

# Synthesis of $\alpha'_L$ -C<sub>2</sub>S cement from fly-ash using the hydrothermal method at low temperature and atmospheric pressure

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## ABSTRACT

The objective of this study was the synthesis of  $\alpha'_L$ -C<sub>2</sub>S (Ca<sub>2</sub>SiO<sub>4</sub>) belite cement, starting from fly-ash of system CaO–SiO<sub>2</sub>–Al<sub>2</sub>O<sub>3</sub>–SO<sub>3</sub>, and using the hydrothermal method in alkaline solution. The lime deficit in these ashes was compensated by the addition of slaked lime from lime bagging workshops. The hydrothermal treatment of the mixture was carried out in demineralized water, NaOH or KOH solution, continually stirred at a temperature below 100 °C and atmospheric pressure. The dehydration and calcination of the mixtures at temperatures between 800 and 1100 °C allowed  $\alpha'_L$ -C<sub>2</sub>S-rich cement to be obtained. The optimization of the synthesis parameters (temperature and time of stirring, pH of solution, temperature and duration of mixture burning) was also studied. The phase formation during various synthesis stages was studied by X-ray diffraction (XRD). Other techniques, such as SEM and EDX, were used to characterize the cement minerals. The results obtained showed that these ashes could form belite cement composed of only one dicalcium silicate phase ( $\alpha'_L$ -C<sub>2</sub>S).

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## 1. Introduction

The use of significant amounts of fuel and carbonates in cement manufacture is one of the great environmental and economic concerns of the present day. The cement industry consumes large amounts of energy (3100–3600 kJ/kg clinker) and produces significant quantities of carbon dioxide, which contribute to the global atmosphere heating by increasing the greenhouse effect [1]. The world cement industry produces around 1.4 billion tons of CO<sub>2</sub> per year, with an average of 0.83 ton of CO<sub>2</sub>/ton of cement, which presents about 8% of the global quantity of CO<sub>2</sub> emitted into the atmosphere [2–4].

One approach for reducing energy consumption in cement production is to decrease the lime saturation factor (LSF) of the raw mixture. The substitution of a high-lime cement by a low-lime one should lead to energy savings and to reduction in the CO<sub>2</sub> emissions resulting from the decarbonation of CaCO<sub>3</sub>. The reduction of the lime saturation factor leads to an increase in the amount of belite (Ca<sub>2</sub>SiO<sub>4</sub> or C<sub>2</sub>S in cement chemistry notation) and a decrease in the alite (Ca<sub>3</sub>SiO<sub>5</sub> or C<sub>3</sub>S in cement chemistry notation) phase content in the clinker [5,6]. It also decreases the energy consump-

tion because the formation of C<sub>2</sub>S<sup>1</sup> (65.1% CaO) occurs at a lower temperature than that for C<sub>3</sub>S (73.7% CaO) [1,5,6].

However, C<sub>2</sub>S is known to be less reactive than C<sub>3</sub>S so, to produce low energy cement with adequate strength development, belite must be either activated or synthesized in a more highly reactive form [5,6]. Dicalcium silicate (C<sub>2</sub>S) exists in several polymorphic forms ( $\alpha$ ,  $\alpha'_L$ ,  $\alpha'_H$ ,  $\beta$ ,  $\gamma$ ), that are stable in different temperature ranges. Contrary to the situation in the C<sub>3</sub>S phase, the arrangement of C<sub>2</sub>S crystalline particles changes from one phase to another, thus leading to different hydraulic properties. In the  $\beta$ -C<sub>2</sub>S form, the polyhedra of Ca<sup>2+</sup> ion coordinations are irregular (the distances vary from 2.30 to 3.56 Å). The longer chemical bond of Ca–O facilitates the hydration. The  $\gamma$ -form is considered as inert and has poor hydraulic properties [7]. This inertia is related to the symmetrical coordination of Ca ions and to the great bonding strength of Ca–O, due to the low coordination of Ca<sup>2+</sup>.  $\alpha'_L$ -C<sub>2</sub>S is assumed to be more reactive than  $\beta$ -C<sub>2</sub>S. However, the actual reactivity depends on the kind and amount of dopant employed [7–10]. The reactive forms of dicalcium silicate ( $\alpha'_L$  and  $\beta$ -C<sub>2</sub>S) in the belite clinker can be stabilized by quick cooling, at least 500 °C/min in the temperature range 1300–700 °C, or by inclusion of an appropriate mineralizer. Foreign oxides, such as MgO, K<sub>2</sub>O, BaO and SO<sub>3</sub>, improve the formation of  $\alpha'_L$ -C<sub>2</sub>S and increase its hydraulic properties [1,7].

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<sup>1</sup> Cement chemistry notation: Ca<sub>2</sub>SiO<sub>4</sub> in terms of its oxides is 2CaO·SiO<sub>2</sub>. The CaO term is shortened to C and the SiO<sub>2</sub> to S. The compound thus becomes C<sub>2</sub>S.

In recent years, researchers have begun to study the use of industrial wastes and by-products as secondary raw materials in the synthesis of reactive belite cement at low burning temperature. They have used the hydrothermal treatment as a synthesis method, since silica has a high solubility under these conditions [11–15]. This kind of cement has also been synthesized by other researchers [16] by replacing the hydrothermal treatment by an ultrasound process, which is equally effective. Some researchers have studied the synthesis of reactive belite by a hydrothermal calcination method using coal combustion fly-ash of low-lime content and fly-ash from municipal solid waste incineration [17–23]. The dehydration of various mixture phases, by controlled heating, leads to the formation of reactive belite ( $\beta$ - $\text{Ca}_2\text{SiO}_4$ ), mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) and calcite ( $\text{CaCO}_3$ ). Other researchers have used the same method but with coal fly-ash of high-lime content [19,21,22,24]. During the hydrothermal treatment under high pressure (200 °C, 1.24 MPa), the pozzolanic reaction of fly-ash is strongly activated, thus leading to the formation of hydraulic precursors. After dehydration of the precursors at 1000 °C, a mixture of  $\beta$ - $\text{C}_2\text{S}$ ,  $\alpha'$ - $\text{C}_2\text{S}$ , mayenite and calcite is formed. The compressive strength of this cement at 28 days reaches similar values to those for Portland cement CEM I-32,5 [19]. This cement also has good resistance to sulphate attack [25].

The contribution of the present work concerns the production of reactive belite cement containing only  $\alpha'$ - $\text{C}_2\text{S}$  as the highly reactive belite phase, starting from a fluidized bed fly-ash of system  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-SO}_3$ , by using the hydrothermal method in an alkaline solution at relatively low temperature (100 °C max) and under atmospheric pressure, unlike other studies found in the literature, for which the temperature and pressures were higher. The synthesis parameters were also optimized, namely: temperature, pressure and time of stirring, nature of liquid solution and its concentration, and temperature and duration of mixture burning.

## 2. Experimentation

### 2.1. Sample testing

The chemical compositions of the raw materials, mixture and synthesized clinkers were determined by X-ray fluorescence (PW 1404X). A scanning electron microscope (Philips XL30) and EDX analysis were used to study the belite phase. The crystallized phases were identified by X-ray diffraction with a Siemens D5000 diffractometer equipped with a variable slit opening and using  $\text{Co K}\alpha$  radiation. It should be noted that silicon was used as the external standard in this study. Chemical analysis using the “glycerin–alcohol” method was performed to determine the free lime content in the burned mixtures.

