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Effect of Pozzolan Content and Fineness on Early Hydration of Interground Blended Cements

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Abstract

The chemical composition and heat evolution of <45 μm (fine), and > 45 μm (coarse) portions of interground, natural pozzolan-blended cements were investigated. Cements with four different pozzolan contents were ground to 300 m^2/kg, 500 m^2/kg, and 600 m^2/kg fineness and sieved through a 45 μm sieve. Clinker, pozzolan, and gypsum contents in the fine and coarse portions after sieving were determined and compared with the unsieved cements. Heat of hydration evolution of the samples were determined up to 48 h using isothermal calorimetry. The fine portions of the cements always contained more gypsum, had higher pozzolan-to-clinker ratios, and slightly higher tricalcium silicate contents, which influenced the rate of heat development at early ages. The fine portions contribute more to the total early heat evolved than the coarse portions. A small amount of pozzolan enhances early hydration. The heat evolved up to 24 h was related linearly to the heat evolved up to 48 h. Such observations could be useful in the modeling of early hydration of blended cements.

1. Introduction

Concrete is one of the most widely used materials in the world. Typically 10-20 % by mass of concrete is cement. For economical, environmental, and technical reasons, ~75 % of cement produced in Europe contains different proportions of one or more of blast furnace slag, silica fume, pozzolans, fly ash, and limestone (Cembureau 2013). Pozzolan incorporation modifies the hydration of cement which is affected by factors such as phase composition and fineness of the cement, water-cement ratio, temperature, and amount of chemical and mineral admixtures (Odler 2004). Changes in the rate and amount of heat evolution during early hydration can explain the influence of partial replacement of portland cement with pozzolans.

Pozzolans are generally accepted to reduce heat evolution due to the dilution effect (Massazza 2004). Several investigations report enhanced cement hydration caused by pozzolan incorporation (Buil *et al.* 1984; Cheng-Yi and Feldman 1985; Rahhal and Talero 2009; Takemoto and Uchikawa 1980; Massazza 2004). Contrarily, other investigations report no change or a delay in early hydration upon pozzolan incorporation (Zhou *et al*. 2012; Carette and Malhotra 1983; Naik and Singh 1997; Schindler and Folliard 2003). Conflicting results can be explained by differences in the types, compositions, and finenesses of the pozzolans used. In almost all of these studies, the added pozzolan was ground separately, hence the particle size distribution (PSD) of the remaining portland cement was unchanged. In the case of blended cements, produced by intergrinding the clinker and pozzolan, differences in grindability can lead to significant changes in the relative proportions of the finer and coarser portions of the cement (Tokyay *et al.* 2012). Very fine cement particles hydrate can fully within 24 h (Mindess and Young 1981) whereas particles larger than 45 μm hydrate slowly (Mehta and Monteiro 2006). It has also been suggested that particles with an equivalent-volume sphere diameter greater than 15-20 μm generally may not hydrate completely (Erdoğan 2013). However, these generalisations do not necessarily apply to blended cements. The relative contribution over time of various-size cement particles to hydration and property development of a mixture is still not well understood.

The work presented here is part of an extensive study, the aim of which is to investigate the effects of different mineral admixtures interground with clinker (and gypsum) on the early heat of hydration of blended cements. In this first stage, natural pozzolan-containing cements belonging to groups CEM II/A and CEM II/B of EN 197-1 (2011) are studied. The effects of interground natural pozzolan on early hydration were analyzed through determining the rate of heat evolution of cement portions smaller and larger than 45 μm and comparing the results with the unsieved cement.

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Table 1 Chemical compositions of the clinker, pozzolan and gypsum used.

Oxide (%)	Clinker	Natural Pozzolan	Gypsum
SiO_2	20.43	62.59	2.26
Al_2O_3	5.73	15.56	0.08
Fe_2O_3	3.25	3.86	0.28
CaO	65.50	6.79	32.16
MgO	2.67	1.77	0.68
SO_3	0.42	0.05	42.68
Na_2O	0.37	3.35	0.34
K_2O	0.58	1.62	0.12
Loss on Ignition	1.02	3.49	21.54

2. Materials and method

Blended cements in which 6, 20, and 35 % of the clinker was replaced by a natural pozzolan were obtained by intergrinding clinker, pozzolan, and gypsum in a laboratory ball mill. Control cements without pozzolan were obtained from the same clinker and gypsum. The amount of gypsum added to the control and 6 % pozzolan cements was 5 % (by mass of clinker + natural pozzolan). It was reduced to 4 % for 20, and 35 % pozzolan cements. **Table 1** shows the chemical compositions of the clinker, pozzolan and gypsum, measured using inductively coupled plasma mass spectrometry.

All cements were prepared at three Blaine finenesses: 300±10 m^2/kg, 500±10 m^2/kg, and 600±10 m^2/kg. Part of each cement was sieved through a 45 μm sieve to separate the fine and coarse portions. Three subgroups were obtained: original (unsieved), fine (< 45 μm), and coarse (> 45 μm). Samples were named to reveal whether they were obtained from a control cement or a cement containing 6, 20, or 35 % pozzolan; the Blaine fineness (in m^2/kg) of the cement the sample was taken from, and whether it is the fine portion, the coarse portion, or unsieved (original). For example, C300o is the unsieved (full PSD), control (no pozzolan), 300 m^2/kg Blaine cement sample, 6P500f is the fine (< 45 μm) portion of the 500 m^2/kg Blaine cement sample containing 6 % pozzolan, and 35P600c is the coarse (> 45 μm) portion of the 600 m^2/kg Blaine cement sample containing 35 % pozzolan. **Figure 1** shows the PSDs of the samples determined using laser diffraction.

