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SPECIALTY SECTION
This article was submitted to Polymeric
and Composite Materials,
a section of the journal
Frontiers in Materials

RECEIVED 20 September 2022
ACCEPTED 01 December 2022
PUBLISHED 20 December 2022

CITATION
Lv J, Tian B, Li L and Quan L (2022),
Mechanisms of hydration heat inhibitors
on the early heat release process
of cement.
Front. Mater. 9:1049202.
doi: 10.3389/fmats.2022.1049202

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Mechanisms of hydration heat inhibitors on the early heat release process of cement

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We evaluated the effects of hydration heat inhibitors on the early hydration heat release process of cement and its main mineral components. We used a microcalorimetric method to determine the effects of various proportions and properties of hydration heat inhibitors on the hydration of portland cement, tricalcium silicate, and tricalcium aluminate: concentration (C) = 40% m/m hydroxydiphosphonic acid (HEDP) (1-hydroxyethylidene-1,1-diphosphonic acid) and C = 40% m/m diethylene triamine pentonyphosphonic acid (DTPMPA) (diethylenetriaminepentamethylene phosphonic acid). We also analyzed and tested the heat release rate and cumulative heat release during the hydration of cement and its main mineral components. The hydration heat inhibitors decreased the heat release rate of cementitious materials by means of adsorption, chelation, precipitation, complex formation, and control of calcium hydroxide crystals. Among these materials, the hydration heat inhibitor had the most substantial effect on the composition of tricalcium silicate clinker, reducing the peak temperature at the initial stage of hydration and delaying its occurrence time. These results are pertinent to controlling and selecting the early hydrothermal release process of cement systems.

KEYWORDS

hydration heat inhibitors, cement hydration, C₃S single mineral, C₃A single mineral, hydration heat, heat release rate

1 Introduction

The appearance of cracks in bulk cement-based concrete in response to high temperatures is one of the most challenging problems affecting construction engineering (Aitcin, 2000; Ju, 2002; Zhu, 2003; Zhu, 2014). Yang (2007) studied the effects of raw materials on the cracking of concrete and reported that the heat of hydration of the cement is the primary factor that affects the temperature increase. Zhu et al. (2018) investigated heat evolution in various cementitious material systems and found that using low-heat portland cement or ordinary portland cement (OPC) with inactive mineral admixtures can reduce the heat of hydration. However, some admixtures might affect the performance of cement. Li et al. (2018) and Liu et al. (2009) found that mineral admixtures such as mineral powder and fumed silica can reduce heat generation but

also increase the self-shrinkage of concrete, thus increasing the risk of cracking; in particular, there is a risk of damaging the concrete mass.

In the early 1920s, researchers began to investigate approaches for mitigating high internal temperatures in bulk concrete by, for example, installing cooling water pipes inside the concrete to remove heat (Qian et al., 2012; Liu et al., 2015; Dash et al., 2018; Maanser et al., 2018; Tasri et al., 2019; Conceição et al., 2020; Idrees et al., 2021; Lu et al., 2021). However, installing cooling water pipes—and their associated increases in materials and costs—does not meet current requirements for energy conservation, carbon emission reduction, or environmental protection.

In recent years, researchers have designed materials to inhibit temperature increases during the hydration of concrete. Mixing cement-based concrete with an appropriate quantity of such materials can reduce the exothermic rate during the cement hydration acceleration period, while the total hydration heat of cement remains unchanged (Chen et al., 2021; Chen et al., 2021; Dong et al., 2021; Gu et al., 2021; Liu et al., 2021; Yu et al., 2021). Solving the problem of temperature cracks in mass concrete is an active area of research. For example, Jia et al. (2013; 2021) developed the hydration heat of concrete expansion agent for restraining (HCSA-R), which regulates the hydration of cement in a manner that extends the heat release process and delays the occurrence time of the peak temperature. Lv et al. (2015) prepared a starch-based cement hydration heat regulation material that can also gradually release the hydration heat and reduce the maximum temperature produced inside the concrete by the high heat inside. In their study of calcium aluminosilicate cement mixed with hydroxydiphosphonic acid (HEDP) and diethylene triamine pentonyphosphonic acid (DTPMPA), Li et al. (2020) found that the two admixtures did not affect the hydration process of cement slurry but did prolong the hydration time; the exothermic state of hydration should be further studied. The mechanism of these materials is generally the same: they gradually dissolve in alkaline concrete and adsorb on the surface of the hydration products on the cement particles, thus inhibiting the cement hydration rate in the initial and accelerated stages (Hao et al., 2017). Many studies indicate that the exothermic curve for hydration is a means of studying the exothermic law and the hydration process in determining the effects of admixtures on cement-based materials. The Krstulovic–Dabic model (2000) of hydration dynamics is based on a thorough analysis of a hydration heat-release profile of cement-based materials. The model contains several parameters that reflect the macroscopic and microscopic processes involved in the hydration of the cemented material. The heat release of hydration is related to the active substances in the cementitious materials, and there is no means of reducing the total heat produced during the hydration process.

Our novel research has identified two main sources of hydration heat in cement-based materials and their main

mineral components [tricalcium silicate (C_3S) and tricalcium aluminate (C_3A)] and has revealed their mechanisms by collecting early heat release data during the hydration of active minerals in cement. The purpose of this study is to provide technical support for the thermal cracking control of bulk concrete by selecting and regulating the hydration heat inhibitor in a manner that affects the heat generation and the heat release rate of the hydration process.

2 Materials

2.1 Hydration heat inhibitors

In accordance with the main effects and properties of the hydration heat inhibitor, we selected hydroxydiphosphonic acid (HEDP) (1-hydroxyethylidene-1,1-diphosphonic acid) and diethylene triamine pentonyphosphonic acid (DTPMPA) (diethylenetriaminepentamethylene phosphonic acid), both of which can interfere in the exothermic process of the thermal hydration of cement-based gel materials by different means (Li et al., 2020). Table 1 summarizes the characteristics of the selected hydration heat inhibitors, and Figure 1 shows their molecular structures.

2.2 Cement and water

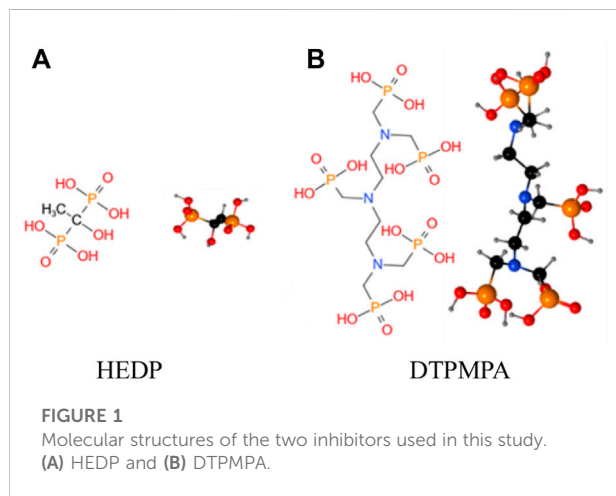
The tests were conducted with P-I 42.5 portland cement (number average size $Dv50 = 13.02 \mu\text{m}$). The specific surface area was $350 \text{ m}^2/\text{kg}$. Table 2 summarizes the composition. Deionized water was used in all trials at a water-to-cement ratio of 0.4.

2.3 Preparation of C_3S and C_3A

To prepare the C_3S and C_3A single minerals, we followed the method developed by Li (2018). The synthetic materials incorporated anhydrous calcium carbonate from VWR (China, Shanghai) and silica from Sigma-Aldrich (China, Shanghai), as well as Al_2O_3 . These reagents were mixed in accordance with various synthetic ratios and calcined five times in a Borel furnace at $\geq 1700^\circ\text{C}$. The product was then ground into a powder with a disk grinder (Hibtek). Single C_3S and single C_3A minerals were obtained after controlling the transient synthesis reaction with gypsum reagents (Sigma-Aldrich). These C_3S and C_3A single ores were $>99\%$ pure, and they both had an average size of $Dv50 = 13.02 \mu\text{m}$ and a specific surface area of $350 \text{ m}^2/\text{kg}$. They were sealed and stored for use in subsequent trials. Table 3 summarizes the chemical compositions of the alite samples. Figure 2 shows X-ray diffraction (XRD) distribution maps of the C_3S and C_3A single minerals. As can be seen from Figure 2, the produced C_3S and C_3A single minerals

TABLE 1 Characteristics of the hydration heat inhibitors tested in this study.

