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Synthesis of belite cement from lignite fly ash

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Abstract

Synthesis of belite cement from lignite fly ash is studied as it can be produced using low temperature between 750 and 1200 °C leading to energy saving and low carbon dioxide emission. Two synthesis methods viz., clinkerization and hydrothermal processes assisted by calcinations are studied. Lignite fly ash is used as a main starting material. For the clinkerization process, the firing temperatures, types of additives and calcium oxide/silicon dioxide ratios (Ca/Si) are studied. In this process, the reaction between fly ash and calcium carbonate produces gehlenite ($2CaO{\cdot}Al_2O_3{\cdot}SiO_2$) which is undesirable due to its poor hydraulic property. A slightly higher belite ($2CaO{\cdot}SiO_2$) phase is obtained using sulfate ion as a dopant and using high Ca/Si ratio. The strength of gehlenite bearing belite cement is, however, rather poor. For the hydrothermal–calcination process, the alkaline concentrations and calcining temperatures are studied. The final products are belite phase and mayenite ($12CaO{\cdot}7Al_2O_3$) which are desirable as they possess hydraulic properties. The reasonable 28-day compressive strength of the belite cement mortar of 9.5 MPa is obtained. The hydrothermal process assisted by calcination is, therefore, suitable for use in the synthesis of belite cement from lignite fly ash.

Keywords: A. Calcination; C. Strength; Lignite fly ash; Solid-state reaction; Dissolution-precipitation

1. Introduction

The Portland cement (PC) manufacturing industry has been facing the pressure to reduce energy consumption and CO_2 emissions [1]. Some estimates put the CO_2 emissions from cement industry as high as 5% of global emissions [2]. Cement with high proportion of belite (C_2S) is receiving more attention as it can be manufactured using lower LSF (lime saturation factor), lower carbonate content and lower burning temperature resulting in less CO_2 emission in comparison to PC. The belite cement phase of dicalcium silicate does not contribute to the early strength owing to its slow hydraulic activity [3]. However, the long-term strength can reach the same level or even higher than that of PC. The early strength is improved by adding calcium sulfoaluminate ($C_4A_3S^*$) to form ettringite ($C_6AS_3{}^*H_{32}$) or inorganic salt accelerators such as $CaCl_2$, $Ca(NO_3)_2$ and K_2CO_3 [4].

Belite phase is generally produced by clinkerization and hydrothermal processes. The clinkerization is controlled by solid-state reaction at high temperature over 800 °C [5]. Belite is formed when $CaCO_3$ dissociates to free CaO around 750–850 °C and afterwards reacts with free SiO_2. The reactivity and particle size of starting materials and firing temperature are very crucial for the synthesis. In general the system of CaO–SiO_2 easily provides belite phases. Belite has five allotropic forms: α, α'_H, α'_L, β and γ [6]. The β-form is metastable under 500 °C and has hydraulic property while γ-form is hydraulically inactive. The others are stabilized at room temperature with the addition of foreign ions in the crystal structure. The reactive belite phase can be obtained when a faster cooling and some cationic and anionic dopants such barium, boron and sulfate ions are used in the synthesis. For example, $BaCl_2$ is used to maintain belite in a reactive form of β-C_2S at room temperature. In addition to stabilizing reactive belite phase, sulfate compounds are also used to attack AlO_4^{5-} group from aluminosilicate phases [7,8].

Hydrothermal process is controlled by dissolution-precipitation. Hydrothermal processing is widely used for C–S–H and calcium aluminate hydrate (C–A–H) preparations. Fly ash contains glassy phase and high silica content with pozzolanic property. It can dissolve in lime solution and precipitate to form calcium silicate hydrate (C–S–H). The obtained products

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Table 1
Chemical compositions of fly ash, FGD-gypsum and rice husk ash (RHA).

Raw materials	Chemical composition (wt%)										
	SiO_2	CaO	Al_2O_3	Fe_2O_3	Na_2O	K_2O	MgO	MnO	TiO_2	P_2O_5	SO_3
FA	38.45	17.21	21.32	14.38	0.93	2.77	2.49	0.15	0.44	0.18	1.69
FGD-gypsum	1.69	46.77	0.63	0.67	0.06	0.05	0.52	0.02	0.03	0.03	49.54
RHA	91.79	1.37	0.64	0.64	0.18	3.06	0.65	0.37	0.06	1.29	0.16

contain very fine particles which are used as reactive starting powders. Belite phase is formed with a dehydroxylation of C–S–H phase using heat treatment process. The hydrothermal–calcination process was first introduced by Jiang and Roy [9]. The latent heat which is in charge of hydraulic property of fly ash is influenced by the chemical and mineralogical compositions, the surface area and the type of activation. The reactivity of fly ash is enhanced with the alkaline activation. With a high concentration of OH^- in the mix, the siliceous fly ash, is activated and partly dissolved resulting in silanol group ($\equiv$Si–OH). It is neutralized in the alkaline medium and precipitated as various types of hydration products depending on types of major and minor elements contained in fly ash. The heat treatment process is performed to remove chemically bound water from the hydration products and to transform the anhydrous products into the required belite bearing cement.

Synthesis of belite cement from fly ash has been carried out by many researchers [10–13]. The authors find out that a low Ca fly ash (CaO $<5\%$) and a high Ca fly ash (CaO $>30\%$) are mostly used as starting materials when clinkerization and hydrothermal processes are used as pathways of the belite synthesis, respectively. Here, lignite fly ash from Mae Moh power plant in the north of Thailand is composed of CaO of 17 wt%. This research, therefore, aims to synthesise belite cement mainly from the lignite fly ash to compare the methods of the synthesis using the clinkerization and hydrothermal–calcination process. The knowledge would undoubtedly lay some important ground work for the improvement of belite cement synthesis from lignite fly ash.

