Asian Journal of Chemistry; Vol. 27, No. 11 (2015), 4193-4196

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.19486

Effects of Mineral Activators on Hydration Properties of Ternary, Low-Heat Blended Cement with Abundant Ground Granulated Blast-Furnace Slag†

SUNG WOO CHOI[1,*], GYU YONG KIM[2], DEUK HYUN RYU[1] and CHUL WOO BACK[1]

[1]Research&Development Cente, Eugene Corporation Co. Ltd., Goyang-City, GyeongGi-Do, Republic of Korea
[2]Department of Architectural Engineering, Chungnam National University, Daejeon, Republic of Korea

*Corresponding author: Fax: +82 31 9697345; E-mail: friendpo@daum.net

AJC-17432

Hydration properties and use of blended cements with various types of mineral activators were evaluated for the purpose of developing an environment-friendly, low-heat blended cement using a high proportion of ground granulated blast-furnace slag and fly ash, thus reducing the proportion of Portland cement mix by up to 10 %. The results showed that a mixture of plaster and quicklime as a mineral activator, at 5 % of total binder content, can maintain performance comparable with standard, commercial low-heat cements and importantly, results in a significant reduction in concrete's hydration heat.

Keywords: Low heat blended cement, Mineral admixture, Mineral activator.

INTRODUCTION

The hydration of Portland cement is accompanied by heat evolution, which causes a temperature rise in concrete. Heat evolution of concrete is particularly important with regard to mass concrete, where cooling can lead to cracking after a large temperature rise[1,2]. Mass concrete is defined by the ACI committee[3] 116 as "any volume of concrete with dimensions large enough to require the measures be taken to cope with generation of heat of hydration from the cement and attendant volume change to minimize cracking".

It is known that using fly ash and ground granulated blast-furnace slag as 'any volume of concrete with dimensions large enough to require the measures be taken to cope with generation of heat of hydration from the cement and attendant volume change to minimize cracking' .

In this research, based on a mixing method that reduces cement's hydration heat through the incorporation of fly ash and ground granulated blast-furnace slag (GGBS), the hydration properties of low-heat blended cement (LHBC) were evaluated in relation to mineral activators to induce reaction activation of the admixture. This was carried out for the purpose of developing an environment-friendly low-heat blended cement by greatly reducing the required proportion of Portland cement in low-heat concrete production, treating granulated blast-furnace slag as a primary binding material.

EXPERIMENTAL

The experimental parameters for the optimal proportions of environment-friendly low-heat blended cement with granulated blast-furnace slag at 10 % of total cement (OPC) binding material are presented in Table-1, with test methods listed in Table-2. In order to determine the mix proportion for development of environment-friendly low-heat blended cement, the resulting strength of mortar was evaluated and then an optimal mix proportion was selected. Based on this, hydration properties were evaluated. Gypsum was used as a SO_3 supplier for the inorganic activator required by the granulated blast-furnace slag and fly ash and quicklime (QL) and calcium-sulfo-aluminate (CSA) were used as a CaO supplier to induce a pozzolanic reaction. For gypsum (GS)[4], the hydration properties were evaluated by various methods with plasters using calcium-sulfate anhydrate (CA) and calcium-sulfate dihydrate (CD), which is industrial by-products.

Heat of hydration was monitored using isothermal conduction calorimetry apparatus. The test comdition or the isothermal conduction calorimetry were as follows: the mass of binder used and activator used respectively; binders prepared 1 day earlier than the test. The initial scanning rate was 30s; the final recording rate was 300s; the bath water temperature was 20 °C and the test time was 72 h.

---

†Presented at The 8th ICMMA-2014, held on 27-29 November 2014, Hoseo University, Chungnam, Republic of Korea

TABLE-1
TEST PLAN AND METHOD

Binder	Cement and admixture	– Standard mix proportion of binder ⇒ OPC: GGBS: FA = 4: 4: 2 – Ordinary Portland cement (Type 1; OPC) ⇒ 10 % – Ground granulated blast-furnace slag (GGBS) ⇒ 60-70 % – Fly ash (Type F; FA) ⇒ 20 %-
	Mineral activator	– Quicklime (QL) – Gypsum: Calcium sulfate anhydrate (CA), Calcium sulfate dihydrate (CD) – Calcium-sulfo-aluminate (CSA) – Mineral activator ratio: Use (1) Each: 2, 3, 5, 7, 10 % (2) Mix: QL+GS(CA, CD), QL+GS+CSA
Test method		(1) Mortar strength: KS L ISO 679 (2) Binder: • Chemical composition analysis, • Heat Evolution rate • XRD

