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## CO<sub>2</sub> mineral sequestration with the use of ground granulated blast furnace slag

### Introduction

The 2015 United Nations Climate Change Conference held in Paris negotiated a global agreement on the reduction of climate change. The Paris Agreement was hailed as a turning point for the world as it was agreed that global and national emissions should peak as soon as possible (EC 2016).

The EU has committed to a 20% reduction in 2020 greenhouse gas emissions (from 1990 levels). By 2050, the goal of the EU climate policy is to cut greenhouse gas emissions to 80% compared to 1990 base year ([http://unfccc.int/focus/indc\\_portal/items/8766.php](http://unfccc.int/focus/indc_portal/items/8766.php)). As an EU country, Poland has followed the policy of reducing CO<sub>2</sub> emissions and meeting the requirements of the Kyoto Protocol, and thus the objectives set by the EU, for many years.

One option for reducing CO<sub>2</sub> emissions is CCS (*Carbon Capture and Storage*).

The mineral sequestration of CO<sub>2</sub> may constitute the final stage of CCS technology and replace geological storage. This option is especially interesting for enterprises that do not have the possibility of storing CO<sub>2</sub> in geological structures due to their location, but

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produce waste products which can be used to bind carbon dioxide. This applies particularly to industrial sectors – large emitters of CO<sub>2</sub>, participating in the EU emission trading system (EU ETS). The steel industry is one of the major emitters of CO<sub>2</sub> from industrial processes.

In Poland, the CO<sub>2</sub> emissions from pig iron and steel production amounted to 5,818.37 Gg in 2013 and then increased up to 6 181.07 Gg in 2014, which is still a significant reduction compared to the year 1988 when the emissions amounted to 20,551.91 Gg (PNIR 2016).

The mineral carbonation using metallurgical slag is one of the potential options considered in studies on reducing CO<sub>2</sub> emissions from the steel industry.

The theoretical suitability of metallurgical slag for CO<sub>2</sub> sequestration was estimated in the range from 325.2 to 407.1 g/kg (Huijgen et al. 2004; Huijgen and Comans 2005).

The paper presents the degree of carbonation of the examined samples of ground granulated blast furnace slags.

## 1. The mineral carbonation using metallurgical slags

An analysis using slags blast furnace, steel, and converter slags has been performed in order to determine the possibility of reducing CO<sub>2</sub> emissions using mineral carbonation (Table 1 and 2).

Table 1. Direct carbonation using slags from the iron and steel industry

Tabela 1. Karbonatyzacja bezpośrednia przy zastosowaniu żużli z hutnictwa żelaza i stali

Authors	Slag type	Type of direct carbonation	Temperature [°C]	Pressure [MPa]	The degree of carbonation
Baclocchi et al. 2008, 2009a	electric arc furnace (EAF) slag, argon oxygen decarburization (AOD) slag	slurry-phase carbonation	30 to 50	0.1 to 1.0	maximum CO <sub>2</sub> uptake – 12%
Baclocchi et al. 2010a	electric arc furnace (EAF) slag, argon oxygen decarburization (AOD) slag	wet route batch carbonation	50, 100, 150	0.3; 0.1; 1.0	maximum CO <sub>2</sub> uptake: EAF – 180 g CO <sub>2</sub> /kg slag; AOD – 300 g CO <sub>2</sub> /kg slag
Baclocchi et al. 2010b	electric arc furnace (EAF) slag, argon oxygen decarburization (AOD) slag	wet route batch carbonation	50	0.3; 0.1; 1.0	maximum CO <sub>2</sub> uptake: EAF – 17.6% AOD – 30.7%
Bonenfant et al. 2008	electric arc furnace (EAF) slag, ladle furnace (LF) slag	gas mixture (15% CO <sub>2</sub> and 85% N <sub>2</sub> ) – suspension L/S = 10 kg/kg	20	atmospheric pressure	CO <sub>2</sub> sequestration capacity: EAF slag – 7.66 g CO <sub>2</sub> /100 g of slag, LF slag suspension – 24.7 g CO <sub>2</sub> /100g of slag

Table 1. cont.

Tabela 1. cd.

