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Ash to Reduce Trace Element Mobility**

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# REACTION OF CO<sub>2</sub> WITH CLEAN COAL TECHNOLOGY ASH TO REDUCE TRACE ELEMENT MOBILITY

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**Abstract.** The combustion of coal in power plants generates solids (e.g., fly ash, bottom ash) and flue gas (e.g., SO<sub>x</sub>, CO<sub>2</sub>). New Clean Air Act mandated reduction of SO<sub>x</sub> emissions from coal burning power plants. As a result, a variety of Clean Coal Technologies (CCT) are implemented to comply with these amendments. However, most of the CCT processes transfer environmentally sensitive elements (e.g., As, Cd, Pb, Se) from flue gas to CCT ash. The objective of this study was to determine the effect of a pressurized CO<sub>2</sub> treatment on the chemistry of CCT ash. Three CCT ash samples, produced from lime injection, atmospheric fluidized bed combustion, and sodium carbonate injection processes were reacted under different CO<sub>2</sub> pressure treatment conditions. Treated and untreated samples were subjected to various experiments including, X-ray diffraction (XRD) analysis, calcium carbonate solubility studies, and trace element extraction studies. Factors influencing the efficiency of a CO<sub>2</sub> treatment for CCT ash samples include combustion process, moisture, CO<sub>2</sub> concentration, and pressure. The CO<sub>2</sub> pressure treatment resulted in the precipitation of calcite in CCT ash samples, and thus lowered the pH and the concentration of extractable trace elements (e.g., Cd, Pb, Cr, As, Se). Furthermore, we found that CO<sub>2</sub> pressure treatment was more effective for lime injection and atmospheric fluidized bed combustion processed samples than for sodium carbonate injection processed samples.

## 1. Introduction

Coal is the most abundant energy source in the world and therefore plays a crucial role in electric power generation. It is expected that the prominence of coal in the generation of electric power will continue in the future (Murarka, 1987). During the coal combustion process various by-products including, fly ash, bottom ash, and flue gases are generated. For example, in 1988 electric utilities in the USA generated approximately 90 million tons of coal ash. About 62% was fly ash, 23% was bottom ash and boiler slag, and 15% was flue gas desulfurization sludge. Of the total ash produced, only 20–25% was used in cement products, road bases, and asphalt. The remaining 75–80% was placed in surface impoundments and/or landfills.

The pH of fly ash can vary from 4.5 to 12.0 depending on the sulfur content of the parent coal, with high sulfur (eastern coals) generally producing acidic fly

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ash, and low sulfur (western coals) producing alkaline fly ash. Several studies have shown that certain trace elements (e.g., As, Cd, Se) in alkaline fly ash may become mobile and leach from disposal facility into soils and ground water (Cherry and Guthrie, 1977; Adriano *et al.*, 1980; Kopsick and Angino, 1981; Adriano *et al.*, 1982; Humenick *et al.*, 1983; USEPA, 1988; Carlson and Adriano, 1993). However, the solubility and mobility of trace elements in fly ash disposal environments are not well understood (Mattigod *et al.*, 1990; Eary *et al.*, 1990).

The New Clean Air legislation enacted by the U.S. Congress mandated the reduction of SO<sub>X</sub> emissions from coal burning power plants. As a result, a variety of Clean Coal Technologies (CCT) such as furnace/duct sorbent injection, atmospheric fluidized bed combustion, spray dryer and wet flue gas desulfurization (FGD) scrubbing will likely be used. Such technologies are currently in various stages of commercial or experimental development in the United States.

Calcium (Ca<sup>2+</sup>) is one of the most abundant elements in fly ash, because it is not volatilized during the combustion process (Rai *et al.*, 1987) and an alkaline sorbent (e.g., lime or sodium carbonate) is commonly used in the CCT process to remove SO<sub>X</sub> from flue gas. Furthermore, high temperatures of combustion process drive off CO<sub>2</sub> from carbonate phases (decarbonation). Consequently, the pH of aqueous extracts of CCT ash increases; this affects the solubility and mobility of trace elements.

