

Article

Field Application of Accelerated Mineral Carbonation

Brandon Reynolds ¹, K. J. Reddy ^{1,*} and Morris D. Argyle ²

¹ Ecosystem Science and Management, University of Wyoming, 1000 E. University Ave, Laramie, WY 82071, USA; E-Mail: brandonr@uwyo.edu

² Chemical Engineering, Brigham Young University, Provo, UT 84602, USA; E-Mail: mdargyle@byu.edu

* Author to whom correspondence should be addressed; E-Mail: katta@uwyo.edu or kjreddy@physics.harvard.edu; Tel.: +1-307-766-6658; Fax: +1-307-766-6403.

Received: 11 January 2014; in revised form: 15 March 2014 / Accepted: 18 March 2014 /

Published: 26 March 2014

Abstract: Globally, coal-fired power plants are the largest industrial source of carbon dioxide (CO₂). CO₂ emissions from flue gas have potential for direct mineralization with electrostatic precipitator fly ash particles in the field. Demonstration scale accelerated mineral carbonation (AMC) studies were conducted at the Jim Bridger Power Plant, a large coal fired power plant located in Wyoming, USA. AMC produces kinetically rapid conditions for increased rates of mineralization of CO₂, sulfur dioxide (SO₂) and mercury (Hg) on fly ash particles. Control and AMC reacted fly ash particles were investigated for: change in carbon (expressed as CaCO₃), sulfur (expressed as SO₄²⁻), and mercury (Hg) contents; topology and surface chemical composition by scanning electron microscope/energy dispersive X-ray spectroscopy analysis; chemical distribution of trace elements; and aqueous mineral solubility by the toxicity characteristic leaching procedure. Results of the AMC process show an increase in C, S, and Hg on AMC fly ash particles suggesting that multiple pollutants from flue gas can be removed through this direct mineral carbonation process. Results also suggest that the AMC process shifts soluble trace elements in fly ash to less leachable mineral fractions. The results of this study can provide insight into potential successful field implementation of AMC.

Keywords: accelerated mineral carbonation; fly ash particles; carbon dioxide; flue gas; coal fired power station; trace element; solubility; chemical fractionation

1. Introduction

In 2012, coal fired power plants were responsible for 37% of electrical generation in the United States [1]. Approximately 70% of China's [2] and 40% of India's [3] total energy were also supplied by coal in 2012. The size of these three countries highlights the importance coal plays in the domestic and global energy portfolio. Total global carbon emissions from the consumption of energy in 2011 were 35,578 Mt [4]. The products of the coal combustion process are flue gas and solid byproducts (e.g., fly ash particles, bottom ash, and boiler slag). Flue gas CO₂ emissions from coal fired power plants totaled 1718 Mt in the USA in 2011 [4]. Total annual solid byproducts in the USA are approximately 130 Mt, of which roughly 70 Mt is fly ash particles. Nationally, 35% of fly ash particles were used for beneficial purposes such as concrete additives. The remaining fly ash particles were disposed of in landfills or holding ponds. The use of fly ash particles for beneficial purposes varies worldwide; for example, it is 30% in India and China [5,6], whereas it is nearly 100% in Germany and The Netherlands [7]. Fly ash is used in construction most widely as a substitute for Portland cement in concrete as well as in wallboard, bricks, and other materials. It can be also be utilized as fill material in mining.

Both fly ash particles and flue gas contain trace elements. The levels of these trace elements depend on: the source of coal used [8], the specific conditions of the combustion process, the physical [9] and chemical properties [10,11] of the fly ash particles, the type of fly ash particle collection system [12], and the flue gas desulfurization system [13]. Based on the U.S. Resource Conservation and Recovery Act [14] of 1976, coal combustion products (CCP) are classified as non-hazardous materials and can be disposed of in lined impoundments. This classification has come under increased scrutiny following several incidents in which fly ash particles were inadvertently released into the environment, most notably the fly ash slurry holding pond spill at a Tennessee Valley Authority power plant in 2008 [15]. Numerous studies have examined the presence, the water solubility, and chemical leaching potential of major and trace elements in fly ash particles [10,12,16–30]. A recent review of both major and trace elements by Izquierdo *et al.* [31] provides a comprehensive reference for research conducted on acidic and alkaline fly ash elemental mobility across a wide range of pH values.

In the United States, proposed regulations on flue gas emissions from coal powered electrical generation, combined with increasing awareness of the potential effect these emissions have on anthropogenic climate change, have led to increased research on technologies to reduce and remove them before being emitted to the atmosphere. Early research focused on removal of flue gas SO₂, a major component of acid rain. This research led to the flue gas desulphurization techniques such as wet gas scrubbing with caustic solutions, which are widely employed today. The recent research in this field has focused on CO₂, the largest of the greenhouse gas emissions from coal-fired power plants. Technologies that have been researched are generally distinguished into separation/capture technologies and storage technologies [32,33]. Separation and capture technologies include membrane separation, sorbent capture, solvents (monoethanolamine) and other integrated processes. Storage processes include geologic sequestration and enhanced oil and gas recovery, which are arguably not a permanent storage solution. After all the efforts and research applied to this issue, few economically sound, industry-wide applications have resulted. This is due to many factors, including, but not limited to, the costs of: separation of CO₂ from the flue gas stream, capture of the CO₂ once it is separated,

transportation from the source to the disposal site, and appropriate long term disposal or storage solutions for the CO₂ [32]. One method that has the potential to directly capture and store CO₂ is mineral carbonation. Mineral carbonation differs from many other methods of CO₂ capture and storage by changing flue gas CO₂ into carbonate minerals. Mineral carbonation of CO₂ (e.g., atmospheric or flue gas) with different sources of minerals (e.g., natural [34], spent oil shale [35] or fly ash [36–39]) have been studied. However, most of these studies were conducted at laboratory scale.

The focus of the research in this paper is aimed at reducing emissions from coal-fired power plants using a novel method of mineral carbonation of flue gas CO₂ with power plant fly ash particles. Fly ash from coal-fired power plants is found in many developed and developing countries. As mentioned previously, the amount of fly ash put to beneficial use varies by country drastically. For example, Germany and the Netherlands use nearly all of their fly ash for beneficial use. In the United States, China, and India it is around 30%–35%, resulting in large quantities of fly ash that is disposed in landfills or placed in holding ponds. The potential of fly ash for carbonation worldwide was reported to be ~7 Mt C/year by Renforth *et al.* [40]. The novel process is termed accelerated mineral carbonation (AMC). The AMC process relies on generating optimal conditions for nearly instantaneous mineral carbonation of flue gas CO₂ onto the surface of the fly ash particles. This process differs from other studies because it is a direct mineralization process for multiple pollutants from flue gas with short reaction times. A small pilot scale AMC process was successfully tested at a large coal power plant prior to the current demonstration scale AMC process [41]. The AMC process has shown promise not only in removing flue gas CO₂, but also SO₂ and Hg, as well as minimizing the mobility and leaching of trace elements in the fly ash [42–44]. However, for this current study, we made several modifications to the demonstration apparatus (Figure 1). These modifications included addition of a screw conveying system to accurately deliver the required amount of fly ash from the electrostatic precipitator hopper to the fluidized bed reactor and installation of better controls for reactor temperature and pressure, and moisture of flue gas leaving the humidifier into the fluidized bed reactor (FBR). We conducted three experiments with 0–120 min reaction time, at 60 °C heater/humidifier temperature, ~21 kPa gauge pressure, and 16% of flue gas moisture. Control and flue gas CO₂ reacted fly ash samples were analyzed for carbon, sulfur, and mercury and subjected to studies of scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS), toxicity characteristic leaching, and mineral fractionation. Data from these studies were used to discuss the direct mineralization of flue gas CO₂, SO₂, and Hg by fly ash particles using the AMC process.