Authors	Slag type	Type of direct carbonation	Temperature [°C]	Pressure [MPa]	The degree of carbonation
Boone et al. 2014	fine grained stainless-steel slag	CO <sub>2</sub> – mixture with 10 wt % water	80	2	59 g of CO <sub>2</sub> is bound in carbonate per kg of slag
Chang et al. 2011	ultra-fine steelmaking slag	aqueous carbonation	40–160	4.83	CO <sub>2</sub> capture capacities per gram of dry solid slag – 0.127 kg CO <sub>2</sub>
Diener et al. 2010	electric arc furnace slag, ladle furnace slag	accelerated carbonation	20–40	–	the lowest pH, decreased leaching: Ca, Cu, Ba, Fe, Mn, Pb
Huijgen et al. 2004	steel slag	CO <sub>2</sub> – suspension of steel slag	25–200	0.1–3.0	70% degree of conversion
Huijgen et al. 2005; Huijgen and Comans 2006; Huijgen 2007	Linz Donawitz steel slag	CO <sub>2</sub> – suspension of steel slag L/S = 2–20 kg/kg	25–225	0.1–3.0	the maximum carbonation degree of the Ca content – 74%
Johnson 2000	ground granulated blast furnace slag (GGBFS), stainless steel slag	CO <sub>2</sub> – suspension of steel slag	–	0.3	weight gain carbonation – 20%
Sánchez and Martines 2010	steelmaking slag	dry accelerated mineral carbonation slag/water = 5/1	150	5	71% carbonation
Santos et al. 2013	stainless steel slags: argon oxygen decarburization (AOD) slag, continuous casting (CC) slag	slurry carbonation	30–180	0.2–3	CO <sub>2</sub> uptake: 0.26g CO <sub>2</sub> /g slag AOD 0.31 g CO <sub>2</sub> /g CC slag
Uliasz-Bocheńczyk 2009	steel slag	CO <sub>2</sub> and CO <sub>2</sub> – 13%, O <sub>2</sub> – 11%, N <sub>2</sub> – 76% – slag suspension	20	atmospheric pressure	CO <sub>2</sub> absorption – 3,66–11,23 g CO <sub>2</sub> /100 g slag
van der Laan et al. 2008	converter slag	gas (20% CO <sub>2</sub> and 80% Ar) – slag in the presence of water	5–90	–	sequestered slag – 15 g CO <sub>2</sub> /kg slag

Table 2. Indirect carbonation using slags from the iron and steel industry

Tabela 2. Karbonatyzacja pośrednia przy zastosowaniu żużli z hutnictwa żelaza i stali

Authors	Slag type	Extracting factor	Temperature [°C]	Pressure [MPa]	The degree of carbonation
Eloneva et al. 2008 a	blast furnace slag	CH <sub>3</sub> COOH, NaOH	30–70	0.1, 3	4.4 kg of slag, 3.6 dm <sup>3</sup> CH <sub>3</sub> COOH and 3.5 kg NaOH would be required to bind 1 kg CO <sub>2</sub> resulting in – 2,5 kg of 90% CaCO <sub>3</sub>
Eloneva et al. 2010	steelmaking slag	NH <sub>4</sub> Cl, NH <sub>4</sub> NO <sub>3</sub>	30	–	high-quality CaCO <sub>3</sub> precipitated (calcite or aragonite)
Eloneva i in. 2008 b	steel converter slag	CH <sub>3</sub> COOH, CH <sub>3</sub> CH <sub>2</sub> COOH, HNO <sub>3</sub> , H <sub>2</sub> SO <sub>4</sub> , NaOH, CH <sub>3</sub> COONa, NH <sub>4</sub> Cl, CH <sub>3</sub> COONH <sub>4</sub> , NH <sub>4</sub> NO <sub>3</sub> , (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> , NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> , (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	30, 50, 70	0.130	Ca conversion – 50–70%
Kodama et al. 2006, 2008	converter slag	NH <sub>4</sub> Cl	–	atmospheric pressure	degree of extraction Ca – 48,5%
Kunzler et al. 2011	steel slag	HCl	25, 70	–	the global yield of extraction and carbonation for CaCO <sub>3</sub> – 83%
Mun and Cho 2013	blast furnace slag	EDTA CH <sub>3</sub> COOH HCl	–	–	capture CO <sub>2</sub> as 0.09 kg/kg
Nienczewski et al. 2008	mixture of rude carbon steel slag from the electric arc furnace	HCl solution	25, 40, 70		max. Ca extracted – 73.8%
Sun et al. 2011	steelmaking slag	NH <sub>4</sub> Cl	60	1	CO <sub>2</sub> capture capacity – 211 kg CO <sub>2</sub> /ton steelmaking slag
Teir et al. 2007	blast furnace slag, steel converter, slag electric arc furnace slag	CH <sub>3</sub> COOH	30, 50, 70	–	calcium reach solution suitable for precipitation of CaCO <sub>3</sub>
Zevehoven et al. 2010	steelmaking slag – basic oxygen slag	NaHCO <sub>3</sub> NaNO <sub>3</sub>	28, 150	4	bound of 2–8% CO <sub>2</sub>

