MODELING KINETICS OF CO₂ (CARBON DIOXIDE) MINERAL SEQUESTRATION IN HETEROGENEOUS AQUEOUS SUSPENSIONS SYSTEMS OF CEMENT DUST

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Abstract
The necessity to reduce CO₂ emission in the environment has encouraged people to search for solutions for its safe capture and storage. Known methods for carbon dioxide mineral sequestration are based primarily on the use of its binding reaction with metal oxides, mainly earth metals. Increasingly important, due to the availability and price, are processes based on the suspension of various wastes such as fly ash, cement dust or furnace slag. Due to the complexity of the mineral sequestration of CO₂ in water-waste suspensions, an important issue is to determine the reaction mechanisms. This applies mainly to the initial period of the transformation phase of mineral wastes, and consequently with the occurrence of a number of transition states of ionic equilibria. The mechanisms and reaction rates in the various stages of the process of CO₂ mineral sequestration in heterogeneous systems containing selected wastes are defined herein. This paper presents a method of modeling kinetics of this type of process, developed on the basis of the results of the absorption of CO₂ thanks to the aqueous suspension of fly ash and cement dust. This allowed for the transfer of obtained experimental results into the mathematical formula, using the invariant function method, used to describe the processes.

Keywords
CO₂ sequestration, cement dust, invariant function.

1. INTRODUCTION
The amount of carbon dioxide introduced into the environment is responsible for the greenhouse effect. Therefore, it is crucial to search for methods which can reduce gas emissions and safely capture and store it. One interesting method of carbon dioxide neutralization is mineral carbonation (IPCC Special Report 2005), which results in stable, environmentally inert products. This process also called a mineral sequestration is the reaction of CO₂ with metal oxides (mainly CaO and MgO) which results in carbonates. In order to bind CO₂, mineral carbonation raw materials (e.g. serpentine) can be used as well as different types of waste such as fly ash, cement dust, or slag. It was suggested, in the early 1990s in (Seifritz 1990), to use a carbonation of serpentine, a mineral occurring in nature, as a method to reduce CO₂ emissions. The early results of research conducted with the use of natural resources were published in the mid-1990s (Lackner et al. 1995; Lackner, Butt, Wendt 1997). Due to the complexity of mineral sequestration, resulting from the heterogeneous reactions of binding CO₂ by waste-aqueous suspension, it was important to determine the reaction mechanisms. It was interesting to find out what happens in the early stage of reactions as well as during the transformation phase of mineral waste and in the associated emergence of a number of transient ionic equilibria.

This paper describes the modeling of the carbon dioxide mineral carbonation process. It is based on the results of the absorption of CO₂ by the aqueous suspension of cement dust and fly ash (Uliasz-Bocheńczyk 2009). Considering the assumptions of the thermodynamic model (Uliasz-Bocheńczyk, Cempra 2010) and the kinetic model (Świnder, Uliasz-Bocheńczyk 2010), it attempts to identify the mechanisms and reaction rates leading to the permanent binding of carbon dioxide with selected waste.

2. SEQUESTRATION OF CO₂ WITH THE USE OF WASTE
The high cost of extracting and processing natural resources in the early twentieth century has led to research regarding the use of waste for CO₂ binding (Baciciocchi et al. 2009; Back et al. 2008; Duchesnel, Reardon 1998; Huijgen, Comans 2006).

In Poland, the work on mineral sequestration of CO₂ was conducted using waste-aqueous suspension (Uliasz-Bocheńczyk 2008; Uliasz-Bocheńczyk, Mokrzycki 2009; Uliasz-Bocheńczyk, Piotrowski 2008; Uliasz-Bocheńczyk et al. ed. 2007). However, some mineral carbonation using fresh and stored dust from a cement kiln can also be found (Antemir et al. 2008; Huntzinger, Eatmon 2009a; Huntzinger et al. 2009b; Huntzinger et al. 2009a).
3. A SIMPLIFIED PROCESS MODEL

The model of the process of CO₂ absorption in aqueous suspensions of cement kiln dust is similar to the mechanism of processes occurring during the sequestration of carbon dioxide by using suspensions of slag and fly ash (Świnder, Uliasz-Bocheńczyk 2010; Uliasz-Bocheńczyk 2009).

