

Low Temperature Cement Synthesis: Calcium Sulfoaluminate-Belite from Industrial Wastes

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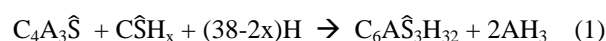
Abstract— This study aimed to synthesis low temperature cement: Calcium Sulfoaluminate-Belite (C \hat{S} AB) using industrial waste as starting material viz., fly ash, bottom ash, and FGD-gypsum together with calcined clay. Commercial grade of Ca(OH) $_2$ and Al(OH) $_3$ are also used as corrective materials. The synthesis method was hydrothermal-calcination. The designed cement phases were calculated basing on Bogue equation. This study varied proportion of starting materials in order to obtain high level of ye'elinite phase and followed the strength development of the synthesized product. The main phases after synthesis were ye'elinite and anhydrite. Belite was also formed as a minority. C \hat{S} AB was mixed with 20wt% of FGD-gypsum and 0.6 of water to solid ratio to study its hydration. The compressive strength was 22.9 MPa at 7 days.¹

Index Terms—C \hat{S} AB cement, hydrothermal-calcination, industrial waste, ye'elinite, belite, ettringite

I. INTRODUCTION

Calcium sulfoaluminate-belite (C \hat{S} AB) cement is alternative cement for a replacement of ordinary Portland cement (OPC) [1] because of the benefits in reductions of CO $_2$ emissions and firing temperatures [2][3]. In addition its grindability was improved [4]. Furthermore, C \hat{S} AB cement concrete has presented good dimensional stability, low permeability, low alkalinity, good durability, and comparable compressive strength to Portland cement concrete [5].

C \hat{S} AB mainly consists of ye'elinite (calcium sulfoaluminate: C $_4$ A $_3$ \hat{S}) and belite (dicalcium silicate: C $_2$ S) and calcium sulfates C \hat{S} . However, minor phases and the amounts of the phases show vary significant dependence on raw materials and applications [5]. C \hat{S} AB cements can introduce rapid setting and give high early-age strength due to the fast reaction of C $_4$ A $_3$ \hat{S} with calcium sulfates compounds and water to form ettringite (C $_6$ A \hat{S} $_3$ H $_{32}$). Al(OH) $_3$ (AH) is a by-product as stated in (1) [6] [7] [8].

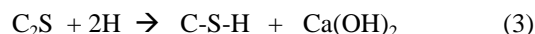


when C = CaO, S = SiO $_2$, A = Al $_2$ O $_3$, \hat{S} = SO $_3$, H = H $_2$ O

Without C \hat{S} or insufficient C \hat{S} , hydration of C $_4$ A $_3$ \hat{S} will forms monosulfate (C $_4$ A \hat{S} H $_{12}$) instead of ettringite [9] as stated in (2), this phase give lower strength than ettringite.



By contrast, the hydration of belite (C $_2$ S) is slower than C $_4$ A $_3$ \hat{S} , but that can provide the long term strength. The products after hydration are C-S-H and Ca(OH) $_2$ as stage in (3).



C \hat{S} AB cement has been commercially in China since the 1970s [10]. Clinkerization method was using solid-state reaction. This study proposed alternative synthesis method to produce C \hat{S} AB via hydrothermal-calcination method because of its various benefits in term of lower firing temperature and better morphology control [11]. Hydrothermal reaction undergoes dissolution and precipitation leading to very fine precipitates. This method also allows the utilization of waste containing active silicate/aluminate or aluminosilicate phases for example ashes, rice husk ash, marble sludge, aluminum sludge, FGD-gypsum. Mae Moh Power Plan in northern Thailand provides fly ash, bottom ash and flue gas desulfurization-gypsum (FGD-gypsum) approximately 2.3, 1.5 and 2.5 Mton/year [12], respectively. As coal ashes contain high level of CaO and Fe $_2$ O $_3$, it is thus a big challenge to be used as starting materials for C \hat{S} AB production in the most effective way.

