Full Length Research Paper

The early heat of hydration of blended cements incorporating GGBFS and ground basaltic pumice (GBP)

Hanifi B N C [1]*, smail H. ÇAGATAY[2], Mustafa TOKYAY[3] and Mehmet M. KÖSE[1]

[1]K.S. University, Department of Civil Engineering, Kahramanmaras, Turkey
[2]Cukurova University, Department of Civil Engineering Adana, Turkey
[3]Middle East Technical University, Civil Engineering Department, Ankara, Turkey

In this study, the effect of blended cements containing additives on the heat of hydration and the rate of heat liberation was investigated. The blended cements were prepared by using clinker, ground granulated blast-furnace slag (GGBFS) and ground basaltic pumice (GBP). Two groups of specimens were prepared by the grinding method of intergrinding and separate grinding. For each group of specimen, two Blaine values of 2800 $\pm$30 cm^2/g and 4800 $\pm$30 cm^2/g and four different ratios of additives, which were 0%, 10%, 20% and 30% of clinker by weight, were used. The effects of the grinding method, the fineness and the amount of additives on the heat of hydration were also investigated. It was found that the heat of hydration was affected by the grinding method. Also, interground coarser blended cement specimens resulted in extended time to reach the second peak compare to the separately ground finer ones. A significant reduction in the total heat of hydration was achieved in the interground coarser specimens with 30% additives. The minimum heat of hydration was obtained from the interground specimens with 30% additives and Blaine value of 2800 $\pm$30 cm^2/g. Due to lower heat of hydration this cement can be used for mass concrete construction.

Keywords: Hydration; Grinding Method; Additives; GGBFS; Ground Basaltic Pumice.

INTRODUCTION

The significance of hydration in concrete technology is well known. The hydration reactions of cement compounds are exothermic. The heat of hydration studies can be used for characterizing the setting and hardening behavior of cements, and predicting temperature rise which is very important when large volumes of plain concrete are placed (Mehta, 1986; Neville and Brooks, 1987).

There are many factors that influence the rate of hydration such as, fineness, admixtures, water/binder ratio and temperature of the materials at the time of mixing and grinding methods (Kosmatka and Panarese, 1994). For this

reason, there have been so many studies presented in the literature on the effects of different factors on heat of hydration of Portland blended cements and blast fur-nace slag. The slag reaction is more sensitive to heat than Portland cement clinker. When 5% GBFS is added, the rate of heat evolution is decreased and the peaks are broadened and shifted to longer hydration time (Mehta, 1986; Neville and Brooks, 1987; Sha et al., 1999; Singh et al., 1995; DE Schutter, 1995; Swamy 1986). Several studies compared the intergrinding and separately grinding of blast furnace cement, clinker and pozzolan (Erdogdu et al., 1999; Öner, 2000; Hosten and Avsar, 1998; Turanli et al., 2004). However, in these studies the effect of heat of hydration and heat liberation rate of GGBFS and GBP blended cements were not considered.

Turkey is rich in natural pozzolan, which are also called

---
*Corresponding author E-mail: hbinici@ksu.edu.tr, Tel: +90 344 2191278, Fax: +90 344 2191250

Table 1. Chemical Compositions of the Clinker, GGBFS and GBP

Oxide (%)			
	Clinker	GGBFS	GBP
SiO_2	20.1	39.7	43.9
Al_2O_3	5.2	12.8	14.1
Fe_2O_3	3.9	1.7	12.1
CaO	64.1	32.9	9.3
MgO	2.2	7.4	8.9
Na_2O+K_2O	1.4	0.8	0.3
SO_3	1.2	1.4	-
LOI	0.5	-	0.5
(%) Potential mineral composition (according to Bogue)			
C_3S	64.0		
C_2S	10.1		
C_3A	8.2		
C_4AF	11.7		

"basaltic pumice" in the cement industry. Almost 155000 km^2 of the country is covered by Tertiary and Quaternary-age volcanic rocks, among which tuffs occupy important volumes. Although there are many geological investigations on these volcanic rocks, their potential as natural pozzolan is not well established (Kaplan and Binici, 1996). The basaltic pumice cone deposits are of Quarternary age and are located in the Cukurova region (Southern Turkey), and there are reserves estimated to be approximately 1.000 million tons.

There are two cement plants in the neighborhood of the huge basaltic pumice reserve mentioned above. Use of this material in the production of the cement will reduce the total cost due to ease of grindability and low cost of transportation. Also, many dams have been constructed in Turkey and heat of hydration is one of the major problems in mass concrete. Use of basaltic pumice in the production of cement may lead to reduction in the heat of hydration.

