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Study on the possibilities of treatment of combustion by-products from fluidized bed boilers into a product devoid of free calcium oxide[☆]

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ABSTRACT

The purpose of this paper is to examine the possibility of reduction of free calcium oxide content in waste from fluidized bed boilers by treating them with carbon dioxide under various conditions. The primary examination concerning the possibilities of reducing the content of free calcium oxide in waste included carbonation process in a laboratory, taking into account various parameters of the process. The primary examination has been carried out in a fluidized bed reactor, rotary reactor and a ball mill reactor.

Depending on the reaction process, the variables in the examined processes included: reaction time, temperature, amount of the catalyst (water), application of an abrasive material. After completion of the process, the treated material was tested with regard to the content of free calcium oxide. Thus, it was possible to determine the most optimal conditions for treatment of combustion products from fluidized bed boilers, that is the conditions which will ensure reduction of the content of free calcium oxide at an appropriate level, under the physical conditions most similar to normal conditions and in the shortest possible time.

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1. Introduction

The continuous tightening of standards concerning emission to the atmosphere of pollutants from combustion of fuels in power plants, has forced the energy industry to start a series of actions, the aim of which is to change the combustion

technology in order to keep these standards without the need to construct new, separate installations for purifying exhaust gases. The analysis of combustion technologies showed that the technology of fuel combustion in a fluidized bed constitutes very effective method of combining the combustion process with the simultaneous purification of exhaust gases (Brożyna & Mazurkiewicz, 2000; Pyssa, 2005; Stańczyk &

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Bieniicki, 2007). Therefore, the number of power units which operates based on combustion in fluidized bed boilers is steadily growing in Poland (Niesler, 2011), and it results in a continuous increase in the amount of combustion products from fluidized bed boilers, which, due to low temperature in the fluidized bed (ca. 850 °C) and because of fuels used, significantly differ (mainly in phase composition and considerably higher amount of free calcium oxide CaO_w) from waste produced during combustion in dust boilers (Gawlicki & Roszczynialski, 2000; Jarema-Suchorowska & Kuczak, 2010; Zapotoczna-Sytek, Laskawiec, Gembarowski, Małolepszy, & Szymczak, 2012).

According to the Act on Waste of December 14, 2012 (WA, 2012) and the Regulation of the Minister of Environment of December 9, 2014 on waste catalogue (RME, 2014), waste from fluidized bed boilers are classified under the following codes:

- 10 01 24 – sands from fluidized beds (with the exception of 10 01 82),
- 10 01 82 – a mixture of fly ash and solid waste with calcium-based flue gas desulphurization (dry and semi-dry methods of desulphurization and fluidized bed combustion).

In the light of applicable laws, wastes from fluidized bed boilers are not classified as hazardous waste. Nevertheless, according to the representatives of the power and waste management industry, the planned changes to the regulations concerning substances and mixtures may result in the classification of waste from fluidized bed boilers as hazardous waste (Jacak, 2013; Paluch, 2013). According to the above, waste from fluidized bed boilers are characterized by their composition, that is, they include much more free calcium oxide CaO_w compared to waste from ash boilers. The amount of free calcium oxide CaO_w in this type of waste may be up to 10% of weight or it may even exceed this value (Jarema-Suchorowska & Kuczak, 2010; Zapotoczna-Sytek et al., 2012). Pursuant to the criteria specified in the Regulation (EC) No 1272/2008 of the European Parliament and of the Council of December 16, 2008 on classification, labelling and packaging of substances and mixtures (RPE, 2008), amending and repealing Directive 67/548/EEC, 1999/45/EC and amending the Regulation (EC) no. 1907/2006, calcium oxide CaO is classified as a substance having irritating properties and it is labelled as H315 and H318. According to the draft Decision of the European Commission amending Decision 2000/532/EC of May 3, 2000 (DKE, 2000), if waste contains one or more substances in the amount exceeding the limit values, which are classified by one of the following hazard categories and hazard codes – H314, H315, H318, H319 and when one or more acceptable concentrations are reached or exceeded, the waste has to be classified as hazardous, however, the limit value to consider that the particular waste is hazardous due to the irritant properties is 1.0%. It means that since the provisions of Decision of the European Commission amending Decision 2000/532/EC started to apply in Poland, waste from fluidized bed boilers containing more than 1.0% of weight of free calcium oxide CaO_w (and generally, it is 100% of such waste), will have to be classified as hazardous waste (Jacak, 2013; Paluch, 2013).

The waste having high content of alkali oxides (inclusive of calcium oxide) show good capacity to bind carbon dioxide in the form of carbonates (IPCC, 2005; Muduli, Nabak, Dhal, & Mishra, 2014; Uliasz-Bocheńczyk, 2007). On this basis, the study has been focused on optimizing the parameters of the carbonation process of calcium oxide contained in waste from fluidized bed boilers.