2. Experimental procedure

2.1. Raw material

Lignite fly ash as per ASTM Class F from Mae Moh power plant in the north of Thailand is used as a main starting material. The physical properties of fly ash (FA) includes particle size ($d_{4,3}$) of 60 μm, specific surface area by BET of 2.05 m^2/g and pH of 12.3. Mineralogical compounds of FA consist of quartz, hematite, mullite, unburned carbon, calcium aluminium oxide ($Ca_3Al_2O_6$), anhydrite ($CaSO_4$) and some glassy phases. The glassy phases are approximately 52 wt% detected by dissolving fly ash powders in 1% HF [14]. Laboratory grade calcium carbonate ($CaCO_3$) and rice husk ash (RHA) are also used as the other starting materials. Laboratory grade $BaCl_2{\cdot}2H_2O$ and $FeSO_4$, and flue-gas-desulfurization gypsum (FGD-gypsum, $CaSO_4{\cdot}2H_2O$) from Mae Moh power plant are used as additives. Rice husk ash is used to prepare belite phase in order to control the clinkerization condition in the experiments as RHA contains mostly free silica in amorphous form and can readily react with free CaO. RHA is obtained from burning rice husk at 700 °C with a heating rate of 5 °C/min and soaking time of 60 min. The physical properties of RHA includes particle size ($d_{4,3}$) of 60 μm, specific surface area by BET of 49.1 m^2/kg and pH of 11.9. XRD indicates that the mineralogical compositions of RHA compose largely of an amorphous phase of silica with a small amount of crystobalite. The chemical compositions of FA and FGD-gypsum are shown in Table 1.

2.2. Preparation of belite cement

2.2.1. Clinkerization

FA and $CaCO_3$ mixes with Ca/Si stoichiometric ratios of 2.0, 2.5 and 3.0 were thoroughly mixed and ground until percentages retained on 40 μm sieve were 50%. RHA and $CaCO_3$ mixes with Ca/Si stoichiometric ratios of 2.0 and 3.0 were also prepared. Chemical compositions of starting mixtures were given in Tables 2 and 3. The additives viz., $BaCl_2{\cdot}2H_2O$ at 3 and 6% and $CaSO_4{\cdot}2H_2O$ at 3 and 20% by weight of dry solid were incorporated into the mixes. The raw mixes were fired in an electric furnace at the temperatures of 950, 1000, 1050, 1100 and 1180 °C. The firing temperatures were established from Differential Thermal Analysis (DTA) and Thermo Gravimetric Analysis (TGA) as shown in Fig. 1. The heating rates at 7 °C/min from room temperature to 800 °C and soaked for 30 min, and at 3 °C/min from 800 °C to the required temperatures and soaked for 60 min were employed.

Table 2
Chemical compositions (wt% oxide) of starting mixtures without additives.

Systems	Raw materials (g)	$CaCO_3$ (g)	CaO (g)	SiO_2 (g)	CaO (%)	SiO_2 (%)
FA (Ca/Si = 2)	100	76.90	76.90	38.45	66.67	33.34
FA (Ca/Si = 2.5)	100	96.13	96.13	38.45	71.43	28.57
FA (Ca/Si = 3)	100	115.35	115.35	38.45	75.12	25.03
RHA (Ca/Si = 2)	100	183.58	183.58	91.79	66.67	33.34
RHA (Ca/Si = 3)	100	275.37	275.37	91.79	75.04	25.02

Table 3
Chemical compositions (wt% oxide) of starting mixtures with additives.

FA systems (Ca/Si = 2)	FA (g)	$CaCO_3$ (g)	$BaCl_2$ (g)	$CaSO_4$ (g)	$FeSO_4$ (g)	CaO (%)	SiO_2 (%)	$BaCl_2$ (%)	SO_4 (%)
Added 3% $BaCl_2$	100	76.90	3.65	–	–	64.62	32.31	3.07	–
Added 6% $BaCl_2$	100	76.90	7.40	–	–	62.65	32.31	6.03	–
Added 3% $CaSO_4{\cdot}2H_2O$	100	76.90	–	7.37	–	64.62	32.31	–	3.07
Added 3% $CaSO_4{\cdot}2H_2O$ + 10% $FeSO_4$	100	76.90	–	7.37	9.88	58.00	29.00	–	13.00
Added 20% $CaSO_4{\cdot}2H_2O$	100	76.90	–	57.83	–	53.4	26.70	–	19.90

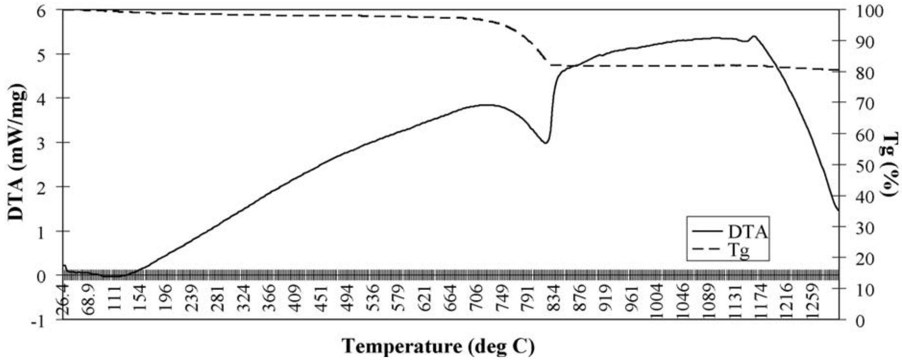


Fig. 1. DTA and TGA-curves of the mixture of FA and $CaCO_3$ at Ca/Si ratio of 2.

Air cooling was used to cool the clinkers. The clinker was then ground to a required fineness.

2.2.2. Hydrothermal–calcination process

To produce non-alkaline activated belite, mixture of FA and hydrated lime ($Ca(OH)_2$) at Ca/Si stoichiometric ratio of 2.0 was prepared. Raw mix was ground to obtain 50% retained on 40 μm sieve. For alkaline activated condition, FA, NaOH and water were totally mixed and stirred using magnetic stirrer for 24 h. Water to solid ratio of 5, 1, and 3 M NaOH were used. The pH values of the non-activated and activated systems were measured before autoclaving. The slurry was autoclaved at 130 ± 5 °C and 1 kg/cm^2 pressure for 4 h. The intermediate products were heated at 60 °C for 24 h to remove adsorbed water and analyzed by XRD. The products were calcined at 750, 850 and 950 °C with the heating rates of 8 °C/min to 600 °C and of 4 °C/min onwards and soaked at the maximum temperature for 30 min.

2.2.3. Test on cement

The mineralogy and microstructure of the ground and calcined cements were investigated using XRD, SEM and EDS. The cements were tested for particle size by laser diffraction method, specific gravity by pycnometer, specific surface area by Blaine method and free lime content by titration method.

