# Instantaneous Capture and Mineralization of Flue Gas Carbon Dioxide: Pilot Scale Study

K.J. Reddy*, Hollis Weber, and Pradip Bhattacharyya
Department of Renewable Resources
University of Wyoming
1000 E University Avenue
Laramie WY 82070 USA

Morris Argyle
Department of Chemical Engineering
Brigham Young University
Provo, UT 84604 USA

David Taylor, Mikol Christensen, and Thomas Foulke
Department of Agricultural and Applied Economics
University of Wyoming
Laramie WY 82070 USA

Paul Fahlsing
Jim Bridger Power Plant
Point of Rocks, WY 82942 USA

**ABSTRACT –**Multiple $CO_2$ capture and storage (CCS) processes are required to address anthropogenic $CO_2$ problems. However, a method which can directly capture and mineralize $CO_2$ at a point source, under actual field conditions, has advantages and could help offset the cost associated with the conventional CCS technologies. The mineral carbonation (MC), a process of converting $CO_2$ into stable minerals (mineralization), has been studied extensively to store $CO_2$. However, most of the MC studies have been largely investigated at laboratory scale. Objectives of this research were to develop a pilot scale AMC (accelerated mineral carbonation) process and test the effects of flue gas moisture content on carbonation of fly ash particles. A pilot scale AMC process consisting of a moisture reducing drum (MRD), a heater/humidifier, and a fluidized-bed reactor (FBR) was developed and tested by reacting flue gas with fly ash particles at one of the largest coal-fired power plants (2120 MW) in the USA. The experiments were conducted over a period of 2 hr at ~ 300 SCFM flow-rates, at a controlled pressure (115.1 kPa), and under different flue gas moisture contents (2-16%). The flue gas $CO_2$ and $SO_2$ concentrations were monitored before and during the experiments by an industrial grade gas analyzer. Fly ash samples were collected from the reactor sample port from 0-120 minutes and analyzed for total inorganic carbon (C), sulfur (S), and mercury (Hg). From C, S, and Hg concentrations, %calcium carbonate ($CaCO_3$), %sulfate ($SO_4^{2-}$), and %mercury carbonate ($HgCO_3$) were calculated, respectively. Results suggested significant mineralization of flue gas $CO_2$, $SO_2$, and Hg within 10-15 minutes of reaction. Among different moisture conditions, ~16% showed highest conversion of flue gas $CO_2$ and $SO_2$ to %$CaCO_3$ and %$SO_4^{2-}$ in fly ash samples. For example, an increase of almost 4% in $CaCO_3$ content of fly ash was observed. Overall, the AMC process is cost-effective with minimum carbon footprint and can be retrofitted to coal fired power plants (existing and/or new) as a post-combustion unit to minimize flue gas $CO_2$, $SO_2$, and Hg emissions into the atmosphere. Used in conjunction with capture and geologic sequestration, the AMC process has the potential to reduce overall cost associated with $CO_2$ separation/compression/transportation/pore space/brine water treatment. It could also help protect sensitive amines and carbon filters used in flue gas $CO_2$ capture and separation process and extend their life.

## INTRODUCTION

Coal reserves are crucial for providing global energy needs. However, flue gas emissions from coal-fired power plants are a major source for the release of anthropogenic $CO_2$ into the atmosphere. Concurrently coal-fired power plants also generate significant quantities of solid residues (e.g., fly ash particles) as by-products. Increasing anthropogenic $CO_2$ levels in the atmosphere are raising concerns over climate change and global warming. In addition to $CO_2$ emissions, release of trace amounts of flue gas $SO_2$ and Hg into the atmosphere are also critical air quality concerns.

To address the anthropogenic $CO_2$ problems, multiple $CO_2$ capture and storage (CCS) processes are proposed (IPCC, 2007; Pacala and Socolow, 2004; Charles, 2009). As a result different $CO_2$ capture technologies and storage processes are under evaluation. The $CO_2$ capture technologies include membrane separation technologies, sorbent technologies involving pressure or temperature swing processes, and the use of solvents such as monoethanolamine (Herzog, 2009; Reynolds et al., 2005; Atimay, 2001; Kintisch, 2007). The $CO_2$ storage processes include subsurface pressure injection into geologic strata and saline, oil, and gas reservoirs. Mineral carbonation (MC), a process of converting $CO_2$ to stable minerals (mineralization), is also studied extensively to store $CO_2$. Among these $CO_2$ storage processes, mineral carbonation is an ideal approach to store $CO_2$ on a geological time scale (Lackner, 2003). However, these $CO_2$ capture technologies and storage processes have limitations for widespread practical use due to the requirement of separation of $CO_2$ from flue gas, compression of $CO_2$, and transportation of $CO_2$ to a site where it can be safely stored or used for mineral carbonation process (Reddy et al., 2010). Furthermore, $CO_2$ separation and capture technologies are limited by the flue gas $SO_2$, because $SO_2$ is known to affect the performance of amine solvents (Supap et al., 2006). In addition to flue gas $CO_2$ and $SO_2$, the Hg emissions from coal-fired power plants also received considerable attention in recent years (Lopez et al., 2003; Sullivan et al., 2006). Here we show evidence suggesting that significant quantities of flue gas $CO_2$ as well as $SO_2$ and Hg can be directly captured (without separation) and mineralized by the fly ash particles under actual field conditions.

In a natural chemical weathering process, carbonic acid, which results from the interaction of atmospheric $CO_2$ and rain water, will convert alkaline earth minerals to carbonate minerals. Similarly, alkaline solid wastes (e.g., fly ash) also carbonate naturally. Reddy et al. (1986) were the first to study aqueous mineral carbonation (AQMC) process by bubbling $CO_2$ through alkaline solid waste slurries resulting from the extraction of hydrocarbons from oil shale. However, AQMC of alkaline solid wastes is a slow process; hence accelerated mineral carbonation (AMC) process was proposed (Reddy et al., 1991; Reddy et al., 1994). Subsequently, several studies explored different alkaline solid wastes [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 (e.g., calcium, iron, and magnesium silicates) for $CO_2$ mineralization. In a recent study, Dellantonio et al. (2010) also articulated the role of coal combustion residues in sequestration of $CO_2$.

