

# Low-temperature Synthesis of Belite Cement from Reactive Mixtures Based on Coal Fly Ash

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**Abstract:** This paper summarizes the selected results of an extensive investigation of application of two methods (hydrothermal and mechanochemical) assisted by calcination for synthesizing belite cement from reactive mixtures (CaO/SiO<sub>2</sub> molar ratio of 2) consisting of various waste kinds from fluidized brown coal combustion in Slovakian power plant and CaO addition. Based on XRD diffraction patterns and infrared spectra of pre-treatment products, the formation of the new profiles corresponding to CSH phases with low degree of ordering as belite precursors after hydrothermal treatment as well as metastables calcium silicates and aluminosilicates in mechanosynthesized products was confirmed. Calcination of hydrothermally treated products led to transformation of CSH phases to wollastonite (CS), belite and gehlenite phase, whereas creation of  $\alpha$ - and  $\beta$ -C<sub>2</sub>S or wollastonite in milled reactive mixture took place. Differences in phase composition of products before and after calcination depend upon waste quality and precursor's synthesis conditions. Bottom ash isn't suitable as raw material for synthesizing belite phase because of high CaO content fixed in anhydrite form (44.1%). Coal fly ash with low CaO content in anhydrite form (4.2%) and its mechanochemical or hydrothermal treatment in combination with subsequent heating offer opportunities for the utilization of coal fly ash as raw material for belite production.

**Key words:** Coal fly ash, hydrothermal pre-treatment, mechanosynthesis, belite.

## 1. Introduction

Clean coal technologies of energy production result in decrease of the produced amount of gas exhalants. However, it creates solid waste of new quality as well, that is necessary to utilize or defuse. The Slovakia falls behind foreign countries in the coal fly ash utilization. The main reason is the dominant fly ash produced from brown coal burning with poor quality. The fly ash produced by black coal burning does not satisfy the requirements of chemical properties for utilization in the building industry.

The utilization of raw fly ash in cement production is relatively low therefore the researchers try to find new untraditional way of fly ash properties modification for

the development of new kinds of cements using appropriate methods. The growing interest is related to synthesis of reactive low-energy belite cements as an alternative to the conventional Portland cement because of favorable properties of belite in comparison with alite. This kind of cement represents great economic and environmental value, mainly because of the CO<sub>2</sub> emission reduction, energy saving as well as the use of wastes and by-products from coal combustion processes of fossil fuels in power plants and electric power stations. Presently, belite cement synthesizing has become the hotspot in cement-concrete materials science.

Many investigations of low temperature synthesis by hydrothermal [1–8], mechanochemical [9–13] and ultrasound [14] procedures have been realized in order to prepare belite ( $\beta$ -polymorphic modification of C<sub>2</sub>S) from industrial wastes and by-products as alternative

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secondary raw materials. Belite cements and mortars were prepared in accordance with Jiang and Roy's method [1] based on hydrothermal treatment of coal fly ash and subsequent calcination of formed calcium silicate and aluminate hydrates. Reactive forms of dicalcium silicate ( $\alpha'_L$  - and  $\beta$  -  $C_2S$ ) in belite clinker were stabilized by quick cooling or inclusion of an appropriate mineralizer [7].

Another mechanochemical way of low-temperature belite synthesis consists in high-energy milling of reactive mixture based on coal fly ash in combination with heating. The non-conventional mechanochemical route became a very useful preparation and processing technique in material science and environmental engineering. It was connected with the preparation of the reactive precursors for special materials and novel, high-performance, and low-cost materials [15]. Numerous papers have been demonstrated an important position of mechanosynthesis in the intensification and stimulation of the chemical solid-state process engineering progress. In our previous papers [9,10, 12, 16, 17], formation of cement minerals  $C_2S$  and  $C_3S$  was investigated at high-energy milling of reactive mixtures consisting of coal fly ash and calcium compound addition (calcite and portlandite) at Ca/Si ratio of 2 and 3.

In this paper, the selected results of hydrothermal and mechanochemical treatment assisted by calcination for synthesizing belite cement from reactive mixtures consisting of two kinds of Slovak ash matter with calcium oxide addition are presented.

