

Evaluating the Effect of Mixing Method on Cement Hydration in the Presence of a Polycarboxylate High-Range Water Reducing Admixture by Isothermal Conduction Calorimetry

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ABSTRACT

This paper describes the importance of mixing methods and materials when evaluating the effect of polycarboxylate high-range water reducing admixtures on the hydration of cement by isothermal conduction calorimetry.

Experience with hydration studies using isothermal conduction calorimetry has shown that polycarboxylate high-range water reducing admixtures tend to retard early hydration in cement paste preparations. This is unexpected based on the fact that these admixtures do not retard setting and early strength development when used at the same dosage rate in a concrete mix. The main difference between cement paste and concrete is the shear energy that is imparted. In cement paste, the shear is imparted only by the mixing implement, while in concrete the mixing implement and the aggregate contacts are sources of shear forces.

This paper shows that the method of mixing has a strong influence on the hydration of cement when polycarboxylate high-range water reducing admixtures are used. The use of a mortar batch comes closest to simulating performance of a concrete batch. With cement paste, prepared either with a high-shear method or standard method, the initial hydration of the cement is impeded by the presence of such admixtures. The magnitude of the decrease in initial hydration caused by the addition of polycarboxylates to cement paste is a function of the cement chemistry. The method of mixing appears to have a smaller influence on the hydration of cement when such admixtures are not added, to the extent that cement paste studies may be appropriate.

Keywords: high-range water reducing admixture, polycarboxylate, cement paste, isothermal calorimetry, hydration, shear, mixing, mortar, concrete

1. INTRODUCTION

The use of polycarboxylate-based high range water reducing admixtures (HRWRA, also called superplasticizers) in practice by the concrete

industry started in the early 1990's, with publications on the subject appearing in the decade leading up to their introduction. Due to the rapid increase of research in the design and application of such materials, it is difficult to find a comprehensive review of the technology. Every three years, CANMET and ACI sponsor a conference on the subject of superplasticizers, and the majority of papers in recent conferences have been focused on polycarboxylate chemistry. Those interested in a deeper understanding of polycarboxylates are pointed to the proceedings of these conferences, with the eighth and latest being held in late 2006 [1]. An introduction to polycarboxylate chemistry can be found in the second chapter of a recent book [2].

The use of isothermal conduction calorimetry to study the progress of cement hydration is a common practice [3,4]. With the recent emergence of commercial calorimeters, more calorimetry data is being published in the literature [5,6]. In fact, at the 11th ICCG, more than 25 papers referenced isothermal (heat flow) calorimetry [7]. Most calorimetry studies that are used to study cement hydration and the effect of chemical and mineral admixtures on hydration utilize cement paste, typically at a w/c of 0.50, and often little attention is given to the method of preparation of the cement paste for testing [8,9]. With hydration studies that have included polycarboxylate admixtures, the author's experience has shown that the polycarboxylates tend to retard the initial cement hydration reactions. This same result appears in many published studies [10-13]. Unfortunately, this result is at odds with normal practice, as in concrete these admixtures do not slow down the setting or early strength development of concrete.

This work uncovers some of the relationships between methodology of mixing and the hydration response of the system as determined with calorimetry. The influence of polycarboxylates on the hydration response is shown, and the hydration response with mixing method seems to be dependent on the chemistry of the portland cement.

2.1 Materials

Table 1 shows the chemical composition of the two cements (148 and 156) used in the present study. Cement 148 is a Type I cement according to ASTM C150 [14] that is found in the northeastern United States and contains relatively high levels of C₃A, alkalis, and sulfates. Cement 148 is a Type I or Type II cement according to ASTM C150 that is found in the southwestern United States and contains relatively low levels of C₃A, alkalis, and sulfates.