Chronological development of AQMC and AMC processes of industrial solid wastes and natural minerals were published elsewhere (Tawfic et al., 1995; Reddy, 2000; Meima et al., 2002; Ecke et al., 2003; Fernandez et al., 2004; Huijgen et al., 2005; Baciocchi et al., 2006; Costa et al., 2007; Gerdemann et al., 2007; Zevenhoven et al., 2008; Perez-Lopez et al., 2008; Montes-Hernandez et al., 2009). Since AQMC and AMC processes were proposed most of the $CO_2$ mineralization studies have been largely conducted at laboratory scale. Reddy et al., (2008 and 2010) were the first to test the AMC process to determine the possibility of simultaneous capture and mineralization of actual flue gas $CO_2$, without separation, using fly ash particles under coal-fired power plant conditions. These preliminary studies were conducted to test the "proof of concept". In these studies flue gas was directly reacted with fly ash particles in fluidized-bed reactor over a period of 120 minutes. However, temperature and moisture content of the flue gas was not controlled during the reaction. Results from these studies suggested that significant amounts of flue gas $CO_2$ (~30% reduction in flue gas $CO_2$), $SO_2$ and Hg can be mineralized within first few minutes of reaction. However, further studies were needed to test the effect of flue gas moisture content on the AMC process. Also, scale-up design studies were required to integrate into a power plant process.

The objectives of this research were to 1) develop a pilot scale study for further testing to determine the feasibility of proposed the AMC process, 2) determine the effect of temperature and moisture content of flue gas on the AMC process, 3) evaluate cost-economics of the AMC process and its potential benefits to CCS processes, and 4) determine the significance of coal combustion ash in mineralization of flue gas $CO_2$. The pilot tests of the AMC

2

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 pilot scale experiments were conducted in the Unit two ash hopper building.

## MATERIALS AND METHODS

Based on the preliminary studies, we designed and developed a pilot scale AMC process skid to capture and mineralize flue gas $CO_2$. The AMC pilot process consists of three process vessels (Fig. 1) - a moisture reducing drum (MRD) (0.9 m $\Phi \times$ 1.8 m), a heater/humidifier (0.9 m $\Phi \times$ 1.8 m), and a fluidized-bed reactor (FBR) (0.9-1.2 m $\Phi \times$ 3.7 m). Flue gas was withdrawn from the stack (after power plants wet scrubber process of removing $SO_2$) and was fed to the MRD at about 0.094 $m^3$/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.
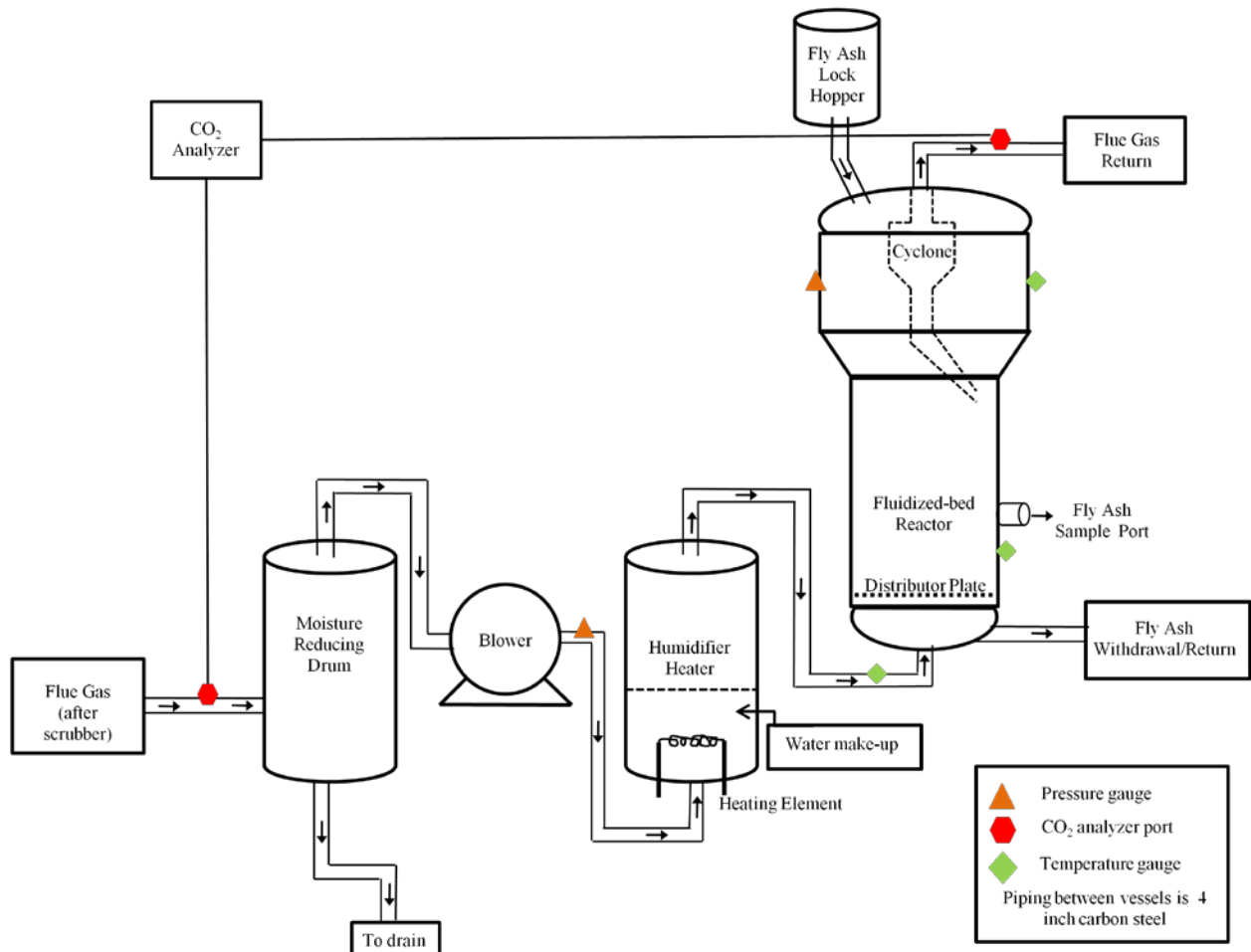
Fig. 1. The schematics of pilot scale AMC process to directly capture and mineralize flue gas $CO_2$.

