Hydration Characteristics and Synthesis of Hauyne-Belite Cement as Low Temperature Sintering Cementitious Materials

Sang-Jin Park*, Se-Hoon Jeon**†, Kyung-Nam Kim*, and Myong-Shin Song**†

*Department of Advanced Materials Engineering, Kangwon National University, Samcheock 25913, Korea

**Research Center of Advanced Convergence Processing on Materials, Kangwon National University, Samcheock 25913, Korea

(Received October 23, 2017; Revised March 19, 2018; Accepted March 20, 2018)

ABSTRACT

OPC production requires high calorific value and emits a large amount of CO₂ through decarbonation of limestone, accounting for about 7% of CO₂ emissions. To reduce CO₂ emissions during the Ordinary Portland Cement (OPC) production process, there is a method of reducing the consumption of cement or lower temperature calcination for OPC product. In this study, for energy consumption reduction, we prepared Hauyne-belite cement by calcination at a low temperature compared to that used for OPC and studied the early hydration properties of the synthesized Hauyne-belite cement. We set the ratios of Hauyne and belite to 8 : 2, 5 : 5 and 3 : 7. For the hydration properties of the synthesized Hauyne-belite cement, we tested heat of hydration of paste and the compressive strength of mortar, using XRD and SEM for analysis of hydrates. As for our results, the temperature for optimum synthesis of Hauyne-belite is 1,250°C. Compressive strength of synthesized Hauyne-belite cement is lower than that of OPC, but it is confirmed that compressive strength of synthesized Hauyne-belite cement with mixing in of some other materials can be similar to that of OPC.

Key words : Hauyne, Belite, CSA, CO₂

1. Introduction

Compared to many industries, the cement industry has high energy consumption due to the high calcination temperature required in the production of clinker. Approximately 0.9 tons of CO₂ are produced for each container of cement, and approximately 50 million tons of CO₂ are produced in the domestic cement industry.¹⁾ Ordinary Portland Cement (OPC) is the most widely used binder for concrete used for construction. As the use of OPC increases, the production of CO₂ increases as well and contributes to environmental problems such as global warming.²⁾ There are a number of representative methods that can be used to reduce emissions of CO₂ and energy in the production of cement, including numerous approaches for low temperature calcination of cement, and geopolymers. Hauyne-Belite cement (HBC) has been reported to be manufacturable at low calcination temperature compared to conventional OPC. Thus, the development of HBC can reduce the use of natural resources compared to the fabrication of OPC, while reducing energy consumption and CO₂ emissions, relieving environmental loads.

HBC produces ettringite through the hydration reactions

of CaO and CaSO₄ and the hydration product of acicular crystals improves compressive strength by micropore densification of the cement hardener.³⁾ Also, it has been reported that belite influences long-term strength.⁴⁾

In this study, HBC was synthesized at temperatures below the low calcination temperature of 1300°C, compared to that of conventional OPC, and the properties of HPC were evaluated. Additionally, the initial hydration reaction properties and compressive strength based on various Hauyne and Belite composition ratios were investigated,⁵⁾ and hydrate analysis was carried out.

2. Experiment Procedure

2.1. Synthesis Materials

The materials used in the synthesis of HBC were reagent grade,⁶⁾ and Table 1 shows the properties of the reagents used in the synthesis.

2.2. Optimal HBC Synthesis Condition

The mixing ratio was determined according to the molar ratio used for the synthesis of HBC. Table 2 shows the synthesis molar ratio where the target ratios of Hauyne and Belite were 8 : 2, 5 : 5, and 3 : 7.

In order to determine the phase transition temperatures of the Hauyne⁷⁾ and Belite, TG-DTA (Netzsch. Co., STA409PC Luxx model) analysis was conducted. Measurements were carried out up to the maximum temperature of 1,400°C with a heating rate of 5°C/min, and under O₂ atmosphere. Fig. 1

†Corresponding author : Myong-Shin Song

E-mail : msong0422@kangwon.ac.kr

Tel : +82-33-570-6558 Fax : +82-33-570-6556

†Corresponding author: Se-Hoon Jeon

E-mail : zine2421@naver.com

Tel : +82-33-570-6556 Fax : +82-33-570-6556

Table 1. Hauyne-Belite Cement Synthetic Materials

Component	Product	Molecular weight (g)	Purity
CaCO ₃	DAEJUNG	100.09	Extra pure
Al ₂ O ₃	JUNSEI	101.96	Guaranteed Reagent
CaSO ₄	Alfa Aesar	136.14	99%
SiO ₂	JUNSEI	60.08	Extra pure

Table 2. Hauyne-Belite Cement Synthesis Ratio Unit (wt.%)

Type name	CaCO ₃	Al ₂ O ₃	CaSO ₄	SiO ₂	SUM
HC	49.9	30.5	13.6	6.0	100
MC	61.7	17.2	7.6	13.5	100
LC	63.7	10.8	4.8	17.0	100

Fig. 1. Results of TG-DTA. **Fig. 2.** Results for free-CaO using ethylene glycol.

shows the analysis results.