On the basis of the developed thermodynamic model (Uliasz-Bocheńczyk, Cempa 2010) and the kinetic calculations (Świnder, Uliasz-Bocheńczyk 2010) the assumption that processes of mineral carbonation of ash and cement dust are similar was considered. Moreover, these processes are connected with two consecutive actions: the hydration of carbon oxide (from ash or cement dust) and joining carbon dioxide to the obtained calcium hydroxide (the result of hydration).

In case of high pH (around 12.5), occurring in aqueous suspensions of ash and cement dust, the equilibrium of the reaction (4) is shifted toward the creation of a poorly soluble calcite (CaCO₃).

Taking into consideration the new solid phases, like CaSO₄ or CaCO₃ created during the hydration and dissolution of minerals from fly ash or cement dust, which can create an additional barrier to access the surface of reagents and formed calcite crystals, the new kinetic model of mineral carbonation in aqueous suspension systems of ash and cement dust was developed.

Based on the process model presented in various works (Aksielrud, Pohobenko 1966; Aksielrud, Molezanow 1981), which describes the kinetics of a heterogeneous reaction, resulting in poorly soluble reaction products, the kinetics of the analysed process can be written as follows:

$$\frac{dC_s}{dt} = k_1 R = k_2 P = k_3 C$$  (5)

where:
- $C_s$ – concentration of a substrate in the reaction system
- $k_1 R$ – kinetics of particles of ash or cement kiln dust dissolution
- $k_2 P$ – an increase in diffusion resistance at a flow of mass through a layer of poorly soluble products
- $k_3 C$ – kinetics of CO₂ reaction with the components of ash or cement dust

Using the formula (5), the kinetics of gaseous CO₂ sequestration in a heterogeneous reaction system containing dust or fly ash cement and water was determined. It was assumed that the volume of solid (ash or cement kiln dust) and the reactant concentration (CO₂) in a solution is constant, and the process is conducted in a closed system.

Under these assumptions, using a simplified reaction equilibrium curve, the equation of reaction kinetics of a cement dust particle or fly ash with carbon dioxide on the aquatic environment can be described as follows:

2009b; 2009c), yet their number is relatively low. In order to determine the rate of reaction occurring in the various stages of sequestration, it is necessary to determine the form of kinetic equation of a given reaction and to determine its constant rate value for the selected type of waste. The reactions of binding CO₂ by aqueous suspensions of waste are heterogeneous reactions. In heterogeneous processes, in addition to starting parameters such as pressure, temperature and concentration, other factors characterizing the physicochemical state of substrates plays an important role. In the case of waste-aqueous suspensions, the first to be mentioned are: the size distribution (fineness degree), phase composition, surface grain condition, and defects in the crystal structure of the minerals contained in the waste (Uliasz-Bocheńczyk 2008, 2009). In the process of CO₂ sequestration in waste-aqueous suspensions, in addition to the stages associated with physical phenomena (diffusion and dissolution of gaseous CO₂, dissolution and migration from the phases of mineral calcium ions Ca²⁺, nucleation and precipitation of carbonates), chemical reactions take place, which are associated with the formation of carbonate and bicarbonate ions and their reactions with calcium ions. These reactions cause changes in the pH of the reaction (Uliasz-Bocheńczyk, Cempa 2010). Factors affecting the rate of sequestration and diffusion processes are the precipitation and dissolution rate resulting in the process of sparingly soluble compounds (e.g. calcium carbonate). These phenomena do not affect the nature of chemical reactions because the sequestration of CO₂ with waste suspension is a second order reaction (Świnder, Uliasz-Bocheńczyk 2010), but the formation of solid products significantly affects the kinetics of the dissolution processes of waste grain, and thus the concentration of substrates in their reaction with CO₂. Due to the complicated nature of the physicochemical processes occurring during the process of CO₂ sequestration with certain soluble components of fly ash or cement dust, it is not possible to unambiguously identify the phenomenon, physical or chemical, which determines the rate of this process. Analyses conducted for modeling processes are performed to extend and complement previously described experiments (Świnder, Uliasz-Bocheńczyk 2010; Uliasz-Bocheńczyk 2008, 2009), associated with sequestration in aqueous suspensions of selected waste. The conducted experiments and the proposed kinetic model of the processes and reactions which occur during the introduction of gaseous carbon dioxide in aqueous suspensions of selected waste facilitates defining the parameters of CO₂ sequestration processes for a number of industrial wastes, including cement dust. In order to verify these assumptions, cement kiln dust captured from the gas stream at the inlet to the kiln from dry method cement production was used. In order to verify the results of the experimental sequestration of carbon dioxide fly ash from the dry dedusting were also used, as described in the works (Świnder, Uliasz-Bocheńczyk 2010; Uliasz-Bocheńczyk 2008, 2009). Phase composition of fly ash and cement dust is influenced by many factors such as the physicochemical conditions of the process and the composition of input materials. Studies on cement dust samples revealed the presence of several mineral phases, with a dominant share of portlandite. Similar results can be found in other studies of cement (Peethamparan, Olek, Lovelli 2008; Seifritz 1990).
\[ C_r = C_p \left(1 - e^{-\frac{nA_c k}{V C_r}}\right) = C_p \left(1 - e^{-kT}\right) \]