2.2.4. Properties of cement paste and mortar

Setting time and compressive strength of belite cement were studied. The cement pastes were prepared using water to solid binder ratio (W/B) of 0.25 for clinkerization cement and 0.8 for hydrothermal process cement in order to obtain the same flow behavior. The larger water content used to prepare the cement paste and mortar for hydrothermal process cement were due to its high surface area. The setting times were performed on the cement paste using procedure described in ASTM C191. The mortars with sand to cement ratio of 2.75 were used for the strength test. The W/B ratios of 0.48 and 0.87 were used for clinkerization cement and hydrothermal process cement respectively. The 50-mm cube mortar specimens were prepared and tested in accordance with ASTM C109. The specimens were demoulded at the age of 1 day and cured in moist chamber until the compressive strength test at the age of 28 days. The hydration reaction was studied using the broken pieces from the compressive strength samples. The hydrations of samples were stopped by immersion in acetone solution for 24 h. The samples were then dried at 80 °C and studied for the mineralogy using XRD.

3. Results and discussion

3.1. Firing technique

3.1.1. Belite synthesis

The DTA pattern of FA and $CaCO_3$ mix as shown in Fig. 1 shows an endothermic peak at 820 °C owing to the decomposition of $CaCO_3$. The second peak at 1160 °C is exothermic peak suggesting the formation of new phase. Firing temperature range used to synthesis belite clinker is therefore obtained from the DTA/TG thermograph as shown in Fig. 1.

The synthesis of CaO–SiO_2 system is used as reference to control the condition of synthesis used in the experiments. RHA is source of SiO_2 in the synthesis. Most of products obtained from the reaction of $CaCO_3$ and SiO_2 with Ca/Si ratio of 2 with a firing temperature of 1150 °C are belite and wollastonite as shown in Fig. 2. A small amount of CaO is left behind. With the Ca/Si ratio of 3, only belite phase is attained.

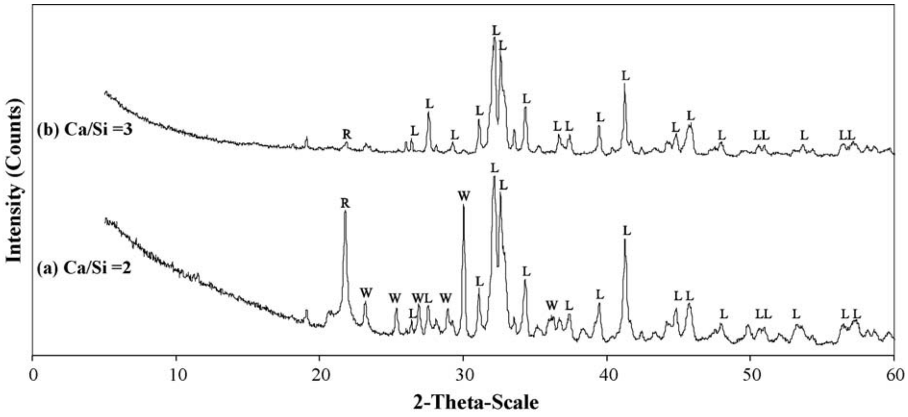
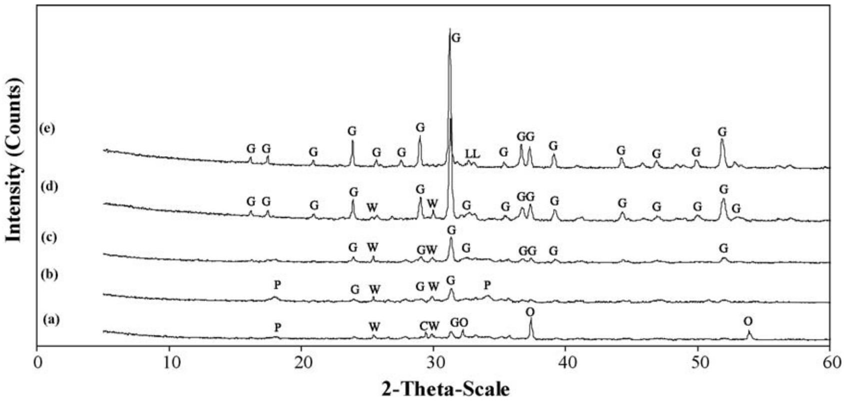


Fig. 2. XRD patterns of products from RHA and $CaCO_3$ mix at Ca/Si = 2 and Ca/Si = 3 at 1150 °C.

The phase development of the FA–$CaCO_3$ mix with Ca/Si ratio of 2 at firing temperatures of 950, 1000, 1050, 1100, 1180 and 1200 °C are shown in Fig. 3. At 950 °C, the $CaCO_3$ starts to decompose and generates CaO. At 1000 °C, gehlenite ($CaAl_2SiO_7$) is the first crystalline phase formed following the collapse of $CaCO_3$. This is in agreement with calcia–aluminosilicate ($CaO–Al_2O_3–SiO_2$) phase diagram [15]. A small amount of belite phase (β-Ca_2SiO_4) called "larnite" is found when the firing temperature is about 1100 °C and disappears when the temperature is 1180 °C. However, gehlenite persistently exists which is undesirable due to its low hydraulic property. Gehlenite is generally produced by the reaction between dehydroxylated clay mineral and CaO particularly when free silica is reduced in the system [16]. The solid-state reaction between CaO and aluminosilicate compound such as kaolinite tends to develop belite phase rather than gehlenite because of a transformation of kaolinite into spinel at firing temperature range of 1000–1150 °C resulting in a release of free silica needed for the belite formation. Lignite fly ash used in the experiments mainly composes of aluminosilicate glassy phase with small amounts of free silica. Moreover, gehlenite has a negative value of Gibb free energy larger than belite phase ($\Delta G = -3.8 \times 10^3$ kJ/mole for gehlenite and $\Delta G = -1.1 \times 10^3$ kJ/mole for belite phase). This results in the formation of gehlenite rather than belite phase.

