

DE GRUYTER  
OPEN

GOSPODARKA SUROWCAMI MINERALNYMI – MINERAL RESOURCES MANAGEMENT

2017

Volume 33

Issue 4

Pages 143–156

DOI 10.1515/gospo-2017-0044



ALICJA ULIASZ-BOCHEŃCZYK\*, ALEKSANDRA PAWLUK\*\*, MICHAŁ PYZAŁSKI\*\*\*

## The mineral sequestration of CO<sub>2</sub> with the use of fly ash from the co-combustion of coal and biomass

### Introduction

The power industry is the largest source of CO<sub>2</sub> emissions in Poland. Emissions from the energy sector accounted for 52.37% (162 689.57 kt) of the total emissions in 2015, which was estimated at 310.64 million tons of CO<sub>2</sub>. Bituminous coal is the primary fuel for energy production in the power industry (about 56%), but biomass energy use is becoming increasingly important; the biomass energy consumption amounted to 67.892 PJ and 101.980 PJ in 2010 and 2015, respectively (PNIR 2016).

Biomass is an interesting fuel for energy because it is considered as a renewable energy source. CO<sub>2</sub> emissions from biomass combustion are not included in the total emissions from the combustion of fuels, resulting in the zero-emission factor for biomass, which is in line with the EU Emissions Trading Scheme and the IPCC guidelines.

However, the combustion and co-combustion of biomass produces, as in the case of all solid fuels, waste of limited economic use. One of their possible applications is the mineral sequestration of carbon dioxide.

Mineral sequestration using energy waste (fly ash) is an interesting option for the energy industry to reduce CO<sub>2</sub> emissions. The use of ashes to bind CO<sub>2</sub> allows not only to carbon

\* Ph.D. Eng., \*\* M.Sc., AGH University of Science and Technology, Faculty of Mining and Geoengineering, Krakow, Poland; e-mail: aub@agh.edu.pl.

\*\*\* M.Sc. AGH University of Science and Technology, Faculty of Faculty of Materials Science and Ceramics, Krakow, Poland.

dioxide emissions to be reduced, but also problematic waste such as by-products resulting from the lignite and biomass combustion to be recycled.

The mineral carbonation using fly ash can be carried out using both direct (gas-solid, gas-slurry) and indirect methods. The most common is the direct (gas-slurry) method. However, the second direct method (gas-solid) is becoming increasingly popular.

Mineral sequestration using waste products is primarily aimed at reducing CO<sub>2</sub> emissions, but also can be used as a way to reduce the leaching of pollutants from waste.

The article presents the results of the direct gas-solid mineral sequestration of CO<sub>2</sub> using fly ashes from the co-firing of biomass with hard coal and examines the possibility of reducing leaching of pollutants.

### 1. The mineral sequestration of CO<sub>2</sub> with the use of fly ash from the co-combustion of coal and biomass

The studies on the use of ashes from coal-fired power generation are carried out in many countries (Noack et al. 2014; Mayoral et al. 2013; Siriruang et al. 2016; Ukwattage et al. 2013, 2015; Guo et al. 2015; Ebrahimi et al. 2017; Ji et al. 2017; Jo et al. 2012; Dananjayan et al. 2016; Mazzella et al. 2016; Wee 2013; Bobicki et al. 2012), including Poland (Uliasz-Bocheńczyk et al. 2006a, b, 2007, 2008, 2009, 2011, 2012, 2013, Uliasz-Bocheńczyk 2008, 2009, 2010, 2011).

The studies use ashes from hard coal, lignite (Table 1), and biomass combustion (Table 2).

Table 1. Mineral sequestration CO<sub>2</sub> using coal fly ash

Tabela 1. Mineralna sekwestracja CO<sub>2</sub> przy wykorzystaniu popiołów ze spalania węgla

Authors	Fly ash type	Type of carbonation	Process parameters	The degree of carbonation
Back et al. 2008	lignite fly ash	suspension-CO <sub>2</sub>	temperature: 25–75°C	maximum conversion – 5.2 moles CO <sub>2</sub> /kg fly ash (~0.23 g/kg)
Bauer et al. 2011	lignite fly ash	semi-dry reaction conditions	pressure CO <sub>2</sub> : 10–20%, L/S* = 0.03–0.36 dm <sup>3</sup> /kg	carbonation efficiency: 13.1–52.8% cumulative CO <sub>2</sub> uptake: 2.2–4.8 mmol/g
Dananjayan et. al. 2016	coal fly ash	gas-solid carbonation	pressure: 1 MPa	maximum capacity – 26.3 g of CO <sub>2</sub> /kg fly ash
	coal fly ash	aqueous route	water slurry L/S = 15 pressure: 0.4 MPa	maximum capacity – 50.3 g of CO <sub>2</sub> /kg of fly ash

Table 1. cd.

Tabela 1. cont.