This study aimed to synthesis C \hat{S} AB cement from high CaO and Fe $_2$ O $_3$ fly ash and bottom ash. FGD-gypsum and calcined clay were also used to supply sulfate and aluminum compounds, respectively. Commercial grade of hydrated lime (Ca(OH) $_2$) and aluminum hydroxide (Al(OH) $_3$) were used as corrective materials according to stoichiometric calculation of Bogue, which was commonly used for cement calculation using solid state reaction

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[13]. The quantities of starting materials were varied according to their active phases. The synthesized products were investigated in terms of their mineralogical compositions and morphology. Binding property was defined by compressive strength test. This synthesis knowledge would be helpful to understand the future improvement of C^ŜAB cement synthesis. Lastly, the effect of environmental issues such as CO₂ emission and limitation of landfill would be reduced.

II. EXPERIMENTAL

A. Raw Materials Preparation

Starting materials used for the synthesis were fly ash (FA), bottom ash (BA) and FGD-gypsum (FGDG) from Mae Moh Power Plant in Lampang province (Thailand). Calcined clay (CC) was prepared from calcination of locally available clay, at 650 °C with soaking time of 30 min. The mineralogical compositions of starting material were using X-ray diffraction (XRD) is shown in Fig. 1. From XRD result of FA consisted of lime (CaO), anhydrite (CaSO₄; C^Ŝ), magnesioferrite (Mg-Fe₂O₃), hematite (Fe₂O₃), quartz (SiO₂) and some amorphous phases. BA consisted of muscovite (KAl₂(AlSi₃O₁₀)(OH)₂) and hematite together with amorphous phase. FGDG mainly composed of gypsum (CaSO₄.2H₂O). Calcined clay consisted of metakaolin, remaining kaolinite, quartz (SiO₂) and

muscovite. Commercial grade of Ca(OH)₂ (CH) and Al(OH)₃ (AH) mainly composed of portlandite (Ca(OH)₂) and gibbsite (Al(OH)₃) respectively. The mineral composition that related to their chemical compositions analyzed by X-ray fluorescence (XRF) is provided in Table 1.

B. Materials Proportions

Each starting material was dried at 110 °C overnight and then ground and sieved passing through No.100 sieve size. Only FGD was dried at 60 °C to keep gypsum phase prior to use. Theoretical phase compositions were forecasted by modification of Bogue's equation for C^ŜAB cement as shown in (4) – (8).

$$\%C_4AF = 3.043 (\%Fe_2O_3) \tag{4}$$

$$\%C_4A_3\hat{S} = 1.995 (\%Al_2O_3) - 1.273(\%Fe_2O_3) \tag{5}$$

$$\%C_2S = 2.867 (\%SiO_2) \tag{6}$$

$$\%C\hat{S} = 1.700 (\%SO_3) - 0.445 (\%Al_2O_3) + 0.284 (\%Fe_2O_3) \tag{7}$$

$$\%C = 1.00(\%CaO) - 1.867(\%SiO_2) - 1.054(\%Fe_2O_3) - 0.550(\%Al_2O_3) - 0.700(\%SO_3) \tag{8}$$

TABLE I. CHEMICAL COMPOSITION OF RAW MATERIALS

Raw materials	Chemical composition												
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O	K ₂ O	MgO	P ₂ O ₃	SrO	TiO ₂	MnO	SO ₃	LOI
FA	29.59	13.40	19.23	34.57	-	2.47	-	-	0.20	0.55	-	-	-
BA	32.43	14.23	18.70	28.50	-	1.90	3.51	-	-	0.57	0.17	-	-
FGDG	2.09	0.49	0.71	51.69	-	-	0.11	0.35	0.07	-	-	44.51	-
CC	58.57	33.11	1.61	0.03	0.03	1.75	0.07	0.04	-	0.09	0.05	-	-
CH	0.67	0.79	0.29	73.25	0.15	0.02	1.10	-	-	0.02	0.01	-	23.70
AH	0.07	64.99	0.03	0.02	0.46	0.01	-	-	-	-	-	-	34.39

