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## Waste used for CO<sub>2</sub> bonding via mineral carbonation

### Key words

Sequestration, mineral carbonation, CO<sub>2</sub>, waste

### Abstract

CO<sub>2</sub> sequestration via mineral carbonation is an ecologically safe way of its utilization. Owing to the processes occurring whilst mineral carbonation, CO<sub>2</sub> is strongly bonded and stable thermodynamic products come into being, neutral to the environment, in the form of carbonates, that exist naturally in the environment. For CO<sub>2</sub> bonding the following natural resources may be employed: olivine as well as mineral waste.

The examples of CO<sub>2</sub> sequestration by means of mineral carbonation with the application of varied mineral waste have been presented in the article.

### Introduction

Mineral carbonation as a method of carbon dioxide sequestration was proposed by Seifritz (1990) in 'Nature' magazine, and the first research on that matter was published in 1995 by the team of: Lackner K.S., Wendt C.H., Butt D.P., Joyce E.L. Jr, Sharp D.H. Since then, numerous publications concerning mineral carbonation have appeared from various research centers around the world.

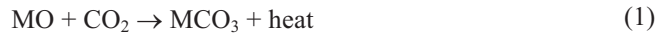
In 2005 mineral carbonation was finally defined in the IPCC Special Report on Carbon Dioxide Capture and Storage, part 7. Mineral Carbonation and Industrial uses of Carbon Dioxide (IPCC... 2005c). Mineral carbonation is a reaction of CO<sub>2</sub> with metallic oxides such

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as: magnesium, calcium or iron, as a result of which insoluble carbonates are created (IPCC... 2005c):



Mineral carbonation is a strong exothermal reaction. In case of the two basic oxides CaO and MgO 179 and 118 kJ/mol are educed adequately (Lackner et al. 1995).

The process of mineral carbonation via CO<sub>2</sub> bonding in the natural mineral resources is a phenomenon occurring in nature, and it is one of the reactions thanks to which the ageing of rocks in the atmospheric conditions occurs (Kojima et al. 1997).

Mineral carbonation is an ecologically safe method of CO<sub>2</sub> sequestration.

As the result of the processes occurring via mineral carbonation, stable thermodynamic products come into being, neutral to the environment, in the form of carbonates, that exist naturally in the environment.

Mineral carbonation may be conducted by means of a direct and indirect method (Huijgen, Comans, 2003). When using the direct method, the mineral or waste undergoes direct carbonation. When dealing with the indirect method, the reactive ingredients are initially extracted from the mineral matrix, then undergo a reaction with CO<sub>2</sub>.

The process of mineral carbonation in natural conditions is slow, thus various kinds of the so-called pretreatment are applied, among which the most important ones are the enlargement of the specific surface area of the mineral or the waste via its pulverization, thermal treatment as well as magnetic separation.

### 1. Mineral carbonation by waste

The use of natural minerals involves the costs of their extraction. It is the opposite in case of the application of waste for CO<sub>2</sub> bonding via mineral carbonation. An additional aspect in favour of the usage of waste is the fact that the process of mineral carbonation is faster in comparison with natural mineral resources. It is at the same time a way of economic usage of waste.

For CO<sub>2</sub> bonding inorganic alkaline waste should be employed, containing CaO and MgO in the form that is prone to reactions with CO<sub>2</sub> (Huijgen, Comans 2005).

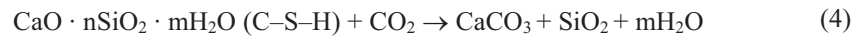
Subject to carbonation are, first of all, the phases present in a great number of mineral wastes (Huijgen, Comans 2005):