\[ K = \frac{nA_c C_y k}{V C_r} \]

where:
\( C_p \) – concentration of poorly soluble product in the reaction environment
\( C_p^* \) – product concentration level at which the surface of reactive substrate is completely covered
\( V \) – volume of water
\( n \) – stoichiometric coefficient of reagent conversion into undissolved product of the reaction (\( n = 1 \))
\( A_0 \) – the volume of solid
\( C_d/ C_r^* \) – ratio of the lowest and highest pressure in the system
\( k \) – rate constant of reaction

4. EXPONENTIAL MODEL OF THE PROCESS

The kinetics equation (6) is an example of an exponential model with two parameters, also called the first-order inertial model. This model can be written with the equation:

\[ y(t) = a \left(1 - e^{-\frac{t}{T}}\right) \]

The constant \( a \) is the so-called asymptote of the curve, and constant \( T \) is the time constant. The importance of the various constants can be described as follows: the asymptotic value is the upper limit value adopted by the function, or otherwise – the limit under the assumption that the function arguments tend to go to infinity. The time constant is the measure of the function ramping: if the argument of a function is time, assuming that the rate of accumulation of values is such as at the initial moment (for \( t = 0 \)), the limit value would be reached after time, \( t = T \). In turn, each of the integral multiples of a time constant value (\( t = nT \), where \( n \) is a natural number), the value of the \( y \) function is the \( (en - 1)/en \) limit (asymptotic) value.

5. EXPERIMENTS AND RESULTS

5.1. Input data

We analyzed three sets of data from studies of \( CO_2 \) absorption by cement-water and ash-water and suspensions, carried out in the system (Ulissasz-Bocheńczyk 2008) located in the Department of Environmental Engineering and Mineral Processing of the Faculty of Mining and Geomeering at the AGH University of Science and Technology. The first two series were carried out using the dust, while the third, was carried out with ash.

A brief description of each of the series is given in Table 1.

**Table 1. Characteristics of measurement series.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Series I</th>
<th>Series II</th>
<th>Series III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exact duration [s]</td>
<td>1 633 997</td>
<td>1 887 180</td>
<td>112 204</td>
</tr>
<tr>
<td>Approximate duration [days]</td>
<td>18</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>Volume [cm³] – ( V )</td>
<td>0.091</td>
<td>0.125</td>
<td>0.125</td>
</tr>
<tr>
<td>Specific surface of dust/ash [m²/kg – ( A )]</td>
<td>3000</td>
<td>3000</td>
<td>400</td>
</tr>
<tr>
<td>( R/P_{f_0} )</td>
<td>0.96</td>
<td>0.31</td>
<td>0.60</td>
</tr>
<tr>
<td>( n )</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Volume of solid [cm³] – ( V_{cs} )</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Number of measurements</td>
<td>2 653</td>
<td>5 350</td>
<td>1 079</td>
</tr>
</tbody>
</table>

