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European Journal of Advances in Engineering and Technology, 2017, 4(12): 907-913

Research Article ISSN: 2394 - 658X

Hydration Heat Evolution and Fineness of Blended Cement Containing Steel Slag and Pumice

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ABSTRACT

In this study, the heat of hydration and the strength relation of blended cement has been experimentally investigated. The blended cement mixture was prepared using one type of clinker and two types of pozzolans in different amounts, such as 10, 20 and 30 %, by weight of clinker, along with the controls. Two types of grinding, two types of fineness, and three different ratios of additives were used. Cement paste and mortars were prepared, and their compressive strength was also determined. The results indicate that the studied pumice and slag can reduce the heat of hydration. Compared to the heat of hydration of separated grinded system, the heat of hydration of blended cements are higher than the heat of hydration of separated cements when the fineness and the ratio of additives are held constant.

Keywords: Hydration heat, blended cement, pumice, strength

INTRODUCTION

When cement is mixed with water, heat is liberated. This heat is known as the heat of hydration and is the result of the exothermic chemical reaction between cement and water. The heat generated by the cement's hydration raises the temperature of concrete. Understanding the mechanism of heat generation in cement is the key to controlling the temperature of mass concrete [1]. Cement hydration is a highly exothermic and thermally activated reaction. The heat of hydration can be used to characterize the setting and hardening behaviour of cement and to predict the temperature rise. Measuring different aspects of cement and concrete hydration is essential, particularly in the case of major projects such as dams and foundations of large structures. Various means to determine the heat of hydration have been developed.

Concrete is the most widely used material in the construction industry for various purposes due to its ability to withstand high loads, its ability to be cast in any shape and its good resistance against wear and tear [2]. Finer cement particles result in faster and more complete hydration. However, an increase in cement fineness and cement content in concrete raises the concrete's adiabatic temperature. The issue of high heat of hydration was assumed to not affect the general construction cases and to be unique to mass concrete construction [3].

To save energy and reduce emissions for cement, in addition to improving equipment, one approach involves increasing the grindability of cement using a grinding agent, thereby reducing the power consumption [4]. Another approach is to improve the properties of cement by using additives. Thus, chemical additives are becoming increasingly popular in materials based on cement. Supplementary cementitious materials are quite common in today's concrete industry [5-7]. The most popular are industrial by-products such as fly ash, silica fume, and blast furnace slag [8] that are coming into increasing use particularly in the countries where they are produced.

Pozzolanic reactions are known to take action at later stages involving low heat rate, which makes them difficult to follow by calorimetry [9-10]. Partial replacement of Portland cement with supplementary cementitious materials such as Ground Granulated Blast Slag (GGBS) not only improves the mechanical and durability properties of concrete but also reduces the adiabatic heat development [11, 12]. In contrast to GGBS, which is a slow reactant providing later development of microstructures [13], fine GGBS contributes to both early and ultimate strength development of the concrete. As the fineness of the GGBS increases, the total surface area for the reaction increases, resulting in an increased rate of hydration and pozzolanic reactions [14].

Recently, there has been increased interest in using natural pozzolan (pumice) and artificial pozzolan (slag) as supplementary cementitious materials [15-18]. Turkey is rich in natural pozzolans. Almost 155.000 km^2 of the country is covered by Tertiary and Quaternary age volcanic rocks, among which tuffs occupy large volumes. Although there are many geological investigations on these volcanic rocks, their potential as natural pozzolan is not well-established. The natural pozzolan (basaltic pumice) cone deposits are of Quaternary age and are located in the Cukurova region (Southern Turkey), where the reserves are estimated to be approximately 1.000 million tons [19-22].

GGBFS has been used for many years as a supplementary cementitious material in Portland cement concrete, either as a mineral admixture or as a component of blended cement [23-24]. Additive is defined as all natural or artificial material that could contribute to the formation of cement [25-26]. These cements are used more particularly for mass concrete structures, which, if made with ordinary cement, might undergo an excessive rise in temperature, causing stress and cracking [27]. Because almost all chemical reactions are followed by heat generation, the hydration of complex systems, such as blended cements, can be quantified by their heat of hydration [28-29].