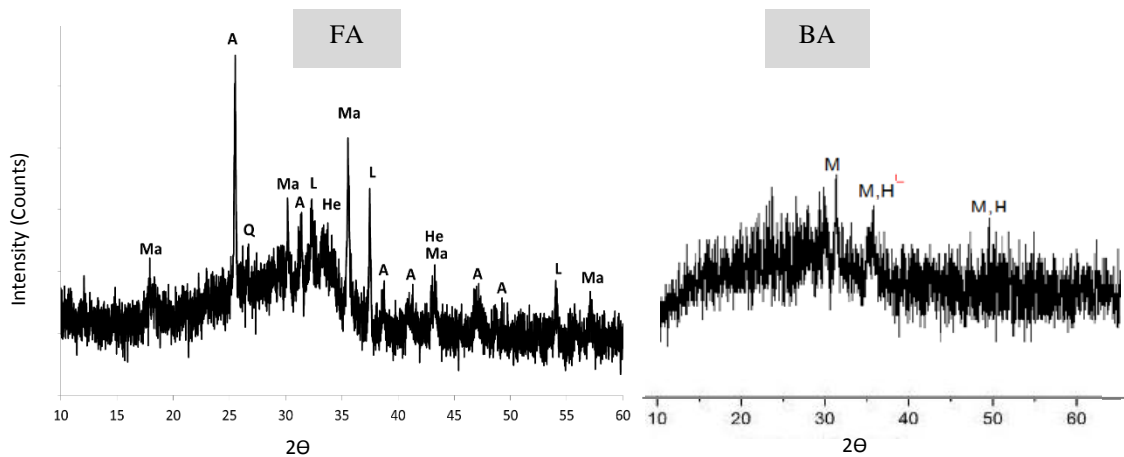


Figure 1. XRD patterns of starting materials.

A: Anhydrite (C^Ŝ), Ma: Magnesioferrite (MgFe₂O₃), He: Hematite (Fe₂O₃)
 L: Calcium oxide (CaO), Q: Quartz (SiO₂), M: muscovite (KAl₂(AlSi₃O₁₀)(OH)₂)

All targeted proportion to obtain $C_4A_3\hat{S}$ larger than 45 wt.% is given in Table II. All starting materials were stoichiometrically prepared and weighed according to the required cement phases as staged in Table II.

TABLE II. TARGETED PHASES FROM MODIFIED BOGUE'S EQUATION

Phase	Phase composition (wt.%)					
	CSA 1	CSA 2	CSA 3	CSA 4	CSA 5	CSA 6
C_4AF	12.75	12.67	13.03	11.51	13.09	13.04
$C_4A_3\hat{S}$	67.37	67.97	54.08	48.98	54.54	65.89
C_2S	19.75	19.05	32.89	39.50	32.37	18.91
CS	0.13	0.32	-	-	-	2.17
C	-	-	-	-	-	-

C. Synthesis Procedure

Starting materials as stoichiometric calculations were mixed with de-ionized water with water to solid ratio was 7.0. The mixed was stirred by magnetic stirrer at 250 rpm for 1 h to obtain homogenous slurry and pre-dissolving of

starting materials. The synthesis via hydrothermal-calcination method was separated into two stages [13].

First stage was hydrothermal reaction in an autoclave under pressure 1.3 bars and at temperature of 124 °C to allow dissolution and then crystallization of intermediate phase. The intermediate phases after hydrothermal treatment were dried at 60 °C for 24 h. Second stage of synthesis was calcination in an electrical furnace at 1050 °C with heating rate of 5 °C/min and soaking for 1 h and then rapid cooling by cool air.

D. Test Condition

The hydrothermal and calcination products were investigated in term of mineralogical composition by XRD (Rigaku Miniflex II). The samples were scanned between 5 and 60° (2 θ). The morphology of calcination products was observed by scanning electron microscopy and energy dispersive spectroscopy (SEM&EDS; JEOL JSM-5910 LV).

