Slovak Geol. Mag. 2008, 19 – 22

CO_2 sequestration with the use of fly ash from hard coal and lignite combustion

ALICJA ULIASZ-BOCHEŃCZYK, EUGENIUSZ MOKRZYCKI

Mineral and Energy Economy Research Institute of Polish Academy of Science
Wybickiego 7; 31-261 Krakow, Poland
aub@min-pan.krakow.pl

Abstract. Mineral sequestration relies upon permanent CO_2 bonding in natural minerals or wastes. It is an ecologically safe method, because CO_2 is permanently bonded, and the occuring in the reaction carbonates do not affect the environment negatively. For CO_2 bonding there may be used natural mineral resources such as f.ex.: olivines, serpentinites or permanent inorganic alkaline waste, containing CaO and MgO in the form reactive with CO_2. Among such waste are f.ex.: fly ash, which are the potential material for carbon dioxide sequestration via mineral carbonation.

In the article a review of findings on the use of fly ash for CO_2 bonding via mineral carbonation has been discussed. One of the aspects of mineral carbonation of particular interest is the influence of CO_2 insertion on the leachability of chemical contamination. In the article there have been presented the exemplary results of chemical contamination contents in the leachates from 'pure' and with inserted CO_2 ash–aqueous suspensions.

The presented findings show that the insertion of CO_2 has caused changes in chemical impurities concentrations in leachates, with concentrations being either increased or decreased, however they are not great.

Key words: CO_2, fly ash from hard coal combustion, fly ash from lignite combustion, mineral carbonation, leachability

1. Introduction

The reduction of increasing anthropogenic CO_2 emission has recently become one of the most important problems as far as the environmental protection. Professional power industry is one of the biggest sources CO_2 emission. This is where a significant amount of solid waste is produced: slags, fly ash, fly ash with desulphurization products and gypsum mixtures. Fly ash is the potential material that can be used for CO_2 bonding. Polish professional power industry, which is the greatest emissioner of CO_2 in Poland, uses, above all, fossil fuel – hard coal and lignite. In 2006 CO_2 emission from Polish professional power industry amounted to 150,918 th. tons, including 91,544 th. tons from the power plants using hard coal, and 56,959 th. tons from power plants and combined heat and power plants (CHPs). At the same time 13,341 th. tons were captured, including 7,156 th. tons from power plants and CHPs operating on hard coal, while from power plants on lignite – 6,157 th. tons (Emitor 2007).

The issue of CO_2 emission reduction from power plants and CHPs may be combined with the use of fly ash for its sequestration via mineral carbonation (Uliasz-Bocheńczyk et al. 2006, Uliasz-Bocheńczyk& Mokrzycki, 2006), which is based on CO_2 reaction with metallic oxides, resulting in the formation of insoluble carbonates (IPCC…2005).

For CO_2 sequestration via mineral carbonation there may be used fly ash from fossil fuel combustion in power industry (Mazurkiewicz et al. 2004; Soong et al. 2006; Baciocchi et al. 2006; Back et al. 2006; Uliasz-Bocheńczyk & Mokrzycki, 2006), as well as ash from waste combustion (Meima et al. 2002; Costa et al. 2007).

The CaO and MgO contents determine fly ash ability to CO_2 bonding (Johnson, 2000; Back et al. 2006; Baciocchi et al. 2006). However, the reactivity of fly ash depends mainly on the CaO content, with MgO content being less important.

Mineral carbonation, or more precisely, the so called accelerated carbonation, has been suggested not only as a method of CO_2 sequestration that is emission reduction, but also as a method of chemical stabilization of fly ash not being widely used in economy, assigned mostly for deposition. This involves, first of all, fly ash from waste combustion (Costa et al. 2007, Meima et al. 2002, Zhang et al. 2007, Li et al. 2006).

In both cases, that is CO_2 sequestration and stabilization, the important issue of CO_2 usage is its impact on the impurities leachability and the change of for example pH.