Material	HEDP	DTPMPA
Appearance	Colorless or light-yellow transparent liquid	Brown-yellow or brown-red viscous liquid
Active component (HEDP) % \geq	50	50
Phosphite (PO_3^{3-}) % \leq	2.0	3.0
Chloride (Cl^-) % \leq	1.0	12–17
Density (20°C) $\text{g}/\text{cm}^3 \geq$	1.34–1.40	1.35–1.45
Iron (Fe^{3+}) concentration ppm \leq	10	35



have high X-ray diffraction peaks and good crystal development, with high phase content and high purity.

3 Experimental

3.1 Methods and equipment

The exotherms of the cement and single ores were measured by microcalorimetry with a TAM air isothermal calorimeter from TA Instruments. The duration of each continuous test was >168 h. The experimental environment was $20^\circ\text{C} \pm 1^\circ\text{C}$. The temperature control of this device was stable within $\pm 0.02^\circ\text{C}$, with a short-term noise of $< \pm 4 \mu\text{W}$, and a baseline drift of $\geq 25 \mu\text{W}$ per 24 h.

3.2 Sample compositions for microcalorimetry

Two types of inhibitors—HEDP, with a strong retarding effect, and DTPMPA, with a strong cooling effect—were selected for the test. The total mass of a single test sample was 7 g,

including 5 g of solid (cement or C_3A , C_3S) and 2 g of water. The quantity of inhibitor was 0.01%, 0.03%, or 0.05% of the mass of the cement, C_3A , or C_3S (Table 4) (i.e., 0.0005 g, 0.0015 g, 0.0025 g of $\text{C} = 40\%$ m/m HEDP or $\text{C} = 40\%$ m/m DTPMPA). The weighed inhibitor was added to 2 g of water, then the prepared solution was mixed with the solid material for 60s for testing. These mixtures were then placed in two parallel channels and recorded simultaneously. The non-meaningful increase of heat flow caused by opening the channel could disturb the integration of cumulative heat at a very early age. Here, we started the integration from 0.75 h to minimize the possible error.

4 Results and discussions

4.1 C_3S trials

4.1.1 Effects of inhibitors on the rate of heat release from C_3S hydration

As indicated by the heat release rate curve of the C_3S hydration reaction (Figure 3), the time to reach the peak heat flow varied substantially at various inhibitor doses (Table 5).

Regarding the test data for the C_3S single-ore hydration reaction, in the case of the unhydrated heat inhibitors, the peak heat flow was higher and the time to form the heat flow peak was relatively brief. The heat flow peak decreased after HEDP inhibitor incorporation, compared with the blank control group. In the trial with a low incorporation dose (0.01%), the time to form the heat flow peak decreased by nearly 13 h, and the peak heat release rate decreased by 40.5%. By increasing the incorporation dose, the peak heat release rate decreased by ca. 57%, but the heat flow peak delay was not obvious. These results indicate that adding HEDP during the hydration of C_3S single ore delayed the formation time of the heat flow peak at a lower dose of HEDP and decreased the peak heat release rate. The increased HEDP dose did not delay the peak formation time but did decrease the peak heat release rate by ca. half.

The peak heat release rates could be decreased after incorporating DTPMPA inhibitor compared with the blank

TABLE 2 Mineral composition of the cement clinker was used in this test.

Clinker mineral	C ₃ S	C ₂ S	C ₃ A	C ₄ FA
Compositional proportion %	50	24.79	7.03	18.18

control. In trials with a low added dose (0.01%), the peak heat release rate could be decreased by 78%, but the formation time of the peak temperature and the increased added dose changed negligibly. These results indicate that adding DTPMPA to the hydration process of C₃S single ore did not delay the formation time of the peak temperature but did reduce the peak heat release rate. At the low incorporation dose (0.01%), the peak heat release rate was the most decreased; therefore, the incorporation dose of DTPMPA in the hydration process of C₃S single ore should not be too high.

After incorporating the mixed HEDP + DTPMPA inhibitor, the peak heat flow formation time in the case of the low incorporation dose (0.01%) decreased by 37.8% compared with the blank control group. This result does not differ greatly from that of incorporating an HEDP inhibitor at a dose of 0.01%. By adjusting the HEDP + DTPMPA incorporation dose to 0.03%, the peak heat flow formation time was close to that of the blank control group, and the peak heat release rate could be substantially decreased to 73%. When the HEDP + DTPMPA incorporation dose increased to 0.05%, the peak heat release formation time was close to that of the blank control group and the decrease in the peak heat release rate was greatest (83.8%). These results indicate that HEDP played a major role at 0.01%. The decrease in the peak heat release rate was limited but could delay the manifestation of the peak heat release. As the incorporation dose of HEDP + DTPMPA increased to 0.03%, DTPMPA played a prominent role. The decrease in the peak heat release rate gradually intensified, and the manifestation of the peak heat flow was

slightly delayed. By further increasing the incorporation dose to 0.05%, we reduced the peak heat release rate most substantially to ca. one-sixth of the blank control group, but the formation time of the peak heat flow did not change.

4.1.2 Effect of inhibitors on the quantity of heat released from C₃S hydration

As is evident from the comparison curve of C₃S (Figure 4), under the conditions of various dosages of the inhibitors, the cumulative release of the hydration heat gradually increased within 1 w, but the increase was faster in the early stage and slower in the later stage (Table 6).

Regarding the test data for the C₃S single mineral hydration reaction, the cumulative calorific value of the hydration heat at 24 h was 115 J/g, accounting for 57.5% of the cumulative calorific value of the first 7 days (200 J/g). Only 45 J/g was released after 48 h, representing 75% of the cumulative calorific value within the first 7 days.

After incorporating the HEDP inhibitor, the first 7 days' cumulative calorific value was slightly increased at the HEDP incorporation dose of 0.01%, but there was a decreasing trend with increasing HEDP incorporation doses. The test results indicate that the cumulative calorific value of the first 7 days was 20% lower at the 0.03% incorporation dose and 40% lower at the 0.05% incorporation dose. The cumulative calorific value at 24 or 48 h decreased to different extents. The cumulative calorific value at 24 h at the 0.03% incorporation dose decreased the most: 65%.

All the cumulative calorific values in the first 7 days exhibited large degrees of reduction compared with the blank control group, but the decreasing trend abated with increasing doses of DTPMPA. The cumulative calorific values at 24 or 48 h decreased to varying extents. At the incorporation dose of 0.01%, the 24 h cumulative calorific value decreased the most substantially: >50%.

TABLE 3 Chemical compositions of the C₃S samples.