With time, the pH of alkaline ash is expected to decrease with natural recarbonation (uptake of CO<sub>2</sub> by an alkaline ash). However, natural recarbonation is restricted by slow CO<sub>2</sub> input and reaction kinetics (Schramke, 1992). Such slow reactions may not prevent the mobility of trace elements from ash into disposal environments (i.e., soils and ground water). Nevertheless, reactions involving Ca<sup>2+</sup> and CO<sub>2</sub> are expected to control the pH and solubility and mobility of trace elements in alkaline fly ash (Schramke, 1992). Despite the importance of these reactions, only a few studies have examined the effects a CO<sub>2</sub> treatment on alkaline solid wastes (i.e., fly ash and spent oil shale) (Reddy *et al.*, 1986; Essington, 1989; Schramke, 1992). These studies either bubbled CO<sub>2</sub> through fly ash and spent shale slurries or aqueous solutions. However, such techniques are not practical for a typical coal burning power plant situation.

Recently, Reddy *et al.* (1991 and 1994) reported that reaction of CO<sub>2</sub> with alkaline spent oil shale and conventional coal combustion fly ash under slightly elevated pressures resulted in rapid precipitation of calcite, and thus reduced the concentration of extractable trace elements. In this study laboratory tests were conducted to determine the effects of pressurized CO<sub>2</sub> treatments on the chemistry of CCT ash samples. We collected different CCT ash samples and reacted them in a specially built chamber under different CO<sub>2</sub> pressure treatment conditions. Treated and untreated samples were subjected to X-ray diffraction (XRD) analysis and trace element extraction studies. Additionally, treated samples were subjected to calcite solubility studies. Results from these studies were used to determine the

effects of pressurized CO<sub>2</sub> treatment on the pH and extractability of selected trace elements in CCT ash.

## 2. Materials and Methods

### 2.1. INITIAL CHARACTERIZATION

Three CCT ash samples (CCT-1, 2, and 3) were used in this study. The CCT-1 and CCT-2 ash samples were collected from a lime injection and atmospheric fluidized bed combustion processes, respectively. The CCT-3 ash samples were derived from a sodium carbonate injection process. Approximately, 4–5 kg of ash samples were collected either directly from the bag-house or electrostatic precipitators and were screened through a 0.25 mm mesh sieve. The sieved samples were subjected to the analysis of pH and total elemental concentrations.

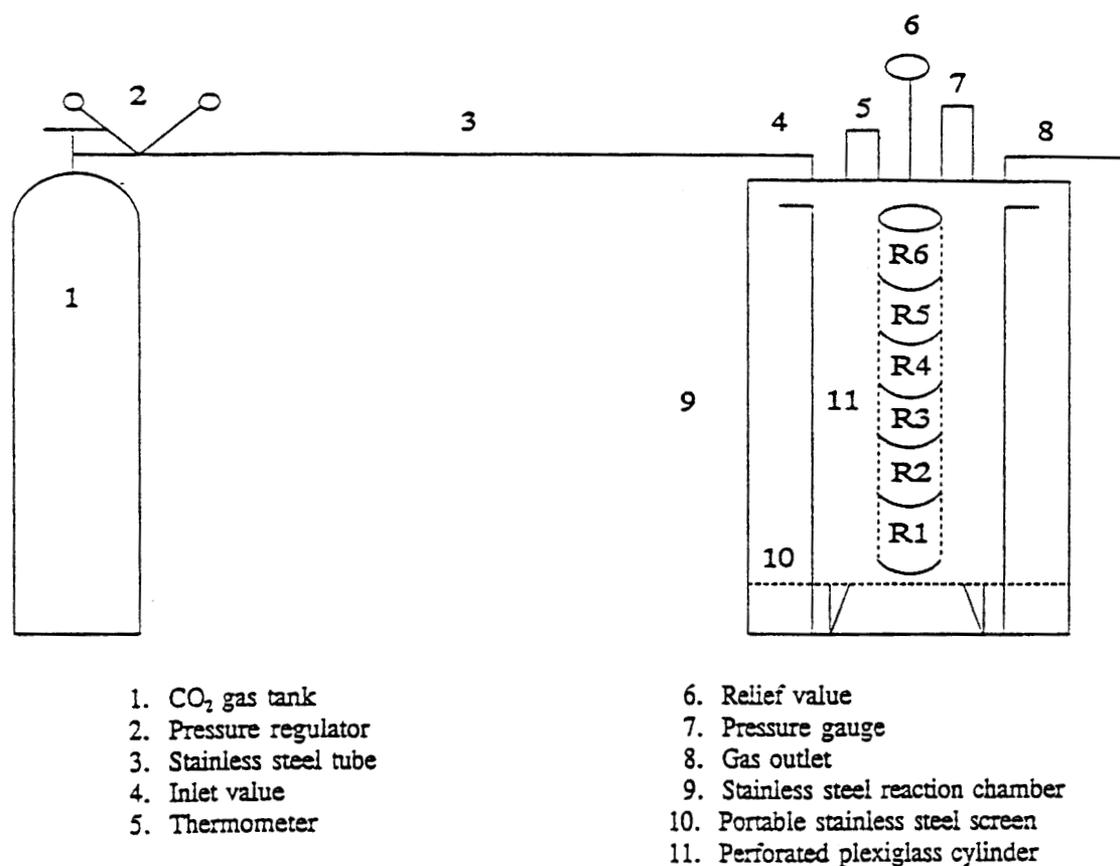
The pH of the CCT ash samples was measured in a saturated paste with an Orion combination electrode. Samples were digested in nitric acid (6*N*) plus perchloric acid (60%). The solutions were then analyzed for total concentrations of Al, S, P, Ca, Fe, Mg, Mn, Cu, Cd, Zn, As, Se, and Mo by inductively coupled plasma optical emission spectrometry (ICP-OES). Sodium and K were measured by atomic absorption (AA). More details regarding these procedures are reported in Page *et al.* (1982).