### 2.2. Material used

The raw materials used to prepare the mixtures were industrial wastes: fluidized bed fly-ash and slaked lime dust recovered from lime bagging workshops. The fly-ash resulted from the calcination at 850 °C of a mixture of different coals. Contrary to classical round-shaped coal fly-ash which are commonly used in cement-based materials, this kind of fluidized bed fly-ash is very difficult to reuse due to its particular morphology and high  $\text{SO}_3$  content. Its specific surface area was 880  $\text{m}^2/\text{kg}$ . The chemical compositions of these materials were determined by X-ray fluorescence (Table 1). The mineralogical composition of the fly-ash is given in the XRD pattern (Fig. 1). This fly-ash was mainly composed of anhydrite, quartz, free lime, hematite, and traces of calcite, portlandite and micas. The presence of glass was also confirmed by a small diffusion hump. The slaked lime dust (industrial waste from lime bagging

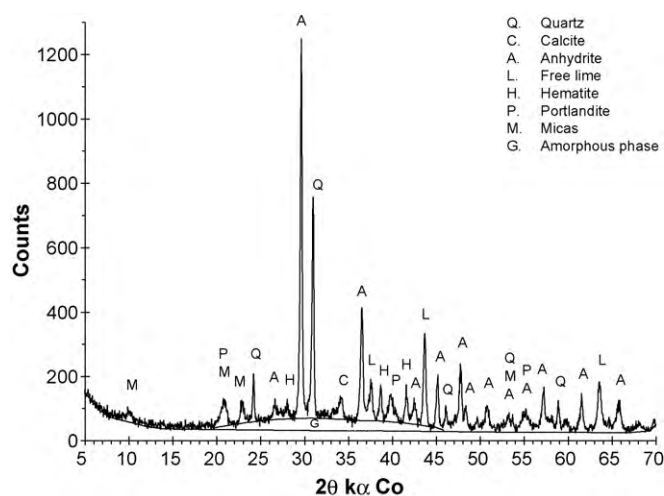


Fig. 1. XRD pattern of fluidized bed coal fly-ash.

workshops) was mainly composed of portlandite but also contained calcite, resulting from the lime carbonation during stocking.

### 2.3. Synthesis procedure

In order to obtain global belite cement, the lime/silica molar ratio must be equal to 2. The lime deficit in the ash was compensated by the addition of slaked lime. The hydrothermal method was used to produce  $\alpha'$ - $\text{C}_2\text{S}$ -rich cement. The synthesis process was divided into two stages: the first stage was the hydrothermal treatment, which produced hydrated precursors. The raw mixture, composed of fly-ash and slaked lime dust with  $\text{CaO/SiO}_2$  molar ratio of 2, was put either in demineralized water, or in a solution containing NaOH or KOH at various concentrations, with a liquid to solid ratio of 5. NaOH and KOH were used to allow the production of precursors favouring the synthesis of  $\alpha'$ - $\text{C}_2\text{S}$ .

The liquid mixture obtained was stirred for a fixed time between 0 and 24 h under atmospheric pressure and activated at 3 different temperatures (20, 50 and 100 °C). After hydrothermal treatment, the suspension was vacuum filtered to eliminate the excess of alkalis, and then dried in a drying oven at 105 °C. The second stage of the synthesis process was the burning of the dry sample in a muffle furnace at a temperature ranging between 600 and 1100 °C, with a heating rate of 5 °C/min, followed by fast air-cooling.

Table 2 is used as the reference for the identification of the various phases in this study. It gives compounds, chemical formulas and ICDD card numbers of the minerals contained in the raw materials, hydrothermal mixtures and synthesized cements.

## 3. Results and discussion

### 3.1. Parametric study of hydrothermal treatment

This section aims to evaluate the effect of different parameters on the composition of mixtures after the first stage (solid obtained from the hydrothermal treatment) and the second stage (cement obtained after burning of the hydrothermal solid) of the synthesis. The parameters studied included the type and concentration of chemical activation, the temperature of activation and the stirring time.

#### 3.1.1. Type of chemical activation

According to the previous works, fly-ash can be activated by mechanical treatment (fine crushing) [26–30], chemical treatment (addition of chemical activator such as NaOH) [31–34], or

**Table 1**  
Chemical compositions of the raw materials used for the synthesis of belite cement.

Material	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	SO <sub>3</sub>	K <sub>2</sub> O	Na <sub>2</sub> O	TiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	LOI
Fly-ash	23.9	11.1	5.6	29.5 <sup>a</sup>	1.1	14.7	1.4	0.1	0.4	0.4	9.6
Lime dust	1.8	0.2	0.4	73.4	0.9	–	0.02	0.03	–	–	23.0

LOI: loss on ignition.

<sup>a</sup> Including free lime (9.2%).

hydrothermal treatment [19,20,22,25]. In our study, chemical and hydrothermal processes were combined to improve the chemical reactivity of the fly-ash. The conditions of hydrothermal treatment were fixed at a maximum temperature of 100 °C and atmospheric pressure, in contrast to other studies found in the literature, for which the temperature and pressures were higher. The continuous mechanical stirring and its duration (5 h) were selected on the basis of preceding work on fly-ash activation [18,23,35–38].

The minerals found in the mixtures, after hydrothermal treatment in H<sub>2</sub>O, NaOH (1 M) and KOH (1 M) but before calcination, are given in Fig. 2. This figure also presents the mixture of fly-ash and lime homogenized in water at 20 °C for 1 h (taken as the reference here).

The only common change for all mixtures was the disappearance of free lime. Compared to the reference mixture (20 °C–1 h), the hydrothermal treatment of 5 h in 100 °C H<sub>2</sub>O led to a partial dissolution of anhydrite and a precipitation of kuzelite, a calcium aluminium hydroxide sulphate (Ca<sub>4</sub>Al<sub>2</sub>(OH)<sub>12</sub>(SO<sub>4</sub>)<sub>6</sub>·6H<sub>2</sub>O). Aluminium came from either the micas or the amorphous phase. Part of the portlandite was carbonated to form calcite. Otherwise, no significant changes were detectable for this treatment, including in the quartz phase of the fly-ash.

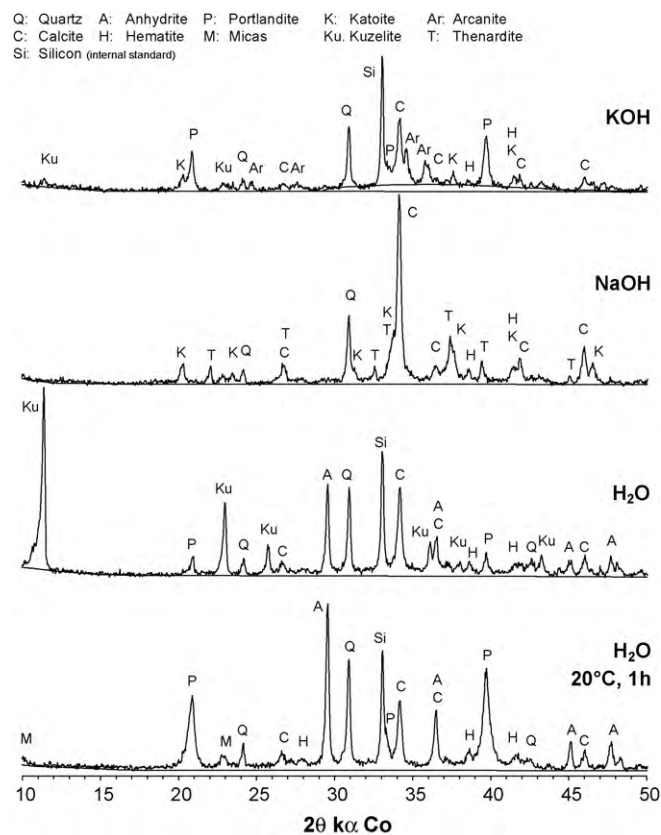
The hydrothermal treatments in a basic environment (100 °C–5 h) induced other significant modifications in the mineralogy of the mixtures, such as the complete dissolution of anhydrite and the partial consumption of quartz. Anhydrite was consumed by NaOH and KOH according to the following reactions: CaSO<sub>4</sub> + 2NaOH → Ca(OH)<sub>2</sub> + Na<sub>2</sub>SO<sub>4</sub> and