2. Methodology

The principal purpose of the studies on the possibilities of treatment of waste from fluidized bed boilers into a product devoid of free calcium oxide was to determine the possibility of reduction of free calcium oxide content in such waste by treating them with carbon dioxide under various conditions.

The tests were carried out on waste from the fluidized bed boiler. The adopted research methodology consisted of two stages:

- preliminary research on waste and
- principal research on the possibilities of reduction of the content of free calcium oxide in waste.

The purpose of the preliminary research was to determine the basic physical and chemical properties of waste as well as their potential in terms of the possibility of binding carbon dioxide by free calcium oxide. The preliminary research consisted in the determination of the content of calcium oxide CaO_w in accordance with the standard PN-S-96035:1997P Road. Fly ash (PN, 1997).

The principal research concerning the possibilities of reducing the content of free calcium oxide in waste included carbonation process in a laboratory, taking into account various parameters of the process. The principal research was carried out in the following systems:

- fluidized bed reactor,
- rotary reactor,
- ball mill reactor.

Depending on the reaction process, the variables in the examined processes included: reaction time, temperature, amount of the catalyst (water), application of abrasive material. After completion of the process, the treated material was tested with regard to the content of free calcium oxide. Thus, it was possible to determine the most optimal conditions for treatment of fly ash from fluidized bed boilers, that is the conditions which will ensure reduction of the content of free calcium oxide at an appropriate level, under the physical conditions most similar to normal conditions and in the shortest possible time.

3. Characteristics of the tested material

The following wastes were subject to tests:

- bottom ash, with the code 10 01 24 as specified in the Regulation of the Minister of Environment on the waste

catalogue of December 9, 2014 (RME, 2014) and referred to as – sands from fluidized beds (with the exception of 10 01 82),

- fly ash, with the code 10 01 82 as specified in the Regulation of the Minister of Environment on the waste catalogue of December 9, 2014 (RME, 2014) and referred to as a mixture of fly ash and solid waste with calcium-based flue gas desulphurization (dry and semi-dry methods of desulphurization and fluidized bed combustion).

In order to characterize the waste tested, the following test methods were applied:

- the content of water and dry matter in waste was determined by gravimetric method, according to PN-EN 15934:2012,
- the content of ash in waste was determined by the gravimetric method, according to the procedure PB.03 (ed. 4 of February 27, 2012) developed on the basis of PN-80/G-04512,
- roasting losses were determined based on the algorithm, according to the procedure PB.03 (ed. 4 of February 27, 2012) as described in PN-80/G-04512,
- the content of oxides in waste, such as: SiO₂, Al₂O₃, Fe₂O₃, CaO, MgO, Na₂O, K₂O, SO₃, TiO₂, P₂O₅ was determined by the method of X-ray fluorescence spectrometry with wave dispersion (pressing with a binding agent and fusion into borate pearl), according to PN-EN 15309:2010,
- the content of mercury Hg in waste was determined by the atomic absorption spectrometry with vapour generation (CVAAS), according to the procedure PB.23 (ed. 4 of February 27, 2012),
- the content of free calcium oxide CaO_w in waste was determined by titration, according to the procedure PB.16 (ed. 3 of February 27, 2012), pursuant to PN-S-96035:1997,
- the content of trace elements in waste, such as: Ag, As, Ba, Cd, Co, Cr, Cu, Mn, Mo, Ni, Pb, Rb, Sb, Sn, Sr, V, Zn was determined by the method of X-ray fluorescence spectrometry with wave dispersion (XRF), according to the documentation of the Central Mining Institute no. 2074012BC and no. 2219053BC,
- waste specific gravity was determined according to PN-EN 196-6:1997.

The results of the analyses developed with regard to fly ash and bottom ash have been presented in Table 1 and in Table 2.

3.1. Determination of the content of free calcium oxide CaO_w

The content of free calcium oxide (CaO_w) in waste was determined based on PN-S-96035:1997P, according to the procedure specified below. This method is a chemical method and it involves lixiviation of CaO_w contained in the tested material, using anhydrous ethylene glycol and its further binding into a soluble compound – calcium glycolate. Thus, glycol has two roles in this method – it is a reagent and solvent (PN, 1997).

A sample of the tested material (with a particle size lower than 125 μm) was weighed on an analytical balance (ca. 1 g) and it was transferred quantitatively into the flask.

