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# POSSIBILITIES OF COAL FLY ASH UTILIZATION IN THE LOW TEMPERATURE BELITE CEMENT PRODUCTION

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**Abstract.** At present, belite cement synthesizing has become the hotspot in cement-concrete materials science. Many investigations have been realized in order to synthesize belite (β polymorph modification of C2S) from coal fly ash as an alternative secondary raw material. Belite cements and mortars were formed in accordance with Jiang and Roy´s method based on hydrothermal treatment of coal fly ash and subsequent calcination of formed calcium silicate and aluminate hydrates. 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.

This paper summarizes the results of an extensive investigation of application of both methods for synthesizing belite cements from reactive mixtures consisting of two waste kinds (bottom ash – BA and fly ash - FA) from fluidized brown coal combustion in Slovakian power plant and CaO (analytical grade reagent) addition. Starting mixtures with CaO/SiO2 molar ratio of 2 were hydrothermally activated in rotating autoclave under optimal conditions (200°C and 4 hours) and mechanochemically treated during 2 hours in high-energy planetary mill. The starting mixtures and products of treatments were subsequently calcinated at temperatures in the range of 600 to 1200°C. Phase composition development in all products was studied by X-ray diffraction (XRD), FT infrared spectroscopy (FTIR), thermal analysis and scanning electron microscopy (SEM). Comparative study of phase composition of products won by hydrothermal and mechanochemical treatment and subsequent calcinations of reactive mixtures based on two kinds of waste with different CaO content showed that fluidized coal ash matter with low CaO content in fixed form is a suitable material for belite cement production. Any of two applied pre-treatment methods led to activation of anhydrite structure presented in bottom fly ash; therefore the low conversion degree to belite phase was reached.

**Keywords:** coal fly ash, mechanosynthesis, hydrothermal pre-treatment, belite.

## 1. Introduction

Energy obtained in an environmental and energetic clear way is the requirement for forming of environmental strategy of energy production. Its consequence is the innovation of ecological technology in energy power stations. This technology results in decrease of the production amount of gas exhalants. However, it creates solid waste of new quality as well, that is necessary to utilize or defuse (Stevulova 2006). Slovakia falls behind foreign countries in the coal fly ash utilization. The main reason is the dominant fly ash produced from brown coals burning with poor quality. (Stevulova 2007; Filkova *et al.* 2008). The utilization of raw fly ash in building industry is relatively low therefore the researchers try to find new untraditional way of fly ash properties modification for extensive possibilities of its utilization (Stevulova 2009).

The growing interest is related to synthesis of reactive low-energy belite cements as an alternative to the conventional Portland cement. This kind of cement represents great economic and environmental value, mainly because of the CO2 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 (Goni *et al.* 2004; Stevulova 2009).

Results of low temperature synthesis of belite cement from two kinds of Slovak ash matter and calcium compounds by hydrothermal and mechanochemical way of treatment are presented in this paper.

## 2. Materials and methods

Two different kinds of ash matters (AM) from fluidized brown coal combustion process in Slovak power plant ENO Nováky with different granulometric and chemical composition (CaO content) were used in this study. Ash matter I – fluidized course- grained bottom ash (40 do 3000 μm). Ash matter II - fluidized fly ash with grain size from 1 to 500 μm. This fact is confirmed by the value of mean particle diameters and specific surface area (table 1).

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

| Ash material | dm [μm] | SBET [ $m^2g^{-1}$] |
|---|---|---|
| I | 423 | 3,35 |
| II | 79,4 | 4,78 |

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

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

| Chemical composition [%] | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ash matter | $SiO_2$ | CaO | $Fe_2O_3$ | $Al_2O_3$ | MgO | $SO_3$ | LI* |
| I | 30,4 | 51,2 | 2,3 | 16,9 | 2,4 | 36 | 5,3 |
| II | 33 | 23,9 | 8,3 | 11,4 | 2,0 | 3,2 | 4,8 |

*lost of ignition

Low molar ratio of calcium and silicate compounds in used material was corrected by CaO p.a. (Lachema Brno) in stechiometric ratio $CaO/SiO_2 = 2$ in starting mixtures. AM I was short- time milled (1 min) in laboratory mill due to increase its dispersity degree. The milling product gained the grain size defined by mean particle diameter $d_m = 7\mu m$ and value of specific surface area of 6, 06 $m^2g^{-1}$. The content of starting mixtures is described in table 3. Reactive mixtures were homogenized in planetary ball mill during 5 minutes with rotation speed 270 rpm.

**Table 3.** Characteristic of reactive mixtures

| Reactive mixture | Composition |
|---|---|
| RZ1 | Raw ash matter I + CaO |
| RZ2 | Milled ash matter I+ CaO |
| RZ3 | Ash matter II + CaO |

## 3. Hydrothermal treatment

In the case of hydrothermal treatment homogenized starting mixture RZ1 and RZ3 were mixed with demineralised water as well as 0.5 % and 2 % NaOH solution at a water-to-solid ratio of 5. They were activated hydrothermally in rotating autoclave A-08. Conditions of the hydrothermal treatment are summarized in table 4. Products were filtered and dried at 55 °C during 24 h after hydrothermal treatment.