The influences of additives viz. $BaCl_2{\cdot}2H_2O$, $CaSO_4{\cdot}2H_2O$ and $FeSO_4$ on belite phase development for the mixes with a Ca/Si of 2 are shown in Figs. 4 and 5. The mix with no additives contains mainly gehlenite with a small amount of wollastonite ($CaSiO_3$). Wollastonite is normally formed when CaO reacts with quartz (SiO_2) [10]. With the increase of $BaCl_2{\cdot}2H_2O$ to 3 and 6 wt%, the wollastonite disappears and there is a formation of belite phase. Cations such as Ba^{2+} will act as substitution of Ca^{2+} in belite structure to stabilize the more reactive belite phase at room temperature [17]. The additions of 3 and 20% FGD-gypsum ($CaSO_4{\cdot}2H_2O$) also increases the belite and gehlenite phase. However, there is an excess sulfate compound left behind in clinker. The addition of sulfate ion to the calcia–aluminosilicate system can generate larnite phase due to a reaction preference of sulfate ion to aluminium ion [7]. In the presence of a large amount of sulfate ion that has sufficient free silica coming from fly ash and free CaO coming from FGD-gypsum, thus belite phase is formed. The reaction between sulfate and aluminium ions activated by iron sulfate provides calcium aluminium sulfate compound ($Ca_4Al_6O_{12}SO_4$) as seen in Fig. 5. This compound possesses hydraulic property and is



O=CaO, C=$CaCO_3$, G=$CaAl_2SiO_7$, L=β-Ca_2SiO_4, P=$Ca(OH)_2$, W=$CaSiO_3$

Fig. 3. XRD patterns of products from FA and $CaCO_3$ mix at Ca/Si = 2 with different firing temperatures: (a) at 950 °C, (b) at 1000 °C, (c) at 1050 °C, (d) at 1100 °C and (e) at 1180 °C.

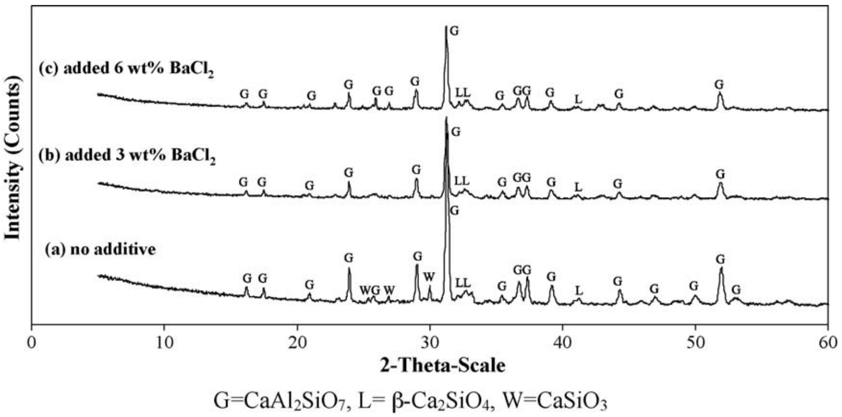


Fig. 4. XRD patterns of products from FA and $CaCO_3$ mix (Ca/Si = 2) with different $BaCl_2$.

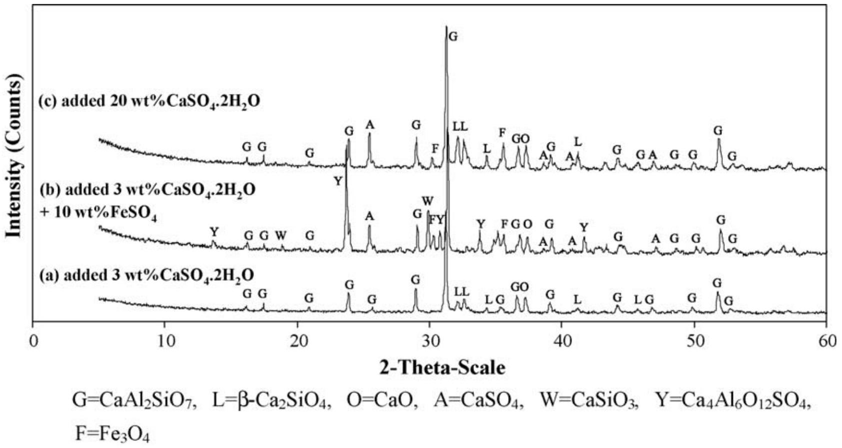


Fig. 5. XRD patterns of products from $CaCO_3$ and fly ash mix (Ca/Si = 2) with different sulfate compound additions.

classified as special cement [18]. Here, it is pointed out that the addition of $FeSO_4$ results in new phases such as calcium aluminium sulfate phase rather than calcium silicate phase. This is due to the fact that dissociation temperature of $FeSO_4$ is lower than that of $CaSO_4$ and hence there are sufficient SO_4^{2-} ions for the sulfatization reaction [19,20]. In addition, a large amount of wollastonite is obtained. The formation of measurable belite phase is obtained with the addition of 20 wt% of $CaSO_4{\cdot}2H_2O$.

The result of the Ca/Si ratios on phase development as shown in Fig. 6 shows that the high Ca/Si ratio of 3 gives belite phase incorporating with gehlenite while the low Ca/Si ratios of 2 and 2.5 without additives give no belite phase. Sufficient amount of reactive free lime is therefore necessary to produce

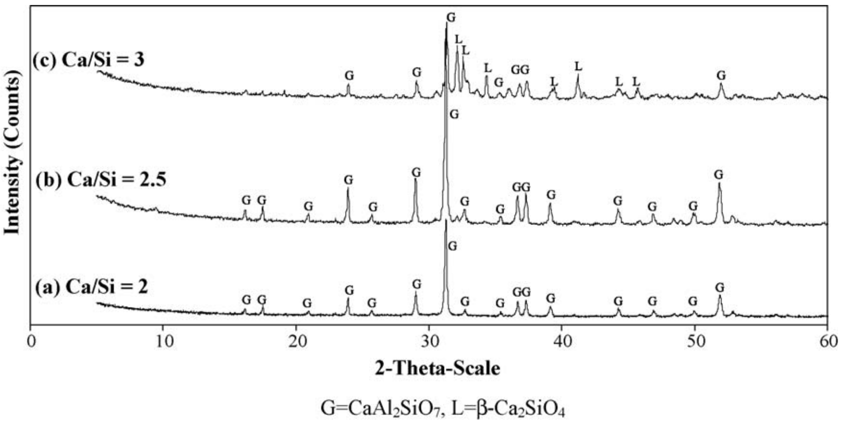


Fig. 6. XRD patterns of the mixtures of $CaCO_3$ and fly ash at different Ca/Si ratios.

belite phase. It is pointed out here that calcium elements contained in fly ash are mostly in the form of glassy phase called ‘‘calcium aluminosilicate glassy phase’’ which is preferably transformed into gehlenite phase. The mineralogical characteristic of a starting material is therefore more critical than the chemical composition used in clinkerization process owing to the limitation of ion diffusion in the solid-state reaction. Clinkerization process is, therefore, not promising as it produces substantial non-hydraulic gehlenite phase.