1) portlandite

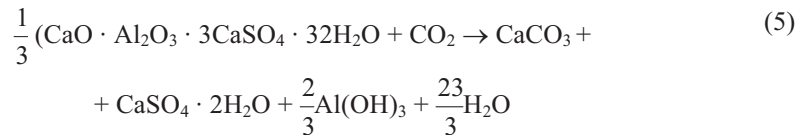


2) calcium silicates





3) ettringite



In case of the use of ash aqueous suspensions for CO<sub>2</sub> bonding, the researches have confirmed the presence of the phases undergoing carbonation such as: CSH, ettringite, calcium silicates. The products of carbonation were mainly calcium compounds (calcite) calcium and magnesium (dolomite) and sporadically potassium carbonate. Carbonates have occurred within the confines of the availability of this element, with the excess of active calcium compounds, which were not bound with silicates and sulphates, probably for the most part as a result of carbonation of portlandite educed in the later stages of hydration (Uliasz-Bocheńczyk et al. 2007).

When selecting waste for CO<sub>2</sub> bonding, the distance between the place of their origin and the source of emission ought to be taken into consideration, as the increase of the distance entails the increase of costs of transport, thereby sequestration. The future management of carbonation products should influence the selection of waste chosen for CO<sub>2</sub> bonding. The best solution is the economic utilization of carbonation products (Hujigen and Comans 2005).

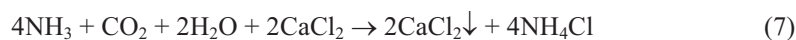
Waste that may be used for CO<sub>2</sub> sequestration via mineral carbonation are among others: fly ash, ash from fluidized bed boilers, blast furnace slag, cement waste, concrete waste and asbestos waste.

Mineral carbonation by waste, where CaO is bonded in silicates, is most often conducted as direct carbonation with the use of waste-aqueous suspensions with different ratios of water to waste (Stolaroff et al. 2005; Hujigen and Comans 2005; Kodama et al. 2006; Hujigen, 2007; Uliasz-Bocheńczyk et al. 2007; Costa et al. 2007). The absorption and bonding of carbon dioxide depends on the conditions of the process of mineral carbonation, first and foremost, the temperature and the pressure (Reddy et al. 1994; Hujigen et al. 2005; Hujigen, 2007; Fernandez Bertos et al. 2004).

During the researches on mineral sequestration by waste, the direct carbonation gas – solid was applied (Jia, Anthony 2000; Baciocchi et al. 2006) as well as the indirect two-stage carbonation (Kodama et al. 2006; Teir et al. 2007). In the processes of direct mineral carbonation gas – solid, the waste from Air Pollution Control system and ash from fluidized bed boilers were used. Indirect carbonation by slag was suggested with the use of NH<sub>4</sub>Cl (Kodama et al. 2006) and CH<sub>3</sub>COOH (Teir et al. 2007).

In case of NH<sub>4</sub>Cl, the process of mineral carbonation should yield to the two-stage pattern as follows:





On the basis of the chemical composition, the potential of some waste for CO<sub>2</sub> bonding was estimated (Table 1).

TABLE 1  
CO<sub>2</sub> potential for sequestration for some mineral waste (Huijgen and Comans 2005)

TABELA 1  
Potencjał sekwestracji CO<sub>2</sub> dla niektórych odpadów mineralnych (Huijgen i Comans 2005)

Waste type	Ca content [g/kg]	Mg content [g/kg]	Amount of utilized CO <sub>2</sub> [g/kg]
Cement waste	424.7–448.8	9.0–11.0	486.1
Fly ash from coal combustion	38.1	9.2	58.6
Fly ash from community waste combustion	119.1	13.5	155.2
Blast furnace slag	222.0–312.5	45.0–73.1	325.2–407.1

## 2. Sequestration by cement and concrete waste

CO<sub>2</sub> bonding via concrete is a well-known phenomenon occurring in the environment even with its small concentration in the air and water. The bond is permanent and thus, safe for the environment. However, this process is very slow in natural conditions (Uliasz-Bocheńczyk et al. 2006).