TABLE-2
PHYSICAL AND CHEMICAL ANALYSIS OF BINDERS

	Properties		Chemical analysis (%)						
	Blaine (cm^2/g)	Density (g/cm^3)	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	SO$_3$	Ig. loss
Ordinary portland cement	3,342	3.14	20.78	5.53	3.15	61.66	3.22	2.43	2.19
Ground granulated blast-furnace slag	4,191	2.91	32.81	14.85	0.35	41.23	5.28	4.25	0.98
Fly ash	3,432	2.27	69.1	20.14	4.11	2.43	0.00	0.36	3.52
Quicklime	2,566	3.28	2.82	0.18	0.72	85.35	0.99	0.19	9.17
Calcium-sulfate-anhydrate	3,643	2.82	1.95	1.9	0.85	39.8	0.56	51.62	2.85
Calcium-sulfate-dihydrate	3,831	2.40	2.9	1.19	0.26	32.5	1.15	43.54	16.05
Calcium-sulfo-aluminate	3,945	2.76	10.05	33.31	2.05	42.12	0.00	9.93	1.65

TABLE-3
STRENGTH OF MORTAR

OPC	FA	BFS	QL	CA	CD	CSA	Stength (MPa)		
							3	7	28
Portland cement Type II [4]							7.5	15.0	32.5
40	20	40					15.3	25.6	41.9
		70					10.2	15.5	24.2
10	20	60 - 68	10				7.3	13.5	30.4
			7				8.1	15.6	31.8
			5				12.2	20.7	36.4
			3				11.6	20.5	34.8
			2				11.7	18.4	32.2
				10			11.2	21.4	27.6
				7			13.2	24.5	30.4
				5			13.8	24.3	35.8
				3			14.1	23.1	31.6
				2			12.6	18.1	27.4
					10		13.8	24.7	31.9
					7		12.9	25.2	33.4
					5		14.5	22.3	30.1
					3		13.1	19.2	26.4
					2		10.4	16.4	23.8
						3	14.9	21.5	24.8
						2	13.2	19.9	25.7
						1	11.1	18.9	25.5

10 % of total cement (OPC); Fly ash (FA); Quicklime (QL); Calcium-sulfate anhydrate (CA); Calcium sulfate dihy (CD); Calcium-sulfo-aluminate (CSA)

X-ray diffraction allows the identification of well-crystallized mineral phases when they are present in sufficient quantity. Presence/absence of a hydration phase was assessed by observing diffraction angles for the primary elements.

The physical and chemical properties of the binding material used for this study are listed in Table-2. A chemical compound analysis showed that the quicklime, calcium-sulfate anhydrate, calcium-sulfate dihydrate and calcium-sulfo-aluminate used as mineral activators were all found to have a high CaO content. Both GS (calcium-sulfate anhydrate, calcium-sulfate dihydrate) turned out to have a relatively high SO$_3$ content and calcium-sulfo-aluminate had a relatively high Al$_2$O$_3$ content[5].

RESULTS AND DISCUSSION

Strength of mortar: Properties of the strength manifestation of mortar with different types and preparation methods of mineral activator are listed on Table-3.

On observing the effects of quicklime on strength manifestation, there is a clear tendency for the strength manifestation to decrease as its proportion is increased in the early stage. Afterwards, the strength manifestation increases by about 5 %, but it starts to decrease above certain level. When plaster is used, a similar tendency is shown. As the differences shown by different types of plaster using natural anhydrous gypsum showed the improve strength manifestation over those using dehydrate gypsum. This behavior may be due to a difference in solubility.

According to the results of mortar-strength manifestation in terms of the mix proportion of mineral activator, the optimal formulation of mineral activator was quicklime and calcium-sulfate anhydrate, with a binding material mix proportion of OPC:GGBS: FA:MA=1:6:2:1 and a calcium-sulfo-aluminate mix proportion of 5:5:0 or 5:4:1. In addition to the two selected mixes, hydration properties were evaluated for mixing binding material without mineral activator or standard low-heat blended cement and the mix proportion of evaluated binding material is presented in Table-4.

Heat evolution rate: Conduction caloric heat over time for different binding material mix proportions are presented in Fig. 1.