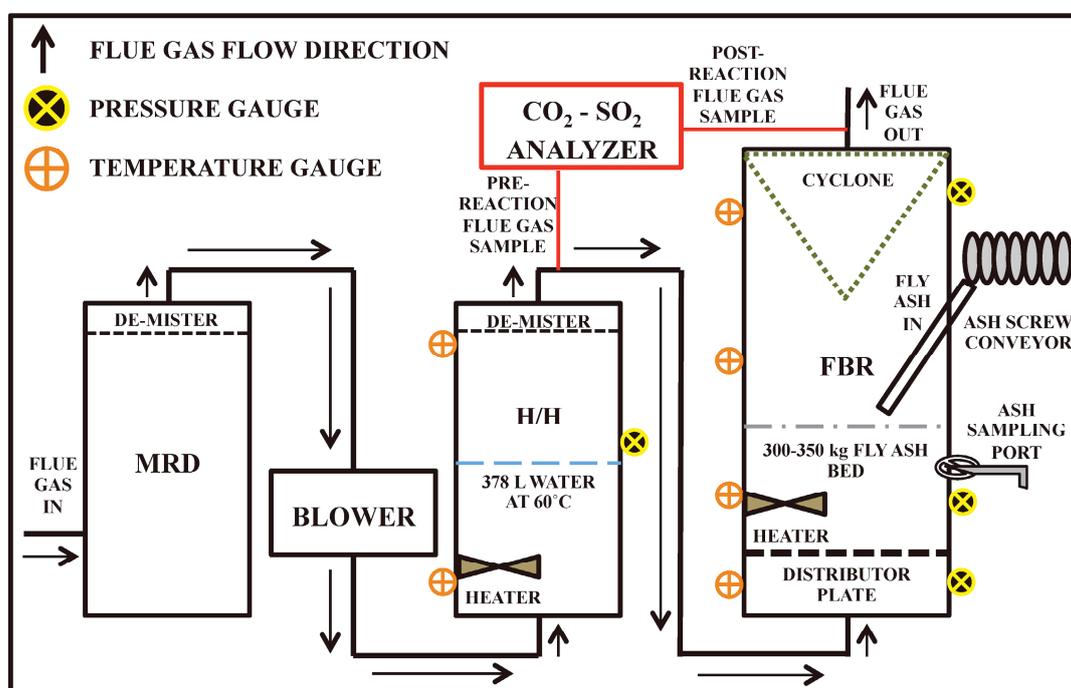
2. Materials and Methods

2.1. Demonstration Scale Accelerated Mineral Carbonation Field Testing

The AMC study was conducted at the Jim Bridger Power Plant (JBPP), a 2120 MW coal fired electrical generation plant, owned by PacifiCorp, located near Point of Rocks, Wyoming, USA. JBPP consumes approximately 19,900 t of low sulfur sub-bituminous coal per day to feed its four independent power generating units, each unit capable of producing 530 MW. Post-combustion flue gas sulfur removal at JBPP is accomplished by a wet Na₂CO₃ scrubber.

The AMC demonstration scale process (Figure 1) is located at Unit 2 of JPBB. In the AMC process, a continuous slipstream of flue gas is piped from the outlet of the flue gas stack (after all scrubbing/treatment processes) through a moisture reducing (or knockout) drum (MRD) to a blower (model 1602 Atlantic Blower (Carrollton, TX, USA), producing approximately $0.094 \text{ m}^3/\text{s}$, STP), which slightly pressurizes the flue gas. From the blower, the flue gas is routed through a water reservoir in the heater/humidifier (H/H) drum, before finally fluidizing and reacting with a batch of ash in the fluidized bed reactor (FBR). The fly ash particles for each batch experiment conveyed by a screw conveyor (UCC Corp., Waukegan, IL, USA) directly from the electrostatic precipitator hopper above the reactor. The temperature of the fly ash particles entering the FBR is approximately $70 \text{ }^\circ\text{C}$. The fly ash bed depth was approximately 45 cm ($\sim 300\text{--}350 \text{ kg}$) in each experiment.

Figure 1. Schematic of accelerated mineral carbonation (AMC) process design (not to scale).



The FBR has an operating section of 0.9 m diameter and 3.0 m length with a perforated distributor plate containing 9 mm diameter holes to distribute the flue gas to provide proper fluidization of the fly ash particles, a heater (ASB Heating Elements Ltd., Toronto, ON, Canada), a cyclone to separate the fly ash particles from the flue gas as it leaves the FBR, and a pressure control valve with controller (Leslie Controls, Inc, Tampa, FL, USA). The flue gas temperature entering the MRD is approximately $50 \text{ }^\circ\text{C}$. Both the MRD and H/H drums contain demister screens to remove entrained water droplets from the flue gas to protect the blower and the FBR, respectively. The H/H drum is filled with 378 L of plant process water, which is heated (ASB Heating Elements Ltd.) to condition the flue gas to the desired humidity. The temperature of the H/H in this study was $60 \text{ }^\circ\text{C}$, which is approximately 16 mol % moisture. Pressure (Ashcroft gauges), temperature (Omega Engineering thermocouples), and CO_2 and SO_2 concentrations (Horiba continuous emissions flue gas analyzer) are continuously monitored at strategic locations noted in Figure 1. However, we did not report flue gas measurement of CO_2 and SO_2 for two reasons: (1) the Horiba instrument presented problems with calibration and measurement

due to condensation of water in the sample lines during the testing; and (2) the flue gas supplied was constantly replenished with CO₂ and SO₂ during the reaction, which rendered the small differentials in concentration not meaningful to analyze in the gas samples. For these reasons, the removal of CO₂ and SO₂ from the flue gas was calculated based on C and S contents of control and treated fly ash samples. A detailed description of the demonstration scale AMC process is available in Reddy *et al.* [42,43]. Fly ash solubility and fractionation data from a pilot scale AMC process at JBPP, smaller than the current demonstration scale conducted at JBPP, is detailed in Bhattacharya *et al.* [44].

Experimental conditions in the fluidizing bed were as follows: fly ash temperature of 70 °C, flue gas temperature of 60 °C corresponding to ~16 mol % moisture, and ~21 kPa gauge pressure. Three separate experiments were conducted on different days, each with the same experimental conditions. Fly ash samples were collected directly out of the FBR before the reaction (control), during the reaction at 10 min and 30 min through a sampling valve, and directly out of the FBR at 120 min or the end of the experiment (final). The samples were sealed immediately after sampling and transported to the lab for analysis. The chemical composition of control fly ash samples from Unit 2 electrostatic precipitator hopper was gathered from JBPP.