The reactor's top inlet was connected to the fly ash hopper to deliver a required amount of fresh ash into the 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 $\times 10^{-3}$ m $\Phi$ 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

3

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 $CO_2$, $NO_x$, and $SO_2$ in the flue gas. We conducted seven test runs to study the AMC process. The experimental conditions of the seven test runs are summarized in Table 1. 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 first 2 experiments but it attained higher temperatures due to heating of the flue gas as it passed through the blower. The five subsequent runs had constant flue gas temperature and moisture. This was accomplished by regulating the incoming and outgoing water through the humidifier in order to keep the temperature constant. The pressure was 115.1kPa and flow rate was ~300 SCFM. Experiments were conducted from 0-120 minutes. The process water in the humidifier before and after pumping flue gas was analyzed for pH and major and trace element concentrations. The pH was analyzed with Thermo Orion 5 Star pH portable meter. The major and trace elements were analyzed with inductively coupled plasma mass spectrometry (ICP-MS). The anions were analyzed with ion chromatography (IC).

Table 1. Summary of test conditions for seven runs.

| Expt. | Temperature (C) Reactor | Temperature (c) Humidifier ($H_2O$%) | Ash Quantity (kgs) |
|---|---|---|---|
| 1 | 48-57 | 38-55 (5-12) | 300 |
| 2 | 39-58 | 25-58 (2-13) | 200 |
| 3 | 35-41 | 40 (5) | 100 |
| 4 | 42-47 | 45 (7) | 200 |
| 5 | 39-53 | 50 (10) | 250 |
| 6 | 61-78 | 55 (12) | 480 |
| 7 | 69-92 | 60 (16) | 640 |

Fly ash samples were collected from the reactor sample port over a period of 0-120 minutes. Control and treated fly ash samples were analyzed for total inorganic carbon (C), sulfur (S), and mercury (Hg). Carbon and sulfur were analyzed using a CE Elantech EA 1112 elemental combustion analysis. Mercury was analyzed by an Agilent 7500ce ICP-MS. From C, S, and Hg concentrations, %calcium carbonate ($CaCO_3$), %sulfate ($SO_4^{2-}$), and %$HgCO_3$ were calculated, respectively. Flue gas was measured using an industrial grade Horiba multi-gas analyzer as described earlier. Control flue gas was sampled and analyzed for approximately 15 minutes after the each experiment was completed. An average of these 15 minutes was used as the control for $CO_2$, $SO_2$ and $NO_x$. Treated flue gas was sampled from the outlet piping, just downstream the reactor vessel. Since the analyzer cannot sample two samples at once, we had to manually switch the analyzer between treated and control flue gas.

In order to estimate the costs associated with a full-size reactor, the capital investment and operating costs of the pilot reactor were first estimated. The total capital investment for the pilot reactor was estimated using the Percentage of Delivered-Equipment Cost method which uses the delivered equipment costs as a basis for estimating total capital investments (Peters et al, 2004). The operating cost for the pilot reactor were estimated using cost data gathered from the operation of the pilot reactor and industry standards for this type of chemical process. This information was combined with depreciation rates developed from the capital investment analysis to determine total production costs with depreciation. The capital investment and operating cost estimates for the pilot reactor were than scaled up to a full-sized reactor using the six-tenths factor rule (Peters, 2004). This information was used to develop a simple spreadsheet model to conduct a break-even analysis of the process. The data from the break-even analysis was then incorporated into a cash flow model to consider the financial feasibility of the process in terms of the time value of money.

## RESULTS AND DUSCUSSION

The chemical and physical properties of flue gas and fly ash samples are presented in Table 2. Flue gas from Jim Bridger power plant contains mostly nitrogen (~66-70%), oxygen (~10-20%) and $CO_2$ (~12-14%). Other notable constituents were $SO_2$ (~105-120 ppmv), $NO_x$ (~100-120 ppmv), pH (3.33) and temperature (~37-60°C). The flue gas pH was measured in the field using a design consisting of 0.00025 $m^3$ (250 ml) conical flask with a pH probe

4

(Thermo Orion 5 Star pH portable meter). Before the measurement, the pH probe was calibrated using standard buffer solutions following the procedures of the manufacturer. Approximately 0.00015 m$^3$ (150 ml) of distilled deionized water was placed in the flask and flue gas, before entering the fluidized-bed reactor, was bubbled through the flask. The pH was monitored for several minutes and recorded when it was stabilized (Viswatej, 2009).

