Article

Analysis of the Process of Mineral Sequestration of CO₂ with the Use of Fluidised Bed Combustion (FBC) Fly Ashes

Alicja Uliasz-Bocheńczyk 1,• and Eugeniusz Mokrzycki 2,•

1 Faculty of Civil Engineering and Resource Management, AGH University of Science and Technology, Mickiewicza 30, 30-059 Krakow, Poland
2 Mineral and Energy Economy Research Institute of the Polish Academy of Sciences, Wybickiego 7A, 31-261 Krakow, Poland; mokrzy@min-pan.krakow.pl
* Correspondence: aub@agh.edu.pl

Abstract: There is a current focus on replacing the generally accepted conventional power generation technologies with more advanced ones that will better protect the natural environment. The need to limit CO₂ emissions from power generation plants presents a problem that must be solved in many countries that use coal or lignite as basic fuels. One potential option is mineral sequestration performed using side products of fossil fuel combustion, such as fluidised bed combustion (FBC) fly ashes. Fluidised bed combustion (FBC) lignite fly ashes are characterised by a high storage capacity of 15.7%. Research conducted with the most commonly used method of direct mineral sequestration—CO₂ trapping with fluidised bed combustion (FBC) ash in water suspension—has indicated a very high level of carbonation of CO₂, reaching 11%. Calcite was the basic product of carbonation. The calcite content increased from 2% to 12% in the suspension subjected to treatment with CO₂. Furthermore, CO₂ reduced the pH and limited the leaching of impurities, such as Zn, Cu, Pb, Ni, As, Hg, Cd, Cr, Cl, and SO₄. The fly ash suspensions subjected to CO₂ treatment can be used in industry in the final stage of carbon capture and utilisation (CCU) technology, which will further contribute to the implementation of the circular economy.

Keywords: fluidised bed combustion (FBC) fly ash; mineral sequestration; CO₂; direct process; lignite combustion

1. Introduction

CO₂ emissions from fossil fuel combustion are the main source of anthropogenic greenhouse gases (GHG), and therefore, developed countries are aiming to shift towards low-emission economies. The attainment of a low-emission economy or society will require a drastic reduction in CO₂ emissions by the mid-21st century. This process will be accompanied by the implementation of low-emission technologies, as well as changes in certain social models and lifestyles. Mineral carbonation is part of that process.

It is estimated that human activities have caused a global temperature increase of about 1.0 °C compared with the temperature before the industrial era, and global warming is predicted to reach 1.5 °C between 2030 and 2052 if it continues to rise at the present rate [1]. Therefore, it is important to take all necessary actions to limit greenhouse gas emissions. The Paris Agreement developed a global action plan intended to limit global warming to well below 2 °C, preferably to 1.5 °C [2].

The problems resulting from climate change require that people continue to implement actions intended to reduce greenhouse gas emissions. This particularly applies to countries whose industries and power generation systems are based on fossil fuels. Despite actions designed to increase energy production from renewable sources, many countries still rely on fossil fuels, especially countries that possess their own fossil fuel resources. Poland is a good example. The CO₂ emissions from power plants originate mainly from coal combustion (including both coal and lignite) (see Figure 1).
Mineral carbonation is defined as a process based on the reaction of CO₂ with metal oxides, producing insoluble carbonates and various quantities of heat [4]:

$$MO + CO_2 → MCO_3 + \text{heat} \quad (1)$$

The first publications on mineral sequestration of CO₂ reported the use of natural materials in the process [5,6]. Subsequently, the possibilities of using mineral waste were implemented, e.g., those involving solid fuel combustion ashes originating from power plants. In this process, CO₂ binding should be performed with inorganic solid waste, such as fly ash, containing CaO and MgO in a form that can react with carbon dioxide [7].

Power plant emissions can be limited by implementing the circular economy concept through the utilisation of combustion waste for CO₂ trapping by way of mineral carbonation. Waste of limited economic use is primarily considered, such as FBC lignite ashes.

Mineral carbonation is defined as a process based on the reaction of CO₂ with metal oxides, producing insoluble carbonates and various quantities of heat [4]:

$$MO + CO_2 → MCO_3 + \text{heat} \quad (1)$$

The absorption and binding of carbon dioxide depend on the conditions in which the mineral carbonation process is carried out, primarily the temperature and pressure, but also the pH, time, and liquid-to-solid ratio [18–20].