Table 1. Chemical analysis of cements

	Cement 148 (Type I)	Cement 156 (Type I/II)
SiO₂	19.01%	19.37%
Al₂O₃	6.04%	4.38%

Fe₂O₃	2.55%	3.33%
CaO	61.60%	63.07%
MgO	2.89%	4.27%
SO₃	4.42%	2.83%
Na₂O_{eq}	1.05%	0.29%
Limestone	---- ^a	3.32%
LOI	1.22%	2.41%
Insoluble residue	0.22%	0.54%
Bogue potential composition		
C₃S	49%	60%
C₂S	17%	10%
C₃A	12%	6%
C₄AF	8%	10%
Blaine fineness (m²/kg)	446	405

^a not reported (likely = 0.00)

The polycarboxylate (PCE) HRWRA had a solids content of 44.8%, specific gravity of 1.107, and pH of 7. In all cases, it was used at a dosage of 0.12% (based on polymer content) by mass of cement.

2.2 Equipment

The mixing apparatus that was used to prepare high-shear cement paste was a Waring blender LB10 (Model 38BL54) with a cool base container. The cool base container is a mixing cup with an external jacket through which fluid can flow. In this case, the mixing container was connected to a water bath set at 15°C in order to eliminate heating of the cement paste by the blender motor and friction. The apparatus is described in a draft document of Committee C01.22 of ASTM [15]. A Hobart N50 mixer was used to prepare the standard cement paste and mortar. Concrete was prepared in a Zyklos ZK30HE pan-style mixer. All materials (concrete, mortar, and cement paste) were designed to have similar levels of workability.

2.3 Methods

2.3.1 High-shear cement paste

Cement was added to the water in the mixing container with the mixing blade rotating at 1000 rpm. Immediately after addition of the last of the cement, the mixing blade speed was increased to 13,000 rpm and mixing proceeded at this speed for two minutes. In the paste prepared with polycarboxylate, the admixture was added to the mixing water and the paste was mixed in the same manner as the paste that did not contain the admixture. Late addition of the polycarboxylate was not possible because of the lack of workability of such a low w/c paste before addition of the admixture. Defoamer was added to all cement pastes to eliminate generation of air. The cement paste mix designs are shown in Tables 2

and 3. For these studies, 500g of cement and the appropriate amount of water were used.

2.3.2 Low-shear cement paste

Cement was added to the mixing vessel and the mixer was started at low speed (140 rpm). For the case without admixture, the water was added and then the mixer speed was increased to 285 rpm and the paste was mixed for two minutes. For the case with polycarboxylate admixture, the paste was mixed in a similar fashion, with the admixture added for the last minute of mixing. Defoamer was added to all cement pastes to eliminate generation of air. The cement paste mix designs are shown in Tables 2 and 3, and the same designs were used for both the high-shear and low-shear cement pastes. For these studies, 1kg of cement and the appropriate amount of water were used.

2.3.3 Mortar

Cement and sand were blended for two minutes at 140rpm. After addition of water, the speed was increased to 285 rpm and the mortar was mixed for two minutes. In the case with the polycarboxylate admixture, the admixture was added for the last minute of mixing. Defoamer was added to all mortar mixes to eliminate generation of air. The mortar mix designs are shown in Tables 2 and 3. For these studies, 625g of cement and the appropriate amounts of fine aggregate and water were used.

2.3.4 Concrete

Cement and aggregates were blended for two minutes at 60 rpm pan rotation and 38 rpm rotor rotation (both rotating clockwise). After addition of water, the concrete was mixed for two minutes. In the case with the polycarboxylate admixture, the admixture was added for the last minute of mixing. Defoamer was added to all concrete mixes to eliminate generation of air. The concrete mix designs are shown in Tables 2 and 3. For these studies, a 15 liter batch of concrete was produced.

