7	−0.02	4.77	−0.064	−0.09	1.2	−4.16
	Itaconic acid			1.1	−0.02	4.67	−0.109	−0.19	1.9	−2.00
	AA	16.5 μmol/g	P·O 42.5 R	0.0	−0.01	–	−0.003	0.01	0.4	–
	Methacrylamido propyl trimethyl ammonium chloride (MAPTAC)			0.0	−0.01	–	0.001	0.14	0.0	–
	PAA			4.2	−0.34	7.58	−0.236	−0.41	11.9	14.57
	PMAPTAC			0.3	−0.05	0.34	0.018	0.08	0.6	0.06
PCA superplasticizers[43,68,78]	Linear polycarboxylate-based superplasticizer (LPSUP)	0.3 wt%	P·O 42.5	3.4	−0.50	–	−0.208	0.22	7.7	–
	$AA_{2.5}$-$TP24_1$-MAS_{008}②			3.4	−2.39	10.51	−0.080	−0.21	8.9	14.21
	$AA_{3.5}$-$TP24_1$-MAS_{008}			4.6	−2.84	−1.22	−0.119	−0.27	11.4	55.85
	$AA_{4.5}$-$TP24_1$-MAS_{008}			4.5	−3.03	−1.85	−0.127	0.95	14.6	62.88
	$AA_{5.5}$-$TP24_1$-MAS_{008}			3.6	−2.86	−9.83	−0.134	−1.74	14.5	6.36
	$AA_{3.5}$-$TP24_1$			4.7	−1.67	16.13	−0.205	1.04	15.3	88.96
	$AA_{3.5}$-$TP24_1$-MAS_{008}			1.9	−2.77	1.52	−0.218	3.89	11.1	4.44
	$AA_{3.5}$-$TP24_1$-MAS_{016}			2.9	−2.90	11.17	−0.196	1.08	10.3	3.58
	$AA_{3.5}$-$TP24_1$-MAS_{032}			4.2	−3.76	14.93	−0.081	1.82	10.5	−28.12
	$AA_{3.5}$-$TP24_1$-MAS_{064}			3.5	0.64	12.68	−0.176	4.58	8.0	−3.81

Table 3: (continued)