Sample no.	Mass ratio								
	CaO	SiO ₂	Na ₂ O	K ₂ O	MgO	Al ₂ O ₃	Fe ₂ O ₃	P ₂ O ₅	SO ₃
Typical alite	71.6	25.20	0.1	0.1	1.1	1	0.7	0.1	0.1
Control	71.6	25.57	—	—	—	—	—	—	—
C0	71.6	25.57	0.1	0.1	1.1	1	0.7	0.1	0.1
C1	71.6	25.57	—	—	1.1	1	0.7	0.1	0.1
C2	71.6	25.57	0.1	0.1	—	1	0.7	0.1	0.1
C3	71.6	25.57	0.1	0.1	1.1	—	0.7	0.1	0.1
C4	71.6	25.57	0.1	0.1	1.1	1	—	0.1	0.1
C5	71.6	25.57	0.1	0.1	1.1	1	0.7	—	0.1
C6	71.6	25.57	0.1	0.1	1.1	1	0.7	0.1	—

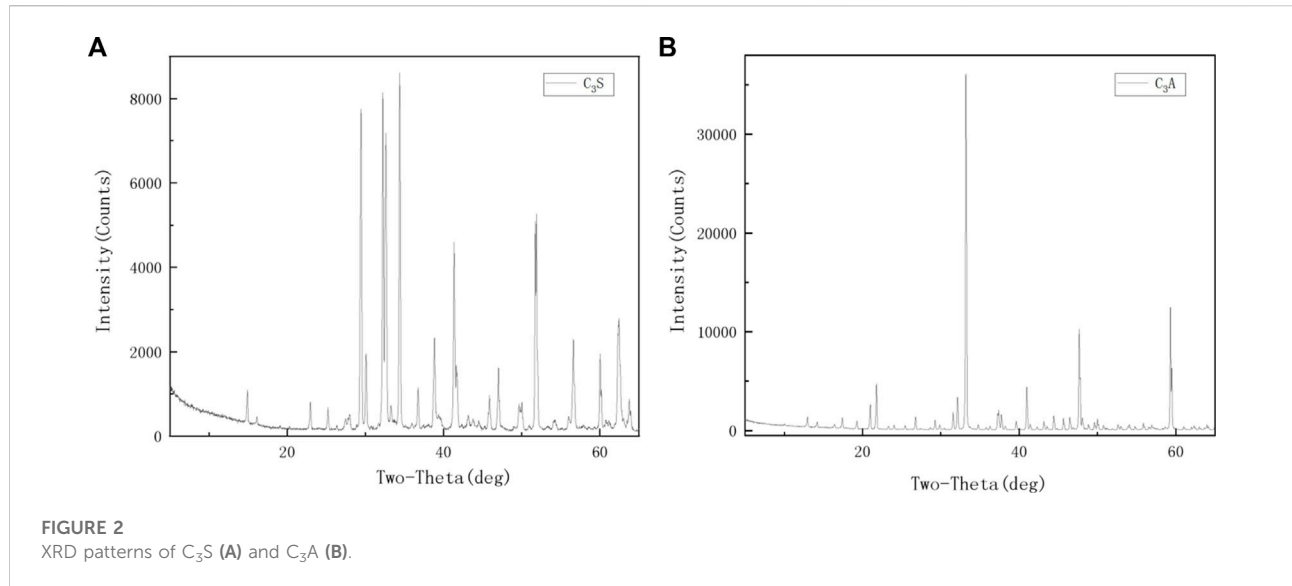


TABLE 4 Test parameters during microcalorimetric analyses of hydration.

Test system	Materials and ratio	Inhibitor type	Inhibitor dosage (%)			
			0	0.01	0.03	0.05
Cement system	Cement: H ₂ O = 5:2	Blank control group	CB	/	/	/
		HEDP	/	CH1	CH3	CH5
		DTPMPA	/	CD1	CD3	CD5
		HEDP: DTPMPA = 1:1	/	CHD1	CHD3	CHD5
C ₃ S system	C ₃ S: H ₂ O = 5:2	Blank control group	SB	/	/	/
		HEDP	/	SH1	SH3	SH5
		DTPMPA	/	SD1	SD3	SD5
		HEDP: DTPMPA = 1:1	/	SHD1	SHD3	SHD5
C ₃ A system	C ₃ A: H ₂ O = 5:2	Blank control group	AB	/	/	/
		HEDP	/	AH1	AH3	AH5
		DTPMPA	/	AD1	AD3	AD5
		HEDP: DTPMPA = 1:1	/	AHD1	AHD3	AHD5

*Note: To distinguish the experimental groups in this paper, the different component materials were numbered uniformly. The type of numbering was "material + inhibitor type + inhibitor additive dose", including C-cement, S-C3S, A-C3A, B-Blank, h-HEDP reagent, D-DTPMPA reagent, HD-HEDP: DTPMPA = 1:1 mixed reagent. The numbers (1,3,5) represent 1%, 3%, and 5% of inhibitor dosage, respectively.

Using the HEDP + DTPMPA mixed inhibitor slightly increased the cumulative calorific value in the first 7 days at 0.01% incorporation, but there was a decreasing trend with increasing HEDP incorporation. At an added dose of 0.05%, the 7-day calorific value reached 65%. The cumulative calorific value at 24 and 48 h was less than half of the cumulative calorific value for the first 7 days at the same incorporation dose.

4.2 C₃A trials

4.2.1 Effect of inhibitors on the rate of heat release from C₃A hydration

As evident from the heat release rate curve of the C₃A hydration reaction (Figure 5), the peak of the heat flow and the time of the heat flow peak formation changed negligibly after

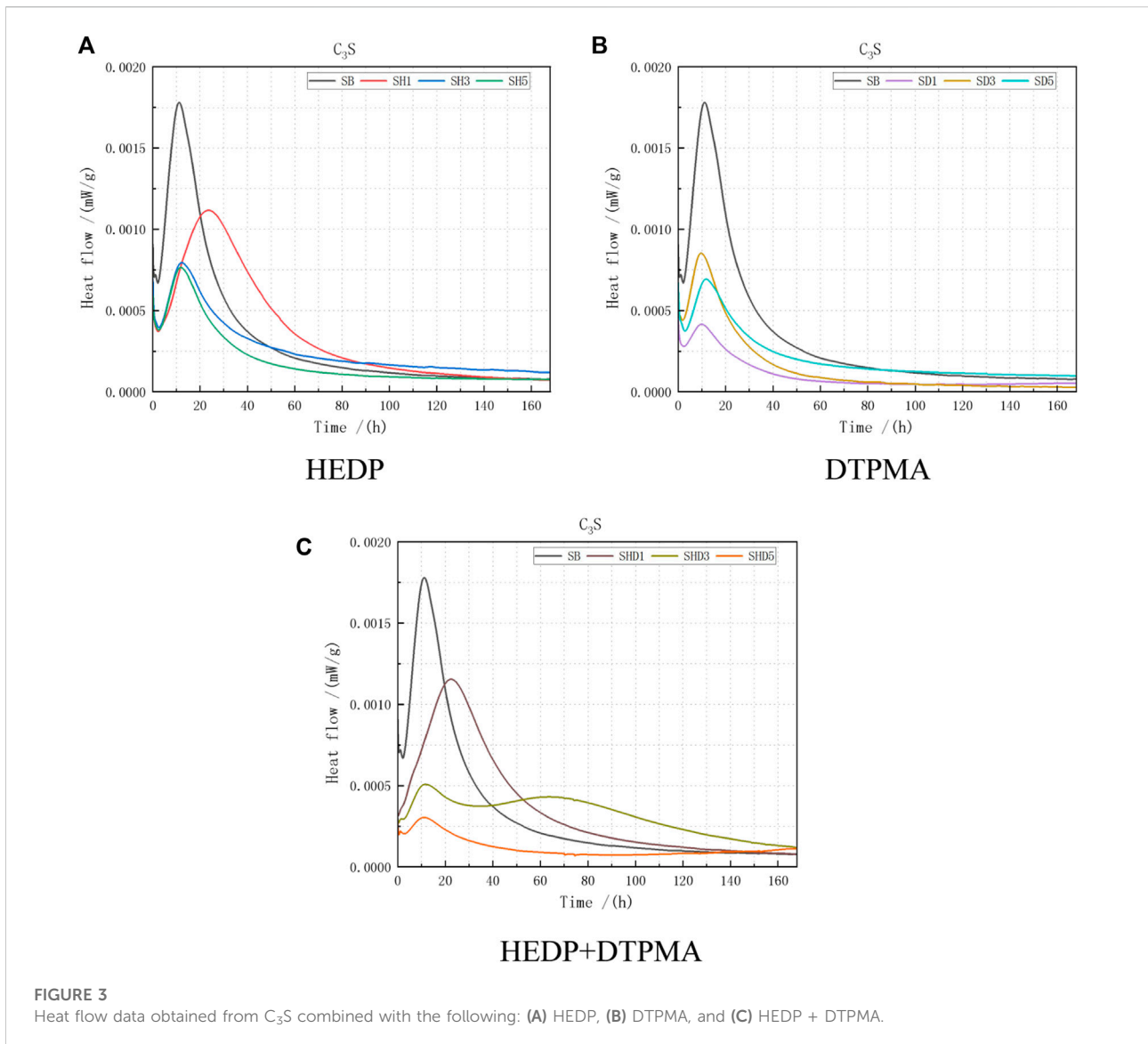


TABLE 5 Heat release rate data of the C₃S hydration reaction.