## 2. Materials and Methods

Two different kinds of ash matters (AM) from fluidized brown coal combustion process in Slovak power plant ENO Novaky with different granulometric and chemical composition (CaO content in anhydrite form) were used in this study.

Ash matter I – fluidized course-grained bottom ash (40 do 3000  $\mu\text{m}$ ).

Ash matter II – fluidized fly ash with particle size from 1 to 500  $\mu\text{m}$ . This fact is confirmed by the value of mean particle diameters and specific surface area (Table 1).

Chemical composition of both kinds ash matters is described in Table 2. Main mineralogical phases in AM I are anhydrite, quartz, calcite and lime. In AM II are also portlandite and illite presented as well. However, anhydrite in AM II is not dominant phase as in AM I.

AM I was milled for a short term (1 min.) in laboratory mill due to increase its dispersity degree. The milling product had the mean particle diameter  $d_m = 7 \mu\text{m}$  and value of specific surface area of  $6.06 \text{ m}^2\text{g}^{-1}$ . Low molar ratio of calcium and silicate oxides in used materials was corrected by CaO p.a. (Lachema Brno) in stoichiometric ratio  $\text{CaO}/\text{SiO}_2 = 2$  in starting mixtures. The composition of starting mixtures is given in Table 3. Reactive mixtures were homogenized in planetary ball mill AGO-2 (URF Technology, Hungary) during 5 min. with rotation speed 270 rpm.

Low-temperature synthesis of belite cement from reactive mixtures was carried out by hydrothermal and mechanochemical treatment in combination with subsequent calcination. Hydrothermal treatment of homogenized reactive mixtures was realized in demineralized water under optimal conditions (200°C; 4h) at a water-to-solid ratio of 5 in rotating autoclave A-08 [18]. Products were filtered and dried at 55°C during 24 h after hydrothermal treatment.

The reactive mixture RM1 was used due to study the influence of mechanochemical activation on the formation of metastable precursors of belite phases. The homogenized starting mixture was milled in high-energy planetary ball mill AGO 2 (URF Technology, Hungary) during 2 hours with rotation speed 700 rpm.

**Table 1 Mean particle diameter  $d_m$  and specific surface area  $S_{\text{BET}}$  of ash matters.**

Ash material	$d_m$ [ $\mu\text{m}$ ]	$S_{\text{BET}}$ [ $\text{m}^2\text{g}^{-1}$ ]
AM I	423	3.35
AM II	79.4	4.78

**Table 2** Chemical composition of ash matters.

Ash matter	Component content [%]						
	SiO <sub>2</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	MgO	SO <sub>3</sub>	LOI*
AM I	30.36	51.21	2.29	16.95	2.45	36.00	5.25
AM II	33.00	23.90	8.30	11.40	1.99	3.22	4.79

LOI\* – loss of ignition

**Table 3** Characteristic of reactive mixtures

Reactive mixture	Composition
RM1	Raw ash matter I + CaO
RM2	Milled ash mater I + CaO
RM3	Ash mater II + CaO

Consequently, products of both treatments were thermally treated in the high-temperature chamber oven LM 417 (NETZSCH, Germany) at temperatures: 700, 800, 900 and 1200°C during 30 minutes. Phase composition development in all products was studied by X-ray diffraction (XRD) and infrared spectroscopy with Fourier transformation (FTIR).

### 3. Result and Discussion

#### 3.1 Hydrothermal Treatment

Based on XRD diffraction patterns of mixtures RM1 – RM3 after hydrothermal treatment decrease in relative intensities of initial crystalline phases reflections (without anhydrite) and formation of new phases of hydrated calciumsilicates (CSH, tobermorite and xonolite) as belite precursor were observed (Table 4). In the case of hydrothermally treated RM1 significant creation of portlandite was detected.