Type of substance (functional group)	Admixtures	Dosage①	Base material	Changes in the parameters of exothermic hydration process compared to the cement without admixtures						
				Δt_A/h	$\Delta(dQ/dt)_A$/mW/g	ΔQ_A/J/g	$\Delta K_{A\text{-}B}$/mW/(g·h)	$\Delta(dQ/dt)_C$/mW/g	Δt_C/h	$\Delta Q_{A\text{-}C}$/J/g
	AA$_{2.8}$-MA$_{07}$-TP24$_1$-MAS$_{008}$			4.0	−3.14	6.00	−0.194	3.36	11.4	0.51
	AA$_{2.45}$-MA$_{1.05}$-TP24$_1$-MAS$_{008}$			6.5	−3.32	15.62	−0.053	−1.21	9.8	−28.52
	AA$_{2.1}$-MA$_{1.4}$-TP24$_1$-MAS$_{008}$			4.7	−2.96	7.80	−0.108	−0.94	7.3	−27.75
	AA$_{2.1}$-MA$_{1.4}$-TP24$_1$-MAS$_{008}$			5.5	−3.25	4.07	−0.069	−3.37	7.9	−27.49
	AA$_{3.5}$-TP4$_1$-MAS$_{04}$			11.8	−3.61	29.07	−0.252	−0.60	22.2	−11.27
	AA$_{3.5}$-TP4$_{067}$-TP24$_{033}$-MAS$_{008}$			9.6	−3.47	6.70	−0.182	−0.76	21.1	−4.15
	AA$_{3.5}$-TP4$_{067}$-TP24$_{033}$-MAS$_{008}$			10.9	−2.75	20.22	−0.157	−1.98	18.6	−14.65
	AA$_{3.5}$-TP4$_{067}$-TP24$_{033}$-MAS$_{008}$			9.7	−2.56	23.81	−0.068	3.13	18.9	31.06
	AA$_{3.5}$-TP4$_{067}$-TP24$_{033}$-MAS$_{008}$			5.4	−2.85	11.15	−0.045	4.34	11.8	15.38
	P (MAA$_3$-MM$_1$)③	0.15 wt%	CEM I 52.5 N	1.5	−1.48	-	0.064	1.63	3.1	-
Polymer emulsions containing carboxyl groups [26,72,87]	Ethylene vinyl acetate (EVA)	5 wt%	Portland-limestone cement	0.3	0.31	9.31	−0.446	−1.03	0.8	−25.23
		10 wt%		0.8	0.10	11.46	−0.317	−1.39	0.9	−29.74
	Styrene-acrylate copolymer latexes (PSA)	7 wt%	P·I 42.5	0.8	−0.18	−11.48	−0.078	−0.75	1.8	0.42
		12 wt%		1.5	−0.33	−4.39	−0.278	−1.57	4.1	−0.50
		17 wt%		2.4	−0.44	1.65	−0.338	−2.17	6.4	−10.19
		34 wt%		5.5	−0.61	3.81	−0.419	−2.76	12.5	−25.22
	Polystyrene latex	5 wt%	P·I 42.5	0.8	−0.21	−3.28	−0.166	−0.92	4.0	5.23
		10 wt%		2.8	−0.23	−4.92	−0.259	−1.41	8.5	5.65
Small molecules and homopolymers containing sulfonic groups[64]	Sodium p-styrene sulfonate (SSS)	16.5 μmol/g	P·O 42.5 R	0.0	0.00	-	−0.001	−0.04	0.1	-
	PSSS			1.5	−0.19	3.80	−0.067	−0.20	1.5	−3.42
Polysulfonic superplasticizers[73]	P(PEG$_1$-AA$_4$)④	0.15 wt%	P·O 42.5 R	1.0	−0.34	14.79	−0.293	0.33	4.9	1.56
	P(PEG$_1$-AA$_{3.8}$-SA$_{0.2}$)			1.3	−0.42	23.66	−0.261	0.29	4.8	−20.18
	P(PEG$_1$-AA$_{3.4}$-AMPS$_{0.6}$)			0.9	−0.38	11.92	−0.307	0.36	6.5	17.52
Polyphosphate superplasticizers[78,79]	P (MOPE$_3$-MM$_1$)⑤	0.15 wt%	CEM I 52.5 N	1.4	−0.69	-	0.173	3.02	2.0	-
	P(IPPA$_4$-IPEPPG$_1$)	0.05 wt%	P·I 42.5	1.3	−0.11	-	−0.059	0.19	2.0	-
Admixtures containing silaneoxy groups[84,86]	Aminopropyltriethoxysilane (KH550)	1.0 wt%	P·I 52.5	3.1	−0.64	-	−0.402	−0.31	8.1	-
	KH550 pre-hydrolysis 12 h			5.1	−0.67	-	−0.475	−1.19	11.6	-
	Glycidylpropyltrimethoxysilane (KH560)			5.4	−0.72	-	−0.406	−0.10	10.6	-
	KH560 pre-hydrolysis 12 h			9.8	−0.66	-	−0.469	−0.07	14.8	-
	3-Aminopropyltriethoxysilane (APTES)	1.0 wt%	P·I 42.5	0.5	0.06	-	−0.099	−0.59	1.1	-
	Tetraethoxysilane (TEOS)	Same molar quantity as APTES		6.8	−0.42	-	−0.133	0.31	10.1	-
	N-2-aminoethyl-3-aminopropyltrimethoxysilane (AEAPTMS)			29.6	−0.48	-	−0.243	−0.02	40.3	-