Heat of hydration inhibitor dosing	0.00%		0.01%		0.03%		0.05%	
	Peak heat flow, mW/g	Formation time, h	Peak heat flow, mW/g	Formation time, h	Peak heat flow, mW/g	Formation time, h	Peak heat flow, mW/g	Formation time, h
HEDP	185	11.2	110	23	80	12.3	78	11.8
DTPMPA	185	11.2	40	9.8	85	9.6	60	11.8
HEDP: DTPMPA = 1:1	185	11.2	115	22.5	50	11.6	30	11.2

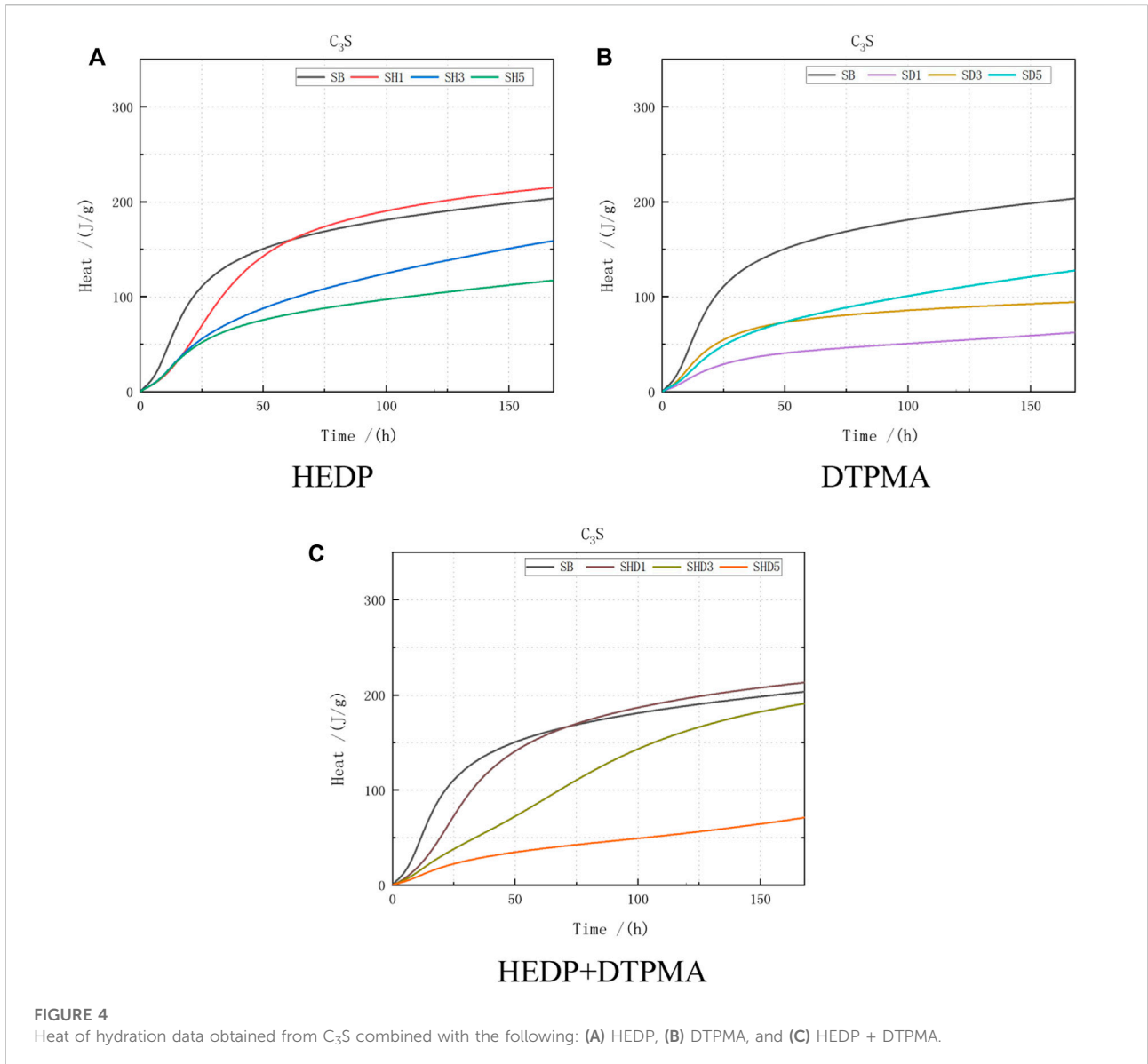


TABLE 6 Cumulative release data of C₃S hydration heat over various time periods.

Heat of hydration inhibitor dosing(J/g)	0.00%			0.01%			0.03%			0.05%		
	24 h	48 h	168 h	24 h	48 h	168 h	24 h	48 h	168 h	24 h	48 h	168 h
HEDP	115	150	200	70	140	220	55	82	160	50	75	120
DTPMPA	115	150	200	30	42	63	52	75	95	50	75	80
HEDP: DTPMPA = 1:1	115	150	200	70	140	218	40	70	185	20	35	70

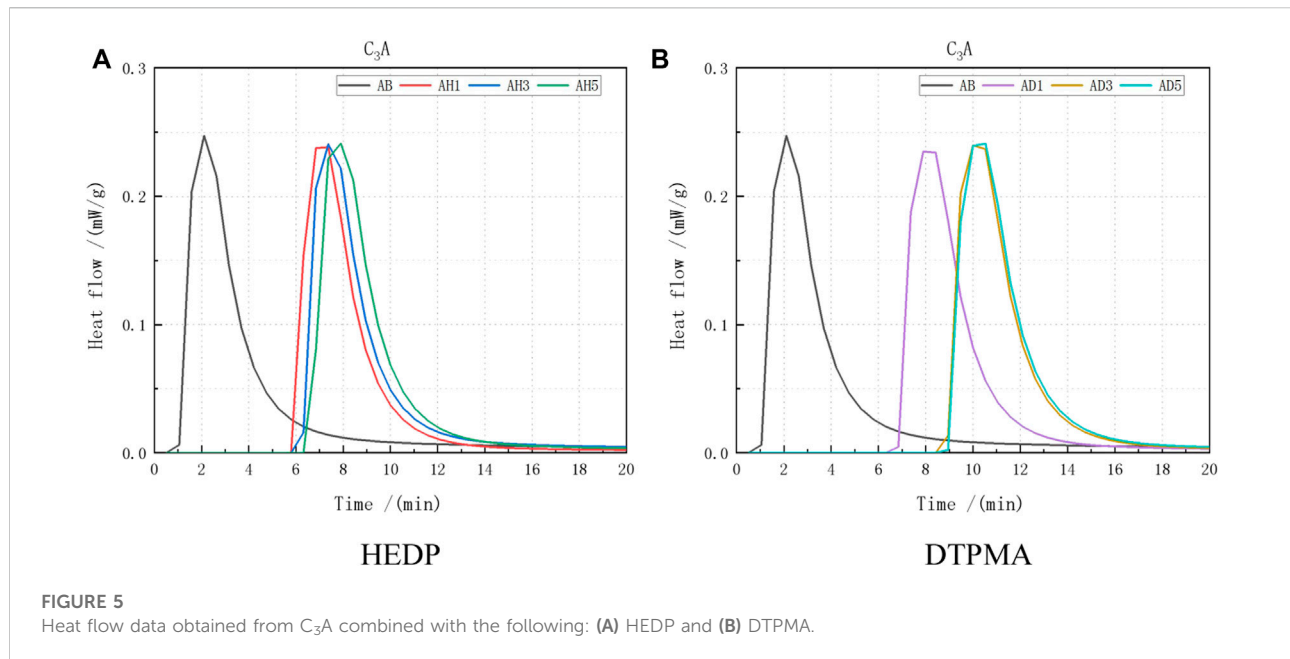


TABLE 7 Hydration reaction release rate of C₃A.