CaSO<sub>4</sub> + 2KOH → Ca(OH)<sub>2</sub> + K<sub>2</sub>SO<sub>4</sub>. The treatment in 1 M NaOH led to total disappearance of portlandite (and free lime) and a significant increase in the amount of calcite (Ca(OH)<sub>2</sub> + CO<sub>2</sub> → CaCO<sub>3</sub>). The sulphates made available by the dissolution of anhydrite were found as thenardite (Na<sub>2</sub>SO<sub>4</sub>). The presence of katoite (Ca<sub>3</sub>Al<sub>2</sub>(SiO<sub>4</sub>)(OH)<sub>8</sub>) was also observed. The sources of aluminium and silicon came from the dissolution of the amorphous phase of the fly-ash (and probably from quartz for Si). The 1 M KOH treatment produced small amounts of kuzelite, katoite and arcanite (K<sub>2</sub>SO<sub>4</sub>), and probably also C–S–H, as confirmed by the presence of the hump in the 2.33–3.56 Å (29–45° 2θ Kα Co) region.

The compounds obtained after burning of the reference and hydrothermal mixtures at 1100 °C were identified by their XRD patterns (Fig. 3). C<sub>2</sub>S was present in all four cements, but the polymorphic forms differed depending on the treatment used. Fig. 4 highlights the differences of the principal XRD peaks of both α' and β forms, characterized by a small but significant shift in the range of lattice spacing 2.69–2.78 Å. As shown in this figure, only hydrothermal treatments in NaOH (HT-NaOH) and KOH (HT-KOH) led to the formation of α'-C<sub>2</sub>S. HT-NaOH gave both forms of C<sub>2</sub>S, while α' seemed to be the exclusive form in HT-KOH mixture. Intensities of the characteristic peaks of α'-C<sub>2</sub>S were much stronger in the case of KOH treatment. For this reason, KOH was selected

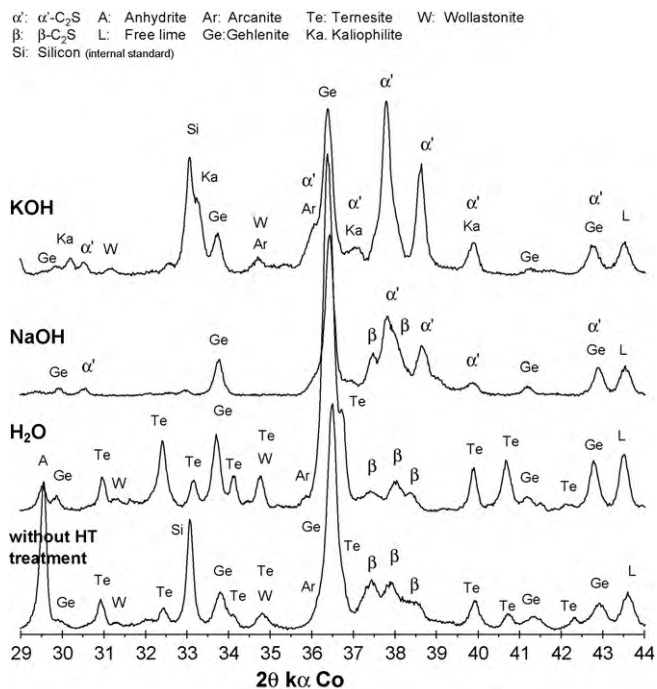
**Table 2**  
Identification of the various phases of crystalline compounds contained in raw materials, hydrothermal mixtures and synthesized cements.

Compound	Formula	ICDD no.	
Q	α-Quartz	SiO <sub>2</sub>	46-1045
C	Calcite	CaCO <sub>3</sub>	05-0586
H	Hematite	Fe <sub>2</sub> O <sub>3</sub>	33-0664
M	Mica (e.g. muscovite)	KAl <sub>2</sub> (Si <sub>3</sub> Al)O <sub>10</sub> (OH) <sub>2</sub>	02-0055
L	Lime	CaO	37-1497
P	Portlandite	Ca(OH) <sub>2</sub>	04-0733
A	Anhydrite	CaSO <sub>4</sub>	37-1496
Cs	Calcium sulphite	CaSO <sub>3</sub>	44-0517
T	Thenardite	Na <sub>2</sub> SO <sub>4</sub>	01-1009
Ar	Arcanite	K <sub>2</sub> SO <sub>4</sub>	24-0703
G	Gypsum	CaSO <sub>4</sub> ·2H <sub>2</sub> O	76-1746
Ge	Gehlenite	Ca <sub>2</sub> Al <sub>2</sub> SiO <sub>7</sub>	35-0755
α'	α'-C <sub>2</sub> S	α'-Ca <sub>2</sub> SiO <sub>4</sub>	89-5917
β	β-C <sub>2</sub> S	β-Ca <sub>2</sub> SiO <sub>4</sub>	36-0642
W	Wollastonite	CaSiO <sub>3</sub>	33-0302
			29-0371
			76-0186
			27-1064
			19-0248
Ma	Mayenite	Ca <sub>12</sub> Al <sub>14</sub> O <sub>33</sub>	09-0413
Y	Yeelimite	Ca <sub>4</sub> Al <sub>6</sub> SO <sub>16</sub>	16-0440
E	Etringite	Ca <sub>6</sub> Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> (OH) <sub>12</sub> ·26H <sub>2</sub> O	41-1451
CSH	C–S–H	Ca <sub>1.5</sub> SiO <sub>3.5</sub> ·xH <sub>2</sub> O	33-0306
K	Katoite	Ca <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> )(OH) <sub>8</sub>	38-0368
Ku	Kuzelite	Ca <sub>4</sub> Al <sub>2</sub> (OH) <sub>12</sub> (SO <sub>4</sub> ) <sub>6</sub> ·6H <sub>2</sub> O	83-1289
Ka	Kaliophilite	KAlSiO <sub>4</sub>	33-0989
Te	Ternesite	Ca <sub>5</sub> (SiO <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	70-1847
Si	Silicon (used as external standard)	Si	27-1402

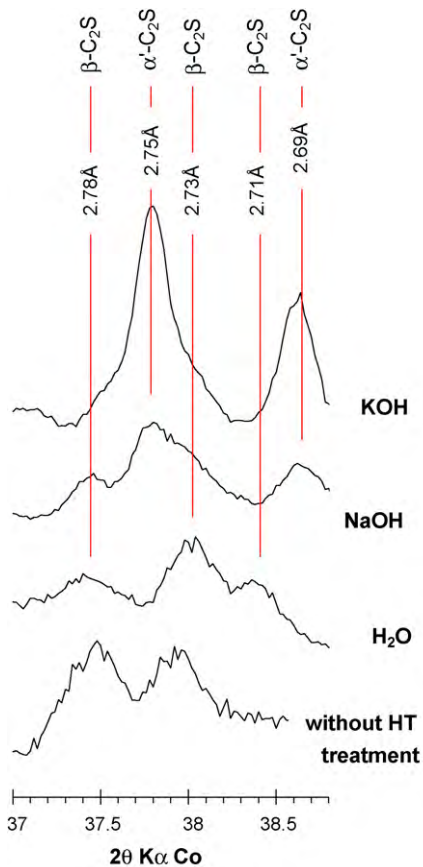


**Fig. 2.** XRD patterns of mixtures after the first stage of synthesis. Hydrothermal treatment at 100 °C and 5 h stirring, in different solvents (H<sub>2</sub>O, 1 M NaOH, 1 M KOH).





