GOSPODARKA SUROWCAMI MINERALNYMI

Tom 26 2010 Zeszyt 4

ALICJA ULIASZ-BOCHEŃCZYK*

Mineral sequestration of CO_2 in suspensions containing mixtures of fly ashes and desulphurization waste

Introduction

Reducing carbon dioxide emissions by its capturing and safe storage in various forms, including CO_2 bound permanently in mineral raw materials and waste, belongs to the most important problems of environmental protection. Different possibilities and places to store carbon dioxide are constantly searched for.

Heat-generating mineral carbonation consists of permanent binding of CO_2 applying mineral raw materials or waste as a result of creating insoluble carbonates, which are neutral for the environment.

Using waste for binding CO_2 by means of mineral carbonation is more economically justified than using mineral raw materials, as no expenses related to their extraction and processing are incurred. Waste which can potentially serve as material for CO_2 sequestration is often created by a big producer of CO_2, which reduces the cost of transport and the additional CO_2 emissions related to it, and also restricts the negative effect of waste and carbon dioxide on the natural environment.

Permanent binding of CO_2 by mineral carbonation is not only a method of reducing its anthropogenic emissions, but it can also be used as a way of decreasing the leaching of pollutants from waste. In this way the solutions to two problems, which are important from the ecological point of view, can be combined: the reduction of CO_2 emissions by mineral sequestration and waste processing aimed at decreasing the leaching of pollutants, which allows for an easier storage, as well as the searching for new economic applications.

---

* Ph.D., Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, Kraków, Poland; e-mail: aub@min-pan.krakow.pl

CO_2 should be bound in inorganic solid waste containing CaO and MgO forms which can react with carbon dioxide (Huijgen, Comans 2005).

Mixtures of desulphurization products with fly ashes are examples of waste with a high total content of CaO and a high content of free CaO, potentially a good material for CO_2 sequestration.

The economic applications of mineral carbonation's products are an important aspect of its usage. In case of mixtures of fly ashes with desulphurization products these applications can be the use of suspensions prepared on this base in mining technologies (Mazurkiewicz et al. 2005; Uliasz-Bocheńczyk et al. 2004, 2006, 2007).

1. Description of waste used in the research

Research into the degree of carbonation was conducted in aqueous suspensions made of ash and water mixtures with desulphurization products from the Siersza and Łaziska power plants.

Waste from the Siersza power plant is a mixture of fly ashes with products of desulphurization conducted by means of a spray dry absorption method based on the GEESI Anhydro technology (Table 1).

Waste from the Łaziska power plant is a mixture of fly ashes with products of desulphurization from a flue gas desulphurization system using a semi-dry method of the NID type (Table 1).

TABLE 1

The total content of CaO and free CaO in the studiem waste [%] (Uliasz-Bocheńczyk et al. 2007)

TABELA 1

Zawartość całkowitego CaO i wolnego CaO w badanych odpadach [%]

Waste	Content	
	CaO	free CaO
Siersza power plant waste	10.3	1.02
Łaziska power plant waste	13.5	2.62

To describe accurately the studied waste the maximum theoretical capacity for CO_2 binding was calculated using the Steinour equation (Fernandez Bertos et al. 2004):

$$CO_2\ (\%) = 0.785(CaO - 0{,}7SO_3) + 1.09Na_2O + 0.93K_2O \qquad (1)$$

For waste from the Siersza power plant the equation assumes the following form:

$$CO_2\ (\%) = 0.785(10.5 - 0.7 \cdot 2.3) + 1.09 \cdot 1.9 + 0.93 \cdot 2.1 \qquad (2)$$

and the maximum theoretical capacity to bind CO_2 in these suspensions is 11.0%.

For waste from the Łaziska power plant equation (1) is as follows:

$$CO_2\,(\%) = 0.785(13.5 - 0.7 \cdot 1.3) + 1.09 \cdot 0.6 + 0.93 \cdot 2.3 \tag{3}$$

and the maximum theoretical capacity to bind CO_2 in these suspensions is 12.7%.