Table 2 Rosin-Rammler-Sperling-Bennett distribution parameters for the cement samples.

	Blaine (m^2/kg)	n	D (μm)
Control	300	1.23	36.2
	500	1.42	17.0
	600	1.71	9.8
6P	300	1.18	42.2
	500	1.40	16.4
	600	1.66	9.5
20P	300	1.19	48.3
	500	1.29	16.8
	600	1.58	11.5
35P	300	1.24	61.0
	500	1.30	19.3
	600	1.47	13.4

The median particle size drops from 20-40 μm for the 300 m^2/kg cements, to 6-10 μm for the finer cements. The effect of overall cement fineness on the amounts of material below and above 45 μm appears to be small for the 500 m^2/kg and 600 m^2/kg cements (12-15 % above 45 μm). For 300 m^2/kg Blaine, increasing pozzolan content noticeably shifts the PSD to coarser sizes. This effect is less for the finer cements. **Table 2** gives the calculated parameters of the Rosin-Rammler-Sperling-Bennett distribution (Masuda *et al.* 2006) for the cements.

"*D*" is the position parameter, equal to the particle size above which 36.8 % of the particles are retained. The smaller the position parameter is, the greater the fineness of the particle population. and "n" is the spread parameter and is the slope of the straight line fitted to the measured particle size distribution data and describes the width of the distribution. The larger the slope is, the narrower the size distribution. It is seen in **Table 2**, that *D* naturally decreases with increasing Blaine fineness, for a given cement, control or blended. *D* increases as the amount of pozzolan

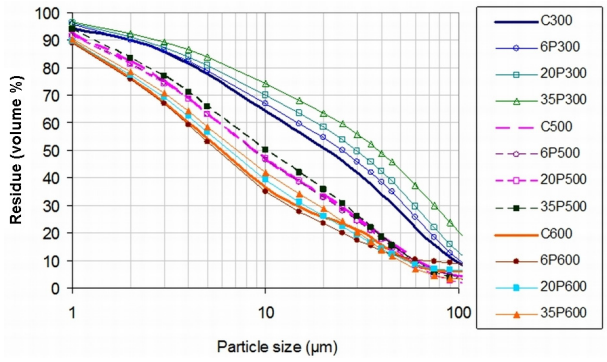

Fig. 1 Particle size distributions of the 300 m^2/kg, 500 m^2/kg, and 600 m^2/kg cements.

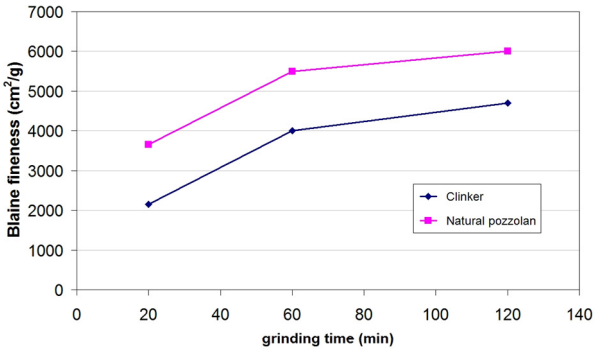

Fig. 2 Change in the Blaine fineness of the clinker and pozzolan with grinding.

increases, especially at low fineness. De Weerdt (2007) reported that during intergrinding, the softer component initially hinders the grinding of the harder component. **Figure 2** shows that the natural pozzolan used is softer and easier to grind than the clinker. The difference between the control and the 35P cements is much greater for the 300 m^2/kg case than for the 600 m^2/kg case. n increases with increasing Blaine fineness for a given cement but for a does not change very much with changing pozzolan content, for a chosen fineness.

The rate of heat evolution vs. time curves of paste samples with water-to-cement ratios of 0.40 were obtained using isothermal calorimetry at 23 °C. The heat flow data were integrated to obtain the total heat evolution in time and analyzed to determine the combined effect of pozzolan and fineness on early hydration.

3. Results and Discussion

The chemical compositions of the samples are given in **Table 3**.

Loss on ignition (LOI) is higher in the finer portions of all cements. LOI increases with increasing pozzolan content for the fine portions. This could be expected since the pozzolan has a higher LOI than the clinker. However, this trend is not true for the coarse portions indicating that the actual amount of pozzolan in the coarse portion of a cement may not equal the amount prior to sieving. SO_3 contents of the fine portions are higher suggesting that more of the gypsum, softer than clinker or pozzolan, ends up there. SO_3 decreases with increasing fineness (e.g. comparing 6P300f, 6P500f, and 6P600f) since most of the gypsum is already in the fine portion at 300 Blaine, but the relative content of pozzolan and/or clinker in this portion increases with continued grinding. Also, cements with more pozzolan

Table 3 Chemical compositions of the cement samples.

