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Stabilization of the fly ash emission after the combustion of black coal by the reaction with H_2O and CO_2: The temperature and pressure conditions and time duration of artificial carbonatization in the experimental study

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Abstract

The experimental study of artificial carbonatization parameters – temperature, pressure and duration of the reaction of CO_2 with the captured fly ash, being an alkaline residue after the combustion of the black (hard) coal in the thermal power plant, has contributed to stabilization of the piled fly ash, forming calcite and aragonite as the main results of its artificial carbonatization. The liquid mixture (H_2O + CO_2) most effectively reacted with the fly ash at the temperature 22 °C and pressure 5 MPa. The optimal duration of reaction was 2 hours.

The results of experimental study show that components of the fly ash caught by electrostatic separators can be forced to react with CO_2 and to form new carbonates based on $CaCO_3$. During carbonatization process the anhydrite and Ca-rich amorphous phase as the fly ash components were changed to calcite and bassanite. By this way formed carbonates can stabilize the fly ash and to minimize an environmental risk of the waste dumps. Because no additional heat input for the reaction is required, it supports the industrial application of this quick and less energy demanding process of the CO_2 bonding on Ca-rich components of the fly ash. The artificial carbonatization contributes to lowering of the amount of both environmental loads – CO_2 and caught fly ash simultaneously, producing stable carbonates inside the dust. The newly formed carbonates are environmentally friendly and eventually can be further used in the industry, substituting natural ones. Moreover, the necessary amount of CO_2 for the artificial carbonatization can be obtained from the industrial process, producing gas emissions.

Key words: fly ash, CO_2, carbonation, carbonatization, carbonates, optimized reaction, environmental protection

Introduction

Up to 60 % of the CO_2 emissions are produced by the large stationary sources like the heating and power plants, iron and steel plants, refineries and further industrial facilities. Coal is the world´s most abundant and widely used fossil fuel, supplying over one third of the world´s electricity and 23 % of the global primary energy needs (Santosh et al., 2009). It is known that app. 1 kg of CO_2 gets emitted into the environment after the generation of 1 kWh of electrical energy from the coal thermal power plants (Chel, 2009). Besides the gas exhalates containing 5 – 15 vol.% of CO_2, the heating and power plants produce the dumps of fly ash as an additional environmental load.

The environmentally friendly stabilization and/or liquidation of the fly ash as an alkaline residue after the coal combustion is a world-wide problem, too. Being used in the minor amount in the industry of building materials, in road building and geotechnics (Uliasz-Bochenczyk and Mokrzycki, 2006; Uliasz-Bochenczyk and Piotrowski, 2009; Uliasz-Bochenczyk and Cempa, 2010), it mostly requires further processing. Especially, the fly ash with a high-unburned-carbon content represents an increasing problem in quantities produced by the thermal power plants, since it cannot be marketed as a cement extender and, therefore, has to be disposed (Maroto-Valer et al., 2008). The direct further utilization of the fly ash deposited on the dumps is not possible, because its particular types differ by the chemical and mineralogical composition, grain-size, as well as the amount of combustible carbon. Another negative factor of the deposited fly ash is the harmful leachability of the chemical impurities present in the fly ash dumps, e.g. Zn, Cu, Pb, Ni, As, Hg, Cd, Cr, P, Cl, S, SO_4^{2-} from the ash-aqueous suspensions being formed by the rainfalls (l.c.; Uliasz-Bochenczyk, 2010).

Our research aimed to reveal the optimum reaction parameters for the CO_2 most effective reaction with the fly ash produced in the energetic-heating industry, being

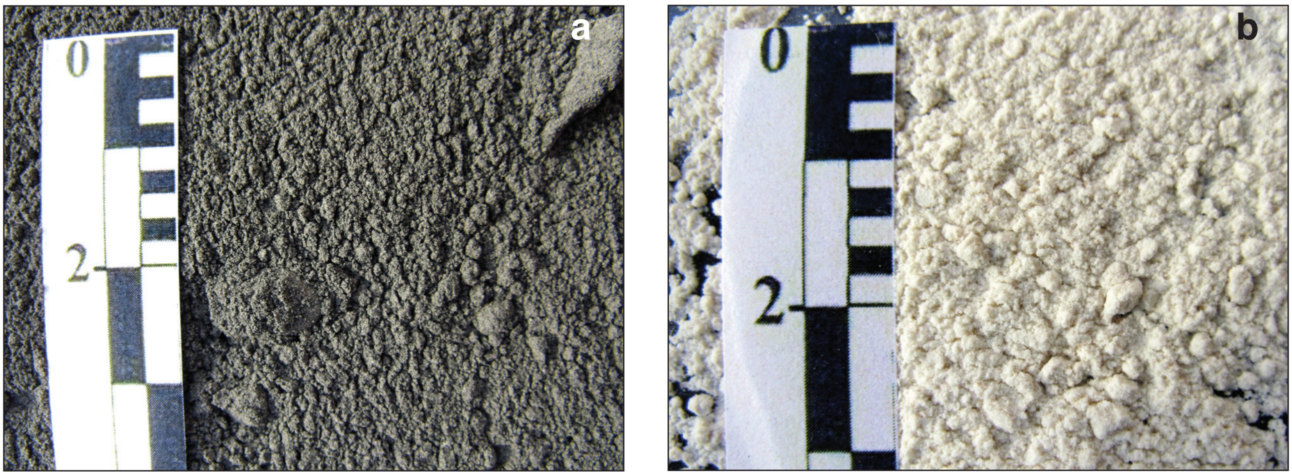

Fig. 1. a – The sample P of the fly ash produced during the black coal combustion and being caught from the fume gases by the electrostatic separator. **b** – Carbonate product P6 produced by the carbonatization and crystallization from the filtrate of the sample P. In both cases the numbered scale is in cm.

captured by an electrostatic separator and deposited on the dumps. The tested fly ash is characterized by the precisely determined mineralogical, chemical and grain-size parameters (Tabs. 1 and 2). By this way both environmental loads would be minimized simultaneously resulting in the origin of the stable carbonates with fixed bound of CO_2 in their lattice.

The carbonatization of silicates in natural conditions is very slow process, and its acceleration requires technological optimizing of principal parameters affecting the reactivity of mineral compounds with CO_2. Following the request of the European Union, until the year 2020 the industrial plants will be obliged to lower their CO_2 emissions by 20 % in comparison to the state in 1990. The optimized methodology, being presented in this article, could be applied for projecting of the technological schemes and realization projects in the model and industrial scales.

Experimental research

The rate of the CO_2 bonding into appropriate substances and formation of the stable products is dependent on mineral and chemical composition of input medium, on activity of its components and purity of CO_2. The next important influencing factors are the granularity and porosity of reacting substances, the activity of their specific surface, the mutual ratio of the solid, liquid and gaseous phases, temperature, CO_2 pressure and the duration of reaction. The conversion is supported by the primary mechanical, thermal, chemical, or physical activation of entering compounds, the pH value of the reacting environment and types of applied agents (additives, reagents, etc.). Regarding the density, resp. viscosity of reacting suspension, the static or dynamic reaction conditions can be alternatively applied. Therefore optimizing of the reaction parameters consisted of identification methods of the input sample and output products and the reactions in the laboratory high pressure reactor at various combinations of the temperature/pressure/time parameters.

The dry fly ash sample P (Fig. 1a) in a total weight 15 kg was taken from the separating device of the fume gases. Despite a low content of CaO in the input sample (1.59 wt.%), being accompanied with the MgO (0.60 wt.%) and FeO (0.58 wt.%), the input sample P was used in reactions in its primary state, i.e. without any further modification or activation – either mechanic, or chemical (cf. Zhang et al., 2004; Arenillas et al., 2005; Lee and Jo, 2008; Majchrzak-Kuceba and Nowak, 2009; Olivares-Marin et al., 2010), or thermal modification (cf. Maroto-Valer et al., 2008). The chemical composition (wt.%) of the primary sample, as well as its grain-composition were determined using 10 sieves (2, 1, 0.5, 0.315, 0.2, 0.1, 0.071, 0.063, 0.045 and 0.02 mm).