2. Mineral carbonation of example ash aqueous suspensions with compositions based on fly ash from hard coal and lignite combustion

Polish professional power industry is based on the use of two main fuels for its energy production: hard coal and lignite. Fly ash from professional power industry from hard coal and lignite combustion has been used in the examinations.

Fly ash from hard coal combustion in power plant Jaworzno with CaO content – 4,94%, MgO – 2,55 and fly ash from lignite combustion in power plant Bełchatów with CaO content – 21,6%, MgO – 0,78% and free CaO – 1,1% has been used in the research. The free CaO content has not been stated in ash from hard coal combustion (Uliasz-Bocheńczyk et al. 2007).

Above all, the contents of CaO and MgO in fly ash determine the process of mineral carbonation. While comparing the contents of CaO, MgO and free CaO in the examined ash, a high CaO content (21,6%) is noticeable, in the fly ash from lignite combustion and relatively low CaO content in ash from hard coal combustion (4,94%), with no free CaO content stated in its composition.

For the purpose of confirmation of mineral carbonation processes in ash aqueous suspensions, an examination of CO_2 absorption for fresh ash aqueous suspensions as well as phase composition by means of roentgenographic method has been carried out and a supplementary study of the microstructure with the use of scanning microscope for hardened ash aqueous suspensions.

The studies of CO_2 absorption extent by ash aqueous suspensions have been carried out using especially created installation consisting of two measurement sites, including measurement sets for pressure chambers and registering devices as well as gas cylinder and reducer (Uliasz-Bocheńczyk et al. 2007).

The maximum absorption of ash aqueous suspensions on the basis of fly ash from hard coal combustion in power plant Jaworzno, has been confirmed with the ratio of ash to water 1,5 amounting to 1,22 g CO_2/100 g, for the suspensions prepared on the basis of fly ash from lignite combustion in power plant Bełchatów, the maximum absorption has been stated with the ratio of ash to water 1,25 amounting to 4,15 g CO_2/100 g (Uliasz-Bocheńczyk et al. 2007).

In the roentgenographic and microstructure studies the presence of calcite has been of particular interest, as the basic product of mineral carbonation. The presence of calcite has been stated in ash aqueous suspensions prepared on the basis of ash from hard coal combustion as well as in ash aqueous suspensions prepared on the basis of ash from lignite combustion (Uliasz-Bocheńczyk et al. 2007).

The following phases have been found in the ash aqueous suspensions with compositions based on ash from hard coal combustion in power plant Jaworzno: mullite ($Al_{4.59}\,Si_{1.41}\,O_{9.7}$), haematite ($Fe_2O_3$), quartz ($SiO_2$), calcite ($CaCO_3$) and maghemite ($Fe_2O_3$).

The following phases have been confirmed in the ash aqueous suspensions with compositions based on ash from lignite combustion in power plant Bełchatów: haematite (Fe_2O_3), quartz (SiO_2), calcite ($CaCO_3$), ettringite ($Ca_6(Al(OH)_6)_2(SO_4)_3(H_2O)_{25.7}$), calcium sulphate ($CaSO_4$), calcium silicate ($Ca_2SiO_4$), which has been confirmed by the results of examinations with the use of scanning microscope (example – Fig. 1).

In the roentgenographic examinations the presence of CSH phase has not been stated, however, it has been found in the SEM examinations in the form of gel (Uliasz-Bocheńczyk et al. 2007).

3. Leachability of chemical impurities

The leachability of chemical impurities has been carried out for ash aqueous suspensions with and without inserted CO_2 in order to determine its possible influence.

Chemical oxygen demand (COD) in the analyzed solutions of aqueous extracts has been examined according to standard PN-74 C-04578/03. The chlorides content has been marked with Volhard method, and the designation of sulphates has been done with the use of inductively coupled plasma atomic emission spectrometry method (ICP AES). The plasma emission spectrometry method has been used to mark: arsenic concentration, chrome, cadmium, copper, lead, nickel, zinc, arsenic and mercury. The findings of chemical impurities concentrations as well as the results of pH values designations and COD marking in the leachates from ash aqueous suspensions, 'pure' (without CO_2) and with the inserted CO_2 have been presented in table 1.