Table 2. Chemical and physical properties of Jim Bridger Power Plant flue gas and fly ash. The Na$_2$O and K$_2$O were 0.7% and 0.94%, respectively.

| Flue Gas | | Fly Ash | |
|---|---|---|---|
| N$_2$ | 66-70% | SiO$_2$ | 58.61% |
| CO$_2$ | 12-13.6% | Al$_2$O$_3$ | 19.06% |
| SO$_2$ | 110-110ppm | Fe$_2$O$_3$ | 5.37% |
| NOx | 100-120ppm | CaO | 7.5% |
| CO | 60-750ppm | MgO | 3.85% |
| Hg and As | Traces | CaCO$_3$ | <0.1% |
| Moisture | 10-20% | Moisture | 0.042% |
| Temperature | 40-45$^o$C | Particle Size | 40 μm |
| pH | 3.33 | pH | 12.2 |

The fly ash samples consists of mainly oxides, quartz and amorphous silicate phases of Al, Ca, and Mg and a high pH of over 12 (Viswatej, 2009). Average fly ash particle size is around 40 micrometers. The CaCO$_3$ content is <0.1%. However, when we analyzed fresh fly ash samples from the hopper the %CaCO$_3$ content was ~1%. We attribute this due to uptake of a small amount of atmospheric CO$_2$ to rapid cooling of fly ash to the outside tememperature during the sample collection process. The carbonate phases, including calcite (CaCO$_3$), were not detected in control samples. Formation of oxides and silicates require high temperatures and such temperatures are commonly attained in the coal combustion unit. The alkaline pH of fly ash is attributed to the hydration of oxides and silicate minerals. During the coal combustion process, CO$_2$ is driven off leaving behind a residue (ash) with oxide and silicate phases. When these phases react with water, the resulting aqueous extract's pH will be highly alkaline. The effect of flue gas pumping on the chemistry of water in the humidifier is shwon in Table 3.

Table 3. The chemistry of water in the humidifier before and after reacting with flue gas. Values in the prenthesis are after flue gas reaction. Other trace elemnts or anions were below the detection limit. Units mg/L.

| Component | Concentration |
|---|---|
| Sodium | 45 (38) |
| Calcium | 46 (43) |
| Magnesium | 22 (18) |
| Potassium | 2 (1.8) |
| Sulfate | 150 (120) |
| Alkalinity as CaCO$_3$ | 130 (110) |
| pH | 8.3 (6.2) |

Pilot scale AMC process experimental results suggested that among different temperature conditions, 60$^\circ$C, which had ~16 mole% moisture, showed highest mineralization of flue gas CO$_2$ and SO$_2$. The %CaCO$_3$ in fly ash samples increased to 3.7- 4% (Fig. 2) with in few minutes of reaction. The CO$_2$ capture and mineralization capacity of the ash in the reactor is not fully diminished even after 1.5-2 hours of reaction. These pilot scale studies suggest that significant amounts of flue gas CO$_2$ can be directly captured (without separation) and mineralized into carbonates by the fly ash particles. The AMC process also mineralized flue gas SO$_2$ with in few minutes of reaction (Fig. 2). These

5

findings are in agreement with recent AMC preliminary results reported by Reddy et al., (2010). In these preliminary experiments, flue gas $CO_2$ and $SO_2$ concentrations decreased from 13.0 to 9.6% (~30% reduction) and from 107.8 to 15.1 ppmv, respectively during the first few minutes of reaction. These studies, based on the formation of different carbonate minerals and oxide content (Al, Ca, Fe, Mg, K, and Na) of JBPP fly ash (Table 2), estimated 207 kg of $CO_2$ mineralization per tonne of fly ash.
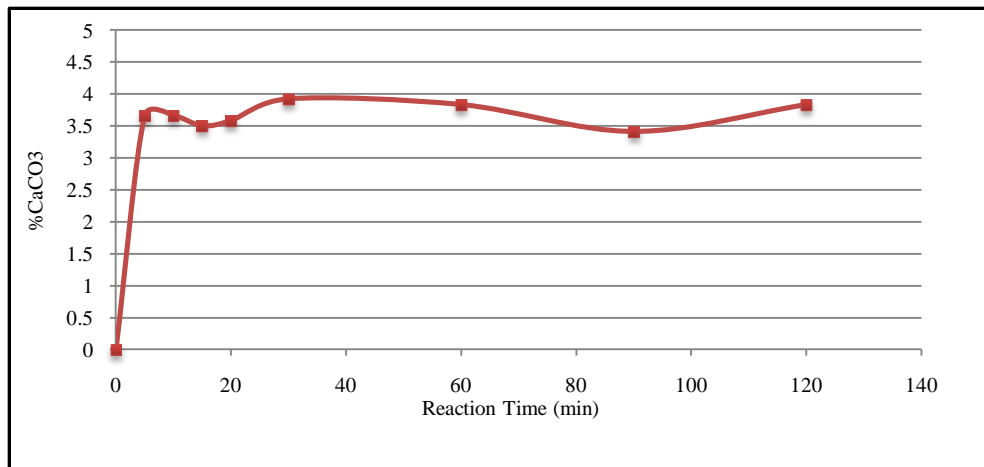


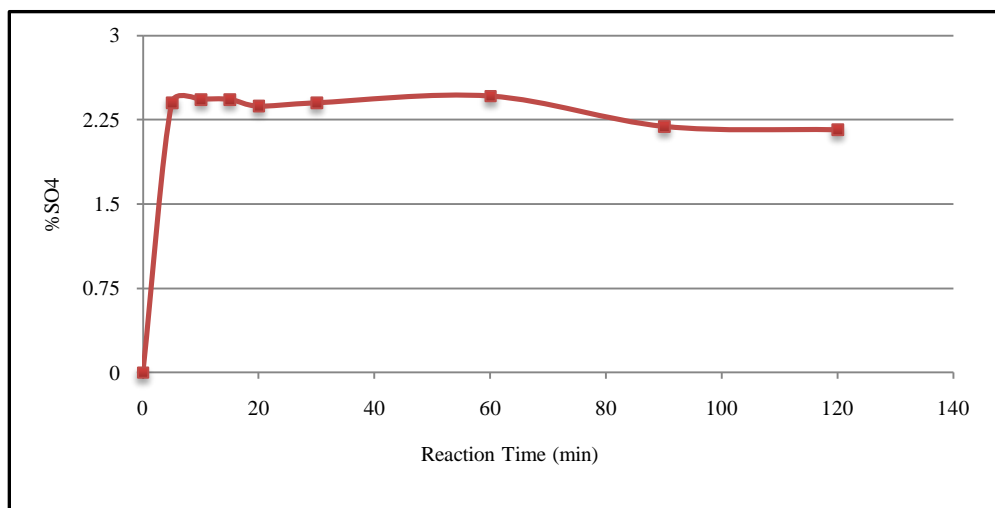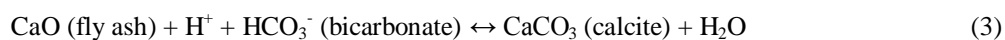Fig. 2. The effect of AMC process on $\%CaCO_3$ content of fly ash at $60^{\circ}C$ (~16% moisture).