The aim of this study was to investigate use of ground basaltic pumice (GBP) and ground granulated blast-furnace slag (GGBFS) in the production of cement. Also, the effect of grinding methods, i.e. intergrinding and separately grinding, on heat of hydration and rate of heat liberation of blended cements containing clinker, GGBFS and GBP were examined and compared. The comparesons were also made for two Blaine values of 2800 ± 30 cm^2/g and 4800 ± 30 cm^2/g and four different ratios of additives, 0%, 10%, 20% and 30% by weight of Plain Portland Cement (PPC).

MATERIALS

Clinker, GGBFS and GBP were obtained from Adana Cement Factory, Iskenderun Iron and Steel Factory, and Osmaniye, respectively. Ground basaltic pumice (GBP) was obtained from pyroclastic

exposures around Osmaniye region. Ground granulated blast furnace slag (GGBFS) were obtained from Iskenderun iron and steel plant. The basaltic pumice contains glass shards, small amount of volcanic rock and minerals such as feldspars, quartz, biotite and clay. The high porosity of the basaltic pumice is an advantage for easy and economical crushing (Kelling et al, 2000). Basaltic pumice used in this study was called as Scoria. It has dark brown/blackish color, porous structure and low crystal water. Its hardness is about 5.2 in Mhos scale. The chemical compositions of the materials were given in Table 1.

METHODS

Mixture proportions

The cement specimens were prepared one of the grinding method of interground and separate grinding of each constituent and then by intimate blending. Besides the clinker and mineral admixtures, all specimens contained 5% gypsum by the weight of the clinker. A 20 kg capacity laboratory ball mill was used for the grinding. Three groups of specimens were prepared. The first group specimens prepared by Blaine values of 2800 ± 30 cm^2/g and 4800 ± 30 cm^2/g were selected as the control specimens and no additives were used in this group. The second group of specimens was prepared by separate grinding with the same Blaine values and three different ratios of additives, 10%, 20% and 30% by weight of clinker. The third group of specimen was prepared by intergrinding with the same Blaine values and three different ratios of additives, 10%, 20% and 30% by weight of clinker. The notations and the compositions of the cements specimens were given in Table 2. In this table, C1 and C2 show the control specimens with two different Blaine values. For the rest of the specimens, a notation in the form of SX.X and IX.X were used. In those notations, the first letter stands for separate and intergrinding, respectively. The second character could be 1 or 2 and stands for the Blaine value. The third character could be 10, 20 and 30 and stands for the amount of additives by the weight of the clinker.

Test procedure

The heat of hydration and its rate were determined at 25°C by using a Tonical Isothermal Conduction calorimeter. 4.2 g of cement sample was placed into the test chamber and 2.1 g of distilled water was put into the small container positioned above the cement sample. After reaching the thermal balance, the water was injected into the test chamber through a hollow needle by means of a piston ensuring an intimate mixing with cement under pressure. Completion of the each test took 24 hours.

RESULTS AND DISCUSSIONS

The effects of the method of grinding, the fineness of cement and the amount of mineral admixtures on early heat of hydration were discussed in relation with the first and the second peak values of the rate of heat liberation and the heat of hydration.

In general, as shown in Figure 1, on mixing the cement with water, a rapid heat evolution (ascending first peak) occurs and last a few minutes. This initial heat evolution ceases quickly (descending first peak). The next heat evolution cycle, culminating in the second peak after about 4-8 h of hydration for Portland cements (ascending second peak) (Mehta, 1986).

Table 2. Notations and Compositions of the Cements Prepared

Cement	Clinker + Gypsum (%)	GGBFS (%)	GBP (%)	Blaine Fineness (±30 cm^2/g)
C1	100	-	-	2800
C2	100	-	-	4800
Separate Grinding				
S1.10	90	5	5	2800
S1.20	80	10	10	2800
S1.30	70	15	15	2800
S2.10	90	5	5	4800
S2.20	80	10	10	4800
S2.30	70	15	15	4800
Intergrinding				
I1.10	90	5	5	2800
I1.20	80	10	10	2800
I1.30	70	15	15	2800
I2.10	90	5	5	4800
I2.20	80	10	10	4800
I2.30	70	15	15	4800
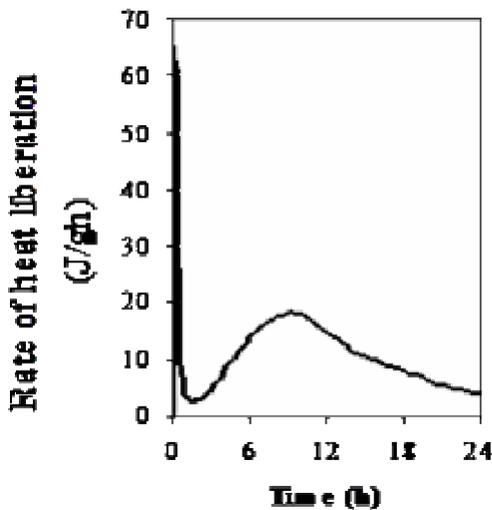
Figure 1. Heat liberation rate of a Portland cement