Authors	Fly ash type	Type of carbonation	Process parameters	The degree of carbonation
Ebrahimi et al. 2017	hard coal fly ash	aqueous fly ash carbonation slurry – CO <sub>2</sub>	water-to-fly ash ratio = 15 and 7.5 ml/g	carbonation efficiency of 83.5% – final CO <sub>2</sub> 3.2%, i.e. 32 g CO <sub>2</sub> /kg fly ash
Ji et al. 2017	hard coal fly ash	direct mineralization slurry – CO <sub>2</sub>	additives: Na <sub>2</sub> CO <sub>3</sub> , NaHCO <sub>3</sub> , a mixture of Na <sub>2</sub> CO <sub>3</sub> and NaCl temperature: 60, 140, 180, 220, 230, 275°C pressure: 1.0, 2.0 MPa	carbonation efficiency – 79%
Jo et al. 2012	coal fly ash	two-step indirect aqueous carbonation	ambient temperature and pressure	0.008 kg of CO <sub>2</sub> /kg of fly ash
Mayoral et al. 2013	fly ash from combustion of the mining waste	fly ash slurry CO <sub>2</sub> – wet carbonation	temperature: 20, 55, 80°C	% CO <sub>2</sub> obtained in the thermogravimetric analysis: % CO <sub>2</sub> coal ash – 0.79–13.62 % CO <sub>2</sub> waste ash: 1.35–16.79
Mazzella et al. 2016	coal fly ash	gas-solid carbonation	pressure: 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, 1.5 MPa temperature: 25, 45°C	CO <sub>2</sub> uptake capacity of over 180 g/kg dry ash
Montes-Hernandez et al. 2009	coal fly ash	aqueous carbonation	pressure: 1.0, 2.0, 3.0, 4.0 MPa temperature: 20–25, 30, 60°C	capacity to sequester CO <sub>2</sub> : 26 kg/CO <sub>2</sub> /Mg fly ash
Muriithia et al. 2013	coal fly ash	fly ash brine dispersion-CO <sub>2</sub>	temperature: 30 and 90°C pressure: 1.0 MPa, 4.0 MPa, L/S = 0.1, 0.5, 1.0	CO <sub>2</sub> content – 2.75–6.5%wt.
Noack et al. 2014	lignite fly ash hard coal fly ash	aqueous carbon sequestration process	–	amorphous calcium carbonate
Siriruang et al. 2016	coal fly ash	solid-CO <sub>2</sub>	temperature: 30, 60, 100, 150°C pressure: 0.10, 0.12, 0.15 MPa moisture contents: 0, 5, 10%	amount of CO <sub>2</sub> capture: 0.29–4.29 mmol/g fly ash

Table 1. cd.

Tabela 1. cont.

Authors	Fly ash type	Type of carbonation	Process parameters	The degree of carbonation
Ukwattage et al. 2013	lignite fly ash hard coal fly ash	fly ash slurry-CO <sub>2</sub>	L/S = 0.1–0.7 temperature: 40°C pressure: 2–6 MPa	sequestration capacity – 7.66 kg CO <sub>2</sub> /Mg fly ash
Ukwattage et al. 2015	coal fly ash	slurry-CO <sub>2</sub>	water-to-solid ratio: 0.1–1.0 temperature: 20, 40, 60, 80°C pressure: 3 MPa	sequestration potential: 10.71–27.05 kg of CO <sub>2</sub> per ton of fly ash
Uliasz- -Bocheńczyk 2008	hard coal fly ash	suspension-CO <sub>2</sub>	L/S = 1.5, 1.7	CaCO <sub>3</sub> content – 2,27% CO <sub>2</sub> absorption: 0.42–1.31 g CO <sub>2</sub> /100 g
Uliasz- -Bocheńczyk 2009	lignite fly ash hard coal fly ash mixture of hard coal fly and desulphurization waste	suspension-CO <sub>2</sub>	S/L = 0.8, 1.1	degree of CO <sub>2</sub> binding – 0.43–12.82% CO <sub>2</sub> absorption: 2.15–9.54 g CO <sub>2</sub> /100 g
Uliasz- -Bocheńczyk 2011	lignite fly ash	suspension-CO <sub>2</sub>	L:S – 1:1	degree of CO <sub>2</sub> binding – 8.85%
Uliasz-- Bocheńczyk et al. 2009b	lignite fly ash	suspension-CO <sub>2</sub>	S/L = 0.6, 1.25, 1.5	CO <sub>2</sub> absorption: 2.98–8.81 g CO <sub>2</sub> /100 g
Uliasz- -Bocheńczyk 2010	hard coal fly ash and desulphurization waste	suspension-CO <sub>2</sub>	L/S= 1.5	degree of CO <sub>2</sub> binding – 2.4 and 5.2%
Uliasz- -Bocheńczyk et al. 2012	lignite fly ash	suspension-CO <sub>2</sub>	L:S = 0.7:1, 0.8:1	CO <sub>2</sub> absorption: 4.71–9.33 g CO <sub>2</sub> /100 g

\*L/S = liquid/solid.