The process of mineral carbonation utilizing slags from the steel industry can be carried out directly (as a one-step process) (Table 1) or indirectly (two-stage process – Ca and Mg ions are subjected to extraction, which is followed by reaction with CO<sub>2</sub>) (Table 2).

## 2. The materials used for testing

According to the Regulation of the Minister of the Environment of 9 December 2014 (Journal of Laws, 2014, item 1923) on the waste catalogue, the majority of slag produced by the iron and steel industry during smelting (blast furnaces, steelmaking furnaces) is defined by the six-digit code (10 02 01) for waste and the respective two-digit (10 02) chapter heading.

Blast furnace slags are characterized by a rough and cavernous surface with many sharp edges (Sobczyński 1999) (Fig. 1).

The granulated blast furnace slag used for testing (Fig. 1) was not grinded, which significantly reduced the cost of the carbonation process.

The chemical composition of blast furnace slags depends on the content and composition of gangue accompanying the iron ore (Małolepszy et al. 2008; Galos et al. 2009). The examined granulated blast furnace slags are characterized by a high content of Ca and Si (Table 3 and 4).



Fig. 1. Ground granulated blast furnace slag used for testing

Rys. 1. Granulowany żużel wielkopiecowy zastosowany do badań

Table 3. The chemical (oxide) composition of the examined blast furnace slags [%]  
(Uliasz-Bocheńczyk and Mokrzycki 2016)

Tabela 3. Skład chemiczny (tlenkowy) badanych żużli wielkopiecowych [%]

Component	Blast furnace slag
SiO <sub>2</sub>	39.0
CaO	44.0
MgO	5.0
Al <sub>2</sub> O <sub>3</sub>	9.0
Fe <sub>2</sub> O <sub>3</sub>	0.5
Na <sub>2</sub> O	0.5
K <sub>2</sub> O	0.4
SO <sub>3</sub>	2.5

Table 4. The chemical composition (elemental) of examined blast furnace slags [%]

Tabela 4. Skład pierwiastkowy badanych żużli wielkopiecowych [%]

Component	Blast furnace slag
Si	4.49
S	0.22
Cl	0.18
K	0.47
Ca	23.66
Ti	0.27
V	0.097
Cr	0.06
Mn	0.20
Fe	0.14
Ni	0.01
Cu	0.004
Zr	0.007
Pb	0.001

Based on the chemical composition it is possible to estimate the maximum theoretical capacity of the analyzed blast furnace slags to bind CO<sub>2</sub>.

The maximum theoretical capacity to bind CO<sub>2</sub> is calculated from the chemical composition using the Steinoor equation (Fernandez-Bertos et al. 2004):

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

The capacity of the analyzed blast furnace slags is 34.1%.

The phase composition of the analyzed slags is dominated by amorphous glassy phase (Fig. 2 and 3), typical for this type of waste (Deja 2004). The glass content of granulated blast furnace slag is typically more than 90% (Deja 2004; Galos et al. 2009; Małolepszy et al. 2008).