3.1.2. Characterization and compressive strengths of cements

Products obtained from the mix with a Ca/Si ratio of 2 in the presence of 3 and 20 wt% $CaSO_4$ and fired at 1200 °C are mostly gehlenite with a small amount of belite. The characteristics and properties of the gehlenite–belite cements are shown in Table 4. The final setting times are 390 and 340 min. The 28-day compressive strength of the cement mortars doped with 3 and 20 wt% $CaSO_4$ are very low at approximately 1.5 and 2.5 MPa. This is due to the non-reactive nature of gehlenite compound. The higher compressive strength can be obtained with a Ca/Si ratio of 3 due to a larger amount of belite phase.

3.2. Hydrothermal process

3.2.1. Belite synthesis

The physical and chemical reactions of the hydrothermal reaction products detected by DTA in the range of RT-1100 °C are shown in Fig. 7. The hydrothermal or intermediate products begin to decompose into anhydrous phase at 440–600 °C. The decomposition of $Ca(OH)_2$ also takes place at this temperature range. Heller [21] reports a similar finding obtained from the transformation of C–S–H into β-C_2S at 450 °C. However, there is no exothermic peak indicating no development of new phase at higher temperature. It should be pointed out that there are very few calcite ($CaCO_3$) remaining in the sample indicating the effective consumption of hydrated lime in the reaction. Ishida et al. [22] have shown that β-C_2S is formed when the anhydrous phase is heated further to 900–1000 °C.

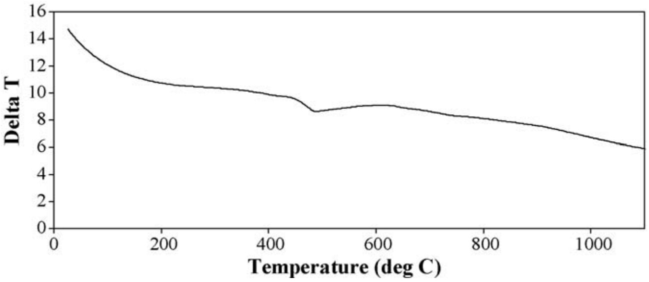
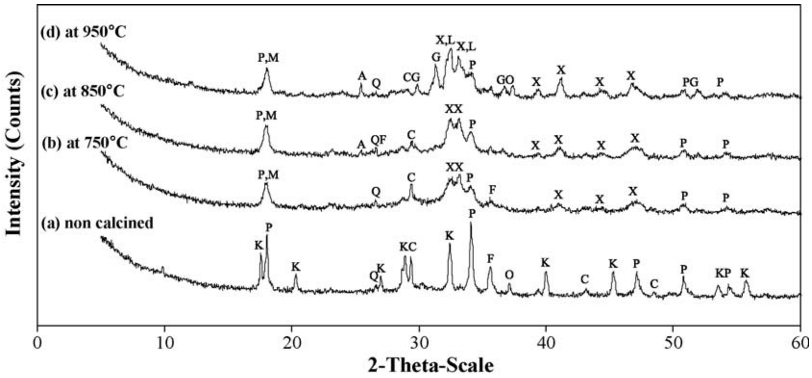


Fig. 7. DTA-curves of hydration product of FA and $Ca(OH)_2$ mix at Ca/Si ratio of 2 after hydrothermal process.

Mineralogical compositions of the hydrothermal products and the final cement products prepared from the mixture of fly ash and hydrated lime in the form of XRD patterns are shown in Fig. 8. New hydration phases called katoite ($Ca_3Al_2SiH_8O_{12}$) a kind of hydrogarnet is formed similar to Goni’s finding [23]. C–S–H gel ($Ca_{1.5}SiO_{3.5}\cdot xH_2O$) is also present but is not possible to identify by XRD due to the calcite reflection overlapping. The reflections of calcite and portlandite show that the fly ash pozzolanic reaction under steam is not completed. However, this method of synthesis is far more advantageous than the

Table 4
Characteristics and properties of cement obtained from clinkerization process.

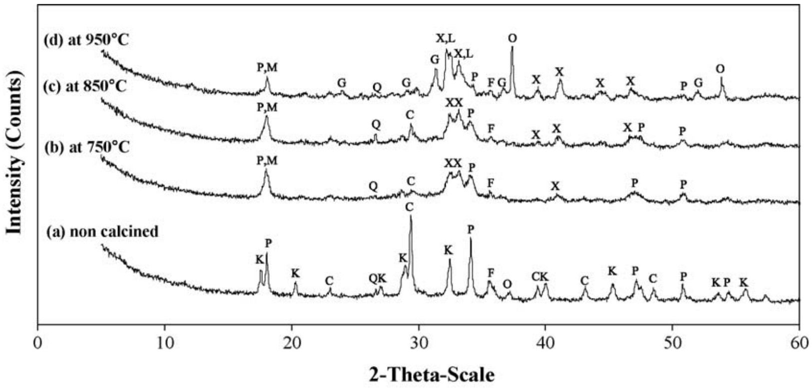
Conditions of synthesis	$d_{4,3}$ (μm)	Specific gravity	Blaine fineness (cm^2/g)	Free lime (%)	Final setting time (min)	Compressive strength at 28 days (MPa)
Ca/Si = 2 (added 3 wt% $CaSO_4$)	88	3.07	4400	0.20	390	1.5
Ca/Si = 2 (added 20 wt% $CaSO_4$)	16	3.07	4700	0.17	340	2.5
Ca/Si = 3	14	3.37	4470	0.36	275	4.0



A=$CaSO_4$, P=$Ca(OH)_2$, O=CaO, C=$CaCO_3$, Q=SiO_2, F=Fe_3O_4, K=$Ca_3Al_2SiH_8O_{12}$,

X=α_L-Ca_2SiO_4, G=$CaAl_2SiO_7$, L=β-Ca_2SiO_4, M=$Ca_{12}Al_{14}O_{33}$

Fig. 8. XRD patterns of products from FA and $Ca(OH)_2$ mix with different calcined temperatures.