TABLE-4
MIX PROPORTION OF BINDER

	OPC (%)	FA (%)	BFS (%)	MA (%)	MA (%)		
					QL	CA	CSA
LHBC^{*1}	40	20	40	0	0	0	0
Non-MA^{*2}	10	20	70	0	0	0	0
MA 1	10	20	60	10	5	4	1
MA 2	10	20	60	10	5	5	0

(1) LHBC: Low heat blended cement; (2) MA: Mineral activator; 10 % of total cement (OPC); Fly ash (FA); Quicklime (QL); Calcium sulfate anhydrate (CA); Calcium-sulfo-aluminate (CSA)

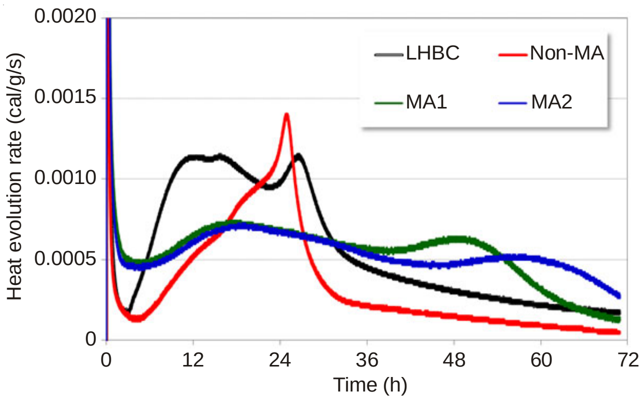
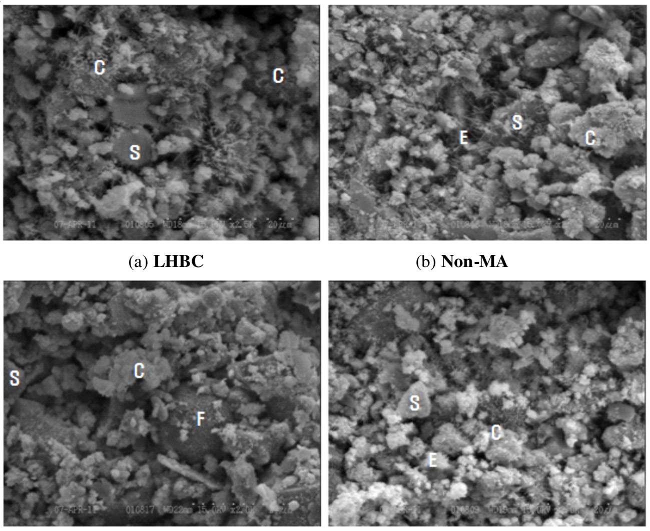


Fig. 1. Heat evolution rate of binder

For mix proportions of low-heat blended cement treated with mineral activator, a third exothermic peak occurs due to spreading from ettringite ($3CaO·Al_2O_3·3CaSO_4·32H_2O$) to mono-sulfate [$Ca_4Al_2O_6(SO_4)12H_2O$] within 30 h after the hydrate reaction. Since no anhydrous gypsum is added to the mixture of non-MA (non-mineral activator) and low-heat blended cement, which is a comparison mix. However, for MA1 and MA2 mix treated with mineral activator, SO_3 supplied by the gypsum delayed the transformation of monosulfate and eventually delayed the third exothermic peak (Fig. 2).

The XRD analysis results with respect to binding-material mix proportion are listed in Fig. 3. Since fly ash was used in every case, the quartz peak, which is a main phase of fly ash, appeared in every mix for up to 28 days. For low-heat blended cement, $Ca(OH)_2$ was present at all ages, but as it progressed, peak level slightly decreased and when treated with mineral activator, both MA1 and MA2 produced calcium sulfate