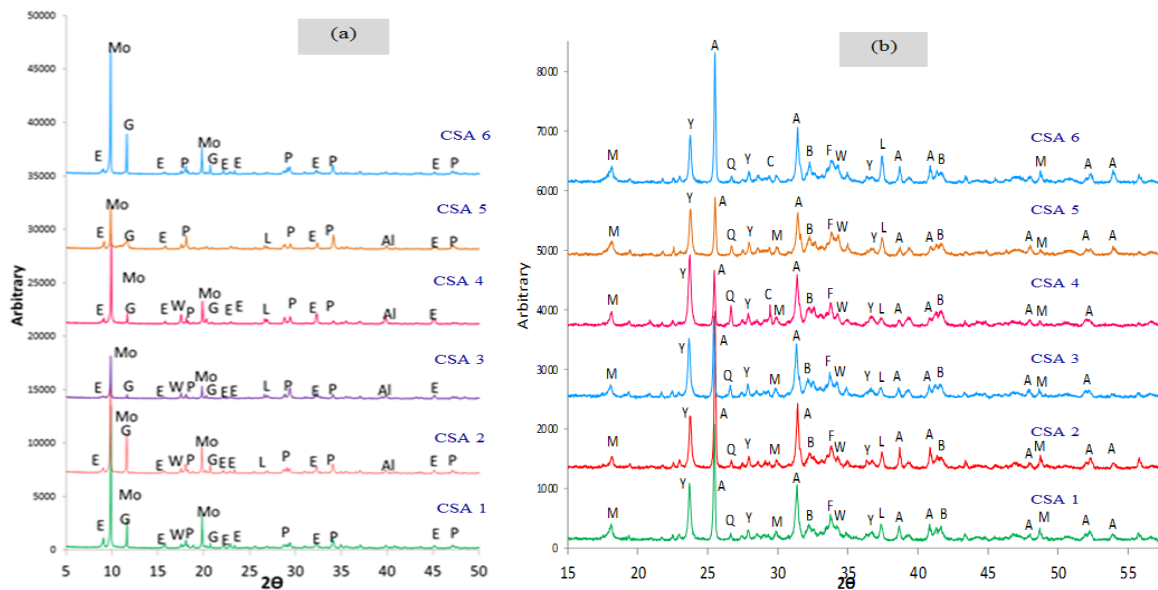


Figure 2. XRD patterns (a) hydrothermal products and (b) calcination product at 1050 °C

Mo: Monosulfate ($C_4A\hat{S}H_{12}$), E: Ettringite ($C_6A_3\hat{S}_2H_{32}$), G: Gypsum ($CaSO_4 \cdot 2H_2O$), W: Wollastonite ($CaSiO_3$)
 Al: Aluminium oxide (Al_2O_3), P: Portlandite ($Ca(OH)_2$), Y: Ye'elimite ($C_4A_3\hat{S}$), A: Anhydrite (CS)
 B: Belite ($\beta-C_2S$), M: Mayenite ($C_{12}A_7$), L: Calcium oxide (CaO), Q: Quartz (SiO_2)

Binding property was tested by preparing cement paste from the synthesized products with two water ratio contents (water to solid ratio of 0.6 and 0.8). The ground cement was mixed with 20 wt% of FGDC before mixing with water. The paste was cast into 25 mm³ acrylic cube molds. Specimens were kept at room temperature for 1 day and then demolded and cured in moist chamber (at 20 °C \pm 5 and 95% relative humidity) until the strength test. The compressive strength tested was investigated at the ages of 1, 3 and 7 days. Each test was done with three specimens. Stopping hydration of samples was done by immersing the samples in ethanol solution for 2 days and followed by drying at 60 °C for 24 h. Phase development of hydration products was analyzed using SEM&EDS (gold coated samples).

III. RESULTS AND DISCUSSION

A. XRD Analysis of Synthesized Product

The synthesis was separated into two stages. First stage was hydrothermal treatment under pressure of 1.3 bar at temperature of 124 °C. The results of mineralogical compositions are shown in Fig. 2 (a). Hydrothermal products were monosulfate (2 θ = 9.93 and 19.936), gypsum (2 θ = 11.71 and 20.83), portlandite (2 θ = 34.08, 18.08 and 47.12), calcium oxide (2 θ = 26.75 and 29.75) and aluminium hydroxide (2 θ = 38.95). When active phases such SiO_2 and Al_2O_3 containing in FA, BA and CC were dissolved, Al_2O_3 could react with dissolved species CaO and SO_4 from CH and FGDC to form monosulfate