2.2. Total Carbon, Sulfur, and Mercury

Samples from three separate tests at 60 °C humidifier water temperature were analyzed for total carbon, sulfur, and mercury by the Wyoming Department of Agriculture Analytical Services Laboratory, Laramie, WY, USA. Analysis was accomplished using a CE Elantech EA 1112 elemental combustion analyzer (Thermo Scientific, Waltham, MA, USA) for carbon and sulfur. Mercury analysis was performed by an Agilent 7500ce inductively coupled plasma mass spectrometer (ICP-MS). All other analyses described next were performed on ash samples from one of the 60 °C humidifier water temperature tests.

2.3. Scanning Electron Microscopy-Energy Dispersive X-Ray Spectroscopy

Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) were used to determine the texture and composition of the surface of the control and AMC fly ash particles. Analysis was conducted at Colorado State University, Ft. Collins, CO, USA on a JSM-6500F (JEOL, Tokyo, Japan) SEM coupled with a NORAN System SIX (Thermo Fisher Scientific, Waltham, MA, USA) EDS. Samples were prepared by coating, mounting, and inserting into the JSM-6500F. Analysis was performed by examining SEM images and performing EDS measurements on areas of interest.

2.4. Sequential Chemical Fractionation of Trace Elements

Sequential chemical fraction of the trace elements (Al, Cr, Mn, Cu, Zn, As, Se, Pb, Cd, and Hg) in the fly ash was conducted following a slightly modified method of Tessier *et al.* [45] at the Water Quality Laboratory, College of Agriculture and Natural Resources, University of Wyoming, Laramie, WY, USA. The sequences of extraction are water soluble, exchangeable, carbonate bound, oxide bound, organic matter bound, and the residual fraction, as detailed in Table 1. The modified methodology uses 1 g of fly ash with the following extraction fluids in 50 mL centrifuge tubes:

Table 1. Sequential chemical fraction procedure, modified from Tessier *et al.* [45].

Fraction	Extractant Fluid	Procedure
Exchangeable	0.5 M Mg(NO ₃) ₂	30 min shaking at 120 rpm
Carbonate	1 M NaOAc	5 h shaking at 120 rpm
Oxide	0.08 M NH ₂ OH·HCl	6 h shaking at 120 rpm
Organic Matter	0.02 M HNO ₃ and H ₂ O ₂	2 h shaking at 120 rpm at 85 °C
Residual	Concentrated HNO ₃	2 h shaking at 120 rpm

Recovery of the extractant fluid was performed through centrifugation at 10,000 rpm. Supernatant was removed and analyzed. To wash the remaining residue of the previous extractant fluid, samples were rinsed with 8 mL deionized water between every step, centrifuged again for 30 min at 10,000 rpm, and supernatant disposed. Analysis of the leachate fluid was performed using ICP-MS for cations and ion chromatography (IC) for anions at Wyoming Department of Agriculture Analytical Services Laboratory, Laramie, WY, USA.

2.5. Toxicity Characteristic Leaching Procedure (TCLP)

Toxicity characteristic leaching procedure (TCLP) was conducted at the ALS Environmental laboratory in Ft. Collins, CO, USA. TCLP is one of the measurements used to determine if a disposal product is classified as a hazardous or non-hazardous waste based on the leaching of certain elements of concern. The TCLP is often used when wastes are disposed of in a landfill. Slightly more than half of JBPP fly ash is disposed of in a local landfill, with the remaining portion being used in cement production. The current study examined leachability of trace elements including As, Ba, Cd, Cr, Pb, Se, Ag and Hg. The purpose of the TCLP test is to help predict the mobility and leaching potential of these trace elements from fly ash before and after the AMC process.

3. Results and Discussion

3.1. Elemental Composition and Distribution on Fly Ash Particles

The composition of fly ash particles and the distribution of elements on their surfaces and interiors are important when discussing elemental solubility and fractionation, with an emphasis on control fly ash samples and of changes on AMC fly ash samples. A model for fly ash particles has been proposed [46], with the particles composed of a thin exterior surface of differing composition from the interior of the fly ash particle. Subsequent studies featuring SEM-EDS and XRD analysis [25,47,48] indicate general agreement with their findings. The exterior is proposed to be made up of inorganic oxides and hydroxides and reactive aluminosilicate glass, while the interior is primarily a less reactive aluminosilicate matrix [24]. The exterior shell has been found to contain elements, both trace and major, that undergo phase changes during the combustion process, form small particles upon cooling, and can attach to the surface of the aluminosilicate matrices that form the larger fly ash particles [49]. The interior of the particle is less reactive and composed primarily of aluminosilicates with a distribution of various cations and anions. Major cations, anions, and trace elements are not all evenly distributed between the silicate and non-silicate phases of the fly ash particles [24]. The fly ash particles in this study were from low sulfur sub-bituminous coal with an initial carbon content of

35–45 wt %. The combustion of the coal results in fly ash particles with inorganic oxides and hydroxides and amorphous aluminosilicates [26,50]. The approximate distribution of chemical species in JBPP fly ash particles is shown in Table 2.

Table 2. Distribution of chemical species on Jim Bridger Power Plant (JBPP) fly ash particles (wt %).

Component	wt %
SiO ₂	60.04
Al ₂ O ₃	19.67
CaO	5.86
Fe ₂ O ₃	4.66
MgO	3.85
K ₂ O	2.00
N ₂ O	1.00
Loss on Ignition	0.60

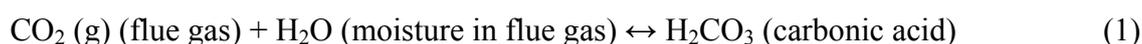
The amorphous silicates are primarily Si, Al, and Ca minerals [25,47]. The pH of the fly ash is 11.5–12.5. The physical size of the fly ash is approximately 40 µm, spherical in shape, with very low moisture content. The flue gas is relatively low in SO₂ (20–25 ppm) and NO_x (100–120 ppm) concentrations, contains 11–13.5 mol % CO₂, 66–70 mol % N₂, 10–20 mol % moisture and trace amounts of Hg, As, and various other trace elements. The pH of the flue gas is 3.3 [41,42].

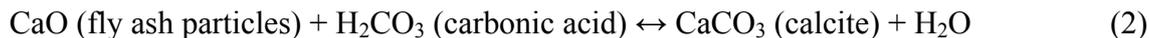
3.2. Demonstration Scale Studies

During demonstration scale AMC testing, fly ash samples collected were: control, 10 min, 30 min, and 120 min (or final). The controlling factors in the AMC process are the chemical and physical properties of the fly ash and flue gas and the conditions in which they are mixed. Three factors influencing the chemical composition of the fly ash are the combustion process, the mineralogy and chemical composition of parent coal, and the ash collection method.

