Simultaneous capture and mineralization of coal combustion flue gas carbon dioxide (CO₂)


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Abstract

The mineral carbonation, a process of converting CO₂ into stable minerals (mineralization), has been studied extensively to capture and store CO₂. However, most of the mineral carbonation studies have been largely investigated at lab scale. Preliminary and pilot scale studies for accelerated mineral carbonation (AMC) were conducted at one of the largest coal-fired power plants (2120 MW) in the USA by reacting flue gas with fly ash particles in a fluidized bed reactor. In the preliminary experiments, flue gas CO₂ and SO₂ concentrations decreased from 13.0 to 9.6% and from 107.8 to 15.1 ppmv, respectively during the first 2 min. of reaction. The flue gas treatment increased mercury (Hg) concentration in fly ash (0.1 to 0.22 mg/kg) suggesting that fly ash particles also mineralized flue gas Hg. From these results, we designed and developed pilot scale process skid consisting of a moisture reducing drum (MRD) (0.9 m Φ × 1.8 m), a heater/humidifier (0.9 m Φ × 1.8 m), and a fluidized bed reactor (FBR) (0.9-1.2 m Φ × 3.7 m) to capture and mineralize flue gas CO₂. Flue gas was withdrawn from the stack and was fed to the MRD at about 0.094 m³/s. The MRD and the heater/humidifier pretreat flue gas before it enters the FBR. The MRD captures droplets of water entrained in the flue gas to protect the blower placed between the MRD and the heater/humidifier. The heater/humidifier enables control of flue gas moisture and temperature. Approximately 100-300 kg of fresh fly ash was collected from the electrostatic precipitator through ash hopper and placed in the fluidized-bed reactor. The fly ash particles were fluidized by flow of flue gas through a distributor plate in the FBR. The pilot scale studies were conducted at a controlled pressure (115.1 kPa) by controlling the flue gas moisture content. The flue gas was continuously monitored to measure flue gas CO₂, SO₂ and NOₓ concentrations by an industrial grade gas analyzer, while the fresh and spent fly ashes were analyzed for calcium carbonate (CaCO₃), sulfur (S), and mercury (Hg) content. The pilot scale study results suggest that an appreciable amount of flue gas CO₂ and significant amounts of SO₂ and Hg can be directly captured (without separation) and mineralized by the fly ash particles.

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1. Introduction

Coal reserves are crucial for providing global energy needs because of dwindling petroleum and natural gas reserves and increasing demand for energy. However, flue gas emission from coal-fired power plants is a major source for the release of anthropogenic CO₂ into the atmosphere. Increasing anthropogenic CO₂ levels, as a consequence of burning fossil fuels, are raising concerns over global warming and climate change. Concurrently coal-fired power plants also generate significant quantities of solid residues (e.g. fly ash particles) as by-products and release trace amounts of flue gas SO₂ and Hg into the atmosphere.

To address the anthropogenic CO₂ problem, multiple CO₂ capture and storage (CCS) processes are proposed [1,2,3]. As a result different CO₂ capture technologies and storage processes are under evaluation. The CO₂ capture technologies include membrane separation technologies, sorbent technologies involving pressure or temperature swing processes, and the use of solvents such as monoethanolamine [4,5,6,7]. The CO₂ storage processes include subsurface pressure injection into geologic strata and reservoirs of saline, oil, and gas. In addition, mineral carbonation, a process of converting CO₂ to stable minerals (mineralization), is also studied extensively. Among different CO₂ storage processes, mineral carbonation is an ideal approach to store CO₂ on a geological time scale [8]. However, CO₂ capture technologies and storage processes have limitations for widespread practical use due to the requirement of separation of CO₂ from flue gas, compression of CO₂, and transportation of concentrated CO₂ to a site where it can be safely stored or used for mineral carbonation. Furthermore, CO₂ separation and capture technologies are severely limited by the flue gas SO₂, because SO₂ is known to affect the performance of amine solvents [9]. In addition to CO₂ and SO₂ air quality concerns, the Hg emissions from coal-fired power plants and its potential for deposition in soils, vegetation, water, and animals also received considerable attention in recent years [10,11].

