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Mechanochemical Synthesis of Belite Cements from Coal Fly Ash/Portlandite Mixture

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Abstract

In this paper, the synthesis of the C_2S cement by using reactive mixture containing fly ash (class F) from fluidized coal combustion and $Ca(OH)_2$ (CaO/SiO_2 ratio of 2) by mechanochemical treatment and subsequent heating is studied. Changes in structure and phase composition of milled and calcinated products of reactive mixture are compared with those of starting mixture. Two hours milling leads to mechanochemical decomposition of portlandite and to the structural and compositional metastability of mixture. The formation of the new compounds as C_2S precursors (CSH and α-C_2SH gels with low degree of ordering and α- and β-C_2S nanocrystalline phases) was confirmed after 2 h milling by X-ray diffraction and infrared spectroscopy. Creation of α- and β-C_2S and gehlenite in milled reactive mixture takes place at lower temperature (600 °C) compared to non-milled starting mixture (1200 °C). Mechanochemical synthesis in combination with thermal treatment offers opportunities for the increased utilization of coal fly ash as a basic raw material for belite production.

INTRODUCTION

Reactive low-energy belite cements, chemically and structurally related to dicalcium silicate (Ca_2SiO_4, C_2S), become the accepted alternative cementitious materials for replacing the conventional Portland cement in many construction applications. The growing interest in the belite cements synthesis is related to several reasons such as CO_2 emission reduction, energy saving and mainly better durability against corrosion attacks [1]. The industrial wastes and by-products as secondary raw materials for synthesizing belite cements are used increasingly. Belite synthesis process based on the hydrothermal calcination route of fly ashes or other residues generated from combustion processes of fuels is described in papers [2–8]. The new cement kinds based on fly ash of high Ca content (so-called fly ash belite cements, FABC) were obtained from hydrated precursors by their subsequent heating at 800 °C [8].

Mechanochemically stimulated solid state reactions as dry processes have recently become more environmentally friendly than the wet processes or currently applied high temperature preparation procedures [9]. Our previous investigations were focused on mechanochemical changes proceeding during high-energy ball milling of coal fly ash and its reactive mixtures with calcium compounds addition (Ca/Si ratio of 2 and 3, respectively). In papers [10, 11], it was shown that a mechanochemical reaction proceeds between the main components SiO_2 and CaO and an amorphous and/or nanocrystalline calcium silicate (CS), C_2S and highly metastable precursor C_3S are formed. Subsequent controlled heating of these mechanosynthesized metastable products obtained after 2 h milling led to crystallization of cement miner-

TABLE 1

Chemical composition of coal fly ash, %

SiO_2	CaO	Al_2O_3	Fe_2O_3	S_{total}	MgO	Loss on ignition
33.0	23.9	11.4	8.3	3.22	1.99	<0.01

als C_2S and C_3S in dependency on composition of mixture and metastability degree in milled products at lower temperatures from 200 to 400 °C, compared to non-milled starting mixtures. Based on studies of soft mechanochemical synthesis of complex oxide [12], we are investigating the mechanochemical formation of belite phase during high-energy milling of reactive mixture of coal fly ash and portlandite. Changes in structure and phase composition of milled and calcinated products of reactive mixture are compared with those of starting mixture.

EXPERIMENTAL

Slovak fly ash (class F according to European standard) from fluidised bed coal combustion in power plant ENO A (Nováky) was used as a raw material.