Fineness Group (m^2/kg)	Cement sample	Oxide (%)									
		SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	LOI	CaO / SiO_2
300	C300o	19.65	5.48	3.08	63.25	2.58	2.43	0.35	0.57	2.59	3.22
	C300f	19.30	5.27	2.94	62.96	2.49	3.13	0.31	0.60	3.01	3.26
	C300c	20.18	5.90	3.25	63.79	2.69	1.74	0.36	0.53	1.51	3.16
	6P300o	21.81	6.09	3.26	60.12	2.55	2.59	0.52	0.65	2.40	2.76
	6P300f	21.96	5.90	3.13	59.04	2.44	3.20	0.54	0.67	3.12	2.69
	6P300c	21.80	6.34	3.36	61.88	2.65	1.58	0.49	0.58	1.32	2.84
	20P300o	27.23	7.55	3.59	52.53	2.50	2.15	0.90	0.80	2.64	1.93
	20P300f	28.00	7.50	3.62	50.80	2.43	2.40	0.94	0.83	3.27	1.81
	20P300c	26.27	7.61	3.55	55.05	2.62	1.40	0.86	0.74	1.43	2.10
	35P300o	33.85	8.99	3.63	44.20	2.41	1.80	1.35	0.93	2.83	1.31
	35P300f	35.77	9.25	3.76	40.05	2.27	2.65	1.38	0.97	3.89	1.12
	35P300c	32.88	8.87	3.44	45.94	2.44	1.74	1.28	0.91	2.17	1.40
500	C500o	19.65	5.48	3.08	63.25	2.58	2.43	0.35	0.57	2.59	3.22
	C500f	19.44	5.38	3.01	63.22	2.51	2.77	0.32	0.59	2.70	3.25
	C500c	20.08	5.86	3.25	63.44	2.74	1.81	0.39	0.55	1.75	3.16
	6P500o	21.81	6.09	3.26	60.12	2.55	2.59	0.52	0.65	2.40	2.76
	6P500f	21.81	6.08	3.22	59.62	2.46	2.79	0.52	0.66	2.83	2.73
	6P500c	21.74	6.15	3.34	61.37	2.57	1.88	0.47	0.58	1.78	2.82
	20P500o	27.23	7.55	3.59	52.53	2.50	2.15	0.90	0.80	2.64	1.93
	20P500f	27.85	7.52	3.59	50.95	2.46	2.36	0.90	0.82	3.03	1.83
	20P500c	25.93	7.41	3.61	55.23	2.63	1.56	0.86	0.71	1.79	2.13
	35P500o	33.85	8.99	3.63	44.20	2.41	1.80	1.35	0.93	2.83	1.31
	35P500f	34.78	9.18	3.70	42.09	2.31	2.38	1.36	0.95	3.28	1.21
	35P500c	32.30	8.65	3.48	46.91	2.55	1.66	1.28	0.86	2.08	1.45
600	C600o	19.65	5.48	3.08	63.25	2.58	2.43	0.35	0.57	2.59	3.22
	C600f	19.49	5.45	2.93	63.37	2.57	2.64	0.34	0.57	2.60	3.25
	C600c	20.01	5.74	3.24	62.95	2.65	2.18	0.35	0.60	2.23	3.15
	6P600o	21.81	6.09	3.26	60.12	2.55	2.59	0.52	0.65	2.40	2.76
	6P600f	21.77	6.09	3.26	60.11	2.54	2.53	0.53	0.65	2.53	2.76
	6P600c	21.68	6.10	3.34	60.10	2.55	2.28	0.51	0.60	2.82	2.77
	20P600o	27.23	7.55	3.59	52.53	2.50	2.15	0.90	0.80	2.64	1.93
	20P600f	27.51	7.56	3.56	51.63	2.50	2.32	0.90	0.81	2.88	1.88
	20P600c	25.88	7.33	3.64	55.33	2.65	1.75	0.80	0.72	1.93	2.14
	35P600o	33.85	8.99	3.63	44.20	2.41	1.80	1.35	0.93	2.83	1.31
	35P600f	34.61	9.16	3.67	42.59	2.37	2.11	1.32	0.97	3.20	1.23
	35P600c	32.01	8.57	3.52	47.63	2.61	1.42	1.27	0.86	2.00	1.49

contain less SO_3 because the pozzolan contains hardly any and because the amount of added gypsum decreases from 5 % to 4 %.

Concerning the four major oxides, the most important observation is that CaO content decreases and SiO_2, Al_2O_3 contents increase with increasing pozzolan amount in the unsieved cement and both the fine and coarse portions, since the pozzolan has higher SiO_2 and Al_2O_3 contents than the clinker. The Fe_2O_3 contents of the unsieved cement and the sieved fine portions increases with pozzolan content but for the coarse portions, the increase is up to 20 % is reversed afterwards. This suggests that more of the pozzolan is in the fine portion for the 35P cements. Similarly, the CaO contents of the coarse portions are generally higher, and the SiO_2 content mostly lower, at higher pozzolan contents. For the controls, as fineness increases, the CaO/SiO_2 ratio of the fine portion slightly decreases towards the value for the unsieved cement since more of the particles are below 45 μm at 500 Blaine. The Al_2O_3 content is higher in the fine portions of the 35P cements suggesting that the pozzolan goes to the finer portions at this loading. The higher Na_2O and K_2O alkali contents in the fine portions of all pozzolan-containing cements, regardless of content, also supports this.

Amounts of clinker, pozzolan, and gypsum in the fine and coarse portions of each cement, determined according to CEN/TR 196-4 (2007), are given in **Table 4**.