P=Ca(OH)$_2$, O=CaO, C=CaCO$_3$, Q=SiO$_2$, F=Fe$_3$O$_4$, K=Ca$_3$Al$_2$SiH$_8$O$_{12}$,

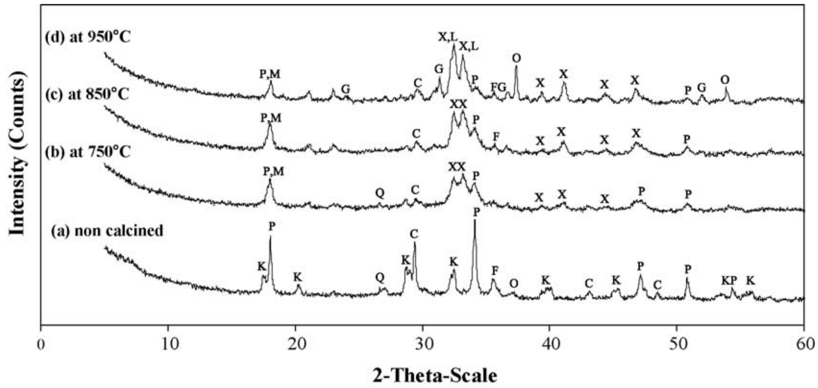
X=α'_L-Ca$_2$SiO$_4$,G=CaAl$_2$SiO$_7$, L=β- Ca$_2$SiO$_4$, M=Ca$_{12}$Al$_{14}$O$_{33}$

Fig. 9. XRD patterns of products from FA and Ca(OH)$_2$ mix activated by 1 M NaOH with different calcined temperatures.

clinkerization process as all calcium compounds contained in fly ash can play a role in the precipitation of cement phase. With heat treatment at 750 °C, katoite changes entirely into alpha ($\alpha'_L - Ca_2SiO_4$), β-belite (β-Ca$_2$SiO$_4$) and mayenite (Ca$_{12}$Al$_{14}$O$_{33}$) which are hydraulic as shown in Fig. 8(b). At low calcining temperature, the obtained belite phase is mostly $\alpha'_L - Ca_2SiO_4$. The β-Ca$_2$SiO$_4$ starts to form at 950 °C. In addition, the amount of portlandite and calcite decrease indicating the transformation of the calcium minerals into belite phase. With increasing calcining temperatures from 750 to 950 °C, the intensities of the belite are increased and gehlenite is formed.

Mineralogical compositions of the hydrothermal products and the final cement products prepared from the mixture of fly ash and hydrated lime activated by 1 and 3 M NaOH in the form of XRD patterns are shown in Figs. 9 and 10. The XRD patterns of both 1 and 3 M NaOH activated mixtures are similar. They are also similar to the patterns of non-activated mixtures for all ranges of calcining temperatures but the intensities and the amount of gehlenite are different. In fact, pH significantly controls solution speciation and dictates the form and mechanism by which the various complexes precipitate [24]. The dissolution of pozzolanic material can be, therefore, accelerated when pH of a system is over 13 [3]. The basic pH of the non-activated 1 and 3 M NaOH activated mixtures are 12.8, 13.3 and 13.5, respectively. The activations using both 1 and 3 M NaOH slightly affect the belite preparations indicating that most of silica contained in fly ash can be hydrothermally dissolved. The alkaline activations can slightly enhance the quantities of the belite cement. The XRD evidences show that the obtained belite cements are the mixture of $\alpha'_L - C_2S$ and β-C$_2$S. A small amount of portlandite still remains after the calcinations for all temperature ranges.

The results of SEM analyses of both non-activated and NaOH activated hydrothermal–calcination cements as shown in Figs. 11 and 12. With a non-activated synthesis, there are spherical and irregular particles at the surfaces of fly ash particles after 850 and 950 °C calcinations as shown in Fig. 11(c) and (e). The hydrothermal products have no such particles as shown in Fig. 11(a). A very common shape of belite cement in the form of β-C$_2$S mixed with some $\alpha'_L - C_2S$ is spherical as seen in Fig. 11(c) and (e). The EDS-results of non-



P=Ca(OH)$_2$, O=CaO, C=CaCO$_3$, Q=SiO$_2$, F=Fe$_3$O$_4$, K=Ca$_3$Al$_2$SiH$_8$O$_{12}$,

X=α'_L-Ca$_2$SiO$_4$,G=CaAl$_2$SiO$_7$, L=β- Ca$_2$SiO$_4$, M=Ca$_{12}$Al$_{14}$O$_{33}$

Fig. 10. XRD patterns of products from FA and Ca(OH)$_2$ mix activated by 3 M NaOH with different calcined temperatures.