($C_4A\hat{S}H_{12}$) phase. Ettringite ($C_6A\hat{S}_3H_{32}$) was also found as a minority. Gypsum was left behind due to insufficient aluminum active phase to form new compound. It worth noting here that monosulfate was preferred form of hydrothermal product instead of ettringite, although there was a surplus of sulfate phase from gypsum. From XRD result of hydrothermal product, the intensities of monosulfate phase for CSA1, CSA2 and CSA6 was higher than the other that related to the expected calcium sulfoalumi-

nate phase as shown in Table II and to the high quantity of used AH in raw mixes. In addition, these 3 formulas had high level of unreacted gypsum due to a use of high FGDG content. For CSA4 sample, CC was used to replace AH partly as a source of Al_2O_3 . The result showed that monosulfate was quite high with lower content of unreacted gypsum and some remaining AH. For CSA3 and CSA5 samples, monosulfate content was smaller than the others due to the similar reason as mentioned above.

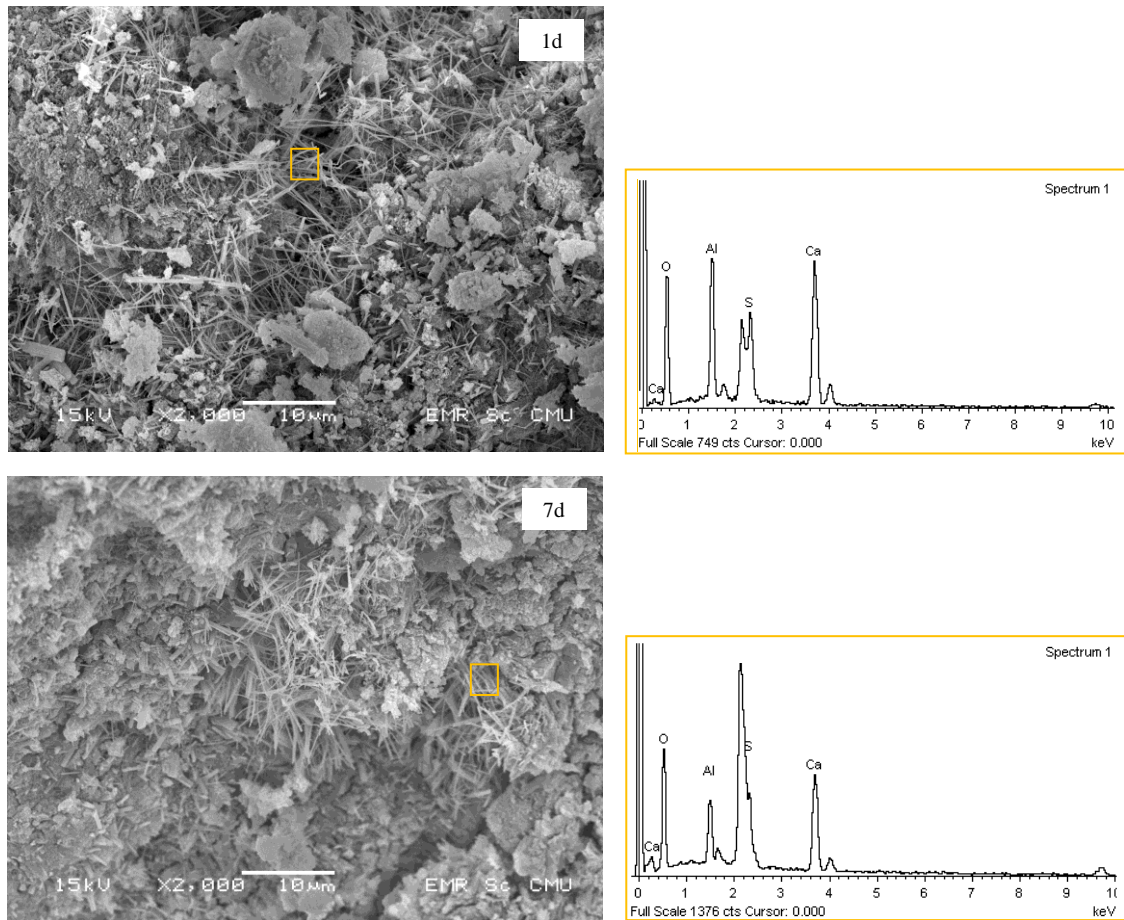


Figure 3. Microstructures of hydration products of $C\hat{S}AB$ cement with water to solid ratio of 0.6 at 1 day and 7 days