The fly ash particles and flue gas exiting the combustion chamber are reactive due in part to their respective intrinsic properties; fly ash particles with alkaline pH, high metal oxide content, and warm temperature and flue gas with high CO₂ content, presence of SO₂ and NO_x, low pH, optimized moisture content from the H/H, and warm temperature. In addition to these properties, the conditions created within the process to facilitate AMC include increased in pressure to 21 kPa gauge in the FBR, mixing via the fluidizing bed in the FBR, and conditioning of the flue gas via the H/H. The combination of these factors results in an increased rate of mineral carbonation of fly ash inorganic oxides and hydroxides and flue gas CO₂ and SO₂. As an example, Summers *et al.* [51] investigated the combined effect of CO₂ and SO₂ in mineral carbonation. Results from these studies show that small fraction of SO₂ in the flue gas in fact enhances the mineral carbonation of CO₂. The formation of carbonates and sulfates in fly ash through the AMC process can be explained by the following example reactions involving CaO and CO₂ and SO₂ [43]:

Carbonates:

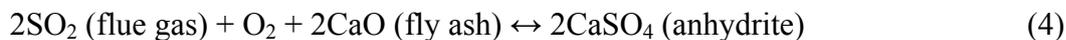




The overall Reaction (3) results from combining Reactions (1) and (2):



Sulfates:



The total carbon, sulfur and mercury content of the fly ash particles after the AMC process (Table 3) increased from the control sample to the final sample. As noted in Section 2.2, C, S, and Hg were calculated by the reported methods. To obtain the values for CaCO_3 and SO_4^{2-} , conversion factors were multiplied by the elemental value. The conversion factor is the molecular weight of the compound divided by the molecular weight of the individual element. This equals to 8.33 for CaCO_3 , and 3.0 for SO_4^{2-} . These data are averaged from three experiments. The control value is based on two samples collected prior to the experiments. These data are averaged from three separate experiments at ~16% moisture in the flue gas. The control value is based on two of the experiments.

Table 3. CaCO_3 (wt %), SO_4 (wt %), and Hg (mg/kg) content of JBPP control and AMC fly ash samples.

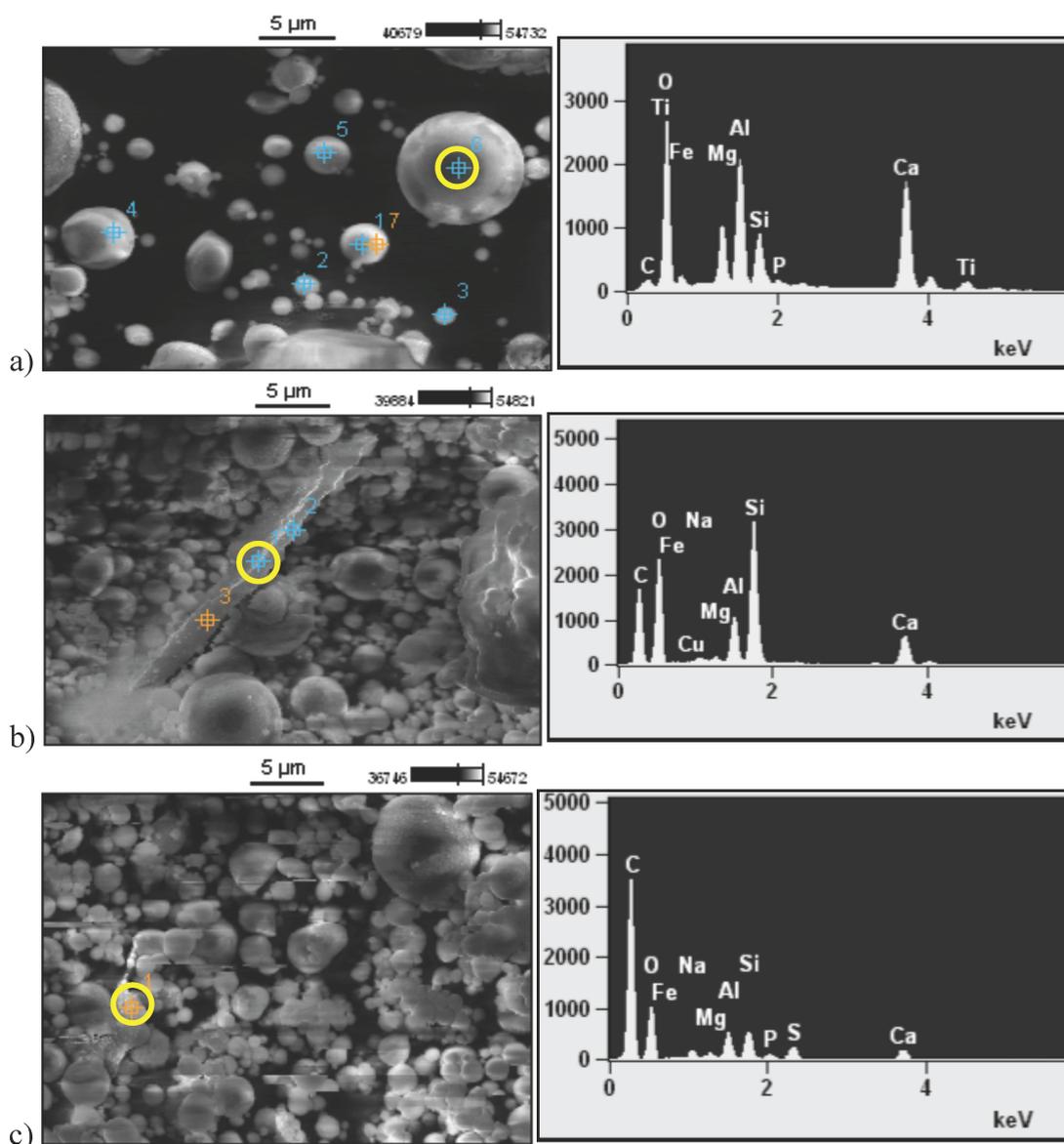
Sample	CaCO_3 (wt %)	SO_4^{2-} (wt %)	Hg (mg/kg)
Control	2.88 ±0.96	0.48 ±0.03	0.12 ±0.09
10 min	3.11 ±1.57	1.21 ±0.19	0.27 ±0.12
30 min	3.67 ±1.53	1.35 ±0.13	0.25 ±0.08
Final	3.86 ±1.28	1.42 ±0.14	0.30 ±0.11

These data indicate formation of carbonates, as the only potential source for an increase in carbon content of the fly ash in the AMC process was due to flue gas CO_2 . Carbonates have been shown to form during hydrolysis of calcium oxides and hydroxides in alkaline fly ash as well as in the presence of CO_2 [46,52]. This is possibly occurring in the AMC samples due to the high relative moisture and 11.0%–13.5% CO_2 contained in the flue gas. Examination of the interaction of atmospheric and flue gas SO_2 with fly ash particles indicates that it is possible for anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), amorphous calcium sulfate, or various other sulfate minerals to be formed on the surface of the particles of alkaline fly ashes [25,31,50]. The observed increase in total sulfur on the AMC samples is likely due to the interaction with the 20–25 ppm SO_2 in the flue gas. Tsuchiai *et al.* [53] found that SO_2 oxidized to SO_3 and then was converted to CaSO_4 by the presence of NO_x , which the flue gas also contains. The observed neutralization of the high pH in the control sample to the AMC sample suggests that more calcium will be available as Ca^{2+} to react with either CO_2 or SO_2 . Extensive studies on mercury [13,54–60] have suggested that the majority of Hg in post desulfurization flue gas is typically in elemental form, which can be oxidized by soluble inorganic oxides (*i.e.*, CaO) or chlorine [60], and potentially adsorb to unburned carbon in the fly ash. However, since fly ash from JBPP has low or insignificant unburned carbon content, this mechanism might not explain the increase in mercury content of the fly ash. Studies have shown that mercury can also coprecipitate as HgCO_3 with calcite in fly ash or adsorb to the calcite surface [61], which might be happening during the AMC process.