The laboratory testing and optimizing of the CO_2 reaction with captured fly ash was done by means of the high pressure reactor PARR 4540 at combinations of three CO_2 pressures (2.5; 5.0 and 7.5 MPa), three temperatures of the reacting environment (22, 35 and 50 °C) and four reaction times (1, 2, 3 and 6 hours). Into the reactor the water suspension of the fly ash with concentration $152\ g \cdot l^{-1}$ was inputted. The dynamic conditions of the reactions of Ca, Mg, resp. Fe components with CO_2 in suspensions were provided by its continual stirring at 300 rpm.

The output products of the CO_2 carbonatization from the high-pressure reactor were tested undivided, as well as divided by the filtration to filtration cakes and filtrates and both compounds were dried at 200 °C.

The input sample, as well as the output products after carbonation, filtration and crystallization were identified by chemical, X-ray and microprobe analyses, targeted on bonding parameters of CO_2 in the originated solid products. Experimental works with the high pressure reactor and all laboratory procedures were performed in the State Geological Institute of Dionýz Štúr (ŠGÚDŠ), laboratories of the Applied Technology of Raw Minerals (ATNS) in Košice. Chemical analyses were performed in the ŠGÚDŠ – Geoanalytical Laboratories (GAL) in Spišská Nová Ves. The content of CO_2 was determined

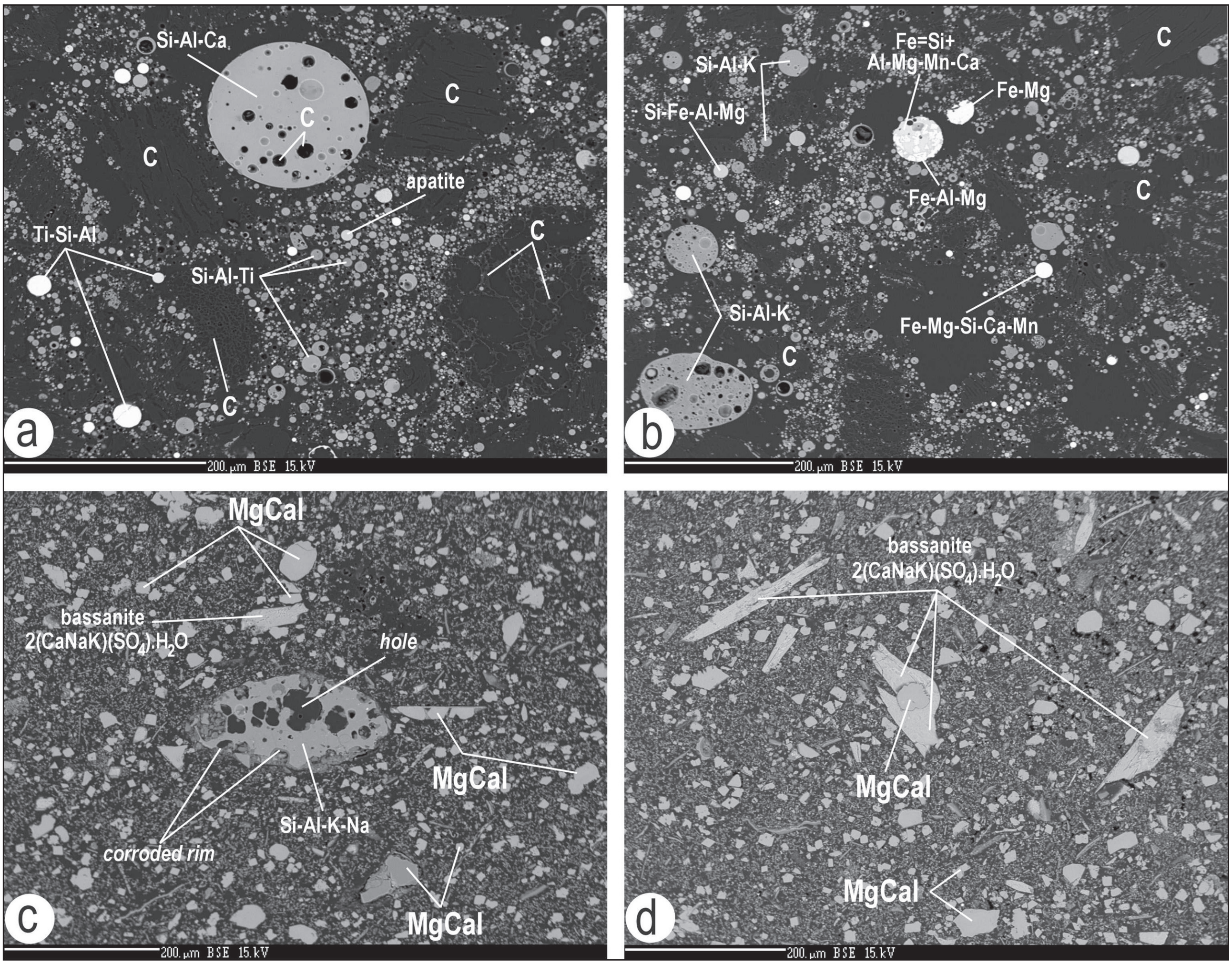

Fig. 2. a – The input fly ash sample P contains the relics of the silicate melt of spheroidal shape, as well as relics of apatite and carbon (C). Elements in the melt relics or in amorphous phases, e.g. Ti-Si-Al are ordered according to the decreasing amount of oxides TiO_2-SiO_2-Al_2O_3 reaching more than 10 wt.%. **b** and **c** – Unreacted relics of the solidified melt – amorphous phases of various chemical composition and the position of carbon-relicts after artificial carbonatization in the filtration cake – contain amorphous phase, e.g. Fe = Si + Al-Mg-Ca. Contents e.g. Al-Mg-Ca are ordered according to the lowered amounts of present elements. The CaO-rich amorphous phase is corroded by the mixture of H_2O and CO_2 and the deliberated Ca from the corroded rim enters to the solution and it is the base cation for crystallization of $CaCO_3$ according to reaction (1). MgCal – Mg-rich calcite and bassanite are product of artifical carbonatization and were caught in the filtration cake – sample P5. **d** – Mg calcite and bassanite as the products of the artificial carbonatization in the sample of precipitate P6. Backscattered electron images.

by the high temperature oxidation and manometry, CaO and MgO were determined by the X-ray fluorescence spectroscopy and FeO volumetric analysis, and the loss by ignition by the gravimetric method. For the computerized X-ray diffraction analyses done in the ŠGÚDŠ – ATNS laboratories the facility DRON – UM 1 with the detection sensitivity of ca 3 % was used at following conditions: radiation CoK_{α}, Fe-filter, accelerating voltage 30 kV, current intensity 20 mA, time constant T – 2, apertures 2 – 2 and 1 – 0.25, shift of the goniometer arm 2°/min. The semiquantitative and quantitative mineral compositions in the primary sample and carbonation products were determined by the combination of X-ray diffraction using a method of outer standard and mineralogical recomputation from the chemical analyses.

The carbonation products and unreacted residues (filter cakes) were studied by means of the optical microscope and the microprobe Cameca SX 100 in the ŠGÚDŠ Bratislava. The standards used: Ca – wollastonite, Mn – rodonite, Na – albite, K – orthoclase, Cr – chromite. Synthetic compounds were used for determining of Ti, Al, Fe, Mg and BaF_2 for determining of F. The analytic parameters were 15 kV and the beam intensity 5 nA when analysing the carbonates or 20 nA at analysis of silicates and amorphous phases. Analysed area of silicates in the diameter 1 – 7 µm changed in the dependence on the size of mineral or investigated object in thin section. Acid carbonates and carbonates were analysed at 7 – 20 µm. The sensing time for one element was 10 s or 25 s for F. Detection limit for particular elements was lower than 0.05 wt.%, with error ±1-sigma.

Results and discussion

Input sample of the fly ash

The fine-grained fly ash (sample P; Fig. 1a) before artificial carbonation contained 98.3 vol.% of amorphous phase, carbon and minor content of apatite and anhydrite. The maximum calcite-aragonite content was 1.7 wt.%. The amorphous phase of the silicate melt had an oval shape and enclosed relics of carbon, being present also in the matrix of the input sample together with the apatite (Fig. 2a). The spheroidal amorphous silicates in the fly ash indicate the quick cooling of the melt in the fume flying from the combustion chamber towards the electrostatic separators. The amorphous phases have variable contents of SiO_2 (wt.%), Al_2O_3, CaO, FeO, MgO, K_2O, TiO_2 and their chemical composition (p.f.u.) varies among Si-Al-Ca, Si-Al-Ti and Ti-Si-Al. The content of $(OH)^-$ or H_2O in amorphous phases ranges from 1.94 wt.% to 3.89 %.