Table 1 – Physical and chemical analysis of fly ash.^a

Oxide	Content (% of weight)	Oxide	Content (% of weight)
SiO ₂	36.02	Na ₂ O	0.91
Al ₂ O ₃	21.02	K ₂ O	2.15
Fe ₂ O ₃	6.41	SO ₃	9.12
CaO	18.02	TiO ₂	0.63
MgO	2.10	P ₂ O ₅	0.33
BaO	0.07		
Element	Content (mg/kg)	Element	Content (mg/kg)
Ba	585	V	143
Co	5	Zn	243
Cr	80	Ag	<2
Cu	72	As	18
Mn	378	Cd	<2
Ni	65	Mo	3
Pb	96	Sb	3
Rb	105	Sn	5
Sr	315	Hg	0.43
Parameter	Content	Unit	
Moisture content	0.07	(% of weight)	
Specific density	2.65	g/cm ³	
Roasting losses	2.55		

^a Upon conversion into the initial state.

Subsequently, coarse-grained quartz sand was added (1–2 g). The content of the flask was mixed and anhydrous ethylene glycol was added (50 cm³). The sample was mixed again and heated for 30 min at 65–75 °C, stirring every 5 min. The sample was filtered through a glass filter G-4. 4 drops of an indicator (methyl red + bromocresol green) were added to the filtrate and it was titrated with 0.1 M of HCl solution using a digital burette for changing the colour from blue into orange. The content of free calcium oxide CaO_w was calculated according to the formula:

$$X_{\text{CaO}_w} = \frac{0.2804 \cdot V}{m} (\% \text{ of weight}) \quad (1)$$

where X_{CaO_w} – the content of free calcium oxide CaO_w in the tested sample, % of weight; V – volume of 0.1 M of HCL solution used for titration, cm³; m – sample weight, g.

The content of free calcium oxide in fly ash and bottom ash was determined as a function of time. This content was 4.18% of weight on the date of delivery of waste for the fly ash, and for the bottom ash it was 2.76% of weight, whereas:

- after 18 days of storage, the content of CaO_w in the fly ash was 4.03% of weight,
- after 36 days of storage, the content of CaO_w in the fly ash was 3.68% of weight,

which indicates that the content of free calcium oxide in waste changes over time of storage, probably as a result of the reaction of calcium oxide with carbon dioxide from the air.

Table 2 – Physical and chemical analysis of bottom ash.^a

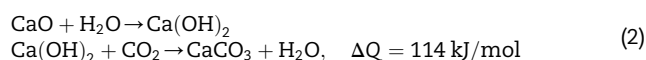
Chemical composition			
Oxide	Content (% of weight)	Oxide	Content (% of weight)
SiO ₂	48.78	Na ₂ O	0.68
Al ₂ O ₃	19.33	K ₂ O	2.28
Fe ₂ O ₃	5.16	SO ₃	6.29
CaO	13.98	TiO ₂	0.65
MgO	1.53	P ₂ O ₅	0.13
BaO	0.04		
Content of trace elements			
Element	Content (mg/kg)	Element	Content (mg/kg)
Ba	324	V	121
Co	6	Zn	220
Cr	70	Ag	<2
Cu	47	As	9
Mn	369	Cd	<2
Ni	44	Mo	3
Pb	74	Sb	<2
Rb	114	Sn	4
Sr	188	Hg	<0.01
Parameter	Content	Unit	
Moisture content	0.05	(% of weight)	
Specific density	2.84	g/cm ³	
Roasting losses	0.26		

^a Upon conversion into the initial state.

4. Carbonation process

Mineral carbonation is an exothermic process, where CO₂ reacts with oxides of metal (Ca, Mg, Fe) and forms stable, insoluble carbonate compounds (Olajire, 2013; Prigobbea, Hänchen, Wernera, Baciocchib, & Mazzottia, 2009). Mineral carbonation may take place both in case of contact of CO₂ with minerals which naturally occur in the environment and with anthropogenic materials, e.g. industrial waste (Huijgen & Comans, 2005; Muduli et al., 2014; Świder & Uliasz-Bocheńczyk, 2010; Uliasz-Bocheńczyk, 2007, 2009). Mineral carbonation is a well-known phenomenon which occurs in the environment, even at low concentration of CO₂ in the air and water. This process is very slow under natural conditions. The process is intensified in the presence of water.

Waste from fluidized bed boilers, characterized by a high content of calcium, produces hydrates (Ca(OH)₂ and phase C–S–H) by reaction with water. Calcium carbonate is produced as a result of the reaction of calcium hydroxide with carbon dioxide, which is a thermodynamically stable product:



Crystalline tricalcium aluminate C₃A and other aluminates contained in waste are also reactive with respect to CO₂. At the same time, various phases of calcium carbonate will occur (Uliasz-Bocheńczyk, Mazurkiewicz, Mokrzycki, & Piotrowski, 2004).