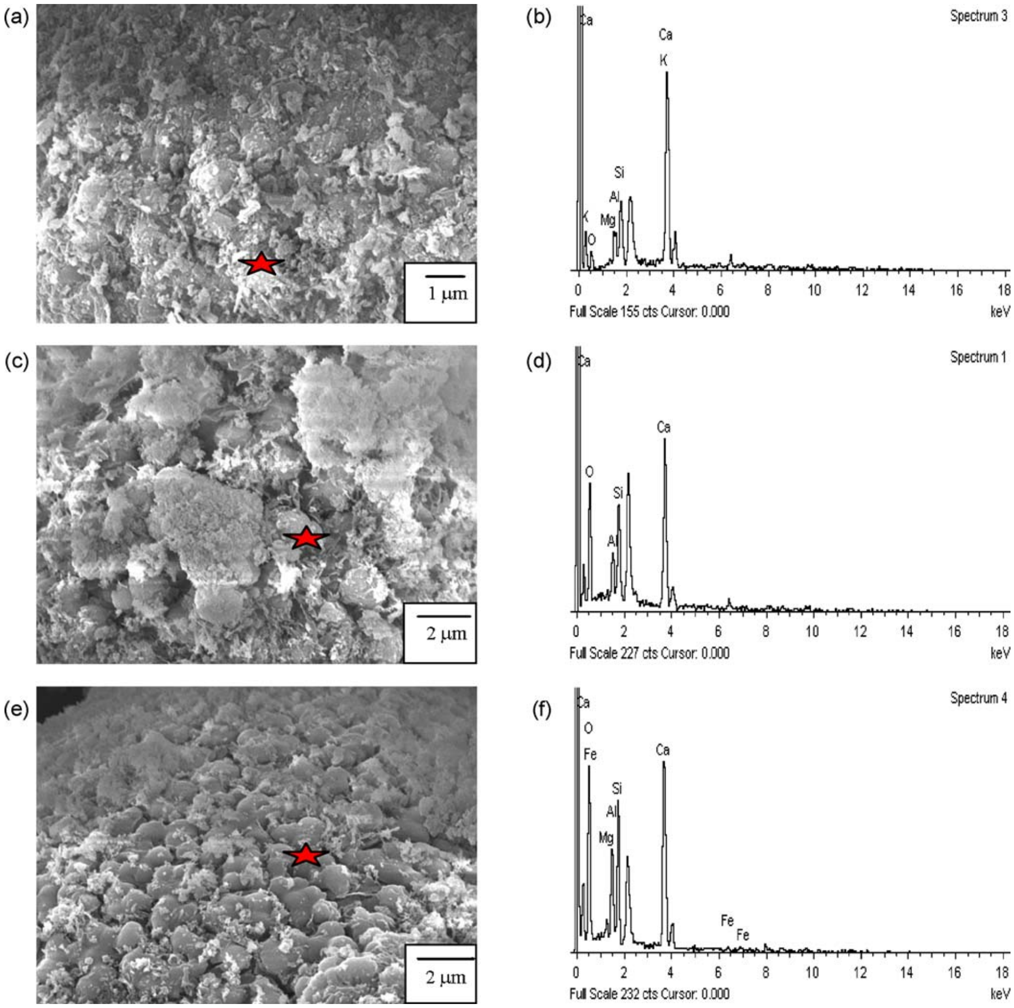


Fig. 11. SEM–EDS of products from FA and $Ca(OH)_2$ mix with different calcinations temperatures: (a and b) non-calcined; (c and d) calcined at 850 °C; (e and f) calcined at 950 °C.

activated hydrothermal–calcination cements are shown in Fig. 11(d) and (f). From the EDS analysis of non-calcined sample shown in Fig. 11(b), averaged compositional ratios of Ca/Si and Ca/Al are 4.9 and 8.8 which do not correspond to the presence of katoite as detected by XRD. This is due to the presence of a large amount of unreacted hydrated lime left behind after the pozzolanic reaction via hydrothermal process. The Ca/Si ratios of samples calcined at 850 and 950 °C are 2.3 and 1.9 which are relevant to the presence of belite phase as confirmed by XRD patterns shown in Fig. 8. For the β-C_2S to $\alpha'_L - C_2S$ transformation, the shape of those grains is typically irregular [25] as seen from the results of SEM photomicrographs of activated samples in Fig. 12(c) and (e). Therefore, these photomicrographs confirm the existences of both $\alpha'_L - C_2S$ and β-C_2S. The EDS-results of NaOH activated samples are illustrated in Fig. 12(b), (d) and (f). The Ca/Si ratio of non-calcined sample has changed from 1.8 into 2.1 and 1.5 when the samples are calcined at 850 and 950 °C, respectively. The reduction in Ca/Si ratio ensures the formation of gehlenite phase at 950 °C.

For the NaOH activation system, the particle size of the belite rich cement increases with an increase of calcination temperature owing to the grain growth as shown in Fig. 12. In the presence of 3 M NaOH, the belite cement contains irregular particles after 850 and 950 °C calcinations. The activation of fly ash with NaOH, thus, results in $\alpha'_L - C_2S$ phase rather than β-C_2S phase.

3.2.2. *Characterization and compressive strengths of cements*

The characteristics and properties of belite cements obtained from hydrothermal process are shown in Table 5. The particle size ($d_{4,3}$)of the cements are between 25 and 36 μm, the specific gravity (S.G.) are in the range of 2.53–3.02, the finenesses are between 8000 and 16,400 cm^2/g, and the free lime content are between 5.5 and 9.4%. The S.G. increases with the calcined temperatures and the concentration of the NaOH. The fineness decreases with an increase in the concentration of the NaOH. The free lime content of the non-activated system is lowest at the average of 5.5–7.0%.

The setting time of nearly all the cements are relatively short except those with NaOH activation and high calcined temperature of 950 °C which have high initial and final setting times. The relatively short setting times are due to the high

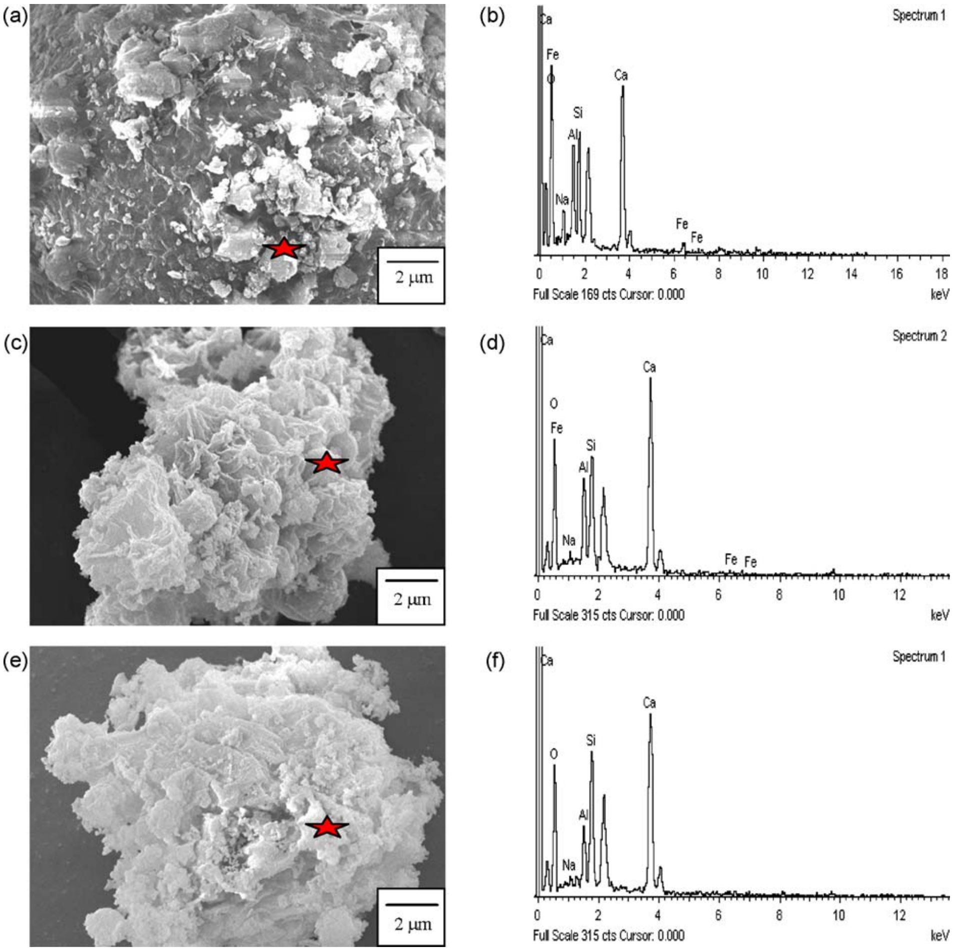


Fig. 12. SEM–EDS of products from FA and $Ca(OH)_2$ mix activated by 3 M NaOH with different calcinations temperatures: (a and b) non-calcined; (c and d) calcined at 850 °C; (e and f) calcined at 950 °C.