The chemical and mineral composition of the input captured fly ash sample P are in Tab. 1 and its wet grain-size analysis is in Tab. 2. The very fine-grained sample consists of the prevailing amorphous alumosilicate, silicate and organic phases (in total 98.3 wt.%). The grain-size beneath 1 mm was very high (more than 99.97 %), and even beneath 0.02 mm it reached nearly 50 % (48.35 %). Input pH of the fly ash suspension was 7.0. The precise knowledge of mineralogical, chemical and grain-size parameters of the captured fly ash represents an important input information (Tabs. 1 and 2).

Experimental study and optimizing of the parameters for the carbonate origin by the reaction of captured fly ash with CO_2

The technological parameters of the laboratory tests of CO_2 carbonatization by means of the fly ash sample P (Fig. 1a) are in Tabs. 3 – 7, which unambiguously prove the origin of new carbonate minerals – prevailingly calcite + aragonite (Fig. 1b) from the filtrates, having the carbonate purity in the range from 43.9 to 56.6 wt.% $CaCO_3$. The increase of the weight yields of precipitated products in relation to input sample was in the range from 0.54 to 0.92 %. To demonstrate the origin of carbonates during the first six tests (P1, P4, P7, P10, P13 and P16), the filtration cakes and the precipitates were analysed separately (Tab. 4). Further reactions (P19-P48; Tabs. 3 and 5 – 7) aimed to optimize parameters of the most effective carbonation, and therefore only the undivided products of the reactions at alternating three different temperatures 22, 35 and 50 °C, three different pressure conditions 2.5, 5.0 and 7.5 MPa and 1, 2, 3 and 6 hours durations of reactions were analysed. The qualitative mineral compositions of the fly ash sample and its carbonatized products confirmed by the X-ray diffraction analysis are presented in Tabs. 5 – 7.

The new calcite with the content of $MgCO_3$ molecule has originated from the Ca and Mg cations, being deliberated into suspension from the amorphous phase containing CaO and MgO. The bassanite represents a coexisting and accompanying newly crystallized mineral with calcite. Comparing the input CO_2 balance of 0.76 wt.% in the sample P, and the CO_2 contents in the newly formed carbonatic precipitates min. 19.3 and max. 24.9 wt.% (products of the reactions P6 and P9), the CO_2 is bound (liquidated) in the newly-originated carbonates by 18.54 to 24.14 wt.%, depending on the reaction conditions.

The testing done at laboratory temperature 22 °C in the solution $H_2O + CO_2$ in the above stated alternating pressure and time parameters is presented in Tabs. 4 and 5. The amorphous phases in the input sample P and the amorphous phases of the sample P5 in the diagram Si+Ti vs. Fe(total)+S+Ca+K+Na+Mn+P+Al indicate a direct substitution trend with an immiscibility gap (Fig. 3). The immiscibility gap in the glass or in a solid solution indicates that there originated a phase with a pseudoordered crystalline lattice (Figs. 2a – c and 3). The relics of amorphous phases were distinguished in two modes: not hydrated and hydrated (Tab. 8). In the case of hydrated amorphous

Tab. 1
Chemical and mineral composition of the input sample of the fly ash P

Chemical composition (wt.%)	
SiO_2	29.90
CaO	1.59
MgO	0.60
FeO	0.58
CO_2	0.76
Al_2O_3	13.30
Fe_2O_3	5.84
SO_3	–
Loss by ignition	46.00
TC	44.40
TOC	44.20
Mineral composition (wt.%)	
calcite + aragonite	1.70
Amorphous phase	98.30
quartz	+
mullite	+

Tab. 2
The wet grain-size analysis of the fly ash sample P

Grain size (mm)	Weight yield (%)		
	Classes	Total residue on the sieve	Through the sieve
1.0 – 2.0	0.03	0.03	99.97
0.5 – 1.0	0.12	0.15	99.85
0.315 – 0.5	0.03	0.18	99.82
0.2 – 0.315	1.73	**1.91**	**98.09**
0.1 – 0.2	20.86	22.77	77.23
0.071 – 0.1	11.25	34.02	65.98
0.063 – 0.071	3.49	37.51	62.49
0.045 – 0.063	5.82	43.33	56.67
0.02 – 0.045	8.32	51.65	48.35
–0.02	48.35	–	–
Total	100.00	–	–

Tab. 3
Qualitative mineral compositions of the fly ash sample and its carbonatized products found by the X-ray diffraction analyses

Sample	Product	Mineral composition (wt.%)
P	Input	Amorphous phase, quartz, mullite?
P1	Undivided product	Amorphous phase, quartz, maghemite?
P2	Filtration cake of P1	Amorphous phase, quartz, maghemite, mullite?
P3	Precipitate of P1	Calcite, siderite?, amorphous phase
P4	Undivided product	Amorphous phase, quartz, maghemite
P5	Filtration cake of P4	Amorphous phase, quartz, maghemite
P6	Precipitate of P4	Calcite, bassanite, amorphous phase
P7	Undivided product	Amorphous phase, quartz, maghemite
P8	Filtration cake of P7	Amorphous phase, quartz
P9	Precipitated of P7	Calcite, aragonite, bassanite
P10	Undivided product	Amorphous phase, quartz, mullite, maghemite
P11	Filtration cake of P10	Amorphous phase, quartz, maghemite, mullite?
P12	Precipitate of P10	Calcite, bassanite
P13	Undivided product	Amorphous phase, quartz, maghemite
P14	Filtration cake of P13	Amorphous phase, quartz, maghemite
P15	Precipitate of P13	Calcite, bassanite
P16	Undivided product	Amorphous phase, maghemite
P17	Filtration cake of P16	Amorphous phase, quartz, maghemite
P18	Precipitate of P16	Calcite, aragonite, bassanite
P19	Undivided product	Calcite, amorphous phase, quartz, maghemite
P20-P21	Undivided products	Amorphous phase, quartz, maghemite
P22	Undivided product	Amorphous phase
P23	Undivided product	Amorphous phase, quartz, maghemite
P24	Undivided product	Amorphous phase, quartz, mullite, maghemite
P25	Undivided product	Amorphous phase, quartz, maghemite
P26	Undivided product	Amorphous phase, quartz, mullite, hematite, maghemite
P27	Undivided product	Amorphous phase, quartz, mullite, maghemite
P28	Undivided product	Amorphous phase, quartz, mullite, hematite, maghemite
P29	Undivided product	Amorphous phase, quartz, mullite, maghemite
P30	Undivided product	Amorphous phase, quartz, mullite, maghemite
P31	Undivided product	Amorphous phase, quartz, mullite
P32-P37	Undivided products	Amorphous phase, quartz, mullite, maghemite
P38	Undivided product	Amorphous phase
P39	Undivided product	Amorphous phase, quartz, mullite, maghemite
P40	Undivided product	Amorphous phase, quartz
P41	Undivided product	Amorphous phase, quartz, mullite, maghemite
P42-P43	Undivided products	Amorphous phase, quartz, maghemite
P44-P45	Undivided products	Amorphous phase, quartz, hematite?, maghemite
P46	Undivided product	Amorphous phase, quartz, maghemite
P47	Undivided product	Amorphous phase, quartz, hematite, maghemite
P48	Undivided product	Amorphous phase, quartz, maghemite

Amorphous phase is formed by Si-Al-... (silicate phase) and Si (quartzy phase)

phase the content of chemically bound water and/or in OH^- group was in the range from 2.06 to 2.41 wt.% (amount of water was estimated as 100 – total in Tab. 8, corresponding to the water content or OH groups in the input sample of the fly ash P (from 1.94 wt.% to 3.89 %).