4.1. Fluidized bed reactor

Research on the carbonation process of free calcium oxide in the fluidized bed reactor (Fig. 1) consisted in blowing the reactor (quartz tube) filled with a layer of waste from the fluidized bed boiler with a weight of 100 g and a water content of 5–10% (process catalyst) with a stream of mixture consisting of 60% of carbon dioxide (CO₂) and air at a pressure of 0.1 MPa. The concentration of CO₂ in the gas retention tank was measured using Madur GA-40. The stream of mixture constituted the working substance which not only initiates the carbonation reaction of free calcium oxide (CaO_w) into calcium carbonate (CaCO₃), but it also results in a free rise and abrasion and thus, in regeneration of bed reaction surface along the height of the reactor. An additional factor which determines the regeneration process of the surface of development of particular fractions of waste grains is a spherical ceramic bed consisting of aluminium trioxide (Al₂O₃). The gas mixture is supplied to the reaction zone by a pulsating vacuum pump, after the concentrations in the retention tank are equalized. Before the gas mixture enters the reactor, it flows through a heat exchanger (gas cooling system) which is intended to initially reduce the temperature of the working substance to the ambient temperature. Additional reaction zone cooling system was used during the selected tests and it was placed at a distance of ca. ¼ of the total height of the reactor. It is intended to continuously condense vapour droplets of the fluidized bed by lowering the bed temperature to 10 °C. Finer grain fractions of waste which, as a result of abrasion of the bed, are moved together with the stream of the working substance, are captured on a dry filter and are subject to further secondary carbonation process.

4.2. Rotary reactor

Research on the carbonation process of free calcium oxide in a rotary reactor (Fig. 2) was carried out in a rotary drum with a capacity of 15 dm³ filled with waste from the fluidized bed boiler with a mass ranging from 200 g to 1000 g and a water content of up to 5% being the process catalyst, under the conditions of atmospheric temperature and pressure. The reactor is rotating around its own axis at a constant speed of 26 rev./min, powered by an electric drive with power of 0.55 kW. The volume flow of carbon dioxide was supplied to the reaction zone of the reactor directly from a cylinder containing 100% of CO₂. Optionally, a spherical abrasive material supporting the regeneration of the surface of development of particular grain fractions of waste during the process was placed in the drum of the reactor.

4.3. Rotary reactor

Research on the carbonation process of free calcium oxide in a ball mill reactor (Fig. 3) was carried out in a ball drum with a capacity of 2 dm³ filled with waste from the fluidized bed boiler with a mass of 25 g and a water content of up to 5%. Additional filler of the deposit includes steel balls with a diameter of 25 mm, in the amount of up to 15 pieces and a total weight of 963.6 g, which serve as an abrasive material providing continuous regeneration of the surface of mass exchange between particular grain fractions of waste and the gas phase –

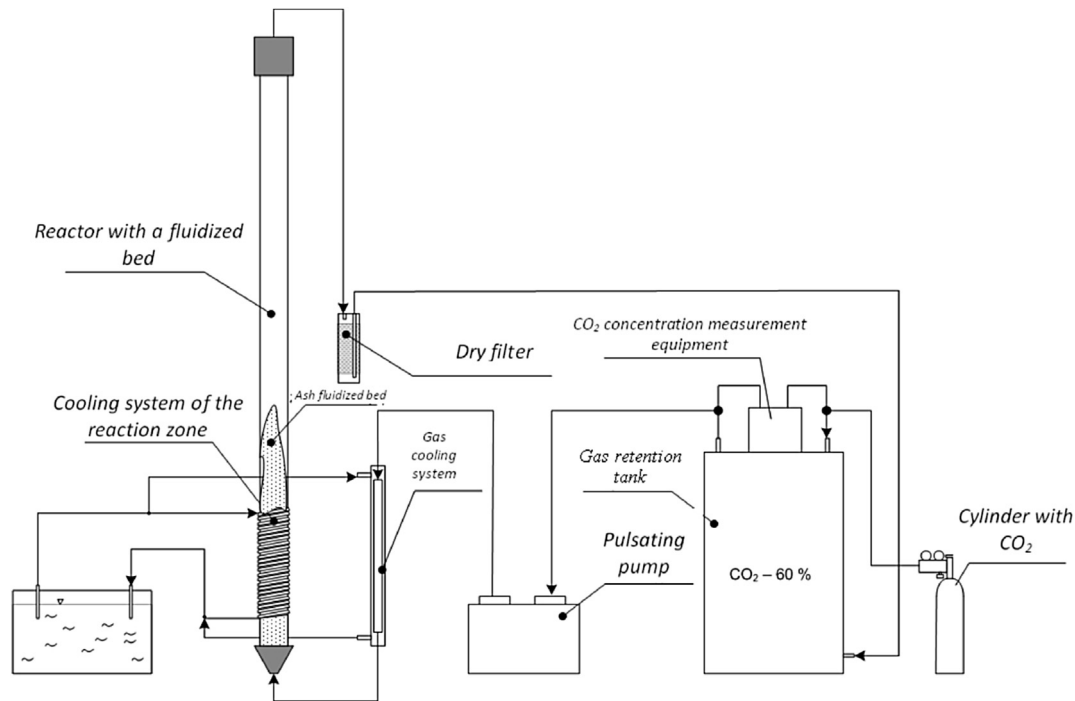


Fig. 1 – Scheme of a fluidized bed reactor for testing the carbonation process of free calcium oxide contained in waste.