Table 2. Mineral sequestration CO<sub>2</sub> using biomass fly ashTabela 2. Mineralna sekwestracja CO<sub>2</sub> przy wykorzystaniu popiołów ze spalania biomasy

Authors	Fly ash type	Type of carbonation	Process parameters	The degree of carbonation
Gunning et a. 2010	biomass ash	paste-CO <sub>2</sub>	pressure: 0.2 MPa	carbon dioxide uptake: about 1%
Guo et al. 2015	wood ash	solid-CO <sub>2</sub>	simulated gas: 10% CO <sub>2</sub> and 8–16% H <sub>2</sub> O temperature: 60–100°C	CO <sub>2</sub> capture capacities: 0.35–0.54 mmol CO <sub>2</sub> /g

The process of the mineral sequestration of carbon dioxide in the carbonation process, using ashes from the energy sector, is carried out by means of indirect and direct methods, predominantly through the CO<sub>2</sub> – slurry method (Table 1).

## 2. The materials used for testing

Fly ashes resulting from the co-firing of hard coal and biomass, as described in Uliasz-Bocheńczyk et al. 2016, were subjected to the carbonation process. The above mentioned ashes are the result of the co-combustion of forest biomass (80%) and agricultural waste (20%) with hard coal in a conventional pulverized boiler (Uliasz-Bocheńczyk et al. 2016). These ashes can be classified as waste 10 01 17 – fly ash from co-firing other than mentioned in 10 01 16 according to the classification contained in the Regulation of the Minister of the Environment of December 9, 2014 on waste catalogue (Journal of Laws 2014, item 1923).

The chemical composition of the examined fly ash (PWB) (Uliasz-Bocheńczyk et al. 2016) is characterized by a high SiO<sub>2</sub> content – 52.8%. The content of SiO<sub>2</sub> and other components, such as Al<sub>2</sub>O<sub>3</sub> (22.8%), SO<sub>3</sub> (0.4), and CaO (5.17%), allows to qualify them, according to the requirements of the BN-79/6722-09 standard as: *Fly ash and slags from bituminous coal and lignite-fired boilers. Division, names, and definitions* as silicate ash (k).

In these fly ash, the Na<sub>2</sub>O and K<sub>2</sub>O content amounts to 1.2%, and 3.1%, respectively (Uliasz-Bocheńczyk et al. 2016).

The chemical composition allows for the calculation of the maximum theoretical CO<sub>2</sub> binding capacity using the Steinour equation (Fernandez-Bertos et al. 2004):

$$\text{CO}_2 (\%) = 0.785 (\text{CaO} - 0.7 \text{SO}_3) + 1.09 \text{Na}_2\text{O} + 0.93 \text{K}_2\text{O} \quad (1)$$

For the analyzed fly ashes resulting from the co-firing of biomass, the mentioned maximum theoretical carbon dioxide binding capacity is 8.03%, which is a relatively low result compared to the maximum capacity calculated for fly ash from hard coal combustion – 24.6% (Mazzella et al. 2016); fly ash from biomass combustion – around 38% (Gunning et al. 2010); fly ash from lignite combustion (Uliasz-Bocheńczyk 2009), or the mixture of fly ash and desulphurization products.

## 3. The degree of carbonation – mineral sequestration of CO<sub>2</sub>

Fly ashes from co-firing were subjected to a direct gas-solid mineral carbonation process for 28 days. The wetted fly ash resulting from the co-combustion of biomass and coal were placed in sealed chambers supplied with CO<sub>2</sub> (Uliasz-Bocheńczyk 2009).

The phase composition of CO<sub>2</sub> treated fly ashes was examined with use of the Debye-Scherrer-Hull X-ray powder method (XRD) using a Philips X-ray diffractometer with

copper radiation (CuK $\alpha$ ) and the thermal analysis method (*DTA* – differential thermal analysis and *TG* – thermogravimetry) using a Netzsch 449F3 Jupiter analyzer.

The results were compared with the phase compositions determined before exposing the fly ashes to CO<sub>2</sub> (Uliasz-Bocheńczyk et al. 2016) (Fig. 1, 2, and 3).

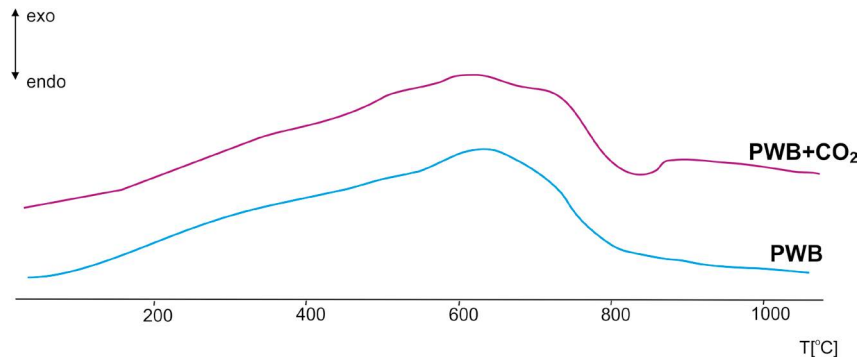


Fig. 1. The DTA curves of: the analyzed fly ashes resulting from the co-firing (PWB) (Uliasz-Bocheńczyk et al. 2016) and the analyzed fly ashes resulting from the co-firing after exposure to CO<sub>2</sub> (PWB + CO<sub>2</sub>)