The product of an artificial carbonatization of the fly ash (P6; Fig. 1b) consists of a mixture of calcite containing $MgCO_3$ molecule and bassanite (Figs. 4, 2c – d). Allotriomorphic grains of Mg calcite are rimmed by bassanite, showing that Mg calcite has crystallized before the bassanite (Fig. 2d). The relation of Mg calcite and bassanite indicates that the crystallization of these minerals has progresses in two stages. Firstly the Mg calcite has crystallized, which Ca and Mg cations were deliberated into the suspension from the amorphous phase with CaO and MgO contents. Later bassanite has continually crystallized, probably originating by the hydratation of anhydrite according to reaction:

$$\underset{\text{Anhydrite}}{CaSO_4} + \underset{\text{Component in amorphous phase}}{CaO} + H_2O + CO_2 \overset{\text{5 MPa, 22 °C, 1 hour}}{====>} \underset{\text{Calcite}}{CaCO_3} + \underset{\text{Bassanite}}{CaSO_4 \cdot H_2O} \tag{1}$$

Tab. 4

Laboratory tests of CO_2 reaction with the fly ash sample at temperature **22 °C**, CO_2 pressures 2.5, 5.0, 7.5 MPa and duration of reaction 1 and 2 hours. Table summarizes the results of the first step of our research – proving the origin of carbonates and expressing their amount in wt.%

Sample	Pressure of CO_2 (MPa)	Duration or reaction with CO_2 (Hour)	Product	Gain weight yield (%)	Chemical composition (wt.%)					Mineral composition (wt.%)				
					CaO	MgO	FeO	Loss by ign.	CO_2	Calcite + aragonite	Amorphous phase + minor bassanite	Quartz	Mullite	Maghemite
P		Input		–	1.59	0.60	0.58	46.0	0.76	1.7	98.3	+	+	
P2	2.5	1	Filtration cake	–	1.20	0.53	0.87	50.6	3.30	7.5	92.5	+	+	+
P3			Precipitate	**+0.54**					20.6	46.8	53.2			
P5	5.0	1	Filtration cake	–	1.22	0.56	0.73	47.8	3.39	7.7	92.3	+		+
P6			Precipitate	**+0.92**					19.3	**43.9**	56.1			
P8	7.5	1	Filtration cake	–	1.27	0.57	0.58	46.0	3.50	8.0	92.0	+		
P9			Precipitate	+0.80					24.9	**56.6**	43.4			
P11	2.5	2	Filtration cake	–	1.20	0.55	0.44	48.3	3.61	8.2	91.8	+	+	+
P12			Precipitate	+0.76					21.9	49.8	50.2			
P14	5.0	2	Filtration cake	–	1.13	0.54	0.58	51.2	3.90	8.9	91.1	+		+
P15			Precipitate	+0.88					21.7	49.3	50.7			
P17	7.5	2	Filtration cake	–	1.20	0.53	0.58	47.0	3.71	8.4	91.6	+		+
P18			Precipitate	+0.82					23.1	52.5	47.5			

Amorphous phase is formed by the amorphous phase Si-Al-... (alumosilicate), amorphous phase Si (silicate) and organic amorphous phase (TOC). Composition of input sample P is 29.9 % SiO_2; 13.3 % Al_2O_3; 5.84 % $Fe_2O_{3\ tot.}$; 44.4 % TC (total carbon) and 44.2 % TOC (total organic carbon). + accessoric amount of mineral phases. **Samples P 2, 5, 8, 11, 14, 17 represent filtration cakes, samples P 3, 6, 9, 12, 15, 18 represent precipitated carbonates from filtrates. This table represents a detailed information from the Tab. 3 – the undivided sample P1 was separately studied as P2 (cake) and P3 (filtrate), P4 was studied as P5 (cake) and P6 (filtrate), P7 as P8 (cake) and P9 (filtrate), etc. to P16 as P17 (cake) and P18 (filtrate). Further samples P19-P48 were tested as undivided and the research aimed to optimize reaction parameters.**

Tab. 5

Laboratory tests of CO_2 reaction with the fly ash at temperature **22 °C,** CO_2 pressure 2.5, 5.0 and 7.5 MPa and 1, 2, 3 and 6 hours durations of reactions with CO_2

Sample	Pressure CO_2 (MPa)	Duration of reaction with CO_2 (hour)	Gain weight yield (%)	Chemical composition (wt.%)					Mineral composition (wt.%)				
				CaO	MgO	FeO	Loss by ign.	CO_2	Calcite + aragonite	Amorphous phase	Quartz	Mullite	Maghemite
P	input	–	–	1.59	0.60	0.58	46.0	0.76	1.7	98.3	+	+	
P1	2.5	1	+0.34	1.67	0.64	0.87	49.2	3.06	7.0	93.0	+		+
P4	5.0	1	+0.64	1.75	0.64	0.29	45.7	3.54	8.0	92.0	+		+
P7	7.5	1	+0.50	1.64	0.59	0.58	48.1	2.58	5.9	94.1	+		+
P10	2.5	2	+0.42	1.61	0.60	0.81	47.7	3.60	8.2	91.8	+	+	+
P13	5.0	2	+0.70	1.69	0.63	0.44	46.7	4.32	9.8	90.2	+		+
P16	7.5	2	+0.54	1.69	0.57	0.44	45.4	4.82	10.9	89.1			+
P19	2.5	3	+0.36	1.66	0.59	0.58	45.9	3.20	7.3	92.7	+		+
P20	5.0	3	+0.52	1.55	0.58	0.73	48.6	2.68	6.1	93.9	+		+
P21	7.5	3	+0.34	1.67	0.60	0.58	47.3	2.81	6.4	93.6	+		+
P22	2.5	6	+0.54	1.60	0.61	0.29	48.9	2.57	5.8	94.2			
P23	5.0	6	+0.44	1.66	0.56	0.29	47.8	2.52	5.7	94.3	+		+
P24	7.5	6	+0.46	1.66	0.57	0.29	49.5	3.93	8.9	91.1	+	+	+

Note: Amorphous phase is formed by Si-Al-... amorphous phase (alumosilicate type), Si amorphous phase (silicate) and organic amorphous phase (TOC). In the input sample P we have further analysed: 29.9 % SiO_2; 13.3 % Al_2O_3; 5.84 % $Fe_2O_{3\ tot.}$; 44.4 % TC (total carbon) and 44.2 % TOC (total organic carbon). + accessoric content of mineral phases. Samples represent undivided reaction products.

Tab. 6

Laboratory tests of CO_2 reaction with the fly ash at temperature **35 °C**, CO_2 pressures 2.5, 5.0 and 7.5 MPa and duration of reactions 1, 2, 3 and 6 hours

Sample	Pressure CO_2 (MPa)	Duration of reaction with CO_2 (hour)	Gain weight yield (%)	Chemical composition (wt.%)					Mineral composition (wt.%)				
				CaO	MgO	FeO	Loss by ign.	CO_2	Calcite + aragonite	Amorphous phase	Quartz	Mullite	Maghemite (Hematite?)
P	input	–	–	1.59	0.60	0.58	46.0	0.76	1.7	98.3	+	+	
P25	2.5	1	+0.24	1.59	0.58	0.58	46.8	3.46	7.9	92.1	+		+
P26	5.0	1	+0.38	1.60	0.63	0.58	46.6	3.71	8.4	91.6	+	+	+ ?
P27	7.5	1	+0.26	1.56	0.60	0.58	45.2	3.06	7.0	93.0	+	+	+
P28	2.5	2	+0.28	1.63	0.66	0.44	45.2	4.30	9.8	90.2	+	+	+ ?
P29	5.0	2	+0.34	1.56	0.57	0.44	47.7	4.32	9.8	90.2	+	+	+
P30	7.5	2	+0.32	1.52	0.59	0.58	48.5	4.93	11.2	88.8	+		+
P31	2.5	3	+0.44	1.64	0.62	0.44	46.8	3.95	9.0	91.0	+	+	
P32	5.0	3	+0.58	1.69	0.68	0.87	45.2	4.86	11.0	89.0	+	+	+
P33	7.5	3	+0.48	1.62	0.60	0.58	48.4	3.42	7.8	92.2	+	+	+
P34	2.5	6	+0.40	1.68	0.64	0.44	45.8	4.21	9.6	90.4	+	+	+
P35	5.0	6	+0.42	1.60	0.68	0.67	45.8	3.82	8.7	91.3	+	+	+
P36	7.5	6	+0.42	1.77	0.62	0.44	44.1	3.93	8.9	91.1	+	+	+

Note: Amorphous phase is formed by Si-Al-... amorphous phase (alumosilicate type), Si amorphous phase (silicate) and organic amorphous phase (TOC). In the input sample P we have further analysed: 29.9 % SiO_2; 13.3 % Al_2O_3; 5.84 % $Fe_2O_{3\ tot.}$; 44.4% TC (total carbon) and 44.2 % TOC (total organic carbon). + accessoric content of mineral phases. Samples represent undivided reaction products.