Control specimens

It is obvious that the fineness affects the rate of heat liberation and the heat of hydration. The rate of heat liberation of the control specimens C1 and C2, were shown in Figure 2. The first peak value of the rate of heat evolution of the control specimen C2 was found about 39% higher than that of the control specimen C1, as shown in Table 3. Increased fineness accelerates the rate of heat evolution to reach the second peak value. The time required for the control specimen C2 to reach the second peak value was determined to be about two hours less than that of the control specimen C1. How-ever, the rate of heat liberation of the control specimen C2 was almost two times of that of control specimen C1 at the second peak.

The difference between the control specimens C1 and C2 in total heat of hydration was shown in Figure 3. The ratio of the heat of hydration at the second peak to the heat of hydration at 24 hours, Q_s/Q_{24}, was given in Table 3. Increased fineness resulted in higher heat of hydration. At the end of 24 hours, total heat of hydration of the control specimen C2 was higher than that of the control specimen C1 about 58.8%, as shown in Figure 3.

Separately grounded specimens

The rate of heat liberation and total heat of hydration of the separately ground specimens with Blaine value of 2800 cm^2/g were shown in Figure 4 and Figure 5, respectively. Also, the rate of heat liberation and total heat of hydration of the separately ground specimens with Blaine value of 4800 cm^2/g were shown in Figure 6 and Figure 7, respectively.

The time to reach to the first peak for the specimens S1.10, S1.20 and S1.30 was less than that of the control specimen C1 about 37.9%, as shown in Table 3. The second peak value of the specimens S1.10, S1.20 and S1.30 occurred at 8.84 h, 9.28 h, and 12.70 h, respectively. Only the second peak value of the specimen S1.30 was greater than the second peak value of the control specimen C1.

Although the fineness of the control specimen C1 was equal to the fineness of the specimens S1.10 and S1.20, the specimens S1.10 and S1.20 had higher second peak value of the rate of heat liberation. However, the heat of
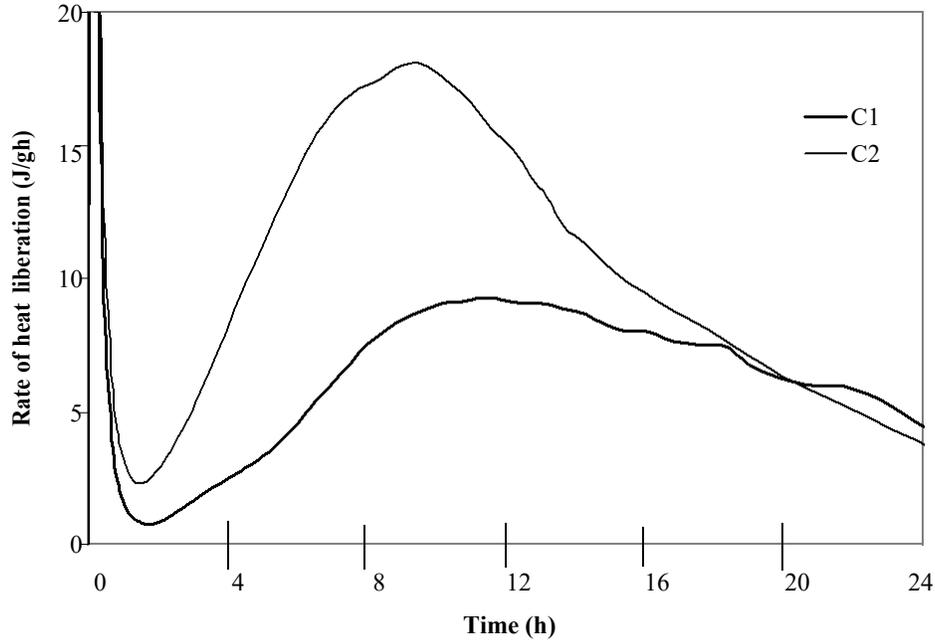
3