In addition, the amount of free-CaO depending on calcination temperature was determined by using the ethylene glycol method. Fig. 2 shows the free-CaO content according to

Fig. 3. Hauyne-Belite Cement firing condition.**Table 3.** XRD-Rietveld Product Yield

	CSA (%)	C ₂ S (%)	CaSO ₄ (%)	CaO (%)	Al ₂ O ₃ (%)	Etc. (%)
HC	84.3	15.7	-	-	-	-
1250°C MC	46.9	53.1	-	-	-	-
LC	31.7	68.3	-	-	-	-

temperature. Since free-CaO of around 10% was present up to 1200°C, it was determined that the temperature range was not appropriate. The amounts of free-CaO for 1250°C and 1300°C were 2.08% and 1.54%, respectively, so the appropriate temperature range was determined to be 1250°C or 1300°C. In this study, the optimal calcination temperature was set to 1250°C.

Therefore, for the synthesis of HBC, the temperature was maintained at 850°C for 30 minutes for the decarbonation reaction, followed by 60 minutes at 1250°C where Hauyne is produced and synthesized through natural cooling within the furnace. Fig. 3 shows the calcination temperature condition. Finally, we have verified the yields of CSA and C₂S and the values are the same as in Table 3.

2.3. Physical Property Experiment Method

The amount of added CaSO₄ was calculated according to the production stoichiometry of ettringite depending on the molar ratios of CSA and CaSO₄. Then, through substitution, the experimental mixing ratios were obtained and are shown in Table 4. The mortar compressive strength experiment was carried out in accordance with the KS L ISO 679

Table 4. Hauyne-Belite Cement Mortar Test Mixing Ratio

	OPC (wt.%)	HC (wt.%)	MC (wt.%)	LC (wt.%)	CaSO ₄ (wt.%)
Plain	100	-	-	-	-
HC	-	64.6	-	-	35.4
MC	-	-	76.9	-	23.1
LC	-	-	-	83.3	16.7

“cement strength experiment method”. Specimens with dimensions of $40 \times 40 \times 160$ mm, W/B 0.5, and S/B 3.0 were prepared. The HBC compressive strength was measured for ages of 1, 3, 7 and 28 days. In order to measure the hydration reaction heat, an insulation box was used to measure the simple hydration heat with a 10 point data logger manufactured by Kyowa.

Also, a paste of W/B 0.4 was fabricated to investigate the hydration products of HBC, and after curing at 21°C and humidity of 60%, the acetone immersion method was used based on ages of 1, 3, 7 and 28 days to make measurements by XRD (Rigaku. Co., D/Max-2500V) and FE-SEM (JSM-6701F/X-Max) after hydration termination. XRD analysis was carried out for the range of 2θ $5 \sim 65^\circ$ at a scan rate of $1^\circ/\text{min}$.

3. Results and Discussion

3.1. Simple Hydration Heat Measurement Result

Figure 4 shows the hydration heat measurement result. Generally, CSA mainly produces ettringite and C-A-H from hydration through reactions of SO_3 , CaO , and H_2O . The hydration measurement result showed hydration heat curves of 106.8°C , 103°C , and 87.3°C for HC, MC, and MC, respectively, and higher reaction heats were measured for greater CSA amounts. This result was determined to be

Fig. 4. Heat of hydration of cement paste.

hydration heat due to the ettringite production reaction, and it was concluded that the initial hydration reaction was proportional to the CSA amount. Meanwhile, LC showed the highest reaction rate and a greater amount of stabilized phase C_2S compared to CSA. Therefore, the Ca and Al ions of CSA were more conveniently released to produce ettringite at a relatively faster time and faster hydration heat rate.

3.2. XRD Analysis Result of the Hydration Products

Through the hydration reaction, CSA produces ettringite and C-A-H products, which contribute to the initial strength development. The results of the X-ray diffraction analysis

Fig. 5. Results of XRD analysis.

performed to determine the HBC hydration products according to curing age are shown in Fig. 5.

For HBC, overall non-hydrated CaSO_4 was identified, which was determined to be a result of the gypsum added, according to the theoretical amount of ettringite production, and the amount remaining without participating in the reaction. The amount of gypsum remaining was estimated by the peak intensity. The peak intensity order was $\text{HC} > \text{MC} > \text{LC}$, which was thought to be due to the differences in the amounts of gypsum added for each type.

Also, when the ettringite production amount was estimated by peak intensity according to each type and curing age, the ettringite production amount was almost constant regardless of the amount of added gypsum depending on the type and curing age from 1 to 28 days, along with the CSA amount. Here, gypsum was added based on the CSA content for each type according to the stoichiometry of Eq. (1) for ettringite production.

The result obtained was thought to be because the theoretical production rates of ettringite for HC, MC, and LC were in similar ranges when the CSA amount and gypsum addition amount for each type were converted to percent-

ages.