This study focuses on the quantitative analysis of blended cement hydration using the isothermal calorimetry method. The study objectives are to determine the degree of hydration of blended cements and the degree of reaction of the pozzolans. The chemical compositions of the pozzolans are consistent with the requirements given in both the EN TS-25 [30] and the ASTM C168 [31] standards for trass types of pozzolanic admixtures. Experiments for the hydration were carried out with a Calorimeter according to the ASTM C 186-80 [32] standards. All of the samples have hydration heat varying between 374 J/g and 171 J/g. The finenesses of the control cement (clinker + gypsum) were maintained constant to values of approximately 2800 m^2/g and 4800 cm^2/g, and The blended cement (clinker + pumice + slag + gypsum) was of the same fineness. Adding the pumice and slag in small proportions (10, 20 and 30 % weight of clinker) was repeated for two different fineness values.

MATERIALS AND METHODS

The clinker come from the Adana cement plant and was taken out from cooling. Its mineral composition is shown in Table 1. The results of the chemical analyses of the clinker, gypsum, pumice and slag are given in Table 2. The physical properties of the materials are given in Table 3. The chemical compositions of the blended cement and control cements are given in Table 4. In this study, the heat of hydration of blended cement has been experimentally investigated. The blended cements were prepared using one type of clinker and one type of natural pozzolan (pumice) and one type of artificial pozzolan (slag) in different amounts, such as 0, 10, 20 and 30 % pozzolan by weight of clinker. Cement paste and mortars were prepared using the control (with no pozzolan) and the other two types of grinding systems (intergrinding and separate grinding) and two types of finenesses (2800 cm^2/g and 4800 cm^2/g). The heat of hydration for each of the different blended and control cements were found. In addition, mortars were prepared and their compressive strengths were determined. During this survey, two of the pozzolan additives (2800 and 4800 cm^2/g) were used; they will be named B, C, D and E. The control cements (pure Portland) will be named A (Tables -5 and 6). The heat of hydration of the blended cements and control are calculated by differential calorimeter.

Table-1 Mineralogical Composition of Clinker

Samples	HM	SM	C_3S	C_2S	C_3A	C_4AF
Clinker	2.18	2.15	65.7	8.6	8.2	11.7
$A_1 = A_2$	2.19	2.05	66.5	5.6	8.1	11.9

Table -2 Chemical Compositions of the Materials

Materials	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Loss on ignition
Pumice	43.89	14.11	13.10	13.57	8.94	0.48
Slag	39.65	12.77	1.67	32.91	9.40	0.01
Clinker	29.14	5.19	3.90	55.05	2.23	0.51

Table -3 The Physical Properties of Materials

Materials	Specific gravity (g/cm^3)	Specific surface (cm^2/gr)	Residue on the 200 μ sieve analysis, %	Residue on the 90 μ sieve analysis, %
Pumice	2.97	2800 and 4800	0.06	0.2
Slag	2.89	2800 and 4800	0.09	0.3
Clinker	3.19	2800 ad 4800	0.09	0.3

Table -4 The Chemical Compositions of the Cements

Samples	Oxides				
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Cinker	20.29	5.57	3.85	64.75	1.96
$A_1 = A_2$	19.46	5.57	3.91	63.43	1.89
B_1	22.12	6.80	4.49	59.83	2.69
B_2	24.37	7.58	4.82	55.43	3.30
B_3	26.59	8.42	5.18	50.92	3.91
C_1	22.20	6.64	4.15	60.15	2.63
C_2	24.43	7.34	4.40	55.76	3.26
C_3	26.35	8.05	4.59	51.33	3.76
D_1	21.98	6.45	4.15	60.24	2.44
D_2	24.10	7.21	4.36	55.82	3.07
D_3	26.16	7.94	4.56	51.40	3.62
E_1	22.01	6.42	4.14	60.22	2.41
E_2	23.93	7.17	4.35	54.96	3.58
E_3	25.65	7.82	4.54	50.71	4.25

Table -7 The Compressive Strength Control and Blended Cement Samples (MPa)

Samples	Days				
	3	7	28	90	180
A_1	26.3	36.5	49.7	55.2	57.1
A_2	41.5	52.3	60.5	63.5	64.7
B_1	24.0	32.0	46.6	52.4	52.5
B_2	19.3	26.7	40.5	47.3	54
B_3	17.4	24.9	38.2	48.1	52.3
C_1	38.2	46.8	58.8	62.6	66.3
C_2	33.8	42.9	55.7	62.9	67.4
C_3	29.1	35.4	51.9	61.6	65
D_1	24.8	33.7	46.3	54.1	57
D_2	22.3	29.5	41.6	50.6	56.1
D_3	16.8	22.7	33.3	42.7	49.5
E_1	38.7	48.9	59.9	63.8	65.1
E_2	33.6	41.9	52.9	60.3	64.4
E_3	29.9	35.5	47.5	56.8	60.3