Fig. 3. The effect of AMC process on $\%SO_4$ content of fly ash at $60^{\circ}C$ (~16% moisture).
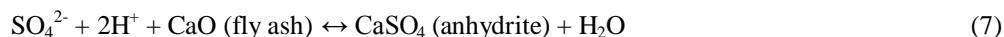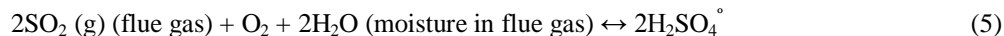
The flue gas $CO_2$ and $SO_2$ mineralization by the fly ash particles can be explained by the following reactions (here we used CaO as an example):
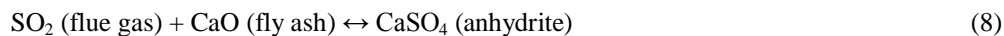
$CO_2$ (g) (flue gas) + $H_2O$ (moisture in flue gas) $\leftrightarrow$ $H_2CO_3^{\circ}$ (carbonic acid)  (1)

$H_2CO_3^{\circ}$ (carbonic acid) $\leftrightarrow$ $H^+$ + $HCO_3^-$ (bicarbonate)  (2)

CaO (fly ash) + $H^+$ + $HCO_3^-$ (bicarbonate) $\leftrightarrow$ $CaCO_3$ (calcite) + $H_2O$  (3)
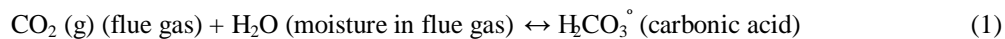
If we combine equations 1-3, the overall reaction is:

$CO_2$ (g) (flue gas) + CaO (fly ash) $\leftrightarrow$ $CaCO_3$ (calcite)  (4)

6
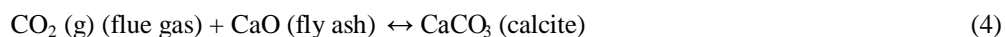
Flue gas $SO_2$ conversion to calcium sulfate can be explained by these reactions:

$$2SO_2 \text{ (g) (flue gas)} + O_2 + 2H_2O \text{ (moisture in flue gas)} \leftrightarrow 2H_2SO_4^{\circ} \qquad (5)$$

$$H_2SO_4^{\circ} \leftrightarrow 2H^+ + SO_4^{2-} \qquad (6)$$

$$SO_4^{2-} + 2H^+ + CaO \text{ (fly ash)} \leftrightarrow CaSO_4 \text{ (anhydrite)} + H_2O \qquad (7)$$

If we combine reactions 5-7, the overall reaction is:

$$SO_2 \text{ (flue gas)} + CaO \text{ (fly ash)} \leftrightarrow CaSO_4 \text{ (anhydrite)} \qquad (8)$$

The pilot scale AMC process also mineralized flue gas Hg. The data for 25-58ºC test suggested that $HgCO_3$ in fly ash samples increased to 0.4 mg/kg within few minutes of reacting with flue gas (Fig. 4). The results shown in Fig. 4 further suggest that the AMC process continues to mineralize flue gas Hg even after 90 minutes of reaction. We believe that mercury in flue gas oxidizes to $Hg^{2+}$ and mineralizes to $HgCO_3$ on fly ash particles. The preliminary AMC studies suggested (Reddy et al., 2010) that Hg in control samples 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 a brief flue gas reaction 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 (Reddy et al., 2010). Our findings also agree with other published research (Piwoni and Keeley, 1996). For example, studies have shown that precipitating pollutants (e.g., Hg, Cd, Cu, Pb) in air pollution control residues as carbonates (e.g., $HgCO_3$), through carbonation process, drastically reduces their toxicity and leaching potential (Walton et al., 1997; Van Gerven et al., 2005).
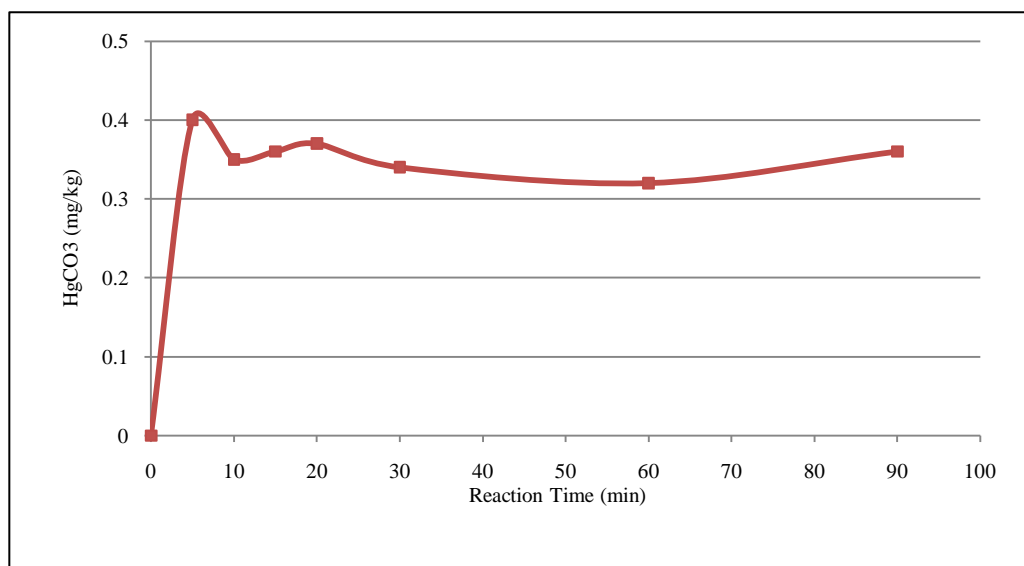


Fig. 4. The effect of AMC process on $HgCO_3$ content of fly ash at $60^{\circ}C$ (~16% moisture).