carbon dioxide. The rotary motion is accomplished as a result of contact of outer surfaces of the ball mill with the drive unit consisting of two rollers driven by a belt transmission. The effect of the rotary ball mill results in the movement of the bed along the circumference of the reactor within the zone filled with 100% carbon dioxide. The volume flow of CO₂ has been supplied for ca. 2 min to the reactor which had been previously filled with the bed, in order to saturate and displaces the atmospheric air from the reaction zone of the reactor and afterwards, the system is completely isolated against the influence of external environmental conditions.

5. Test results

The parameters of the experiments have been shown in Table 3. The process parameters were selected based on the

experiments carried out with the use of fly ash. The experiment for the bottom ash was carried out under optimized conditions of the process.

The influence of an addition of water on the effectiveness of the reduction process of the content of free calcium oxide in waste in the rotary reactor has been compared in Fig. 4. An addition of water has a catalytic influence on the process. In the absence of water addition to waste, the weight of CaO_w decreased only by 0.09% and in case of addition of 5% of water, the weight of CaO_w decreased by 3.83% (for the time period of the process of 24 h).

Fig. 5 shows the influence of the addition of water and the application of cooling on the kinetics of the abovementioned process carried out in the fluidized bed reactor. The largest loss of the content of free calcium oxide CaO_w in the tested waste was noticed when the addition of water and cooling were applied ($\Delta\text{CaO}_w = 2.68\%$ of weight, the process time

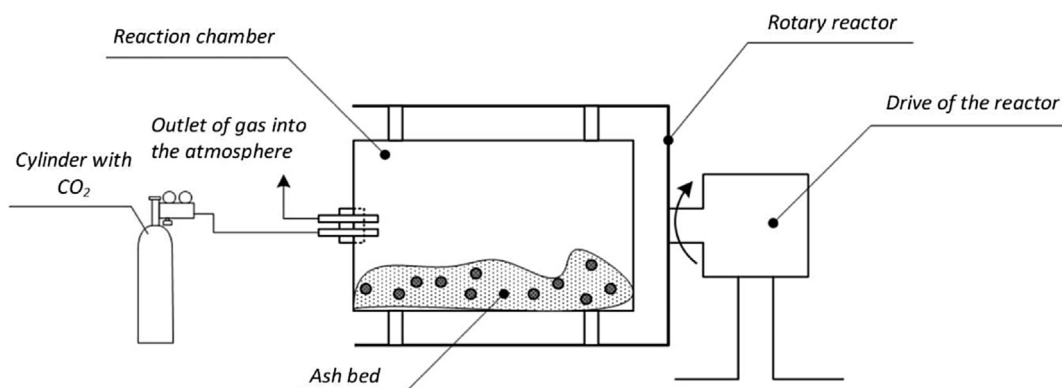


Fig. 2 – Scheme of a rotary reactor for testing the carbonation process of free calcium oxide contained in waste.

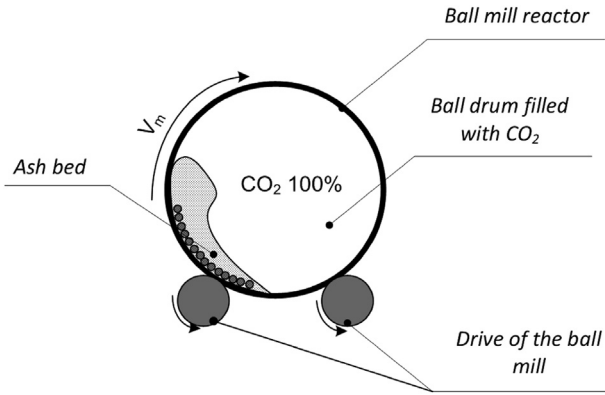


Fig. 3 – Scheme of a ball mill reactor for testing the carbonation process of free calcium oxide contained in waste.

period of 30 min). Fig. 6 shows the kinetics of the process carried out in the ball mill reactor (including the addition of 5% of water).

Table 4 includes a list of selected process conditions, results of determination of the content of free calcium oxide in the tested waste and its loss was calculated with respect to the content in the initial material.

6. Discussion

The paper presents three methods of utilization of combustion products from energy use of fuel in fluidized bed boilers into a product devoid of free calcium oxide. The presented methods are characterized by different effectiveness, however, the most effective among these methods proves to be the carbonation process of combustion products in the fluidized bed reactor, which allowed for reduction of the content of free calcium oxide in waste to 1% of CaO_w.