Table -5 Separated Grinding of Samples

Samples	System of additions	finensess (gr/cm^2)
A_1	clinker + 0 % additions	2800
A_2	clinker + 0 % additions	4800
B_1	clinker + 5 % slag +5 % pumice	2800
B_2	clinker + 10 % slag +10 % pumice	2800
B_3	clinker +15 %15 slag +15 % pumice	2800
C_1	clinker +5 % slag + 5 % pumice	4800
C_2	clinker + 10 % slag + 10 % pumice	4800
C_3	klinker + 15 % slag + 15 % pumice	4800

Table -6 Intergrinding of Samples

Samples	System of additions	finensess (gr/cm^2)
D_1	clinker + 5 % slag + 5 % pumice	2800
D_2	clinker +10 % slag + 10 % pumice	2800
D_3	clinker + 15 % slag + 15 % pumice	2800
E_1	clinker + 5 % slag + 5 % pumice	4800
E_2	clinker + 10 % slag + 10 % pumice	4800
E_3	clinker + 15 % slag + 15 % pumice	4800

RESULTS AND DISCUSSION

The Heat of Hydration of the Blended Cement

The heats of hydration of the blended and control cements are given in Fig.1. Differential variations of the heat of hydration of the control cements are presented in Fig. 2. The relationship between the heat of hydration and the percentage of the additives is given in Fig. 3. The relationship between the heat of hydration and the fineness is given in Fig. 4. The calorimetry test results, including both the rate of heat generation and the cumulative heat from the three different types of cements used in this study, is shown in Fig. 5. The three figures demonstrate that when different cements were used, the shape of the heat generation curve changed, but the trend of these curves with different w/c remained similar, i.e., the maximum rate of heat generation decreases with increased w/c, while the time for the mortar mixtures to reach the maximum rate of heat generation increases as w/c increases. One possible explanation is that a higher w/c causes a relatively higher degree of dilution of cement in the cement–water solution, which may result in a lower rate of hydration and reduced or retarded heat of cement hydration at the early ages. The results indicate that despite the differences in cement fineness, most of the mortar showed similar trends on the effect of w/c on the heat of hydration rate.

A similar trend can be confirmed in the cumulative heat generated in the first 24 h after mixing [33]. Because the diminishing of the hydration rate is affected by the depletion of cement particles, it is reasonable to believe that the switch from the acceleratory period to the decelerator period depends on the particle size of cement. In addition to the effect of additives, finer cement is generally expected to have an increased heat release rate; although the ultimate heat releases may be similar [34]. The results from this study indicated that the heat generated from hydration was considerably lower at the early hours when coarser cement was used. Because the hydration occurs at the surface of the cement particles and because finely ground cement has a higher specific surface area, more area is in contact with water, resulting in a higher rate of hydration. As expected, the amount of heat generated in the first 24 h decreased with decreasing fineness. The control cements showed a significantly lower hydration heat compared to the blended cements. It is well-known that the finest cements (Cements A2, C and E) have the shortest calorimetry initial and final set times. However, similar trends of the calorimetry initial and final set times were not observed from mixes with the coarser cements used in this study (Cements A1, B and D). This finding may be observed because although the coarser cement particles reduce the rate of hydration, slightly less hydration is required to achieve equivalent set than finer cement due to the higher degree of structure build-up from the larger particles.

The relationship between the heat of hydration and the grinding systems is given in Fig.6. The fineness and the grinding system were kept constant while the ratio of additive increased and the hydration heat decreased. Both the hydration heat and the fineness increased when the grinding system and additive ratios were kept constant. The heats of hydration of the blended cements, which are intergraded, are higher than the heats of hydration of separated cement when the fineness and the ratio of additives are kept constant. At the end of a long period, however, the heat of hydration reaches closer values. A direct comparison of the hydration heat and the compressive strength curves of blended cements containing pumice and GGBFS with the results obtained by other investigators could not be performed because no such measurements were found in common databases [5, 35]. Therefore, blended cements with GGBFS were used for such a comparison. GGBFS can be considered to be a material that is relatively close to the pumice of its origin [36] with pozzolanic activity [37], although certain references may indicate otherwise [38]. Several features of the heat of hydration and compressive strength relation curves (Fig. 6) are highly similar in this study.