## ECONOMIC ANALYSIS AND BENEFITS TO CCS PROCESSES

A preliminary economic analysis of the AMC process for 90% capture from a 532 MW power plant yields a mineralization cost of about $11/tonne $CO_2$ (Fig. 5) at a mineralization capacity of 207 kg $CO_2$/tonne fly ash (Christensen, 2010). The mineral carbonation process can reduce the pore space requirement for geological sequestration for a given quantity of $CO_2$ emission. For example, a modern commercial 500 MW coal power plant generates about 3 million metric tons of $CO_2$ per year. If 30% removal (0.9 million metric tons) is achieved by the

7

AMC process as seen in the preliminary studies, the rest of the 2.1 million metric tons of $CO_2$ can be removed by utilizing a geologic formation. This may translate to roughly 30% reduction in pore space requirement for geologic sequestration. This coupled with 30% reduction in separation, compression, transportation, and produced water treatment costs can amount to substantial savings in $CO_2$ sequestration costs. If the plant life is assumed to be 30 years, the required aquifer pore volume is about 7.7 trillion cu. ft. (Ehlig-Economides and Economides, 2010), assuming an aquifer exists in the vicinity of the plant with 20% porosity, 100 md permeability and 100 ft thickness at a depth of 6000 ft and the aquifer is pressurized not more than 100 psi over initial aquifer pressure. 30% reduction in pore space in this case would be a substantial volume ~2.3 trillion cu. ft. Since the AMC process captures and mineralizes $SO_2$, it could also help protect and extend life of sensitive amines and carbon filters used in flue gas $CO_2$ capture and separation process.
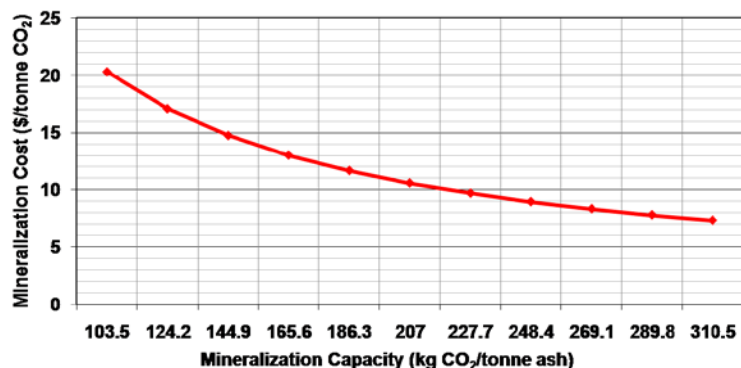


Fig. 5. Preliminary cost estimation of flue gas $CO_2$ mineralization process.

The availability and potential of coal combustion ash to mineralize flue gas $CO_2$ were examined. The wt% of oxides in bituminous ash, sub-bituminous ash, lignite ash, and other industrial residues was gathered from published data. The coal ash that is available in US landfills since 1966 was also estimated as a potential material to mineralize anthropogenic $CO_2$ (Coal Ash Facts, 2010). Coal-fired power plants annually produce about 122 Mt of ash. Of this 35-40% is used for beneficial purpose (e.g., construction). However, if we use total 122 Mt, based on average oxide content of fly ash resulting from three coal types (Table 4), we could annually mineralize ~41 Mt of flue gas $CO_2$. In addition, published information over 40 years (1966-07) suggests that coal-fired power plants in US alone produced approximately 3 Gt of total ash (Table 5). Of this total ash about 810 Mt was used for beneficial purposes. Remaining 2.19 Gt of ash was disposed in landfills. This is a significant of amount of ash which could potentially be used for flue gas $CO_2$ mineralization. Based on average oxide content of three coal tyes (33.6%), we estimate that the 2.19 Gt of ash which is available in landfills could potentially mineralize ~730 Mt of flue gas $CO_2$. The physical and chemical properties of the ash, amount that is available and close proximity of the landfills to power plants make these materials very attractive for $CO_2$ mineralization. Furthermore, use of fly ash materials for $CO_2$ mineralization process could also enhance their overall beneficial uses including for construction as an additive to concrete, reclamation of sodic soils (~30% of global soils are sodic in nature), and as a containment material for sites contaminated with organic and inorganic pollutants.

