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Development of a Carbon Dioxide Pressure Technique for Chemical Stabilization of Alkaline Clean Coal Technology (CCT) Ash

Prepared by Wyoming Water Resources Center/University of Wyoming Laramie, Wyoming

Development of a Carbon Dioxide Pressure Technique for Chemical Stabilization of Alkaline Clean Coal Technology (CCT) Ash

Clean Coal Technology (CCT) process ash may contain harmful trace elements that could leach from a disposal facility. This study investigated the effects of a carbon dioxide pressure treatment to lower the pH and therefore the leachability of trace elements in the ash. Test results confirmed that the pressure treatment significantly reduced the pH of CCT ash samples.

BACKGROUND Clean coal technologies to reduce SO_x emissions from coalburning utilities include furnace/duct sorbent injection, atmospheric fluidized bed combustion, use of a spray dryer, and wet flue gas desulfurization scrubbing. Application of these technologies may result in production of alkaline CCT ash with a pH ranging from 9 to 12. In turn, such materials may pose a problem for land disposal due to the leaching of certain trace elements such as arsenic, cadmium, and selenium.

OBJECTIVE To test and optimize a carbon dioxide (CO₂) pressure technique for the chemical stabilization of alkaline CCT ash.

APPROACH Investigators collected CCT ash samples and subjected them to various CO_2 pressures and temperatures in a specially built chamber designed to optimize conditions for chemical stabilization. To determine the effects of the CO_2 pressure treatment on the pH and mobility of trace elements, investigators performed X-ray diffraction (XRD) and leachability studies on treated and untreated samples.

RESULTS The CO₂ pressure process produced a significant drop in the pH of CCT treated ash samples. This pH reduction was due to the precipitation of calcite, gypsum, and anhydrite, as confirmed by XRD analyses. The precipitation of these minerals was enhanced in CCT ash samples produced in lime injection systems, since sufficient calcium was present from the lime. Moisture level was highly correlated with the treatment effect on pH in all samples. Reduction in the pH level indicated that the CO₂ pressure treatment effectively decreased the concentrations of leachable trace elements in CCT ash samples. In fact, tests showed that concentrations of trace elements in CO₂ pressure-treated samples were lower than in untreated samples and, in most cases, were below control treatment levels.

EPRI PERSPECTIVE The potential for the leaching of trace elements from ash management facilities is an important consideration for electric utilities when considering facility siting and management. This research has demonstrated at the laboratory stage that CO₂ pressure treatment is effective in decreasing the solubility of trace elements in CCT ash samples. Furthermore, CO₂ for the treatment can be obtained from the coal combustion process, meaning that this treatment also has

INTEREST CATEGORIES

Land and water quality chemistry and physics Waste and water management

KEYWORDS

Solid waste Leaching Trace elements the potential to reduce CO_2 emissions. Additional research is needed to evaluate the cost and economic viability of the CO_2 pressure treatment process under field conditions.

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Development of a Carbon Dioxide Pressure Technique for Chemical Stabilization of Alkaline Clean Coal Technology (CCT) Ash

TR-104840 Research Project 2485-21

Final Report, June 1995

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ABSTRACT

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Clean Coal Technology (CCT) ash may contain trace elements such as arsenic (As), cadmium (Cd) and selenium (Se), some of which may become mobile and leach from a disposal facility. This study was undertaken to determine the effects of a carbon dioxide (CO_2) pressure treatment on the leachability of trace elements in CCT ash. The CO₂ pressure treatment was optimized using a three by five factorial design as well as a multiple regression analysis. Low, medium and high levels of moisture, reaction time, pressure, temperature and concentration of CO₂ were tested. Treated and untreated CCT ash samples were subjected to X-ray diffraction (XRD) and leachability studies. A 1:4 (solid:solution) suspension was used to monitor the pH changes after each treatment. Optimum CO₂ treatment conditions rapidly precipitated calcite, and thus lowered the pH of CCT ash samples. For example, a stable pH drop from 12.47 to 7.05 for CCT-1, 12.74 to 9.34 for CCT-2 and 11.50 to 9.16 for CCT-3 was obtained. An increase in percent calcium carbonate (CaCO₃) content and percent CO₂ uptake was observed in CO₂ treated samples. Solubility studies suggested that Ca²⁺ concentration in CO₂ treated CCT ash leachates appeared to be regulated by $CaCO_3$. Our results show that reacting moist CCT ash samples with CO_2 under pressure is effective in lowering the concentrations of leachable trace elements (e.g., Cd, Pb, Cr, As and Se), which could prevent their migration from disposal environments into soils and groundwaters.