**Fig. 3.** XRD patterns of hydrothermal mixtures after the second stage of synthesis. Mixtures burned at 1100 °C to form belite cements (hydrothermal conditions: heating temperature of 100 °C, stirring time of 5 h, solvents: H<sub>2</sub>O, 1 M NaOH, 1 M KOH).



**Fig. 4.** XRD patterns showing the types of C<sub>2</sub>S obtained after the two stages of synthesis. Mixtures burned at 1100 °C after hydrothermal treatments (conditions: heating temperature of 100 °C, stirring time of 5 h, solvents: H<sub>2</sub>O, 1 M NaOH, 1 M KOH).

as the most appropriate solvent for the hydrothermal synthesis of belite cement in the rest of the study. It seemed that the synthesis of  $\alpha'_L$ -C<sub>2</sub>S was favoured by the presence of portlandite, probably because of the lower temperature of decomposition of portlandite compared to anhydrite.

Mixtures without HT treatment and with HT treatment in H<sub>2</sub>O gave only the  $\beta$ -form of C<sub>2</sub>S. The small shift of the main peaks observed for  $\beta$ -C<sub>2</sub>S around 2.73 Å was probably due to the presence of foreign elements in the structure of the compounds.

In addition to C<sub>2</sub>S, the synthesized cements contained other minerals (Fig. 3): free lime and small amounts of wollastonite (CaSiO<sub>3</sub>), showing an incomplete combination of calcium. Moreover, gehlenite (Ca<sub>2</sub>Al<sub>2</sub>SiO<sub>7</sub>) was formed in all cements. This mineral is poorly reactive and can be considered as inert compared to  $\alpha'_L$  or  $\beta$ -C<sub>2</sub>S. To avoid the synthesis of this compound, it would be necessary to use raw materials with no available aluminium, which is quite rare for coal fly-ashes since their amorphous phases always contain this element.

Almost all mixtures contained arcanite (K<sub>2</sub>SO<sub>4</sub>), a mineral known to be a setting accelerator of cement. A significant amount of anhydrite was still present in the reference mixture (without HT treatment). H<sub>2</sub>O HT treatment also left a small quantity of anhydrite.

Some particular minerals were found in the different mixtures: kaliophilite-type mineral (KAlSiO<sub>4</sub>) in KOH HT cement and ternesite (Ca<sub>5</sub>(SiO<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) in cements obtained with and without H<sub>2</sub>O HT treatments. A small quantity of yeelimite (Ca<sub>4</sub>Al<sub>6</sub>SO<sub>16</sub>) was also detected in the reference mixture.

To decrease the concentration of the hydrothermal solution, a test was carried out with a concentration of 0.6 M KOH. This mixture was subjected to a hydrothermal treatment at 100 °C for 5 h, followed by burning at 1100 °C and rapid air-cooling. The comparison of the belite cements obtained using KOH solutions at 0.6 and 1 M showed that liquid solution of 0.6 M KOH was sufficient to obtain cement containing  $\alpha'_L$ -C<sub>2</sub>S without  $\beta$ -C<sub>2</sub>S.

### 3.1.2. Temperature and time of activation

In order to optimize the synthesis parameters and make the belite cement manufacture more economical, the effect of temperature and stirring time on the formation of belite cement minerals, in particular  $\alpha'_L$ -C<sub>2</sub>S belite phase, were studied. The hydrothermal treatments were carried out in a 1 M KOH solution at heating temperatures of 20, 50 and 100 °C for stirring times of 1, 2, 5, 12 and 24 h. The burning temperature after hydrothermal treatments was set to 1100 °C. Tables 3 and 4 give the mineral species found in the mixture after hydrothermal treatments and burning at 1100 °C, respectively.

**3.1.2.1. Treatment at 20 °C.** Table 3 reports the mineralogy of solids obtained after hydrothermal treatment (1 M KOH) carried out at heating temperatures of 20 °C for stirring times of 1, 5 and 24 h. The mineralogical composition of the cements obtained after burning these hydrothermal mixtures at 1100 °C is given in Table 4 and Fig. 5.

The pure fly-ash contained a significant quantity of free lime (CaO) and anhydrite (CaSO<sub>4</sub>) (Fig. 1), which disappeared with the hydrothermal treatment. The continuous stirring led to the formation of arcanite, gypsum and ettringite after treatment of 1, 5 and 24 h, respectively. A small amount of calcium sulphite (CaSO<sub>3</sub>) was also detected in the hydrothermal mixtures. Significant quantities of portlandite and calcite were still present after 24 h of stirring. The intensity of the hump seemed to increase slightly with the time of treatment. This amorphous phase can probably be attributed to C-S-H.

The samples burned at 1100 °C contained  $\beta$ -C<sub>2</sub>S and other neo-phases such as gehlenite, mayenite and yeelimite. Large quantities

**Table 3**  
Mineral species in mixtures after hydrothermal treatment in 1 M KOH solution (20, 50 or 100 °C).

	Hydrothermal treatment	20 °C			50 °C		100 °C	
		1 h	5 h	24 h	5 h	12 h	2 h	5 h
Q	Quartz	✓	✓	✓	✓	✓	✓	✓
C	Calcite	✓	✓	✓	✓	✓	✓	✓
P	Portlandite	✓	✓	✓	✓	✓	✓	✓
H	Hematite	✓	✓	✓	✓	✓	✓	✓
M	Micas	✓	✓	✓	✓	✓	✓	✓
A	Anhydrite	✓ tr	✓ tr	✓ tr	✓ tr	✓ tr	✓ tr	✓ tr
G	Gypsum	✓ tr	✓	✓	✓	✓	✓	✓
Cs	Calcium sulphite		✓ tr	✓ tr				
Ar	Arcanite	✓ tr	✓	✓	✓	✓	✓	✓
K	Katoite				✓	✓	✓	✓
Ku	Kuzelite							✓
CSH	C–S–H				✓	✓	✓	✓
E	Ettringite			✓				✓

tr: trace.

**Table 4**  
Mineral species in mixtures after hydrothermal treatment in 1 M KOH solution (20, 50 or 100 °C) and burning at 1100 °C.

	Hydrothermal treatment	20 °C			50 °C		100 °C	
		1 h	5 h	24 h	5 h	12 h	2 h	5 h
$\alpha'$	$\alpha'_L$ -C <sub>2</sub> S				✓	✓	✓	✓
$\beta$	$\beta$ -C <sub>2</sub> S	✓	✓	✓	✓	✓	✓	✓
L	Lime	✓	✓	✓	✓	✓	✓	✓
Q	Quartz	✓ tr						
W	Wollastonite	✓	✓ tr	✓ tr	✓ tr	✓	✓	✓
Ge	Gehlenite	✓	✓	✓	✓	✓	✓	✓
Ar	Arcanite	✓ tr	✓	✓	✓	✓	✓	✓
Ma	Mayenite (C <sub>12</sub> A <sub>7</sub> )	✓	✓	✓	✓	✓	✓	✓
Y	Yeelimite (C <sub>4</sub> A <sub>3</sub> S)	✓	✓	✓				
Ka	Kaliophilite				✓	✓		✓