The controlling factor in determining the CO₂ mineral sequestration process is the chemical composition of the fly ash, particularly the CaO and free CaO content [21].

The calcium oxide (CaO) content is essential when using fly ashes to trap CO₂ [18]. The largest quantities of CaO and free CaO are contained in fly ashes generated by lignite combustion and those collected from fluidised beds [22,23]. Fly ashes are most often used for the sequestration of CO₂ in the form of a water suspension, with mineral carbonation conducted by the direct method: treating the suspension with CO₂ (Table 1). Research has also been conducted on the use of bottom ashes collected from fluidised bed boilers [24]. The use of fly ashes to trap CO₂ requires plans to dispose of the products generated in the process.
Table 1. Mineral sequestration of CO$_2$ using lignite fly ash.

| Process Characterisation | Reference |
|--------------------------|-----------|
| Suspension: CO$_2$       | [18]      |
| Maximum conversion: 5.2 moles CO$_2$/kg fly ash | | |
| Semi-dry reaction conditions | [25]      |
| L/S = 0.03–0.36 dm$^3$/kg | | |
| Carbonation efficiency: 13.1–52.8% | | |
| Cumulative CO$_2$ uptake: 2.2–4.8 mmol/g | | |
| Aqueous carbon sequestration process | [26]      |
| Results of process: amorphous calcium carbonate | | |
| Suspension: CO$_2$ | [27]      |
| CO$_2$ capture capacity: 26.4 kg CO$_2$/Mg fly ash | | |
| Indirect mineralisation in acetic acid leachate | [28]      |
| 123 kg CO$_2$/tonne fly ash | | |
| Suspension: CO$_2$ | [29]      |
| Carbonation of the ash slurries and carbonation yield products: 19–37% | | |
| Suspension: CO$_2$ | [30]      |
| L/S = 0.1–0.7 | | |
| Sequestration capacity: 7.66 kg CO$_2$/Mg fly ash | | |
| Fly ash suspension (brine and water): CO$_2$ | [31]      |
| S/L = 0.8; 1.0; 1.25; 2.5 | | |
| CO$_2$ absorption: 1.4–8.8 g CO$_2$/100 g | | |
| Suspension: CO$_2$ | [32]      |
| S/L = 1.0 | | |
| The degree of CO$_2$: 8.85% | | |
| Suspension: CO$_2$ | [33]      |
| L/S = 0.7:1; 0.8:1 | | |
| CO$_2$ absorption: 4.71–9.33 g CO$_2$/100 g | | |
| Fly ash: CO$_2$ | [34]      |
| The best carbonation efficiency: 10.5% | | |

L/S—liquid/solid.

Determining the potential for using waste for mineral sequestration requires a comprehensive treatment of the issue, taking into account all process elements, including the applicable analyses. Such an approach will ensure the ecological safety of mineral sequestration and the use of the process products in further industrial processing. The utilisation of fluidised bed lignite fly ashes in the process of mineral sequestration of CO$_2$ should also consider aspects such as the influence of the process on the leachability of pollutants. Previous studies on the process of CO$_2$ binding in fluidised bed lignite fly ashes have usually been limited to selected tests and concentrated only on a portion of the process. Interest in a holistic approach to this issue motivated the present authors to broaden its scope within the concept of the circular economy.

The novelty of this article is that it offers a broader, more comprehensive approach to the problem of mineral sequestration using a direct CO$_2$–water suspension of FBC ash, with an indication of the possible use of the products of the process, compared to previous studies.

This paper presents the results of an analysis of the potential use of FBC lignite ashes in the mineral sequestration of CO$_2$, followed by economic utilisation of the products of that process.
2. Materials and Methods

2.1. Materials

This study used FBC fly ash (PF) from a lignite-fired fluidised bed boiler with a circulating fluidised layer, atmospheric furnace and natural circulation. The analysed FBC fly ash was characterised by a high content of CaO and free CaO (Table 2).