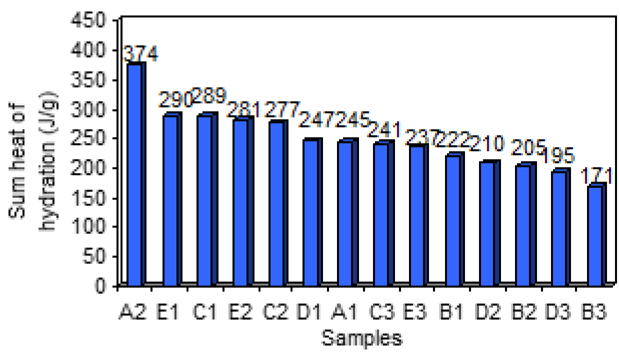

Fig.1 100 hours the heat of the hydration of the blended and control cements

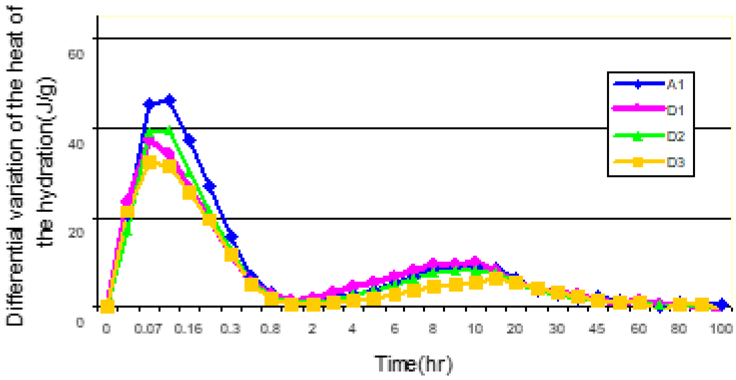

Fig.2 The heat of the hydration and finensess relations (intergrinding, fineness:2800 cm²/g)

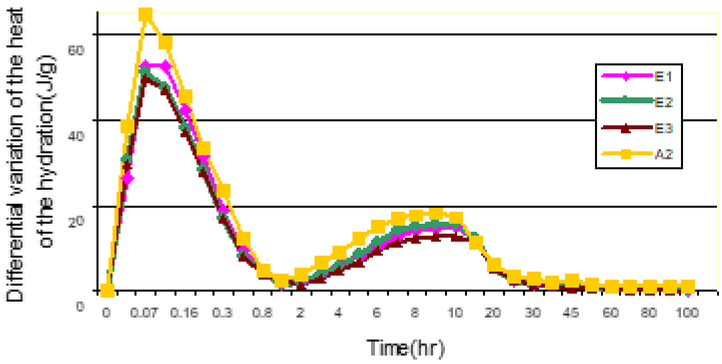

Fig. 3 Differential variation of the heat of the hydration of the blended and control cements (intergrinding, fineness:4800 cm²/g)

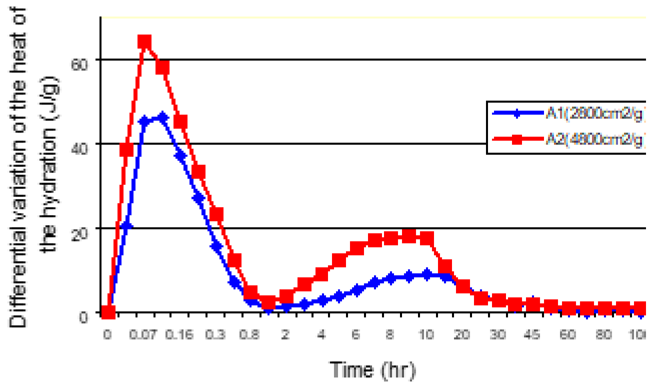

Fig.4 The heat of the hydration and the fineness

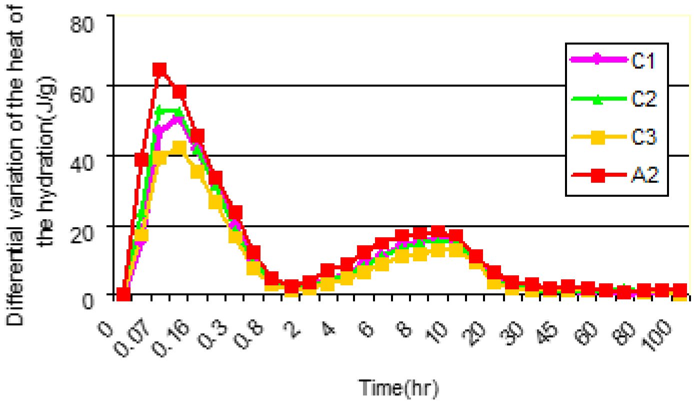

Fig.5 The heat of the hydration and grındıng system relations (seperatelygrinding, fineness:4800 cm²/g)