Carbonation consists in the interaction between CO<sub>2</sub> in the air and the hardened cement paste present in the concrete. All of the ingredients of the cement paste undergo carbonation. From among hydrates, Ca(OH)<sub>2</sub> shows the easiest type of reaction with CO<sub>2</sub> in the cement paste, forming CaCO<sub>3</sub>, but CO<sub>2</sub> influences other hydrates, as a result beside CaCO<sub>3</sub>, the hydrated silicon, aluminium and iron oxides are produced. When Ca(OH)<sub>2</sub> is used up there is a possibility of carbonation of hydrated C–S–H. The easiest carbonation occurs in portland cement, which produces the biggest amount of lime. The pace of concrete carbonation increases together with the rise of CO<sub>2</sub> concentration, especially when the ratio values of cement to water are high (Neville 2000).

The stages of the cement carbonation process are as follows (Fernandez Bertos et al. 2004): CO<sub>2</sub> diffusion in the air, CO<sub>2</sub> infiltration through the solid, solvation of CO<sub>2(g)</sub> to CO<sub>2(aq)</sub>, hydration CO<sub>2(aq)</sub> in H<sub>2</sub>CO<sub>3</sub>, ionisation of H<sub>2</sub>CO<sub>3</sub>, dissolution of C<sub>3</sub>S and C<sub>2</sub>S, crystallization of CaCO<sub>3</sub> and CSH, precipitation of solid phases, secondary carbonation.

The studies concerning the possibilities of cement waste usage were carried out mainly for reasons of leaching limitation with the use of carbonation, and at the same time utilization of CO<sub>2</sub> (Ginneken et al. 2004; Gervais et al. 2004; Fernandez et al. 2004).

### 3. Sequestration by slag

For the reason of high CaO content slag was employed to CO<sub>2</sub> sequestration (Johnson 2000; Huijgen et al. 2004; Stolaroff et al. 2005; Kodama et al. 2006; Huijgen 2007). Theoretically, the slag capability of CO<sub>2</sub> sequestration amounts to 0.25 kg/kg (Huijgen et al. 2004). The parameters of the greatest influence on the degree of slag carbonation are the temperature and specific surface area (Huijgen et al. 2004). Huijgen and others (2004) have affirmed a 70% limestone transformation within 30 minutes with the pressure of 20 bars and the temperature of 200°C. What is particularly interesting, is the use of steelmaking slag, since it does not have such wide economic application as granulated blast furnace slag, which is an important material for the cement production.

The potential of CO<sub>2</sub> sequestration by slag and granulated blast furnace slag in the USA was valued at 4.6 Mt CO<sub>2</sub>/year (Stolaroff et al. 2005).

### 4. Sequestration by slag and concrete waste

Stolaroff and others (2005) also proposed the method of mineral sequestration, where slag and concrete waste are used. The system is based on two parallel layers (deposits) operating simultaneously, one of which is drained and unloaded while the other is working. The system should consist of 140 kt of slag and 680 kt of concrete waste. The amount of CO<sub>2</sub>, that can be captured and bonded by means of the suggested system was assessed at 32 kt of CO<sub>2</sub> per annum, and as a result of mineral carbonation 73 kt of CaCO<sub>3</sub> will be produced within a year (Stolaroff et al. 2005).

### 5. Sequestration by fly ash

For CO<sub>2</sub> bonding the fly ash from fossil fuels combustion in the power industry may be applied (Mazurkiewicz et al. 2004; Uliasz-Bocheńczyk et al. 2006; Uliasz-Bocheńczyk et al. 2007; Soong et al. 2006; Baciocchi et al. 2006; Back et al. 2006 a, b; Uliasz-Bocheńczyk, Mokrzycki 2006; Rao et al. 2007), as well as the ash from waste combustion (Todorovic et al. 2006; Meima et al. 2002; Rendek et al. 2006).

First of all, the CaO content, free CaO and MgO determine the fly ash ability to bond CO<sub>2</sub> (Johnson 2000; Back et al. 2006a; Baciocchi et al. 2006). However, similarly as in case of cements, the reactivity of ash depends largely on the CaO content, less importantly on MgO content.