Rys. 1. Krzywe DTA: analizowanych popiołów lotnych ze współspalania (PWB) (Uliasz-Bocheńczyk i in. 2016) oraz analizowanych popiołów lotnych ze współspalania po poddaniu ich działaniu CO<sub>2</sub> (PWB + CO<sub>2</sub>)

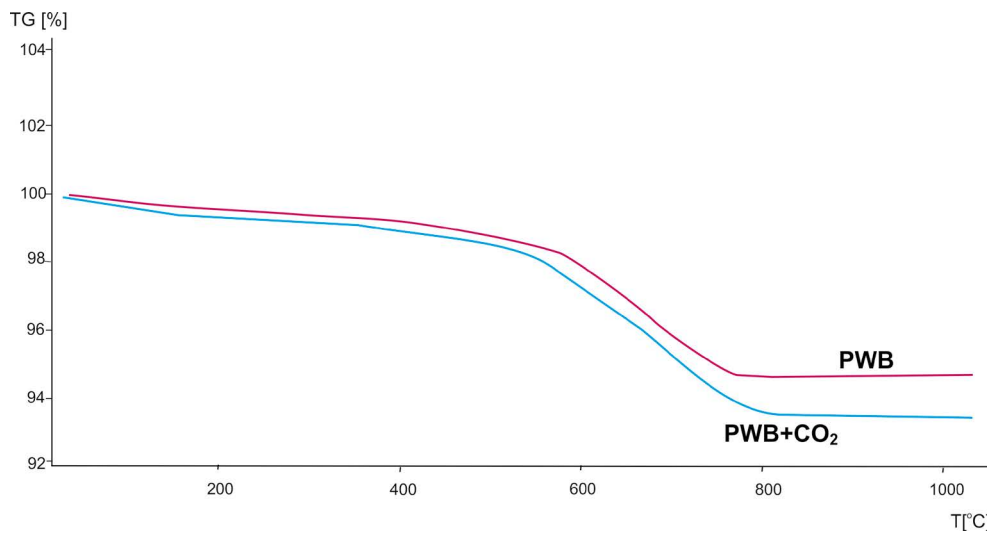


Fig. 2. The TG curves: of the analyzed fly ash resulting from the co-firing (PWB) (Uliasz-Bocheńczyk et al. 2016) and the analyzed fly ashes resulting from the co-firing after exposure to CO<sub>2</sub> (PWB + CO<sub>2</sub>)

Rys. 2. Krzywe TG: analizowanych popiołów lotnych ze współspalania (PWB) (Uliasz-Bocheńczyk i in. 2016) oraz analizowanych popiołów lotnych ze współspalania po poddaniu ich działaniu CO<sub>2</sub> (PWB + CO<sub>2</sub>)

The CO<sub>2</sub> treatment of the analyzed fly ash results in an endothermic effect with a maximum temperature of about 820°C (Fig. 1), indicating the decomposition of calcium carbonate – calcite, the primary product of the mineral CO<sub>2</sub> sequestration. This is confirmed by the effect seen on the TG curve for the PWB + CO<sub>2</sub> sample (Fig. 2), resulting from the mass loss in the temperature range 665–820°C, which has not been observed in the case of the PWB sample. In the PWB sample (Fig. 2), the only observed effect was associated with the loss of moisture (Uliasz-Bocheńczyk et al. 2016). The X-ray results show the presence of SiO<sub>2</sub> and mullite (Uliasz-Bocheńczyk et al. 2016). After the carbonation process, the peaks associated with the presence of CaCO<sub>3</sub> were recorded, which confirms the DTA/TG results. In addition, the formation of calcite as the primary gas-solid carbonation product confirms the results obtained by the Mazzella et al. (2016) and Dananjayan et al. (2016).