Fineness of AM I in RM2 and RM3 influences hydrothermal reaction and relative intensities corresponding to tobermorite  $\text{Ca}_5\text{Si}_6\text{O}_{16}(\text{OH})_2 \cdot 4\text{H}_2\text{O}$ , Al-tobermorite  $(\text{Ca}_5\text{Si}_5\text{Al}(\text{OH})_{17} \cdot 5\text{H}_2\text{O})$  as well as xonolite  $\text{Ca}_2\text{Si}_6\text{O}_7(\text{OH})_2$  are observed. Lower conversion degree of CaO and SiO<sub>2</sub> to CSH phase in hydrothermal treated products of RM1 and RM2 in comparison to RM3 was determined. It is connected with high CaO content fixed predominantly in anhydrite form (44.1%) in AM I [19].

IR spectra of reactive mixture RM2 and its hydrothermally treated product (Fig. 1) confirms the obtained results of XRD analysis and contribute to explanation of structural and phase changes. Significant absorption band centred at 3642 cm<sup>-1</sup> (RM2) corresponds to vibrations of OH group in portlandite. Bands observed at 3440; 3445 a 1619; 1632 cm<sup>-1</sup> on both IR spectra belong to stretching and deformation vibrations of water. Absorption peaks centred at 1157 (RM2) and 1160 cm<sup>-1</sup> (hydrothermally treated product) are attributed asymmetric stretching vibration of SO<sub>4</sub><sup>2-</sup> group in anhydrite. Calcite presence in RM1 and RM2 confirms absorption region of 1500 -1400 cm<sup>-1</sup> with peak intensity at 1445; 1448 cm<sup>-1</sup> and at 875; 872 cm<sup>-1</sup>, respectively. Two main zones of 800 -1200 cm<sup>-1</sup> and 450 -550 cm<sup>-1</sup> belong to vibrations of Si-O in silicates. Absorption band centred at 994 cm<sup>-1</sup> (asymmetric stretching vibration) together with band at 523 cm<sup>-1</sup> (bending vibration) corresponding to Si-O group in CSH gels is related to partial synthesis of hydrated calcium silicate phases.

Products of hydrothermal treatment of mixtures RM2 and RM3 were chosen for the study of belite phase development during calcination. Changes in integral intensities of XRD reflections of main crystalline phases in hydrothermally treated and subsequent calcinated products of RM2 and RM3 can be seen in Table 5. The comparative study of calcinated products of hydrothermally treated mixtures RM2 and RM3 determined the optimal temperature for synthesis belite phase. Heating at the temperature of 800°C leads to transformation of CSH phases to wollastonite (CS) and belite phase (C<sub>2</sub>S) in dependence on ash matter quality in the mixture. Formation of gehlenite that is known as a retarder of cement hydration, and

Table 4 XRD relative intensities  $I_{rel}$  of initial and new formed phases in reactive mixtures RM1, RM2 and RM3 after hydrothermal treatment (HT) in water under optimal conditions (200°C/4h).

Mineral	$I_{rel}$ [-]					
	Mixture					
	RM1	RM2/HT	RM2	RM2/HT	RM3	RM3/HT
Anhydrite	978	640	626	752	48	44
Quartz	759	126	884	252	36	49
Portlandite	203	18 021	211	-	32	243
Lime	314	-	204	-	45	-
Calcite	-	297	-	297	57	40
Katoite	81	-	167	-	-	-
Tobermorite	-	-	-	336	-	387
Xonolite	-	-	-	378	-	-
CSH	-	248	-	288	-	-