### 2.2. CO<sub>2</sub> PRESSURE TREATMENT EFFECTS ON THE PH

A stainless steel chamber, 30 cm in diameter by 60 cm in height (Fig. 1), was designed to react samples under different levels of CO<sub>2</sub> pressure (up to 125 psi). The reaction chamber was connected to a CO<sub>2</sub> tank (pure 99%, electronic instrument grade). A pressure gauge and a thermometer were installed on top of the chamber to monitor pressure and temperature, respectively. The gas outlet was connected to a fume hood.

A perforated plexiglass cylinder was designed, which consisted of six ring sample holder (11.87 cm in diameter by 7.5 cm in height) each separated by removable plexiglass disks (0.6 cm thick). This design assures effective diffusion of CO<sub>2</sub> through CCT ash samples during the treatment, since partial diffusion could lead to incomplete neutralization of alkalinity. The stainless steel chamber was wrapped in thermal wire along its length to monitor temperature. The chamber was covered with a foam insulation to reduce lateral heat flow losses to maintain a constant temperature.

Preliminary experiments were conducted to determine the efficiency of CO<sub>2</sub> diffusion through CCT ash samples. Different amounts of distilled-deionized H<sub>2</sub>O were added to the samples (on weight basis) and reacted under different levels of CO<sub>2</sub> partial pressure. After each preliminary treatment, samples were collected



- |                             |                                     |
|-----------------------------|-------------------------------------|
| 1. CO <sub>2</sub> gas tank | 6. Relief valve                     |
| 2. Pressure regulator       | 7. Pressure gauge                   |
| 3. Stainless steel tube     | 8. Gas outlet                       |
| 4. Inlet valve              | 9. Stainless steel reaction chamber |
| 5. Thermometer              | 10. Portable stainless steel screen |
|                             | 11. Perforated plexiglass cylinder  |

Fig. 1. Experimental design of CO<sub>2</sub> pressure process for CCT ash samples.

near the wall and at the middle of each ring to determine the efficiency of CO<sub>2</sub> diffusion through the samples.

The efficiency of a CO<sub>2</sub> pressure treatment is dependent on variables such as moisture, CO<sub>2</sub> partial pressure, total pressure, temperature, and reaction time. Forty-six different treatment conditions were tested separately. These treatment conditions consisted of a range of variables (moisture = 5–50%, CO<sub>2</sub> partial pressure = 20–100%, pressure = 50–125 psi, temperature = 25–50 °C, and reaction time = 24–72 hr). For each test, water was added to CCT ash samples on a weight basis, samples were then transferred to the plexiglass ring holders, and reacted under different conditions.

A part of each treated CCT ash samples was transferred to a plastic centrifuge tube to prepare 1:4 (solid:water) suspension and closed with caps. The pH of the suspension was measured within two hours and then monitored weekly for eighteen months to determine the effects of the CO<sub>2</sub> treatment on the long term stability of the pH. From 46 treatment conditions, final treatment conditions, which produced stable and lower pH's were selected. The CCT ash samples were then reacted with final treatment conditions and treated samples were used for subsequent experiments.

### 2.3. TREATMENT EFFECTS ON MAJOR MINERALS AND SOLUBILITY OF CALCITE

Treated and untreated CCT ash samples were subjected to XRD and calcium carbonate analyses. The XRD analysis was performed on randomly oriented slurried samples with a Scintag PAD V powder diffractometer using CuK $\alpha$  radiation. The XRD profiles obtained for each CCT ash sample were compared with Scintag software containing JCPDS (Joint Committee on Powder Diffraction Standards) files to determine major mineral phases. Calcium carbonate content was measured following the method of Nelson (1982). The %CO<sub>2</sub> absorbed by each CCT ash sample was calculated from the calcium carbonate content.