Table 2. The chemical (oxide) composition of the examined FBC fly ash, %.

| Component | FBC Fly Ash |
|-----------|-------------|
| CaO       | 15.50       |
| CaO\text{free} | 4.7     |
| SiO\text{2} | 37.3       |
| Fe\text{2O}\text{3} | 3.87       |
| Al\text{2O}\text{3} | 21.14     |
| MgO       | 1.41        |
| Na\text{2O} | 1.20        |
| K\text{2O} | 0.90        |
| SO\text{3} | 6.00        |
| The loss on ignition (LOI) | 12.12 |

The maximum CO\text{2}-binding capacity of FBC fly was calculated using the Steinour formula [24]:

\[
\text{CO}_2 \% = 0.785 (\text{CaO} - 0.7\text{SO}_3) + 1.09\text{Na}_2\text{O} + 0.93\text{K}_2\text{O} \quad (2)
\]

\[
\text{CO}_2 \% = 0.785 (15.5 - 0.7 \times 6.0) + 1.09 \times 1.20 + 0.93 \times 0.90 \quad (3)
\]

The resulting value is high: 11.02%.

The ashes used in the present research project were characterised by largest grains from 0.025 to 0.075 mm, with the lowest share of grain fractions being above 0.2 mm (Figure 2).

![Figure 2. Granulometric analysis, mm.](image)

The fly ashes used in this research were in the form of aqueous suspensions with an ash-to-water ratio of 0.7.

2.2. Methods

The mineral carbonation was conducted in an installation composed of two measurement systems: two chambers and a logger, or recording device, a gas cylinder, a pressure valve, and test chambers. Preliminary preparation of the suspension was conducted by...
mixing waste and water in a laboratory mixer, followed by filling the test chambers. After the chambers were sealed, they were connected to the measurement and recording devices, as well as the CO$_2$ feeder [35]. The mineral sequestration process was carried out for 28 days.

The following operations were completed to determine the degree of carbonation or CO$_2$ trapping by the waste-and-water suspension:

- The phase composition was determined by XRD (the Debye–Sherrer–Hull powder diffraction method, using a Philips X-ray Diffractometer and a copper tube (CuK$_\alpha$ radiation)).
- The CaCO$_3$ contents in the waste-and-water suspension were determined with the use of thermogravimetric analysis (TGA/DTA) and an OD-2 Derivatograph (Paulik–Paulik–Erdey system). DTA/TG was carried out in the atmosphere with a heating rate of 10 °C/min.
- Microstructure tests were conducted by scanning electron microscopy (SEM) using a Nova 200 Nano SEM (FEI) equipped with an EDS (energy-dispersive spectroscopy) system (EDAX, Link).

In addition, the influence of CO$_2$ on leaching pollutants was determined. Leaching pollutants were determined using the ICP AES (Perkin-Elmer Plasma–40 ICP model) and ICPMS (Perkin-Elmer Plasma 6100) techniques.

The samples were prepared for leachability tests in accordance with the EN 12457-1:2006 Standard: Characterization of waste—Leaching—Compliance test for leaching of granular waste materials and sludge.

3. Results and Discussion

3.1. Degree of Mineral Sequestration of CO$_2$

FBC lignite fly ashes can be classified as calcium ashes characterised by high pozzolanic/hydraulic activity. Such ashes contain glass rich in SiO$_2$ and aluminium, as well as glass from the CaO–Fe$_2$O$_3$–SiO$_2$ system. FBC lignite fly ashes are different from conventional ashes with respect to phase composition and grain formation. They are mainly composed of irregular grains, dehydrated and dehydroxylated gangue minerals, quartz, anhydrite, calcite, CaO, and its Ca(OH)$_2$ hydration products, as well as unburned coal. No glass phase or mullite occurred in FBC fly ashes [36]. FBC lignite fly ashes can contain chlorides and sulphates, as well as sodium and potassium nitrates, originating from the exhaust gas stream and resorbing on the solid component surfaces.