Heat of hydration inhibitor dosing	0.00%		0.01%		0.03%		0.05%	
	Peak heat flow, mW/g	Formation time, h	Peak heat flow, mW/g	Formation time, h	Peak heat flow, mW/g	Formation time, h	Peak heat flow, mW/g	Formation time, h
HEDP	248	2	237	7	239	7	242	7
DTPMPA	248	2	236	8	237	9	239	9

incorporating various or no inhibitors and various doses of inhibitors (Table 7).

Regarding the test data for the C₃A single-ore hydration reaction, it is evident that there was a C₃A single-ore after hydration in water. The hydration reaction was fast and formed a heat flow peak at ca. 2 min. The temperature peak manifested early and disappeared quickly, and the concentrated heat release time was short. The test indicates that incorporating the hydration heat inhibitor had little impact on the hydration heat release process; the time delay of the formation of the hydration heat flow peak was <5–8 min, which does not essentially decrease the heat flow peak.

4.2.2 Effect of the inhibitors on the quantity of heat released from C₃A hydration

As evident from the cumulative release curve of the C₃A hydration heat (Figure 6), the cumulative release of C₃A hydration heat was 77% within 5 min and 85% within 10 min. After 10 min, the cumulative

release increase gradually abated. At various incorporation doses of various inhibitors, the cumulative release of the hydration heat changed negligibly compared to the release without the inhibitors (Table 8).

From the test data for the cumulative hydration heat release of the C₃A single mineral hydration reaction, it is evident that most of the hydration heat was released within 5–20 min, and the cumulative heat release within 20 min did not increase much. Eighty-five to 90 percent of the cumulative heat release of hydration was not associated with the type or dose of the inhibitor.

4.3 OPC trials

4.3.1 Effect of inhibitors on the rate of heat release from OPC hydration

As evident by the heat release rate curve of the OPC hydration reaction (Figure 7), the time and formation of the

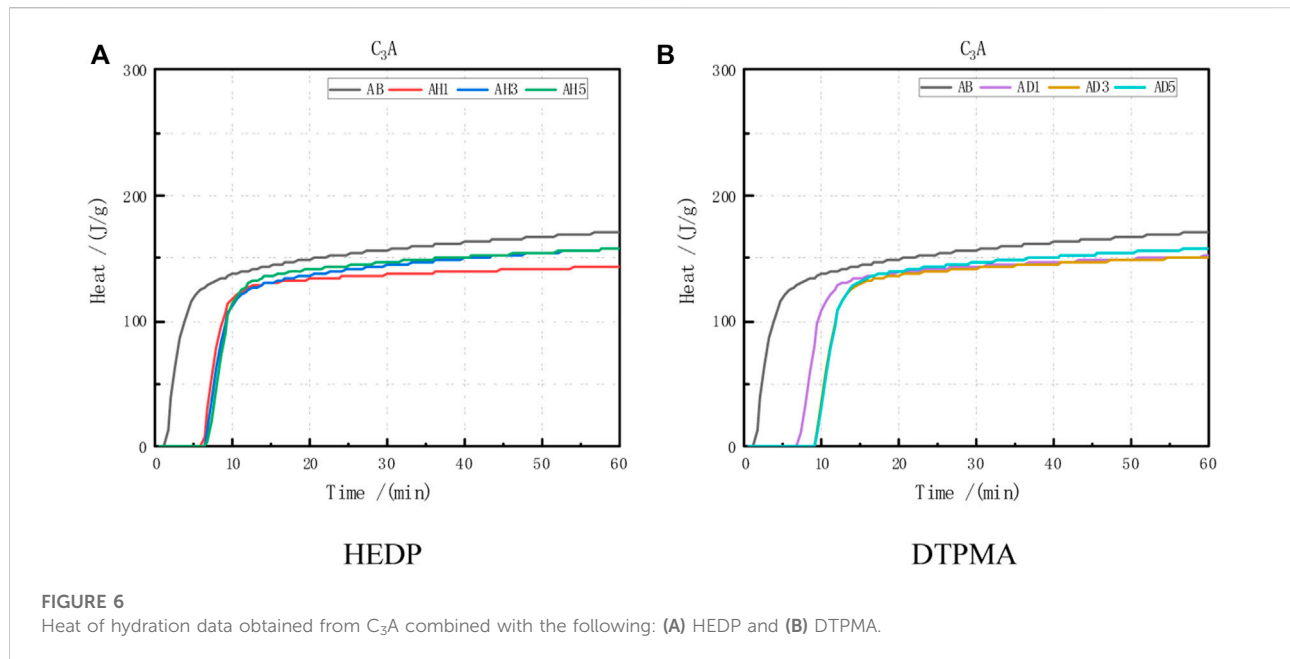


FIGURE 6

Heat of hydration data obtained from C₃A combined with the following: (A) HEDP and (B) DTPMA.TABLE 8 C₃A cumulative hydration heat release data over various time periods.

Heat of hydration inhibitor dosing(J/g)	0.00%			0.01%			0.03%			0.05%		
	5 min	10 min	60 min	10 min	20 min	60 min	10 min	20 min	60 min	10 min	20 min	60 min
HEDP	127	139	165	125	140	147	125	142	152	125	143	153
DTPMPA	127	139	165	126	141	149	125	141	148	125	143	149

heat flow peak varied substantially under the incorporation of various doses and types of inhibitors (Table 9).

The peak heat flow (210 mW/g) was evident at 32 h after the hydration reaction of the cement clinker. Incorporating the HEDP inhibitor decreased the peak heat flow compared with that of the blank control group. In the trial with the low incorporation dose (0.01%), the time to form the heat flow peak was delayed by nearly 16 h and the peak heat release rate decreased by 35.5%. After increasing the incorporation dose, the peak heat release rate decreased by ca. 64%–70%, but the time delay of forming the peak heat flow was not obvious. These results indicate that the incorporation dose of HEDP in OPC also had a platform effect. The low incorporation doses of the HEDP inhibitors delayed the formation of the peak heat flow time and decreased the peak heat release rate. However, although increasing the

incorporation dose of the HEDP inhibitor did not delay the formation of the peak heat flow, the peak heat release rate decreased by ca. two-thirds.

After incorporating the DTPMPA inhibitor, the peak heat release rate substantially decreased compared with the blank control group. In the trial with the low incorporation dose (0.01%), the peak heat flow decreased by 54.7%, the time for the formation of the peak heat flow was delayed by nearly 31 h, and the delay time was nearly twice that of the blank control group. By increasing the DTPMPA incorporation to 0.03%, the time to form the heat flow peak can be delayed by 104 h, which is more than 4× that of the blank control group. Regarding the 0.05% incorporation dose, the peak heat flow decreased by 90%. However, the time to form the peak heat flow was 12 h earlier compared with the blank control group. These results indicate that adding DTPMPA