① The units of dosage, without special explanation, "μmol/g" indicates the quantity of functional groups doped by 1 g of cementitious minerals; "wt%" indicates the mass fraction of admixture in cement. ② analytical-grade acrylic acid (AA), methyl acrylate (MA), sodium methallyl sulfonate (MAS) (> 98% purity), Industry-grade allyl polyethenoxy ether (TP) macromonomers with molecular weights of 400 (TP4) and 2,400 (TP24). The numbers in "AA$_{2.5}$-TP24$_1$-MAS$_{008}$" represent the ratio of the amount of each monomer in the polymer. Other numbers of the same type in the table have the same meaning. ③ Ethylene glycol methacrylate macromonomer (MM), methacrylic acid (MAA). ④ Methyl allyl polyethenoxy ether (PEG), sodium methallyl sulfonate (SA), 2-acrlamide-2-methylpropanesulfonic (AMPS). ⑤ 2-(methacryloyl oxy) ethyl phosphate (MOEP). ⑥ polyoxyethylene isopentenol-polyoxyel ether macromonomer, EO/PO ratio = 4:1 (IPEPPG), methyl allyl polyoxyethylene ether (IPPA).

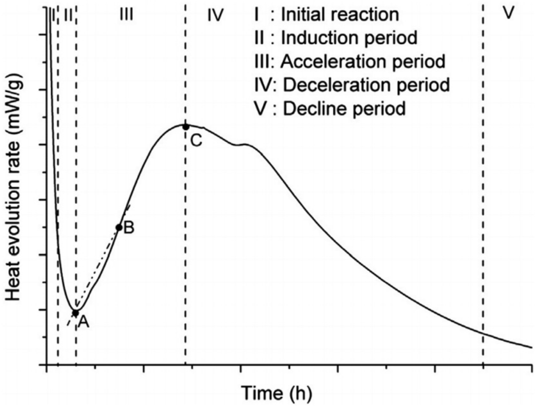

Figure 11: Typical heat flow curve of cement hydration.[64]

From the above data, it can be seen that: (1) Sugar alcohols, PCA macromolecules, polymer emulsions containing carboxyl groups and silanes organic admixtures have stronger delaying effects on the induction period, and alcohol-ammonia have the relatively weakest effect; and the delaying effect of small molecular weight admixtures is significantly weaker than that of the same type of macromolecule admixtures. It means that the time when they start to accelerate nucleation is seriously delayed, but it does not determine the amount of nucleation and the degree of late hydration. (2) Sugar alcohols, PCA macromolecules, polymer emulsions containing carboxyl groups, PCA superplasticizers containing sulfonic groups and silanes organic admixtures have a strong decelerating effect on the nucleation of hydration products. Moreover, the effect of silanes is the most obvious, while small molecules containing carboxyl group and organic admixtures containing phosphate groups have a weak deceleration effect on the rate of cement hydration nucleation, and even part of the organic admixtures containing phosphate groups can accelerate the rate of hydration nucleation. (3) The effects of organic admixtures on the amount of nucleation are relatively complex. The effects of different substances containing the same functional groups may have substantial differences (For example, $\Delta(dQ/dt)_C$ of some sugar alcohols modified cement are between −1 and 0 mW/g, indicating the reduction in the amount of hydration nucleation, not conducive to the subsequent hydration. However, there are also a considerable number of alcohols that make $\Delta(dQ/dt)_C$ vary between 0 and 4 mW/g, increasing the nucleation amount.) Sugar alcohols and PCA macromolecular admixtures can not only significantly affect the amount of nucleation, and the trend of the amount of nucleation is not fixed. Alcohol-ammonia, small molecules containing carboxyl groups, organic admixtures containing sulfonic groups and silanes have less impact on the amount of nucleation. The polymer emulsions containing carboxyl groups are not conducive to nucleation, and the amount of nucleation decreases significantly. In contrast, the superplasticizers containing phosphate groups can significantly increase the amount of nucleation, which is very conducive to the subsequent rapid reaction of cement hydration.

4 Effect mechanism of organic admixtures on silicate cement hydration

The key to exploring the effect of organic admixtures on cement hydration is to understand the interaction between organic molecules and cement particles. Currently the most accepted interactions include two main types: adsorption between organic admixture molecules and cement particles or hydration products and complexation with ions.