Tab. 7
Laboratory tests of CO_2 reaction with the fly ash sample at temperature **50 °C** and CO_2 pressures 2.5, 5.0 and 7.5 MPa and duration of reactions 1, 2, 3 and 6 hours

Sample	Pressure CO_2 (MPa)	Duration of reaction with CO_2 (hour)	Gain weight yield (%)	Chemical composition (wt.%) CaO	MgO	FeO	Loss by ign.	CO_2	Mineral composition (wt.%) Calcite + aragonite	Amorphous phase	Quartz	Mullite	Maghemite (Hematite?)
P	input	–	–	1.59	0.60	0.58	46.0	0.76	1.7	98.3	+	+	
P37	2.5	1	+0.24	1.73	0.64	0.73	44.5	4.01	9.1	90.9	+	+	+
P38	5.0	1	+0.26	1.72	0.69	1.22	42.7	2.94	6.7	93.3			
P39	7.5	1	+0.34	1.74	0.63	0.64	44.1	2.02	4.6	95.4	+	+	+
P40	2.5	2	+0.38	1.65	0.63	0.87	48.6	3.38	7.7	92.3	+		
P41	5.0	2	+0.32	1.75	0.76	1.16	45.3	2.55	5.8	94.2	+	+	+
P42	7.5	2	+0.34	1.70	0.66	0.58	44.1	2.32	5.3	94.7	+		+
P43	2.5	3	+0.36	1.70	0.61	0.44	45.6	4.12	9.4	90.6	+		+
P44	5.0	3	+0.38	1.62	0.65	0.87	47.0	3.69	8.4	91.6	+		+ ?
P45	7.5	3	+0.32	1.58	0.60	0.87	49.6	3.65	8.3	91.7	+		+ ?
P46	2.5	6	+0.28	1.68	0.64	0.73	47.7	4.25	9.7	90.3	+		+
P47	5.0	6	+0.44	1.65	0.59	1.16	49.3	3.79	8.6	91.4	+		+ ?
P48	7.5	6	+0.42	1.49	0.51	0.87	51.2	3.72	8.5	91.5	+		+

Note: Amorphous phase is formed by Si-Al-... amorphous phase (alumosilicate type), Si amorphous phase (silicate) and organic amorphous phase (TOC). In the input sample P we have further analysed: 29.9 % SiO_2; 13.3 % Al_2O_3; 5.84 % $Fe_2O_{3\ tot.}$; 44.4 % TC (total carbon) and 44.2 % TOC (total organic carbon). + accessoric content of mineral phases. Samples represent undivided carbonation products.

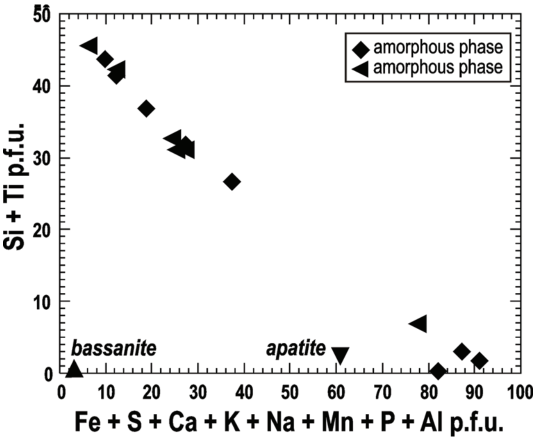

Fig. 3. Relation of the Si+Ti pfu content vs. Fe(total)+S+Ca+K+Na+Mn+P+Al pfu content in the amorphous phase of solidified melt and in bassanite and apatite from the fly ash. Amorphous phase has variable composition. Chemical analyses of amorphous phases are recomputed on O = 100. Samples: P, P5 and P6.

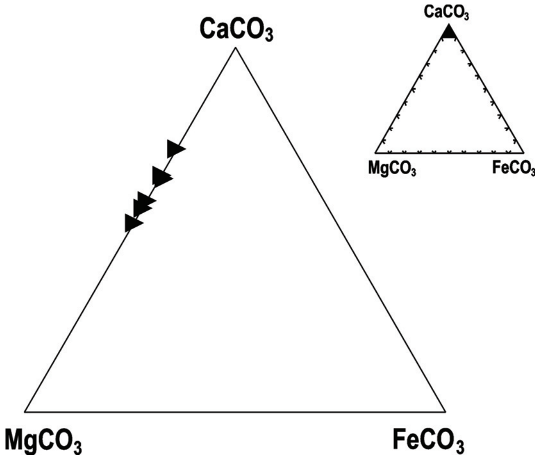

Fig. 4. Chemical classification of calcite with the $MgCO_3$ content in the diagram $MgCO_3$-$FeCO_3$-$CaCO_3$. The originated carbonate is a product of artificial carbonatization of the fly ash after the combustion of the black coal. Sample P6.

Tab. 9
Representative analyses of newly formed Mg-calcite in the precipitate P6

Mineral	MgCal	MgCal
FeO	0.030	0
MnO	0	0
MgO	1.430	1.970
CaO	54.170	53.840
CO_2	44.100	44.410
Sum carb.	99.730	100.220
anion	1.002	1.009
Fe	0	0
Mn	0	0
Mg	0.035	0.048
Ca	0.964	0.951
CO_3	1.002	1.009
$CaCO_3$	96.500	95.200
$MgCO_3$	3.500	4.800
$FeCO_3$	0	0
$MnCO_3$	0	0

Tab. 8
Representative point analyses of amorphous phase in the input sample P and filtration cake P5, as well as bassanite in the precipitate P6