Treated samples (1:4 solid to water) were reacted on a mechanical shaker for determining the solubility of calcite (CaCO<sub>3</sub>) in aqueous extracts of CCT ash samples. After 7, 14, 21, and 28 day reaction time, sample suspensions were filtered through 0.45  $\mu$ M Millipore filters under an Ar atmosphere to reduce the uptake of atmospheric CO<sub>2</sub> by leachates.

Each filtered leachate was divided into two subsamples. One was acidified to pH 5–6 with HNO<sub>3</sub>. The other subsample was left unacidified. Acidified subsamples were analyzed for Ca, Mg, Al, Fe, Mo, Si (ICP-OES), Na, and K (AA). Unacidified subsamples were analyzed for pH, Cl<sup>-</sup>, F<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> (Ion Chromatography). The concentration of carbonate species was measured with CO<sub>2</sub> gas release method (Reddy *et al.*, 1990).

The pH and total elemental concentrations of aqueous extracts were used as input to the MINTEQA2 model (Brown and Allison, 1992) to calculate Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup> activities. Calcite ion activity product (IAP) was calculated from ion activities and compared with the solubility product ( $K_{sp}=10^{-8.48}$ ) of calcite (Plummer and Busenburg, 1982) to determine the solubility of calcite in aqueous extracts from treated CCT ash samples. We assumed that calcite IAPs within  $\pm 0.50$  log units of calcite  $K_{sp}$  represented equilibrium, and that calcite was a probable control on the concentration of Ca<sup>2+</sup> and CO<sub>3</sub><sup>2-</sup>. The variation within that range is accounted for by the uncertainty of IAP estimates and  $K_{sp}$  measurements (Stumm and Morgan, 1981).

### 2.4. TREATMENT EFFECTS ON EXTRACTABLE ELEMENTS

The AB-DTPA (NH<sub>4</sub>HCO<sub>3</sub> Diethylenetriaminepentaaceticacid) (Soltanpour and Schwab, 1977) extractant was used to extract trace elements from CCT ash samples. This extractant extracts both soluble (intensity fraction) and potentially soluble (capacity fraction) concentrations of trace elements from solid phases. The pH of the AB-DTPA extracting solution is maintained at 7.6 using either NH<sub>4</sub>OH or HCl which allows extraction of trace elements in alkaline materials. Several studies have used AB-DTPA (Folsom *et al.*, 1981; Schwab *et al.*, 1991; Reddy *et al.*, 1994) to predict potential solubility and availability of trace elements from alkaline waste materials.

CCT ash samples were spiked with a multielement standard solution to a level of 50 mg/kg each of Cd, Pb, Cu, Cr, As, Se, Ni, and B and were allowed to air dry. Duplicate spiked ash samples of 100 g each were subjected to the CO<sub>2</sub> pressure treatment (spiked-treated) using final treatment conditions. Remaining spiked CCT ash samples were left without the CO<sub>2</sub> pressure treatment (spiked-untreated). The AB-DTPA procedure was used to extract Cd, Pb, Cu, Cr, As, Se, Ni, and B from CCT ash samples (unspiked and untreated; spiked and untreated; spiked and treated).

### 3. Results and Discussion

#### 3.1. INITIAL CHARACTERIZATION

Initial characteristics of CCT ash samples are presented in Table I. All untreated CCT ash samples were high in Ca, K, Fe and low in Cd and Mo. CCT ash samples produced using lime and Na injection processes (i.e., CCT-1 & 3) were higher in Al, Mn, Cu and Pb contents than the one produced by atmospheric fluidized bed combustion process (CCT-2). However, the amounts of S, Fe, Zn and Mo were higher in the CCT-2 ash samples than in the CCT-1 and 3 ash samples. Arsenic and Se concentrations in all CCT ash samples were below 20.0 mg/kg. These results show that CCT ash samples were different in their chemical composition. This may be due to the chemistry of the coal and the combustion process used in the power plants.