In the event of fly ash from community waste combustion which undergoes carbonation (Rendek et al. 2006), the researches revealed an increase of CaCO<sub>3</sub> weight content up to 6,2% in relation to a 3,3% CaCO<sub>3</sub> content in the ash before carbonation. The authors indicated the influence of humidity (in case of a 15% humidity the amount of absorbed CO<sub>2</sub> dropped)

and fly ash pulverization on the process of absorption and bonding of CO<sub>2</sub>. The ash of a 4 mm granulation absorbed 24 dm<sup>3</sup>/kg of CO<sub>2</sub>, and the non-sifted ash 12,5 dm<sup>3</sup>/kg. A decrease in leaching was also confirmed as a consequence of carbonation of heavy metals, such as: Cr, Pb, Cd (Rendek et al. 2006; Baciocchi et al. 2006) as well as Cu and Mo (Meima et al. 2002).

A method of CO<sub>2</sub> sequestration was drawn up as well, with the use of fly ash and brine, which is the waste from petroleum and gas production (Soong et al. 2006). Rich in CaO fly ash is added to brine, so as to increase the value of pH of brine reaction substrates, maximizing the efficiency of carbonation reaction. In addition, the ash is the source of supplemental Ca ions.

The conducted researches on Polish fly ash (Uliasz-Bocheńczyk et al. 2007) showed that CO<sub>2</sub> absorption by ash-aqueous suspensions relies heavily on the ash type and the combination method of these two elements – executed by means of suspensions mixing (shaking) in the CO<sub>2</sub> atmosphere. As a result of the studies, it was stated that CO<sub>2</sub> absorption by suspensions, generated on the basis of conventional fly ash, practically cannot be considered. The following suspensions with ash showed the highest value of absorption: with desulphurization products, fluidized and from lignite combustion. The maximum value of CO<sub>2</sub> absorption amounted for these ashes to 10,93 g CO<sub>2</sub>/100 g of ash (Uliasz-Bocheńczyk et al. 2007).

### Summary

Mineral carbonation is an ecologically safe method, because as a result of the occurring processes CO<sub>2</sub> is permanently bonded in the form of carbonates, that exist in the natural environment.

The application of waste to CO<sub>2</sub> bonding is particularly interesting, since in this way it is economically used. In comparison with natural resources usage, an argument in favour of the waste is the fact that there are not any costs involved with its extraction. Another advantage of waste employment is that the process of carbonation thanks to its use is faster than in the event of natural minerals application. It results from the fact that, first and foremost, the calcium phases undergo carbonation. In their case the process of carbonation is faster than in case of magnesium phases, which predominate in natural resources used for CO<sub>2</sub> sequestration. Additionally, waste is characterized by a relatively open structure and sizeable specific surface area. The employment of waste in mineral carbonation holds further advantage: the waste are often produced in the industrial plants which are at the same time the sources of CO<sub>2</sub> emission, as in case of fly ash and slag, and it consequently eliminates the additional costs of transport.

It seems that, the most promising way of mineral carbonation application is the waste use for CO<sub>2</sub> bonding, which has not found economic employment in the industry.

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ALICJA ULIASZ-BOCHEŃCZYK

#### ODPADY STOSOWANE DO WIĄZANIA CO<sub>2</sub> NA DRODZE MINERALNEJ KARBONATYZACJI

##### Słowa kluczowe

Sekwestracja, mineralna karbonatyzacja, CO<sub>2</sub>, odpady

##### Streszczenie

Sekwestracja CO<sub>2</sub> na drodze mineralnej karbonatyzacji jest bezpiecznym ekologicznie sposobem jego utylizacji. W wyniku procesów zachodzących na drodze mineralnej karbonatyzacji CO<sub>2</sub> jest trwale wiązany i powstają termodynamicznie stabilne produkty, obojętne dla środowiska w postaci węglanów naturalnie występujących w środowisku. Do wiązania CO<sub>2</sub> mogą być stosowane surowce naturalne takie jak np. oliwiny, ale również odpady mineralne.

W artykule przedstawiono przykłady sekwestracji CO<sub>2</sub> na drodze mineralnej karbonatyzacji przy zastosowaniu różnych odpadów mineralnych.