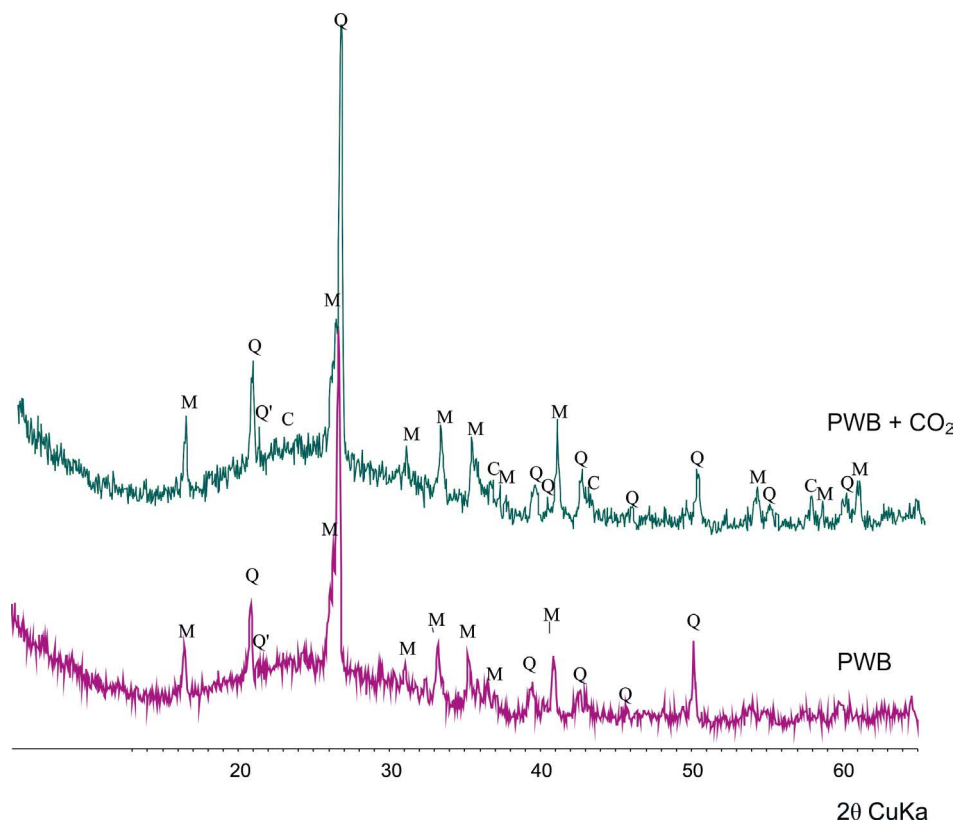


Fig. 3. The diffraction patterns: of the analyzed fly ash (PWB) (Uliasz-Bocheńczyk et al. 2016) and the analyzed fly ashes resulting from the co-firing after exposure to CO<sub>2</sub> (PWB+CO<sub>2</sub>)

M – mullite, Q – quartz, C – calcite

Rys. 3. Dyfraktogramy: analizowanych popiołów lotnych ze współspalania (PWB) (Uliasz-Bocheńczyk i in. 2016) oraz analizowanych popiołów lotnych ze współspalania po poddaniu ich działaniu CO<sub>2</sub>  
 M – mulit, Q – kwarc, C – kalcyt

The analysis of phase composition allows the degree of carbonation – mineral sequestration of CO<sub>2</sub> to be determined, usually calculated on the basis of weight gain after carbonation. The degree of carbonation – mineral sequestration of CO<sub>2</sub> can be determined from the following formula (Baclocchi et al. 2009):

$$\text{CO}_{2\text{uptake}}[\%] = \frac{\text{CO}_{2\text{final}}[\%] - \text{CO}_{2\text{initial}}[\%]}{100 - \text{CO}_{2\text{final}}[\%]} \cdot 100 \quad (2)$$

where:

- CO<sub>2uptake</sub> – the extent of carbonation,
- CO<sub>2initial</sub> – initial carbonate content of the sample,
- CO<sub>2final</sub> – final carbonate content of the sample.

The degree of carbonation – mineral sequestration of carbon dioxide for the analyzed fly ashes resulting from the co-firing of biomass and coal calculated using the formula No. 2 is 1.51%.

#### 4. The impact of the mineral sequestration of CO<sub>2</sub> on the leaching of pollutants

The analyzed fly ashes resulting from the combustion of hard coal and biomass were tested for leaching of pollutants after the process of mineral sequestration of CO<sub>2</sub>. The leaching

Table 3. Leaching of pollutants [mg/dm<sup>3</sup>]

Tabela 3. Wymywalność zanieczyszczeń [mg/dm<sup>3</sup>]

Type of pollution	Leaching of pollutants	
	PWB (Uliasz-Bocheńczyk et al. 2016)	PWB + CO <sub>2</sub>
Cl <sup>-</sup>	150.3	52.0
SO <sub>4</sub> <sup>2-</sup>	790.5	224.6
K	223	81
Na	26	21
As	0.001221	0.0003574
Cd	0.000451	0.000303
Cu	0.04416	0.025217
Cr	0.001548	0.00141
Hg	0.001	<
Pb	0.002758	0.000958



of pollutants was analyzed in accordance with the EN 12457 *Characterization of waste – Leaching – Compliance test for leaching of granular waste materials and sludges* standard using the ICP-AES and Plasma Mass Spectrometry (IC-PMS) methods.

The carbonation process has reduced the leaching of the examined pollutants (Table 3).

This is particularly evident in the case of potassium concentration in the water extracts (over 60%), sulphates, and chlorides (40%). The reduced leaching in the gas-solid method should be mainly attributed to sorption processes.

The pH of the water extracts of the examined fly ashes decreased from 11.96 (Uliasz-Bocheńczyk et al. 2016) for pure fly ashes to 8.7 for CO<sub>2</sub> treated fly ashes, indicating the presence of carbonation process.

### Summary and conclusions

The problem of using fly ash from co-firing biomass with coal in the power industry in the process of mineral sequestration is related to two important issues for this sector: the reduction of CO<sub>2</sub> emissions and the management of by-products of the combustion process. The study aimed to determine the possibilities of using fly ash from co-firing of biomass with coal in the carbonation process.

The study used fly ash resulting from co-combustion of biomass with hard coal in pulverized boilers during the direct gas (CO<sub>2</sub>) – solid carbonation process.

The process of CO<sub>2</sub> absorption by the analyzed waste and the formation of a small amount of calcium carbonate – calcite have been shown.

The mineral carbonation process significantly reduces the leaching of pollutants from waste products, which may increase the potential for their utilization.