2. The degree of carbonation

The process of introducing CO_2 into the aqueous ash suspensions was conducted in a system consisting of chambers, a logger (a registering tool), a gas cylinder and a regulator. On closing the chambers tightly, the measuring and registering equipment was connected and the inflow of CO_2 was opened. The research was conducted in laboratory of Department of Environmental Engineering and Mineral Processing of the Faculty of Mining and Geoengineering at the AGH University of Science and Technology (Uliasz-Bocheńczyk et al. 2007, 2009; Uliasz-Bocheńczyk 2009). It was carried out using suspensions whose waste to water ratio was 1.5 (the suspension containing waste from the Łaziska power plant) and 1.2 (the suspension containing waste from the Siersza power plant).

The carbonation process took place in all the studied suspensions subjected to the effects of carbon dioxide.

To estimate the effectiveness of CO_2 binding in aqueous ash suspensions the content of calcium carbonate was determined by means of a thermogravimetric method (TG) (Table 2).

The increase of $CaCO_3$ content in case of suspensions containing a mixture of fly ashes with desulphurization products from the Siersza power plant was 2.39% after the introduction of CO_2 and in the case of suspensions containing a mixture of fly ashes with desulphurization products from the Łaziska power plant 4.8%.

TABLE 2

The content of calcite (% of mass) and the temperature range of mass loss related to the decomposition of $CaCO_3$ [°C]

TABELA 2

Zawartość kalcytu (% mas.) oraz zakres temperatury ubytku masy związany z rozkładem $CaCO_3$ [°C]

Detailed list	Suspension type			
	clean		subjected to CO_2	
	temperature range	$CaCO_3$ content	temperature range	$CaCO_3$ content
Aqueous suspension of Siersza waste	645–850	2.27	720–850	4.66
Aqueous suspension of Łaziska waste	725–850	2.77	625–850	7.57

The degree of CO_2 binding in the researched suspensions was calculated based on the content of calcium carbonate created as a result of thermogravimetric research (Table 2) using the following equation (Baciocchi i in. 2009):

$$S_k = \frac{Z_{k\,CaCO_3} - Z_{p\,CaCO_3}}{100 - Z_{p\,CaCO_3}} \tag{4}$$

where:

S_K – degree of carbonation [%],
$Z_{p\,CaCO_3}$ – content of $CaCO_3$ in the sample before carbonation [%],
$Z_{k\,CaCO_3}$ – content of $CaCO_3$ in the sample after carbonation [%].

The degree of carbonation calculated using the above-mentioned equation for suspensions containing mixtures of fly ashes with desulphurization products from the Siersza power plant was 2.4% and for suspensions containing a mixture of fly ashes and desulphurization waste from the Łaziska power plant 5.2%. The studied suspensions were additionally distinguished by a high level of CO_2 binding in comparison e.g. to an aqueous suspension of a mixture of fly ashes with desulphurization products from the Rybnik power plant, which was calculated using the same equation (4) and was 0.43% (Uliasz--Bocheńczyk 2009).

Differential thermal analysis (DTA) research conducted at the same time made it possible to determine the phase composition of clean suspensions and suspensions subjected to the effects of CO_2 (Fig. 1, 2).