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INTRODUCTION

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Coal is the most abundant energy source in the United States (U.S.), and accounted for almost 55 percent of the production of electricity in 1990. It is expected that the prominence of coal in the generation of electric power will continue in the future (DOE, 1993).

The coal combustion process produces by-products such as fly ash, bottom ash, flue gas desulfurization sludge and flue gases, including oxides of sulfur (SO_x) and carbon dioxide (CO_2) . In 1990, U.S. electric utilities generated almost 90 million tons of solid by-products (approximately 70 million tons of ash and 20 million tons of flue gas desulfurization sludge). About 30% of these by-products were used in cement products, road bases and asphalt and other miscellaneous applications (DOE, 1993). The remaining percentage was placed in surface impoundments and/or landfills, representing a potential disposal problem due to the leaching of certain trace elements (EPA, 1988).

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 ash, and low sulfur (western coals) producing alkaline fly ash. Fly ash may contain different amounts of trace elements (e.g., As, Cd and Se). However, the content of these elements in fly ash often depend on several factors, including the composition of the parent coal and combustion conditions (Page, 1979 and Adriano, 1986).

Several studies have suggested that some trace elements in alkaline fly ash may become mobile and leach from disposal facility into soils and groundwaters (Adriano, 1980 and Carlson, 1993). Nonetheless, the solubility and mobility of trace elements in fly ash disposal environments are not well understood (Mattigod, 1990 and Eary, 1990).

The New Clean Air legislation enacted by the U.S. Congress in 1990 mandated the reduction of SO_x 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 implemented. Such technologies currently are in various stages of commercial or experimental development in the U.S.

In the CCT process, an alkaline sorbent is used to remove SO_x from flue gas. Furthermore, the high temperatures of the coal combustion process drive off CO_2 from the carbonate phases. These conditions increase the pH of aqueous extracts of CCT ash, which could affect the solubility and mobility of trace elements.

For example, high pH increases the solubility of Se, which in turn may enhance its mobility in fly ash disposal environments. Therefore, reactions involving pH and CO_2 are expected to control the solubility and the mobility of trace elements in CCT ash (Schramke, 1992, Rai, 1987, Reddy, 1986 and Essington, 1989). Most past studies of these reactions have involved either bubbled CO_2 through alkaline ash slurries or aqueous solutions. Such techniques, however, are not practicle for field application.

A CO₂ pressure treatment process that recarbonates the mineral phases could affect the pH, solubility and mobility of trace elements in alkaline solid wastes (Reddy, 1991 and 1993). At present, very little is known about how a CO₂ pressure process affects the pH and the leachability of trace elements in CCT ash.

OBJECTIVES

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The objectives of this study were to conduct laboratory tests to optimize a CO_2 pressure treatment for CCT ash samples to rapidly chemically stabilize the samples and to determine treatment effects on the leachability of trace elements (Figure 1). Different CCT ash samples were collected and reacted in a specially built chamber to optimize CO_2 pressure treatment conditions for chemical stabilization. Treated and untreated samples were subjected to XRD and leachability studies to determine the effects of a CO_2 pressure treatment on the pH and mobility of trace elements in CCT ash samples.