	Input sample					Filtration cake							Precipitate			
Sample	P	P	P	P	P	P-5	P-5	P-5	P-5	P-5	P-5	P-5	P-6	P-6	P-6	P-6
Mineral	Amorph. p	Amorph. p	Amorph. p	Amorph. p	Amorph. p	Amorph. p	Amorph. p	Amorph. p	Amorph. p	Amorph. p	Amorph. p	Amorph. p	Bassanite	Bassanite	Bassanite	Bassanite
F	0	0	0	0.170	0	0	0	0	0	0.030	0.260	0.260	0	0	0	0
Na_2O	0.120	0.070	1.020	0.020	0	0.340	0.570	0.400	0.280	0.030	0	0	2.280	2.050	0.390	2.420
SiO_2	54.980	15.190	53.370	5.840	3.940	76.280	66.710	48.080	84.010	36.070	0.290	1.300	0.020	0.040	0.060	0.590
Al_2O_3	38.510	6.150	30.380	3.620	2.410	15.160	24.090	13.130	11.440	11.700	21.380	1.460	0	0.040	0	0
MgO	0.110	0.340	0.770	3.390	0.090	1.100	0.700	4.130	0.240	3.830	2.970	2.190	0.080	0.040	0.070	0.040
Cl	0	0	0.010	0	0.020	0.010	0.020	0	0	0	0	0	0.010	0	0	0.010
SO_3	0.010	0.030	0.010	0	0.040	0	0	0	0.020	0	0	0	55.030	51.850	54.720	53.290
P_2O_5	0	0.020	0.030	0.190	39.730	0	0	0	0	0	0	0	0	0	0	0
K_2O	0.530	0.740	3.710	0.060	0.050	2.530	3.150	0.790	3.360	0.190	0	0	0.400	0.670	0.080	0.860
CaO	0.140	0.200	0.710	1.200	51.010	0.310	0.510	1.490	0.280	2.180	0.050	0.690	37.760	38.020	39.300	36.790
TiO_2	2.820	72.690	4.510	0.180	0	0.260	0.630	0.390	0.060	0.150	0.070	0.140	0	0.020	0	0
FeO	0.420	1.510	1.530	0	0.720	1.490	1.490	27.540	0.830	0	0	0	0.020	0	0	0.020
MnO	0.010	0.050	0.020	1.490	0.050	0	0.070	0.450	0.090	3.740	1.620	1.830	0	0.080	0.010	0
Cr_2O_3	0.070	0	0.040	0	0	0.010	0	0	0	0.060	0.060	0.040	0	0	0	0
NiO	0	0.040	0	0	0	0.100	0	0	0.010	0	0	0	0.060	0.020	0.050	0
Fe_2O_3	0	0	0	80.160	0	0	0	0	0	41.240	72.570	89.950	0	0	0	0
H_2O	0	0	0	–0.080	–0.010	0	–0.010	0	0	–0.010	–0.120	–0.120	3.900	6.320	3.150	4.160
Total	97.720	97.030	96.110	96.240	98.050	97.590	97.930	96.400	100.620	99.210	99.150	97.740	99.560	99.150	97.830	98.180
O_F_Cl	0	0	0	0.070	0	0	0	0	0	0.010	0.110	0.110	0	0	0	0
O_F	0	0	0	0.070	0	0	0	0	0	0.010	0.110	0.110	0	0	0	0
O_Cl	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0
C_{Total}	97.720	97.030	96.110	96.170	98.050	97.590	97.930	96.400	100.620	99.200	99.040	97.630	99.560	99.150	97.830	98.180
Si	29.957	9.908	30.683	6.740	2.596	41.230	36.569	31.627	43.702	23.881	0.230	1.155	0.001	0.002	0.003	0.028
Al	24.711	4.724	20.569	4.920	1.870	9.650	15.552	10.171	7.008	9.123	19.931	1.528	0	0.002	0	0
Ti	1.156	35.663	1.950	0.156	0	0.106	0.260	0.193	0.023	0.075	0.042	0.094	0	0.001	0	0
Fe_3	0	0	0	0	0	0	0	0	0	20.526	43.185	60.093	0	0	0	0
Fe_2	0.191	0.824	0.736	69.515	0.397	0.674	0.683	15.150	0.361	0	0	0	0.001	0	0	0.001
Cr	0.030	0	0.018	0	0	0.004	0	0	0	0.031	0.038	0.028	0	0	0	0
Mn	0.005	0.028	0.010	1.457	0.028	0	0.033	0.251	0.040	2.097	1.086	1.377	0	0.003	0	0
Mg	0.089	0.331	0.660	5.833	0.088	0.886	0.572	4.050	0.186	3.780	3.505	2.901	0.005	0.003	0.005	0.003
Ca	0.082	0.140	0.437	1.484	36.007	0.180	0.300	1.050	0.156	1.546	0.042	0.657	1.865	1.933	2.004	1.844
Na	0.127	0.089	1.137	0.045	0	0.356	0.606	0.510	0.282	0.039	0	0	0.204	0.189	0.036	0.220
K	0.368	0.616	2.721	0.088	0.042	1.745	2.203	0.663	2.230	0.160	0	0	0.024	0.041	0.005	0.051
P	0	0.011	0.015	0.186	22.160	0	0	0	0	0	0	0	0	0	0	0
S	0.004	0.015	0.004	0	0.020	0	0	0	0.008	0	0	0	1.902	1.844	1.952	1.869
Ni	0	0.021	0	0	0	0.044	0	0	0.004	0	0	0	0.002	0.001	0.002	0
Cations	56.720	52.370	58.940	90.424	63.208	54.875	56.778	63.665	54	61.258	68.059	67.833	4.004	4.019	4.007	4.016
CF	0	0	0	1.241	0	0	0	0	0	0.126	1.302	1.461	0	0	0	0
CCl	0	0	0.019	0	0.045	0.018	0.037	0	0	0	0	0	0.002	0	0	0.002
OH	0	0	–0.010	–0.620	–0.022	–0.009	–0.019	0	0	–0.063	–0.651	–0.731	1.199	2	1	1.299
O	100	100	100	100	100	100	100	100	100	100	100	100	8.300	8.600	8.400	8.300

Data in Tab. 4 confirm that the carbonation of the fly ash sample with subsequent precipitation from the filtrates unambiguously leads to origin of $CaCO_3$ (calcite + aragonite). In the filtration cakes and in undivided products of the carbonation also quartz, mullite, hematite and maghemite occurred in small quantities. The X-ray analysis did not identify the calcite (+aragonite) in the undivided products because they occur in the accessoric to subsidiary amounts, but chemical analyses have confirmed their presence by the determined contents of CO_2.

At the temperature **22 °C**, the highest gain of the weight yield of undivided product **+0.70 %** was obtained with the $CaCO_3$ content **9.8 %** and the increase of the CO_2 bonding in comparison with the input state by **3.56 %** at pressure **5 MPa** and duration of the reaction **2 hours** (test **P13**; Tab. 5).

At temperature **35 °C**, pressure **5 MPa** and the duration of the process **3 hours** the increment of the weight yield of undivided product **+0.58 %** was reached with the $CaCO_3$ content **11.0 %** and the increment of the CO_2 composition in comparison with the input by **4.10 %** (test **P32**; Tab. 6).

At **50 °C** and pressure **5 MPa** and **6 hours** reaction there was reached the highest weight yield of the undivided product **(+0.44 %)** with $CaCO_3$ content **8.6 %** and the increase of the CO_2 in the lattice of newly formed minerals in comparison with the input by **3.03 %** (test **P47**; Tab. 7).

The above stated results indicate that the debugged parameters of the CO_2 reactions with the fly ash P are close and comparable. Therefore the best parameters of the laboratory tests of undivided products are the CO_2 pressure 5 MPa in the duration of reaction 2 hours at laboratory temperature 22 °C (test **P13**), indicating that no heating of the reaction mixture is necessary. Moreover, there was found that an increase of the reaction temperature (22 °C → 35 °C → 50 °C) has a negative effect, because lowers the weight yields (0.70 % → 0.58 % → 0.44 %), and there is also a paradox that the prolongation of the reaction time of CO_2 in the suspension (2 → 3 → 6 hours) also decreases the weight yield. An increase of the temperature and the prolongation of the reaction probably cause the transition of a part of CO_2 from the liquid phase back to gaseous phase, which diminishes its reactivity in comparison with the reactivity of the liquid system $H_2O + CO_2$.

Conclusion

The laboratory optimizing of the CO_2 reaction parameters using the fly ash sample taken from the electrostatic separation device of the flue gases after the combustion of the black (hard) coal in the energetic industry with precisely determined mineralogical, chemical and grain-size parameters has demonstrated that the maximum weight yield of the newly originated carbonates calcite and aragonite (+0.70 % at $CaCO_3$ content 9.8 wt.%) is at the reaction temperature 22 °C, pressure 5 MPa and 2 hours duration of the reaction. It supports the industrial application of this methodology, because it is quick and less energetically demanding than supposed before – no additional heat input for the reaction is necessary. The application of the pressures 5 MPa allows the use of the industrial steel reactors.

The main advantage of the reaction of CO_2 with the appropriate components of the fly ash allows a solid bonding of CO_2 in the structures of newly formed carbonates, which are stable and do not have any negative impact on the nature and living environment. By this way, the methodology contributes to simultaneous lowering of the both harmful products after the combustion of the black (hard) coal – CO_2 and the captured fly ash as an alkaline residue after the combustion.

The artificial carbonatization stabilizes the fly ash owing to $CO_2 + H_2O$ dissolving the anhydrite as well as unstable CaO-rich amorphous phase (reaction 1) and forming the stable bassanite and calcite. The efficiency of the carbonatization is directly related to the occurrence and amount of CaO-rich amorphous phase in the fly ash. Moreover, the effectivity of carbonatization depends on the bonding of sulphur and the amount of anhydrite in the fly ash respectively. The artificial carbonatization effectivity and/or stabilization of the fly ash used in our study are low, but significantly confirm this process. Because only 3 vol.% of anhydrite and CaO-rich amorphous phase were present in the fly ash, the reaction with $H_2O + CO_2$ has produced the limited amount of new bassanite and calcite. The artificial carbonatization effectively stabilizes the dumps of caught fly ash by the fact that the possibility of the reaction it components with the acid rains is lowered.