Table 2. Mix designs used in the study (for 1m³) – no admixture

	Cement paste (high-shear and low-shear)	Mortar		Concrete	
	Cements 148 and 156	Cement 148	Cement 156	Cement 148	Cement 156
Cement	1303 kg	577 kg	595 kg	332 kg	335 kg
Water	586 kg	290 kg	268 kg	182 kg	174 kg
Fine aggregate	---	1370 kg	1413 kg	788 kg	795 kg
Coarse aggregate	---	---	---	1090 kg	1100 kg
w/c	0.45	0.50	0.45	0.55	0.52

Table 3. Mix designs used in the study (for 1m³) – with PCE HRWRA

	Cement paste (high-shear and low-shear)	Mortar		Concrete	
		Cements 148 and 156	Cement 148	Cement 156	Cement 148
Cement	1702 kg	585 kg	601 kg	332 kg	335 kg
Water	460 kg	261 kg	241 kg	158 kg	151 kg
Fine aggregate	---	1439 kg	1477 kg	816 kg	823 kg
Coarse aggregate	---	---	---	1125 kg	1135 kg
w/c	0.27	0.45	0.40	0.48	0.45

3. EXPERIMENTAL

All calorimetry experiments were performed in a Thermometric TAM Air calorimeter set at 21°C.

3.1 Cement paste

For both the high-shear and low-shear cement pastes, workability was determined with a 1:5-scale slump cone (60mm cone with 20mm upper diameter and 40mm lower diameter). Setting time was determined by penetration resistance of a 1mm diameter Vicat needle [16]. A 5-7g sample of the cement paste was used for calorimetry studies.

3.2 Mortar

Workability of the mortar was determined using a 1:2-scale mini-slump cone (150mm cone with 50mm upper diameter and 100mm lower diameter). Setting time of the mortar was determined by penetration resistance of a 2mm diameter Vicat needle [17]. A 15-20g sample of the mortar was used for calorimetry studies.

3.3 Concrete

Workability of the concrete was determined with a standard slump cone, and workability of the mortar fraction was determined using the 1:2-scale mini-slump cone. The mortar fraction was obtained by collecting that part of the concrete that passed a screen with opening size of 4.75mm. In addition to the mini-slump measurement, the mortar fraction was used for measurement of initial setting time [18] and hydration studies with the isothermal conduction calorimeter. A 15-20g sample of mortar was used for calorimetry studies.

4. RESULTS AND DISCUSSION

4.1 Results of physical tests

The results of the slump and setting time determinations, as well as temperature values for the cement paste, mortar, or concrete is shown in Tables 4 and 5.

Table 4. Results from physical tests – no admixture

	High-shear cement paste		Low-shear cement paste		Mortar		Concrete	
Cement	148	156	148	156	148	156	148	156
Slump, mm	---	---	---	---	---	---	55	70
1:2-scale slump, mm	---	---	---	---	64	51	65	55
1:5-scale slump, mm	51	51	46	35	---	---	---	---
Material temp. °C	20	22	23	24	21	21	23	23
Setting time, hr.	6.5	5.6	6.1	5.9	4.4	3.0	5.0	4.1

In this study, the concrete, mortar, and cement paste were all designed to have equivalent workability, rather than equivalent w/c. The workability of the concrete, mortar, and cement pastes prepared without polycarboxylate admixture is reflected in the slump measurements shown in Table 4. Material temperatures were essentially the same, with the high-shear cement paste temperatures slightly lower than the corresponding low-shear cement paste temperatures due to the use of the jacketed mixing vessel for the high-shear mixing. For each cement used in the study, the mortar setting times were faster than the setting time of the concrete mortar fraction, and these were measurably faster than setting times of either of the cement pastes.

Table 5. Results from physical tests – with PCE HRWRA

	High-shear cement paste		Low-shear cement paste		Mortar		Concrete	
Cement	148	156	148	156	148	156	148	156
Slump, mm	---	---	---	---	---	---	70	75
1:2-scale slump, mm	---	---	---	---	104	99	101	94
1:5-scale slump, mm	51	51	46	35	---	---	---	---
Material temp. °C	22	25	23	27	22	22	23	23
Setting time, hr.	9.5	4.8	11.3	5.4	5.0	3.4	5.5	4.2

Again, in this study, the concrete, mortar, and cement paste were all designed to have equivalent workability, rather than equivalent w/c. The

workability of the concrete, mortar, and cement pastes prepared with polycarboxylate admixture is reflected in the slump measurements shown in Table 5. Material temperatures were essentially the same, with the high-shear cement paste temperatures slightly lower than the corresponding low-shear cement paste temperatures due to the use of the jacketed mixing vessel for the high-shear mixing. For each cement used in the study, the mortar setting times were faster than the setting time of the concrete mortar fraction, and these were measurably faster than setting times of either of the cement pastes. The cement pastes prepared with Cement 148 and polycarboxylate had setting times that were extended by 4-6 hours compared to the concrete mortar fraction. The cement pastes prepared with Cement 156 and polycarboxylate had setting times that were extended by approximately one hour compared to the concrete mortar fraction.