4.1 Adsorption

The molecules on the surfaces of solids are in a non-uniform force field, and there are tensions on their surfaces, so the essence of various types of actions on the surfaces is to reduce the surface energy of the solids, and the same is true for adsorption. The adsorption process is to fix the adsorbed molecules, which are in a state of three-dimensional spatial motion, on the surfaces of solid particles, and therefore it is a process of entropy reduction, $\Delta S < 0$. The entropy reduction value of small molecule admixtures adsorbed on the solid surfaces is a higher than that of the large molecule admixtures with the same total number of functional groups and charges. It is perhaps the main reason why the adsorption of the small molecules is more difficult and the dispersing ability of the solid particles is weaker. Since the adsorption behavior is spontaneous, according to the Gibbs function principle, $\Delta G < 0$. Combined with the analysis by the thermodynamic equation $\Delta G = \Delta H - T\Delta S$, $\Delta H < 0$, the adsorption process is exothermic.

4.2 Complexation

Complexation refers to the process of ligands (Lone electron pairs or the donor of off-domain electrons) and center particles (The acceptors of lone electron pairs or off-domain electrons), interacting with each other to form a variety of

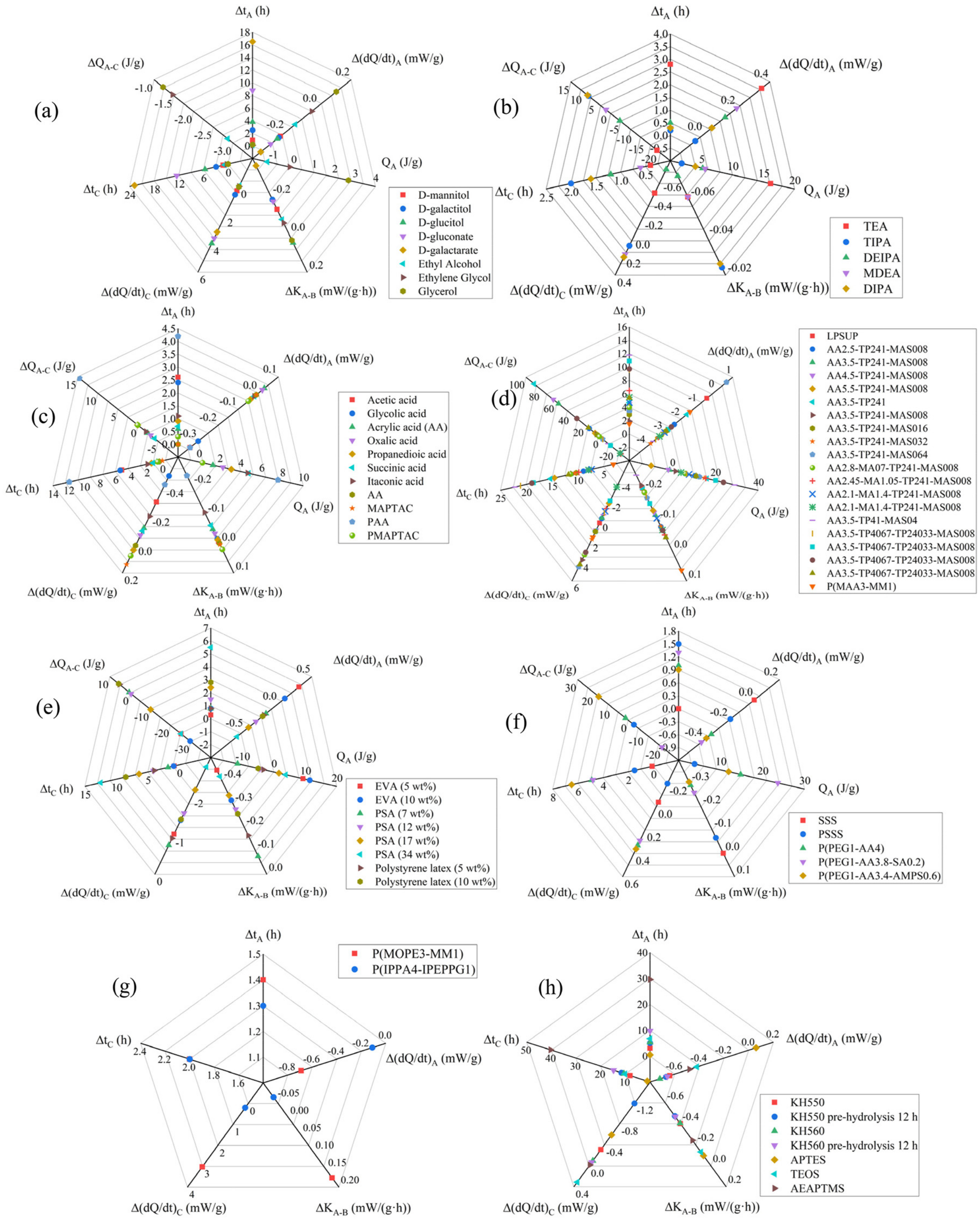

Figure 12: Statistics on the effect of different types of organic admixtures on the hydration parameters: a) Sugar alcohols; b) alcohol-ammonia; c) small molecules containing carboxyl groups; d) PCA macromolecules; e) polymer emulsions containing carboxyl groups; f) admixtures containing sulfonic groups; g) admixtures containing phosphate groups; h) silanes.

complexes. There will be complexation between some organic functional groups and ions in the cement slurry, for example, hydroxyl, carboxyl will be complexed with Ca^{2+} in the slurry.[88–90] At present, many opinions show that complexation has a significant effect on cement hydration, but it’s in-depth mechanism is still controversial.

4.3 Mechanisms of adsorption and complexation affecting cement hydration

The principles of adsorption and complexation are different, but they are not completely independent of each other. Organic admixture molecules may exist as charged particles in alkaline cement slurries, which can cause electrostatic forces between them and charged cement particles (Negatively charged on the surfaces of silica-phase minerals, and positively charged on the surfaces of aluminum-phase minerals.