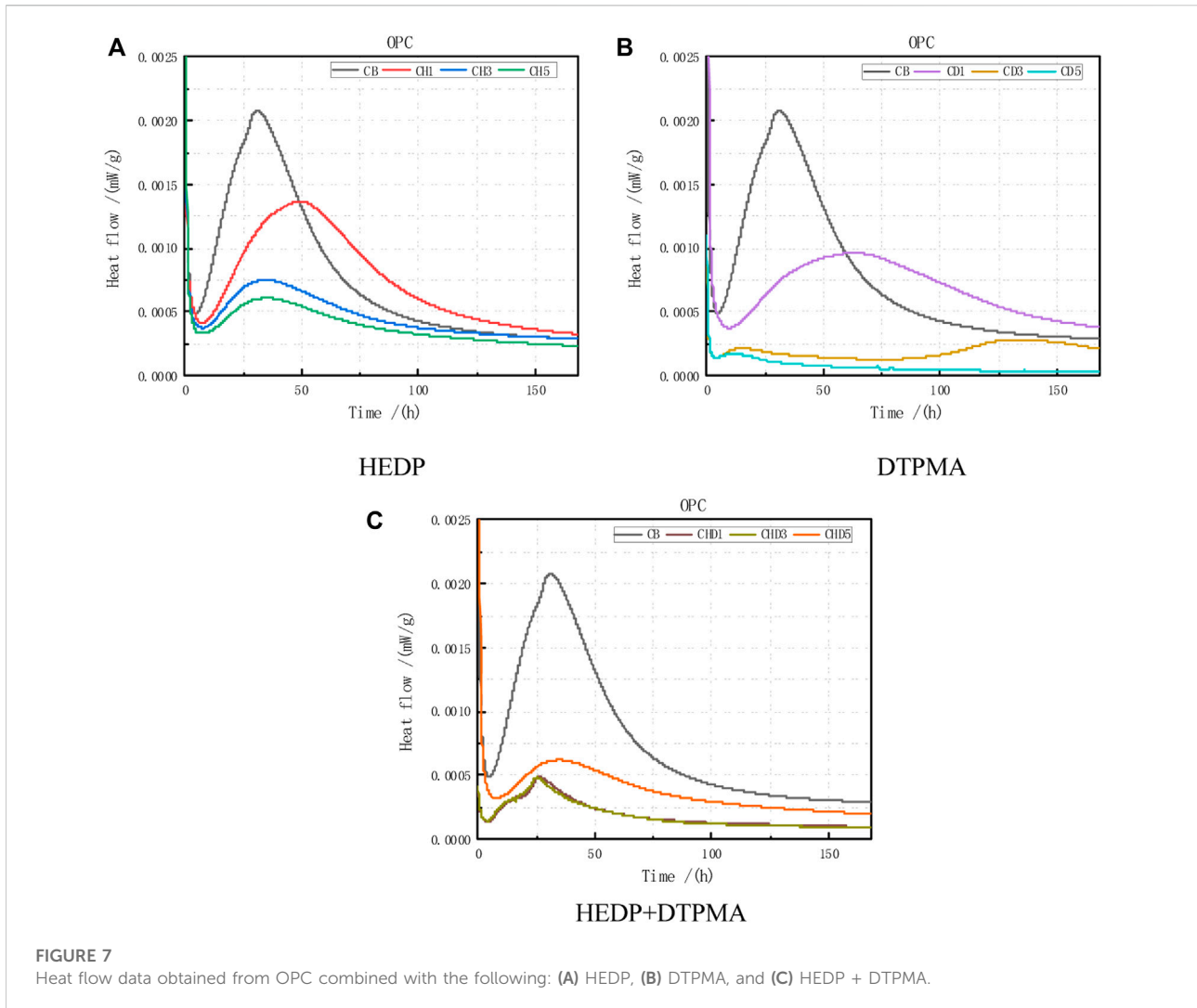


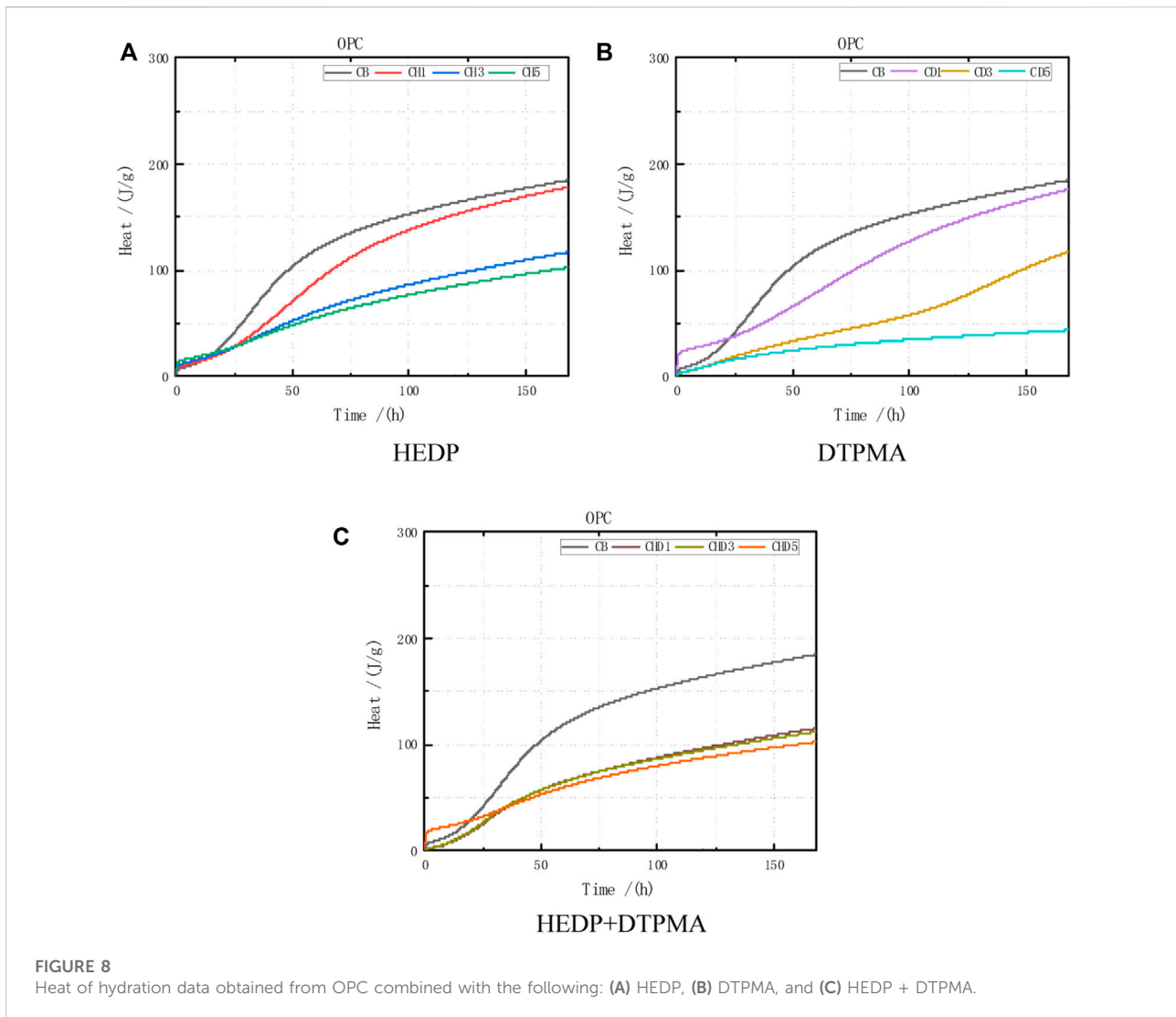
TABLE 9 Heat release rate data for the OPC hydration reaction.

Heat of hydration inhibitor dosing	0.00%		0.01%		0.03%		0.05%	
	Peak heat flow, mW/g	Formation time, h	Peak heat flow, mW/g	Formation time, h	Peak heat flow, mW/g	Formation time, h	Peak heat flow, mW/g	Formation time, h
HEDP	210	32	135	48	75	35	60	35
DTPMPA	210	32	95	63	30	136	18	21
HEDP: DTPMPA = 1:1	210	32	50	25	50	25	60	35

can delay the time of the formation of the peak temperature during the OPC hydration process and can substantially decrease the peak heat release rate. The peak heat release rate and the time to delay the formation of the peak heat flow

can be adjusted to an optimal extent when the incorporation dose is appropriate.