FIGURE 1 RECARBONATION PROCESS OF CCT ASH



Alkaline pH (9-12)

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Increase solubility of trace elements

Dominated by oxides hydroxide and silicate phases Slightly alkaline pH (8-9)

4

Decrease solubility of trace elements

Dominated by carbonate phase

MATERIALS AND METHODS

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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 process and atmospheric fluidized bed combustion process, respectively. The CCT-3 ash samples were derived from a sodium carbonate injection process.

Ash samples were collected either directly from the bag-house or electrostatic precipitators and placed immediately in plastic containers without head space and closed tightly. Samples were screened through a 0.25 mm mesh sieve and were subjected to the analysis of pH, total elemental concentrations, major mineral phases and calcium carbonate content.

Initial Characterization - The pH of the CCT ash samples was measured in a saturated paste with an Orion combination electrode (Rhoades, 1982). Samples were then digested in nitric acid (6*N*) plus perchloric acid (60%) and the solutions were 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 determined by atomic absorption (AA). More details regarding these procedures are reported in Lim and Jackson (Lim, 1982).

XRD analysis was performed on randomly oriented slurried samples with a Scintag PAD V powder diffractometer using CuK α radiation. XRD profiles obtained for CCT ash samples were compared with Scintag software containing JCPDS (Joint Committee on Powder Diffraction Standards) files to determine major mineral phases.

Calcium carbonate content was measured using the method of Nelson (Nelson, 1982). In this procedure, few grams of samples were dissolved in 3N HCl and calcium carbonate content was calculated from the sample weight loss. The percent CO₂ absorbed by CCT ash samples was calculated from calcium carbonate content.

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Design of Stainless Steel Chamber - A stainless steel chamber, 30 cm in diameter by 60 cm in height (Figure 2), was designed to react CCT ash samples under different levels of CO_2 pressure (up to 150 psi). The reaction chamber was connected to a CO_2 tank (99% pure, electronic instrument grade). A pressure gauge and a thermometer were installed on top of the chamber to monitor pressure and temperature, respectively.

A perforated plexiglass cylinder was designed, which consisted of six ring sample holders (11.87 cm in diameter by 7.5 cm in height) each separated by removable plexiglass disks. This design assures effective diffusion of CO_2 through the 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 foam insulation to minimize lateral heat flow losses to maintain a constant temperature during reactions.

Preliminary Experiments - Preliminary experiments were conducted to determine the efficiency of CO_2 diffusion through the CCT ash samples, and its effects on the pH. Different amounts of distilled-deionized water were added to the samples and reacted under different levels of CO_2 pressure at room temperature for different reaction periods. After each preliminary treatment, samples adjacent to the wall (R_w) and at the middle (R_m) of each ring were collected (Figure 3) to determine the efficiency of CO_2 diffusion through the samples.

EXPERIMENTAL DESIGN OF CO₂ PRESSURE PROCESS FOR CCT ASH SAMPLES



- 1. CO₂ gas tank
- 2. Pressure regulator
- 3. Stainless steel tube

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- 4. Inlet value
- 5. Thermometer

- 6. Relief value
- 7. Pressure gauge
- 8. Gas outlet
- 9. Stainless steel reaction chamber
- 10. Portable stainless steel screen
- 11. Perforated plexiglass cylinder

SAMPLING POSITIONS AND pH VALUES TO DETERMINE CO₂ DIFFUSION EFFICIENCY

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Optimum Treatment Conditions - The efficiency of the CO₂ pressure treatment is dependent on variables such as moisture (X₁), pressure (X₂), CO₂ concentration (X₃), temperature (X₄) and reaction time (X₅). A three level by five variable factorial design was used to form the basis for selecting initial treatment conditions (Table 1). Forty-six different treatment conditions were selected and tested separately (Table 2). For each test, moisture ($\%\theta_{\omega}$) was added to CCT ash samples on a weight basis, and the samples were then transferred to the plexiglass ring holders and reacted under different conditions. The chamber was flushed with CO₂ prior to each test.