The finer cements contain higher amounts of < 45 μm material. Most of the pozzolan in 6P, 20P, and 35P are in the fine portion. Pozzolan content of the coarse portion decreases with increasing fineness indicating that the pozzolan is easier to grind. Pozzolan-to-clinker ratio is higher in the fine portions than the coarse portions and is higher for 300 Blaine than for 500 or 600 Blaine cements. As expected, the amount of gypsum in the fine portion of a chosen cement is significantly greater than that in the coarse portion, ~70-80 % of the total for the 300 Blaine cements, and ~85-95 % for the 500 and 600 Blaine cements. **Figure 3** shows the rate of heat evolution in time of the different cements.

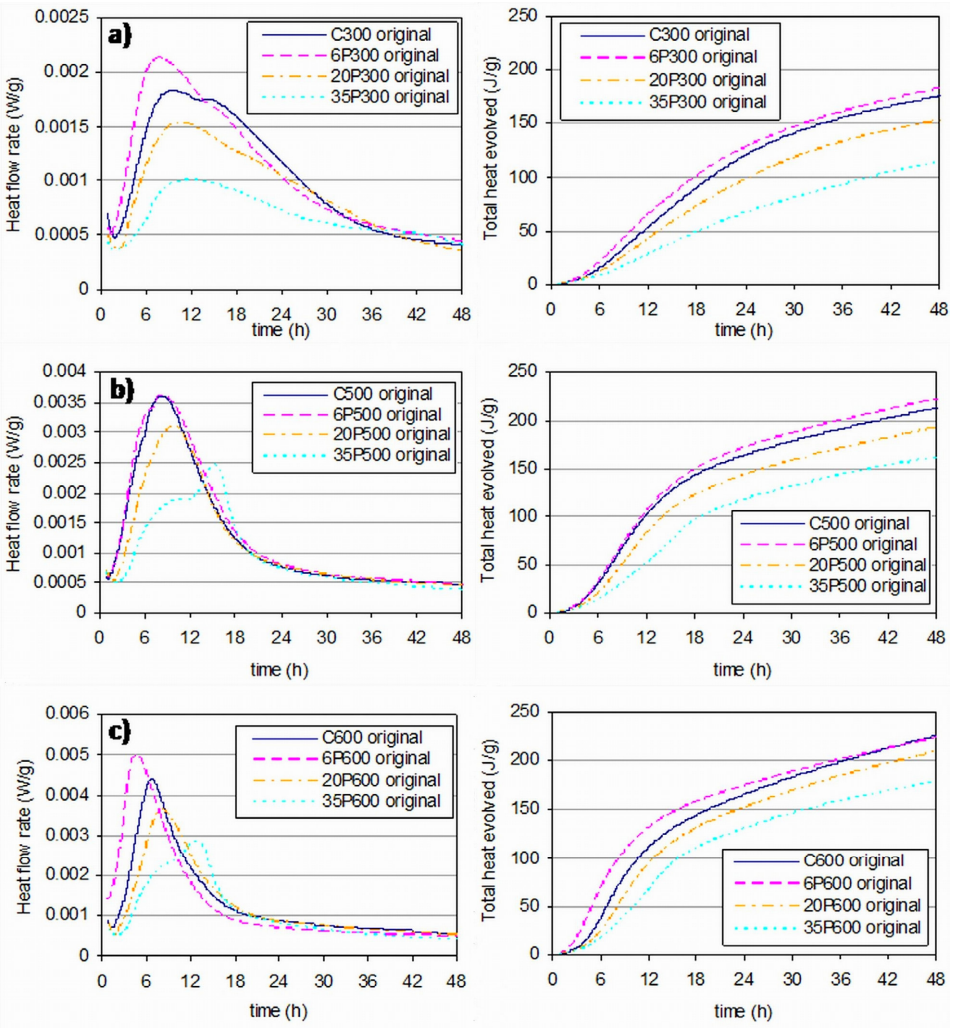

Fig. 3 Rate of heat evolution vs. time (left) and total heat vs. time (right) behavior for the a) 300 m^2/kg; b) 500 m^2/kg; b) 600 m^2/kg cements.

Table 4 Amounts of clinker, pozzolan, and gypsum in the fine and coarse portions of the cements.

Cement	Amounts of clinker, pozzolan, and gypsum (%) in							
	Fine portion (< 45 µm)				Coarse portion (> 45 µm)			
	Clinker	Pozzolan	Gypsum	TOTAL	Clinker	Pozzolan	Gypsum	TOTAL
C300o	65.9	-	4.2	70.1	29.1	-	0.7	29.8
C500o	79.9	-	4.5	84.4	15.1	-	0.5	15.6
C600o	82.2	-	4.7	86.9	12.8	-	0.3	13.1
6P300o	58.4	3.8	3.0	65.2	32.8	1.4	0.7	34.9
6P500o	76.9	4.5	3.6	85.0	14.0	0.6	0.4	15.0
6P600o	80.0	4.4	3.3	87.7	11.2	0.6	0.5	12.3
20P300o	46.2	12.3	2.7	61.2	32.0	5.8	1.0	38.8
20P500o	64.7	16.9	3.8	85.4	12.1	2.1	0.4	14.6
20P600o	67.5	16.6	3.8	87.9	10.2	1.8	0.3	12.3
35P300o	31.0	20.8	2.4	54.2	30.7	14.1	1.1	45.9
35P500o	51.2	30.3	3.1	84.6	10.6	4.5	0.3	15.4
35P600o	54.3	31.2	3.0	88.5	8.0	3.3	0.2	11.5