In a natural chemical weathering process, carbonic acid, which results from the interaction of atmospheric CO₂ and rain water, will convert alkaline earth minerals to carbonate minerals. Similarly, alkaline minerals present in fly ash will also convert to carbonates through a chemical weathering process. In earlier aqueous mineral carbonation (AQMC) studies, CO₂ was bubbled through slurry of industrial residues (e.g., oil shale, coal fly ash) or exposed to a higher CO₂ atmosphere to understand mineral changes associated with the carbonation process [12,13,14]. Some of these studies reported that AQMC process dissolves silicate/oxide minerals and precipitates carbonate minerals in industrial residues. Earlier research also established that the mineral carbonation process will help improve chemical properties of industrial residues and prevent leaching of trace elements (e.g., arsenic, cadmium, lead, and selenium) from land disposal sites into surface water, soils, and groundwater. Furthermore, the mineral carbonation process also creates a favourable environment in industrial residues for biological processes, because carbonate minerals act as nutrients for microorganisms [15].

Aqueous mineral carbonation of industrial residues is a slow process; hence, an accelerated mineral carbonation (AMC) process was proposed [16]. In this method, oil shale residues with 15-20% of moisture (by weight basis) were exposed to moistened CO₂ pressure (135.8 kPa) for 1 hr. The carbonated solids were subjected to mineral solubility studies. Results of AMC studies were similar to the results of earlier AQMC studies and reported that since AMC uses CO₂, which can be obtained from the combustion process itself, another potential benefit is that it may help to minimize CO₂ emissions into the atmosphere. In a recent study, Dellantonio et al.[17] articulated the role of coal combustion residues in storage of CO₂. Chronological development of AQMC and AMC of industrial residues [e.g., coal fly ash/bottom ash, clean coal technology
(CCT) ash, municipal solid waste (MSW) incinerated fly ash/bottom ash, oil shale ash, steel slag, medical solid waste incinerated ash, paper mill ash, and cement kiln dust] and natural minerals [calcium, iron, and magnesium silicate minerals] were published elsewhere [18]. Since AQMC or AMC processes were proposed, CO₂ mineralization studies have been largely investigated at laboratory scale.

The objectives of this research were to: 1) conduct preliminary studies to determine the possibility of simultaneous capture and mineralization of flue gas CO₂ without separation under field conditions; and 2) develop a pilot scale study for further testing to determine the feasibility of proposed AMC process for industrial application. The preliminary and subsequent pilot tests of the AMC process were conducted at Jim Bridger power plant (JBPP), Point of Rocks, Wyoming. The JBPP burns an average of 21,772 tonnes of coal per day using four units to produce 2120 MW. All preliminary experiments were conducted on Unit two flue gas stack at approximately 30 m above ground. All pilot scale experiments were conducted in the Unit two ash hopper building.

2. Preliminary Studies

Approximately 23 kg of fly ash was collected from the electrostatic precipitators and placed in the fluidized-bed reactor (Figure 1). The fluidized-bed reactor was constructed of acrylic (Plexiglas) to allow the bed operation to be observed. The operating portion of the reactor was 0.3 m in diameter and 1.1 m long. A perforated distributor plate with \(2 \times 10^{-3} \text{ m}^2\) diameter openings (approximately 307 openings) provided uniform distribution of the flue gas through the \(0.6 \text{ m}\) deep bed of fly ash above it. A small blower (0.028 m\(^3\)/s (STP), HRB600, Republic regenerative blowers) was used to force the flue gas through the fly ash because flue gas from the power plant is near atmospheric pressure and does not provide sufficient pressure to fluidize the bed.

![Figure 1](image-url) Preliminary experiment set-up for CO₂ capture and mineralization. Inset shows the testing at the plant.
A pleated fabric filter attached to the top flange of the reactor allowed the flue gas to pass through the reactor and return the fly ash to the bed for additional contact with new flue gas. Fly ash samples were collected from the sampling ports at the side of the reactor during experiments at approximately 2, 5, 10, 15, 30, 60, 90, and 120 minutes. The temperature and pressure during the reaction were monitored by mechanical gauges at the top of the reactor. The temperature during the reactions varied between 316 and 327 K, and pressure varied between 88 and 114 kPa.

An Orion® plus IR detector was connected between the blower and outlet, as shown in the Figure 1 to monitor flue gas CO₂ and SO₂ concentrations before and after reaction. The flue gas Hg mineralization was determined by analyzing Hg content of control and flue gas treated fly ash samples. Control fly ash samples were analyzed for particle size, moisture content, pH, total concentration of C, S, and Hg. Fly ash samples were also analyzed for major mineral phases and surface morphology and subjected to trace element fractionation and water solubility studies. Fly ash particle size was estimated using a scanning electron microscope (SEM; JOEL JSM-5800LV). Moisture content of fly ash was measured by heating samples to 373 K in a drying oven (Sargent Analytical Oven) and calculating the difference in mass before and after heating. Flue gas treated fly ash samples were analyzed for pH, C, S, Hg, surface morphology, major mineral phases with elemental composition, metal fractionation, and water solubility studies.