*This work was supported under a grant of the Dean of the Faculty of Mining and Geoengineering of the AGH University of Science and Technology, work no. 15.11.100.912.*

### REFERENCES

- Baclocchi et al. 2010 – Baclocchi, R., Costa, G., Di Bartolomeo, E., Polettini, A. and Pomi, R. 2010a. Comparison of different process routes for stainless steel slag carbonation. *Proceedings of Third International Conference on Accelerated Carbonation for Environmental Engineering ACEME10*, Åbo Akademi University, Åbo/Turku, pp. 193–202.
- Back et al. 2008 – Back, M. Kühn, M. Stanjek, H. and Peiffer, S. 2008. Reactivity of alkaline lignite fly ashes towards CO<sub>2</sub> in water. *Environmental Science & Technology* 42, pp. 4520–4526.
- Bauer et al. 2011 – Bauer, M. Gassen, N. Stanjek, H. and Peiffer, S. 2011. Carbonation of lignite fly ash at ambient T and P in a semi-dry reaction system for CO<sub>2</sub> sequestration. *Applied Geochemistry* 26, pp. 1502–1512.
- Bobicki et al. 2012 – Bobicki, E.R. Liu, Q. Xu, Z. and Zeng, H. 2012. Carbon capture and storage using alkaline industrial wastes. *Progress in Energy and Combustion Science* 38, pp. 302–320.
- Dananjayan et al. 2016 – Dananjayan, R.R.T. Kandasamy, P. and Andimuthu, R. 2016. Direct mineral carbonation of coal fly ash for CO<sub>2</sub> sequestration. *Journal of Cleaner Production* 112, pp. 4173–4182.

- Ebrahimi et al. 2017 – Ebrahimi, A., Saffari, M., Milani, D., Montoya, A., Valix, M. and Abbas, A. 2017. Sustainable transformation of fly ash industrial waste into a construction cement blend via CO<sub>2</sub> carbonation. *Journal of Cleaner Production* 156, pp. 660–669.
- Gunning et al. 2010 – Gunning, P.J Hills, C.D. and Carey P.J. 2010. Accelerated carbonation treatment of industrial wastes. *Waste Management* 30, pp. 1081–1090.
- Guo et al. 2015 – Guo, Y., Zhao, Ch., Chen, X. and Li, Ch. 2015. CO<sub>2</sub> capture and sorbent regeneration performances of some wood ash materials. *Applied Energy* 137, pp. 26–36.
- Fernandez Bertos et al. 2004 – Fernandez Bertos, M., Simons, S.J.R., Hills, C.D. and Carey, P.J. 2004. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO<sub>2</sub>. *Journal of Hazardous Materials* B112, pp. 193–205.
- Ji et al. 2017 – Ji, L., Yub, H., Wang, X., Grigore, M., French, D., Gözükar, Y.M., Yu, J. and Zeng, M. 2017. CO<sub>2</sub> sequestration by direct mineralization using fly ash from Chinese Shenfu coal. *Fuel Processing Technology* 156, pp. 429–437.
- Jo et al. 2012 – Jo, H.Y., Kim, J.H., Lee, Y.J., Lee, M. and Choh, S.J. 2012. Evaluation of factors affecting mineral carbonation of CO<sub>2</sub> using coal fly ash in aqueous solutions under ambient conditions. *Chemical Engineering Journal* 183, pp. 77–87.
- Mayoral et al. 2013 – Mayoral, M.C., Andrés, J.M. and Gimeno, M.P. 2013. Optimization of mineral carbonation process for CO<sub>2</sub> sequestration by lime-rich coal ashes. *Fuel* 106, pp. 448–454.
- Mazzella et al. 2016 – Mazzella, A., Errico, E., Spiga, D. 2016. CO<sub>2</sub> uptake capacity of coal fly ash: Influence of pressure and temperature on direct gas-solid carbonation. *Journal of Environmental Chemical Engineering* 4, pp. 4120–4128.
- Montes-Hernandez et al. 2009 – Montes-Hernandez, G., Perez-Lopez, R., Renard, F., Nieto, J.M. and Charlet, L. 2009. Mineral sequestration of CO<sub>2</sub> by aqueous carbonation of coal combustion fly-ash. *Journal of Hazardous Materials* 161, pp. 1347–1354.
- Muriithia et al. 2013 – Muriithia, G.N., Petrika, L.F., Fatobaa, F., Gitarib, W.M., Doucet, J.F., Neld, J. and Chuks, P.E. 2013. Comparison of CO<sub>2</sub> capture by ex-situ accelerated carbonation and in in-situ naturally weathered coal fly ash. *Journal of Environmental Management* 127, pp. 212–220.
- Noack et al. 2014 – Noack, C.W., Dzombak, A.D., Nakles, D.V., Hawthorne, S.B., Heebink, L.V., Dando, N., Gershenzon, M. and Ghosh, R.S. 2014. Comparison of alkaline industrial wastes for aqueous mineral carbon sequestration through a parallel reactivity study. *Waste Management* 34, pp. 1815–1822.
- PNIR 2016. *Poland's National Inventory Report. Greenhouse Gas Inventory for 1988–2014*. National Centre for Emission Management (KOBiZE) at the Institute of Environmental Protection – National Research Institute, Warszawa 2016.
- Regulation of the Minister of the Environment of December 9, 2014 on waste catalogue. ([Journal of Laws] 2014, item 1923).
- Siriruang et al. 2016 – Siriruang, Ch., Toochinda, P., Julnipayawong, P. and Tangtermsirikul, S. 2016. CO<sub>2</sub> capture using fly ash from coal fired power plant and applications of CO<sub>2</sub>-captured fly ash as a mineral admixture for concrete. *Journal of Environmental Management* 170, pp. 70–78.
- Ukwattage et al. 2013 – Ukwattage, N.L., Ranjith, P.G. and Wang, S.H. 2013. Investigation of the potential of coal combustion fly ash for mineral sequestration of CO<sub>2</sub> by accelerated carbonation. *Energy* 52, pp. 230–236.
- Ukwattage et al. 2015 – Ukwattage, N.L., Ranjith, P.G., Yellishetty, M., Bui, H.H. and Xu, T. 2015. A laboratory-scale study of the aqueous mineral carbonation of coal fly ash for CO<sub>2</sub> sequestration. *Journal of Cleaner Production* 103, pp. 665–674.
- Uliasz-Bocheńczyk, A. 2008. Zastosowanie popiołów lotnych ze spalania węgla kamiennego w kotłach wodnych do sekwestracji CO<sub>2</sub> na drodze mineralnej karbonatyzacji. *Rocznik Ochrona Środowiska* 10, s. 567–574.
- Uliasz-Bocheńczyk, A. 2009. *Mineralna sekwestracja CO<sub>2</sub> w wybranych odpadach*. Kraków: Wyd. IGSMiE PAN, 139 pp.
- Uliasz-Bocheńczyk, A. 2010. Mineral sequestration of CO<sub>2</sub> in suspensions containing mixtures of fly ashes and desulphurization waste. *Gospodarki Surowcami Mineralnymi – Mineral Resources Management* 26, pp. 109–118.
- Uliasz-Bocheńczyk, A. 2011. Mineralna sekwestracja CO<sub>2</sub> przy zastosowaniu zawiesin wodnych wybranych popiołów lotnych ze spalania węgla brunatnego. *Gospodarki Surowcami Mineralnymi – Mineral Resources Management* 27, pp. 145–154.