TABLE 1

THE THREE LEVEL BY FIVE VARIABLE DESIGN FOR CO_2 PRESSURE TREATMENT

Level	X ₁ Moisture (%)	X ₂ Pressure (psi)	X ₃ CO ₂ (%)	X₄ Temperature (°C)	X ₅ Time (hr.)
Low	2	10	10	20	1
Medium	5	50	50	30	5
High	10	100	100	50	10

A portion of each treated CCT ash sample was transferred to a plastic centrifuge tube to prepare a 1:4 (solid:water) suspension. The pH of the suspension was determined within two hours and then monitored on a weekly basis for eighteen months to determine the effects of the CO_2 treatment on the long-term stability of the pH. Multiple regression analysis was used to select the optimum treatment conditions for CCT ash samples (Snedecor, 1978). From optimum conditions, final treatment conditions were selected based on the pH stability of the treated CCT ash samples. CCT ash samples were reacted employing the final treatment conditions and reacted samples were used for subsequent experiments.

TABLE 2

TREATMENT CONDITIONS USED FOR REACTING CCT ASH SAMPLES

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No,	%θ _ω	Pressure	%CO ₂	Temperature	Time (hr.)
1	5	(psr) 50	100	25	24
2	10	50	100	25	24
3	15	50	100	25	24
4	20	50	100	25	24
5	15	100	100	25	24
6	15	75	100 *	25	24
7	15	60	100	25	24
8	15	100	100	25	48
9	15	75	100	25	48
10	20	100	50	25	48
11	20	100	20	25	48
12	20	50	50	25	24
13	20	75	75	25	24
14	50	100	50	25	48
15	50	100	20	25	48
16	50	50	50	25	24
17	50	75	75	25	24
18	10	100	50	25	48
19	10	100	20	25	48
20	10	50	50	25	24
21	10	75	75	25	24
22	15	105	100	25	72
23	20	105	100	25	72

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TABLE 2 (continued)

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TREATMENT CONDITIONS USED FOR REACTING CCT ASH SAMPLES

No.	%θ _ω	Pressure	%CO ₂	Temperature	Time (hr.)
24	25	105	100	25	72
25	30	105	100	25	72
26	20	100	100	25	48
27	25	100	100	25	48
28	10	100	100	25	48
29	20	125	100	25	48
30	25	125	100	25	48
31	10	125	100	25	48
32	25	100	100	25	24
33	20	75	100	25	24
34	25	100	100	25	48
35	25	100	100	25	72
36	40	100	100	25	96
37	50	100	100	25	96
38	20	100	100	45	24
39	20	75	75	50	48
40	20	50	20	50	48
41	50	100	100	45	24
42	50	75	75	50	48
43	50	50	20	50	48
44	10	100	100	45	24
45	10	75	75	50	48
46	10	50	20	50	48

Solubility Studies - Solubility studies were performed on treated and untreated samples for 7, 14, 21 and 28 days to determine potential solid phases controlling the dissolved Ca concentrations. Duplicates 100-g samples were placed in plastic bottles. The bottles caps were replaced by fitted rubber stoppers. Two glass tubes were inserted in each rubber stopper to create an inlet-outlet controlled system. Distilled-deionized water was added to each sample to prepare a 1:4 (solid:water) suspensions. Argon gas was slowly pumped into suspensions to replace laboratory air and thereafter, the inlet-outlet tubes were tightly closed. Suspensions were then placed on a rotary mechanical shaker.

Samples were removed from the shaker and filtered through a 0.45 μ m Millipore filters under argon gas environment. Clear aliquots were divided into two sub-samples without head-space in plastic vials to avoid atmospheric CO₂ (g) interaction. Filtrates were analyzed for pH, electric conductivity (EC), cations and anions. Total alkalinity was determined using an automatic potentiometric titrator. Concentrations of F⁻, Cl⁻, PO₄⁻³⁻, NO₃⁻ and SO₄⁻²⁻ were obtained by ion chromatography (IC); while Ca, Mg, As, Al, B, Si, Se, Pb, Cd, Cr, Cu, Fe, Mn, Zn and Ni were measured by inductively coupled plasma emission spectrometry (ICP-ES). Sodium and K were determined with atomic absorption (AA). The chemical speciation model MINTEQA2 (Brown, 1987) was used to calculate ion-activities, saturation indices and possible solid phases.