[26]), leading to adsorption of the molecules on the surfaces of the cement particles. If only electrostatic adsorption forces resulting from the organic molecules charged are considered, then organic molecules containing mainly hydroxyl, carboxyl, sulfonate or phosphate groups can only be adsorbed on the surfaces of positively charged aluminum-phase minerals. However, it is not the case that carboxyl and other functional groups can often complex Ca^{2+} in the liquid phase after hydrolysis,[64] so that Ca^{2+} is enriched on the surfaces of organic molecules. At this time, the enriched Ca^{2+} plays the bridging role, so that the original negatively charged admixtures are also adsorbed on the surfaces of silica-phase minerals as well as cationic admixtures (as shown in Figure 9). But, some scholars expressed different views on the influencing factors of adsorption. Plank et al.[91,92] believed that the complexation of organic molecules with Ca^{2+} reduced the charge density and the adsorption enthalpy, and increased the entropy of adsorption, thus the entropy increase was the main driving force of the adsorption effect of organic molecules.

For the complexation between organic functional groups and Ca^{2+}, studies at the present stage generally show that complexation can reduce the Ca^{2+} concentration in the slurry. In turn, it prolongs the time required for the solution to reach ionic supersaturation, slows down the nucleation rate of hydration products, and the hydration induction period of cement is prolonged. With the continuous improvement of research, some scholars have questioned the theory. Lu et al.[43] pre-complexed PCA superplasticizer molecules formed by copolymerization of acrylic acid and isopentene polyoxyethylene ether (Mixed organic admixtures with $Ca(NO_3)_2$ solution in advance, and the organic molecules were detected to be complexed with Ca^{2+}.), and studied the influence of PCA superplasticizer molecules complexed with different amounts of Ca^{2+} on hydration. The results showed that the effects of organic molecules with different degrees of complexation on cement hydration did not differ much, which proved that complexation was not the main reason for the inhibition of cement hydration. The effect of pre-complexation on the adsorption of organic molecules was also investigated, and the adsorption of the pre-complexed molecules was only slightly decreased, which corresponds to the slightly weaker inhibition of hydration. It was inferred that for this class of PCA molecules, the hydration inhibition mainly originated from the adsorption of the molecules on the surfaces of the cement particles. It is noteworthy that the negative potential of the PCA admixtures in solution was significantly reduced after complexation, but the decrease in adsorption was not significant, which verified the idea that electrostatic interaction might not be the decisive factor affecting adsorption (Entropy increase is the main driving force for the adsorption of organic molecules).