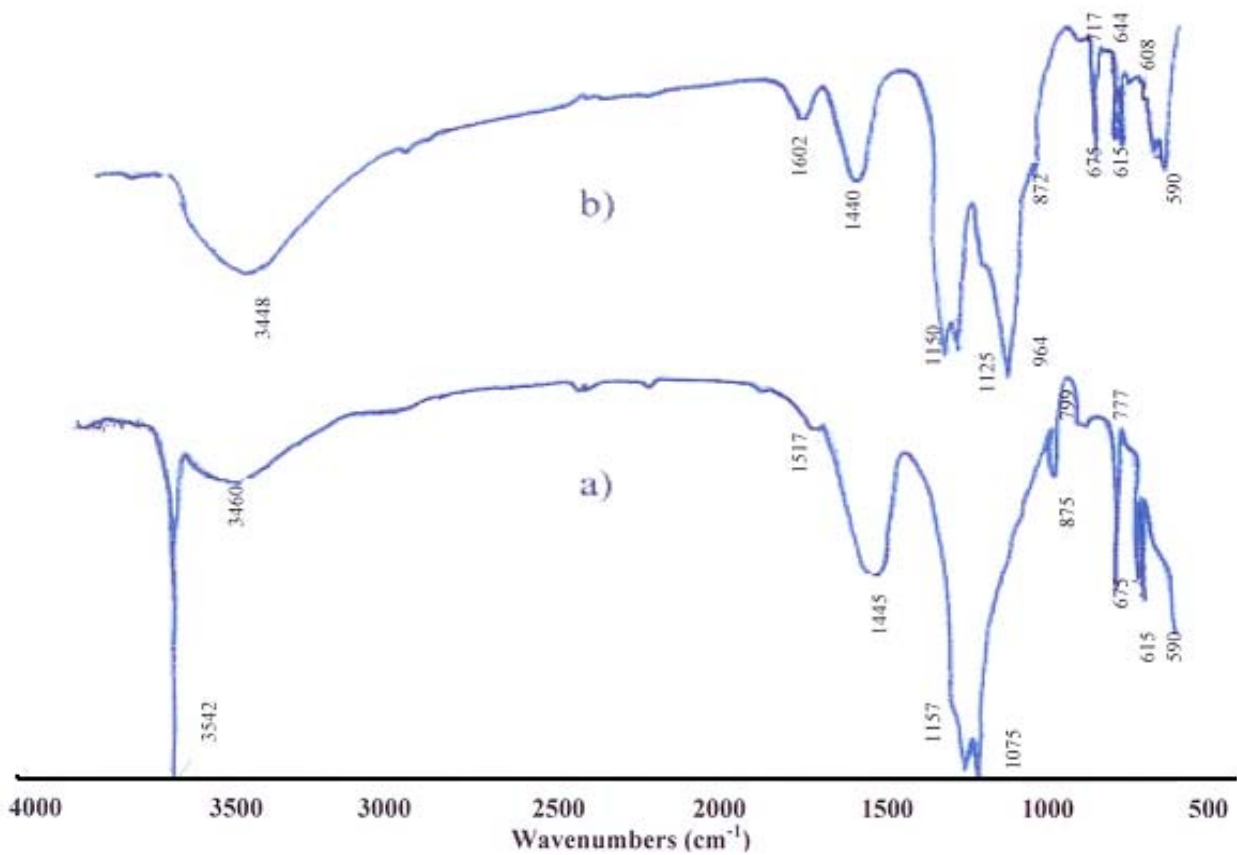


Fig. 1 (a) IR spectrum of starting mixture RM2 and (b) its hydrothermally treated product.

therefore undesirable phase was observed at 900°C in calcinated products of both mixtures. As observed the high CaO content fixed in anhydrite form in reactive mixture RM2 has been not changed during the hydrothermal treatment and subsequent calcination

and belite phase of low conversion degree from CSH phase was formed in comparison to mixture RM3. The reason of this fact consists in anhydrite as a very stable compound. XRD results of calcinated products are in good accordance with results

Table 5 XRD relative intensities  $I_{rel}$  of initial and new formed phases in hydrothermal synthesis products from reactive mixture RM2 and RM3 after subsequent calcination at various temperatures.

Phase	$I_{rel}$ [-]									
	RM2					RM3				
	Calcination temperature [°C]									
	-	700	800	900	1200	-	700	800	900	1200
Anhydrite	752	874	888	934	1034	48	89	75	90	98
Quartz	252	792	992	598	898	36	40	49	59	55
Calcite	-	-				40	-	-	-	-
Portlandite	-	-				243	-	-	-	-
CSH	248	172	-	-	-	339	-	-	-	-
Lime		-				45	10	-	-	-
C <sub>2</sub> S	-	124	144	154	266	-	260	302	351	347
Wollastonite	-	52	212	408	-	-	-	-	-	-
Gehlenite	-	-	-	378	506	-	-	-	163	278