Saturated paste pH of untreated CCT ash samples ranged between 11.50 and 12.74 (Table I). Most CCT processes use an alkaline sorbent (e.g., calcium carbonate or sodium carbonate) to remove SO<sub>x</sub> from power plant flue gas. Additionally, high temperatures of the combustion process drive off CO<sub>2</sub> from carbonate phases, which results in the formation of alkaline earth oxide and silicate phases. These phases react with water, and as a result, the pH of aqueous extracts of CCT ash approach 12.0.

#### 3.2. TREATMENT EFFECTS ON THE PH

Preliminary CO<sub>2</sub> diffusion experiments showed that CO<sub>2</sub> (g) circulated effectively through CCT ash samples during the pressure treatment. The pH of aqueous extracts of CCT ash samples dropped from 12.5 to an average value of 7.3. Measured pH values varied between 7.1 and 7.7 at the 12 sampling positions and the maximum variation was 0.20 within the rings and 0.60 between the rings. Regression analysis was performed to determine correlation coefficient ( $r^2$ ) values to establish the efficiency of the CO<sub>2</sub> diffusion through the plexiglass rings. Correlation coefficient ( $r^2$ ) between the pH at different positions within each ring was 0.99 and 0.98 between different rings. These results suggested that CO<sub>2</sub> was diffused effectively and the treatment effect on pH was nearly identical at all sampling positions.

TABLE I  
Initial characterization of CCT ash samples. Units are mg/kg

Sample Process	CCT-1 Lime injection	CCT-2 Atmospheric fluidized bed combustion	CCT-3 Na <sub>2</sub> CO <sub>3</sub> injection
Al	109,500	300	77,400
Na	47,600	1,500	32,200
S	3,500	43,100	11,800
P	1,900	400	10,000
Ca	56,037	98,037	10,649
K	5,301	8,613	11,220
Mg	1,398	6,786	400
Fe	52,037	73,038	46,046
Mn	218	124	543
Cd	15	10	13
Cu	151	39	87
Pb	357	4	222
Ni	95	69	61
Zn	119	187	81
Mo	23	43	23
pH (saturated paste)	12.47	12.74	11.50

Moisture was a limiting factor for all CCT ash samples for rapid chemical stabilization. High levels of pressure and %CO<sub>2</sub> were also closely related to the pH of some CCT ash samples. A significant drop in the pH was measured immediately after removing samples from the treatment chamber. Over time, some CCT ash samples maintained their low treatment pH values, while others returned to values close to those measured before treatment.

Final treatment conditions that significantly reduced the pH of each CCT ash sample were different. The CCT-1 ash samples stabilized at lower pH values than the CCT-2 and 3 samples. The methods used in the CCT process (i.e. calcium carbonate or sodium carbonate) were critical in determining the effectiveness of the CO<sub>2</sub> treatment with respect to pH. Samples processed using lime injection (CCT-1 ash samples) responded more rapidly to the treatment with respect to pH, than those produced under atmospheric fluidized bed combustion (CCT-2 ash samples) or sodium carbonate injection (CCT-3 ash samples).

Thirteen treatment conditions produced a significant stable drop in the pH values of CCT-1 ash samples (Table II). A drop of between 3.89 and 5.42 ± 0.10 pH units was achieved by different combinations of treatment variables. Treatments 1 through 6 produced an average pH drop of 4.47. These results show that the % moisture level is the most sensitive treatment variable. Increasing the % moisture

TABLE II

Effects of CO<sub>2</sub> treatment variables on the pH of lime injection ash samples (CCT-1). The pH before treatment = 12.47

No.	moisture %	Press. (psi)	CO <sub>2</sub> (%)	Temp. (°C)	Time (hr)	pH-A	pH-F	pH-B	Δ pH
1	15	75	100	25	48	7.77	8.58	+0.81	3.89
2	15	100	100	25	48	7.98	8.34	+0.36	4.13
3	20	50	100	25	24	7.74	8.13	+0.39	4.34
4	20	75	100	25	24	7.89	7.65	-0.24	4.82
5	20	100	100	25	48	7.67	7.55	-0.12	4.92
6	20	125	100	25	48	7.68	7.74	-0.06	4.73
7	20	100	50	25	48	6.81	8.04	+1.23	4.43
8	20	100	20	25	48	8.23	8.15	-0.08	4.32
9	20	50	20	50	48	7.44	7.29	-0.15	5.18
10	20	50	50	25	24	7.88	7.50	-0.38	4.97
11	20	100	100	45	24	8.20	7.18	-1.02	5.29
12	20	75	75	50	48	7.45	7.76	+0.31	4.71
13 <sup>a</sup>	20	75	75	25	24	7.45	7.05	-0.40	5.42

A = pH within two hr after treatment.