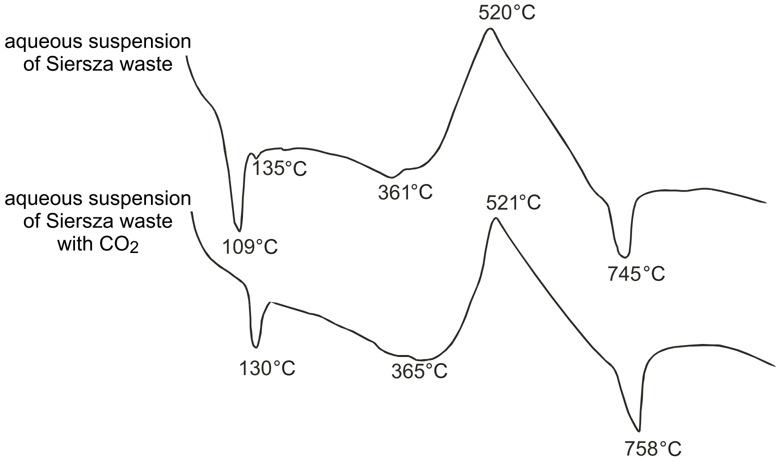

Fig. 1. DTA curves for aqueous suspensions containing mixtures of fly ashes with desulphurization waste from the Siersza power plant; clean suspensions and suspensions subjected to the effects of CO_2

Rys. 1. Krzywe DTA zawiesin wodnych mieszanin popiołów lotnych z odpadami z odsiarczania z El. Siersza: czystych i poddanych działaniu CO_2

The analysis of DTA curves for aqueous suspensions of mixtures of fly ashes and desulphurisation waste from the Siersza power plant points to the presence of:

- C-S-H and ettringite (endothermic effects with a maximum in the temperature range: 109–130°C (Giergiczny 2006));
- hannebachite (hemihydrate calcium sulphate (IV) $\alpha CaSO_3 \cdot 1/2H_2O$) (endothermic effect in a temperature of ca. 360°C (Zaremba et al. 2008));
- calcium carbonate (endothermic effects with a maximum in temperatures 745 and 758°C);
- organic substances (unburnt coal) (exothermic effects with a maximum in the temperature range 520–521°C).

DTA curves (Fig. 2) of aqueous suspensions containing mixtures of fly ashes and desulphurization waste from the Łaziska power plant show effects pointing to the presence of ettringite and C-S-H (endothermic effects with a maximum in temperatures 90°C; 136°C and 140°C). The effect with a maximum in 90°C may point to the presence of ettringite (Prince et al. 2003) which is not included in the curve of suspensions subjected to CO_2. This shows a lack of ettringite related to the carbonation process. The curves also include: endothermic effect with a maximum in temperatures 740°C and 700°C related to the decomposition of $CaCO_3$, as well as an exothermic effect with a maximum in the temperature range 532–516°C related to the presence of organic substances (unburnt coal) and a small endothermic effect with a maximum in ca. 350°C related to the dehydration of hannebachite with the creation of $\alpha CaSO_3$ (Zaremba et al. 2008).

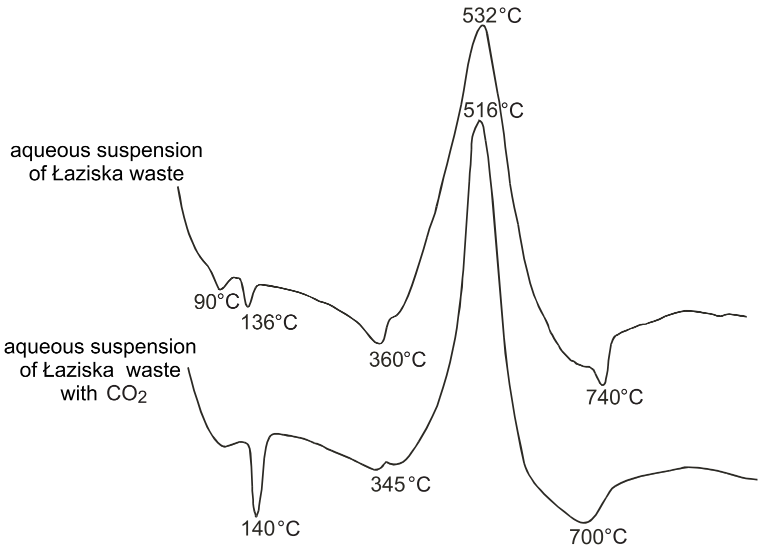

Fig. 2. DTA curves for aqueous suspensions of fly ashes and desulphurization waste mixtures from the Łaziska power plant: clean and subjected to the effects of CO_2