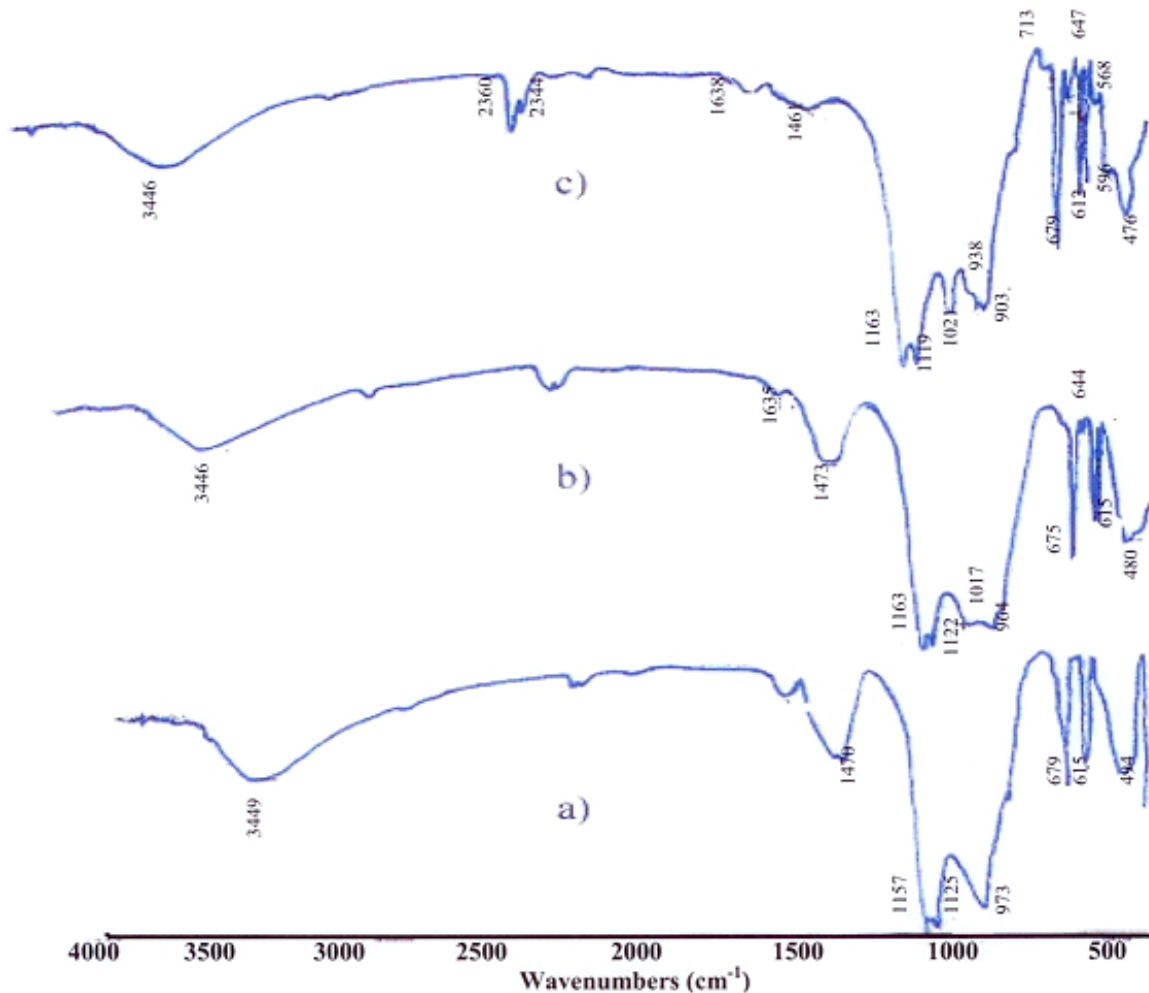


Fig. 2 IR spectrum of hydrothermally treated product of RM2 after calcination at 700°C (a), 800°C (b) and 900°C (c).

of IR spectroscopy and thermal analysis [19].

