Effects of the chemical treatment on coal-fired bottom ash for the utilization in fiber-reinforced cement

Passakorn SONPRASARN[1], Parinya CHAKARTNARODOM[1,*], Pitcharat INEURE[2], and Wichit PRAKAYPAN[3]

[1] *Department of Materials Engineering, Faculty of Engineering, Kasetsart University, Chatuchak, Bangkok, 10900, Thailand*
[2] *Glass Bridge Company Limited, Wang Thonglang, Bangkok, 10310, Thailand*
[3] *Shera Public Company Limited, Bangkorlhaem, Bangkok, 10120, Thailand*

*Corresponding author e-mail: fengpryc@ku.ac.th

Abstract

Around 3 million tons of municipal solid wastes called bottom ash (BA) are produced annually from the coal-fired power plants and it is still much underutilized in Thailand. Hence, the increasing usage of BA in industrial scale is necessary to limit the environmental impacts from landfilling of those by-product. Using of BA in fiber cement (FC) manufacturing seems to be a promising one. However, several negative effects regarding the extremely high water content from the fiber-cement forming process (Hatschek process) and the BA characteristic (the creation of bubble network) need to be eliminated. Both mentioned inferiors significantly reduce the cement hydration mechanism leading to remarkable reductions of set and hardened performances of fiber cement. Therefore, chemical treatment (CT) was introduced to boost up the hydration kinetic and characterized via the relevance of higher heat of hydration. Additionally, scanning electron microscope (SEM) was used to reveal the beneficial effects of treated BA through the microstructures. The results showed the chemically treated BA improve kinetic of hydration reaction was from the modification of BA surface.
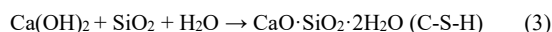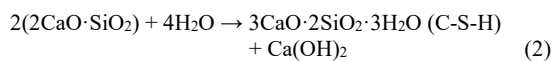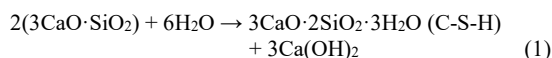
1. Introduction

Coal-fired bottom ash is produced annually from the coal-fired thermo-electric power plants. In Thailand, the plants produce approximately 3 million tons of municipal solid waste per year. The ash is comprised of pozzolanic materials, approximately 0.1-50 mm in size, of which the major chemical composition is silica (SiO_2) and alumina (Al_2O_3). Despite this, the bottom ash is not widely used on an industrial scale. Normally, most bottom ash produced from the power plants are taken to the landfill [1,2].

Fiber-cement products is a fiber-reinforced construction material which is widely used in walls, ceilings, roofing and flooring systems for building. Their major raw materials are Portland cement (PC), sand, and cellulose fiber. The raw materials are mixed with water to form the slurry and the fiber cement products are molded by Hatschek process [3]. After molding, those fiber-cement products are cured either in air or in the autoclave.

Hydration reaction is the chemical reaction of cement with water which could occur after the raw materials of fiber-cement products are mixed with water. Hydration reaction is an exothermic reaction from the chemical reaction between water and the major components of Portland cement including tricalcium silicate ($3CaO \cdot SiO_2$) and dicalcium silicate ($2CaO \cdot SiO_2$)

to produce calcium silicate hydrate (C-S-H), and calcium hydroxide ($Ca(OH)_2$) as shown in equation 1 and 2 [4]. After that, the calcium hydroxide from hydration reaction will further reacts with silicon dioxide (SiO_2) and water to produce calcium silicate hydrate. This reaction is called pozzolanic reaction as show in equation 3 [5].

$$2(3CaO \cdot SiO_2) + 6H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O \text{ (C-S-H)} + 3Ca(OH)_2 \qquad (1)$$

$$2(2CaO \cdot SiO_2) + 4H_2O \rightarrow 3CaO \cdot 2SiO_2 \cdot 3H_2O \text{ (C-S-H)} + Ca(OH)_2 \qquad (2)$$

$$Ca(OH)_2 + SiO_2 + H_2O \rightarrow CaO \cdot SiO_2 \cdot 2H_2O \text{ (C-S-H)} \qquad (3)$$

The basic hydration mechanism, which consist of dissolution of ions to increase PH, diffusion of ions in aqueous phase, the nucleation and growth of crystals of hydration product as shows in Figure 1 [6].