Rys. 2. Krzywe DTA zawiesin wodnych mieszanin popiołów lotnych z odpadami z odsiarczania z El. Łaziska: czystych i poddanych działaniu CO_2

3. Leachability

The chemical demand for oxygen (ChDO) in the analyzed solutions of aqueous extracts was determined in accordance with the norm PN-74 C-04578/03. The content of chlorides was determined using the Volhard method and the concentration of sulphates on the basis of results obtained using inductively coupled plasma atomic emission spectroscopy (ICP AES). To determine the concentration of arsenic, chromium, cadmium, copper, lead, nickel, zinc and mercury the method of plasma emission spectroscopy was employed.

The results of research were compared with the acceptable limits of pollutant contents set by the norm PN-G-11011 „Materials for paste backfill and for caulking abandoned workings" (Table 3). This comparison was conducted because fly ashes are first of all economically applied in mining.

Suspensions prepared using a mixture of fly ashes with desulphurization waste from the Siersza power plant meet the requirements of the PN-G-11011 norm both clean and subjected to CO_2. Introducing CO_2 to the discussed suspensions lowered their pH and resulted in an

TABLE 3

Pollutant leaching from the examined suspensions

TABELA 3

Wymywalność zanieczyszczeń z badanych zawiesin

Type of chemical pollutant	Aqueous suspension containing a mixture of fly ash with desulphurization waste from the Siersza power plant		Aqueous suspension containing a mixture of fly ash with desulphurization waste from the Łaziska power plant		Acceptable leaching levels PN-G-11011
Elements/ions, [mg/dm^3]:	clean	with CO_2	clean	with CO_2	
Zn	0.07900	0.01500	0.00440	0.02100	2.0
Cu	0.00025	0.00065	0.00086	0.00020	0.5
Pb	0.00002	0.00002	0.00016	0.00003	0.5
Ni	0.00060	0.00024	0.00047	0.00031	–
As	0.00900	0.00410	0.00260	0.00230	0.2
Hg	0.00089	0.00049	0.00091	0.00079	0.02
Cd	0.00034	0.00021	0.00018	0.00008	0.1
Cr	0.00260	0.00330	0.00270	0.00280	0.2
Cl^- [mg/dm^3]	44.3	159.6	269	330	1 000.0
SO_4^{2-} [mg/dm^3]	281	484.3	372.8	427	500.0
ChZT [mg O_2/dm^3]	20.0	52.7	5.1	17.1	100.0
PH	11.5	8.0	11.2	7.9	6.0–12.0

increased leaching of ions of copper, chromium, chlorides and sulphates. Decreased leaching was observed in the case of zinc, nickel, arsenic, mercury and cadmium. The leachability of lead did not change.

In the case of suspensions containing Łaziska waste, like in the case of suspensions of Siersza waste, the observed leaching does not exceed the acceptable levels stated in the PN-G-11011 norm. The process of carbonation of suspensions containing waste from the Łaziska power plant resulted in a decrease in zinc, copper, lead, arsenic and mercury leachability. pH was also reduced. The leachability of chromium, sulphates and chlorides increased.

The basic reaction of mineral carbonation taking place in the discussed suspensions:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \tag{5}$$

results in the lowering of pH and, consequently, a change in the solubility and leachability of individual ions. Because of this, carbonation can cause a decrease in the leaching of those elements, whose compounds dissolve better with a higher pH. For elements leaching easily with a medium or low pH carbonation will result in an easier passage to the solution (Astrup et al. 2006). Some factors influencing the decrease of leachability caused by carbonation are: lowering of leachate pH, changes in the solubility caused by the precipitation of carbonates or the creation of oxygen anions, reduction in the release of selected metals as a result of sorption in newly-created minerals and a reduction of porosity as a result of the creation of calcite (Zhang et al. 2008).