Figure 2. Rate of heat evolution of control specimens

Table 3. Rate of heat liberation (j/gh) and heat of hydration (j/g) data values for the first and second peak of the specimens

Specimen	First Peak			Second Peak			Q_s/Q_{24}	24 h
	t (h)	(j/gh)	(j/g)	t (h)	(j/gh)	(j/g)		(j/g)
C1	0.114	46.45	3.45	11.20	9.23	64.26	40.1	160
C2	0.0708	64.60	2.30	9.28	18.07	108.82	42.8	254
S1.10	0.0708	60.18	2.74	8.84	9.86	62.40	39.2	159
S1.20	0.0708	46.49	1.91	9.28	9.85	54.86	35.3	155
S1.30	0.0708	35.62	1.33	12.70	7.00	57.58	38.3	119
S2.10	0.114	50.65	3.34	9.73	15.91	90.74	43.0	211
S2.20	0.0708	53.14	1.70	9.28	15.23	81.15	41.8	194
S2.30	0.114	42.20	3.01	9.73	10.76	105.39	41.4	170
I1.10	0.0708	37.36	1.35	9.73	9.69	58.13	36.7	158
I1.20	0.0708	39.12	1.27	10.70	8.10	52.98	38.9	136
I1.30	0.0708	32.29	1.28	14.30	6.20	55.38	51.7	107
I2.10	0.0708	52.58	1.79	10.20	14.82	92.61	43.2	214
I2.20	0.0708	51.06	1.85	9.28	15.21	81.17	37.5	216
I2.30	0.0708	49.72	1.84	9.73	12.60	74.12	38.4	193

hydration of the specimens S1.10 and S1.20 had lower second peak values when compared with the control specimen C1. The ratio of the heat of hydration at the second peak to the heat of hydration at 24 hours, Q_s/Q_{24}, for the specimens S1.10, S1.20 and S1.30 were obtained as 39.2, 35.3 and 38.3 which were slightly less than that of the control specimen C1.

The rate of heat liberation of the specimens S2.10, S2.20 and S2.30 were shown in Figure 6. The second peak values of the heat of hydration of the specimens S2.10, S2.20 and S2.30 were smaller than that of the control specimen C2. The time to reach the second peak value of the specimens S2.10, S2.20 and S2.30 were 9.73 h, 9.28 h, and 12.70 h, respectively. The time to reach the second peak value of the specimens S2.10 and S2.20 were almost the same as that of control specimen C2 (9.28 h).

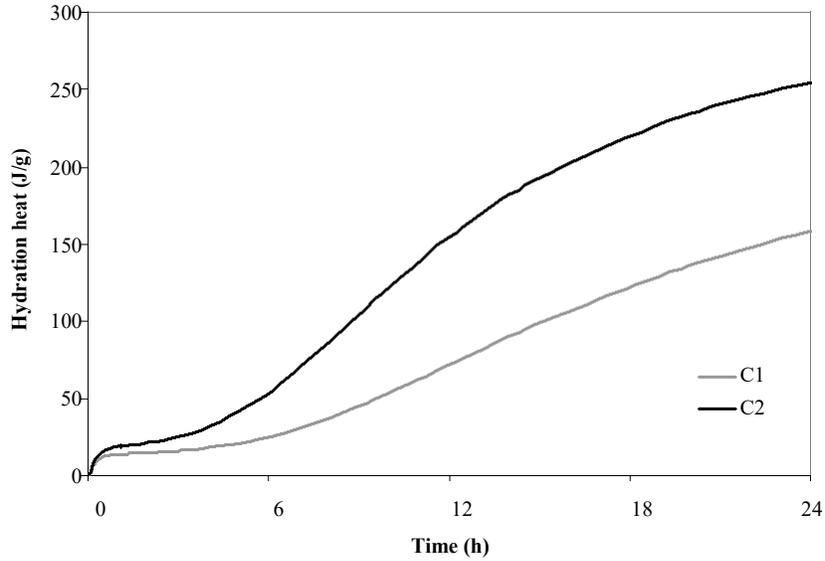The total heat of hydration values of the finer blended
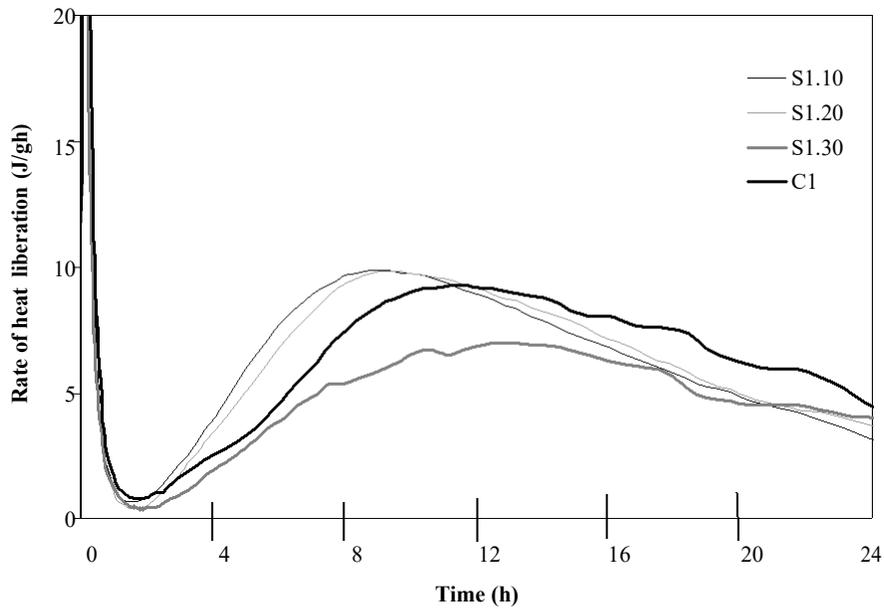
Figure 3. Heat of hydration of control specimens