The flue gas CO₂ concentration decreased from 13.0 to 9.6% within few minutes of reacting with fly ash particles (Figure 2a). Conversely, the carbonate content of fly ash increased from non-detectable to 2.34% during the first 2 minutes of reaction (Figure 2b). The pH of flue gas treated fly ash decreased from 12.2 to 10.6 due to the carbonation process. The XRD analysis show calcite (CaCO₃) and thaumasite [Ca₃Si(SO₄)CO₃(OH)₆.12H₂O] in flue gas treated sample. To verify the formation of these minerals, reacted fly ash was treated with conc. HCl and re-X-rayed. The peaks for calcite and thaumasite were disappeared which indicated the presence of these minerals in flue gas reacted fly ash. These results suggest that flue gas CO₂ is quickly mineralized into carbonates in fly ash. It is well documented that AMC process converts CO₂ into calcite in fly ash and other coal combustion residues [15, 19]. The thaumasite is also reported to form in alkaline industrial residues where carbonate and sulfate are available [20]. The flue gas CO₂ mineralization by the fly ash particles can be explained by the following reactions (here we used CaO as an example):

\[
\begin{align*}
\text{CO}_2 (g) \text{ (flue gas)} + \text{H}_2\text{O} \text{ (moisture in flue gas)} & \leftrightarrow \text{H}_2\text{CO}_3^0 \text{ (carbonic acid)} \quad [1] \\
\text{H}_2\text{CO}_3^0 \text{ (carbonic acid)} & \leftrightarrow \text{H}^+ + \text{HCO}_3^- \text{ (bicarbonate)} \quad [2] \\
\text{CaO} \text{ (fly ash)} + \text{H}^+ + \text{HCO}_3^- \text{ (bicarbonate)} & \leftrightarrow \text{CaCO}_3 \text{ (calcite)} + \text{H}_2\text{O} \quad [3]
\end{align*}
\]

If we combine equations 1-3, the overall reaction is: CO₂ (g) (flue gas) + CaO (fly ash) \leftrightarrow CaCO₃ (calcite).
Figure 2 Concentration of CO₂ in flue gas during the reaction (2a). Effect of flue gas treatment on % carbonate content of fly ash (2b). The pH of the flue gas treated fly ash was 10.6. Average of three experiments. Error bar represents standard deviation (SD).

The results of this study also suggest that, in addition to calcite and thaumasite, other carbonate minerals such as dawsonite (NaAl(CO₃)(OH)₂) and alumohydrocalcite (CaAl₂(CO₃)₂(OH)₄·3H₂O) could form in the flue gas reacted fly ash samples. The conditions required for formation of these carbonates include: alkaline pH, source of carbonate, Na and Al, and slightly higher temperatures [21,22]. These conditions do exist in the fluidized bed reactor. The chemical analysis (Figure 3b) of the flue gas treated fly ash and the reference dawsonite material spectrum reported in literature [22] by the EDS are very similar (Na:Al ~ 1:5). Overall, SEM and EDS analysis revealed the formation of distinct new crystal phases with the chemical composition of Al, Fe, Na, Ca, Mg, K, Si, C and S within few minutes of flue gas reaction (Figures 3c and 3d).

<table>
<thead>
<tr>
<th></th>
<th>O-K</th>
<th>Na-K</th>
<th>Al-K</th>
<th>Si-K</th>
<th>K-K</th>
<th>Ca-K</th>
<th>Fe-K</th>
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<td></td>
<td>59.08</td>
<td>4.43</td>
<td>14.50</td>
<td>16.77</td>
<td>1.56</td>
<td>0.86</td>
<td>2.80</td>
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</table>
The findings of this study suggest that flue gas CO$_2$ mineralizes when it reacts with fly ash particles. Two probable mechanisms may explain these observations. First, flue gas CO$_2$
converting calcium and other oxides in fly ash into carbonate minerals (e.g., calcite, thaumasite, dawsonite, alumohydrocalcite). Second, EDS chemical analysis of the new crystal structures in flue gas CO₂ treated samples shows C along with Al, Fe, Ca, Mg, Na, K, and Si indicating that acidic nature of flue gas (due to nitric and sulfuric acids that were not completely removed in the wet scrubber) probably dissolved amorphous silicate minerals in fly ash, which converted into carbonates. For example, studies have shown that amorphous silicate minerals are much more reactive and soluble in acidic pH [23]. A preliminary economic analysis of the process for 90% capture from a 532 MW power plant yields a mineralization cost of about $11/tonne CO₂ at a mineralization capacity of 207 kg CO₂/tonne fly ash [24].