The following were the products of fly ash and FBC fly ash hydration that were primarily subjected to carbonation: Ca(OH)$_2$, hydrated calcium silicates C-S-H (CaO·nSiO$_2$·mH$_2$O), ettringite (3CaO·Al$_2$O$_3$·3CaSO$_4$·32H$_2$O), and hydrated hexagonal calcium aluminates (Table 3).

| PF           | Calcite (CaCO$_3$) | Quartz (SiO$_2$) | Ettringite (Ca$_6$Al$_2$(OH)$_6$(SO$_4$)$_3$·26H$_2$O) | Gypsum (CaSO$_4$·2H$_2$O) | Hematite (Fe$_2$O$_3$) | Anhydrite (CaSO$_4$) |
|--------------|--------------------|------------------|-------------------------------------------------------|---------------------------|------------------------|----------------------|
| Portlandite (Ca(OH)$_2$) |                    |                  |                                                        |                           |                        |                      |

Six basic phases were distinguishable in pure ash–water suspensions prepared from the fly ashes in question: calcite (CaCO$_3$), quartz (SiO$_2$), portlandite (Ca(OH)$_2$), ettringite (Ca$_6$Al$_2$(SO$_4$)$_3$(OH)$_{12}$·25H$_2$O), hematite (Fe$_2$O$_3$), and anhydrite (CaSO$_4$). The introduction of CO$_2$ caused insignificant changes to the phase composition (Table 3).
Carbon dioxide reacts with the fly ash phases, and these reactions take place in a solution in which gaseous CO$_2$ dissolves. Portlandite and ettringite [7], which are present in FBC fly ashes, are the main carbonated phases, which is confirmed in this research.

The process of mineral carbonation using lignite fly ash suspensions can be separated into three phases [18,19]:

1. Lime dissolution in water, characterised by high pH:
   \[
   \text{CaO (s)} + \text{H}_2\text{O (l)} \rightarrow \text{Ca}^{2+} (\text{aq}) + 2\text{OH}^- (\text{aq}) \tag{4}
   \]

2. CO$_2$ solubility:
   \[
   \text{CO}_2 (\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{HCO}_3^- (\text{aq}) + \text{H}^+ \rightarrow \text{CO}_3^{2-} (\text{aq}) + 2\text{H}^+ \tag{5}
   \]

3. Carbonate precipitation:
   \[
   \text{Ca}^{2+} + \text{CO}_3^{2-} \leftrightarrow \text{CaCO}_3 \downarrow \tag{6}
   \]

After CO$_2$ introduction, no portlandite was detected in the suspensions. The substance reacted completely with carbon dioxide acid and was converted into calcite:

\[
\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \tag{7}
\]

This agrees with the research results obtained by other authors [37,38].

In addition to ettringite, gypsum was identified in the suspension to which CO$_2$ was introduced. Gypsum was not present in pure suspensions, and its appearance can be explained by ettringite carbonation:

\[
\text{Ca}_6[\text{Al}_2(\text{OH})_6]\text{[SO}_4\text{]}_3 \cdot 2\text{6H}_2\text{O} + 3\text{CO}_2 \rightarrow 3\text{CaCO}_3 + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O} + 23\text{H}_2\text{O} \tag{8}
\]

Ettringite was also found in the PF + CO$_2$ suspension, and this can be explained by the fact that only a portion of the mineral was subjected to carbonation.

The calcite content was visibly increased, which was clearly indicated by the increased intensity of diffraction peaks (Figure 3).

![Figure 3. X-ray diffraction (XRD) patterns (P—Portlandite (Ca(OH)$_2$); Q—Quartz (SiO$_2$); E—Ettringite (Ca$_6$[Al$_2$(OH)$_6$]$_2$[SO$_4$]$_3$·26H$_2$O); G—Gypsum (CaSO$_4$·2H$_2$O); H—Hematite (Fe$_2$O$_3$); A—Anhydrite (CaSO$_4$)).](image-url)
The increased intensity of calcite peaks, the absence of portlandite peaks and appearance of gypsum peaks, with the accompanying reduction in the ettringite peak intensity after CO$_2$ introduction, indicate that a great degree of carbonation occurred.