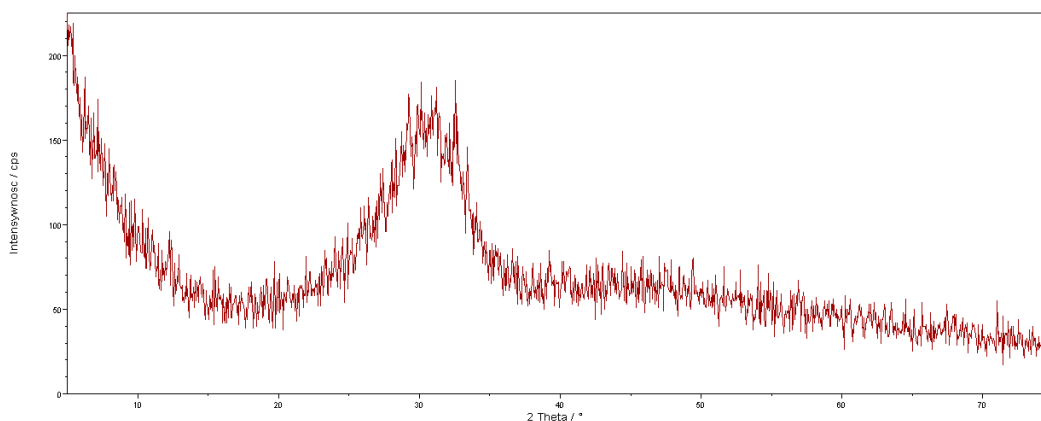


Fig. 2. The diffraction pattern of the analyzed blast furnace slag before the carbonation process

Rys. 2. Dyfraktogram analizowanego żużla wielkopiecowego przed procesem karbonatyzacji

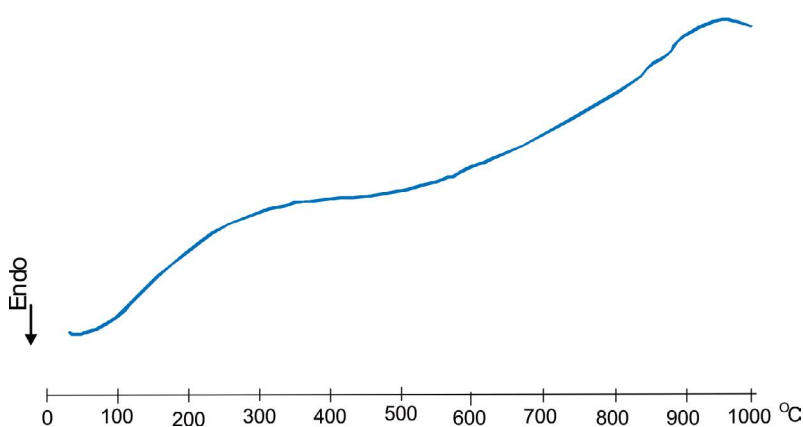


Fig. 3. DTA curve of the analyzed blast furnace slag before the carbonation process

Rys. 3. Krzywa DTA analizowanego żużla wielkopiecowego przed procesem karbonatyzacji

Mellites, forming a series of solid solutions with: akermanite and gehlenite as extreme members of the series, can also be found (Małolepszy et al. 2008). Other minerals include: larnite, monticellite, merwinite, rankinite, anorthite, wollastonite, and calcium aluminate and magnesium aluminate spinel (Deja 2004).

### 3. The degree of carbonation of the examined slags

The carbonation process was conducted using a direct CO<sub>2</sub>-solid method for 30 days. The slags were wetted on the surface and placed in sealed chambers supplied with CO<sub>2</sub> (Uliasz-Bocheńczyk 2009).

The phase composition of slags exposed to CO<sub>2</sub> was analyzed using the X-ray diffraction (XRD) and thermal gravimetric (DTA/TG) methods.

After treating the slags with phase composition presented in Fig. 2 with CO<sub>2</sub>, calcium carbonate – calcite was formed as a product of the carbonation process, as evidenced by intense peaks associated with its presence in the sample (Fig. 4). The observed intense calcite peaks, as opposed to amorphous phase characteristic for slag subjected to aging treatment under laboratory conditions (Fig. 2 and 3), suggests the intensity of the carbonation process, which was indicated by the calcite content determined by the DTA/TG analysis (Fig. 5 and 6).

The DTA/TG analysis of the phase composition indicates the presence of calcite, as indicated by visible and significant endothermic effect with the peak at a temperature of 820°C (Fig. 5).