In addition to the mineralization of flue gas CO₂, the AMC process also mineralized SO₂ and Hg from flue gas (Table 1). The flue gas SO₂ concentration decreases from 107.8 to 15.1 ppmv within two minutes of reaction and stabilized around 22 ppmv. Subsequently S content increased in fly ash from 0.29% to 0.36%. The XRD analysis identified gypsum in flue gas treated sample. The reduction in flue gas SO₂ and increase in S content of fly ash were attributed to the formation of gypsum (CaSO₄·2H₂O) in fly ash. The total concentration of Hg in fly ash increased within few minutes of reaction suggesting that ACM process also mineralized Hg from flue. These results suggest that Hg in flue gas probably oxidizes to Hg²⁺ and mineralizes to HgCO₃ in fly ash.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>SO₂ (ppmv)</th>
<th>Time (min)</th>
<th>S (wt %)</th>
<th>Hg (mg/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>107.8 ± 0.1</td>
<td>0</td>
<td>0.29 ± 0.01</td>
<td>0.10 ± 0.001</td>
</tr>
<tr>
<td>1</td>
<td>5.1 ± 2.0</td>
<td>2</td>
<td>0.23 ± 0</td>
<td>0.22 ± 0.005</td>
</tr>
<tr>
<td>2</td>
<td>15.1 ± 5.0</td>
<td>5</td>
<td>0.26 ± 0.03</td>
<td>0.14 ± 0.003</td>
</tr>
<tr>
<td>5</td>
<td>27.3 ± 9.6</td>
<td>10</td>
<td>0.30 ± 0.01</td>
<td>0.16 ± 0.001</td>
</tr>
<tr>
<td>10</td>
<td>29.4 ± 5.6</td>
<td>15</td>
<td>0.36 ± 0</td>
<td>0.16 ± 0</td>
</tr>
<tr>
<td>11</td>
<td>26.6 ± 5.3</td>
<td>30</td>
<td>0.34 ± 0</td>
<td>0.11 ± 0.001</td>
</tr>
<tr>
<td>12</td>
<td>23.7 ± 6.8</td>
<td>60</td>
<td>0.30 ± 0.01</td>
<td>0.12 ± 0.007</td>
</tr>
<tr>
<td>13</td>
<td>22.8 ± 8.1</td>
<td>90</td>
<td>0.29 ± 0.01</td>
<td>0.13 ± 0.004</td>
</tr>
<tr>
<td>14</td>
<td>22.5 ± 8.8</td>
<td>120</td>
<td>0.23 ± 0.01</td>
<td>0.16 ± 0.002</td>
</tr>
</tbody>
</table>

**Table 1** Effect of the mineralization process on flue gas and fly ash SO₂ and Hg content

The mobility of trace elements from control and flue gas treated samples was examined with metal fractionation studies. It is recognized that trace elements found in water soluble (WS) and exchangeable (EX) fractions are much more available and mobile than trace elements found in carbonate (CBD), oxide (OXD), and residual (RS) bound fractions. The fractionation data for Hg suggest that in control samples most of the Hg was found in exchangeable (EX, 78%), water soluble (WS, 16%), residual (RS, 5%) fractions, and non-detectable in carbonate (CBD) and/or oxide (OXD) bound fractions. Following brief flue gas reaction (AMC), the Hg disposition shifted to oxide bound (33%), carbonate bound (27%) and residual fraction (23%). These results suggest that part of the Hg in flue gas was precipitated as carbonate in fly ash. The fractionation data for other trace elements suggested that AMC process shifted most of the trace elements in fly ash from WS, EX, and CBD to OXD and RS fractions. The results of this study also suggest that AMC process effectively moved trace elements in the fly ash into insoluble factions. For example, arsenic (As) and chromium (Cr) concentrations in water leachates decreased from 6.0 ± 0.2 to non-detectable (ND) and from 72.2 ± 2.7 to 24.0 ± 1.4 µg L⁻¹, respectively. Similarly, AMC process also decreased leachable Se in fly ash and did not affect the leachability of Hg or cadmium (Cd). A significant reduction in the leachable concentration of several trace elements in flue gas reacted fly ash samples is attributed to the redistribution of trace elements from soluble and available fractions (WS and EX) into resistant fractions (CBD, OXD, and RS) and also
probably due to adsorption and co-precipitation processes by the new mineral phases formed through the uptake of CO₂.