4.2 Results from calorimetry studies

A brief discussion on the interpretation of cement hydration effects from heat flow profiles generated with isothermal calorimetry follows.

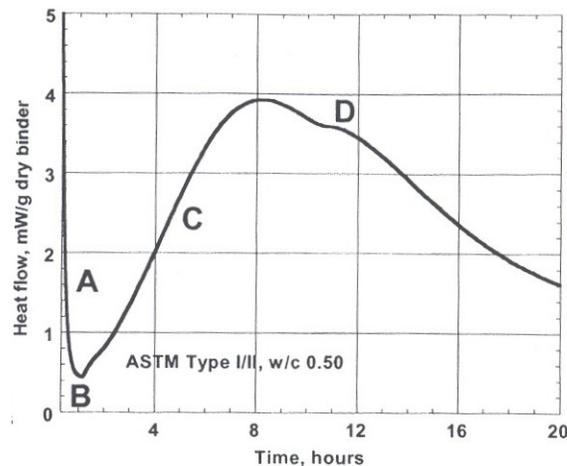


Figure 1. Example heat flow profile of cement paste from the isothermal calorimeter [19]

The initial exotherm, A, is caused by rapid dissolution and initial hydration reactions, mainly of aluminate phases. The dormant period, B, is caused by the control of the aluminate reactions by sulfate to form ettringite. The main peak, C, is caused by accelerated reaction of the calcium silicates, mainly alite. The hump, D, on the back side of the silicate hydration peak, is called the 'sulfate depletion' peak, as it results from the conversion of ettringite to monosulfoaluminate that occurs when the supply of soluble sulfate in the system is exhausted [19].

The results from the calorimetry studies associated with this work are shown in Figures 2-5.

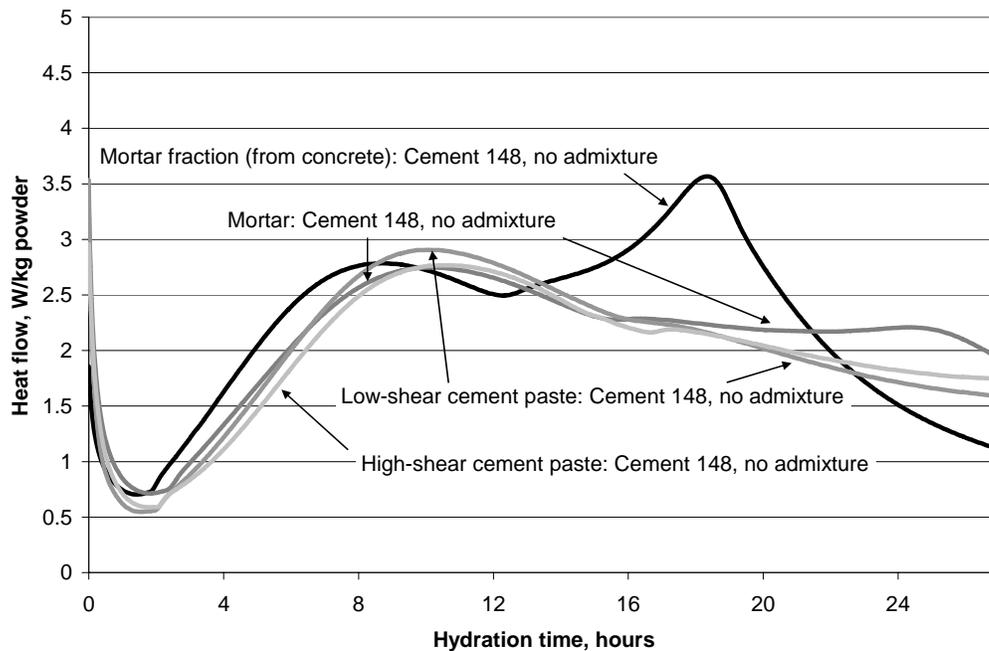


Figure 2. Heat flow profile from calorimetry, preparations made with Cement 148 and no admixture