Second stage of the synthesis was calcination process at temperature of $1050\text{ }^\circ\text{C}$. The XRD results are given in Fig. 2 (b). This stage was focused on the development of ye'elimite ($C_4A_3\hat{S}$) phase and belite (C_2S), which were desirable main phases of $C\hat{S}AB$ cement. Ye'elimite ($C_4A_3\hat{S}$) was formulated from the conversion of hydration product such monosulfate or ettringite after calcination [7][13] [14]. Based on the stoichiometry of ye'elimite ($C_4A_3\hat{S}$) monosulfate ($C_4A\hat{S}H_{12}$) tended to convert to ye'elimite due to the matter of fact that there was additional Al_2O_3 supplied to the system. With insufficient aluminum phase, monosulfate phase could decompose into hydrogarnet and anhydrite [15]. CSA4 sample seemed to have the highest intensity of ye'elimite that might relate to the remaining aluminum phase as shown in its hydrothermal product. Surprisingly, the expected conversion from monosulfate into ye'elimite phase of CSA4 sample was the lowest due to the complete conver-

sion from monosulfate into ye'elimite. In addition to ye'elimite, belite was also found as a minority in this sample. The other samples showed higher intensity of anhydrite than ye'elimite because of the dominance of decomposition as mentioned above.

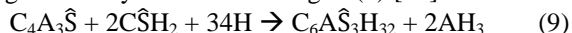
B. Compressive Strength Test and SEM

CSA4 sample was selected for strength test and microstructure investigation of its hydration products. The results of strength test at 1, 3 and 7 days are given in Table III.

TABLE III. COMPRESSIVE STRENGTH OF CSA4 SAMPLE

Condition		Compressive strength (MPa)		
Water/solid Ratio	% FGDG	Day 1	Day 3	Day 7
0.8	20%	9.9	10.3	11.5
0.6	20%	18.0	19.0	22.9

The strength test results indicated that the synthesized C \hat{S} AB cement could provide binding property showing the compressive strength as 18, 19 and 22.9 MPa at 1, 3 and 7 days, respectively when water to solid ratio was 0.6. The strength development was due to the formation of ettringite after hydration according to (9) [16].



With an increase in water to solid ratio to 0.8, compressive strength was drastically reduced. This was due to the excess water creating less dense structures. SEM photomicrographs of hydration product are given in Fig. 3, showing the microstructures comparing between 1 and 7 days. At 1 day of hydration, needle-like particles belonging to ettringite phase were found in overall sample according to (9). Unreacted C \hat{S} AB cement was also clearly observed as agglomerated particles. EDS analysis confirmed the presence of Ca, Al and S in needle-like particles which was ettringite phase.

IV. CONCLUSION

C \hat{S} AB cement could be synthesized from industrial wastes such fly ash, bottom ash and FGD-gypsum together with calcined clay, aluminum hydroxide and hydrated lime using hydrothermal-calcination method. The synthesized cement phases consisted of ye'elimite and anhydrite as majority. Belite was also found in C \hat{S} AB cement. Important intermediate phases after hydrothermal treatment to form ye'elimite were monosulfate and aluminum compound. Effective starting material to supply promising monosulfate and aluminum compounds was calcined clay rather than aluminum hydroxide.

The synthesized C \hat{S} AB cement could undergo hydration after mixing with water and FGD-gypsum providing compressive strength of 18, 19 and 22.9 MPa at the ages of 1, 3 and 7 days, respectively. Hydration product was needle ettringite phase.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

AUTHOR CONTRIBUTIONS

M. Thala conducted all experiments, data analysis and paper plot. K. Pimraksa performed data interpretation and writing improvement.

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