A quantitative analysis of the sample subjected to the carbonation process has confirmed the calcite content at a level of 9.32% (Fig. 6), which is a very significant increase when

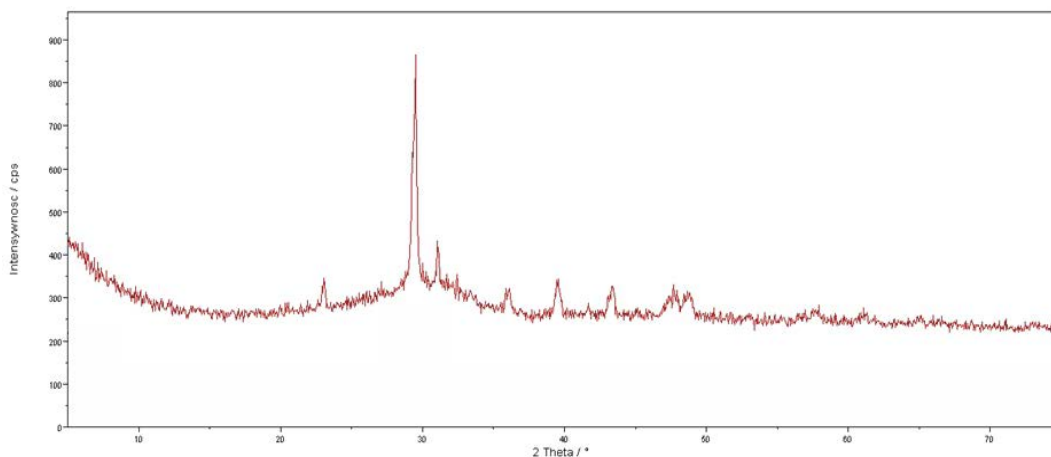
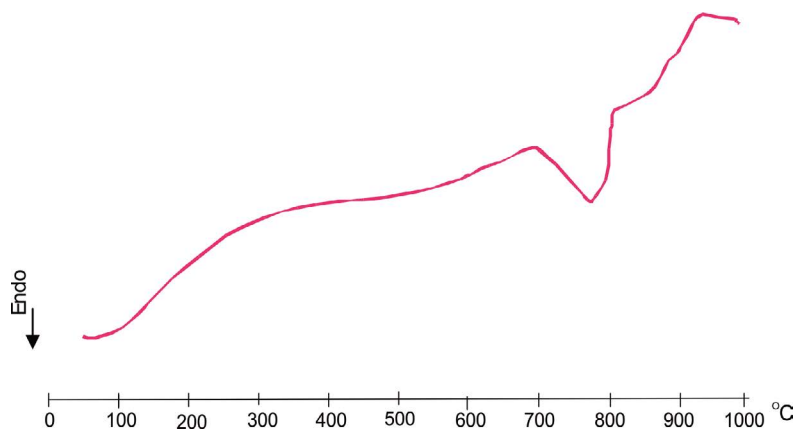
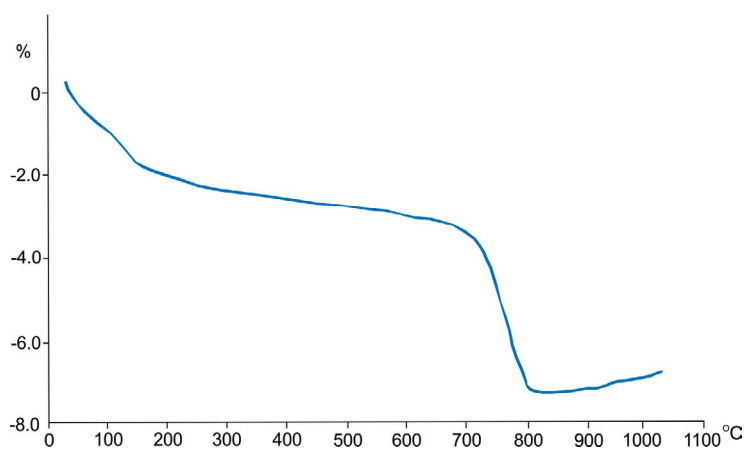


Fig. 4. The diffraction pattern of the analyzed blast furnace slag before the carbonation process

Rys. 4. Dyfraktogram analizowanego żużla wielkopiecowego po procesie mineralnej karbonatyzacji



Fig. 5. The DTA curve of the analyzed slags after exposure to CO<sub>2</sub>Rys. 5. Krzywa DTA analizowanych żużli po poddaniu ich działaniu CO<sub>2</sub>Fig. 6. The TG curve of the analyzed slags after exposure to CO<sub>2</sub>Rys. 6. Krzywa TG analizowanych żużli po poddaniu ich działaniu CO<sub>2</sub>

compared to the sample subjected to aging treatment under laboratory conditions, when no calcite was found (Fig. 2 and 3).