From the results of the phase content tests using the DTA/TG method (Figures 4 and 5), as well as the XRD, the following phases were identified:

- **Ettringite** (endothermic effects with a maximum at 116 and 130 °C) [39]:
  \[
  \text{Ca}_6[\text{Al}_2(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O} \rightarrow \text{Ca}_4[\text{Al}(\text{OH})_6]\text{SO}_4 \cdot 8\text{H}_2\text{O} + 2(\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}) + 17\text{H}_2\text{O} \tag{9}
  \]

- **SiO$_2$ (quartz)** (a small endothermic effect with a maximum at 591 and 613 °C) [40]:
  \[
  \beta Q \rightarrow \alpha Q \tag{10}
  \]

**Figure 4.** DTA curves for suspensions of PF FBC fly ashes: clean (PF) and treated with CO$_2$ (PF with CO$_2$).

**Figure 5.** TG curves for suspensions of PF FBC fly ashes: clean (PF) and treated with CO$_2$ (PF with CO$_2$).
Calcium carbonate (endothermic effect with a maximum at 723 and 776 °C) [40]:

\[
\text{CaCO}_3 \leftrightarrow \text{CaO} + \text{CO}_2
\]  

The endothermic effects at 116 and 130 °C can be attributed to the dehydration of C-S-H, ettringite, or hydrated calcium aluminosilicates. However, only ettringite was found upon XRD analysis. In addition, SEM (Figures 6 and 7) failed to confirm the presence of the relevant phases.

The curves differ mainly in the intensity of the peaks associated with the decomposition of CaCO₃.

The analysis of the TG curves (Figure 4) shows a mass reduction below 200 °C with the loss of both humidity and chemically bound water. A further mass reduction is observed above 700 °C. These processes indicate CaCO₃ decomposition.

Calcite was produced as the basic product of carbonation. Its quantity increased as the process continued. The FBC ashes used in this research were collected from boilers with circulating fluidised beds and an atmospheric hearth, and were characterised by low CaCO₃ content [41]. The proportion of calcite in pure ash–water suspensions amounted to 2.0% in the temperature range 643–850 °C. In suspensions subjected to CO₂ treatment (at 725–850 °C), the proportion of CaCO₃ increased to 12%.

The proportion of mineral sequestration and carbonation resulting from the increase in the CaCO₃ content amounted to 11.4%. This was calculated from the following formula [8]:

\[
\text{CO}_2\text{uptake} \% = \frac{\text{CO}_2\text{f} \% - \text{CO}_2\text{i} \%}{100 - \text{CO}_2\text{i} \%} \cdot 100
\]  

where \( \text{CO}_2\text{uptake} \) is the degree of mineral sequestration/carbonation, \( \text{CO}_2\text{i} \) is the initial carbonate content of the sample, and \( \text{CO}_2\text{f} \) is the final carbonate content of the sample.

Microscopic observations corresponded well to the results of roentgenographic tests and thermogravimetric analysis. Observations with a scanning electron microscope revealed contents in the form of mixed hydration products (Figure 6).

The images show that the products of hydration predominated on ash grain surfaces that were covered by ettringite needles (Figure 6).
The products of carbonation are also visible in SEM images (Figure 7). We can also observe a large grain of calcite with calcium sulphate in the suspension (indicated by the number 1 in part (b)).

![Figure 7](image)

Figure 7. (a) Analysis of microareas: Point 1 (EDS); (b) Microstructure of the hardened water suspension of FBC fly ash from burning lignite with added CO\textsubscript{2} (SEM); (c) analysis of average microareas (EDS).

The majority of the fracture surface was covered by ettringite. Additionally, aluminosilicate phases, calcite and a single gypsum crystallite were observed.

The occurrence of the carbonation process was also apparent upon a comparison of average sample contents (Table 4).

| Element | Peak Intensity EDS |
|---------|--------------------|
| Ca      | S                  |
| S       | S                  |
| Al.     | W                  |
| Mg      | W                  |
| Si      | W                  |
| Fe      | W                  |
| C       | Mw                 |
| O       | Mw                 |

**Table 4.** Elementary composition (EDS).

s—strong; w—weak, mw—middle weak.

In addition, tests on the chemical composition of the PF + CO\textsubscript{2} suspensions were conducted. The results do not show the presence of free lime, indicating that a complete reaction occurred in the mineral carbonation process.
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3.2. Effects of CO$_2$ on Pollutant Leachability

Leaching capability results from the realization of mutually dependent processes such as hydrolysis, hydration, solvation/precipitation, oxidation/reduction, complex generation, sorption, and the formation of solid solutions and new minerals [42].