The decrease in leachability of heavy metals, such as Cd, Zn, Mn, Co, Ni, Pb and Sr may be caused by the sorption of the above-mentioned cations in the calcite, which leads to the co-precipitation of solid solutions (Reeder 1996; Tesoriero, Pankow 1996; Wang et al. 2010). The reduction in the leachability of cadmium ions may also be a result of the creation of $CdCO_3$. In the case of nickel the decrease in leachability may be caused by substituting the Ca^{2+} ions by the Ni^{2+} cation of C-S-H or by the creation of $NiCO_3$ (Fernandez Bertos et al. 2004).

An important factor reducing the leachability of zinc, chromium and lead is the immobilization of these ions by C-S-H (Małolepszy, Deja 1995; Deja 2002; Giergiczny, Król 2008).

The increase in chromium leachability observed in the research may be explained by the oxidizing of Cr^{3+} ions to a better soluble form of Cr^{6+} ions (He et al. 2006) or by the dissolution of ettringite, part of whose structure were the chromium ions. Chromium integrated in ettringite passes into the solution as a result of a lower pH related to carbonation (Van Gerven et al. 2005). Decomposition of ettringite under the influence of carbonation results in a greater leachability of the sulphates in accordance with the following reaction (Kurdowski 2010):

$$1/3\,(CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + CO_2 \rightarrow \tag{6}$$

$$\rightarrow CaCO_3 + CaSO_4 \cdot 2H_2O + 2/3\,Al(OH)_3 + 23/3\,H_2O$$

Chromium may substitute Si in C-S-H. Its solubility increases with the lowering of pH and the decrease in the average degree of polycondensation of oxygen-silicon anions in C-S-H.

The increase in Cu leachability may be caused by a higher solubility of copper compounds caused by the lowering of pH or the decomposition of ettringite (Fernandez Bertos et al. 2004).

Research into the influence of CO_2 on the leachability of the discussed elements in a mixture of fly ashes with desulphurization products from the Rybnik power plant (Uliasz--Bocheńczyk 2009) demonstrated a decrease in the quantity of leaching zinc, copper, nickel, arsenic, chlorides and a lowering of pH in comparison with the suspensions before carbonation. On the other hand, on introducing CO_2 to the suspensions an increase in the leachability was observed for chromium, mercury, sulphates and the value of ChDO. The levels of leachability of other elements (lead and cadmium) did not change.

Summary

Research into the degree of CO_2 binding and the influence of mineral sequestration of carbon dioxide on the leachability of pollutants (mainly heavy metals) was conducted on aqueous suspensions prepared from a mixture of fly ashes with desulphurization products from the power plants Siersza and Łaziska.

An increase in the content of calcium carbonate was observed, which shows that a reaction of mineral carbonation of the suspensions takes place.

The degree of CO_2 binding in the discussed aqueous suspensions containing mixtures of fly ashes and desulphurization products, determined on the basis of thermogravimetric research, was 2.4% for suspensions of waste from the Siersza power plant and 5.2% for suspensions from the Łaziska power plant.

The suspensions researched were distinguished by the presence of phase C-S-H, which may immobilize some heavy metals.

A decrease in the leachability of a number of heavy metals is probably caused by the creation of sparingly soluble carbonates, the immobilization of heavy metals in C-S-H or the adsorption and the co-precipitation of heavy metals as a result of creating solid solutions with calcite.

A very important feature of mineral sequestration of CO_2 is the possibility of using the products of the process in the economy. The researched suspensions subjected to the effects of CO_2 meet the requirements of PN-G-11011 containing the acceptable levels of leachability of chemical pollutants and the values of pH and ChDO for materials used in underground mining, which allows for their usage in mining technologies.

Thermogravimetric research and differential thermal analysis (DTA) were conducted by Prof. Irena Wacławska.

Research into the leachability of pollutants and the values of pH and ChDO was conducted in the Department of Building Materials Technology of the Faculty of Materials Science and Ceramics at the AGH University of Science and Technology.