fineness and the high lime contents. The typical fineness values of modern ordinary Portland cement and rapid hardening Portland cement are about 3000–3500 and 4000–4500 cm^2/g, respectively [26]. Here, the surface areas of fly ash belite cements are on the average two to three times higher than those of the Portland cements.

After 28 days hydration, non-activated mortars generally have higher compressive strengths than the NaOH activated cements due probably to the high fineness of the non-activated cement. The highest compressive strength of 9.5 MPa is obtained from non-activated system with 750 °C calcined belite cement mortar. This is in good agreement with the XRD analyses, where the intensities of belite phase are high for 750 and 850 °C calcined belite cements. Although, the intensity of 950 °C calcined belite is slightly higher than that of 750 and 850 °C calcined belites, its 28-day compressive strength is lower. This is due to the presence of gehlenite at high calcination temperature. Moreover, the XRD result of hydration products of non-activated mortars as shown in Fig. 13 confirms the presence of the largest amount of calcium silicate hydrate

Table 5
Characteristics and properties of hydrothermal process belite cements.

Conditions of synthesis	$d_{4,3}$ (μm)	Specific gravity	Blaine fineness (cm^2/g)	Free lime (%)	Final setting time (min)	Compressive strength at 28 day (MPa)
Non-activated, at 750 °C	34	2.53	15,400	6.87	125	9.5
Non-activated, at 850 °C	33	2.75	16,400	6.96	170	8.5
Non-activated, at 950 °C	32	2.92	11,400	5.52	50	7.0
1 M NaOH, at 750 °C	30	2.59	9,300	9.36	195	7.0
1 M NaOH, at 850 °C	28	2.77	11,400	8.46	230	8.0
1 M NaOH, at 950 °C	25	2.96	9,100	7.72	645	6.5
3 M NaOH, at 750 °C	36	2.65	800	8.83	60	7.5
3 M NaOH, at 850 °C	33	2.82	9,300	7.38	60	8.0
3 M NaOH, at 950 °C	33	3.02	8,200	6.07	500	5.0

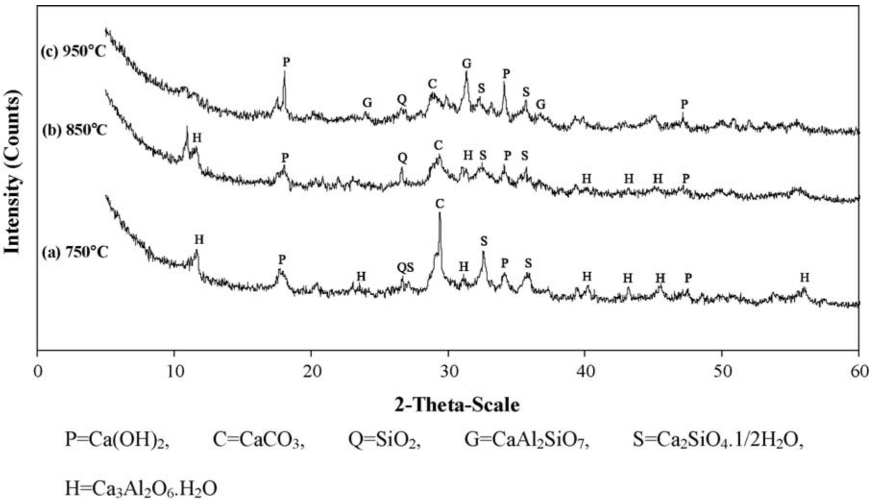


Fig. 13. XRD patterns of hydration products from FA and $Ca(OH)_2$ mix with different calcined temperatures.

($Ca_2SiO_4 \cdot 1/2H_2O$ or C–S–H) in 750 °C calcined cement mortar. The carbonation is also found outstanding. It is commonly known that the transformation of $Ca(OH)_2$ into $CaCO_3$ is in charge of the strength development. In addition to C–S–H formed in 750 and 850 °C cement mortars, $Ca_3Al_2O_6 \cdot H_2O$ (C–A–H) which has a binding property similar to C–S–H is developed. Therefore, the strength values of those 750 and 850 °C cement mortars are not significantly different. For 950 °C calcined cement mortar, gehlenite is still found after the hydration.

The 28-day strength of 9.5 MPa obtained from hydrothermal process cement is relatively high when compared with the values of 2.5 MPa of clinkerization cement. The compressive strength values of hydrothermal process cement reported by Guerrero et al. [27,28] and Goni et al. [23] are 6.7–14 and 11–30 MPa, respectively. However, fly ashes used in those experiments are low calcium fly ashes coming from high grade coal, not similar to lignite fly ash used in this experiment. As a matter of fact there is a difference in mineralogical compositions of those fly ashes and hence the differences of their pozzolanic reaction and hydration. In this experiment, the hydrothermal process without NaOH activation and with 750 °C calcinations is very promising for producing for belite cements from lignite fly ash.

4. Conclusion

The clinkerization process gives gehlenite bearing belite cement with low compressive strength of 1.5–2.5 MPa while hydrothermal process gives mayenite bearing belite cement with relatively high compressive strength of up to 9.5 MPa. The belite cement obtained from hydrothermal process using calcination temperature of 750 °C without NaOH activation gives better strength than the NaOH activated cement. The other characteristics of cements and pastes include low specific gravity, high fineness, and short setting time in comparison to those of Portland cement. The use of hydrothermal process is very attractive for belite synthesis from the lignite fly ash owing to the lower synthesis temperature without non-hydraulic phase formation and hence low CO_2 with no SO_2 emission.

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