The introduction of CO$_2$ to the ash–water suspension caused a considerable reduction in the leaching capability of the following elements: Zn, Cu, Pb, Ni, As, Hg, Cd, Cr, Cl, and SO$_4^{2-}$ (Table 5).

Table 5. The effect of the mineral sequestration process on pollutant leachability from aqueous suspensions of FBC fly ash, mg/dm$^3$.

| Element | Clean Suspension | Suspension with CO$_2$ | % Reduction after Mineral Sequestration |
|---------|------------------|------------------------|----------------------------------------|
| Zn      | 0.0067           | 0.0040                 | 40.3                                   |
| Cu      | 0.00067          | 0.00050                | 25.4                                   |
| Pb      | 0.00017          | 0.00015                | 11.8                                   |
| Ni      | 0.00022          | 0.00017                | 22.7                                   |
| As      | 0.00068          | 0.00041                | 39.7                                   |
| Hg      | 0.00040          | 0.00039                | 2.5                                    |
| Cd      | 0.00006          | 0.00005                | 16.7                                   |
| Cr      | 0.0015           | 0.0013                 | 13.3                                   |
| Cl$^-$  | 65.6             | 62.0                   | 5.5                                    |
| SO$_4^{2-}$ | 88.4           | 54.7                   | 38.1                                   |

The carbonation process considerably affected the reduction in the chemical oxygen demand, which decreased from 15.0 mg O$_2$ mg/dm$^3$ to 7.3 O$_2$ mg/dm$^3$.

The basic carbonation reaction—the reaction of Ca(OH)$_2$ with carbon dioxide, resulting in the production of calcite—reduced the pH from 11.1 to 8.6. This process affected the solubility and leaching capability of impurities.

The reduction in the leaching capability of Cr and Pb, found as a result of the carbonation process, could be caused by the following associated phenomena [43]:

- Reduction in solution pH to the approximate value at which Cr and Pb have the minimum leaching capability after carbonation;
- Metal sorption on newly developed minerals;
- Immobilisation by the C-S-H phase.

The last of these also contributed to a reduction in the leaching capability of Zn [43]. We should emphasise that the sorption process is potentially the most important mechanism that controls the leaching capability of Zn and Pb, and is strongly associated with calcite [44].

The reduction in the leaching capability of SO$_4^{2-}$ can be caused either by the development of ettringite or sorption on calcite [45].

The reduction in the leaching capability of As can be explained by adsorption and coprecipitation [46], with the development of a solid solution with calcite, while the reduction in the leaching capability of Cu is explained by the formation of copper carbonate [47].

The following ions are adsorbed on the surface of calcite: Cd, Zn, Mn, Co, Ni, Pb, and Sr [45].

The reduction in the leaching capability can also result from the development of heavy metal carbonates in the carbonation process. Trace quantities of carbonates could not be identified by the roentgenographic method.

The chemical oxygen demand (COD) was reduced by half when subjected to oxidation under the influence of strong oxidisers. COD is the conventional indicator of water quality,
determining the contents of organic compounds and certain non-organic compounds (e.g., iron(II) salts or sulphides). Furthermore, a considerable reduction in pH occurred, in agreement with the progression of mineral carbonation.

4. Conclusions

The mineral sequestration of CO$_2$, as the last stage of the implementation of CCU technology, is an interesting option that is primarily applicable to facilities that generate waste with high CaO contents and have limited possibilities of delivering waste to other industries. The analyses indicated that fluidised bed combustion (FBC) lignite ashes have a high potential for CO$_2$ trapping in the process of mineral sequestration. At the same time, by treating the water suspension and FBC ashes with CO$_2$, both the pH and the leaching capability of impurities were considerably reduced.

Limiting CO$_2$ emissions using fluidised bed combustion (FBC) ashes can also be considered for power generation, primarily in the context of power plants that generate these types of ashes.

Fluidised bed combustion fly ashes subjected to the process of CO$_2$ trapping can also be utilised in the backfilling or landfilling of post-industrial lands [48].

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