**Table 4.** Conditions of hydrothermal modification of reactive mixtures

| Reactive mixture | Temperature [ºC] /time of hydrothermal treatment [h] | | | | | |
|---|---|---|---|---|---|---|
| | water | | | | NaOH | |
| | | | | | 0,5% | 2% |
| | 200 / 2 | 175 / 2 | 200 / 4 | 175 / 4 | 200/4 | 200/4 |
| RZ 1 | • | • | • | • | • | • |
| RZ 2 | • | • | • | • | • | • |
| RZ 3 | | | • | • | | |

## 4. Mechanochemical treatment

The starting mixture RZ1 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 planetary ball mill AGO 2.

## 5. Calcination

Consequently, products of 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.

Changes in composition phases and development of new crystallize phases after treatments were monitored by XRD analysis and IF spectrometry.The special kind of cement exploited for the Highway Engineering purposes (CEM 42.5 N) was used in mixtures preparation. The Slovakian fly ash from the brown (ENO Novaky) coal combustion (chemical properties of coal fly ash are presented in Table 1) was tested in cooperation with the building praxis (Central building laboratory of Slovak corporation).

## 6. Result and discussion

Hydrothermal treatment in water and NaOH solution is the reason of changes in phase composition of starting mixtures RZ1 and RZ2. These changes in integral intensities of XRD reflections of crystalline phases of starting mixture FZ1 to FZ3 treatment are presented in tables 5–7.

Based on XRD diffraction patterns of mixtures after hydrothermal treatment at different conditions, the optimal parameters were defined for formation belite precursors: 200 °C and 4 hours. Under these conditions expressive changes of integral intensities of XRD reflections in primary phases were detected (without anhydrite). Creation of new profiles of calcium silicates, aluminasilicates (tobermorite, xonotlite) and CSH as belite precursor occurred.

**Table 5.** Relative intensities of initial and new formed phases∗ in reactive mixture RZ1 after hydrothermal treatment in water under various conditions

| RZ1 T[˚C] / t [h] | Relative intensity | | | | | | |
|---|---|---|---|---|---|---|---|
| | A | Q | P | L | K | C | CSH |
| Starting mixture | 978 | 759 | 203 | 314 | 81 | - | - |
| 175/2 | 772 | 222 | 612 | - | 98 | 382 | 176 |
| 175/4 | 818 | 151 | 1443 | - | 112 | 397 | 245 |
| 200/2 | 698 | 228 | 8144 | - | - | 334 | 222 |
| 200/4 | 640 | 126 | 18021 | - | - | 297 | 280 |

**∗** - name of phases in Tables: A - Anhydrite, Q - Quartz, P - Portlandite, L - Lime, K - Katoite, C - Calcite, Y – Illite, T – Tobermorite, X – Xonolite, CSH – Calcium Silicate Hydrates, $C_2S$ – Belite, W – Wollastonite, G – Gehlenite.

IR spectrometry of the reaction mixture RZ2 and the product of hydrothermal treatment under optimal conditions (water; 200ºC/4h) contributed to explanation of changes in mineralogical structure of products. Absorption bands identified by IR spectrometry correlate with results of RTG diffraction spectrometry.

**Table 6.** Relative intensities of initial and new formed phases* in reactive mixture RZ2 after hydrothermal treatment in water under various conditions

| RZ2 T[˚C] / t [h] | Relative intensity | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | A | Q | P | L | C | T | X | CSH |
| Starting mixture | 626 | 884 | 211 | 204 | - | - | - | - |
| 175/2 | 834 | 360 | - | - | 392 | - | - | 220 |
| 175/4 | 936 | 453 | - | - | 220 | 280 | - | 281 |
| 200/2 | 856 | 352 | - | - | 320 | 336 | - | 236 |
| 200/4 | 752 | 252 | - | - | 297 | 336 | 378 | 248 |

**Table 7.** Relative intensities of initial and new formed phases* in reactive mixtures RZ1 and RZ2 after hydrothermal treatment in NaOH solution under conditions 200˚C/4

| RZ / NaOH concentration [%] | Relative intensity | | | | | |
|---|---|---|---|---|---|---|
| | A | Q | P | C | T | CSH |
| RZ1 / 0,5 | 680 | 974 | 620 | 310 | 276 | 202 |
| RZ1 / 2 | 552 | 654 | - | 384 | 302 | 250 |
| RZ2 / 0,5 | 678 | 540 | - | 280 | 372 | 346 |
| RZ2 / 2 | 612 | 446 | - | 186 | | 990 |