The simplest way to calculate the degree of carbonation is to use the increased weight of the sample after the carbonation process with the formula below (Bacocchi et al. 2010a):

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

- ↗  $\text{CO}_2$  uptake – the extent of carbonation [%],
- $\text{CO}_2$  initial – initial carbonate content of the sample [%],
- $\text{CO}_2$  final – final carbonate content of the sample [%].

In the case of the analyzed blast furnace slags the degree of carbonation is 9.32%.

However, given that the carbonation process was carried out with a direct gas-solid method using slags, the degree of carbonation can be calculated with the following formula (Huijgen 2007):

$$S_K = \frac{\frac{\text{CO}_2}{100 - \text{CO}_2} \cdot \text{MW}_{\text{Ca}}}{\text{Ca}_{\text{total}} \cdot \text{MW}_{\text{CO}_2}} \cdot 100 = 39\% \quad (3)$$

- ↗  $S_K$  – the degree of carbonation [%],
- $\text{Ca}_{\text{total}}$  – the total Ca content of the fresh slag [kg/kg],
- $\text{CO}_2$  – carbonate content measured with DTA/TG [wt. %],
- $\text{MW}_{\text{Ca}}$  – the molar weights of Ca [kg/mol],
- $\text{MW}_{\text{CO}_2}$  – the molar weights of  $\text{CO}_2$  [kg/mol].

The carbonation process is also indicated by lowering the pH from 10.5 to 9.6 as a result of subjecting the sample to the mentioned process (Uliasz-Bocheńczyk and Mokrzycki 2016).

An analysis of the leachability of pollutants from blast furnace slags has shown a decrease in ion concentration of Ba, Sr, Mn, Ni, Co, Hg, Sb, V, and Cu after exposure to  $\text{CO}_2$ . It has also been shown that the increased leaching of chloride ions and the leachability of Zn, Pb, Cd, Cr, and As remained unchanged (Uliasz-Bocheńczyk and Mokrzycki 2016).

## Summary and conclusions

Blast furnace slags are among waste products characterized by an increased capacity to bind  $\text{CO}_2$  especially predisposed to bind  $\text{CO}_2$  through mineral carbonation, especially when using the direct gas-solid method.

The research results presented in this article were obtained using the direct gas-solid method. Slags were treated with  $\text{CO}_2$  for 28 days in closed chambers.

The analyzed waste products are characterized by a high content of calcium (23.66%), which affects the theoretical binding capacity of  $\text{CO}_2$  amounting up to 34.1%. An analysis of the phase composition of the analyzed slags has confirmed the presence of amorphous glass phase. Their exposure to  $\text{CO}_2$  has resulted in a significant amount (9.32%) of calcium carbonate – calcite. The carbonation process is also confirmed by lowered pH of slag leachates.

A significant leachability of calcium ions (Uliasz-Bocheńczyk and Mokrzycki 2016) confirms the ease and a high degree of the carbonation process of the analyzed blast furnace slags.

The calculated degree of carbonation of the examined blast furnace slags is up to 39%. The high degree of the carbonation process, although the granulated blast furnace slag used for testing was not grinded, has confirmed the suitability of the discussed waste products to reduce carbon dioxide emissions.

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#### MINERALNA SEKWESTRACJA CO<sub>2</sub> PRZY ZASTOSOWANIU GRANULOWANYCH ŻUŻLI WIELKOPIECOWYCH

##### Słowa kluczowe

mineralna sekwestracja, CO<sub>2</sub>, granulowane żużle wielkopiecowe,  
metoda bezpośrednia gaz–ciało stałe