Even though, the bottom ash is comprised of pozzolanic materials and its major component is silica, bottom ash is not simple to use in the fiber-cement industry due to the high particle size, the high porosity and the brittleness of bottom ash. Moreover, there are negative effect of bottom ash on the chemical reaction such as decreasing the reaction rate of hydration reaction [5,6], which leads to the reductions of set and hardened performances of fiber-cement products.
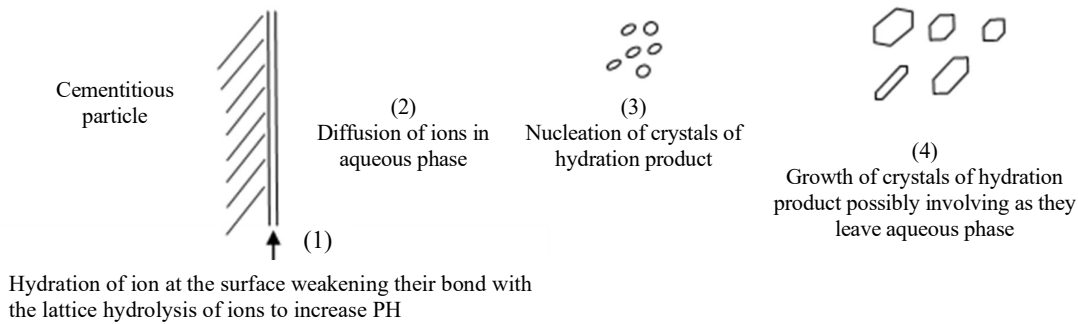
Figure 1. Schematic representation of basic hydration mechanism [6].

It was found that the hydration kinetics in cement could be improved by using coal-fired bottom ash, which is chemically treated with the nucleating agent compound that can accelerate nucleation of crystals in third stage of basic hydration mechanism (Figure 1) to the forming of calcium silicate hydrate (C-S-H) product that lead to the improving of the hydration kinetics of fiber cement products [6,7]. Therefore, the purpose of this work was to investigate the effects of chemical treatment on the coal-fired bottom ash to the hydration kinetics of fiber-cement products for utilization in the fiber-cement industry via the change of heat released during hydration reaction.

2. Experimental

2.1 Material characterization

Ordinary Portland cement type 1 (OPC), bottom ash, sand, and the synthetic nucleating agent (SA) were used in this research. The synthetic nucleating agent (SA) was supplied by Shera Public Company Limited. This SA was prepared by the precipitation process from the aqueous solutions of sodium silicate (Na_2SiO_3) and calcium nitrate ($Ca(NO_3)_2$) [8,9]. Bottom ash was obtained from a coal-fired power plant in Prachinburi, Thailand. This bottom ash was dried in the furnace at 60°C for approximately 24 h to reduce its moisture content. X-ray fluorescence (XRF) spectrometer (Panalytical-Minipal 4) was used to determine the chemical composition of bottom ash. Loss on ignition (LOI) testing of bottom ash was conducted according to the method described in ASTM C311 standard by heating the bottom ash to 750°C in the furnace for 4 h. After that LOI was calculated by equation 4 where m_1 and m_2 are mass of the raw material before and after heating [10].

$$LOI\ (\%) = \frac{m_1 - m_2}{m_1} \times 100 \qquad (4)$$

To prepare the bottom ash for heat of hydration analysis, the bottom ash was ground by ball milling for 8 h. Laser particle size analyzer (Sympatec-HELOS/BR-multirange with QUIXEL dispersing unit) was used to measure the average particle size of ground bottom ash.