With HEDP + DTPMPA (1:1) inhibitor mixing, the time to form the peak heat flow increased nearly 7 h earlier and the peak



heat release rate decreased (in the trials of 0.01% and 0.03%) compared with the blank control group. When the HEDP + DTPMPA incorporation dose was 0.05%, the time for forming the heat flow peak was close to that of the blank control group but the peak heat release rate decreased by only 71.4%. These results indicate that we had added the HEDP + DTPMPA mixed inhibitor at 1:1 during OPC hydration. The peak heat release rate could be decreased by ca. 70%. However, the time of forming the heat flow peak could not be delayed.

4.3.2 Effect of inhibitors on the quantity of heat released from OPC hydration

As evident from the comparison curve of the cumulative release of the OPC hydration heat (Figure 8), the cumulative release of the hydration heat gradually increased over 1 w under the incorporation of various doses and types of inhibitors (Table 10).

Regarding the test data for the OPC hydration reaction, the cumulative release of the hydration heat over 24 h accounted for 22.2%, and the release over 48 h for 55.5%, of the cumulative release within the first 7 days. After incorporating HEDP or DTPMPA, the quantity of cumulative release at added doses of 0.01–0.03 was consistent with the blank control group, but the trend decreased with increasing added doses. Only at the 0.05 dose of DTPMPA incorporation was the cumulative release reduced to the greatest extent, at 76.6%.

After incorporating the HEDP + DTPMPA inhibitor mixture, the cumulative release within the first 7 days decreased ca. by one-third compared with that of the blank control group, and the size of the mixed dose of the HEDP + DTPMPA inhibitor did not affect the cumulative release within the first 7 days.

During the hydration of OPC, the cumulative release at 48 h substantially decreased compared with the blank control group,

TABLE 10 Cumulative hydration heat release data of OPC over various periods.

Heat of hydration inhibitor dosing(J/g)	0.00%			0.01%			0.03%			0.05%		
	24 h	48 h	168 h	24 h	48 h	168 h	24 h	48 h	168 h	24 h	48 h	168 h
HEDP	40	100	180	30	70	178	20	50	117	25	45	102
DTPMPA	40	100	180	38	62	176	20	33	117	18	23	42
HEDP: DTPMPA = 1:1	40	100	180	20	55	115	20	55	112	30	50	102

but the cumulative release could increase in accordance with a linear relationship after 48 h, indicating that the hydration heat release was relatively uniform.

5 Analysis and discussion

Portland cement undergoes solidification, as well as rapid condensation and hardening. Based on theoretical calculations (Cai, 1995), the heat released by this reaction mainly derives from the C_3S and C_3A single ores in the mineral. The test results indicate that the C_3A hydration reaction is fast, forming a peak heat flow (248 mW/g) in ca. 2 min, and has an instantaneous heat release peak and concentrated heat release. The hydration reaction of C_3S is relatively mild, forming a peak heat flow (185 W/g) at ca. 11 h, with a long duration of heat release and a large cumulative heat release. Therefore, silicate cement, as well as C_3S and C_3A single ores, is commonly chosen when studying the hydration heat inhibitors that affect the early heat release of cement. Zhang et al. (2022) observed hydration heat inhibitors to have no effect on late hydration but to inhibit the early hydration of the C_3A system. The test results indicate that the C_3A hydration reaction releases heat quickly and that the inhibitor does not substantially reduce the instantaneous heat released or delay the rate of its heat release. There was no obvious effect on the early or late hydration of the C_3A system. When studying the hydration heat problem of cement concrete, Chen et al. (2020) observed that C_3A provides the heat for the development of the induction period, whereas C_3S provides the heat for the early condensation and strength development period of concrete. These are all well-validated by the aforementioned test results. The C_3S single ore in the OPC composition is the key factor in the early hydration heat of concrete.

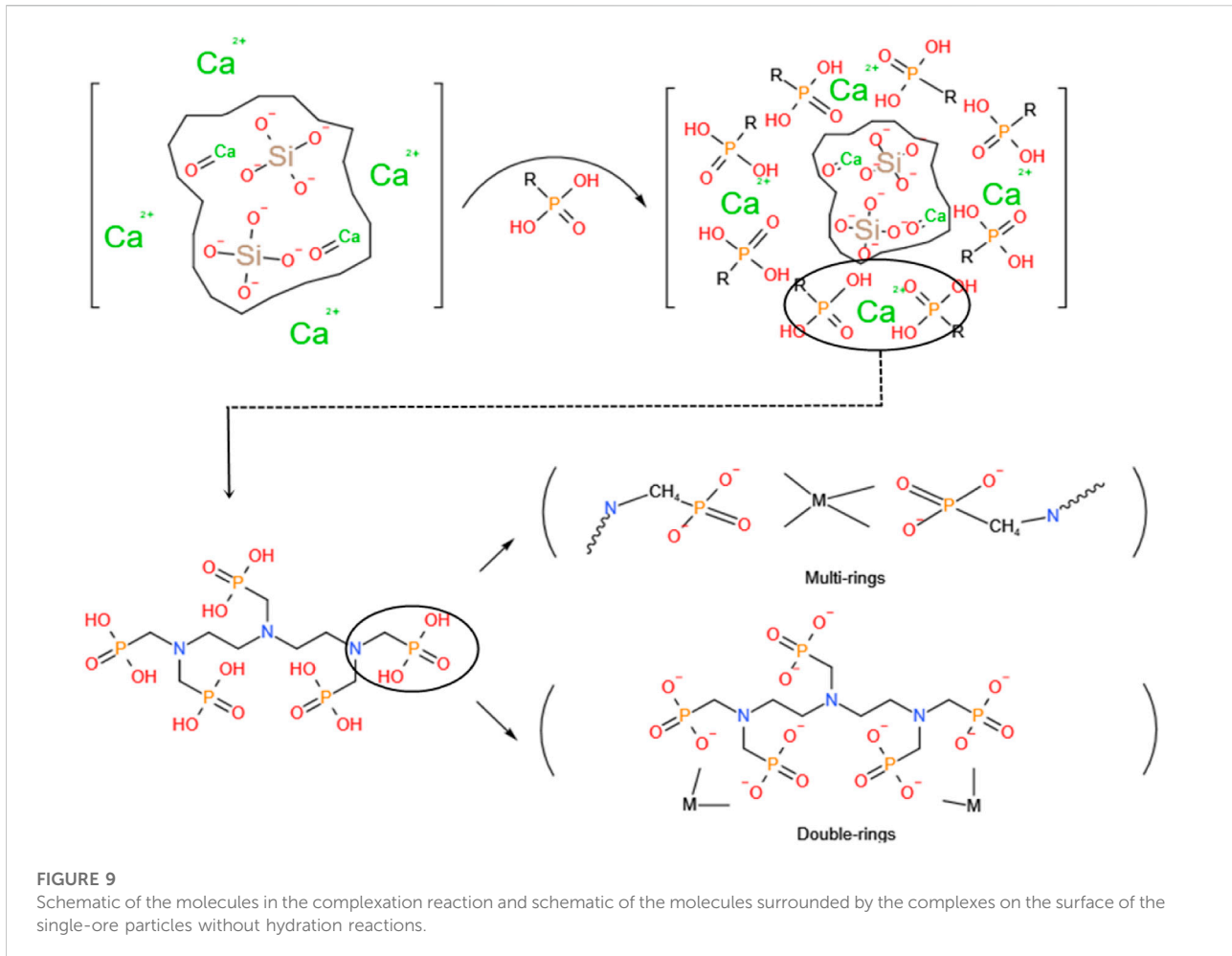
According to Lu (2017), small organic phosphate molecules can substantially inhibit the hydration process of cement. Chen et al. (2021) indicate that using an appropriate quantity of such molecules can in theory substantially reduce the release rate of cement hydration acceleration. We selected the phosphate group, as well as the two compounds HEDP and DTPMPA, to investigate silicate cement and C_3S/C_3A hydration (in

comparison with a control group). The results indicate that both of these hydration heat inhibitors can reduce the early hydration heat of cement.