F = final stable pH.

B = difference in pH between A and F.

Δ pH = net change in pH.

<sup>a</sup> = final treatment.

from 15% to 20% (treatments 1 & 2 vs. 3 & 4) produced lower pH values under less pressure and reaction time. Further, increasing pressure and reaction time (treatments 5 & 6 vs. 4) with 20% moisture did not produce a significant change in the pH ( $\Delta \text{pH} = \pm 0.10$ ).

Treatments 7, 8, 9 and 12 show that increasing temperature with 20% moisture under lower %CO<sub>2</sub> and pressure produced a further reduction in the pH. No significant differences were found between treatments 4 and 12 ( $\Delta \text{pH} = \pm 0.10$ ), but treatment 9 produced a  $\Delta \text{pH}$  of 5.18 with low CO<sub>2</sub> pressure. Treatments 4, 5, 10, 11 and 13 averaged a  $\Delta \text{pH}$  drop of 5.08 with less reaction time, pressure and %CO<sub>2</sub>. However, treatment 13 was the most effective and produced the largest pH drop using medium levels of %CO<sub>2</sub> and pressure. Therefore, these conditions were selected as a final treatment for CCT-1 ash samples.

Initial results from different CO<sub>2</sub> pressure treatment experiments for CCT-2 ash showed that pH of these samples did not stabilize under any treatment conditions. Moisture addition to CCT-2 ash samples, before CO<sub>2</sub> pressure treatment, increased the temperature (approximately 120 °C) of the samples due to the dissolution of oxides. This resulted in the consumption of moisture (approximately 50 to 60%)

TABLE III

Effects of CO<sub>2</sub> treatment variables on the pH of atmospheric fluidized bed combustion ash samples (CCT-2). The pH before treatment = 12.74

No.	moisture %	Press. (psi)	CO <sub>2</sub> (%)	Temp. (°C)	Time (hr)	pH-A	pH-F	pH-B	Δ pH
1	25	100	100	25	24	8.03	9.50	+1.47	3.24
2	25	100	100	25	48	8.05	9.55	+1.50	3.19
3	25	125	100	25	48	7.73	9.50	+1.77	3.24
4	25	100	100	25	72	8.05	9.58	+1.53	3.16
5	40	100	100	25	96	7.74	9.52	+1.78	3.22
6	50	100	100	25	96	7.66	9.42	+1.76	3.32
7 <sup>a</sup>	50	100	100	45	24	8.55	9.34	+0.79	3.40

A = pH within two hr after treatment.

F = final stable pH.

B = difference in pH between A and F.

Δ pH = net change in pH.

<sup>a</sup> = final treatment.

by the formation of hydrated precipitates. The addition of moisture, lost during the formation of hydrated precipitates, before each treatment was a critical factor in obtaining a stable pH drop for CCT-2 ash samples.

Treatments 1 through 7 (Table III) produced a significant drop in the pH values for the CCT-2 ash samples. The lower stable pH values measured after the treatments ranged from 9.58 to 9.34, with an average Δ pH of 3.25. No significant differences were found between treatments 1, 2, 3 and 4. Increasing the % moisture to 40 and 50 under room temperature (treatments 5 and 6) showed no further drop in the pH. However, increasing temperature to 45 °C reduced the pH from 12.74 to 9.34 in 24 hr (treatment 7), and this treatment was selected for CCT-2 ash samples.

Treatments 1 through 4 (Table IV) produced an average Δ pH of 2.30 for CCT-3 ash samples. Initial pH values around 8.50 were obtained by different treatment conditions. However, these initial pH values were stabilized near 9.20 in most treatments, and treatment 2 was selected for CCT-3 ash samples. The high buffering capacity and the apparent slow dissolution of silicate minerals, and also the low concentration of Ca as compared to %Na, might have prevented attainment of a larger drop in the pH of CCT-3 ash samples.

### 3.3. TREATMENT EFFECTS ON MAJOR MINERALS AND SOLUBILITY OF CALCITE

The XRD analysis (Table V) suggested that CCT ash samples consisted largely of quartz, silicates, amorphous phases, and calcium oxide. Formation of these

TABLE IV

Effects of CO<sub>2</sub> treatment variables on the pH of sodium carbonate injection ash samples (CCT-3). The pH before treatment = 11.50

No.	moisture %	Press. (psi)	CO <sub>2</sub> (%)	Temp. (°C)	Time (hr)	pH-A	pH-F	pH-B	Δ pH
1	10	100	20	25	48	8.72	9.14	+0.42	2.36
2 <sup>a</sup>	10	75	75	25	24	8.71	9.16	+0.45	2.34
3	10	100	50	25	48	8.49	9.21	+0.72	2.29
4	10	100	100	45	24	8.55	9.28	+0.73	2.22

A = pH within two hr after treatment.