Leachability Studies - Typically, the U.S. Environmental Protection Agency's Toxicity Characterizing Leaching Procedure (TCLP) is used to predict the leachability of trace elements from solid waste (EPA, 1986). This procedure may not be appropriate to use on solid waste with pH > 7.0 because the TCLP extracts samples under two acidic solutions (pH 2.88 and 4.93). These acid extractants may prohibit the effects of the pH reduction obtained by the CO₂ pressure treatment on trace element concentrations. However, treated and untreated samples were extracted using the TCLP and the extracts were analyzed for As, Ba, Cr, Cd, Pb, Hg, Se, and Ag. The TCLP analysis was performed by Analytical Technologies, Inc. Fort Collins, Colorado.

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AB-DTPA (NH_4HCO_3 -Diethylenetriamine penta acetic acid), a multi-element extractant which removes both available and potentially soluble fractions, is useful in predicting the leachability of a given trace element (Soltanpour, 1977). The pH of the AB-DTPA extracting solution is maintained at 7.6 using either NH_4OH or HCl, which allows for simultaneous determination of trace elements in slightly alkaline leachates. Several studies have been used this extraction procedure (Reddy, 1993, Folsom, 1981 and Schwab, 1991) to predict the solubility and availability of trace elements in alkaline waste materials.

CCT ash samples were spiked with a multi-element standard solution to a level of 50 mg/kg each of Cd, Pb, Cu, Cr, As, Se, Ni and B, and allowed to air dry. Duplicate spiked ash samples of 100 g each were subjected to the CO_2 pressure treatment (spiked-treated) using final treatment conditions. Remaining spiked CCT ash samples were left without the CO_2 pressure treatment (spiked-untreated). The AB-DTPA procedure was used to predict the leachability of Cd, Pb, Cu, Cr, As, Se, Ni and B in CCT ash (unspiked and untreated), spiked-untreated and spiked-treated CCT ash samples.

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RESULTS AND DISCUSSION

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Initial Characterization - Initial characteristics of CCT ash samples are presented in Table 3. All untreated CCT ash samples were high in Ca, K, Fe and low in Cd, As, Se and Mo. CCT ash samples produced using lime and Na injection processes (i.e., CCT-1 and CCT-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 as compared with CCT-1 and CCT-3 ash samples. Arsenic and Se concentrations in all CCT ash samples were found to be below 20.0 mg/kg. These results suggest that CCT ash samples were different in their chemical composition probably due to the type of coal used as well as the combustion process used by the power plants.

The XRD analysis (Table 3) suggested that CCT ash samples consisted largely of quartz, silicates, amorphous phases, calcium oxide and anhydrite. Formation of these phases require high temperatures (i.e., $>1500^{\circ}$ K). Such temperatures are usually attained during the combustion process of coal.

Saturated paste pH of untreated CCT ash samples ranged between 11.50 and 12.74 (Table 3). Most CCT processes use an alkaline sorbent (e.g., calcium carbonate or sodium carbonate) to remove SO_x from power plant flue gas. During the combustion process, high temperatures drive off CO₂ from carbonate phases resulting in the formation of oxide and silicate phases. These phases react rapidly with water, and as a result, the pH of aqueous extracts of CCT ash approach 12.0.