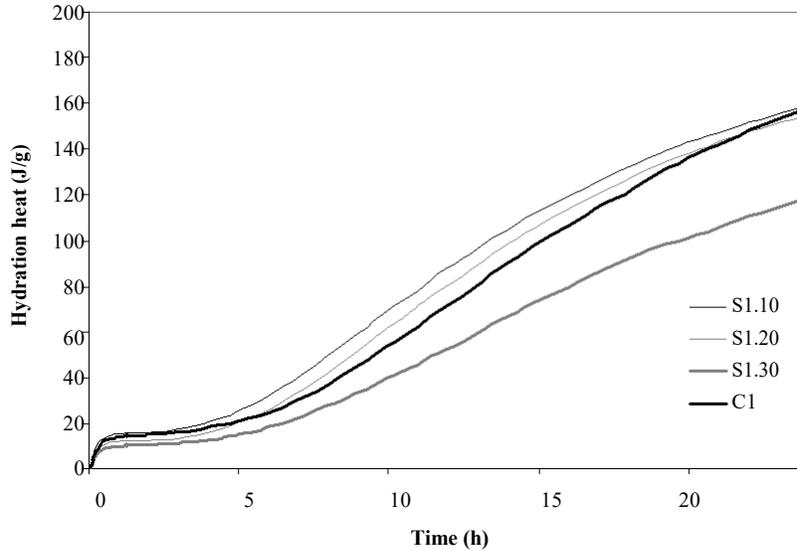**Figure 4.** Rate of heat evolution of separately ground 2800 cm^2/g specimens

specimens were lower than that of the control specimen C2 even at the beginning of the hydration, as shown in Figure 7. It is clearly shown that the best solution for the heat of hydration can be obtained from the specimens with 30% additives for mass concrete construction due to lower heat of hydration.

The heat of hydration of coarser separately ground blended cement specimens with 30% mineral additives was about 25.1% less than the specimens with 10% mineral additives. Similarly, the heat of hydration of finer blended cement specimens with 30% mineral additives

was about 19.4% less than the specimens with 10% mineral additives.

Specimens with Interground

The rate of heat liberation and total heat of hydration of the separately ground specimens with 10, 20 and 30% mineral admixtures were shown in Figures 8-11. The time to reach to the first peak for the specimens I1.10, I1.20 and I1.30 was less than that of the control specimen C1. On the other hand, the time to reach to the first peak for