The insertion of CO_2 to ash aqueous suspensions prepared on the basis of fly ash from hard coal combustion as well as those from lignite combustion has caused either an increase or a decrease in concentration of various impurities in the leachates.

The insertion of CO_2 to suspensions based on ash from hard coal has brought about a decrease in the contents of Zn, Cu, As, Hg, Cd, Cr, chlorides and sulphates, and at the same time an increase in the contents of : Pb, Ni and pH.

The insertion of CO_2 to suspensions based on ash from lignite has caused a decrease in the contents of Zn, Cr, Ni as well as sulphates and chlorides, with an increase in the contents of: Cu, Pb, As, Hg, Cd and pH.

The findings have been compared with the values of the highest acceptable values of pollution indexes for treated industrial sewage stated in the Regulation of Minister of Environment on 29th November 2002 (Regulation…2002a) on conditions to fulfill while entry to water or ground of sewage as well as on the substances harmful to water environment (Journal of Laws 02.212.1799 on 16th December 2002) – annex 3, the values of acceptable leachability stated in standard – PN-G-11011 'Materials for solidifying stowage and grouting of workings', as the fly ash is, above all, economically used in mining, as well as with the requirements for water quality categories stated in the Regulation of Minister of Environment on 27th November 2002 on conditions to fulfill while using surface water deposits as drinking water (Journal of Laws 02.204.1728 on 9th December 2002).