2.2 Heat of hydration

Heat of hydration analysis is the measurement of heat evolution from the exothermic reaction of hydration reaction [11]. The mixture consisting of ordinary Portland cement, bottom ash and SA were prepared based on the proportions given in Table 1. The mixtures were mixed with water with the water to cement ratio (w/c ratio) of 0.35 to form the slurry. The slurry was stored in the chamber of the equipment as shown in Figure 2. Then, the change of temperature inside the chamber due to the developed heat from hydration reaction was recorded by temperature recording device every 30 s until the temperature inside the chamber was stable.

For formulas A3 to A5, the amount of SA added to the mixture of OPC and bottom was based on the amount of OPC in the mixture (1.5% to 4.5% of total OPC weight in the mixture). The chemical treatment on bottom ash by SA was carried out during the hydration reaction of the slurry.

Table 1. Mixtures for the heat of hydration analysis. Formula A2 was used as the reference.

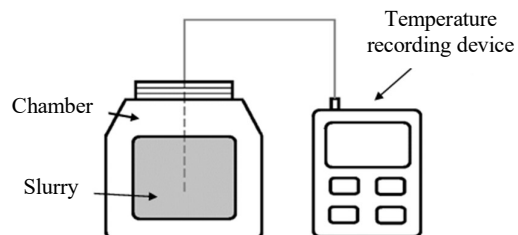| Sample	Composition (wt%)			Nucleating agent (% of OPC weight in the mixture)
	OPC	Sand	Bottom Ash	
A1	75	-	25	-
A2	75	25	-	-
A3	75	-	25	1.5
A4	75	-	25	3
A5	75	-	25	4.5

Figure 2. Schematic diagram of the heat of hydration measurement.

2.3 Morphological analysis of the chemically treated bottom ash

To study the effect of SA on the morphology of bottom ash, the bottom ash and SA were mixed with the weight ratio of SA to bottom ash of 0.015, 0.03 and 0.045. Then the mixtures were mixed with water. The water to solid ratio (w/s ratio) was 0.35. The bottom ash was soaked in the solution for 24 h and then it was dried in the furnace at 60°C for 24 h approximately in order to reduce the moisture content. After that, the morphologies of the bottom ash were observed by scanning electron microscope (SEM).

3. Results and discussion

3.1 Chemical composition, loss on ignition and particle size analysis

Table 2 shows the results from XRF analysis and LOI, which indicated major components of the bottom ash were SiO_2 and Al_2O_3, and the LOI was lower than 3.0wt% which was acceptable by the standard of fiber-cement industry. From laser particle size analyzer, the average particle sizes of bottom ash and sand were 21.50 and 24.62 μm, respectively. Figure 3 shows particle size distribution of the ground bottom ash compared with the particle size of sand which is usually used in the fiber-cement industry. Obviously, the particle size distribution and the average particle size of the bottom ash was comparable to the particle size distribution and the average particle size of sand.

3.2 Heat of hydration

Figure 4 shows the result from the heat of hydration analysis. Clearly, by considering the curve from formulas A1 to A3, the maximum temperatures were approximately 60°C, while formula A4 and A5 maximum temperature were higher (>65°C). These results indicated that the maximum temperature was significantly increased when SA content was greater than 3 wt% of OPC weight in the mixture of raw materials.