Figure 2 shows the heat flow profiles for the mortar fraction (from concrete), mortar, high-shear cement paste, and low-shear cement paste made without admixture and with Cement 148, which is high in alkalis, sulfate, and C₃A. The heat flow profile of the concrete mortar fraction can be seen to rise about one hour sooner than the profiles of the mortar or cement pastes. The sulfate depletion peak, which is the peak that reaches a maximum at approximately 18 hours for the concrete mortar fraction, is quite pronounced as compared to the profiles from the mortar or cement pastes. This peak occurs much later, beyond 24 hours, in the profile from the mortar and is nearly absent in the profiles from the two cement pastes.

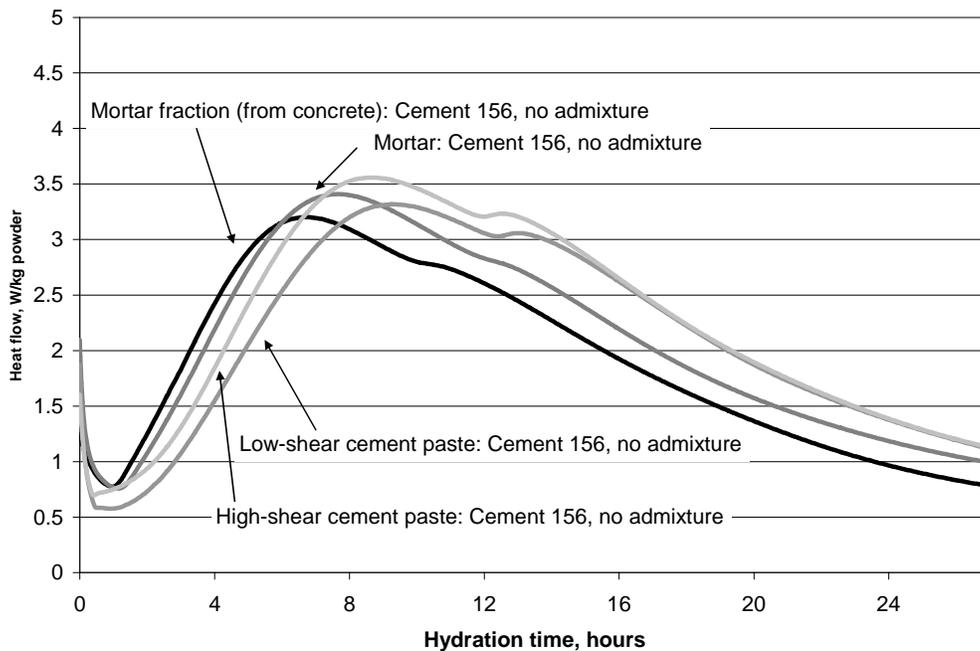


Figure 3. Heat flow profile from calorimetry, preparations made with Cement 156 and no admixture

Figure 3 shows the heat flow profiles for the mortar fraction (from concrete), mortar, high-shear cement paste, and low-shear cement paste made without admixture and with Cement 156, which is low in alkalis, sulfate, and C_3A . With this cement, there is a nearly continuous progression of the initial rise of the heat flow profile in the following order: concrete mortar fraction > mortar > high-shear cement paste > low-shear cement paste. The shapes of the profiles are all quite similar, including the sulfate depletion peaks, which are seen as small humps that peak after 11-14 hours of hydration. The complete profile from the concrete mortar fraction is less pronounced compared to the profiles from the other materials, suggesting less hydration during this 26-hour initial period. This may be due to the higher w/c of the concrete as compared to the mortar or cement pastes.