A prominent shoulder peak is observed on the descending branch of the main hydration peak (the C_3S hydration peak) for the 500 m^2/kg and 600 m^2/kg cements with high pozzolan content. Although this peak is generally associated with the calcium aluminates (Bensted 1987), pozzolanic reaction can also influences its height (Erdoğan and Sağlık 2013; Mostafa and Brown 2005). The 24 h heat for 35P600 is ~80 % of that of C600 despite containing only 65 % of its clinker amount. 6 % pozzolan shortens the dormant period, but higher amounts lengthen it. The gypsum-to-clinker ratio of the 35P cements was higher (100*(4/65)~6.1 %) than for the controls ((100*(5/100)=5 %). This may have also contributed to the longer dormant periods and higher shoulder peaks. Adding 6 % pozzolan gives an earlier and higher main peak for the 300 m^2/kg and 600 m^2/kg cements. Beyond 6 %, the main peak is delayed and supressed.

Figure 4a shows the change in the rate of heat flow during the hydration of C300o, C300f, and C300c. The graphs for C500, and C600 show similar behavior and are omitted.

The main peak is higher in C300f than in C300c or in C300o which is in effect a combination of the < 45 µm and > 45 µm portions. The ratio of the C300f peak height to that of C300c is about 4 and holds roughly for the ascending branch of the peak following the dormant period. The median particle size for C300o is 21 µm. Assuming ~15 µm for C300f and of ~60 µm for C300c are realistic median particle sizes, particle specific surface area alone can not explain the observed differences. C300f gives the earliest calcium silicate peak and C300c the latest. A shoulder peak is noticeable for C300f but not for C300c. The total amount of heat evolved by a cement, shown in **Fig. 4b**, can be calculated as the area under its respective curve in **Fig. 4a**. C300f evolves more than three times as much heat in the first 24 h than C300c. The difference slightly diminishes with time. Additionally, C300f evolves a larger fraction of its 24-h or 48-h total heat sooner.

One reason for these observed differences between the fine and coarse portions other than their greatly different average particle sizes and pozzolan contents could be their different gypsum contents. Since gypsum accumulates in the smaller sizes during intergrinding, sieving through a 45 µm sieve eliminates most of the gypsum in the cement and the coarse portion has less gypsum than the fine portion. Also, the original cement becomes more like the fine portion in terms of its gypsum content with increasing fineness. Gypsum can act as either a retarder or an accelerator, its influence depending, among other things, on the C_3A and alkali contents of the clinker (Lerch 1946;

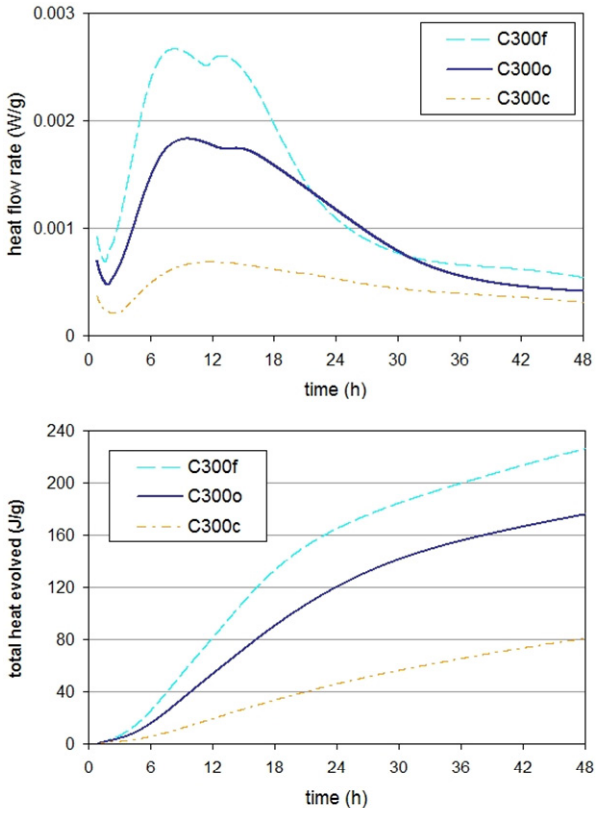

Fig. 4 a) Rate of heat evolution vs. time; and b) total heat vs. time behavior for C300o, C300f, and C300c.

Table 5 24-h and 48-h heat of hydration of the cements and their fine and coarse portions.

Cement	Heat of Hydration (J/g)					
	Original		Fine portion		Coarse portion	
	24 h	48 h	24 h	48 h	24 h	48 h
C300	120.4	181.8	165.1	226.3	46.0	80.8
C500	163.7	213.2	164.7	221.0	76.4	111.6
C600	165.6	225.4	184.6	247.9	83.2	114.9
6P300	128.0	182.9	174.6	239.2	48.9	80.8
6P500	171.2	221.9	198.8	254.4	113.5	1532
6P600	174.4	223.0	185.0	247.0	107.2	140.2
20P300	97.8	152.6	141.4	196.5	33.4	57.8
20P500	142.8	192.3	161.9	219.8	75.9	112.1
20P600	151.9	208.9	166.7	223.8	93.3	130.2
35P300	66.6	114.5	114.4	164.8	42.4	71.2
35P500	117.2	161.9	133.7	182.4	68.4	109.7
35P600	130.5	178.6	146.7	198.6	83.7	121.3

Ghorab *et al*. 2010). The fine portions of C300, C500, and C600 contain slightly less C_3A than the coarse portions (discussed later). Hence the "gypsum needs" of the two portions might differ and seemingly small differences could influence rates of hydration at early ages. The 24-h and 48-h heats of hydration of the samples are given in **Table 5**.