The initial, and the maximum temperature, and the time required to reach the maximum temperature were summarized on Table 3. These results could be used to calculate the average rate (r) of the temperature change from the beginning until the maximum temperature was achieved. From equation 5, the average rate of the temperature change (r) could be estimated by

$$r = \frac{T_{max} - T_{ini}}{t} \qquad (5)$$

where T_{ini} and T_{max} were the initial and the maximum temperature, respectively, and t was the time required to reach the maximum temperature. Based on the formula listed on Table 1, from Figure 5, r_i was the average rate of the temperature change of formulas A1, A3, A4, and A5, while r_{A2} was the average rate of the temperature change of formula A2 (reference formula). Then, from Figure 5, r_i/r_{A2} was greater than 1 when the chemically treated bottom ash was used. Therefore, using the chemically treated bottom ash improved the kinetic of the hydration reaction of the mixture. Moreover, by statistically considering the slope of trend line and the sample coefficient of determination (R^2) shown on Figure 5, the increasing of SA content for chemical treatment on the bottom ash would further improve the kinetic of the hydration reaction.
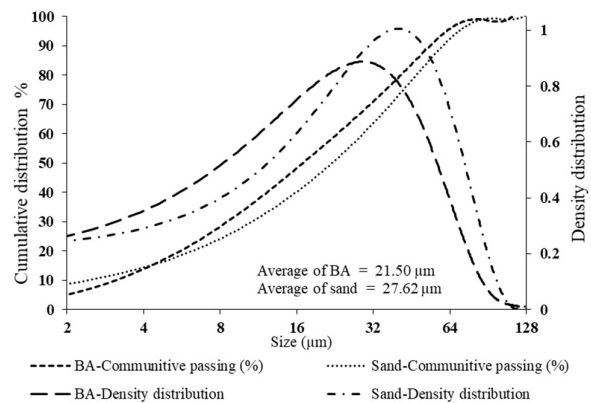

Figure 3. Particle size of bottom ash after grinding compared to the particle size of sand commonly used in fiber-cement industry.
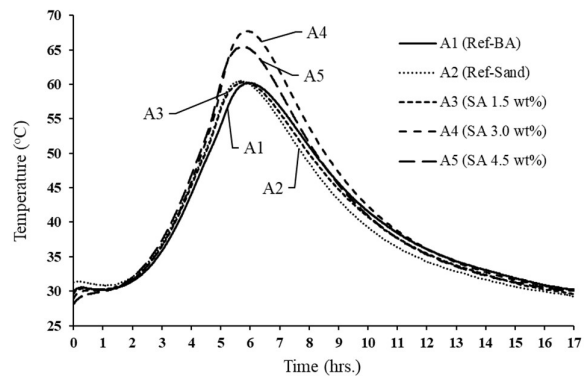

Figure 4. The heat of hydration of chemical treatment of bottom ash.

Table 2. XRF analysis and LOI (wt%) of bottom ash.

Material	Composition (wt%)								LOI (%)
	MgO	Al₂O₃	SiO₂	K₂O	CaO	Fe₂O₃	SO₃	Other	
Bottom ash	1.34	23.82	63.65	0.92	4.50	4.86	0.22	0.69	2.21

Effects of the chemical treatment on coal-fired bottom ash for the utilization in
fiber- reinforced cement composites

57

Table 3. The initial and achieved maximum temperature.

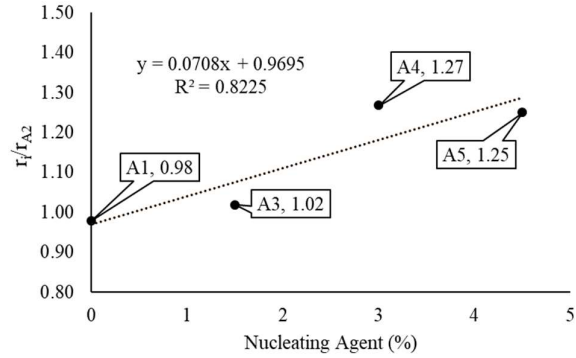|	Formula				
	A1	**A2**	**A3**	**A4**	**A5**
Initial temperature (°C)	30.0	31.3	29.7	28.9	28.2
Maximum temperature (°C)	60.2	60.6	60.3	67.7	65.4
Time required to reach Maximum temperature (h:min)	5:56	5:38	5:46	5:53	5:43

Figure 5. Effect of the dosage of nucleating agent on the rate of temperature change.