- Uliasz-Bocheńczyk et al. 2012 – Uliasz-Bocheńczyk, A., Gawlicki, M. and Pomykała, R. 2012. Ocena możliwości sekwestracji ditlenku węgla w wodnych zawiesinach wybranych popiołów lotnych. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 28, pp. 103–112.
- Uliasz-Bocheńczyk, A. and Mokrzycki, E. 2006a. Fly Ashes from Polish Power Plants and Combined Heat and Power Plants and Conditions of their Application for Carbon Dioxide Utilization. *Chemical Engineering Research and Design* 84, pp. 837–842.
- Uliasz-Bocheńczyk, A. and Mokrzycki, E. 2008. CO<sub>2</sub> sequestration with the use of fly ash from hard coal and lignite combustion. *Slovak Geological Magazine* spec. issue, pp. 19–22.
- Uliasz-Bocheńczyk, A. and Mokrzycki, E. 2011. Możliwości zastosowania odpadów energetycznych do mineralnej sekwestracji CO<sub>2</sub>. *Rocznik Ochrona Środowiska* 13, pp. 1591–1604.
- Uliasz-Bocheńczyk A. and Mokrzycki E., 2013. Mineralna sekwestracja CO<sub>2</sub> przy zastosowaniu odpadów energetycznych – próba oszacowania potencjału w Polsce. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* t. 29 z. 3, s. 179–189.
- Uliasz-Bocheńczyk et al. 2006b – Uliasz-Bocheńczyk, A., Mokrzycki, E., Mazurkiewicz, M. and Piotrowski Z. 2006b. Z. Utilization of Carbon Dioxide in Fly Ash and Water Mixtures. *Chemical Engineering Research and Design* 84, pp. 843–846.
- Uliasz-Bocheńczyk et al. 2009 – Uliasz-Bocheńczyk, A., Mokrzycki, E., Piotrowski, Z. and Pomykała, R. 2009. Estimation of CO<sub>2</sub> sequestration potential via mineral carbonation in fly ash from lignite combustion in Poland. *Energy Procedia* 1, pp. 4873–9.
- Uliasz-Bocheńczyk et al. 2016 – Uliasz-Bocheńczyk, A., Pawluk, A. and Pyzalski, M. 2016. Charakterystyka popiołów ze spalania biomasy w kotłach fluidalnych. *Gospodarka Surowcami Mineralnymi – Mineral Resources Management* 32, s. 149–162.
- Uliasz-Bocheńczyk, A. and Piotrowski, Z. 2009. Wpływ mineralnej karbonatyzacji na wymywalność zanieczyszczeń. *Rocznik Ochrona Środowiska* 11, pp. 1083–1094.
- Wee, J.H. 2013. A review on carbon dioxide capture and storage technology using coal fly ash. *Applied Energy* 106, pp. 143–151.