Starting mixture consisting of coal fly ash and portlandite was prepared by way described in [10] at Ca/Si molar ratio of 2. The mixture was milled for 2 h using a planetary mill AGO-2 with acceleration of 80*g*. Both starting and 2 h milled mixtures were thermally treated in the high-temperature chamber oven LM 417 (NETZSCH, Germany) for 4 h at 600–1200 °C. The particle size distribution of powders was measured on granulometer Helos and Rodos (SYMPATEC, Germany) and mean particle diameter was calculated as the first moment of the distribution density. The specific surface area was determined by the standard BET method using the equipment GEMINI 2360 (Sy-Lab, Austria). SEM measurements were carried out on microscope Tesla BS 340 (Tesla, Czech). In order to determine the changes in phase composition of mechanochemically and thermally treated mixtures, X-ray diffraction analyses (XRD), FT infrared (FTIR) and X-ray fluorescence (XRF) spectroscopy were used. X-ray diffraction patterns were recorded on a DRON 2.0 diffractometer with goniometer GUR-5 (Techsnabexport, Russia). IR study was carried out on FT IR 330 AVATAR (THERMONICOLET, USA) using KBr pellets. The results of XRF analyses were used for calculation of cementation index of products calcinated at 900 °C for 14 h. Thermal analyses were carried out on OD-102 derivatograph (MOM, Hungary).

RESULTS AND DISCUSSION

Coal fly ash

The chemical composition of the coal fly ash is presented in Table 1. As it is shown in Fig. 1,

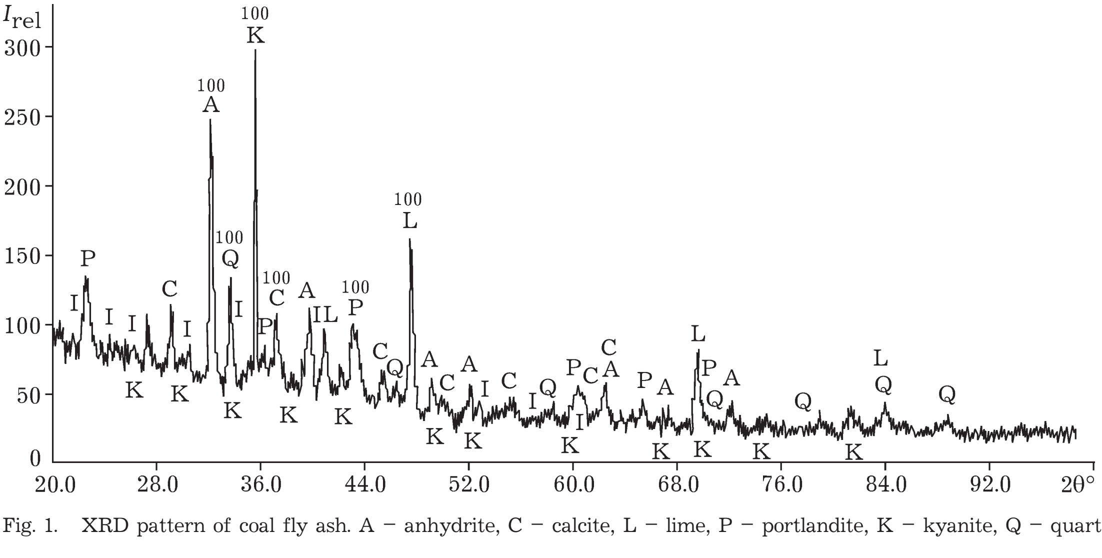

Fig. 1. XRD pattern of coal fly ash. A – anhydrite, C – calcite, L – lime, P – portlandite, K – kyanite, Q – quartz, I – illite.

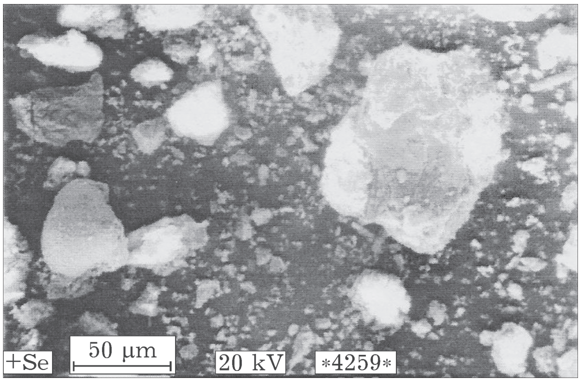

Fig. 2. SEM image of coal fly ash.

the main crystalline phases detected by XRD are α-quartz, anhydrite, calcite, portlandite, lime, kyanite and clayey minerals – illite and montmorillonite. Mean particle diameter is 29.18 μm and specific surface area is 5 m^2/g. Morphology of coal fly ash particles is shown in Fig. 2.