3.3. SEM/EDS

SEM/EDS images and data (Figure 2) suggest an increase in the carbon content from the control to the AMC samples. In the control SEM image (Figure 2a), spherical fly ash particles are visible with little crystal structure formation or variation in their general shapes. The corresponding EDS data suggest that aluminum, oxygen, calcium, magnesium, and silicon are the primary elements at the point of analysis. In the 10 min (Figure 2b) and 30 min (Figure 2c) SEM images, formation of crystals and a change from the uniform shape observed in the control occurs. Correspondingly, an increase in carbon is noted in both EDS data. This increase in carbon content is attributable to the formation of amorphous or crystalline carbonate minerals. The SEM/EDS data (Figure 2c) showed significant amount of carbon and sulfur in 30 min flue gas reacted sample. From this investigation we conclude that carbonation of flue gas CO₂ takes place in the presence of SO₂ gas.

Figure 2. Scanning electron microscopy (SEM) images with corresponding X-ray spectroscopy (EDS) spectra: (a) control; (b) 10 min; (c) 30 min. Point in the yellow circle corresponds to the respective EDS spectra.



3.4. Sequential Chemical Fractionation of Trace Elements

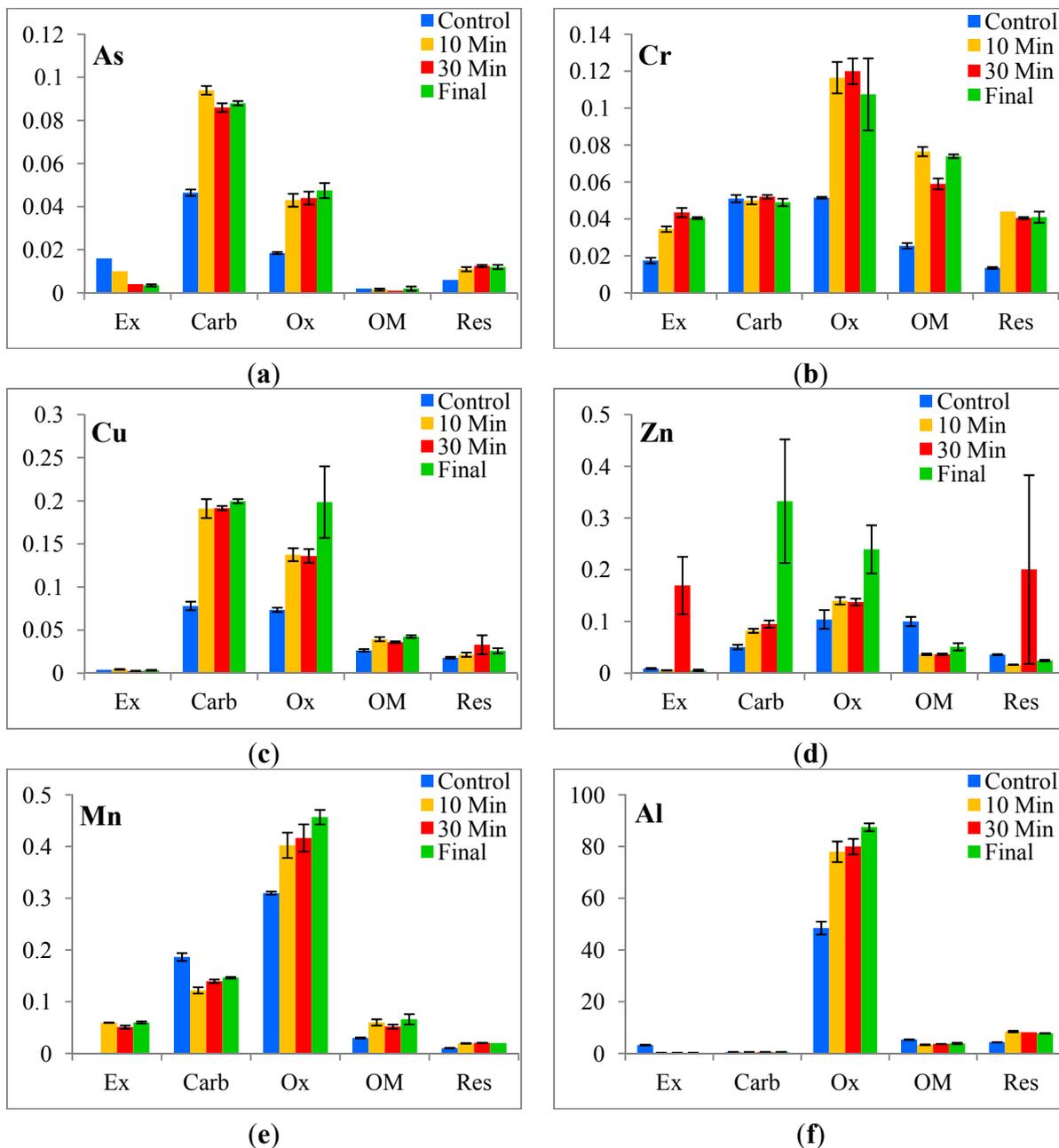
Trace element (As, Cd, Cr, Cu, Hg, Mn, Pb, Se, Ti, Zn) fractionation data (Figure 3) suggest a large increase in the carbonate fraction and, to a lesser extent, oxide bound fraction for arsenic, chromium, copper, and zinc in the AMC process samples. An increase in the oxide fraction for manganese and aluminum was also observed. Lead, selenium, cadmium, mercury and titanium were either below instrumental detection limits or if present, were found at very low concentrations in all fractions. This suggests that their mobility would not pose a problem in either the control or AMC samples. To attempt to interpret possible effects on the distribution of lead, selenium, cadmium, and mercury as a result of the AMC process would be difficult due to the lack of definitive data.

Arsenic (Figure 3a) chemical fractions changed in distribution from the control to the AMC samples. This change results in a decrease in the exchangeable fraction and an increase in the carbonate, oxide, and residual bound arsenic, with minimal change observed in the organic matter bound from the control to the AMC samples. Narukawa *et al.* [62] found similar results for the majority of arsenic bound to carbonates and oxides in a sequential leaching procedure similar to the current study. The increase in the carbonate fraction of arsenic is possibly attributed to adsorption onto the surface of calcite [31,63]. The measured increase in the oxide bound form is possibly due to absorption with iron oxide [27] or to a lesser extent aluminum oxide [63]. The AMC samples potentially reduced the mobility of arsenic in the environment by increasing the concentrations in the less soluble carbonate, oxide, and residual fractions when compared to the control sample.