tr: trace

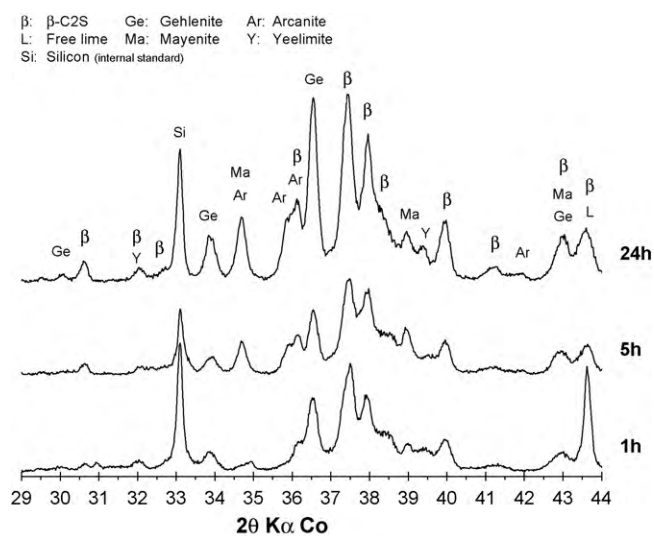
of free lime were present in the mixture stirred for 1 h at 20 °C (Fig. 5). However, no trace of  $\alpha'_L$ -C<sub>2</sub>S was found, even for the hydrothermal mixture stirred for 24 h. Most of the compounds present in the hydrothermal mixtures disappeared after burning at 1100 °C. Only arcanite and small amounts of quartz (for 1 h stirring) were still present. The significant consumption of quartz at relatively low temperature was probably due to the pres-

ence of elements (e.g. alkalis) decreasing the fusion temperature of the mineral. Prolongation of the stirring time without heating decreased the free lime content and improved the formation of  $\beta$ -C<sub>2</sub>S, but did not lead to the formation of  $\alpha'_L$ -C<sub>2</sub>S. Thus, it was necessary to increase the temperature of treatment.

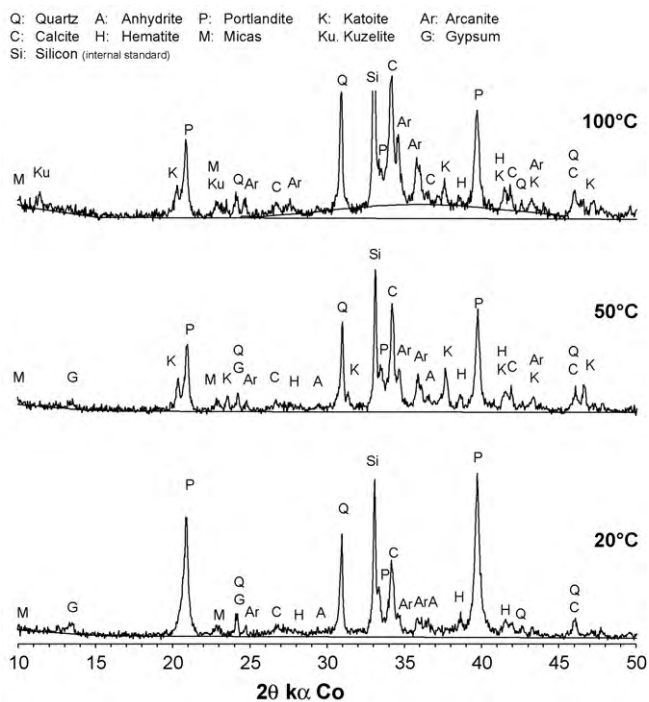
**3.1.2.2. Effect of hydrothermal temperature.** Table 3 and Fig. 6 report the effect of hydrothermal temperature by giving the mineralogy of solids obtained after hydrothermal treatment (1 M KOH) carried out at heating temperatures of 20, 50 and 100 °C for a constant stirring time of 5 h. As the hydrothermal heating temperature increased, gypsum and calcium sulphite gradually disappeared, and the quantity of portlandite decreased. Neo-formed products were detected, mainly kuzelite, katoite and C–S–H (crystallized and amorphous form). These formations intensified with increasing temperature and stirring time.

Fig. 7 shows that burning the hydrothermal mixtures at 1100 °C led to the formation of C<sub>2</sub>S. Only the  $\beta$ -form was present for HT treatment at 20 °C, while a gradual appearance of the  $\alpha'_L$ -form was observed with the increase of HT temperature. For HT heating at 100 °C,  $\beta$ -C<sub>2</sub>S phase was completely transformed into  $\alpha'_L$ -C<sub>2</sub>S in this cement (Fig. 7). This treatment time was sufficient for this temperature but a longer time appeared necessary for the treatment at 50 °C.

**3.1.2.3. Combined effect of hydrothermal temperature and stirring time.** Fig. 8 gives the XRD patterns of burned mixtures at 1100 °C in the zone allowing the identification of the two types of C<sub>2</sub>S detected in this study. As already stated, it can be seen that hydrothermal treatment at 20 °C only led to  $\beta$ -C<sub>2</sub>S. The  $\alpha'_L$ -form was obtained for hydrothermal treatments at 50 and 100 °C. However, short stirring



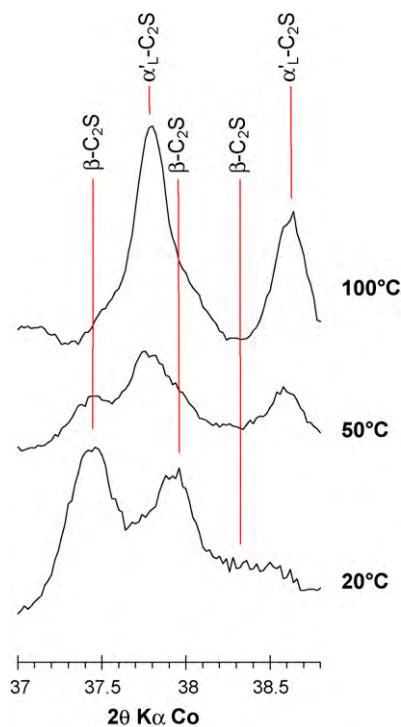
**Fig. 5.** XRD patterns of hydrothermal mixtures after the second stage of synthesis. Mixtures burned at 1100 °C to form belite cements (hydrothermal conditions: heating temperature of 20 °C, stirring time of 1, 5 and 24 h, solvents: 1 M KOH).



**Fig. 6.** XRD patterns of mixtures after the first stage of synthesis. Hydrothermal treatment in 1 M KOH at 20, 50 and 100 °C and 5 h stirring.

times did not allow the formation of  $\alpha'_L\text{-C}_2\text{S}$  phase alone, even at a hydrothermal heating temperature of 100 °C. For 2 h of stirring,  $\beta\text{-C}_2\text{S}$  belite phase was present with  $\alpha'_L\text{-C}_2\text{S}$ .

In mixtures stirred for 12 h at 50 °C and 5 h at 100 °C, the  $\beta\text{-C}_2\text{S}$  phase was completely transformed into  $\alpha'_L\text{-C}_2\text{S}$  with a strong increase in the peak intensities. For these conditions of HT treatment, equivalent cements were obtained. So, in order to improve the formation of  $\alpha'_L\text{-C}_2\text{S}$  in the mixtures at low hydrothermal heating temperatures (e.g. when the temperature is decreased from 100 to 50 °C), an extension of the stirring time at 50 °C is needed. An optimization of the process will be needed in order to highlight

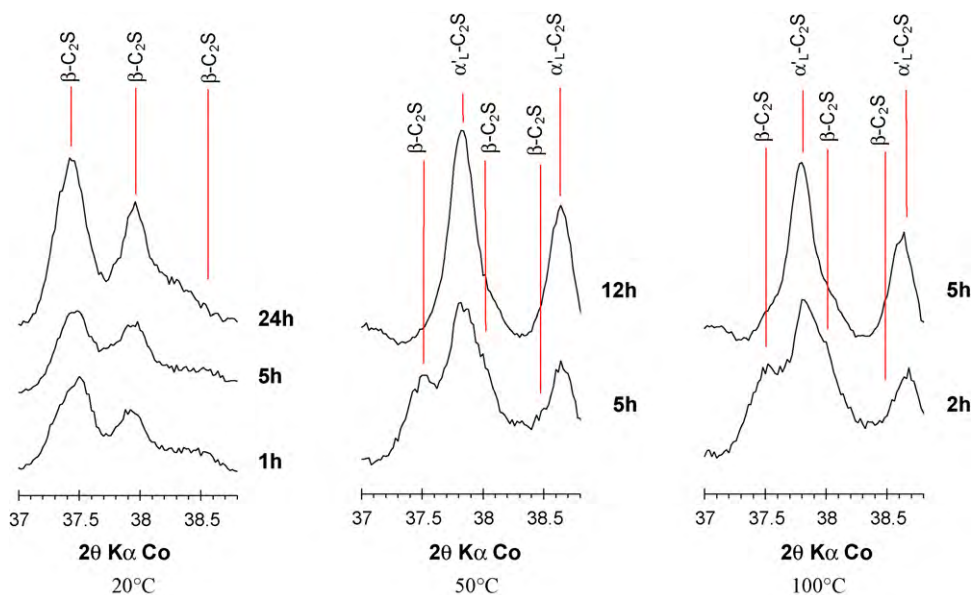


**Fig. 7.** XRD patterns showing the types of  $\text{C}_2\text{S}$  obtained after the two stages of synthesis. Mixtures burned at 1100 °C after hydrothermal treatment (conditions: heating temperature of 20, 50 and 100 °C, stirring time of 5 h, solvent: 1 M KOH).