The increase in values of the mean particle diameter (d_m = 26.8 μm) and decrease in specific surface area (S_{BET} = 3.52 m^2/g) after 2 h milling of mixture, compared to the starting mixture (d_m = 20 μm, S_{BET} = 10.8 m^2/g), is observed. It is related to an aggregation of primary particles into agglomerates at high-energy milling under dry conditions. Detailed characterization of particle size distribution and morphology of agglomerates in milled mixture is published in [13].

Milling products of coal fly ash/portlandite mixture

A rapid gradual diminishing and disappearance of the XRD intensity of reflections corresponding to initial crystalline phases of quartz, calcite, portlandite, anhydrite and kyanite was observed after milling for 2 h. Residual weak reflections of quartz, portlandite and illite ($P_{100}/93$, $Q_{100}/87$, $K_{100}/44$) in milled mixture were remarked (Fig. 3). As it was shown in [11], it relates to the crystallite size reduction, introduction of lattice microstrains and/or the amorphization of the reacting components. In the case of calcite and portlandite, the decrease in XRD peak intensity is connected with mechanochemical decomposition of those two substances. A rapid decrease in absorption band intensity around 870 and 3640 cm^{-1} attributed to stretching vibration of OH^- group during milling also confirms mechanochemical dehydration of portlandite (Fig. 4). The broad band centred at 3400 cm^{-1} is responsible for valence vibration of water molecules released during mechanochemical dehydration and their adsorption on surface products.

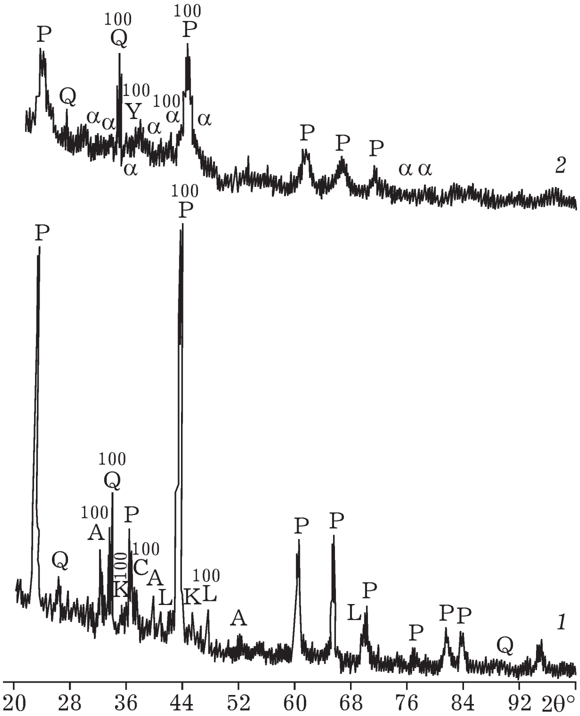

Fig. 3. XRD patterns of starting (*1*) and 2 h milled (*2*) mixture of coal fly ash/portlandite. C – calcite, Q – quartz, K – kyanite, A – anhydrite, L – lime, P – portlandite, α – bredigite.

Amorphization of the main reacting silicon and calcium oxide and the formation of tight contacts between particles during high-energy milling greatly facilitate the successive nucleation of two new nanocrystalline phases of dicalcium silicates (α-C_2S, bregidite, and β-C_2S, larnite) of peak intensity ($\alpha_{100}/51$, $\beta_{100}/36$). The presence of formed silicates in milled mixture is confirmed by the oxygen-related absorption bands in the regions of 800–1200 and 460–470 cm^{-1} on IR spectra (see Fig. 4). The absorption bands that appeared at 1000 and 960–970 cm^{-1} can be assigned to the mechanosynthesized hydrated calcium silicates (CSH gel and α-C_2HS) with a very low degree of ordering in accordance with [5].