For OPC, it was found that the alite peak showed a decreasing trend as the curing age increased, and this was thought to contribute to the strength development according to the OPC hydration mechanism, through continuous C-S-H hydrate production.

3.3. Hydration Product SEM Analysis Result

Figures 6 and 7 show the SEM analysis results of the hydration products. The SEM image for the curing age of 1 day revealed a high distribution of acicular C-S-H hydrates for OPC, while ettringite was mainly distributed for HBC. For the curing age of 28 days, fine, acicular C-S-H hydrates were observed for OPC. For HBC, ettringite and fine, acicular C-S-H hydrates were observed, but the ettringite was dominantly distributed over the C-S-H hydrates. Therefore, for the curing age of 28 days, C-S-H hydrates were dominant for OPC hydrates, while ettringite was dominant for HBC hydrates.

3.4. HBC Compressive Strength Results

Figure 8 shows the compressive strength results for the hardened HBC. The compressive strength measurement results showed that among the gypsum added hardened HBC, the HC exhibited higher strength compared to the

Fig. 6. SEM photo of hydration on day 1.

Fig. 7. SEM photo of hydration on day 28.

Fig. 8. Compressive strength of mortar by curing age.

hardened OPC, while the hardened MC and LC exhibited lower compressive strength development compared to the hardened OPC. This result signified the initial compressive strength development through the production of ettringite according to the CSA in the initial stages of the hydration reaction. Also, this result showed that as the amount of C_2S becomes relatively greater, the compressive strength development decreases.

As observed in the X-ray diffraction analysis results, the

amounts of ettringite produced in each type were similar, however, there were differences in the compressive strength development depending on the C_2S amount. In this study, HBC was designed under the assumptions that the ettringite production would dominate the compressive strength development in the initial stages of hydration, followed by C_2S hydration dominating the compressive strength development in the latter stages of hydration. However, the results obtained through this study revealed that the overall contribution to the compressive strength development was minimal when the C_2S amount with regard to the CSA amount was greater than a specific ratio. Therefore, for the compressive strength development of HBC, the ettringite production dominated the compressive strength development for all the hydration curing ages, and it was predicted that the hydration of C_2S has an assistive role in the compressive strength development. Further research is necessary to determine the underlying theoretical mechanism.

4. Conclusions

In this study, the optimal synthesis conditions and corresponding synthesis yield of Hauyne-Belite Cement were investigated and the following conclusions regarding hydration behavior were obtained.

1) The yields of CSA and C_2S according to the chemical composition ratios were 8 : 2, 5 : 5, and 3 : 7, and it was found that the optimal calcination temperature of 1250°C was appropriate.

2) With regard to the mineral composition of the synthesized HBC, the development of compressive strength was not affected when the C_2S amount for the CSA amount was greater than a specific ratio. The model with compressive strength development higher than that of OPC was found in this study to be the 8 : 2 ratio of CSA and C_2S .

3) The HBC with an 8 : 2 ratio of CSA and C_2S showed higher compressive strength than OPC due to the the production of ettringite in the initial stages of hydration. The produced ettringite was found to dominate the compressive strength of all the hydration curing ages.

4) The HBC with an 8 : 2 ratio of CSA and C_2S showed a greater strength development than OPC with a curing age of 28 days, however, the role of C_2S on the enhancement of long-term strength could not be assessed.

REFERENCES

1. H. J. Song, Effects of Calcium Aluminate Compounds on Hydration of Blast Furnace Slag (*in Korean*), in Master Thesis, Kangwon National University, Samchuk, 2016.
2. S. H. Lee, Physical and Chemical Properties of Cement Mortar with Gamma- C_2S (*in Korean*), in Master Thesis, Kangwon National University, Samchuk, 2016.
3. K. D. Ki, The Study on Characteristics and Preparation of CSA Using Alunite (*in Korean*), in Master Thesis, Myungji University, Seoul, 2000.
4. B. Ma, X. Li, Y. Mao, and X. Shen, "Synthesis and Characterization of High Belite Sulfoaluminate Cement through Rich Alumina Fly Ash and Desulfurization Gypsum," *Ceram.-Silik.*, **57** [1] 7-13 (2013).
5. S. H. Lee, Study of the Synthesis of Hauyne-Belite Cement and its sea-Water Resistance (*in Korean*), in Master Thesis, Myungji University, Seoul, 1984.
6. Irvin Allen Chen, B. S., Synthesis of Portland Cement and Calcium Sulfoaluminate-Belite Cement for Sustainable Development and Performance, in Ph.D. Thesis, The University of Texas at Austin, Austin, 2009.
7. Y. Shen, J. Qian, J. Chai, and Y. Fan, "Calcium Sulphoaluminate Cements Made with Phosphogypsum: Production Issues and Material Properties," *Cem. Concr. Compos.*, **48** 67-74 (2014).