3.3 Morphology of the chemically treated bottom ash

Figure 6 shows the SEM micrographs of crystalline structure of the SA used in this work. Obviously, the shape of SA particles was similar to the spiky ball. For the bottom ash, the morphology of the bottom ash without the chemical treatment was shown on Figure 7(a), while the morphology of the chemically treated bottom ash with SA in which the weight ratio of SA to bottom ash of 0.015, 0.03 and 0.045 were shown on

Figure 7(b) to Figure 7(d), respectively.

Evidently, from Figure 7(a), bottom ash has roughness surface, when it was treated with SA, the crystalline C-S-H phase was observed on their surface. According to Land and Stephan [12], the addition of some small particles could stimulate the hydration reaction. This stimulation was from the reactive surface of the added small particles which acted as the nucleation sites for the crystals of the hydration products (C-S-H phases) [13].

Figure 8 shows the proposed hydration mechanism when the chemically treated bottom was added to the mixture of raw materials from Table 1. From Figure 7, the chemically treated bottom ash had the C-S-H crystal growing out of its surface. As shown on Figure 8, due to these crystals, the surface of bottom ash became active sites for the nucleation and the further growth of C-S-H phase, which ultimately lead to the improved hydration kinetic of the fiber-cement products.

As mentioned before, the common process for making fiber-cement products is Hatschek process. In this process, the raw materials were mixed with water to form the slurry. Of course, the high water content of this process caused the negative impacts on hydration kinetic. However, based on our results, using chemically treated bottom ash would relieve this problem.
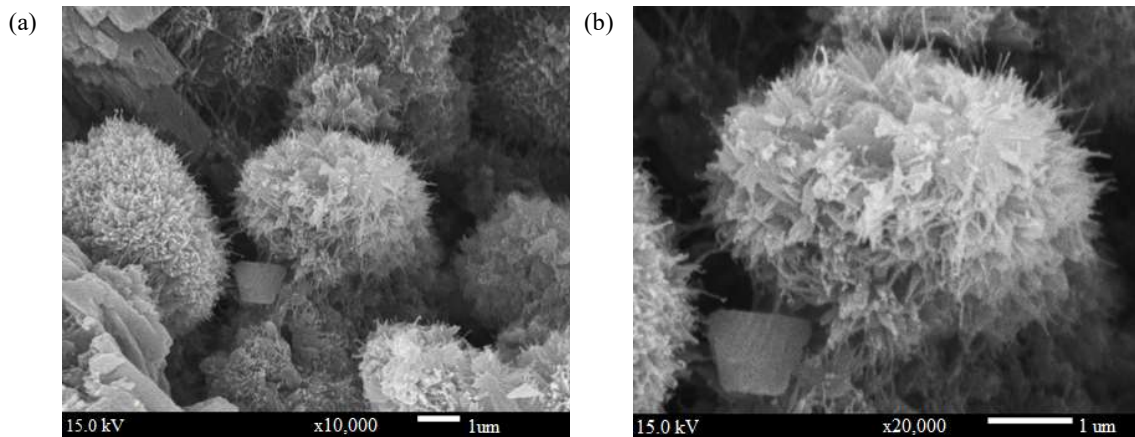