The traditional theory of organic molecule adsorption affecting the dissolution of cement minerals has two main mechanisms. One is that the organic molecules form an isolation layer, which prevents the cement minerals from coming into contact with water, but at present there is still no clear research to show that the isolation layer has been observed. The other is that the organic molecules adsorb on the surfaces of the cement particles, and at the same time, interact with ions in solution, leading to the enrichment of some ions near the cement particles, which is detrimental to the further dissolution of the cement minerals.[93] It is worth noting that many experimental phenomena are not fully consistent with the traditional mechanism of adsorption affecting hydration (Hindering the dissolution of cement minerals) mentioned above. For example, after introducing some organic admixtures, only the phenomenon of “delayed acceleration of hydration” occurs, and the peak hydration rate even rises instead of decreasing,[94,95] similar results have been obtained in §3. Such phenomena are difficult to be explained by traditional theories, and the following section discusses a novel and reasonable mechanism of organic admixtures affecting hydration. Flatt et al.[96] tested the changes in the content of different ions in the pore solution of cement paste containing PCA molecules, and found that the content of Si, Al, and Fe, et al. increased dramatically, but the content of Ca and S did not change much. And many nanoscale particles were found in the supernatant of the solution, which may be tiny AFt, AFm or C–S–H. Sowonidich et al.[40] suggested that these particles were formed by the assembly of organic molecules with Ca^{2+} and SiO_3^{2-}. Lu et al.[43] continued to mix Na_2SiO_3 solution (It has been proved that $Ca(NO_3)_2$ does not react with Na_2SiO_3.) in the pre-complexed organic molecule solution (Mixed solution of organic admixture and $Ca(NO_3)_2$.). It was found that the size of the polymer particles in the original solution was enhanced, indicating that SiO_3^{2-} self-assembled with the pre-complexed organic molecules to generate C–S–H around the polymer particles. The formed

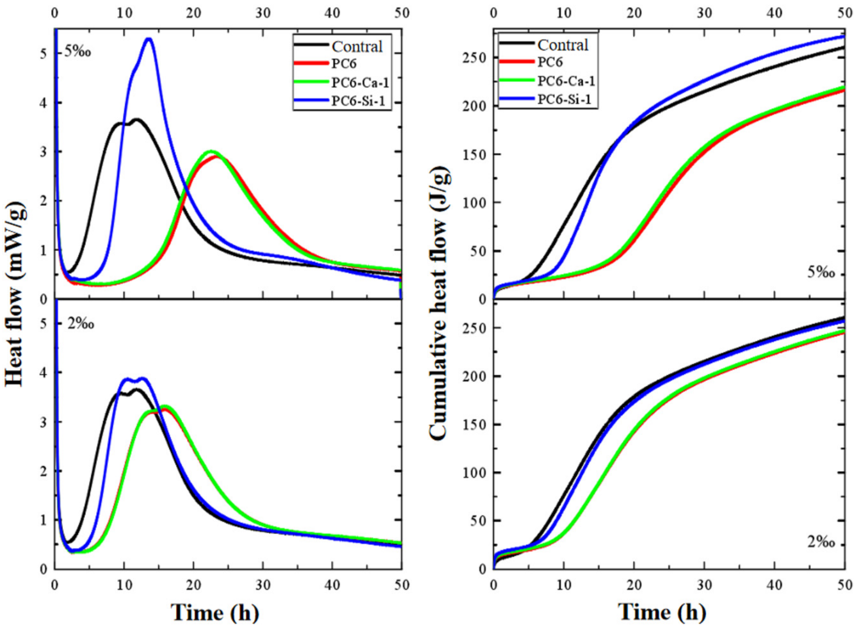

Figure 13: Effect of pre-complexation and pre-nucleation on cement hydration[43] (PC6: Ordinary PCA organic admixture; PC6–Ca-1: Pre-complexation admixture; PC6–Si-1: Pre-nucleation admixture).