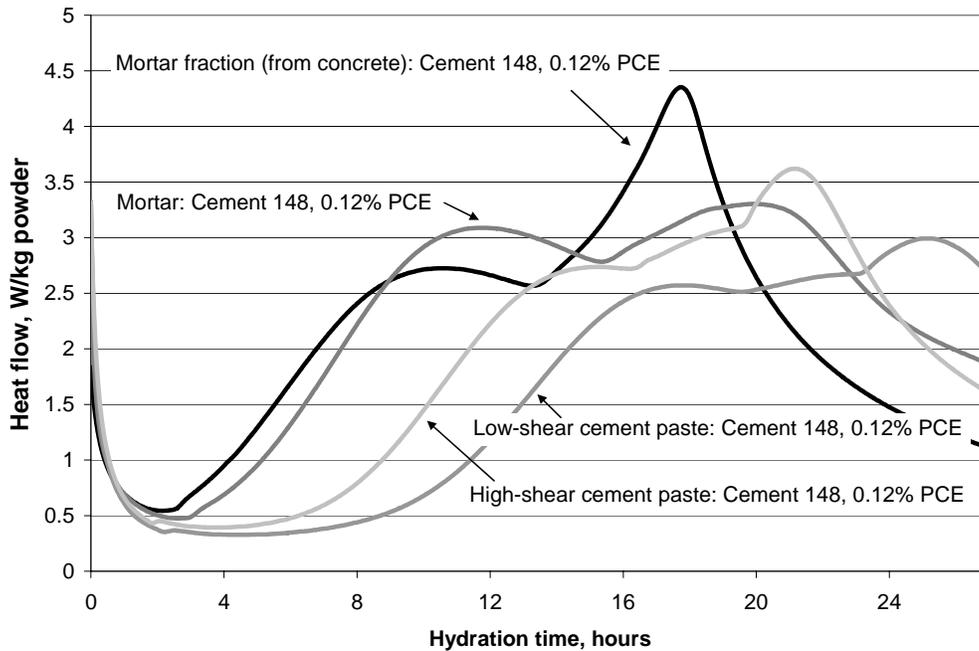


Figure 4. Heat flow profile from calorimetry, preparations made with Cement 148 and PCE HRWRA

Figure 4 shows the heat flow profiles for the mortar fraction (from concrete), mortar, high-shear cement paste, and low-shear cement paste made with PCE HRWRA and with Cement 148. With this cement, there is a progression of the initial rise of the heat flow profile in the following order: concrete mortar fraction > mortar > high-shear cement paste > low-shear cement paste. The extended dormant period for the cement pastes is consistent with the slower setting times that were measured for these materials. Contrary to the heat flow profiles from these materials prepared without admixture (in Fig. 2), the sulfate depletion peak is pronounced in all four of the profiles, although still most pronounced in the profile from the concrete mortar fraction. The overall profiles from the concrete and the high-shear cement paste are quite similar in shape, and are simply shifted relative to each other by about four hours due to the delay in initial hydration of the high-shear cement paste. Similarly, the overall profiles from the mortar and the low-shear cement paste are quite alike, and are simply shifted relative to each other by about six hours due to the delay in initial hydration of the low-shear cement paste. The profiles of the concrete mortar fraction and mortar have similar initial silicate hydration peaks, but the sulfate depletion peak shown in the mortar profile is shifted to a later hydration time compared to its silicate hydration peak. The delay of the initial rise of the silicate hydration peak in the mortar profile compared to the concrete mortar fraction profile is not consistent with the faster setting time of the mortar.