Both the 24-h and the 48-h heats of hydration of the coarse portions are lower than the heat evolved by the original cement, which in turn is lower than the heat evolved by the fine portions. More interestingly, **Fig. 5a** shows that the plot of the 48-h total heat against the 24-h heat using all mixtures is linear with r^2~0.99.

For the same cement, with or without pozzolan, the (24-h heat, 48-h heat) data points shift along the same line with changing fineness. The shift is larger from 300 m^2/kg to 500 m^2/kg and smaller from 500 m^2/kg to 600 m^2/kg. The ratio of the heat evolved by the fine portions from 24 h-to-48 h to the heat evolved in the first 24 h is 0.3-0.4 and doesn't fluctuate much from cement to cement (**Fig. 5b**). This ratio is higher for the coarse portions of the 300 m^2/kg cement, 0.65-0.75.

Using an approximate formula to estimate the overall heat of hydration of the control cements based on their main clinker compound contents (Verbeck and Foster 1950), a 1-yr heat of hydration of about 433 J/g is calculated for the control cements. After 1 d, C300c and C300f have evolved 11 %, and 38 % of this value, respectively. In contrast C600c, and C600f have evolved 19 % and 43 %, respectively. So, finer grinding has not only shifted the average particle size to smaller values, but also changed the nature of the coarse particles. Even though both C300c, and C600c are > 45 μm, C600c evolves nearly twice as much heat in the first day. This could be influenced by compositional differences, changes in particle shape due to grinding, and possibly by imperfect sieving.

Table 5 confirms that small amount of pozzolan incorporation enhances the short term hydration of cement (Lawrence *et al.* 2003; Cyr *et al.* 2005) as 6P cements have higher heat of hydration than their corresponding control specimens. Partial replacement of portland cement by pozzolan has a dilution effect but also a counteracting physical enhancement effect on early hydration. Higher early heat of hydration indicates that the latter dominates. To determine the net effect of the pozzolan on early heat of hydration, it is assumed that:

- the total heat evolved is the weighted average of the heats of hydration of the coarse and fine portions measured separately.
- no pozzolanic reaction occurs within this very early stage.

The total heat evolution at any time within the first 48 h is found using:

$$HH_t = HH_{ct} \times C + HH_{ft} \times F \quad (1)$$

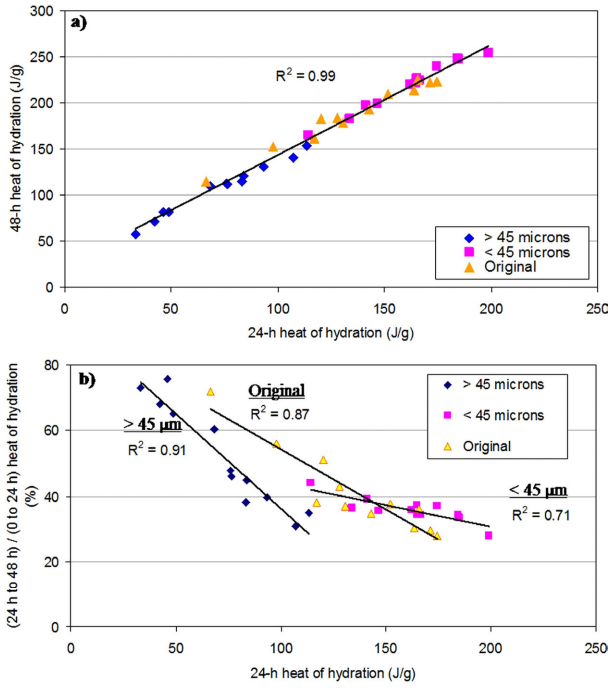

Fig. 5 a) 48-h total heat vs. 24-h heat evolved; b) ratio of the heat evolved from 24 h-to-48 h to the heat evolved in the first 24 h.

where,
HH_t: calculated heat of hydration of the cement,
HH_{ct}: measured heat of hydration of the coarse portion at time t,
HH_{ft}: measured heat of hydration of the fine portion at time t,
C: mass fraction of the coarse portion of the cement,
F: mass fraction of the fine portion of the cement.

Figure 6 shows the measured/calculated heat of hydration ratios for the samples. A ratio of 1.0 indicates equality of the measured and calculated values.

To clarify how the curves in **Fig. 6** were drawn, for C300, the calculated heat is found by averaging the 24 h heat values of C300f and C300c (from **Table 5**) weighting each by the fraction of the cement (excluding the pozzolan) in that size portion. These weights are similar to the values in **Table 4** but slightly higher since they also include the gypsum in the size portion. For C300, the calculated heat at 24 h is [((69.42 % * 165.06 J/g) + (30.58 % * 46.04 J/g))/100 %] = 128.66 J/g. The measured heat is 120.41 J/g. Hence the measured heat/calculated heat for C300 at 24h is 120.41/128.66 = 0.936. The curves for the controls are close to 1.0 so Equation 1 is appropriate for portland cements and the first assumption roughly holds true for portland cements. The second assumption for Equation 1 is not true for the blended cements since the measured/calculated heat values are well over 1.0 at almost any time in the first 48 h. The ratio generally increases with increasing pozzolan amount. It must also be noted that the hydration of the < 45 μm particles may not be the same as their hydration when together with > 45 micron particles (as in the original cement) or vice versa. When only coarse particles are available, the reduced available area causes delayed setting and heat evolution. When fine particles are also available, the hydration products from their reaction could reduce the access coarse particles have to water and hinder their reaction. Contrarily, very fine particles could serve as nucleation sites for the hydration products of the coarse particles, enhancing their contribution.