REFERENCES

Astrup T., Rosenbald C., Trapp S., Christensen T.H., 2005 – Chromium release from waste Incineration Air-Pollution-Control Residues. Environmental Science & Technology 39, p. 3321–3329.

Baciocchi R., Costa G., Polettini A., Pomi R., Prigiobbe V., 2009 – Comparison of different reaction routes for carbonation of APC residues. Energy Procedia 1, p. 4851–4858.

Deja J., 2002 – Immobilization of Cr^{6+}, Cd^{2+}, Zn^{2+} and Pb^{2+} in alkali-actived slag binders. Cement and Concrete Research 32, p. 1971–1979.

Fernandez Bertos M., Simons S.J.R., Hills C.D., Carey P.J., 2004 – A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of CO_2. Journal of Hazardous Materials B112, p. 193–205.

Giergiczny Z., 2006 – Rola popiołów lotnych wapniowych i krzemionkowych w kształtowaniu właściwości współczesnych spoiw budowlanych i tworzyw cementowych. Wydawnictwo Politechniki Krakowskiej, Monografia nr 325, Kraków.

Giergiczny Z., Król A., 2008 – Immobilization of heavy metals (Pb, Cu, Cr, Zn, Cd, Mn) in the mineral additions containing concrete composites. Journal of Hazardous Materials 160, p. 247–255.

He P.J., Cao Q.K., Shao L.M., Lee D.J., 2006 – Aging of air pollution control residues from municipal solid waste incinerator: Role of water content on metal carbonation. Science of Total Environment 359, p. 26–37.

Huijgen W.J.J., Comans R.N.J., 2005 – Mineral CO_2 sequestration by carbonation of industrial residues. ECN. ECN-C-05-074. www.ecn.nl.

Kurdowski W., 2010 – Chemia cementu i betonu. Wydawnictwo Polski Cement/Wydawnictwo Naukowe PWN, Kraków/Warszawa.

Małolepszy J., Deja J., 1995 – Effect of heavy metals immobilization on properties of alkali actived slag mortars. Proceedings Fifth CANMET/ACI International Conference: Fly ash, silia fume, slag and natural pozzolans in concrete, Milwaukee, Wisconsin. Edited by V.M. Malhotra, vol. 2, p. 1087–1095.

Mazurkiewicz M., Mokrzycki E., Piotrowski Z., Pomykała R., Uliasz-Bocheńczyk A., 2005 – Sekwestracja CO_2 i możliwości jego współlokowania w zrobach podziemnych z popiołami. Przegląd Górniczy, nr 11, p. 42–48.

Reeder R.J., 1996 – Interaction of divalent cobalt, zinc, cadmium and barium with calcite surface during layer growth. Geochimica et Cosmochimica Acta vol.60, No. 9, p. 1543–1552.

Tesoriero J.A., Pankow J.F., 1996 – Solid solution partitioning of Sr^{2+}, Ba^{2+}, and Cd^{2+} to calcite. Geochimica et Cosmochimica Acta vol.60, No. 6, p. 1053–1063.

Uliasz-Bocheńczyk A. (red.), Mokrzycki E., Piotrowski Z., Pomykała R., 2007 – Składowanie CO_2 z zawiesinami popiołowo-wodnymi pod ziemią. Wyd. IGSMiE PAN, Kraków.

Uliasz-Bocheńczyk A., Mokrzycki E., Mazurkiewicz M., Piotrowski Z., 2004 – Utylizacja dwutlenku węgla poprzez mineralną karbonatyzację. Polityka Energetyczna t. 7, z, spec., s. 541–554.

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, Volume: 84, Issue: A9, p. 843–846.

Uliasz-Bocheńczyk A., Piotrowski Z., 2009 – Wpływ mineralnej karbonatyzacji na wymywalność zanieczyszczeń. Rocznik Ochrony Środowiska, t. 11, cz. 1, s. 1083–1094.