C–S–H was able to provide nucleation sites, which increased the peak exothermic rate and the total exothermic amount of hydration (Figure 13). It was worth noting that the self-assembled molecules slightly prolonged the induction period even though they improved the degree of hydration. He concluded that even if the self-assembled molecules were doped, they still required a higher enrichment of Ca^{2+} and SiO_3^{2-} in their vicinity for the rapid growth of the hydration products. He also carried out the above studies on different types of polymer emulsions and found the same results, verifying the above theory. That was, some of the organic molecules adsorbed on the cement particles' surfaces would inhibit the dissolution of cement particles in the early period. However, with the hydration proceeding and the ion concentration increasing, the organic molecules in the cement particles' surfaces and inside the slurry would assemble with Ca^{2+} and SiO_3^{2-} to a certain extent to generate C–S–H, which would provide nucleation sites and improve the cement hydration rate and hydration degree.

5 Conclusions and outlook

Cement hydration is essentially a "dissolution-precipitation" process, and organic admixtures affect the steps of the process, such as dissolution of cement minerals, ion aggregation, nucleation and precipitation of hydration products. The molecular weight, the functional groups, molecular structure and even molecular configuration of organic molecules can significantly affect the cement hydration process.

Sugar alcohols containing hydroxyl functional groups on the silica phase minerals to play the "hydration accelerator delay agent" effect to extend the hydration induction period. Alcohol-ammonia admixtures can effectively promote the aluminium phase minerals hydration. It is conducive to improving the early strength of cementitious materials, so alcohol-ammonia admixtures are often used as early strength agents.

The inhibition of cement hydration is strengthened with the increase of the molecular weight and amount of carboxyl group. Small molecules containing carboxyl groups slightly prolong the hydration induction period. Water-soluble PCA molecules inhibit hydration more obviously, and the inhibition effect is closely related to the main chain length, main chain carboxyl group density, side chain structure, side chain density and so on.

Organic admixtures containing sulfonic groups have similar effects as those containing carboxyl groups. The inhibition by the admixtures containing phosphate groups on cement hydration is weaker than that of carboxyl groups. The dehydration and condensation between silaneoxy and cement clinkers make the two have extremely close adsorption and encapsulation. It makes the cement particles easily agglomerated and isolated from water, which is not conducive to the development of the full periods of cement hydration.

Currently, the main mechanisms used to explain the above effects are complexation and adsorption. Complexation can reduce the Ca^{2+} concentration in the slurry, which in turn extends the time required for the solution to reach ionic supersaturation and slows down the hydration nucleation rate. There are two traditional views of adsorption. One is that the organic molecules form an isolation layer to isolate the cement minerals from water. The other is that the organic molecules are adsorbed on the cement particles surfaces and also attract some ions in the solution, leading to enrichment of some ions in the vicinity of the cement particles. The solution environment with high ionic concentration is not conducive to the sustained dissolution of the cement minerals, which in turn affects the hydration.

Although the research on the effect of organic admixtures on the Portland cement hydration has been reported in decades, but there are still many problems that need to be studied and explored. (1) The effect mechanism of various admixtures on a single clinker is not clear, therefore, it still needs to be systematically explored. (2) There are relatively few studies on how the admixtures affect the morphology of hydration products. Only by combining the changes in hydration process and product morphology can we accurately judge the effect of admixtures on the macroscopic properties of cementitious materials. (3) To clarify the influence of molecular weight, molecular structure, functional groups and other factors of organic admixtures on the cement hydration and properties.

Then synthesize the corresponding organic admixtures according to the properties required in the actual application of cementitious materials, which can greatly improve the efficiency of the application of admixtures, and reduce the side effects caused by admixtures, and is one of the key directions for the application of cement admixtures in the future.

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