Chromium (Figure 3b) fractionation data from the AMC process show the greatest increases in the oxide and organic matter bound fraction when compared to the control samples. Lesser increases are observed in the exchangeable and residual bound AMC samples compared to the control, with little discernable difference in the carbonate bound fraction. Chromium is known to adsorb with iron and aluminum oxides at slightly alkaline pH [64]. Chromium has been shown to be associated with organic matter in the depositional environment of the coal, and depending on total concentration and coal combustion methods, can be associated with the organic matter content in the fly ash particles [31]. Chromium in the AMC samples increased in all the fractions except carbonate bound, where no difference is detectable. Although chromium has been suggested to be an element of concern in the environment, the more toxic hexavalent species in fly ash particles is readily reduced to trivalent chromium by interaction with flue gas SO₂ [31], which the AMC process promotes. This change in oxidation state can limit the potential environmental hazards of chromium.

Copper (Figure 3c) exhibits a noticeable increase in the carbonate and oxide bound fractions of the AMC samples compared to the control. There are very slight increases in the organic matter and residual fractions from AMC to control and no detectable difference in the exchangeable fraction. Copper can be adsorbed onto the aluminum oxides in fly ash particles [31,65], and this association might help explain the exhibited increase in oxide bound fractions of copper in the AMC samples. In addition to adsorption on aluminum oxides, formation of copper carbonate, oxide, or hydroxide minerals is possible [65,66]. Formation of these may increase the carbonate bound fraction of copper. The observed increases in copper in both carbonate and oxide fractions indicates that more copper is being fixed in these respective fractions in AMC samples compared to the control.

Figure 3. Sequential chemical fractionation concentrations (mg/L) for the selected trace elements: (a) arsenic; (b) chromium; (c) copper; (d) zinc; (e) manganese; (f) aluminum. Fractions: Ex = exchangeable; Carb = carbonate; Ox = oxide; OM = organic matter; Res = residual.



Zinc (Figure 3d) displays an increase in the carbonate and oxide bound fractions and a decrease in the organic matter fraction from the control to the AMC samples. Exchangeable and residual fractions do not exhibit an appreciable difference. Zinc has been suggested to associate with aluminum oxides [67] or be present as zinc oxide or hydroxide in fly ash [31]. The observed increase in carbonate bound zinc can possibly be explained by adsorption of zinc onto calcite [68] or some other carbonate species or perhaps the formation of a zinc carbonate species.

Manganese (Figure 3e) shows slight increases in exchangeable and oxide bound fractions from the control to AMC samples. Carbonate, organic matter, and residual fractions show slight changes, but

the magnitude of the difference is very minimal. Kim and Kazonich [24] found manganese in higher quantities in the silicate bound forms. This could mean a possible association with aluminum oxides that leach from the fly ash inner matrix and are available to scavenge manganese. The manganese increase in the exchangeable fraction from control to AMC samples is difficult to explain.

Aluminum (Figure 3f) shows an increase in the oxide fraction from the control to AMC samples, with little observable change in any of the other fractions. Aluminum is a major constituent of fly ash particles, and by decreasing the pH in the AMC samples, increased amounts can possibly be dissolved from the glassy inner matrix and then form hydroxide or oxide species.

3.5. Toxicity Characteristic Leaching Procedure

TCLP experiments were carried out to determine if the AMC process would possibly altered the classification of fly ash particles from its currently non-hazardous status. Results of the TCLP are shown in Table 4. All of the constituents sampled for in the TCLP analysis are well below the limits in both the control and AMC samples.

Table 4. Toxicity characteristic leaching procedure (TCLP) concentrations (mg/L).

TCLP (mg/L)	As	Ba	Cd	Cr	Hg	Pb	Se	Ag
Reporting Limit	5.0	100	1.0	5.0	0.2	5.0	1.0	5.0
Control	*	*	*	*	*	*	0.21	*
30 min	*	*	*	*	*	*	0.18	*
Final	*	*	*	*	*	*	0.18	*

Note: * = below the lower limit of quantitation.

4. Conclusions

Results of this study suggest changes in the fly ash geochemistry as a result of the demonstration scale AMC process. Increases in C, S, and Hg were observed, suggesting a mechanism of capture from flue gas onto the surface of the fly ash particles during the AMC process. Analysis of SEM/EDS, sequential chemical fractionation, and TCLP further provided evidence for the direct mineralization of flue gas CO₂, SO₂, and Hg by fly ash particles.

SEM/EDS analysis show changes in the morphology from uniform, spherical particles observed in the control to crystal structures and less uniformity in the shape in the AMC samples, and chemical composition shown by an increase in carbon content of the AMC samples, indicative of carbonation of the fly ash particles. Sequential chemical fractionation data show an increase in the carbonate and oxide bound forms of arsenic, copper, and possibly zinc. Increases in the oxide bound forms of chromium, manganese, and aluminum were observed. Chromium and manganese were the only two trace elements with an apparent increase in the exchangeable forms. TCLP data did not indicate any difference due to AMC process.

The results of the AMC process on fly ash major and trace element mobility are important to determine if this process can potentially be implemented at an industrial scale. The conclusion of the experiments and analysis suggest direct mineralization of flue gas CO₂, SO₂, and Hg is possible in the field at a large scale through the AMC process. As a complement to the mineralization of multiple flue

pollutants, this study also suggests that the AMC process possibly alters some elements of concern in the fly ash to less mobile fractions.

Future study on the AMC process on other coal-fired power plants would help to determine if the AMC process results are applicable to a wide range of conditions. Additionally, increasing the AMC reaction to industrial scale would be needed to determine if it is cost effective and efficient [42]. Fly ash and flue gas conditions vary between different power plants and studies with differing conditions would elucidate if the AMC process works elsewhere. Potential beneficial end uses of the carbonated fly ash include use as an amendment for naturally or anthropogenically created sodic soils. The effect of the AMC process on the pozzolanic properties of fly ash needs to be studied if the beneficial use as construction material, and especially as a replacement for Portland cement, is to be retained. Additional studies could examine application in any industrial setting where an alkaline solid waste and acidic flue gas are produced, including but not limited to: steel industry, cement industry, and solid waste incinerators.

Acknowledgments

The authors would like to thank Dr. Ajay Kumar Sankara Warriar for his contributions in sampling and analysis for the project. We would also like to thank Ryan Taucher, Roger Warner, Dan Miller, Jim Sedey, and Jerry Dickson at Jim Bridger Power Plant, PacifiCorp, and the University of Wyoming Office of Research and Economic Development. Funds for this project were contributed by PacifiCorp, University of Wyoming Ecosystem Science and Management, and the Department and Office of Research and Economic Development.

Author Contributions

K. J. Reddy conceived the original idea. K. J. Reddy and Morris D. Argyle designed and developed AMC reactor skid. Brandon Reynolds, K. J. Reddy, and Morris D. Argyle all participated in conducting experiments. Brandon Reynolds collected the data. All authors participated in writing of the manuscript.