Tab. 10
Summary of the optimum parameters and obtained results
of the CO_2 reaction with the sample of fly ash P

Conditions: p (MPa) t (°C) τ (hour)	Product	Designation of the product	Gain weight yield (%)	CO_2 content (wt.%)	Calcite + aragonite content (wt.%)	pH
–	Input	P	–	0.76	1.7	7
5; 22; 1;	Precipitated	P6	+0.92	19.3	43.9	7 – 8
5; 22; 1;	Filtration cake	P5	–	3.39	7.7	7 – 8
5; 22; 2;	Undivided	P13	+0.70	4.32	9.8	7 – 8

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Stabilizácia emisií popolčeka po spaľovaní čierneho uhlia jeho reakciou s H_2O a CO_2: Optimalizácia teplotno-tlakových parametrov a dĺžky trvania umelej karbonatizácie

Úvod

Približne 60 % emisií CO_2 pochádza z veľkých stacionárnych zdrojov, ako sú teplárne, elektrárne, oceliarne, rafinérie a iné priemyselné závody. Uhlie je najčastejšie používané fosílne palivo, jeho spaľovaním sa vygeneruje viac ako jedna tretina svetovej produkcie elektrickej energie a pokrýva sa 23 % celosvetových energetických potrieb (Santosh et al., 2009). Známa je skutočnosť, že spaľovaním uhlia v tepelných elektrárňach sa pri výrobe 1 kWh elektrickej energie vyprodukuje približne 1 kg CO_2 (Chel, 2009). Popri plynných exhalátoch s 5 – 15 obj. % CO_2 tepelné elektrárne produkujú ďalšiu environmentálnu záťaž v podobe hald popolčeka po spaľovaní fosílnych palív. Využitie alebo likvidácia popolčeka ako alkalického rezídua po spaľovaní uhlia je celosvetovým problémom predovšetkým pre vysoký obsah nespáleného uhlíka. Univerzálna schéma využitia popolčeka nie je vytvoriteľná, lebo jednotlivé jeho typy sa líšia chemicko-mineralogickým zložením, zrnitosťou a tiež množstvom spáliteľného uhlíka. Ďalším negatívnym faktorom je uvoľňovanie chemických prvkov z hald dažďovými zrážkami, čím sa poškodzuje životné prostredie (napr. Zn, Cu, Pb, Ni, As, Hg, Cd, Cr, P, Cl, S, SO_4^{2-}; Uliasz-Bochenczyk, 2010). V zmysle požiadavky Európskej komisie podniky budú musieť nevyhnutne znižovať emisie CO_2, a to o 20 % v roku 2020 v porovnaní so stavom v roku 1990.

V prírodných podmienkach je karbonatizácia silikátov veľmi pomalý proces a jeho akcelerovanie si vyžaduje optimalizáciu technologických parametrov ovplyvňujúcich reaktivitu minerálnych zložiek s CO_2. Cieľom výskumu bola optimalizácia v prípade reakcie CO_2 s popolčekom z energeticko-teplárenského priemyslu, ktorý bol zachytený v elektrostatických separátoroch a uskladnený na haldách. Laboratórne optimalizovanú metodiku prezentovanú v článku bude možné aplikovať pri návrhoch technologických schém a realizačných projektov v modelovom, poloprevádzkovom a prevádzkovom meradle.

Metodika riešenia

Rýchlosť naviazania CO_2 do vhodných substancií a vytváranie konečných stabilných produktov sú závislé od minerálneho a chemického zloženia vstupných materiálov, od aktivity ich zložiek a čistoty plynu z hľadiska CO_2. Dôležitými faktormi sú ďalej skupenstvo, zrnitosť, pórovitosť sekvestračných substancií a aktivita merného povrchu, vzájomný pomer tuhej, kvapalnej a plynnej fázy, teplota, tlak CO_2 a dĺžka reakcie.

Vzorka popolčeka P (obr. 1a) s hmotnosťou 15 kg bola odobratá z elektrostatického separátora komínových plynov. Napriek nízkemu obsahu reakčných komponentov vo vstupnej vzorke (CaO 1,59 hm. %, MgO 0,60 hm. %, a FeO 0,58 hm. %) sme ju použili v primárnom stave, t. j. bez jej termickej modifikácie alebo mechanickej či chemickej aktivácie. Pred reakciou sme určili chemické zloženie vstupnej vzorky (hm. %) a jej zrnitostné zloženie s využitím 10 sít (2; 1; 0,5; 0,315; 0,2; 0,1; 0,071; 0,063; 0,045 a 0,02 mm).

Laboratórne skúšky a optimalizácia reakcie CO_2 s popolčekom sa realizovali v laboratórnom vysokotlakovom reaktore PARR 4540 pri kombináciách troch tlakov CO_2 (2,5; 5,0 a 7,5 MPa), troch teplôt (22, 35 a 50 °C) a štyroch dĺžok reakcií (1, 2, 3 a 6 hodín). Vstup do reaktora pozostával z vodnej suspenzie popolčeka s koncentráciou 152 $g \cdot l^{-1}$. Kontinuálne miešanie reakčnej zmesi pri 300 ot./min. zabezpečovalo dynamické podmienky reakcie. Výstupné produkty reakcie karbonatizácie CO_2 boli z reaktora odobraté nedelené, resp. oddelené filtráciou na filtračné koláče a filtráty a následne vysušené pri teplote 200 °C.

Vstupné vzorky a výstupné produkty po karbonatizácii, filtrácii a kryštalizácii boli identifikované chemickými a rtg. analýzami. Mikrosondovými analýzami sa skúmal spôsob viazania sa CO_2 v tuhých produktoch. Experimenty vo vysokotlakovom reaktore a všetky laboratórne procedúry a rtg. difrakčné rozbory (DRON – UM 1; citlivosť detekcie cca 3 %) boli realizované v Štátnom geologickom ústave Dionýza Štúra (ŠGÚDŠ) – oddelenie aplikovanej technológie nerastných surovín (ATNS) v Košiciach. Chemické analýzy zrealizovali Geoanalytické laboratóriá ŠGÚDŠ v Spišskej Novej Vsi: Obsah CO_2 bol určený metódou vysokoteplotnej oxidácie a manometrie, CaO a MgO boli stanovené röntgenofluorescenčnou spektroskopiou, FeO odmernou analýzou a strata žíhaním gravimetrickou metódou.

Produkty karbonatizácie a nezreagovaných zvyškov po odfiltrovaní (filtračné koláče) boli študované optickým mikroskopom a elektrónovou mikrosondou Cameca SX 100 v ŠGÚDŠ v Bratislave. Analytické parametre merania boli pri 15 kV a intenzite lúča 5 nA pri analýzach kyslých karbonátov a karbonátov a 20 nA pri analýzach silikátov a amorfných fáz. Analyzovaná plocha silikátov s priemerom okna 1 – 7 μm sa menila podľa veľkosti minerálu alebo objektu vo výbruse. Kyslé karbonáty a karbonáty sa analyzovali oknom 7 – 20 μm. Čas snímania jedného prvku bol 10 s alebo 25 s pre F. Detekčný limit pre jednotlivé prvky bol menši než 0,05 hm. %, s chybou ±1-sigma.

Získané výsledky a diskusia

Vstupná vzorka popolčeka

Testovaný popolček vzorky P je presne charakterizovaný svojimi mineralogickými, chemickými a zrnitostnými parametrami (tab. 1 a 2). Prítomnosť častíc popolčeka veľkosti pod 1 mm bola dominujúca (viac ako 99,97 %), ba dokonca aj v triede pod 0,02 mm dosahovala 48,35 %. Vstupné pH suspenzie bolo 7. Vstupná vzorka popolčeka P (obr. 1a) obsahovala pred umelou karbonatizáciou 98,3 obj. % amorfnej fázy, uhlíka a podružný obsah apatitu a anhydritu. Maximálny obsah kalcitu a aragonitu bol 1,7 hm. %. Amorfné fázy silikátovej taveniny mali guľovitý tvar a uzatvárali uhlík, ktorý bol prítomný aj v matrixe vstupnej vzorky spolu s apatitom (obr. 2a). Guľovitý tvar amorfnej silikátovej fázy indikuje rýchle chladnutie taveniny na ceste zo spaľovacej komory k elektrostatickým separátorom. Amorfné fázy majú premenlivý obsah SiO_2 (hm. %), Al_2O_3, CaO, FeO, MgO, K_2O, TiO_2 a rôzne chemické zloženie, napr. Si-Al-Ca, Si-Al-Ti, Ti-Si-Al. V amorfných fázach je obsah chemicky viazanej vody alebo OH skupiny nízky v rozsahu 1,94 – 3,89 hm. %.