It is difficult to refer the test results to any literature data, because the presented studies constitutes an original achievement of work (submitted to the Patent Office of the Republic of Poland) and significantly diverge from the objectives presented in the available literature. Nevertheless, the carbonation process is well described in the literature and is brought to the study on the mechanism of this process, as it is presented, among others, in the paper (Palonen, Hyytiäinen, Mahlamäki, & Varonen, 2013). The aim of the studies was to stimulate of the fluidized bed boiler operation by blowing a fine layer of quartz sand and limestone with a stream of mixture consisting of nitrogen N₂, oxygen O₂ and carbon dioxide CO₂ along the reactor in the shape of a cylinder with a diameter of 4.9 cm. Tests were carried out for various values of the volume fraction of carbon dioxide in the mixture ranging from 10% to 90% and in various temperature conditions ranging from 650 °C to 850 °C during 3000 s. The measurable effect of the process is the parameter which describes a change of the volume fraction of carbon dioxide in the gas stream at the outlet of the fluidized bed reactor, and it allowed the authors of this paper to estimate the speed

Table 3 – The parameters of the experiments.

Process ID	Type of ash		Process parameters					Duration of experiment
	Type of reactor	Water addition	CO ₂ concentration	Temp.	Abrasive material ^a			
PL_D6	Fly ash	5%	60%	Ambient	–	70 min		
PL_D10	Fly ash	10%	100%	Ambient	Ceramic balls	50 min		
PL_D12–D16	Fly ash	No	60%	Ambient	Ceramic balls	Experiment carried out as a function of time (0–30 min)		
PL_D18–D23	Fly ash	5%	60%	Ambient	Ceramic balls	Experiment carried out as a function of time (0–30 min)		
PL_D26–D31	Fly ash	5%	60%	10 °C	Ceramic balls	Experiment carried out as a function of time (0–30 min)		
PL_C1–C6	Fly ash	7%	60%	9 °C	Ceramic balls	Experiment carried out as a function of time (0–30 min)		
PD_D1	Bottom ash	5%	60%	Ambient	–	1 h		
PD_D2	Bottom ash	5%	60%	10 °C	–	1 h		
PD_D3	Bottom ash	7%	60%	10 °C	–	1 h		
PL_PM1–PM3	Fly ash	No	100%	Ambient	–	Experiment carried out as a function of time (0–12 h)		
PL_PB1–PB14	Fly ash	5%	100%	Ambient	–	Experiment carried out as a function of time (0–48 h)		
PD_PB1	Bottom ash	5%	100%	Ambient	–	7 h		
PL_C8–C11	Fly ash	No	100%	No data	Steel balls	Experiment carried out as a function of time (0–30 min)		
PL_C12–C16	Fly ash	5%	100%	No data	Steel balls	Experiment carried out as a function of time (0–12 h)		

^a In case of bottom ash, large size grains constituted abrasive material.

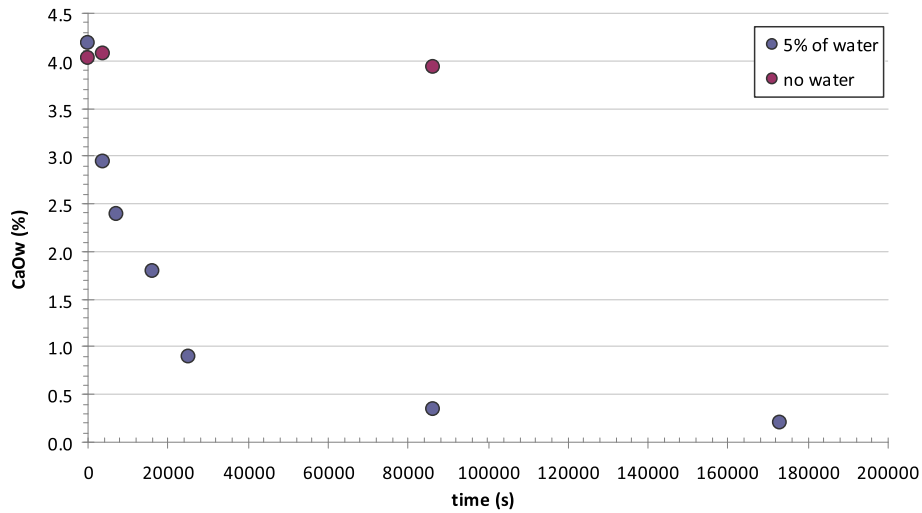


Fig. 4 – Kinetics of the reduction process of the content of free calcium oxide in fly ash (rotary reactor, ● addition of 5% of water, ● no water).