Conflicts of Interest

The authors declare no conflict of interest.

References

1. U.S. Energy Information Administration. Energy in Brief: What is the Role of Coal in the United States? Available online: http://www.eia.gov/energy_in_brief/article/role_coal_us.cfm (accessed on 21 September 2013).
2. U.S. Energy Information Administration. China. Available online: <http://www.eia.gov/countries/cab.cfm?fips=CH> (accessed on 21 September 2013).
3. U.S. Energy Information Administration. India. Available online: <http://www.eia.gov/countries/cab.cfm?fips=IN> (accessed on 21 September 2013).

4. U.S. Energy Information Administration. Monthly Energy Review October 2013. Available online: http://www.eia.gov/totalenergy/data/monthly/pdf/sec12_9.pdf (accessed on 5 October 2013).
5. Asokan, P.; Saxena, M.; Asolekar, S. Coal combustion residues-environmental implications and recycling potentials. *Resour. Conserv. Recycl.* **2005**, *43*, 239–262.
6. Pei-Wei, G.; Xiao-Lin, L.; Hui, L.; Xiaoyan, L.; Jie, H. Effects of fly ash on the properties of environmentally friendly dam concrete. *Fuel* **2007**, *86*, 1208–1211.
7. Barnes, D.; Sear, L. *Ash Utilisation from Coal-Based Power Plants*; Report COAL-R-274 for UK Quality Ash Association; Hatterrall Associates: Cheltenham, UK, 2004.
8. Mardon, S.; Hower, J. Impact of coal properties on coal combustion by-product quality: Examples from a Kentucky power plant. *Int. J. Coal Geol.* **2004**, *59*, 153–169.
9. Seames, W. An initial study of the fine fragmentation fly ash particle mode generated during pulverized coal combustion. *Fuel Process. Technol.* **2003**, *81*, 109–125.
10. Coles, D.; Ragaini, R.; Ondov, J.; Fisher, G.; Silberman, D.; Prentice, B. Chemical studies of stack fly ash from a coal-fired power plant. *Environ. Sci. Technol.* **1979**, *13*, 455–459.
11. Hower, J. Petrographic examination of coal-combustion fly ash. *Int. J. Coal Geol.* **2013**, *92*, 90–97.
12. Davison, R.; Natusch, D.; Wallace, J.; Evans, C. Trace elements in fly ash. Dependence on concentration of particle size. *Environ. Sci. Technol.* **1974**, *8*, 1107–1113.
13. Galbreath, K.; Zygarlicke, C. Mercury speciation in coal combustion and gasification flue gases. *Environ. Sci. Technol.* **1996**, *30*, 2421–2426.
14. Resource Conservation and Recovery Act (Public Law 94-580). *Code of Federal Regulations*, Chapter 139, Title 42, 1980.
15. Ruhl, L.; Vengosh, A.; Dwyer, G.; Hsu-Kim, H.; Deonarine, A. Environmental impacts of the coal ash spill in Kingston, Tennessee: An 18-month survey. *Environ. Sci. Technol.* **2010**, *44*, 9272–9278.
16. Talbot, R.; Anderson, M.; Andren, A. Qualitative model of heterogeneous equilibria in a fly ash pond. *Environ. Sci. Technol.* **1978**, *12*, 1057–1062.
17. Dudas, M. Long-term leachability of selected elements from fly ash. *Environ. Sci. Technol.* **1981**, *15*, 840–843.
18. Wadge, A.; Hutton, M. The leachability and chemical speciations of selected trace elements in fly ash and coal combustion refuse incineration. *Environ. Pollut.* **1987**, *48*, 85–99.
19. Fernandez-Turiel, J.; de Carvalho, W.; Cabanas, M.; Querol, X.; Lopez-Soler, A. Mobility of heavy metals from coal fly ash. *Environ. Geol.* **1994**, *23*, 264–270.
20. Querol, X.; Umana, J.; Alastuey, A.; Ayora, C.; Lopez-Soler, A.; Plana, F. Extraction of soluble major and trace elements from fly ash in open and closed leaching systems. *Fuel* **2001**, *80*, 801–813.
21. Nugteren, H.; Janssen-Jurkovicova, M.; Scarlett, B. Removal of heavy metals from fly ash and the impact on its quality. *J. Chem. Technol. Biotechnol.* **2002**, *77*, 389–395.
22. Smeda, A.; Zyrnicki, W. Application of sequential extraction and the ICP-AES method for study of the portioning of metals in fly ashes. *Microchem. J.* **2002**, *72*, 9–16.
23. Kim, A.; Kazonich, G. Relative solubility of cations in Class F fly ash. *Environ. Sci. Technol.* **2003**, *37*, 4507–4511.

24. Kim, A.; Kazonich, G. The silicate/non-silicate distribution of metals in fly ash and its effect on solubility. *Fuel* **2004**, *83*, 2285–2292.
25. Kim, A. The effect of alkalinity of Class F PC fly ash on metal release. *Fuel* **2006**, *85*, 1403–1410.
26. Kutchko, B.; Kim, A. Fly ash characterization by SEM-EDS. *Fuel* **2006**, *85*, 2537–2544.
27. Jegadeesan, G.; Al-Abed, S.; Pinto, P. Influence of trace metal distribution on its leachability from coal fly ash. *Fuel* **2008**, *87*, 1887–1893.
28. Yang, C. Leaching characteristics of metals in fly ash from coal-fired power plant by sequential extraction procedure. *Microchim. Acta* **2009**, *165*, 91–96.
29. Ahmaruzzaman, M. A review of the utilization of fly ash. *Prog. Energy Combust. Sci.* **2010**, *36*, 327–363.
30. Bhattacharyya, P.; Reddy, K.; Attili, V. Solubility and fractionation of different metals in fly ash of the Powder River Basin coal. *Water Air Soil Pollut.* **2011**, *220*, 327–337.
31. Izquierdo, M.; Querol, X. Leaching behavior of elements from coal combustion fly ash: An overview. *Int. J. Coal Geol.* **2012**, *94*, 54–66.
32. Pacala, S.; Socolow, R. Stabilization wedges: Solving the climate problem for the next 50 years with current technologies. *Science* **2004**, *305*, 968–972.
33. Huijgen, W.; Comans, R. *Carbon Dioxide Sequestration by Mineral Carbonation: Literature Review*; Report ECN-C-03-016 for Energy Research Centre of The Netherlands: Petten, The Netherlands, 2003.
34. Oelkers, E.; Gislason, S.; Juerg, M. Mineral carbonation of CO₂. *Elements* **2008**, *4*, 333–337.
35. Reddy, K.J.; Lindsay, W.L.; Boyle, F.W.; Redente, E.F. Solubility relationships and mineral transformations associated with recarbonation of retorted oil shales. *J. Environ. Qual.* **1986**, *15*, 129–133.
36. Reddy, K.; Drever, J.; Hasfurther, V. Effects of a CO₂ pressure process on the solubilities of major and trace elements in oil shale solid wastes. *Environ. Sci. Technol.* **1991**, *25*, 1466–1469.
37. Tawfic, T.; Reddy, K.; Gloss, S. Reaction of CO₂ with clean coal technology ash to reduce trace element mobility. *Water Air Soil Pollut.* **1994**, *84*, 385–398.
38. Wee, J. A review on carbon dioxide capture and storage technology using coal fly ash. *Appl. Energy* **2013**, *106*, 143–151.
39. Reddy, K. Coal Fly Ash Chemistry and Carbon Dioxide Infusion Process to Enhance Its Utilization. In *Biogeochemistry of Trace Elements in Coal and Coal Combustion Byproducts*; Sajwan, K., Alva, A., Keefer, R., Eds.; Springer: New York, NY, USA, 1999; pp. 133–143.
40. Renforth, P.; Washbourne, C.; Taylder, J.; Manning, D. Silicate production and availability for mineral carbonation. *Environ. Sci. Technol.* **2011**, *45*, 2035–2041.
41. Attili, V. Capture and Mineralization of Carbon Dioxide from Coal Combustion Flue Gas Emissions. Ph.D Thesis, University of Wyoming, Laramie, WY, USA, 2009.
42. Reddy, K.; Weber, H.; Bhattacharyya, P.; Argyle, M.; Taylor, D.; Christensen, M.; Foulke, T.; Fahlsing, P. Instantaneous Capture and Mineralization of Flue Gas Carbon Dioxide: Pilot Scale Study. Available online: <http://precedings.nature.com/documents/5404/version/1> (accessed on 17 March 2014).