Decrease in absorption band intensity of C-O in carbonate group of calcite centered at 1470; 1473; 1471  $\text{cm}^{-1}$  is observed on IR spectra of hydrothermally activated product of RM2 with increasing calcination temperature (Fig. 2). Absorptions around 1150 - 1160  $\text{cm}^{-1}$  (vibrations of bonds in  $\text{SO}_4^{2-}$  group) are found at all calcinations temperatures. Peak centered at 973  $\text{cm}^{-1}$  on spectrum of product calcinated at 700°C originates from vibration of Si-O group in CSH gel and it is identical with XRD data (Table 5). New absorption bands centered at 1017; 1021 a 964; 938 a 514 a 476  $\text{cm}^{-1}$  were observed on spectra at calcination temperatures of 800 and 900°C. These peaks verify fact that transformation of CSH phase (prepared by hydrothermal treatment) to belite phase occurred.

3.2 Mechanochemical Treatment

Belite cement precursors were mechanosynthesized from reactive mixture RM1 and RM3. As shown in the Table 6, the high-energy milling leads to decrease in peak intensity corresponding to initial crystalline phases of anhydrite, portlandite, quartz and calcite in starting mixtures RM1 and RM3. Based on these results the decrease in relative intensities of diffraction lines of main components relates to the crystallite size reduction, introduction of lattice microstrains and/or the amorphization. The decrease in peak intensity of anhydrite, portlandite and/or calcite during milling of

Table 6 XRD relative intensities  $I_{\text{rel}}$  of initial and new formed phases in reactive mixture RM1 and RM3 before and after mechanochemical treatment.

Mineral	$I_{\text{rel}}$ [-]			
	Reactive mixture			
	RM1	RM1/2	RM3	RM3/2
Anhydrite	784	222	46	-
Quartz	177	68	168	70
Lime	282	142	-	-
Calcite	212	178	435	100
Portlandite	215	76	-	-
Wollastonite	-	146	-	-
$\text{C}_2\text{S}$	-	130	-	96

these mixtures therefore appears to have resulted from their partial mechanochemical decomposition. In the case of milled product of RM3 was observed disappearance of anhydrite peak. The formation of CSH gel and  $\alpha\text{-C}_2\text{HS}$  hasn't been observed on XRD patterns (at 29.5 of  $2\theta$  angular zone) of milled mixtures. Formation of nanocrystalline calcium silicates (CS and/or  $\text{C}_2\text{S}$ ) with low degree of ordering after mechanochemical treatment of mixtures was confirmed. Controlled heating of milled mixtures results in the crystallization of wollastonite, dicalcium silicates and gehlenite in dependence on the composition of mixture (Table 7). In the case of RM1 low content of free CaO in AM I is the reason of wollastonite creation [19]. Suppose of forming cement minerals  $\text{C}_2\text{S}$  from RM1 as result of mechanochemical treatment with subsequent heating was not confirmed.

Table 7 XRD relative intensities of new formed phases in milled products of mixtures RM1 and RM3 after subsequent calcination at various temperatures (\* low value of XRD intensity).

Phase	$I_{\text{rel}}$ [-]									
	Reactive mixture									
	RM1/2					RM3/2				
	Calcination temperature [°C]									
	-	600	800	900	1200	-	600	800	1000	1200
$\alpha\text{-C}_2\text{S}$	-	-	-	-	-	/*	/*	/*	/*	82
$\beta\text{-C}_2\text{S}$	130	182	222	234	244	96	134	157	153	190
Wollastonite	146	184	196	215	245	-	-	-	-	-
Gehlenite	-	-	90	130	117	-	-	-	157	224

#### 4. Conclusions

Evaluation of phase composition in hydrothermally and mechanochemically treated products of reactive mixtures showed that bottom ash with high CaO content fixed in anhydrite form (44.1%) as a very stable compound is not suitable as raw material for synthesizing belite phase. Optimal calcination temperature in term of product quality to belite in precursors prepared by mechanosynthesis and hydrothermal treatment of reactive mixture based on FA is 800°C because gehlenite as cement hydration retarder is not formed at this temperature.

The main advantages of mechanochemical method are visible in comparison with conventional solid-state reactions: they are proceeding at the laboratory temperature in the mill, they are environmentally appropriate, because they don't produce any wastewaters. Mechanochemical synthesis of alternative inorganic materials from secondary raw materials as well as structural modification of various waste kinds by mechanical treatment is becoming a priority in current mechanochemical research.

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