F = final stable pH.

B = difference in pH between A and F.

Δ pH = net change in pH.

<sup>a</sup> = final treatment.

TABLE V

Effects of final CO<sub>2</sub> treatment conditions on %CaCO<sub>3</sub> equivalent, %CO<sub>2</sub>, and mineral transformations. N.D. = not detected

Sample	%CaCO <sub>3</sub> equivalent	%CO <sub>2</sub>	Major mineral peaks
CCT-1 Untreated	N.D.	N.D.	quartz, silicates
CCT-1 Treated	2.82	0.62	calcite, gypsum, quartz, mullite
CCT-2 Untreated	N.D.	N.D.	quartz, calcium oxide, amorphous phases
CCT-2 Treated	4.48	0.99	calcite, gypsum
CCT-3 Untreated	3.38	0.74	quartz, amorphous phases
CCT-3 Treated	4.57	1.01	quartz, calcite

phases in CCT ash samples require high temperatures (i.e., >1500 °K). Such temperatures are usually attained during the combustion process of coal. The %CaCO<sub>3</sub> equivalent and %CO<sub>2</sub> (Table V) were increased significantly after the CO<sub>2</sub> pressure treatment. Both CaCO<sub>3</sub> and CO<sub>2</sub> were not detected in untreated CCT-1 and 2 ash samples, but both were increased upon CO<sub>2</sub> pressure treatment. This increase in carbonate content suggests the probable dissolution of oxides and silicates and the precipitation of calcium carbonates. The XRD analyses indicated the presence of calcite in treated CCT ash samples (Table V). The results in Table V

TABLE VI  
Saturation index (SI) for calcite in aqueous extracts of CO<sub>2</sub> treated CCT ash samples

Sample	Calcite	
	-log IAP <sup>a</sup>	log SI <sup>b</sup>
CCT-1	8.90	-0.42
CCT-2	8.76	-0.28
CCT-3	8.25	+0.23
Mean	8.63	-

<sup>a</sup> ion activity product.

<sup>b</sup> SI = log (IAP/ $K_{sp}$ ).

log  $K_{sp}$  of calcite = -8.48.

also show that CO<sub>2</sub> treatment caused the precipitation of gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O) in CCT ash samples.

Chemical data from 7, 14, 21, and 28 day calcite solubility studies suggested that no significant changes were found between 21 and 28 days. Therefore, the chemical data of 28 days reaction time were used to determine the saturation index of calcite in aqueous extracts of treated CCT ash samples (Table VI). The log IAPs for treated CCT samples showed near saturation with respect to calcite (a mean value of -8.63). These results support the XRD findings with treated CCT samples. Long term leaching experiments suggested that calcite could precipitate in weathered fly ash (Dudas, 1981). Rai *et al.* (1987) also reported similar results.

### 3.4. TREATMENT EFFECTS ON EXTRACTABLE TRACE ELEMENTS

The CO<sub>2</sub> pressure treatment effects on extractable trace elements were clearly observed from the results of the AB-DTPA extraction procedure (Table VII). A reduction in the concentrations of extractable trace elements was obtained in spiked plus CO<sub>2</sub> treated CCT ash samples. For instance, extractable arsenic (As) concentrations were decreased from 3.40 to 0.10 mg/L for CCT-1 ash samples. The decrease in extractable As from 0.35 to 0.10 and 3.70 to 1.15 mg/L was observed for CCT-2 and CCT-3 ash samples, respectively. The CO<sub>2</sub> pressure treatment was found most effective for CCT-1 ash samples (lime injection process), followed by CCT-2 (atmospheric fluidized bed combustion process), and CCT-3 (sodium carbonate injection process) ash samples in reducing the concentration of extractable trace elements.