**Table 8.** Relative intensities of initial and new formed phases* in hydrothermal synthesis products from reactive mixture RZ2 after subsequent calcinations at various temperatures

| Calcinations temperature [ºC] | Relative intensity | | | | | |
|---|---|---|---|---|---|---|
| | A | Q | CSH | C2S | W | G |
| 0 | 752 | 252 | 248 | - | - | - |
| 700 | 874 | 792 | 172 | 124 | 52 | - |
| 800 | 888 | 992 | - | 144 | 212 | - |
| 900 | 934 | 598 | - | 154 | 408 | 378 |
| 1200 | 1034 | 898 | - | 266 | - | 506 |

**Table 9.** Relative intensities of initial and new formed phases* in hydrothermal synthesis products from reactive mixture RZ3 after subsequent calcinations at various temperatures

| Calcinations temperature [ºC] | Relative intensity | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | A | Q | C | P | CSH | L | $C_2S$ | $C_2AS$ |
| 0 | 48 | 36 | 40 | 243 | 339 | 45 | - | - |
| 700 | 89 | 40 | - | - | - | 10 | 260 | - |
| 800 | 75 | 49 | - | - | - | - | 302 | 56 |
| 900 | 90 | 59 | - | - | - | - | 351 | 163 |
| 1200 | 98 | 55 | - | - | - | - | 347 | 278 |

Products of hydrothermal treatment of mixtures RZ2 and RZ3 under optimal conditions were chosen for the study of belite phase development during calcinations. Changes in integral intensities of XRD reflections of main crystalline phases of starting mixtures RZ2 and RZ3 as a consequence of the hydrothermal treatment and subsequent calcinations can be seen in tables 8–9.

The results comparison of calcinations of hydrothermally treated products (table 10–11) determined the optimal temperature for synthesis belite cement. Heating at the temperature of 800 °C leads to transformation of CSH phases to wollastonite (CS) and belite phase ($C_2S$). Creation of gehlenite, that is known as a retarder of cement hydration, and therefore undesirable for the cement, was observed at 900°C.

As observed the high CaO content fixed in anhydrite in reactive RZ2 has not changed during the hydrothermal treatment and subsequent calcinations and the same quantity of belite phase from CSH phase was reached. The reason of low CSH phase content after hydrothermal treatment and low conversion degree of precursors to belite consists in anhydrite as a very stable compound.

The research of mechanochemical synthesis of belite cement precursors from the reactive mixture RZ1 links to obtained results from previous works, where mechanochemical synthesis of cement phases from fluidized fly ash with CaO and portlandit addition were studied. (Mezencevová 2003)

**Table 10.** Relative intensities of initial and new formed phases* in reactive mixture RZ1 after mechanochemical treatment under various conditions

| Reactive mixture | Relative intensity | | | | | | |
|---|---|---|---|---|---|---|---|
| | A | Q | L | C | P | W | $C_2S$ |
| Starting mixture | 784 | 177 | 282 | 212 | 215 | - | - |
| RZ1/1 | 648 | 134 | 219 | 178 | 176 | - | - |
| RZ1/2 | 222 | 67 | 142 | 178 | 76 | 146 | 130 |

**Table 11.** Relative intensities of initial and new formed phases* in mechanochemical synthesis products from reactive mixture RZ3 after subsequent calcinations at various temperatures

| Heating temperature RZ1/2 | Relative intensity | | | | | | |
|---|---|---|---|---|---|---|---|
| | A | Q | C | P | L | W | $C_2S$ |
| 0˚C | 222 | 67 | 178 | 76 | 142 | 146 | 130 |
| 600˚C | 218 | 60 | - | - | - | 184 | 182 |
| 800˚C | 198 | 46 | - | - | - | 196 | 222 |
| 900˚C | 176 | - | - | - | - | 215 | 234 |
| 1200˚C | 116 | - | - | - | - | 245 | 244 |

Obtained data from RTG diffraction patterns and relative intensities identified crystalline phases (table 10) of product RZ1 prove that mechanochemical reaction between primary compounds passed partial only. It confirms that the creation of new nanostructures is expressed by low intensive diffraction lines of wollastonite and $C_2S$. The decrease of intensity in primary phases (Goni *et al*. 2004; Stevulova and

Filkova 2009) conforms to amorphization of phase structure based in literature data. The reason of low conversion in belite phase is the quality of ash matter RZ1 with high CaO content fixed in anhydrite (44.1 %).

The milled mixture RZ1/2 containing the precursors phases formed during mechanochemical activation was heated at temperature ranging from 600 °C to 1200 °C. Controlled heating of milled mixture results in the creation of belite phase and wollastonite with low intensity of RTG reflections. Preferential crystallization of $\beta$-$C_2S$ was increased in milled mixture during heating at higher temperatures. This fact relates to the low content of free, reactive CaO in the reactive mixture. Molar ratio of $CaO/SiO_2$ in this mixture is not adequate for dicalcium silicate production; therefore wollastonite was created mainly. Assumption of creation of the cement minerals $C_2S$ from the ash matter I as a result of mechanochemical treatment with subsequent heating was not confirmed.

## 7. 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 ºC because gehlenite as cement hydration retarder is not formed at this temperature.

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