Figure 7 compares the relative effects of the coarse and fine portions of the cements on total heat of hydration. To clarify how the curves in **Fig. 7** were drawn, for C300, the heat evolved up to 24 h by the unsieved cement is 120.4 J/g, by the fine portion is 165.1 J/g, and by the coarse portion is 46.0 J/g (see **Table 5**). Hence, at exactly 24 h, the ratio of heat evolved by the fine portion of C300 to the heat evolved by the unsieved C300 cement is C300f/o = (165.06 J/g) / (120.41 J/g) = 1.37. In a similar fashion, 20P500c/o is the heat evolution of the coarse portion of 20P500 to the heat evolution of unsieved 20P500. A chosen point on a curve corresponds then to the ratio of heat evolved up to that time by the fine or coarse portion of the cement to the heat evolved by the unsieved cement.

The position and shape of the curves in **Fig. 7** depend on factors influencing the rate of heat evolution. Since mean particle size is one such factor, the f/o curves are above 1.0 and the c/o curves are below 1.0. Another is composition, which causes the shape differences between the curves. When the original cement is coarser (300 m^2/kg in this investigation), the relative contribution of its fine portion is higher (**Fig. 7a**). This effect becomes more pronounced as the amount of pozzolan increases. As fineness is increased, more of the original material accumulates in the fine portion (see **Table 4**) and both the chemical and physical compositions of the fine portion approximate the composition of the original cement. This is seen as the heat of hydration ratios of the fine portions to the original cement moving from 1.5-2.0 for 300 Blaine in **Fig. 7a** to 1.1-1.2 for 600 Blaine in **Figs. 7b** and **7c**. Since increasing fineness doesn't influence the mean size of the coarse cements much (despite lowering their total amounts) a similar change is not observed between the c/o curves in **Figs. 7a-c**. Based on size differences alone, the distance of the curves from the 1.0 line are expected to start out being large and to decrease (as the curves move towards 1.0) in time.

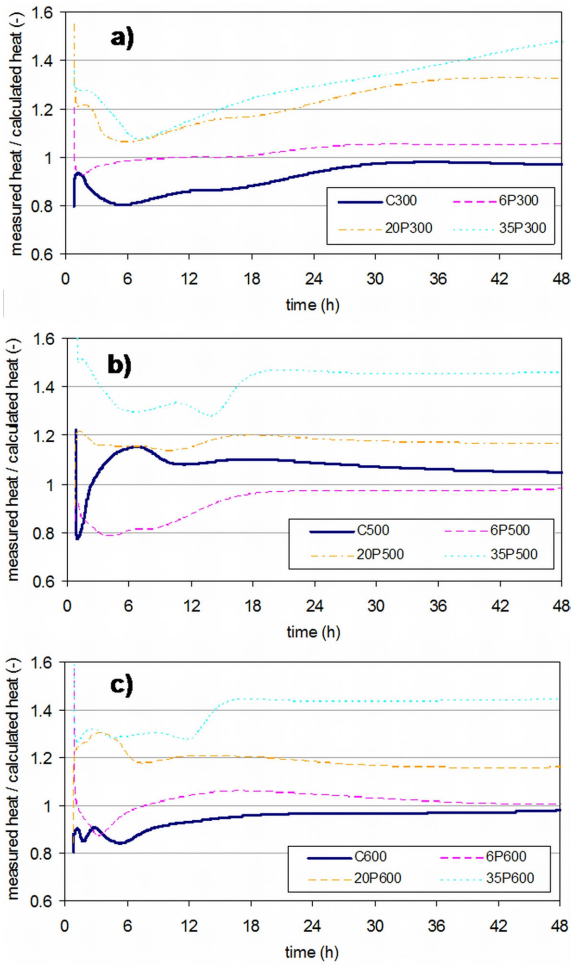

Fig. 6 Measured/Calculated heat of hydration ratios of a) 300 m^2/kg, b) 500 m^2/kg and c) 600 m^2/kg cements.

Table 6 Potential compound compositions of the control cements and their fine and coarse portions.

Compound (%)	C300			C500			C600		
	Original	Fine	Coarse	Original	Fine	Coarse	Original	Fine	Coarse
C_3S	50.9	51.3	49.7	50.9	51.5	49.5	50.9	51.7	47.8
C_2S	18.0	16.7	20.4	18.0	17.0	20.3	18.0	16.9	21.4
C_3A	9.3	9.0	10.1	9.3	9.2	10.0	9.3	9.5	9.7
C_4AF	9.4	9.0	9.9	9.4	9.2	9.9	9.4	8.9	9.9

Any inflection points are probably due to compositional differences and the higher pozzolan content finer cements show such behavior due to their greater pozzolanic activity.