Table 4. Oxide content and $CO_2$ mineralization potential of ash. All values are in %. Values in the parenthesis are $CO_2$ capture potential.

| Oxides | Bituminous | Sub-bituminous | Lignite |
|---|---|---|---|
| $Al_2O_3$ | 20 (8.63) | 25 (10.78) | 17.5 (7.55) |
| $Fe_2O_3$ | 25 (6.88) | 7 (1.93) | 9.5 (2.61) |
| CaO | 6.5 (5.11) | 17.5 (13.75) | 27.5 (21.61) |
| MgO | 2.5 (2.75) | 3.5 (3.85) | 6.5 (7.15) |
| $Na_2O$ | 2 (1.42) | 1 (0.71) | 5 (3.55) |
| $K_2O$ | 1.5 (0.7) | 2 (0.95) | 2 (0.94) |
| Total $CO_2$ Capture Potential | (25.48) | (31.96) | (43.40) |

Table 5. Total coal combustion products (CCP) generated, used, and land disposed in U.S since 1966.

| Years | Produced CCPs* (in million metric tons) | Used CCPs (in million metric tons) | Available CCPs (in million metric tons) |
|---|---|---|---|
| 1966 – '72 | 219.54 | 34.47 | 185.07 |
| 1973 – '77 | 271.70 | 47.63 | 224.07 |
| 1978 – '82 | 311.17 | 68.04 | 243.13 |
| 1983 – '87 | 312.07 | 72.57 | 239.50 |
| 1988 – '92 | 385.55 | 92.53 | 293.02 |
| 1993 – '97 | 430.00 | 108.86 | 321.14 |
| 1998 – '02 | 517.10 | 160.12 | 356.98 |
| 2003 – '07 | 552.48 | 225.89 | 326.59 |
| 1966 – '07 | 2999.61 | 810.12 | 2189.49 |

The data presented here suggest that significant amounts of flue gas $CO_2$ from coal combustion process can be instantaneously captured (without separation) and mineralized by the fly ash particles using the AMC process. To our knowledge, this is the first research project which demonstrated simultaneous captured and mineralization of flue gas $CO_2$ and other volatile species from coal combustion flue gas under actual field conditions. This process is significant and can be a part of near-term partial $CO_2$ capture strategy as suggested by a recent study (Herzog, 2009). According to this study, the advantages of partial $CO_2$ capture strategy are as follows: 1) easier incremental technology change, 2) reduced capital cost, and 3) acceleration of large-scale deployment of full capture process by generation of technical and operating knowledge required for full capture.

**CONCLUSIONS**

We conducted the AMC pilot scale experiments, under field conditions, to directly capture and mineralize coal-fired power plant flue gas pollutants (e.g. $CO_2$, $SO_2$, and Hg) using fly ash particles. Results show that flue gas components can be directly mineralized (without separation) by the fly ash particles using the AMC process. The proposed AMC process mineralized significant amounts of flue gas $CO_2$, $SO_2$, Hg within few minutes of reaction. The moisture content of flue gas reacting with fly ash particles appears to be the most important factor in mineralization of $CO_2$, $SO_2$, and Hg. The data presented here suggest that flue gas $CO_2$ from coal combustion process can be directly captured (without separation) and mineralized by the fly ash particles using the AMC process. To our knowledge, this is the first research project which demonstrated direct capture and mineralization of flue gas $CO_2$ and other volatile species from a point source under actual field conditions. Since the AMC process captures and mineralizes $SO_2$, it could also help protect and extend life of sensitive amines and carbon filters used in flue gas $CO_2$ capture and separation process. Our research findings are significant, timely, and useful to environmental science and engineering disciplines, industry, government, and policy makers. Further studies are underway to install ash conveying system to control ash residence time and optimize moisture content, temperature, and reaction time to improve the flue gas $CO_2$ mineralization capacity by fly ash particles. Such information will help to integrate AMC process into a coal-fired power plant process.

**ACKNOWLEGEDEMENTS**

# REFERENCES

Atimtay, A.T.2001. Cleaner energy production with integrated gasification combined cycle systems and use of metal oxide sorbents for H2S cleanup from coal gas. *Clean Prod. Processes* 2, 197-208.

Baciocchi, R., Polettini, A., Pomi, R., Prigiobbe, V., Zedwitz, V. N. V., Steinfeld, A. 2006. $CO_2$ sequestration by direct gas–solid carbonation of APC residues. *Energy Fuels*, *20* (5), 1933-1940.

Charles, D. 2009. Stimulus gives DOE billions for carbon–capture projects. *Science* 323, 1158.

Christensen, M.H. 2010. An economic analysis of the Jim Bridger power plant $CO_2$ mineralization process. Master's thesis, Dept. of Agricultural and Applied Economics, University of Wyoming.

Coal Ash Facts. 2010. http://www.coalashfacts.org/. Accessed December, 16, 2010.

Costa, J., Baciocchi, R., Polettini, A., Pomi, R., Hills, C. D., Carey, P. J. 2007. Current status and perspectives of accelerated carbonation process on municipal waste combustion residues. *Environ. Monit. Assess*, *135* (1-3), 55-75.

Dellantonio, A., Walter, J.F., Repmann, F., Wenzel, W.W. 2010. Disposal of coal combustion residues in terrestrial systems: Contamination and risk management. *J. Environ. Qual*. 39, 761-75.

Ecke, H., Menad, N., Lagerkvist, A. 2003. Carbonation of municipal solid waste incineration fly ash and the impact on metal mobility. *J. Environ. Eng*, *129* (5), 435-440.

Ehlig-Economides, C., Economides, M.J. 2010. Sequestering carbon dioxide in a closed underground volume, *Journal of Petroleum Science and Engineering*, 70, 1-2, pp123-130.

Fernandez Bertos, M., Simons, S., Hills, C. D., Carey, P. J. 2004. A review of accelerated carbonation technology in the treatment of cement-based materials and sequestration of $CO_2$. *J. Hazard. Mater*, *112* (3), 193-205.

Gerdemann, S. J., O'Connor, W. K., Dahlin, D. C., Penner, L. R., Rush, H. 2007. Ex situ aqueous mineral carbonation. *Environ. Sci. Technol*, *41* (7), 2587-2593.

Herzog, H. 2009. Accelerating the deployment of CCS. 8th Annual carbon capture and sequestration conference proceedings, Pittsburg, PA.

Huijgen, W. J. J., Witkamp, G. J., Comans, R. N. J. 2005. Mineral $CO_2$ sequestration by steel slag carbonation. *Environ. Sci. Technol*, *39* (24), 9676-9682.