##### Streszczenie

Mineralna sekwestracja przy wykorzystaniu odpadów jest metodą redukcji CO<sub>2</sub> szczególnie interesującą dla znaczących emitentów, którzy są zarazem wytwórcami odpadów mineralnych, tak jak przemysł hutniczy. Emisja CO<sub>2</sub> z produkcji żelaza i stali wyniosła 6 181,07 kt w 2014 roku (PNIR 2016). Przemysł ten bierze udział w systemie handlu pozwoleniami na emisję ditlenku węgla – EU ETS, a zarazem w procesach wielkopiecowych powstają odpady mineralne – żużle o wysokiej zawartości CaO, które mogą być stosowane do redukcji emisji CO<sub>2</sub>. Żużle hutnicze mogą być stosowane do realizacji procesu mineralnej sekwestracji ditlenku węgla metodą bezpośrednią (jednoetapową) oraz pośrednią (dwuetapową).

W artykule przedstawiono wyniki badań stopnia karbonatyzacji granulowanych żużli wielkopiecowych klasyfikowanych według Rozporządzenia Ministra Środowiska z dnia 9 grudnia 2014 r. w sprawie katalogu odpadów do podgrupy 10 02 Odpady z hutnictwa żelaza i stali jako odpad o kodzie 10 02 01. Do prowadzenia procesu karbonatyzacji zastosowano metodę bezpośrednią gaz–ciało stałe. Zwilżone żużle były poddawane procesowi sekwestracji ditlenku węgla przez 28 dni, a uzyskane wyniki porównano z analizą świeżych odpadów. Poddane badaniom żużle charakteryzują się wysoką zawartością wapnia, wynoszącą prawie 24%, a ich obliczona teoretyczna pojemność związania CO<sub>2</sub> wynosi 34,1%. Analiza składu fazowego żużli wykorzystanych w badaniach, prowadzona metodą rentgenograficzną, wykazała jedynie obecność amorficznej fazy szklistej, co potwierdzają wyniki analizy DTA/TG. Proces mineralnej sekwestracji CO<sub>2</sub> spowodowało powstanie w znaczącej ilości 9,32% węglanu wapnia–kalcytu, a obliczony stopień karbonatyzacji badanych żużli wielkopiecowych wynosi maksymalnie 39%. Wysoka zawartość wapnia oraz powstanie znaczącej zawartości CaCO<sub>3</sub>–kalcytu, potwierdza szczególnie predyspozycje tych odpadów do redukcji emisji ditlenku węgla.

**CO<sub>2</sub> MINERAL SEQUESTRATION WITH THE USE OF GRANULATED BLAST FURNACE SLAG****Keywords**

mineral sequestration, CO<sub>2</sub>, ground granulated blast furnace slag, the direct gas-solid method

**Abstract**

The mineral sequestration using waste products is a method of reducing CO<sub>2</sub> emissions that is particularly interesting for major emitters and producers of mineral wastes, such as iron and steel industries. The CO<sub>2</sub> emissions from iron and steel production amounted to 6,181.07 kt in 2014 (PNIR 2016). The aforementioned industry participates in the EU emission trading system (EU ETS). However, blast furnace processes produce mineral waste – slag with a high content of CaO which can be used to reduce CO<sub>2</sub> emissions. Metallurgical slag can be used to carry out direct (a one-step process) or indirect (two-stage process) process of mineral sequestration of carbon dioxide.

The paper presents the degree of carbonation of the examined samples of granulated blast furnace slags defined by the six-digit code (10 02 01) for the waste and the respective two-digit (10 02) chapter heading, according to the Regulation of the Minister of the Environment of 9 December 2014 on the waste catalogue. The carbonation process used the direct gas-solid method. The slags were wetted on the surface and treated with CO<sub>2</sub> for 28 days; the obtained results were compared with the analysis of fresh waste products. The analyzed slags are characterized by a high content of calcium (nearly 24%), while their theoretical binding capacity of CO<sub>2</sub> is up to 34.1%. The X-ray diffraction (XRD) analysis of the phase composition of slags has revealed the presence of amorphous glass phase, which was confirmed with the thermogravimetric (DTA/TG) analysis. The process of mineral sequestration of CO<sub>2</sub> has resulted in a significant amount (9.32%) of calcium carbonate – calcite, while the calculated degree of carbonation of the examined blast furnace slag is up to 39%. The high content of calcium, and a significant content of CaCO<sub>3</sub>–calcite, has confirmed the suitability of the discussed waste products to reduce carbon dioxide emissions.