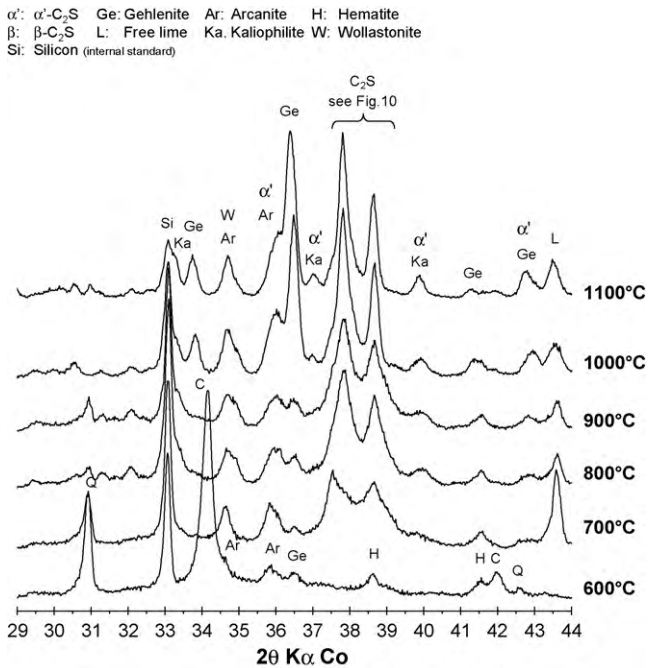
a relation giving equivalent cement for various time–temperature combinations in the hydrothermal treatment.

### 3.2. Reduction of burning temperature of hydrothermal mixtures

To decrease the temperature of cement synthesis, a mixture which gave satisfactory results in the formation of  $\alpha'_L\text{-C}_2\text{S}$  belite phase was chosen in order to study the effect of burning temperatures, from 600 to 1100 °C. The selected mixture was that coming from hydrothermal treatment with KOH (0.6M) heated at 100 °C



**Fig. 8.** XRD patterns showing the types of  $\text{C}_2\text{S}$  obtained after the two stages of synthesis. Mixtures burned at 1100 °C after hydrothermal treatments (conditions: heating temperature of 20, 50 and 100 °C, stirring time of 1, 5, 12 or 24 h, solvent: 1 M KOH).



**Fig. 9.** XRD patterns of mixtures burned at different temperatures (600–1100 °C), after hydrothermal treatment in 0.6 M KOH solution (hydrothermal conditions: heating temperature of 100 °C, stirring time of 5 h).

for 5 h of stirring. The results are illustrated by their XRD patterns in Fig. 9. Fig. 10 gives the variation of the principal peaks of  $\alpha'_L$  and  $\beta$ -C<sub>2</sub>S in the range of lattice spacing 2.69–2.78 Å

At 600 °C, very few reactions occurred and most of the compounds in the mixture had been present in the initial materials. Only a small amount of gehlenite was detected as a new-formed product. The burned mixture contained significant quantities of quartz and calcite (Fig. 9), and no trace of free lime (Fig. 9 and Table 5). This temperature was too low to initiate the decarbonation process and thus allow the reaction between calcium and silicon. Arcanite, hematite and an amorphous phase were still present in the mixture. Neither  $\alpha'_L$  nor  $\beta$ -C<sub>2</sub>S seemed to be formed at this temperature.

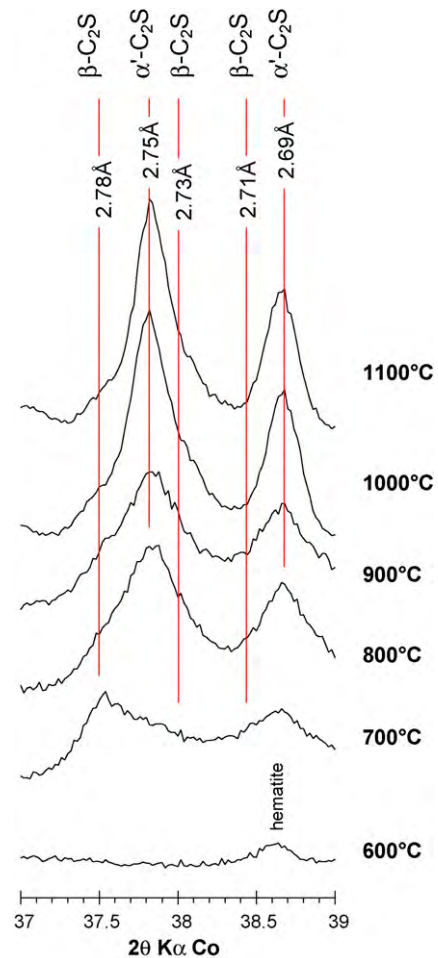
At 700 °C, the presence of C<sub>2</sub>S was detectable, but mainly in the  $\beta$ -form.  $\alpha'_L$  was probably also formed (Fig. 10). Thermal analyses showed that this phase could be obtained around this temperature [39]. Calcite disappeared totally and quartz was significantly consumed (Fig. 9), according to reactions:  $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$ , followed by  $2\text{CaO} + \text{SiO}_2 \rightarrow \text{Ca}_2\text{SiO}_4$ . A high free lime content was found in this mixture, due to the decomposition of calcite (Table 5). Other authors have found that calcite can be decarbonated around 650 °C when mineralizers (e.g. alkalis, fluorite, phosphates, sulphates and chlorides) are used [40,41]. These mineralizers can also decrease the temperature of formation of silicates [41].

At 800 and 900 °C,  $\alpha'_L$ -C<sub>2</sub>S seemed to be the main belite phase but we cannot be completely sure that a small quantity of  $\beta$ -C<sub>2</sub>S was not formed (Fig. 10). A large decrease in the amount of quartz and free lime (Table 5) was noted for these mixtures.

**Table 5**

Free lime contents in burned mixtures at various temperatures (600–1100 °C), after hydrothermal treatment in 0.6 M KOH solution (hydrothermal conditions: heating temperature of 100 °C, stirring time of 5 h).

Burning temperature (°C)	600	700	800	900	1000	1100
% Free lime	Not detected	5.6	1.4	1.2	0.8	0.3



**Fig. 10.** Details of C<sub>2</sub>S in XRD patterns of mixtures burned at different temperatures (600–1100 °C), after hydrothermal treatment in 0.6 M KOH solution (hydrothermal conditions: heating temperature of 100 °C, stirring time of 5 h).

At 1000 and 1100 °C, it can be assumed that there was no  $\beta$  phase left, since peaks of  $\alpha'_L$ -C<sub>2</sub>S were higher. A significant increase of the amount of gehlenite and the appearance of KAlSiO<sub>4</sub> were observed. At these temperatures, quartz was no longer available and the free lime content reached values under 1% (Table 5).