Figure 5. Heat of hydration of separately ground 2800 cm^2/g specimens
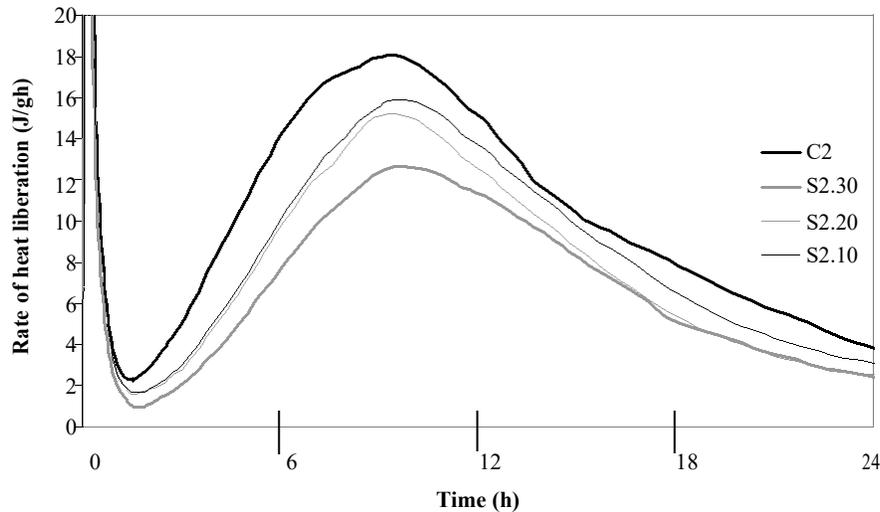
Figure 6. Rate of heat evolution of separately ground 4800 cm^2/g specimens

finer specimens was found the same as that of the control specimen C2. The second peaks of the speci-mens I1.10, I1.20 and I1.30 occurred at 9.73 h, 10.70 h and 14.30 h respectively. In coarser specimens, when the amount of additive was equal to 30% of clinker replace-ment, the time to reach to second peak value decelerated more than 4.5 hours compared to the specimens with 10% of clinker replacement. However, in finer specimens, when the amount of additive was equal to 30% of clinker replacement, the time to reach to second peak value accelerated more than 0.4 hours compared to the speci-mens with 10% of clinker replacement.

The rate of heat liberation was only slightly reduced by mineral admixtures until the second peak was reached.

The time to reach the second peak in interground specimens with mineral admixture was close to that of the control specimen C2, as shown in Figure 10.

Total heat of hydration values of finer interground specimens up to 24 hours were lower than that of the control specimen C2, as shown in Figure 11. For the specimens I2.20 and I2.30, the ratio of the heat of hydration for the second peak to the heat hydration for 24 hours, Q_s/Q_{24}, were slightly lower than that of the control specimen C2 as shown in Table 3.
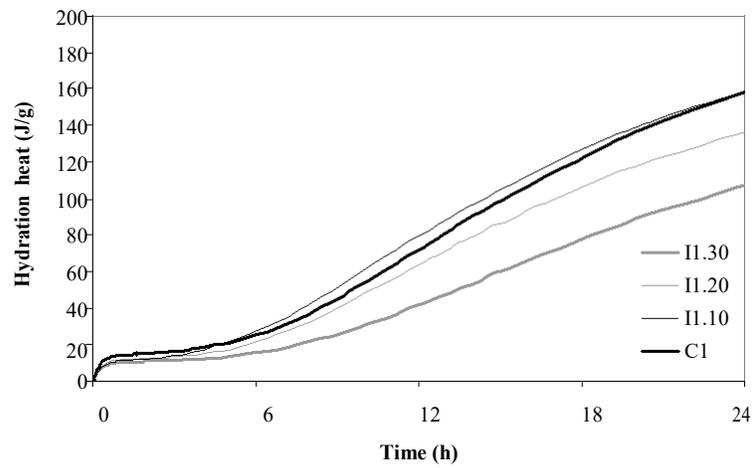
Comparison of grinding methods