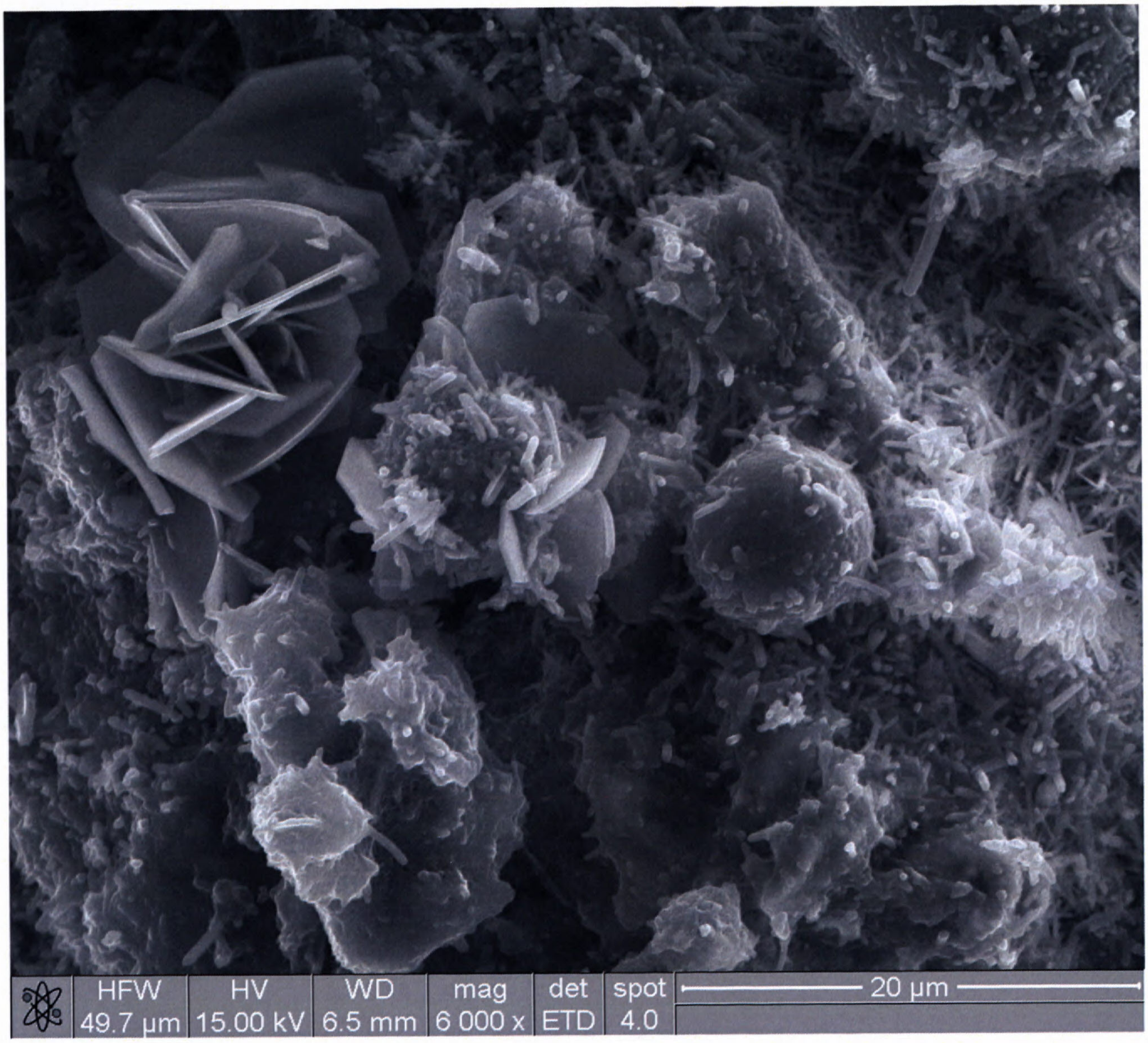

Fig. 1 Ash aqueous suspension prepared on the basis of fly ash from hard coal combustion with inserted CO_2

Table 1 Chemical impurities contents in leachates from ash aqueous suspensions 'pure' and with the inserted CO_2, mg/dm^3

Chemical impurity type	Suspension on the basis of fly ash from hard coal combustion without CO_2	Suspension on the basis of fly ash from hard coal combustion with inserted CO_2	Suspension on the basis of fly ash from lignite combustion without CO_2	Suspension on the basis of fly ash from lignite combustion with inserted CO_2
Zn	0,031	0,021	0,0080	0,0056
Cu	0,00058	0,00029	0,00037	0,00041
Pb	0,00002	0,00003	0,00003	0,00004
Ni	0,00040	0,00041	0,00024	0,00013
As	0,0118	0,0068	0,00022	0,00034
Hg	0,0044	0,0029	0,00017	0,00020
Cd	0,0011	0,00042	0,00011	0,00017
Cr	0,039	0,016	0,0065	0,006
Cl^-	7,1	3,5	1,8	0,0
SO_4^{2-}	455,9	285,7	132,8	92,0
ChZT mg O_2/L	<5,0	<5,0	<5,0	<5,0
pH	10,2	10,8	8,1	11,2

The findings have exceeded highest acceptable values of impurities indexes stated in Regulation (Regulation…2002a) for pH (acceptable 8,5 has not been exceeded only in the case of suspension with composition based on fly ash from lignite combustion without CO_2). The remaining obtained impurities concentrations were below acceptable standards.

The obtained results of chemical impurities concentrations do not exceed the values of chemical contents stated in standard PN-G-11011.

The findings of leachability have been compared with the requirements for water quality categories stated in the Regulation of Ministry of Environment on 27th November 2002 (Regulation...2002b). The obtained concentrations have exceeded the acceptable values only in the case of suspensions based on fly ash from hard coal combustion, in the case of mercury (acceptable 0,005 mg/dm^3) and sulphates (acceptable 250 mg/dm^3) and pH in the case of the two types of suspensions (acceptable 8,5 has not been exceeded only in the case of suspension with composition based on fly ash from lignite combustion without CO_2).

4. Summary

Fly ash may be the material used for CO_2 sequestration. Regardless of a low extent of absorption, as for example in suspensions based on fly ash from hard coal combustion, waste is worth considering for CO_2 sequestration, because of its great amounts. However, when deciding about ash usage for CO_2 sequestration, the leachability of chemical impurities should be taken into consideration, as far as their later use. The presented findings show that the insertion of CO_2 has caused changes in chemical impurities concentrations in leachates, with concentrations being either increased or decreased, however they are not great.