#### MINERALNA SEKWESTRACJA CO<sub>2</sub> PRZY ZASTOSOWANIU POPIOŁÓW LOTNYCH ZE WSPÓLSPALANIA WĘGLA I BIOMASY

##### Słowa kluczowe

popioły lotne, współspalanie biomasy, mineralna sekwestracja CO<sub>2</sub>,  
karbonatyzacja bezpośrednia gaz–ciało stałe

##### Streszczenie

W wyniku procesów produkcji energii, energetyka zawodowa w Polsce jest największym źródłem emisji CO<sub>2</sub> w Polsce. Emisja z energetyki stanowiła w 2015 roku 52,37% (162 689,57 kt) całkowitej emisji, która była szacowana na 310.64 milionów ton CO<sub>2</sub>. W ostatnich latach, wraz z zaostrzeniem przepisów dotyczących wykorzystania odnawialnych źródeł energii, zwiększyła się ilość stosowanej w energetyce zawodowej biomasy, ponieważ emisja CO<sub>2</sub> ze spalania biomasy nie jest wliczana do sumy emisji ze spalania paliw, co jest równoważne stosowaniu zerowego wskaźnika emisji. Zarazem w procesach produkcji energii powstają uboczne produkty, które powinny być zgodnie z hierarchią metod postępowania z odpadami przede wszystkim poddane odzyskowi.

Badaniom poddano popioły ze spalania biomasy w kotłach pyłowych, które ze względu na skład chemiczny można zaliczyć do popiołów krzemianowych. Zgodnie z Rozporządzeniem Ministra Środowiska z dnia 9 grudnia 2014 r. w sprawie katalogu odpadów, popioły te można zaklasyfikować jako odpad 10 01 17 – popioły lotne ze współspalania inne niż wymienione w 10 01 16.

Maksymalna teoretyczna pojemność związania ditlenku węgla dla analizowanych popiołów ze współspalania biomasy wynosi 8,03%. Badania składów fazowych popiołów poddanych karbonatacji wykazały, oprócz składników zidentyfikowanych w czystych popiołach ( $\text{SiO}_2$ , mullit), również obecność węglanu wapnia – kalcytu – podstawowego produktu procesu karbonatacji, na co wskazują wyniki badań wykonanych zarówno metodą rentgenograficzną jak i termogravimetryczną.

Na podstawie analizy wyników badań składów fazowych popiołów lotnych ze współspalania biomasy z węglem kamiennym określono stopień karbonatacji. Obliczony stopień karbonatacji wyniósł 1,51%. Zachodzenie procesu karbonatacji potwierdza również obniżenie wartości pH wyciągów wodnych badanych popiołów, która uległa redukcji z 11,96 dla czystych oraz do wartości 8,7 dla popiołów poddanych działaniu  $\text{CO}_2$ . Proces karbonatacji wpłynął również na obniżenie wymywalności zanieczyszczeń, przede wszystkim chlorków, siarczanów i potasu.

#### THE MINERAL SEQUESTRATION OF $\text{CO}_2$ WITH THE USE OF FLY SSH FROM THE CO-COMBUSTION OF COAL AND BIOMASS

##### Keywords

fly ash, biomass co-combustion,  $\text{CO}_2$  mineral sequestration, gas-solid carbonation

##### Summary

As a result of energy production processes, the power industry is the largest source of  $\text{CO}_2$  emissions in Poland. Emissions from the energy sector accounted for 52.37% (162 689.57 kt) of the total emissions in 2015, which was estimated at 310.64 million tons of  $\text{CO}_2$ . In recent years, the tightening of regulations on the use of renewable energy sources has resulted in an increased amount of biomass used in the professional energy industry. This is due to the fact that the  $\text{CO}_2$  emissions from biomass combustion are not included in the total emissions from the combustion of fuels, resulting in the zero-emission factor for biomass. At the same time, according to the hierarchy of waste management methods, recycling is the preferred option for the management of by-products generated during energy production.

The fly ashes resulting from the biomass combustion in pulverized boilers (which, due to their chemical composition, can be classified as silicate ash) were subjected to analysis. These ashes can be classified as waste 10 01 17 – fly ash from co-firing other than mentioned in 10 01 16 according to the Regulation of the Minister of the Environment of December 9, 2014 on waste catalogues.

The maximum theoretical carbon dioxide binding capacity for the analyzed fly ashes resulting from the co-combustion of biomass is 8.03%. The phase composition analysis of the fly ashes subjected to carbonation process has shown, in addition to the components identified in pure fly ash samples ( $\text{SiO}_2$ , mullite), the presence of calcium carbonate – calcite – the primary product of the carbonation process, as indicated by the results of both X-ray and thermogravimetric analysis.

The degree of carbonation has been determined based on the analysis of the results of the phase composition of fly ash resulting from the co-firing of biomass and bituminous coal. The calculated degree of carbonation amounted to 1.51%. The carbonation process is also confirmed by the lowered pH of the water extracts, decreasing from 11.96 for pure ashes to 8.7 for CO<sub>2</sub> treated fly ashes. In addition, the carbonation process has reduced the leaching of pollutants, most notably chlorides, sulphates, and potassium.