It took 8.84, 9.28 and 12.7 hours for the specimens

6
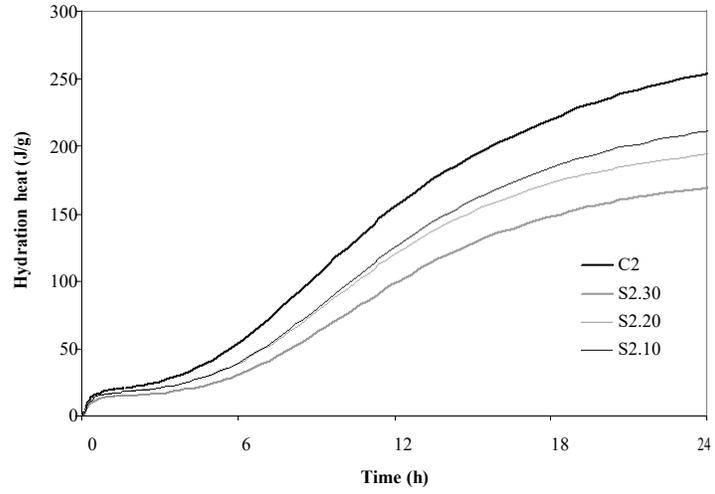
Figure 7. Heat of hydration of separately ground 4800 cm^2/g specimens.
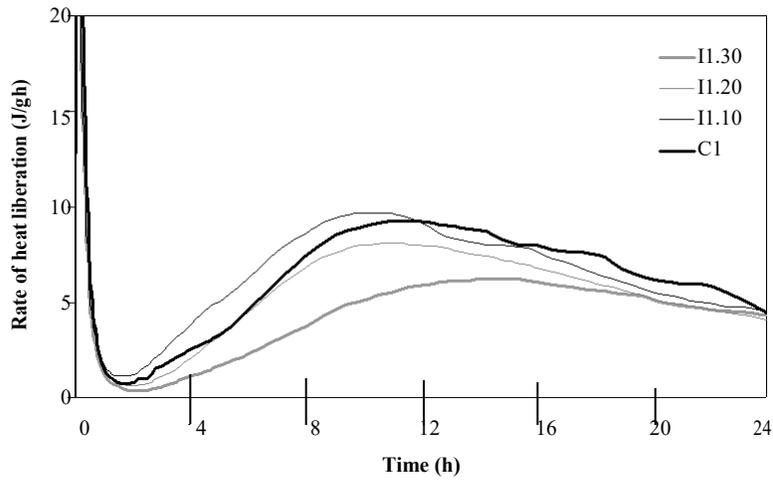
Figure 8. Rate of heat evolution of interground 2800 cm^2/g specimens

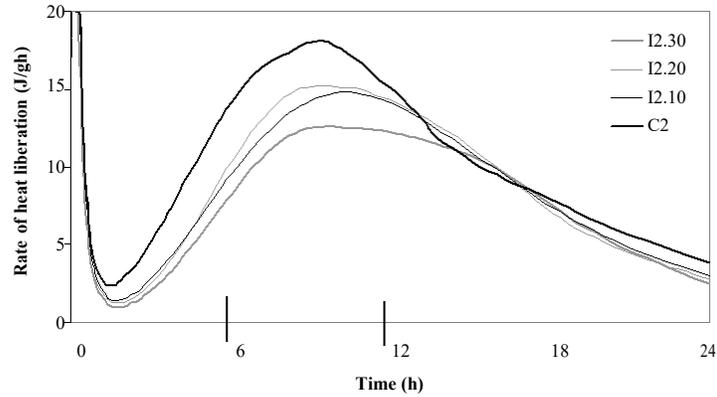**Figure 9.** Heat of hydration of interground 2800 cm^2/g specimens.

7

Figure 10. Rate of heat evolution of interground 4800 cm^2/g specimens.
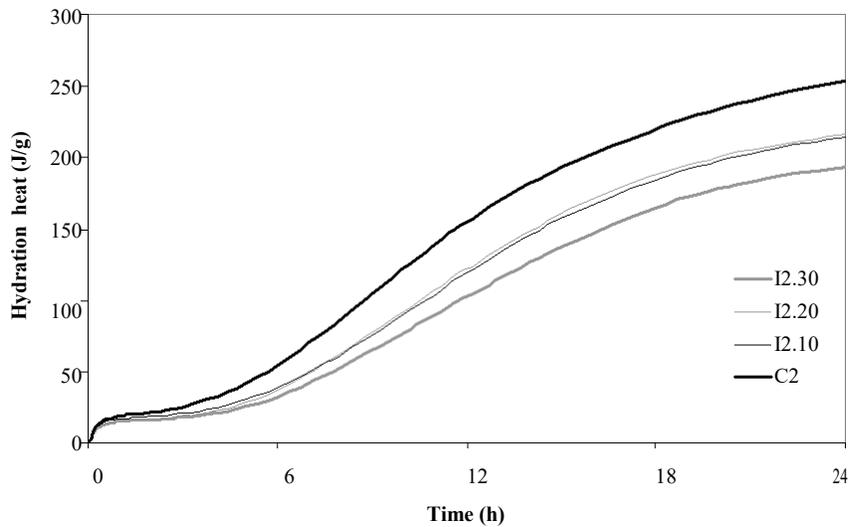