Intergovernmental Panel on Climate Change. Climate Change 2007. The physical science basis: Contribution of working Group I to the Fourth Assessment Report of the IPCC. Cambridge University Press, Cambridge.

Kintisch, E. 2007. Power Generation: Making dirty coal plants cleaner. *Science* 317, 184-186.

Lackner, K.S. 2003. A guide to $CO_2$ sequestration. *Science* 300, 1677-1678.

López Alonso, M., Benedito, J.L., Miranda, M., Fernández, J.A., Castillo, C., Hernández, J., Shore, R.F. 2003. Large-scale spatial variation in mercury concentrations in cattle in NW Spain. *Environ. Pollut*. 125, 173-81.

Meima, J. A., Van der weijden Renata, D., Taylor, E. T., Comans, R. N. J. 2002. Carbonation processes in municipal solid waste incinerator bottom ash and their effect on the leaching of copper and molybdenum. *Appl. Geochem*, *17* (12), 1503-1513.

Montes-Hernandez, G., Pérez-López, R., Renard, F., Nieto, J. M., Charlet, L. 2009. Mineral sequestration of $CO_2$ by aqueous carbonation of coal combustion fly-ash. *J. Hazard. Mater*, *161* (2-3), 1347-1354.

Pacala, S., Socolow, R.H. 2004. Stabilization Wedges: Solving the climate problem for the next 50 years with current technologies. *Science* 305, 968-972.

Perez-Lopez, R., Montes-Hernandez, G., Nieto, J. M., Renard, F., Charlet, L. 2008. Carbonation of alkaline paper mill waste to reduce $CO_2$ greenhouse gas emissions into atmosphere. *Appl. Geochem*, *23* (8), 2292-2300.

Piwoni, M. D., Keeley, J. W. 1996. Basic concepts of contaminant sorption at hazardous waste sites, In *Environmental Assessment Sourcebook*; Boulding, J. Russell, Ed., EPA: Cincinnati, OH, pp 9.

Peter, M.S., K.D. Timmerhause, R.E. West. 2004. *Plant Design and Economics for Chemical Engineers*, *5th Edition*, McGraw Hill, New York, NY, 2004.

Reddy, K.J., Lindsay, W.L., Boyle, F.W., Redente, E.F. 1986. Solubility relationships and mineral transformations associated with recarbonation of retorted oil shales. *J. Environ. Qual*. 15, 129-133.

Reddy, K.J., Drever, J.I., Hasfurther, V.R. 1991. Effects of $CO_2$ pressure process on the solubilities of major and trace elements in oil shale wastes. *Environ. Sci. Technol*. 25, 1466-1469.

Reddy, K. J., Gloss, S. P., Wang, L. 1994. Reaction of $CO_2$ with alkaline solid wastes to reduce contaminant mobility. *Water Res*, *28* (6), 1377-1382.

Reddy, K.J. 2000. Application of carbon dioxide in remediation of contaminants: A new approach. In: Wise DL, Trantolo DJ, Inyang HI, Cichon EJ, Editors. Remediation of Hazardous Waste Contaminated Soils. 2nd Edition, New York: Marcel Dekker Inc.

Reddy, K.J., Argyle, M.D., Viswatej, A. 2008. Capture and mineralization of flue gas carbon dioxide. In Baciocchi R, Costa G, Polettini A, Pomi R, editors. Conference proceedings of 2nd Accelerated Carbonation for Environmental and Materials Engineering, University of Rome, Rome, Italy, October 1-3, p. 221-228.

Reddy, K.J., John, S., Weber, H., Argyle, M., Bhattacharyya, P., Taylor, D.T., Christensen, M., Foulke, T., Fahlsing, P. 2010. Simultaneous capture and mineralization of coal combustion flue gas carbon dioxide ($CO_2$). Energy Procedia.

Reynolds, S.P., Ebner, A.D., Ritter, J.A. 2005. New pressure swing adsorption cycles for carbon dioxide sequestration. *Adsorption* 11, 531-536.

Sullivan, T.M., Adams, J., Milian, L., Subramaniam, S., Feagin, L., Williams, J., Boyd, A. 2006. Local impacts of mercury emissions from the Monticellow coal fired power plant. Environmental Sciences Department, Environmental Research & Technology Division, Brookhaven National Laboratory BNL-77475-2007-IR.

Supap, T., Idem, R., Tontiwachwuthikul, P., Saiwan, C. 2006. The roles of $O_2$ and $SO_2$ in the degradation of monoethanolamine during $CO_2$ absorption from industrial flue gas streams. EIC Climate Change Technology, IEEE, 1-6.

Tawfic, T.A., Reddy, K.J., Gloss, SP, Drever, J.I. 1995. Reaction of $CO_2$ with clean coal technology solid wastes to reduce trace element mobility. *Water, Air, Soil Pollut.* 84, 385-398.

Van Gerven, T., Van Keer, E., Arickx, S., Jaspers, M., Wauters, G., Vandecasteele, C. 2005. Carbonation of MSWI-bottom ash to decrease heavy metal leaching, in view of recycling. *Waste Manage.* **25 (3)**, 291–300.

Viswatej., A. 2009. Capture and mineralization of carbon dioxide from coal combustion flue gas emissions. Ph.D. Thesis. Department of Renewable Resources, University of Wyoming, Laramie, WY.

Walton, J. C., Shafique, S., Smith, R., Gutierrez, N., Tarquin, A. 1997. Role of carbonation in transient leaching of cementitious wasteforms. *Environ. Sci. Technol.* 31 (8), 2345-2349.

Zevenhoven, R., Sipila, J., Teir, S. 2008. Motivations for carbonating magnesium silicates using a gas/solid process route. Conference proceedings of 2nd Accelerated Carbonation for Environmental and Materials Engineering, University of Rome, Rome, Italy, October 1-3, p. 45-54.