A possible explanation for the decrease in the concentration of extractable trace metals (e.g., Cd, Pb) is the precipitation of metal carbonates. In CCT ash samples, these metals are probably present as oxides and/or hydroxides (e.g., CdO, Pb(OH)<sub>2</sub>) due to the combustion process. When CCT ash samples were reacted under CO<sub>2</sub>

TABLE VII

Effects of final CO<sub>2</sub> treatment conditions on extractable trace elements. Units are mg/L

I.D <sup>a</sup>	Cd	Pb	Cu	Cr	As	Se	Ni	B
1-C	0.01	0.10	1.42	0.32	0.75	BD	1.70	27
1-B	5.35	4.55	12.82	0.17	3.40	3.75	2.25	57
1-A	0.04	0.50	2.65	0.02	0.10	0.65	0.20	19
%Drop <sup>b</sup>	99	89	79	88	97	82	90	66
2-C	0.01	0.56	0.09	0.43	0.03	0.03	0.17	26
2-B	4.50	2.65	1.73	2.05	0.35	2.15	0.32	15
2-A	0.45	1.15	1.65	1.10	0.10	0.50	0.30	N.A.
%Drop	90	56	4	46	71	76	6	N.A.
3-C	0.09	0.50	2.90	0.75	2.65	4.25	0.02	176
3-B	3.96	5.85	5.21	0.33	3.70	12.45	2.15	192
3-A	3.10	3.30	3.91	0.08	1.15	8.20	1.81	158
%Drop	21	43	24	75	68	34	15	17

<sup>a</sup>I.D 1 = CCT-1, 2 = CCT-2, 3 = CCT-3.

C = control.

B = spiked-untreated.

A = spiked-treated.

<sup>b</sup>%Drop = 100 - {(A/B) 100}.

N.A. = not available.

BD = below detection limit of 0.01 mg/L.

pressure, soluble oxides and/or hydroxides were probably converted to carbonates (e.g., CdCO<sub>3</sub>, PbCO<sub>3</sub>). This causes a reduction in the concentration of extractable metals because carbonate phases are less soluble than oxides or hydroxides between pH 8.0 and 9.0 (Lindsay, 1979).

A reduction in the concentration of extractable As, B, Cr, and Se is probably attributable to an increased sorption of these elements by iron oxides at lower pH values because CCT ash commonly contains iron oxides (see Table I). It is well established that by decreasing the extractable concentration of a given element, the mobility of that element will also be reduced.

Theis and Wirth (1977) reported that release of trace elements (e.g., As, Cd, Cr, Cu, Pb, Ni, and Zn) from coal combustion ash is strongly related to the pH. Results from their studies also suggest that as pH decreases from 12 to 9 these elements become less soluble in fly ash due to sorption and precipitation processes. However, release of trace elements from coal combustion ash increased significantly, when pH dropped to 6 or below (Theis and Wirth, 1977). These results show that trace

elements in coal combustion ash attain their lowest solubility between the pH of 9 and 6. Rai *et al.* (1987) also reported similar results.

Thus, observed reduction in the concentrations of extractable trace elements in CO<sub>2</sub> treated CCT ash samples is probably due to the mineral phases formed as pH is reduced through the consumption of CO<sub>2</sub>, which in turn enhanced both sorption and precipitation processes of trace elements. The CO<sub>2</sub> pressure treatment described here has, under laboratory conditions, demonstrated its potential to reduce the concentration of extractable trace elements (As, Cd, Pb, and Se) in different CCT ash samples. This could reduce the potential mobility of these elements in CO<sub>2</sub> treated CCT ash.

#### 4. Conclusions

The CO<sub>2</sub> pressure treatment produced a significant drop in the pH of CCT ash samples. The CO<sub>2</sub> treatment also caused the dissolution of oxide and silicate phases and the precipitation of CaCO<sub>3</sub> and CaSO<sub>4</sub>·2H<sub>2</sub>O phases. Clean coal technology process used in each power plant was an important factor in determining the efficiency of the CO<sub>2</sub> treatment for chemical stabilization of CCT ash. Lime injection played a key role by supplying the Ca needed to enhance the rapid precipitation of CaCO<sub>3</sub> and CaSO<sub>4</sub> phases in CCT ash samples. Additionally, moisture, CO<sub>2</sub> concentration, and pressure were also found to affect the efficiency of the CO<sub>2</sub> treatment process for CCT ash.

The CO<sub>2</sub> pressure treatment effectively decreased the concentration of extractable trace elements in CCT ash samples produced from lime injection and atmospheric fluidized bed combustion processes. Since this process uses CO<sub>2</sub>, which can be obtained from the combustion process itself (i.e., flue gas), it has the potential to concomitantly reduce CO<sub>2</sub> (so-called greenhouse gas) emissions from the coal combustion process. Further research is needed to evaluate the cost and economic viability of the CO<sub>2</sub> pressure process under field conditions.

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