Figure 6. Scanning electron micrographs of the SA taken at (a) 10000x magnification (b) 20000x magnification.
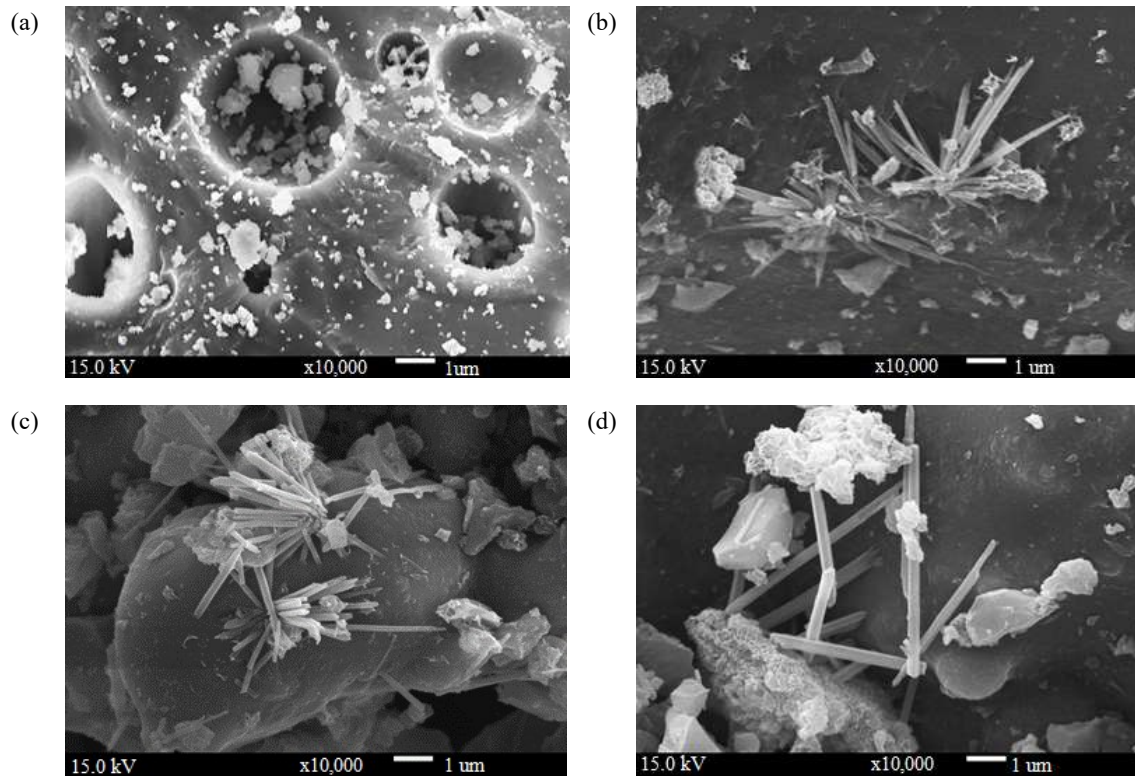
(a)

(b)

(c)

(d)

Figure 7. Scanning electron micrographs of the surface of bottom ash taken at 10000x magnification (a) the bottom ash without the chemical treatment (b) the chemically treated bottom ash with SA with the weight ratio of SA to bottom ash of (b) 0.015, (c) 0.03, and (d) 0.045.
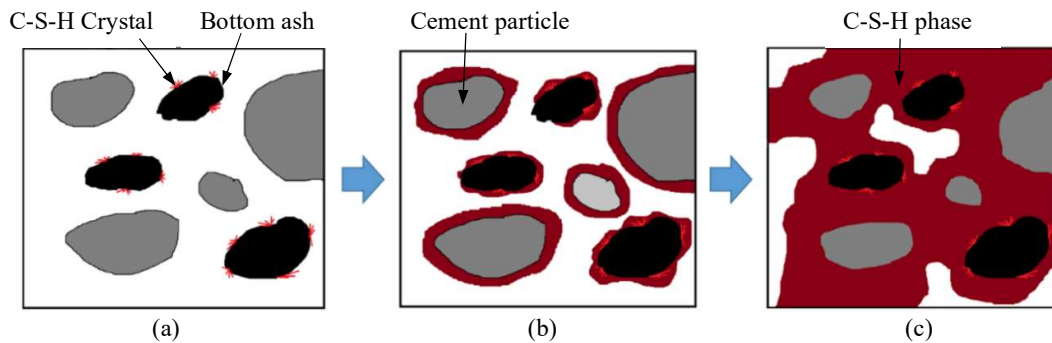
C-S-H Crystal   Bottom ash   Cement particle   C-S-H phase

(a)   (b)   (c)

Figure 8. Schematic diagram of the hydration process when the chemically treated bottom ash was used (a) just after the mixing, C-S-H phase start to form (b) after a few minutes, C-S-H phase growth (c) after a few hours, C-S-H phase further growth.