Výsledky laboratórnych výskumov umelej karbonatizácie popolčeka s CO_2

Technologické parametre laboratórnych skúšok v tab. 3 – 7 jednoznačne preukazujú vytváranie produktov z filtrátov s obsahom vykryštalizovaných karbonátových minerálov (predovšetkým kalcit + aragonit; obr. 1b) s čistotou v rozmedzí 43,9 – 56,6 % a s prírastkom hmotnostných výnosov zrážaných produktov v rozmedzí 0,54 – 0,92 %. Na preukázanie vzniku karbonátov sme počas prvých šiestich skúšok (P1, P4, P7, P10, P13 a P16) analyzovali separátne filtračné koláče a vyzrážané produkty (tab. 4). Ďalšie reakcie (P19-P48; tab. 3 a 5 – 7) optimalizovali reakčné parametre pre najefektívnejšiu karbonatizáciu, a preto sme analyzovali iba nedelené reakčné produkty, ktoré vznikli reakciami pri rôznych kombináciách troch rozdielnych teplôt (22, 35 a 50 °C), tlakov (2,5, 5,0 a 7,5 MPa) a pri dĺžke reakcií 1, 2, 3 a 6 hodín. Kvalitatívne minerálne zloženie vzorky popolčeka a jeho karbonatizovaných produktov prezentujú tab. 5 – 7.

Novovytvorený kalcit s obsahom molekuly $MgCO_3$ vznikol z katiónov Ca a Mg, ktoré sa do suspenzie uvoľnili z amorfnej fázy s obsahom CaO a MgO. Sprievodným minerálom vo vykryštalizovaných produktoch je bassanit. V porovnaní bilancie CO_2 vo vstupnej vzorke P 0,76 hm. % s obsahom CO_2 v novovytvorených karbonátových produktoch min. 19,3 a max. 24,9 hm. % (produkty reakcií P6 a P9) je CO_2 viazané (likvidované) v novotvorených karbonátoch v závislosti od reakčných podmienok v rozsahu 18,54 – 24,14 hm. %.

Reakcie pri laboratórnej teplote 22 °C v suspenzii H_2O + CO_2 pri meniacich sa tlakových podmienkach a dĺžke trvania reakcií sú zobrazené v tab. 4 a 5. Amorfné fázy vo vstupnej vzorke P a amorfné fázy vzorky P5 sú podľa vzťahu obsahu Si+Ti a obsahu Fe(total)+S+Ca+K+Na+Mn+P+Al v diagrame v priamej substitúcii s výraznou medzerou v nemiešateľnosti týchto obsahov (obr. 3). Takéto vlastnosti priamej chemickej substitúcie s medzerou nemiešateľnosti pevného roztoku majú fázy s čiastočne usporiadanou kryštálovou mriežkou (obr. 2a – c, 3). Relikty amorfných fáz pozostávajú z dvoch typov: nehydratované a hydratované (tab. 8). V prípade hydratovaných amorfných fáz je obsah chemicky viazanej vody a/alebo vody v OH^- skupine v rozsahu 2,06 – 2,41 hm. % (tab. 8), čo korešponduje s obsahom vody vo vstupnej vzorke popolčeka P (1,94 – 3,89 %).

Produktom umelej karbonatizácie popolčeka je vyzrážaný produkt (P6; obr. 1b) tvorený zmesou kalcitu s obsahom molekuly $MgCO_3$ a bassanitu (obr. 4, 2c – d). Alotriomorfné zrná Mg kalcitu obaľuje bassanit, z čoho vyplýva, že Mg kalcit kryštalizoval pred bassanitom (obr. 2d). Vzťah Mg kalcitu a bassanitu indikuje, že kryštalizácia týchto minerálov prebiehala v dvoch etapách. Najskôr kryštalizoval Mg kalcit, ktorého katióny Ca a Mg sa do suspenzie uvoľnili z amorfnej fázy s obsahom CaO a MgO. Neskôr kryštalizoval bassanit, ktorý pravdepodobne vznikol hydratáciou anhydritu.

Údaje v tab. 4 potvrdzujú, že výsledkom umelej karbonatizácie vzorky popolčeka s následnou kryštalizáciou z filtrátu je vznik $CaCO_3$ (kalcitu a aragonitu). Vo filtračnom koláči a v nedelených produktoch karbonatizácie sa v malých množstvách vyskytoval tiež kremeň, mullit, hematit a maghemit. Kalcit (+ aragonit) v týchto produktoch rtg. analýzou identifikovaný nebol z dôvodu jeho prítomnosti v akcesorickom až vedľajšom množstve a citlivosti metódy, pričom chemické analýzy potvrdili jeho prítomnosť pomocou stanovených obsahov oxidu uhličitého.

Pri teplote **22 °C**, tlaku **5 MPa** a trvaní procesu **2 hodiny** bol dosiahnutý najvyšší prírastok hmotnostného výnosu nedeleného produktu **+0,70 %** s obsahom $CaCO_3$ **9,8 %** s nárastom viazania sa CO_2 oproti vstupu o **3,56 %** (**P13**; tab. 5).

Pri teplote **35 °C**, tlaku **5 MPa** a trvaní procesu **3 hodiny** bol dosiahnutý najvyšší prírastok hmotnostného výnosu nedeleného produktu **+0,58 %** s obsahom $CaCO_3$ **11,0 %** s nárastom viazania sa CO_2 oproti vstupu o **4,10 %** (**P32**; tab. 6).

Pri teplote **50 °C**, tlaku **5 MPa** a trvaní procesu **6 hodín** bol dosiahnutý najvyšší prírastok hmotnostného výnosu nedeleného produktu **+0,44 %** s obsahom $CaCO_3$ **8,6 %** s nárastom viazania sa CO_2 oproti vstupu o **3,03 %** (**P47**; tab. 7).

Z uvedených výsledkov vyplýva, že všetky sledované ukazovatele umelej karbonatizácie materiálu vzorky P sú si veľmi blízke, a preto za optimálne parametre z realizovaných laboratórnych skúšok nedelených produktov sa môže považovať tlak CO_2 5 MPa v trvaní pôsobenia 2 hodiny pri laboratórnej teplote 22 °C (reakcia s produktom P13), čo indikuje, že ohrev reakčnej zmesi nie je potrebný. Z dosiahnutých výsledkov karbonatizácie vzorky P sa ukazuje experimentálna skutočnosť, že pri rastúcej teplote suspenzie (22 °C → 35 °C → 50 °C) klesá hodnota prírastkov hmotnostných výnosov produktov (0,70 % → 0,58 % → 0,44 %). Hmotnostné výnosy klesali tiež paradoxne s predlžovaním času pôsobenia CO_2 na suspenziu (2 → 3 → 6 hodín). Tento fakt je spôsobený pravdepodobne prechodom časti oxidu uhličitého z tekutej fázy do plynnej fázy zvyšovaním teploty, čím sa zníži reaktivita CO_2 v porovnaní s reaktivitou kvapalného systému $H_2O + CO_2$.

Umelá karbonatizácia stabilizuje popolček rozpúšťaním anhydritu a tiež nestabilnej amorfnej fázy bohatej na CaO zmesou $H_2O + CO_2$ a vznikom stabilných minerálov bassanitu a kalcitu. Účinnosť karbonatizácie je priamo úmerná množstvu amorfnej fázy bohatej na CaO, ktorú obsahuje popolček pred reakciou. Účinnosť karbonatizácie tiež závisí od množstva anhydritu v popolčeku a charakteru viazania sa síry. V dôsledku nízkeho obsahu anhydritu a amorfnej fázy bohatej na CaO (3 obj. %) v popolčeku reakcia s $H_2O + CO_2$ vyprodukovala malé množstvo bassanitu a kalcitu. Napriek tomu metodika umelej karbonatizácie háld popolčeka po spaľovaní čierneho uhlia vedie k stabilizácii týchto háld, lebo sa zníži reaktivita ich komponentov pri pôsobení kyslých dažďov, a tým poškodzovanie životného prostredia.