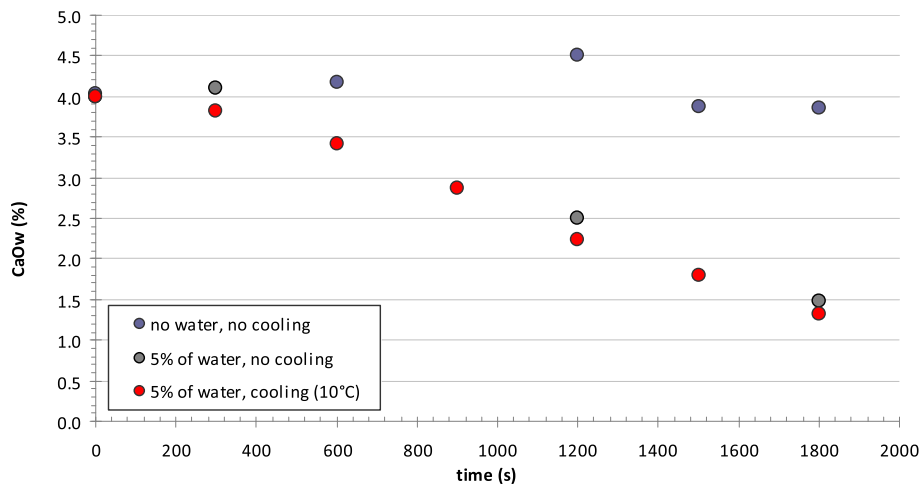


Fig. 5 – Kinetics of the reduction process of the content of free calcium oxide in fly ash (fluidized bed reactor; ● no water, no cooling; ● addition of 5% of water, no cooling; ● addition of 5% of water, cooling).

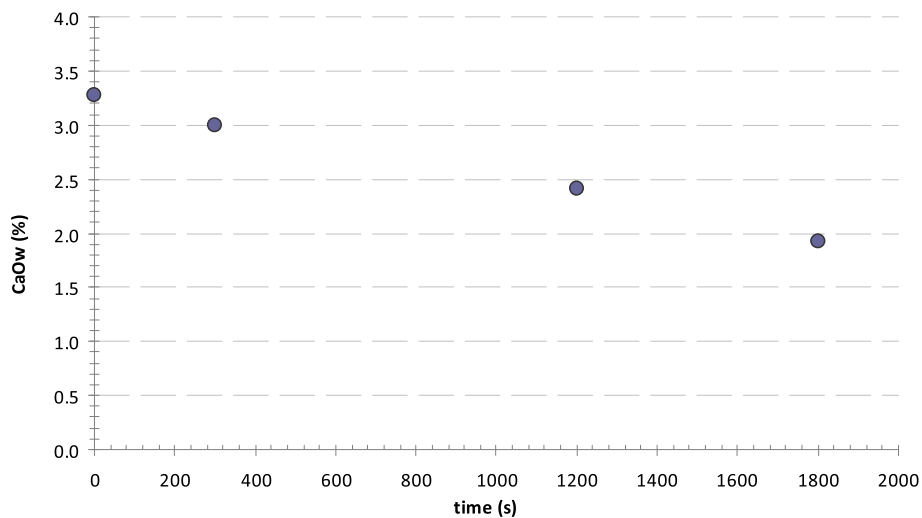


Fig. 6 – Kinetics of the reduction process of the content of free calcium oxide in fly ash (ball mill reactor).

Table 4 – Specification of the content of free calcium oxide CaO_w in the tested waste after the carbonation process as well its losses in relation to the initial material ΔCaO_w .

Process ID	Reactor	Duration of the process	Water addition	Cooling	Abrasive material	CaO_w (% of weight) after the process	ΔCaO_w^a (% of weight)
PL_D6	Fluidized bed	70 min	5%	No	No	3.73	0.45
PL_D10		50 min	10%	No	Yes	2.02	2.16
PL_D16		30 min	No	No	Yes	3.86	0.17
PL_D23		30 min	5%	No	Yes	1.48	2.52
PL_D31		30 min	5%	Yes	Yes	1.32	2.68
PD_D1		60 min	5%	No	Yes	1.81	0.95
PD_D2		60 min	5%	Yes	Yes	1.29	1.47
PD_D3		60 min	7%	Yes	Yes	0.74	2.02
PL_M3	Rotary	24 h	No	No	No	3.94	0.09
PL_PB9		60 min	5%	No	No	2.95	1.23
PL_PB14		7 h	5%	No	No	0.90	3.28
PL_PB1		24 h	5%	No	No	0.35	3.83
PD_PB1		7 h	5%	No	No	1.11	1.65
PL_C11	Ball mill	30 min	No	No	Yes	3.68	0.00
PL_C15		30 min	5%	No	Yes	1.92	1.35
PL_C16		12 h	5%	No	Yes	1.08	2.19