Absorption band of low intensity observed at 800 cm^{-1}, attributed to Si–O symmetric valence vibration, belongs to unreacted amount of amorphous silica.

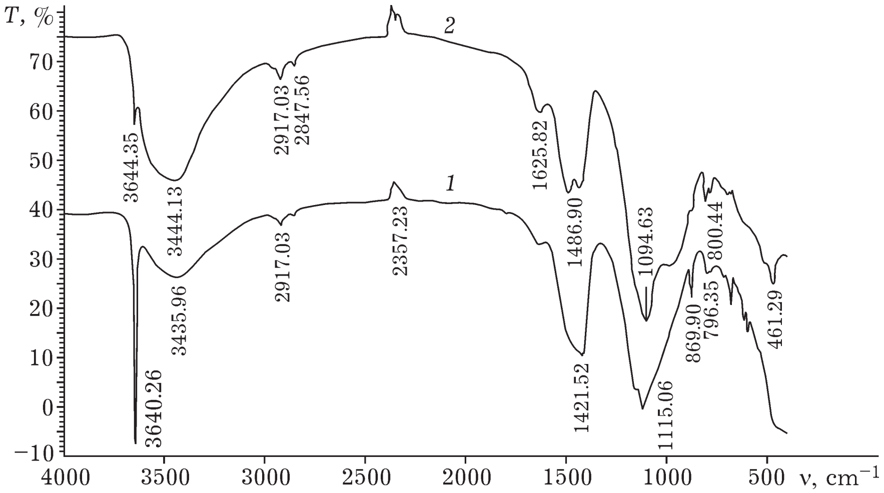

Fig. 4. IR spectra of starting (*1*) and 2 h milled (*2*) mixture of coal fly ash/portlandite.

The bands at 1500–1400 cm^{-1} with two maxima at 1487 and 1420 cm^{-1}, and 870 cm^{-1} can be attributed to carbonates formed during milling and handling of mixtures.

Calcination products

Both the starting and milled coal fly ash/portlandite mixture containing the precursors phases formed during mechanochemical activation were heated at temperature ranging from 600 to 1200 °C. The changes in XRD intensities of selected initial crystalline phases of starting mixture and evolution of silicates and aluminosilicate phases *vs.* increasing temperature can be seen in Fig. 5. The α- and β-C_2S and C_2AS are the dominant phases at all temperatures during the subsequent thermal treatment of milled mixture whereas these phases are created in starting mixture at a temperature of 1200 °C.

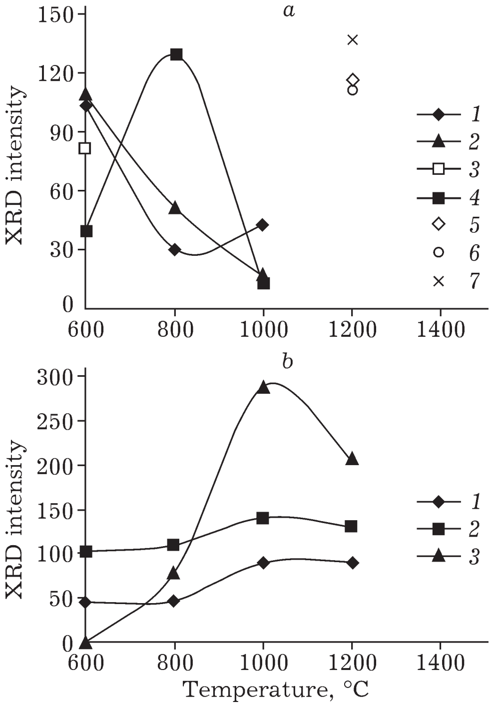

Fig. 5. Changes in XRD intensities of selected initial crystalline phases and of new formed phases in starting (*a*) and milled coal fly ash/portlandite mixture (*b*) *vs.* temperature: *a* – lime (*1*), quartz (*2*), portlandite (*3*), calcite (*4*), α-C_2S (*5*), β-C_2S (*6*), gehlenite (*7*); *b* – α-C_2S (*1*), β-C_2S (*2*), gehlenite (*3*).