43. Reddy, K.; John, S.; Weber, H.; Argyle, M.; Bhattacharya, P.; Taylor, D.; Christensen, M.; Foulke, T.; Fahlsing, P. Simultaneous capture and mineralization of anthropogenic carbon dioxide (CO₂). *Energy Procedia* **2010**, *4*, 1574–1583.
44. Bhattacharyya, P.; Reddy, K. Effect of flue gas treatment on the solubility and fractionation of different metals in fly ash of Powder River Basin coal. *Water Air Soil Pollut.* **2012**, *223*, 4169–4181.
45. Tessier, A. Sequential extraction procedure for the speciation of particulate trace metals. *Anal. Chem.* **1979**, *51*, 844–851.
46. Warren, C.; Dudas, M. Formation of secondary minerals in artificially weather fly ash. *J. Environ. Qual.* **1985**, *14*, 405–410.
47. Medina, A.; Gamero, P.; Querol, X.; Moreno, N.; DeLeon, B.; Almanza, M.; Vargas, G.; Izquierdo, M.; Font, O. Fly ash from a Mexican mineral coal I: Mineralogical and chemical characterization. *J. Hazard. Mater.* **2010**, *181*, 82–90.
48. Reardon, E.; Czank, C.; Warren, C.; Dayal, R.; Johnston, H. Determining controls on elemental concentrations in fly ash leachate. *Waste Manag. Res.* **1995**, *13*, 435–450.
49. Jones, D. The Leaching of Major and Trace Elements from Coal Fly Ash. In *Environmental Aspects of Trace Elements in Coal*; Swaine, D., Goodzari, F., Eds.; Springer: Berlin, Germany, 1995; Volume 2, pp. 221–262.
50. Dudas, M.; Warren, C. Submicroscopic model of fly ash particles. *Geoderma* **1987**, *40*, 101–114.
51. Summers, C.; Dahlin, D.; Ochs, T. *The Effect of SO₂ on Mineral Carbonation in Batch Tests*; DOE/ARC-2004-022; Office of Fossil Energy (FE), U.S. Department of Energy: Washington, DC, USA, 2004.
52. Schramke, J. Neutralization of alkaline coal fly ash leachates by CO₂(g). *Appl. Geochem.* **1992**, *7*, 481–492.
53. Tsuchiai, H.; Ishizuka, T.; Ueno, T.; Hattori, H.; Kita, H. Highly active absorbent for SO₂ removal prepared from coal fly ash. *Ind. Eng. Chem. Res.* **1995**, *34*, 1404–1411.
54. Serre, S.; Silcox, G. Adsorption of elemental mercury on the residual carbon in coal fly ash. *Ind. Eng. Chem. Res.* **2000**, *39*, 1723–1730.
55. Dunham, G.; DeWall, R.; Senior, C. Fixed-bed studies of the interactions between mercury and coal combustion fly ash. *Fuel Process. Technol.* **2003**, *82*, 197–213.
56. Niksa, S.; Naoki, F. Predicting extents of mercury oxidation in coal-derived flue gases. *J. Air Waste Manag. Assoc.* **2005**, *55*, 930–939.
57. Gale, T.; Lani, B.; Offen, G. Mechanisms governing the fate of mercury in coal-fired power systems. *Fuel Process. Technol.* **2008**, *89*, 139–151.
58. Goodzari, F.; Hower, J. Classification of carbon in Canadian fly ashes and their implications in the capture of mercury. *Fuel* **2008**, *81*, 1949–1957.
59. Shah, P.; Strezov, V.; Prince, K.; Nelson, P. Speciation of As, Cr, Se, and Hg under coal fired power station conditions. *Fuel* **2008**, *87*, 1859–1869.
60. Hower, J.; Senior, C.; Suuberg, E.; Hurt, R.; Wilcox, J.; Olson, E. Mercury capture by native fly ash carbons in coal-fired power plants. *Prog. Energy Combust. Sci.* **2010**, *36*, 510–529.

61. Noel, J.; Biswas, P.; Giammar, D. Evaluation of a sequential extraction process used for determining mercury binding mechanisms to coal combustion byproducts. *J. Air Waste Manag. Assoc.* **2007**, *57*, 856–867.
62. Narukawa, T.; Takatsu, C.; Riley, K.; French, D. Investigation on chemical species of arsenic, selenium and antimony in fly ash from coal fuel thermal power stations. *J. Environ. Monit.* **2005**, *7*, 1342–1348.
63. Cornelis, G.; Johnson, A.; VanGerven, T.; Vandecasteele, C. Leaching mechanism of oxyanionic metalloid and metal species in alkaline solid wastes: A review. *Appl. Geochem.* **2008**, *23*, 955–976.
64. Rai, D.; Eary, L.; Zachara, J. Environmental chemistry of chromium. *Sci. Total Environ.* **1989**, *86*, 15–23.
65. Meima, J.; Comans, N. The leaching of trace elements from municipal solid waste incinerator bottom ash at different stages of weathering. *Appl. Geochem.* **1999**, *14*, 159–171.
66. Meima, J.; van der Weijden, R.; Eighmy, T.; Comans, R. Carbonation processes in municipal solid waste incinerator bottom ash and their effect on the leaching of copper and molybdenum. *Appl. Geochem.* **2002**, *17*, 1503–1513.
67. Meima, J.; Comans, N. Application of surface complexation/precipitation modeling to contaminant leaching from weathered solid waste incinerator bottom ash. *Environ. Sci. Technol.* **1998**, *32*, 688–693.
68. Zachara, J.; Kittrick, J.; Harsh, J. The mechanism of Zn^{2+} adsorption on calcite. *Geochem. Cosmochim. Acta* **1988**, *52*, 2281–2291.

© 2014 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).