4. Conclusions

The purpose of this work was to investigate effects of the chemical treatment on coal-fired bottom ash for the utilization in fiber-cement products. The result from the heat of hydration analysis showed that the addition of synthetic nucleating agent to bottom ash caused a significant acceleration of the kinetic of hydration reaction. This improved kinetic of reaction was from the modification of bottom ash surface by the synthetic nucleating agent. The synthetic nucleating agent caused the nucleation of the C-S-H crystals on bottom ash surface which acted as the further nucleation sites and facilitate the further growth of the C-S-H products. Hence, chemically treated bottom ash showed the potential to be utilized as an additive for the manufacturing of fiber-cement products.

5. Acknowledgements

References

[1]   W. Wongkeo and A. Chaipanich, "Compressive strength, microstructure and thermal analysis of autoclaved and air cured structural lightweight concrete made with coal bottom ash and silica fume," *Materials Science and Engineering: A,* vol. 527, pp. 3676-3684, 2010.

[2]   W. Wongkeo, P. Thongsanitgarn, K. Pimraksa, and A. Chaipanich, "Compressive strength, flexural strength and thermal conductivity of autoclaved concrete block made using bottom ash as cement replacement materials," *Materials & Design,* vol. 35, pp. 434-439, 2012.

[3]   A. Akhavan, J. Catchmark, and F. Rajabipour, "Ductility enhancement of autoclaved cellulose fiber reinforced cement boards manufactured using a laboratory method simulating the Hatschek process," *Construction and Building Materials,* vol. 135, pp. 251-259, 2017.

[4]   S. Rai and S. Tiwari, "Nano Silica in Cement Hydration," *Materials Today,* vol. 5, pp. 9196-9202, 2018.

[5]   A. Abdulmatin, W. Tangchirapat, and C. Jaturapitakkul, "An investigation of bottom ash as a pozzolanic material," *Construction and Building Materials,* vol. 186, pp. 155-162, 2018.

[6]   G. C. Bye, *Portland Cement 2nd Ed.* London: Thomas Telford Limited, 1999.

[7]   Z. Chen and E.-H. Yang, "Early age hydration of blended cement with different size fractions of municipal solid waste incineration bottom ash," *Construction and Building Materials,* vol. 156, pp. 880-890, 2017.

[8]   E. John, T. Matschei, and D. Stephan, "Nucleation seeding with calcium silicate hydrate – A review," *Cement and Concrete Research,* vol. 113, pp. 74-85, 2018.

[9]   J. Sun, H. Shi, B. Qian, Z. Xu, W. Li, and X. Shen, "Effects of synthetic C-S-H/PCE nanocomposites on early cement hydration," *Construction and Building Materials,* vol. 140, pp. 282-292, 2017.

[10] ASTM C311-02, Standard Test Methods for Sampling and Testing Fly Ash or Natural Pozzolans for Use as a Mineral Admixture in Portland-Cement Concrete, ASTM International, West Conshohocken, PA, 2000.

[11] ASTM C186-98, Standard Test Method for Heat of Hydration of Hydraulic Cement, ASTM International, West Conshohocken, PA, 1998.

[12] G. Land and D. Stephan, "Controlling cement hydration with nanoparticles," *Cement and Concrete Composites,* vol. 57, pp. 64-67, 2015.

[13] J. J. Thomas, H. M. Jennings, and J. J. Chen, "Influence of nucleation seeding on the hydration mechanisms of tricalcium silicate and cement," *The Journal of Physical Chemistry*, vol. 113, pp. 4327-4334, 2009.