From a certain moment for two measurement sessions the constant (fixed) level of carbon dioxide absorption was observed. Therefore, it was for each of them to arbitrarily indicate the point at which the chemical reactions that are of interest do not occur (or occur at rates that each compensate for their effects). The example of a shortened process for series I is presented on Figure 1 (original data) and Figure 2 (recalculated data). Observing (and modeling) of the series I was completed in the 9308th second of measurement; series III in the 1845th second. In order to ensure that each of the observations equally affects the pattern of the curve described by equation (2), they had to be converted in such a way that the intervals between consecutive measurements were equal. At the interval for series I and III two seconds were taken. For series II – 1000 seconds.

The curve described by equation (3) has two parameters: the asymptote and the time constant responsible for the speed of the pursuit to asymptotic values. From an analytical point of view there should be a search for the best curve which fits the experimental data by manipulating the values of both parameters. However, from the point of view of the nature of the process, the value of the asymptote is indicated to explicitly recognize the fixed value of the process.

5.2. Results

In order to fit a curve to converted experimental data, MATLAB software from Mathworks was used. To measure curve fit, RMSE – Root Mean Squared Error – was used.

\[ RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^{n} (y_i - \bar{y}_i)^2} \]
where $n$ is the number of points derived from experimental data, $y_0$ is the actual value, and $y$ is the value derived from a mathematical model of the process. The next three graphs show the result of the search for a curve that describes the phenomenon investigated in the best manner. The red points are the experimental data while the black curve is the result of the curve fitting to them.

![Graph 1](image1)

**Figure 3.** Process model applied to the actual course

Table 2 contains a compiled set of the parameters of curves, i.e. the reaction rate constants (converted from time constants) and asymptotes.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Series I</th>
<th>Series II</th>
<th>Series III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Asymptote ($C_0$)</td>
<td>0.12992</td>
<td>32.77</td>
<td>0.091633</td>
</tr>
<tr>
<td>Reaction rate constant ($k$)</td>
<td>$6.2752 \times 10^{-5}$</td>
<td>$1.5639 \times 10^{-4}$</td>
<td>$8.7227 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

Table 2. Summary of finally estimated parameters

6. SUMMARY

Heterogeneous phase composition of waste-aqueous suspensions, and their mutual interdependence in the states of equilibrium for the introduction of CO$_2$, facilitates the argument that it is possible to transfer the results of the sequestration of carbon dioxide in heterogeneous systems of aqueous suspensions of selected wastes into a mathematical generalization. For this purpose the invariant function method was used. Based on the results of the experimental course of absorption of CO$_2$ by closed heterogeneous systems, in which poorly soluble products are formed, the mathematical model of the kinetics of this type of process course was proposed. Fitting the model to experimental results is satisfactory from the view of convergence with experimental data (Świnder et al. 2010). This confirms the validity of the assumption that the established model of CO$_2$ sequestration in heterogeneous systems of aqueous suspensions of selected wastes can be described using the method of invariant function.

Acknowledgements

This article is part of an undertaking funded under the statutory activities of the Central Mining Institute in Poland. Project No. 14010500-350 entitled “Model absorption dwutlenku węgla w wodnych roztworach wybranych odpadów” (Model Absorption of Carbon Dioxide in Aqueous Solutions of the Selected Waste). Participation of the second author was supported by the European Union from the European Social Fund (grant agreement number: UDA-POKL.04.01.01-00-106/09).

Bibliography

2. Aksielrud G.A., Molczanow A.D. (1981); Rozpuszczanie cial stałych (Dissolution of the solids). Warszawa, WNT.


22. Uliasz-Bocheńczyk A., Mokrzycki E., Piotrowski Z., Pomykała R. eds. (2007): Składowanie CO$_2$ z zawiesinami popiołowo-wodnymi pod ziemią (Storage of CO$_2$ from suspensions of ash and water under the ground). Kraków, Wydaw. IGSMiE PAN.