Similar results were obtained with natural pozzolans and fly ash (Takemoto and Uchikawa 1980; Massazza 2004) and ground quartz (Lawrence *et al.* 2003). Two hypotheses for the enhancement of hydration by incorporating mineral admixtures are an increase in surface area preferable for the precipitation of hydrated compounds (Takemoto and Uchikawa 1980) and the reduction in the thickness of the hydrate layer formed around the cement particles which facilitate the hydration of the anhydrous portion remaining underneath

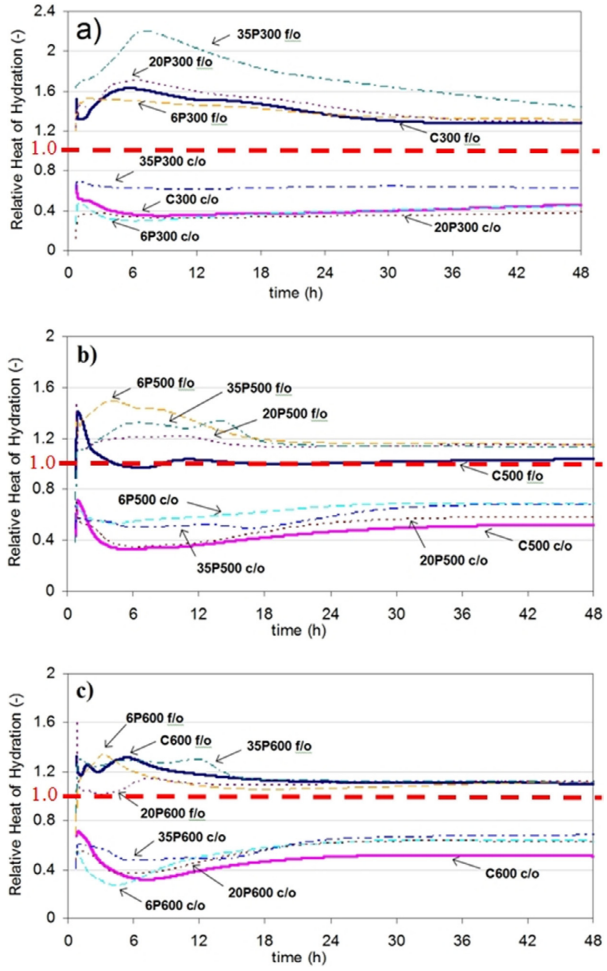

Fig. 7 Heat of hydration ratios of the coarse and fine portions of cements with respect to their originals: a) 300 m^2/kg; b) 500 m^2/kg; c) 600 m^2/kg Blaine cements.

(Lawrence *et al.* 2003). Considering that the contribution of the finer portions of the cements is higher for early hydration as shown in **Fig. 7**, a third influence for enhanced early hydration may be the higher relative amount of C_3S in the finer portion of the cements. Since the major compounds of clinker have different grindabilities (due to different hardness, crystal size, etc.) and C_3S is easier to grind than the other three major compounds (Duda 1977; Hills 1995), higher amounts of this compound accumulate in the finer portions of cements (Zhang *et al.* 2011). It is not easy to determine compound compositions of blended cements. However, the comparison of the potential compound compositions (found using Bogue's Equations) of the fine and coarse portions of the control cements, given in **Table 6**, supports the opinion above.

The amounts of C_3S in the fine portions of the control cements are higher than in the coarse portions and it is reasonable to assume the same tendency in the interground blended cements. The amount of C_3S in the fine portion slightly increases with grinding. Different sizes of an interground pozzolan-blended cement not only contain different ratios of clinker, pozzolan, and gypsum, but also, the compositions of the clinkers (and possibly the pozzolan) they contain may differ. As such, the early-age activity of a pozzolan may differ from that determined by applying standard tests to the unsieved cement.

The general understanding that finer particles react sooner/faster, pozzolan addition dilutes the cement hence slows down hydration-dependent property development and associated heat evolution, and that pozzolans or mineral admixtures can be easier or more difficult to grind than clinker is correct but not sufficient when evaluating blended cements. Analyses of differences between the rate and amount of heat evolution of different-sized sieved portions (preferably narrower than the two subgroups used in this study) of a cement and its heat evolution in the unsieved state could improve our understanding of pozzolanic activity during early hydration, and its dependence on clinker and pozzolan particle size.

4. Conclusions

The chemical composition and heat of hydration evolution of the < 45 μm (fine), and > 45 μm (coarse) portions of interground natural pozzolan blended cements were investigated. For interground blended cements:

- The pozzolan-to-clinker ratio of the fine and coarse

portions can differ greatly from the ratio of the unsieved cement. This influences heat evolution rates at early-ages.
- Partial clinker replacement by pozzolan does not result in a one-to-one reduction in early heat evolution. The relative positive effect of pozzolan incorporation becomes more pronounced as the amount added increases.
- For the same clinker, a unique linear relationship exists between 24-h heat evolution and 48-h heat, regardless of fineness or pozzolan content. The ratio of the second day heat of hydration to the heat evolved on the first day is noticeably greater for the coarse portions of the cements.
- The increased amounts of C_3S and gypsum in the fine portions of interground blended cements should also be considered when evaluating early hydration hydration

The project on the effects of mineral admixtures on early hydration of interground blended cements is continuing and will:
- consider the amount and rate of heat of hydration evolution of narrower size groups (0-10; 10-30; 30-50; and > 50 μm)
- study granulated blast furnace slag- and limestone-blended cements

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