To summarize, it seems that the  $\alpha'_L$ -form of belite can be synthesized and stabilized at a temperature of around 700–800 °C, but the  $\beta$ -form is probably present up to 1000 °C.

### 3.3. Characterization of synthesized cement

A temperature of 800 °C was selected for the synthesis of  $\alpha'_L$ -C<sub>2</sub>S. The belite cement obtained from this product also contained small amounts of free lime and other minerals (Fig. 9). This belite cement, rich in  $\alpha'_L$ -C<sub>2</sub>S, obtained at low burning temperature, was selected to determine its morphological, chemical and physical properties.

The cement morphology, determined by scanning electron microscopy, shows that this cement is characterized by round belite crystals of reduced size (smaller than 10  $\mu\text{m}$ ) (Fig. 11). The reduced size of the  $\alpha'_L$ -C<sub>2</sub>S belite phase should improve its hydraulic reactivity [20,22,42–44].

EDX analysis of this cement showed an elementary composition containing Ca and Si with a CaO/SiO<sub>2</sub> molar ratio equal to 1.86, and insertion of the elements S, Al, Fe, Mg, K, Na and P (Fig. 11). The large amounts of Al and S were due to the chemical composition of



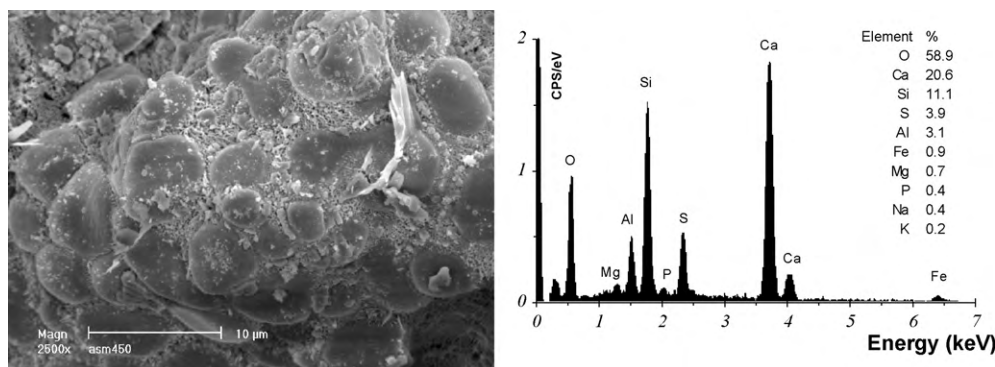


Fig. 11. Morphology and qualitative elementary composition by EDX analysis of  $C_2S$  cement synthesized at 800 °C.

the ash, rich in sulphate and alumina. According to several authors, the presence of these elements in  $\alpha'_L-C_2S$  crystalline structure and the substitution of Ca by these elements could create disorders in the crystal lattice, thus leading to an improvement in the hydraulic reactivity [45–49].

#### 4. Conclusion

This paper has focused on the synthesis of  $\alpha'_L-C_2S$ -rich cement starting from fly-ash of system  $CaO-SiO_2-Al_2O_3-SO_3$ , with added slaked lime dust. This synthesis was possible by using the hydrothermal method in basic (alkaline) solvents at relatively low temperatures (50 or 100 °C) and under atmospheric pressure, contrary to other studies found in the literature, for which the temperature and pressures were higher. The KOH or NaOH liquid solutions both allowed  $\alpha'_L-C_2S$ -rich cement to be obtained but the formation of this phase was facilitated with KOH solution. The use of water as the solvent did not lead to the  $\alpha'_L-C_2S$  belite phase being obtained alone.

Obtaining cement with  $\alpha'_L-C_2S$  is possible if the precursors are prepared in KOH liquid solution (0.6 M) after continuous stirring for 5 h at 100 °C (or 12 h at 50 °C), followed by burning at a minimum temperature of 800 °C and air-cooling. At 1000 °C, the sole belite phase formed is  $\alpha'_L-C_2S$ , with small amounts of free lime and other phases such as  $K_2SO_4$ , known to be a setting accelerator. Some other minerals (e.g. gehlenite and wollastonite) can also be found. The  $\alpha'_L-C_2S$ -rich cement synthesized was characterized by crystals that were round and reduced in size. In addition to Ca and Si, this belite phase contains other elements, such as Al, Fe, Mg, K, Na, which probably increase the disorder of its structure.

Further work will focus on optimizing the method, on evaluating and increasing the reactivity of belite cements, and on the assessment of the environmental impact of the use of fly-ash for the synthesis of binders.

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#### References

- [1] C.D. Popescu, M. Muntean, J.H. Sharp, Industrial trial production of low energy belite cement, *Cem. Concr. Compos.* 25 (2003) 689–693.
- [2] Intergovernmental Panel on Climate Change: Special Report on Emissions, 2001. Available from: <http://www.grida.no/climate>.
- [3] R. McCaffrey, Climate change and the cement industry, *Glob. Cem. Lime Mag.* (2002) (GCL Environmental Special Issue).
- [4] J. Davidovits, Global warming impact on the cement and aggregates industries, *World Resour. Rev.* 6 (1994) 263–278.
- [5] C.D. Lawrence, The production of low energy cements, in: P.C. Hewlett (Ed.), *Lea's Chemistry of Cement and Concrete*, 4th ed., Arnold, London, 1998, pp. 421–470.
- [6] J.H. Sharp, C.D. Lawrence, R. Yang, Calcium sulfoaluminate cements—low energy cements—special cements, *Adv. Cem. Res.* 11 (1999) 3–13.
- [7] I. Odler, Hydration, setting and hardening of Portland cement, in: P.C. Hewlett (Ed.), *Lea's Chemistry of Cement and Concrete*, 4th ed., Arnold, London, 1998, pp. 241–297.
- [8] B. Matkovic, V. Carin, T. Gacesa, R. Halle, Reactivity of belite stabilized by  $Ca_5(PO_4)_3 OH$ , in: *Proc. 7th Int. Congr. Chem. Cem.*, Paris, vol. 2, 1980, pp. 1-189–1-194.
- [9] I. Jelenic, A. Bezjak, M. Bujan, Hydration of  $B_2O_3$ -stabilized  $\alpha$ - and  $\beta$ -modifications of dicalcium silicate, *Cem. Concr. Res.* 8 (1978) 173–180.
- [10] I. Jelenic, A. Bezjak, On the hydration kinetics of  $\alpha'$ - and  $\beta$ -modifications of dicalcium silicate, *Cem. Concr. Res.* 11 (1981) 467–471.
- [11] F.A. Rodrigues, P.J.M. Monteiro, Hydrothermal synthesis of cements from rice hull ash, *J. Mater. Sci. Lett.* 18 (1999) 1551–1552.
- [12] H. Ishida, K. Mabuchi, K. Sasaki, T. Mitsuda, Low-temperature synthesis of  $\beta$ - $Ca_2SiO_4$  from hillebrandite, *J. Am. Ceram. Soc.* 75 (1992) 2427–2432.
- [13] W. Jiang, D.M. Roy, Hydrothermal processing of new fly ash cement, *Am. Ceram. Soc. Bull.* 71 (1992) 642–647.
- [14] R.K. Iler, *The Chemistry of Silica and Silicates*, Wiley, New York, 1979.
- [15] W. Eitel, *Silicate Science*, Academic Press, New York, 1964.
- [16] F.A. Rodrigues, Low-temperature synthesis of cements from rice hull ash, *Cem. Concr. Res.* 33 (2003) 1525–1529.
- [17] P. Arjunan, M.R. Silsbee, D.M. Roy, Sulfoaluminate–belite cement from low-calcium fly ash and sulfur-rich and other industrial by-products, *Cem. Concr. Res.* 29 (1999) 1305–1311.
- [18] S. Goñi, A. Guerrero, A. Macías, M.P. Luxán, Effect of the synthesis temperature on the hydration reaction of fly ash–belite cement, in: M. Cohen, S. Mindess, J. Skalny (Eds.), *Materials Science of Concrete: The Sidney Diamond Symposium*, American Ceramic Society, 1998, pp. 93–108.
- [19] A. Guerrero, S. Goñi, A. Macías, M.P. Luxán, Mechanical properties, pore size distribution, and pore solution of fly ash–belite cement mortars, *Cem. Concr. Res.* 29 (1999) 1753–1758.
- [20] A. Guerrero, S. Goñi, A. Macías, M.P. Luxán, Effect of the starting fly ash on the microstructure and mechanical properties of fly ash–belite cement mortars, *Cem. Concr. Res.* 30 (2000) 553–559.
- [21] A. Guerrero, S. Goñi, A. Macías, M.P. Luxán, Hydraulic activity and microstructural characterization of new fly ash–belite cements synthesized at different temperatures, *J. Mater. Res.* 14 (1999) 2680–2687.
- [22] A. Guerrero, S. Goñi, I. Campillo, A. Moragues, Belite cement clinker from coal fly ash of high Ca content: optimization of synthesis parameters, *Environ. Sci. Technol.* 38 (2004) 3209–3213.
- [23] W. Jiang, D.M. Roy, Hydrothermal processing of new fly ash cement, *Ceram. Bull.* 71 (1992) 642–647.
- [24] S. Goñi, A. Guerrero, M.P. Luxán, A. Macías, Dehydration of pozzolanic products hydrothermally synthesized from fly ashes: microstructure evolution, *Mater. Res. Bull.* 35 (2000) 1333–1344.
- [25] A. Guerrero, S. Goñi, A. Macías, Durability of new fly ash–belite cement mortars in sulfated and chloride medium, *Cem. Concr. Res.* 30 (2000) 1231–1238.
- [26] N. Bouzoubaa, M.H. Zhang, A. Bilodeau, V.M. Malhotra, The effect of grinding on the physical properties of fly ashes and a Portland cement clinker, *Cem. Concr. Res.* 27 (1997) 1861–1874.
- [27] J. Paya, J. Monzo, M.V. Borrachero, E. Peris, Mechanical treatment of fly ashes. Part I. Physico-chemical characterization of ground fly ashes, *Cem. Concr. Res.* 25 (1995) 1469–1479.
- [28] J. Paya, J. Monzo, M.V. Borrachero, E. Peris, E. Gonzalez, Mechanical treatment of fly ashes. Part III. Studies on strength development of ground fly ashes (GFA) – cement mortars, *Cem. Concr. Res.* 27 (1997) 1365–1377.