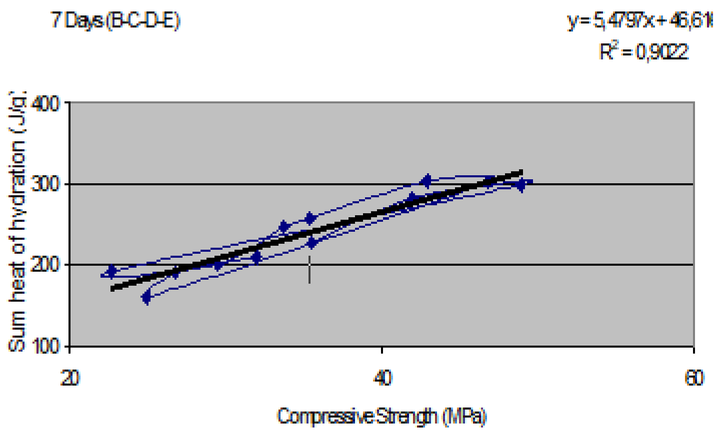

Fig.6 Heat of hydration and compressive strength relation (B-C-D-E-7 days)

Compressive Strength and Heat of Hydration Values of Blended Cements

The mechanical strength in compression is the main quantitative measurement of concrete. The results of the mechanical tests obtained the blended and control cements are shown in Table -7 and Fig. 6. The compressive strength clearly increases with increasing the percentage of additives. The strength values of the cement mortars and the heat of hydration values of the cement pastes are shown graphically in Fig. 7. The increase or decrease in the strength values are related to the increases or decreases of the heat of hydration values. The two curves show a parallel trend. The results showed that within the four mixtures from each cement, the heat of hydration values obtained from calorimetry curves were well correlated with the set times measured according to ASTM C186-80, with a coefficient of determination (R^2) above 0.90, although the relationship is not one-to-one. However, the equation for the linear relationship may not necessarily be the same in each case. Some researchers have reported very similar results [33]. The variation in the compressive strength is shown in Table -7. The compressive strength was found to decrease with increasing slag or pumice content. This is reasonable due to the reduction of cement content in the mix with increasing slag or pumice content. Such pozzolanic action of slag or pumice contributes to the enhancement of the compressive strength in the current study.

The compressive strength is usually a very important property that is related to the cement quality. The compressive strength after 180 days generally increases with an increase in the percentage of the additives. For separately ground specimens with 4800 cm^2/g Blaine values, the compressive strength is higher than that of control cement. In the case of separate grinding, the blended cements with 4800 cm^2/g Blaine values containing 20% additives showed the highest strength development after 90 days. The compressive strengths of all of the blended cements were higher than the minimum value stated by EN TS 12142 [39]. Table -7 shows that the average compressive strength of the separately ground blended cement specimens at 28 days was higher by approximately 8 % than that of the interground ones. The compressive strength of the mortars improved with an increase in the Blaine values of the cement. Moreover, the compressive strength of specimen C2was 18 % higher than that of specimen B2 for the same additive amount (20 %).

CONCLUSIONS

The following conclusions can be taken from this study:

- The fineness of cement is an activating property of the cement heat of hydration, especially at early ages; blended cement with different fineness should be studied to determine the optimum fineness that satisfies the required heat of hydration and the economy.
- In general, additives increase the heat of the hydration of cement, and additives can present a purely economic interest depending on the amount added to the cement. Due to the lower heat of hydration, concrete made with blended cement is generally more sensitive to thermal cracking than Portland cement. This advantage is very important to massive concrete constructions.
- Compared to the cement-separated grinded system, the heat of hydration of blended cements that are intergraded are higher than the heat of hydration of separated when the fineness and the ratio of additives are kept constant.
- The compressive strength of blended cements decrease at early ages as the pozzolan content increases in the cement, but at later ages, the strength development increases considerably. Blended cements containing 20 percent slag and pumice showed the best strength development, while the blended cements containing 30 percent slag and pumice exhibited notably slow strength development compared to those that contained 10 and 20 percent blended cements.
- The addition of pumice and slag as partial replacements for cement slows down the rate of hydration. All of the blended cement samples showed lower degrees of hydration compared to the relevant control samples.
- The best statistical correlations were obtained between the compressive strength and the degree of hydration of the control and blended cement samples.
- 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 cm^2/g.
- The values of heat of hydration mainly depend on the Blaine values.
- Due to the decreased fineness, heat generated from the hydration of coarser cement during earlier ages was lower from the slower rate of hydration.

Finally, due to the lower heat of hydration, this cement can be used for mass concrete construction.

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