3. Pilot Scale Studies

Based on the preliminary studies, we designed and developed pilot scale process skid to capture and mineralize flue gas CO₂. The CO₂ capture and mineralization pilot process (Figure 4) consists of three process vessels - a moisture reducing drum (MRD) (0.9 m Φ × 1.8 m), a heater/humidifier (0.9 m Φ × 1.8 m), and a fluidized bed reactor (FBR) (0.9-1.2 m Φ × 3.7 m). Flue gas was withdrawn from the stack and was fed to the MRD at about 0.094 m³/s. The MRD and the heater/humidifier pretreat flue gas before it enters the FBR. The MRD captures droplets of water entrained in the flue gas to protect the blower placed between the MRD and the heater/humidifier. The heater/humidifier enables control of flue gas moisture and temperature. Approximately 100-300 kg of fresh fly ash was collected from the electrostatic precipitators through ash hopper and placed in the fluidized-bed reactor. The fly ash particles were fluidized by flow of flue gas through a distributor plate in the FBR, ensuring proper mixing and good contact between the fly ash particles and the flue gas.

A perforated plate (2.39 × 10⁻³ m Φ holes) was placed above the distributor plate to minimize collection of ash below the distributor plate. A control valve and a pressure transmitter were used to set the pressure inside the FBR. A particulate removal cyclone in the reactor separated fly ash particles from the exiting flue gas. The pressure drop across the distributor plate, the fluidized bed, and the cyclone were measured by differential pressure transmitters. The temperature at various points inside the humidifier and the reactor were measured by thermocouples.

The vessels and piping connecting them are insulated to minimize heat loss through the walls and prevent moisture condensation. The flue gas was continuously monitored by an industrial grade multi-gas analyzer (HORIBA VA-3000). It was connected to the inlet and outlet lines to monitor the real-time concentration of CO₂, NOₓ, and SO₂ in the flue gas. Fly ash particles were sampled from the reactor using installed sampling ports. The samples were analyzed for carbonate content by dissolution of the carbonates in an excess of standard acid followed by back titration of the remaining acid with standard alkali.

The experimental conditions of the four runs are summarized in Table 2. The flue gas temperature in the reactor was a function of the temperature of the ash received from the plant hopper and the temperature of the flue gas entering the reactor. The humidifier was set at 323 K for experiment no. 1 but it attained higher temperatures due to heating of the flue gas as it passed through the blower. For experiment no. 2, the humidifier temperature was not controlled and so it depended on the temperature of the flue gas, while for no. 3 and 4 the humidifier temperature was set at 313 and 318 respectively K by regulating the water flow rate through the humidifier.
The calculated CO₂ conversion cumulative averages and the carbonate content of the fly ash samples are shown in Figures 5. The highest conversion is seen around 10 minutes and then there is moderate or slight drop. The CO₂ capture capacity of the amount of ash in the reactor is not fully diminished after 1.5-2 hours of reaction. The CaCO₃ content of flue gas treated fly ash samples ranged between 2.5 and 4% within 10 minutes of reaction. The maximum CaCO₃ content of fly ash was about 5.7% after about 1 hours of reaction. The total S and Hg contents of fly ash increased from non-detectable to 0.45 and 0.50 mg/kg, respectively. These results suggest that flue gas SO₂ and Hg also captured and mineralized by the fly ash particles.

### Conclusions

We conducted AMC experiments, under field conditions, to capture and mineralize coal-fired power plant flue gas pollutants (e.g., CO₂, SO₂, and Hg) using fly ash particles. Results show that flue gas components can be directly mineralized (without separation) by the fly ash particles using AMC process. The proposed AMC process mineralized flue gas CO₂ into carbonates (e.g., calcite, thaumasite) within few minutes of reaction. However, further research to optimize AMC process parameters (e.g., moisture, temperature, and contact time) to improve the flue gas CO₂ mineralization capacity by fly ash particles will be invaluable. Such information will help to develop scale-up process under industrial conditions and help to minimize emissions of flue gas pollutants into the atmosphere.
4. References