- [29] K. Kiattikomol, C. Jaturapitakkul, S. Songpiriyakayakij, S. Chutubtim, A study of ground coarse fly ashes with different finenesses from various sources as pozzolanic materials, *Cem. Concr. Compos.* 23 (2001) 335–343.
- [30] F. Xiaoru, L. Qin, Z. Jianping, S. Guanghong, L. Feihu, The physical–chemical characterization of mechanically-treated CFBC fly ash, *Cem. Concr. Compos.* 30 (2008) 220–226.
- [31] A. Palomo, M.W. Grutzeck, M.T. Blanco, Alkali-activated fly ashes a cement for the future, *Cem. Concr. Res.* 29 (1999) 1323–1329.
- [32] S. Antiohos, S. Tsimas, Activation of fly ash cementitious systems in the presence of quicklime. Part I. Compressive strength and pozzolanic reaction rate, *Cem. Concr. Res.* 34 (2004) 769–779.
- [33] C.S. Poon, S.C. Kou, L. Lam, Z.S. Lin, Activation of fly ash cement systems using calcium sulfate anhydrite ( $\text{CaSO}_4$ ), *Cem. Concr. Res.* 31 (2001) 873–881.
- [34] K. Wang, S.P. Shah, A. Mishulovich, Effects of curing temperature and NaOH addition on hydration and strength development of clinker-free CKD-fly ash binders, *Cem. Concr. Res.* 34 (2004) 299–309.
- [35] W. Ma, P.W. Brown, Hydrothermal synthesis of tobermorite from fly ashes, *Adv. Cem. Res.* 9 (1997) 9–16.
- [36] W. Ma, P.W. Brown, Hydrothermal reactions of fly ash with  $\text{Ca}(\text{OH})_2$  and  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , *Cem. Concr. Res.* 27 (1997) 1237–1248.
- [37] F.T. Keys, C.J. Capobianco, S.T. Schwab, Synthesis of hydraulically active beta-belite from hillebrandite, in: *Adv. Cem. Concr. Engineering Foundation Conference, Banff, Alberta, Canada, July, 1998*.
- [38] S. Goñi, M.P. de Luxán, A. Guerrero, M.S. Hernández, A. Macías, Microstructural study of hydration reactions of a fly ash–belite cement, in: *Proc. 6th CAN-MET/ACI Int. Conf. Fly Ash, Silica Fume, Slag and Natural Pozzolans in Concrete, Bangkok, 1998*, pp. 207–224.
- [39] V.S. Ramachandran, Thermal analysis, in: V.S. Ramachandran, J.J. Beaudoin (Eds.), *Handbook of Analytical Techniques in Concrete Science and Technology – Principles, Techniques, and Applications*, Noyes Publications, Park Ridge, USA, 2001, pp. 127–173.
- [40] S. Radnaasediin, Formation of low temperature Portland cement clinker by using non-traditional aluminosilicate rock and mineralizer, in: *Proc. 9th Int. Congr. Chem. Cem.*, New Delhi, India, vol. 2, 1992, pp. 315–321.
- [41] S. Lagzdina, U. Sedmalis, Kinetics of  $2\text{CaO} \cdot \text{SiO}_2$  and  $3\text{CaO} \cdot \text{SiO}_2$  formation in the presence of sodium and potassium compounds, in: *Proc. 10th Int. Congr. Chem. Cem.*, Gotheburg, Sweden, vol. 1, 1998, paper 1i035.
- [42] A. Guerrero, S. Goñi, A. Moragues, J.S. Dolado, Microstructure and mechanical performance of belite cements from high calcium coal fly ash, *J. Am. Ceram. Soc.* 88 (2005) 1845–1853.
- [43] L. Kacimi, A. Simon-Masseron, A. Ghomari, Z. Derriche, Reduction of clinkerization temperature by using phosphogypsum, *J. Hazard. Mater.* 137 (2006) 129–137.
- [44] T. Stanek, P. Sulovsky, The influence of the alite polymorphism on the strength of the Portland cement, *Cem. Concr. Res.* 32 (2002) 1169–1175.
- [45] I. Odler, H. Zhang, Investigations on high  $\text{SO}_3$  Portland clinkers and cements. I. Clinker synthesis and cement preparation, *Cem. Concr. Res.* 26 (1996) 1307–1313.
- [46] K. Quillin, Performance of belite–sulfoaluminate cements, *Cem. Concr. Res.* 31 (2001) 1341–1349.
- [47] L. Baoyuan, X. Jungan, Effect of fluoride and gypsum compound mineralizer on Portland cement clinker, *Silic. Sci. Rep. J. Chin. Silic. Soc.* 12 (1984) 429–440.
- [48] M. Ichikawa, M. Kanaya, Effects of minor components and heating rates on the fine textures of alite in Portland cement clinker, *Cem. Concr. Res.* 27 (1997) 1123–1129.
- [49] K. Raina, L.K. Janakiraman, Use of mineralizer in black meal process for improved clinkerization and conservation energy, *Cem. Concr. Res.* 28 (1998) 1093–1099.