Acknowledgements

This article has been drawn up within the framework of a project financed by the Ministry of Science and Higher Education no. 524 025 32/2619.

The leaching tests were carried out in Faculty of Materials Science and Ceramics of AGH University of Science and Technology.

References

Emitor 2006. Emission of environmental pollution in power plants and in combined heat and power plants. Warsaw, Published by The Energy Market Agency (Agencja Rynku Energii S.A.) (in Polish).

Uliasz-Bocheńczyk A., Mokrzycki E., Mazurkiewicz M., Piotrowski Z., 2006: Utilization of carbon dioxide in fly ash and water mixtures. *Chemical Engineering Research and Design*, vol. 84, no A9, p. 843–846.

Uliasz-Bocheńczyk A., Mokrzycki E., 2006: 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*, vol. 84, no A9, p. 837-842.

IPCC Special Report on Carbon Dioxide Capture and Storage, part 7. Mineral Carbonation and Industrial uses of Carbon Dioxide. Coordinating Lead Author: Marco Mazzotti, 2005.

Mazurkiewicz M., Piotrowski M., Pomykała R., 2004: *The proposition of CO_2 gas disposal.* Proceedings Materials of Twenty-First Annual International Pittsburgh Coal Conference. Osaka.

Baciocchi R., Polettini A., Pomi R., Prigiobbe V., Zedwitz-Nikulshyna, Steinfeld A., 2006: *Performance and kinetics of CO_2 sequestration by direct gas-solid carbonation of APC residues.* Proceedings Materials of 8th International Conference on Greenhouse Gas Control Technologies. Trondheim, Norway.

Back M., Vosbeck K., Kühn M., Stanjek H., Clauser Ch., Peiffer S., 2006: *Storage of CO_2 and generation of alkalinity from reaction of alkaline fly ashes with flue gas.* Proceedings Materials of 8th International Conference on Greenhouse Gas Control Technologies. Trondheim, Norway.

Soong Y., Fauth D.L., Howard B.H., Jones J.R., Harrison D.K., Goodman A.I., Gray M.L., Fromell E.A., 2006: CO_2 sequestration with brine solution and fly ashes. *Energy Conversion and Management,* vol. 47, p. 1676–1685.

Meima J.A., van der Weijden R., Eighmy T.T., Comans R.N.J., 2002: Carbonation in municipal solid waste incinerator bottom ash and their effect on leaching of copper and molybdenum. *Applied Geochemistry* , vol. 17, p. 1503–1513.

Costa G., Baciocchi R., Polettini A., Pomi R., Hills C.D., Carey P.J., 2007: Current status and perspectives of accelerated carbonation processes on municipal waste combustion residues. *Environm. Monit. Assess.*, vol. 135, p. 55-75.

Johnson D.C., 2000: *Accelerated carbonation of waste calcium silicate materials.* SCI Lecture Papers Series, Society of Chemical Industry, ISSN 1353-114X.

Li M., Fernández Bertos M., Hills C.D., Carey P.J., Simon S., 2007: Accelerated carbonation of municipal solid waste incineration fly ashes. *Waste Management*, vol. 27, p. 1200-1206.

Zhang H., He P.J., Shao Li.M., Lee D.J., 2006: Temporary stabilization o air pollution control residues using carbonation. *Waste Management*, vol. 28, p. 509-515.

Uliasz-Bocheńczyk A., Mokrzycki E., Piotrowski Z., Pomykała R., 2007: *The underground storage of CO_2 with ash-water suspensions.* Edit. MEERI PAS, Krakow, 142 p. (in Polish).

Regulation of Minister of Environment on 29th November 2002 on conditions to fulfill while entry to water or ground of sewage as well as on the substances harmful to water environment (Journal of Laws 02.212.1799 on 16th December 2002) a.

Regulation of Minister of Environment on 27th November 2002 on conditions to fulfill while using surface water deposits as drinking water (Journal of Laws 02.204.1728 on 9th December 2002) b.