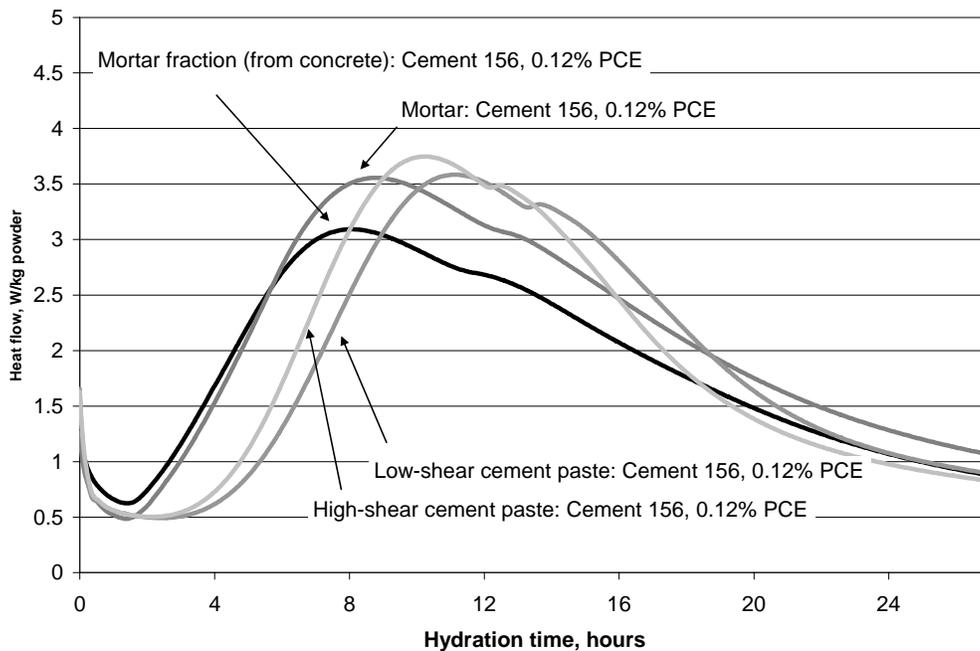


Figure 5. Heat flow profile from calorimetry, preparations made with Cement 148 and PCE HRWRA

Figure 5 shows the heat flow profiles for the mortar fraction (from concrete), mortar, high-shear cement paste, and low-shear cement paste made with PCE HRWRA and with Cement 156. With this cement, there is also a progression of the initial rise of the heat flow profile in the following order: concrete mortar fraction > mortar > high-shear cement paste > low-shear cement paste. The extended dormant period for the cement pastes reflects the slower setting times that were measured for these materials, although the delay in the rise of the hydration profile is longer than would be expected based on measured setting times. As was the case with this cement and the materials produced without admixture, the shapes of the profiles are all quite similar, including the sulfate depletion peaks, which are seen as small humps that peak after 13-15 hours of hydration. The complete profile from the concrete mortar fraction is less pronounced compared to the profiles from the other materials, suggesting less hydration during this 26-hour initial period. This may be due to the higher w/c of the concrete as compared to the mortar or cement pastes. This argument does not hold when comparing the mortar and cement paste profiles, which are only slightly different in magnitude even though the w/c of the cement pastes were much lower than that of the w/c of the mortar.

5. CONCLUDING REMARKS

For studies of portland cement hydration with water only, the choice of material and mixing method does not have a great influence on the initial

hydration reactions as measured with isothermal calorimetry. Depending on the chemistry of the cement, there may be a measurable difference in the later aluminate reactions with different mixing methods, as evidenced in the differences between the shape and location of the sulfate depletion peak in the heat flow profile of concrete as compared to mortar or cement paste. If the goal of such a study is to simulate performance of materials in concrete, then the best approach is to prepare batches of concrete to use for testing. If material quantities prohibit the preparation of concrete batches, then mortar or cement paste preparations seem to provide accurate indications of initial cement hydration. Mortar is more useful than cement paste to judge relative water requirements of cements.

For studies of portland cement hydration in the presence of polycarboxylate admixtures, cement paste does not simulate the hydration of cement in concrete. The performance of cement paste with polycarboxylates is highly dependent on the chemistry of the cement. The retardation of hydration by polycarboxylates in cement paste is likely a result of less dispersion of the cement grains, which means that less grain surfaces are available for water access and reaction. Additionally, more surfaces may be coated by polycarboxylate, further inhibiting water access. One should use strong caution when drawing conclusions about cement hydration by interpreting results of cement paste experiments with polycarboxylate admixtures.

The hydration of cement in a mortar preparation is similar to the hydration of cement in concrete when both include polycarboxylate high range water reducing admixtures.

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