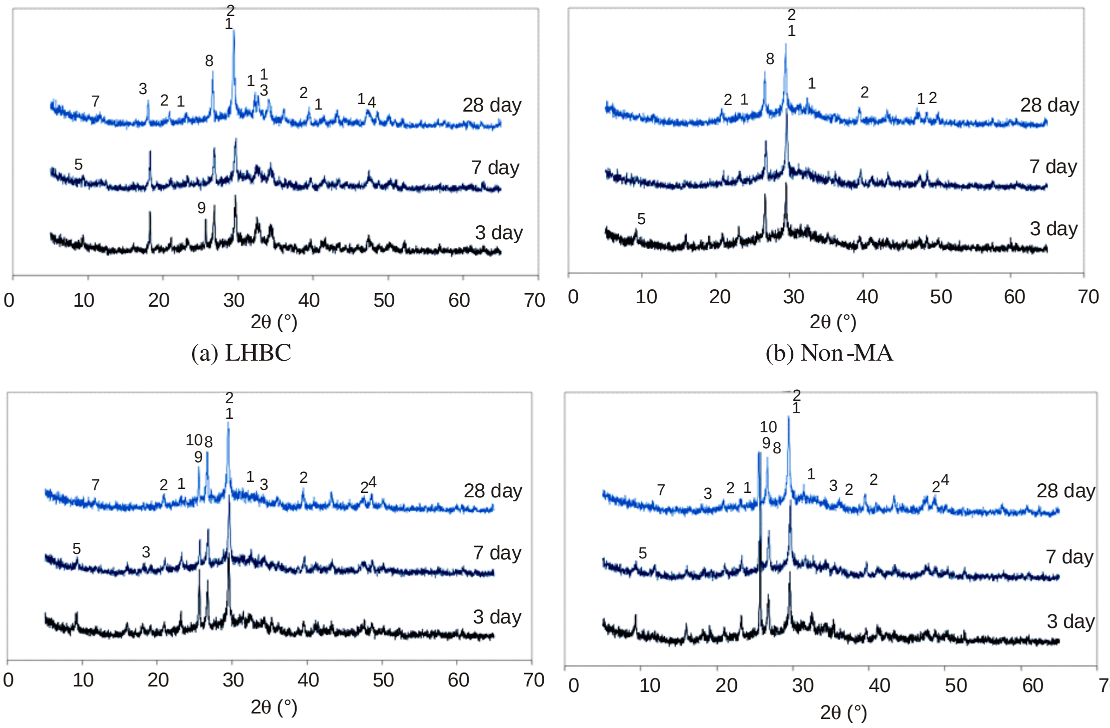


(a) LHBC (b) Non-MA

(c) MA1 (d) MA2

1. Clinker, 2. $CaCO_3$, 3. $Ca(OH)_2$, 4. CSH, 5. Ettringite, 6. Monosulphate
7. $C_3A·CaCO_3·12H_2O$, 8. Quartz, 9. Calcium sulfate-hydrate, 10. Mullite

Fig. 3. SEM of binder (day 28)



(a) LHBC (b) Non -MA

(c) MA1 (d) MA2

1.Clinker 2. $CaCO_3$ 3. $Ca(OH)_2$ 4. CSH 5. Ettringite 6. Monosulphate
7. $C_3A·CaCO_3·12H_2O$ 8. Quratz 9. Calcium sulfate-hydrate 10. Mullite

Fig. 2. XRD analysis of binder

hydrate and ettringite peaks due to the use of calcium-sulfate anhydrate. These were observed up to a later age and a $Ca(OH)_2$ peak was clearly visible at later ages.

The SEM images for each mix proportion of the binding material on day 28 are shown in Fig. 3. For low-heat blended cement, some unreacted granulated blast-furnace slag particles and fly ash particles were still observed on day 28. For MA1 and MA2, ettringite and monosulfate, which are produced during the hydration process were observed.

Conclusions

- When using a mixture of granulated blast-furnace slag and fly ash, granulated blast-furnace slag needs to supply SO_3 and fly ash needs to supply CaO for reaction activation of the mixture and plaster and quicklime exhibited a strong potential as activators for each mixture's reaction
- The plasters difference in solubility proved to be an important factor affecting activation of ground granulated blast-furnace slag.
- In terms of the hydration heat characteristics of low-heat concrete, *i.e.*, low-heat blended cement of a ternary compound system, which is a mixture of fly ash and cement with proportions of granulated blast-furnace slag, it is considered likely that development of environment-friendly low-heat blended cement with minimized cement usage for reduced CO_2 emission is possible. Since this formulation produced similar or improved performance relative to standard commercial blended cement, but with 40 % less cement usage.

ACKNOWLEDGEMENTS

This research was supported by a grant (Code 11-Technology Innovation-F04) from Construction Technology Innovation Program (CTIP) funded by Ministry of Land, Transportation and Maritime Affairs (MLTM) of Korean government.

REFERENCES

1. C.D. Atis, *Cement Concr. Res.*, **32**, 751 (2002).
2. ACI Committee, 116 R-85, Cement and Concrete Terminology, ACI Manual of Concrete Practice, American Concrete Institute Pubs, USA (1989).
3. R.E. Davis and R.W. Carson, *ACI J.*, **33**, 577 (1937).
4. M. Michel, J.-F. Georgin, J. Ambroise and J. Péra, *Construct. Build. Mater.*, **25**, 1298 (2011).
5. Korea Standards Association, KS L 5201 Portland Cement, Korea (2011).