^a Calculated according to the equation ΔCaO_w (% of weight) = CaO_w , after the process (% of weight) – CaO_w , before the process (% of weight).

of conversion of free calcium oxide CaO in the tested mineral layer. The authors of this paper identified the optimal conditions for carrying out the carbonation process of free calcium oxide and obtained the CaO conversion ability, in the tested mineral layer, of 0.8 during 300 s, at a temperature of 750 °C and CO₂ atmosphere of 90%. Similarly, the authors of (Rouchon, Favregeon, & Pijolat, 2013) undertook to investigate the kinetics of the carbonation process in the atmosphere of carbon dioxide CO₂ under variable pressure conditions ranging from 2 kPa to 30 kPa and temperature ranging from 450 °C to 650 °C, during 140 min. The tests were carried out in a laboratory using thermal gravimetric analysis (TG). The study allowed identifying the optimum parameters for the carbonation process, for which the degree of calcium oxide CaO conversion was 0.9 at a pressure of 30 kPa and temperature of 650 °C. Moreover, the authors of the paper (Chrissafis, 2007) undertook to investigate the influence of particular carbonation process parameters on the calcium oxide CaO conversion speed. Various samples of limestone with slight differences in their stoichiometry, which were treated with carbon dioxide CO₂ during 3600 s under variable ambient temperature conditions, were used for that purpose. The tests were carried out using thermal gravimetric analysis (TG). Based on the results, the author identified the carbonation process parameters for which, under the conditions of high carbon dioxide saturation and at a temperature of 670 °C, the conversion of CaO is possible at 0.9 during 8400 s. Another approach to the problem of calcium oxide carbonation CaO was presented in the papers (Huijgen & Comans, 2005; Muduli et al., 2014; Olajire, 2013; Świder & Uliasz-Bocheńczyk, 2010; Uliasz-Bocheńczyk, 2007, 2009; Uliasz-Bocheńczyk et al., 2004) which describe the sequestration process of CO₂ in mineral resources and waste, in which the adopted effectiveness measure is the amount of carbon dioxide absorbed by mineral waste with high content of alkali oxides.

7. Summary and conclusions

The solution of the problem concerning unfavourable content of free calcium oxide in ash from fluidized bed boilers which impedes their broader use has been the subject of numerous studies. Besides the problem of their management (as an additive to concrete) which is mentioned already in the introduction, the issue of their storage also constitutes a problem due to the adverse impact on the environment. Due to the chemical exergy contained therein (Łączny, 2011), it was noticed that they may constitute an interesting sorbent for binding carbon dioxide during a sequestration process (Huijgen & Comans, 2005; Muduli et al., 2014; Olajire, 2013; Świder & Uliasz-Bocheńczyk, 2010; Uliasz-Bocheńczyk, 2007, 2009; Uliasz-Bocheńczyk et al., 2004). Moreover, hydration allows to avoid technical problems related to failures of equipment for hydrotransport and uncontrolled solidification of stored waste (Anthony, Jia, Wu, & Caris, 2003).

The article presents three proposed transformation methods of fluidized bed fly ash into a product devoid of free calcium oxide. The presented methods are characterized by different effectiveness, however, the most effective among these methods proves to be the carbonation process in the fluidized bed reactor, in which it was possible to obtain the content of free calcium oxide in waste of ca. 1% of CaO_w in a relatively short time (approx. 35 min).

Regardless of the practical use which can have in the future the method of processing waste from a fluidized bed boiler (which is described in this paper) into a product devoid of free calcium oxide, an important result which was achieved is the fact that the combustion product processed in accordance with this method will not be a hazardous waste.

Three different types of reactors were used in order to pre-determine the kinetics of the process which is difficult due to the fact that the reaction system consists of several phases

and thus, the time necessary to reach the required content of free calcium oxide. Future possibilities of practical implementation of the process under industrial conditions with the use of the existing infrastructure in power plants were also taken into consideration.

The following conclusions results from the studies:

1. The study showed that there is a possibility to reduce free calcium oxide (CaO_w) contained in waste from fluidized bed boilers by treating them with carbon dioxide and with the use of water as a factor simulating and later supporting the process.
2. In this case, a reaction of carbon dioxide with free calcium oxide into calcium carbonate takes place, however the progress of the reaction can be controlled in such a way, as to obtain a certain conversion degree of calcium oxide to calcium carbonate.
3. The most optimal conditions for processing waste from fluidized bed boilers into a product with a controlled content of free calcium oxide in a fluidized reactor, in which reduction of the content of free calcium oxide was obtained at relatively short reaction periods (30 min) at the desired level, that is ca. 1%.
4. It was confirmed that there are practical possibilities of implementation of the process under industrial conditions and further studies should focus on optimizing the operation of the fluidized bed reactor.

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