Figure 11. Heat of hydration of interground 4800 cm^2/g specimens

S1.10, S1.20 and S1.30 to reach the second peak whereas the specimens I1.10, I1.20 and I1.30 required 9.7, 10.7 and 14.3 hours to reach the second peak, respectively. These results showed that the intergrinding of the materials resulted in longer time to reach the second peak compared to the separately ground specimens. Also, for the Blaine value of 2800 cm^2/g, the total heat of hydration values of the interground specimens were smaller than the separately ground specimens. However, for the Blaine value of 4800 cm^2/g, the total heat of hydration values of the interground specimens were higher than the separately ground specimens. During separately grinding, different ingredients do not show the same behavior as in the case of intergrinding. Hence, it was concluded that during intergrinding some interactions occur between the particles of different ingredients of blended cements. Particle characteristics of separately ground ingredients are more stable than the ones of interground ingredients. On the other hand, this situation was not observed for the finer specimens, i.e. the time to reach to second peak was about the same.

The total heat of hydration of the finer interground specimens with 30% mineral additives was found as 1.14 times of that of the separately ground ones. Generally, the total heat of hydration of the separately ground cement specimens, were lower than those of both the control and the interground specimens.

CONCLUSIONS

The following conclusions were drawn from the results of this experimental investigation on the heat of hydration of clinker-GGBFS-GBP blends.

For the separately ground specimens, the total heat of hydration of the finer specimens with 30% additives were found less than that of the ones with 10% additives about 19.4%. Similarly, the total heat of hydration of coarser specimens with 30% additives was found less than that of

8

the ones with 10% additives about 25.2%.

For the interground specimens, the total heat of hydration of the finer specimens with 30% additives were found less than that of the ones with 10% additives about 9.8%. Similarly, the total heat of hydration of coarser specimens with 30% additives was found less than that of the ones with 10% additives about 32.3%.

The heat of hydration was affected by the grinding method. Interground coarser blended cement specimens resulted in longer time to reach the second peak compared to the separately ground coarser ones.

When the amount of additives was equal to 10 to 20% clinker replacement, the time to reach the second peak reduced for the separately ground and interground coarser specimens compared to the specimens with 30% additives.

A significant reduction in the total heat of hydration was achieved in the interground coarser specimens with 30% of additives. Due to lower heat of hydration this blended cements can be used for mass concrete construction.

Although the particle grinding characteristics is stable in separately ground method, the total heat of hydration is dependent on the fineness of the cement ingredients.

For the same grinding method and mineral admixture content, heat of hydration of the finer specimens are higher than those of the coarser ones and for the same fineness and grinding method, increasing the mineral admixture content results in reduced heat of hydration. For the same Blaine values, separately ground blended cement had lower heat of hydration than interground blended cement and control cement specimens.

Heat of hydration values are mainly depend on the Blaine values. Grinding methods had little effect on the heat of hydration.

REFERENCES

AM Neville, JJ Brooks (1987). Concrete Technology, Longman Group, New York.

C Hosten, C Avsar (1998). Grindability of mixtures of cement clinker and trass, Cem. Concr. Res. 28: 1519-1524.

G. DE Schutter, General hydration model for Portland cement and blast furnace slag cement, Cem Concr Res 25 (1995), 593-604.

H Kaplan, H Binici (1996). Trass and trass cement. Cement World [in Turkish]. 1:23–30.

K Erdogdu, M Tokyay, P Türker (1999). Comparison of intergrinding and separate grinding for the production of natural pozzolan and GBFC-incorporated blended cements. Cem. Concr. Res. 29: 743-746.

Kelling G, Kapur S, Sakarya N, Akc,a E, Karaman C, Sakarya B (2000). Basaltic Tephra: potential new resource for ceramic industry, British. Ceram. Trans. 99: 29–36.

L Turanli, B Uzal, F Bektas (2004). Effect of material characteristics on the properties of blended cements containing high volumes of natural pozzolans, (in press). Cem. Concr. Res. 34: 2277-2282.

M Öner (2000). A study of intergrinding and separate grinding of blast furnace slag cement. Cem. Concr. Res. 30: 473-480.

NB Singh, KN Bhattacharjee, AK Shukla (1995). Hydration of Portland blended cements. Cem. Concr. Res. 25: 1023-1030.

PK Mehta (1986). Concrete, Structure, Properties, and Materials, Prentice-Hall, New Jersey.

RN Swamy (1986). Cement replacement materials, Surrey University Press, London. Vol. 3.

SH Kosmatka, WC Panarese (1994). Design and Control of Concrete Mixtures, Portland Cement Association, Illinois.

W Sha, EA O'Neill, Z Guo (1999). Differential scanning calorimetry study of ordinary Portland cement. Cem. Concr. Res. 29: 1487-1489.