Adding a certain quantity of HEDP inhibitor into the mineral hydration reaction for silicate cement or C_3S alone can substantially extend the arrival time of the temperature peak, which is closely related to the slow coagulation characteristics of HEDP. HEDP inhibitors adsorb onto the surface of unhydrated cement or C_3S particles and undergo hydration with Ca^{2+} ions in the cement slurry or C_3S slurry. Calcium salts of low solubility in water precipitate to form impermeable thin layers on the surface of the unhydrated cement or C_3S mineral, hindering the further hydration of portland cement or C_3S . This condition is consistent with Li et al.'s (2020) investigation of the mechanism of incorporating cement into an HEDP retarder. Concomitantly, Ca^{2+} in the cement slurry or C_3S slurry forms a semi-permeable film of a six-ring chelate with some functional groups in the hydration heat inhibitor (such as COO^-), which can also enclose the surface of the cement particles or C_3S in a manner that prevents the contact of water with the cement particles or C_3S . These phenomena affect the speed of the hydration reaction, inhibit the formation and growth of AFt and CH, prolong the time of the hydration reaction and the formation of the heat flow peak, reduce the release rate, and delay the temperature increase of the concrete.

If a certain quantity of silicate cement or the C_3S single mineral hydration undergoes a strong cooling effect because of the DTPMPA inhibitor, the arrival time of the temperature peak can be prolonged and the peak temperature and early accumulated heat release substantially reduced. The participation of DTPMPA in hydration has multiple effects: adsorption, chelation, and precipitation. The DTPMPA methyl phosphate group and calcium magnesium ions form a complex (Figure 9) that can enclose the unhydrated cement or C_3S single ore particle surface, as well as inhibit C_3S mineralization during CH (i.e., crystals of calcium dihydroxide) core growth and conventional CH precipitation hydration.

HEDP and DTPMPA are organophosphate products that are incorporated into the cement slurry, in addition to Ca^{2+} , which can ionize hydrogen ions and coordinate oxygen atoms in the



water. Ca^{2+} , Mg^{2+} , Al^{3+} , and Fe^{2+} react to form stable phosphate chelates. The decomposition of these phosphates is endothermic; this energy is from the hydration of cement or C_3S . Thus, the temperature peak and cumulative heat released by the hydration heat temperature increase are reduced, which inhibits the hydration heat.

Yu et al. (2021) found that to reduce the heat release rate of cement hydration in the accelerated period, the identity and quantity of the inhibitor are critical. Accordingly, we used a cross-combination scheme of various materials to investigate the temperature-control performance requirements of two hydration heat inhibitors, HEDP and DTPMPA. The results indicate the following.

In terms of delayed peak time of the heat flow, regarding C_3S single ore, the single-incorporation of HEDP should not be too large. HEDP can substantially delay the formation time of the peak heat flow at 12 h and reduce the peak heat flow by 40.5%. However, with an increased incorporation dose, the formation time of the heat flow peak will no longer be extended but will return to the state without HEDP incorporation. When we tested the single incorporation of DTPMPA, the formation time of the

peak heat flow was not delayed in the range of the 0.01%–0.05% incorporation dose. When HEDP and DTPMPA inhibitors were mixed at a mass ratio of 1:1 and at a dose of 0.01%, the results were nearly the same as for HEDP alone. However, when the added dose was increased, the results were similar to that of DTPMPA alone. For portland cement, the time effect of delaying the peak heat flow with the combined dose of 0.03% was substantial, which can delay the formation time of the peak heat flow by ca. 4 days. Reducing the incorporation dose to 0.01% reduced the formation time of the delayed heat flow peak to 0.01%. Increasing the incorporation dose to 0.05% reduced the peak formation time rapidly, eventually by more than 10 h. The thermal peak was less obvious because of the large quantity of hydration heat to be balanced by the heat absorption effect of DTPMPA in the hydration reaction. When mixing HEDP, or HEDP and DTPMPA, with two inhibitors at a mass ratio of 1:1, the effect was far less than that of DTPMPA incorporation alone. Therefore, an HEDP dose of ca. 0.01% or a DTPMPA dose of 0.03% is the ideal choice to reduce the heat release rate of hydration and delay the formation time of the peak heat flow.

In terms of reducing the quantity of hydration heat release, siland cement is consistent with a C_3S single ore after incorporation into HEDP. We observed that little was changed without HEDP or at 0.01% HEDP but that the cumulative hydration heat release in the first 7 days decreased with an increasing added dose, such as 35% at the 0.03% dose. The cumulative hydration heat release in the first 7 days decreased by 43% at the 0.05% dose. These data suggest that HEDP reduced the release of hydration heat only when the incorporation dose was relatively high. For the C_3S single ore, the accumulated heat release decreased by 68.5% in the first 7 days when the dose was 0.01% after DTPMPA incorporation, but as the added dose increased, the first 7-d accumulated release was non-linearly correlated with the dose (i.e., 47.4% at 0.03% and 60% at the added dose of 0.05%). The quantity of cumulative heat release varied slightly at a dose of 0.01% after DTPMPA incorporation at 7 days compared with no DTPMPA incorporation (control group). With increasing incorporation doses, the cumulative quantity of heat release at 7 days was linearly correlated with the incorporation dose, decreasing by 35% at an incorporation dose of 0.03% and 76% at an incorporation dose of 0.05%. These characteristics indicate that the effect of DTPMPA cooling becomes increasingly obvious with increasing incorporation doses. If silicate cement or the C_3S single ore was mixed with HEDP and DTPMP inhibitors at a mass ratio of 1:1, then different doses were not substantially different from the results of HEDP incorporation alone. For OPC, the cumulative release of the first 7 days could be reduced by 35%–43%, but it was not associated with the magnitude of the added dose. By considering the cumulative release of the hydration heat, such as 24 or 48 h of HEDP, we found that 0.01% HEDP or 0.03% DTPMPA of 0.03% decreased at 7 days. These results are consistent with the mechanisms by which HEDP and DTPMPA affect the exothermic process of OPC.

This study found that a reasonable choice of hydration heat inhibitor and dosage, for cement as an adhesive material of concrete (especially bulk concrete), can reduce the temperature difference of the concrete core and surface by reducing the hydration heat release and delaying the arrival of the temperature peak. In so doing, this study reduced the generation of early temperature stress in concrete and provided a means of minimizing the appearance of temperature cracks.

6 Conclusion

The inhibitors primarily interfered with the OPC hydration process, similar to the manner in which they affected the exothermic hydration of C_3S . These results indicate that C_3S might play a major role in generating the exothermic effect observed during OPC hydration. The inhibitors decreased the heat release during OPC hydration by a maximum of 77%. DTPMPA acted by forming complexes and controlling the

production of CH (i.e., crystals of calcium dihydroxide). The phosphate groups in this molecule formed complexes with the calcium and magnesium ions that covered the surfaces of unhydrated C_3S particles in a manner that inhibited hydration and CH^- formation, achieving a cooling effect. Blending with a mixture of HEDP and DTPMPA delayed the onset of the peak heat flow, decreased the heating rate, and increased the cooling rate. Therefore, a synergistic effect was apparent. Increasing the inhibitor level to 0.03% resulted in a segmental heating phenomenon. The cooling performance caused an overall decrease in the heating rate, whereas the inhibition effect prolonged the overall temperature increase, leading to hydration heat generation with segmented heating and cooling. The temperature increases exhibited relatively small variations and the overall time span over which the heat of hydration was released increased by 50%.

Data availability statement

The original contributions presented in the study are included in the article/Supplementary material, and further inquiries can be directed to the corresponding author.

Author contributions

JL designed the experiment and analyzed the main points. BT was a major contributor in terms of testing and writing the manuscript. LL and LQ helped to conduct tests and data examination. All the authors read and approved the final manuscript.

Funding

This research was supported by the National Key Scientific Instrument and Equipment Development Projects of China (2018YFB1600100) and the National Natural Science Foundation of China (52178428, 52178427, and 51908260).

Acknowledgments

The first author acknowledges support from the Ministry of Communications Highway Traffic Test Site, Beijing, China.

Conflict of interest

The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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