Controlled heating of milled mixture results in the formation of belite phase and gehlenite at lower temperature (600 °C) in comparison with the formation of these crystalline phases from starting mixture (1200 °C). Preferential crystallization of β-C_2S was observed in samples of milled mixture during heating at lower temperatures up to 1000 °C. Based on the thermogravimetric and literature data [4, 14, 15], it can be explained by dehydration of α-C_2HS mechanosynthesized cement precursors completed under 600 °C and their subsequent crystallization to β-C_2S. The same C_2S phase content at temperatures of 600 and 1200 °C is reached in milled and starting mixture, respectively. Based on the cementation index value (CI) of the milled mixture calcinated at 900 °C (CI = 1.4), the degree of hydraulicity of this mixture corresponds to that of natural cements [16]. Both free lime and gehlenite are not desirable.

CONCLUSIONS

In this paper, the possibilities of belite phase from fluidised coal fly ash and portlandite (Ca/Si = 2) during 2 h high-energy milling of mixture and subsequent heating of both starting and milled ones are studied. The following conclusions were reached:

1. The formation of CSH and α-C_2HS gels with low degree of ordering as C_2S precursors, α- and β-C_2S crystalline phases was confirmed by IR spectroscopy and XRD analysis.

2. Complete solid-state synthesis of cements related to C_2S in milled mixture takes place at lower temperature, compared to non-milled starting mixture.

3. Based on the estimated cementation index and larnite presence as major hydraulic phase in calcinated product of 2 h milled coal fly ash/portlandite mixture, the used fly ash is appropriate material for belite cement production by mechanochemical procedure in combination with thermal treatment for construction applications with emphasis in restoration and conservation works.

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REFERENCES

1 A. K. Charterjee, *Cem. Concr. Res.*, 26 (1996) 1213.

2 W. Jiang and D. M. Roy, *Ceram. Bull.*, 71 (1992) 642.

3 W. Ma and P. W. Brown, *Cem. Concr. Res.*, 27 (1997) 1237.

4 S. Goni, A. Guerrero, M. P. Luxán and A. Macias, *Mat. Res. Bull.*, 35 (2000) 1333.

5 S. Goni, A. Guerrero, M. P. Luxán and A. Macias, *Cem. Concr. Res.*, 33 (2003) 1399.

6 A. Öztük, R. Suyadal and H. Oguz, *Ibid.*, 30 (2000) 967.

7 F. A. Rodrigues and P. I. M. Monteiro, *J. Mat. Sci. Lett.*, 18 (1999) 1551.

8 A. Guerrero, S. Goni, I. Campillo and A. Moragues, *Environ. Sci. Technol.*, 38 (2004) 3209.

9 V. V. Boldyrev, *Rus. Chem. Rev.*, 75 (2006) 177.

10 N. Števulová and A. Mezencevová, *Chem. Listy*, 97 (2003) 872.

11 N. Števulová and A. Mezencevová, in: Proc. 16th Int. Congr. of Chemical and Process Engineering CHISA´ 2004, ECED, Prague, 2004.

12 E. G. Avvakumov, M. Senna and N. Kosova, Soft Mechanochemical Synthesis: a Basis for New Chemical Technologies, Kluwer Academic, Boston, 2001.

13 N. Števulová, M. Bálintová, J. Briančin and Z. Széghyová, *Chem. Listy*, 99 (2005) 420.

14 H. Ishida, S. Yamazaki, K. Sasaki *et al.*, *J. Am. Ceram. Soc.*, 76 (1993) 1707.

15 M. M. Komljenovič, B. M. Živanovič and A. Rosič, in: Proc. 10th Int. Congr. of the Chemistry of Cement, Göteborg, vol. 1, 1997.

16 R. S. Boynton, Chemistry and Technology of Lime and Limestone, Wiley, New York, 1980.