Uliasz-Bocheńczyk A., 2009 – Mineralna sekwestracja CO_2 w wybranych odpadach. Studia Rozprawy Monografie nr 153, Wyd. IGSMiE PAN, Kraków.

Prince W., Espagne M., Aïtcin P.C., 2003 – Ettringite formation: A crucial step in cement superplasticizer compatibility. Cement and Concrete Research 33, p. 635–641.

Wang L., Yiying J., Yongfeng N., 2010 – Investigation of accelerated and natural carbonation of MSWI fly ash with a high content of Ca. Journal of Hazardous Materials 174, p. 334–343.

Van Gerven T., Van Keer E., Arickx S., Jaspers M., Wauters G., Vandecasteele C., 2005 – Carbonation of MSWI-bottom ash to decrease heavy metal leaching, in view of recycling. Waste Management 25, p. 291–300.

Zaremba T., Hehlmann J., Mokrosz W., Stapiński G., Szwalikowska A., 2008 – Otrzymywanie i właściwości spoiw siarczynowych i anhydrytowych z odpadów z półsuchej metody odsiarczania spalin. Gospodarka Surowcami Mineralnymi, t. 24, z. 2/1, s. 87–106.

Zhang H., He P.J., Shao Li. M., Lee D.J., 2008 – Temporary stabilization of air pollution control residues using carbonation. Waste Management 28, p. 509–517.

MINERALNA SEKWESTRACJA CO_2 W ZAWIESINACH MIESZANIN POPIOŁÓW LOTNYCH Z ODPADAMI Z ODSIARCZANIA

Słowa kluczowe

Popioły lotne, produkty odsiarczania, ditlenek węgla, wymywalność zanieczyszczeń, mineralna sekwestracja

Streszczenie

Mineralna sekwestracja CO_2 w zawiesinach odpadowo-wodnych jest metodą, która pozwala na równoczesne gospodarcze wykorzystanie odpadów oraz redukcję antropogenicznej emisji ditlenku węgla. Może być również stosowana jako metoda obróbki odpadów, ograniczająca wymywalność z nich niektórych zanieczyszczeń. Badania przeprowadzono na dwóch rodzajach zawiesin wodnych mieszanin popiołów z produktami odsiarczania z El. Siersza i El. Łaziska. Obliczono teoretyczną pojemność związania tych mieszanin. Przedstawiono wyniki badań związania CO_2 w zawiesinach wodnych mieszanin popiołów lotnych z odpadami z odsiarczania oraz wpływu poddania ich działaniu ditlenku węgla na wymywalność zanieczyszczeń. Na podstawie badań termograwimetrycznych obliczono stopień związania CO_2 w analizowanych zawiesinach. Badania wykazały wpływ mineralnej karbonatyzacji na redukcję wymywalności określonych zanieczyszczeń z omawianych zawiesin poddanych działaniu CO_2.

MINERAL SEQUESTRATION OF CO_2 IN SUSPENSIONS CONTAINING MIXTURES OF FLY ASHES AND DESULPHURIZATION WASTE

Key words

Fly ashes, desulphurization products, carbon dioxide, pollutant leaching, mineral sequestration

Abstract

Mineral sequestration of CO_2 in wastewater suspensions is a method which allows both for economic applications of waste and for the reduction of anthropogenic emissions of carbon dioxide at the same time. It can also be used as a method of waste processing which decreases the leaching of some pollutants. The research was conducted using two kinds of aqueous suspensions of fly ashes and desulphurization waste mixtures from the Siersza and Łaziska power plants. A theoretical binding capacity of the mixtures was calculated. The results of research into CO_2 binding in aqueous solutions of fly ashes and desulphurization waste mixtures and into the influence of subjecting them to the effects of carbon dioxide on the leachability of pollutants were presented. Based on thermogravimetric research the degree of CO_2 binding in the analyzed suspensions was calculated. The research showed an influence of mineral carbonation on the decrease in certain pollutants' leaching from the discussed suspensions subjected to the effects of CO_2.