TABLE 3

INITIAL CHARACTERIZATION OF CCT ASH SAMPLES

Property	CCT-1	CCT-2	CCT-3
Process	Lime injection	Atmospheric fluidized bed	Na ₂ CO ₃ injection
	Mg/Kg	combustion Mg/Kg	Mg/Kg
Al	109,500	300	77,400
Na	47,600	1,500	32,200
S	3,500	43,100	11,800
Р	1,900	400	10,000
Ca	56,037	98,037	10,649
К	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
Мо	23	43	23
Major Mineral Phases	quartz & silicates	quartz, calcium oxide, anhydrite	quartz & amorphous phases
pH (saturated paste)	12.47	12.74	11.50

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Preliminary Results - Preliminary CO₂ diffusion experiments (Fig. 3) indicated that CO₂ (g) circulated effectively through CCT ash samples during the pressure treatment. The pH of CCT-1 aqueous extracts dropped from 12.5 to an average value of 7.3. Measured pH values varied between 7.1 and 7.7 at the 10 sampling positions and the maximum variation was 0.20 within the rings (R_{1w} and R_{1m}) and 0.60 between the rings (R_{5w} and R_{1m}). Regression analysis was performed to determine correlation coefficient (r^2) values to establish the efficiency of the CO₂ 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 CO₂ diffused effectively and the treatment effect on pH was nearly identical at all sampling positions.

Optimum Treatment Conditions and Treatment Effects on the pH - The 3⁵ factorial design with a multiple regression analysis using five independent variables and the pH of aqueous extracts as the dependent variable was performed to determine the effect of each treatment variable on the pH. The method identified the treatment variables that were closely related to the pH, and was used to determine the optimum treatment conditions. From optimum conditions, the final treatment conditions were selected based on the stability of the pH of CCT treated samples.

Moisture was predicted as the limiting factor by multiple regression analysis for all CCT ash samples. High levels of pressure and percent CO_2 were also predicted to be closely related to the pH for CCT-2 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.

Optimum 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 CCT processes (i.e calcium carbonate or sodium carbonate) appeared to be

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critical in determining the effectiveness of the CO_2 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 for CCT-1 ash samples (Table 4). A drop of between 3.89 to 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 percent moisture (θ_{ω}) level is the most sensitive treatment variable. Increasing the percent θ_{ω} 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% θ_{ω} did not produce a significant change in the pH (Δ pH = ± 0.10).

Treatments 7, 8, 9 and 12 show that increasing temperature with 20% θ_{ω} under lower percent CO_2 and pressure produced a further reduction in the pH. No significant differences were found between treatments 4 and 12 (\triangle pH = ± 0.10), but treatment 9 produced a \triangle pH of 5.18 with low CO_2 pressure. Treatments 4, 5, 10, 11 and 13 averaged a \triangle pH drop of 5.08 and with less reaction time as well as less pressure and percent CO_2 . However, treatment 13 was the most effective and produced the biggest pH drop using medium levels of percent CO_2 and pressure. Therefore, these conditions were selected as a final treatment for CCT-1 ash samples.

Initial results from different CO_2 pressure treatment experiments for CCT-2 ash samples suggested that the pH of these samples did not stabilize under any treatment conditions. Moisture addition to CCT-2 ash samples, before CO_2 pressure treatment, released heat (approximately 120°C) due to the dissolution of oxides, which resulted in the loss of moisture (approximately 50 to 60%). The addition of moisture lost from the samples prior to the each treatment was a critical factor in obtaining a stable pH drop for CCT-2 ash samples.

TABLE 4

OPTIMUM TREATMENT VARIABLES FOR CCT-1 ASH SAMPLES.

No	%θ _ω	Pressure	%CO2	Temperature	Time	pH-A	pH-F	pH-B	۵рН
		(ps1)	And and a second second	(°C)	(hr.)				
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 [†]	20	75	75	25	24	7.45	7.05	-0.40	5.42

The pH before treatment = 12.47. A = pH within two hours after treatment. F = final stable pH. B = difference in pH between A and F. $\triangle pH$ = net change in pH.[†] = final treatment

Treatments 1 through 7 (Table 5) 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 3.16 to 3.40, with an average \triangle pH of 3.25. No significant differences were found between treatments 1, 2, 3 and 4. Increasing the percent θ_{ω} to 40 and 50 under room temperature (treatments 5 and 6) showed no further drop in the pH. However, increasing the temperature to about 45°C reduced the pH from 12.74 to 9.34 in 24 hours (treatment 7), and therefore this treatment was selected for CCT-2 ash samples.

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No	%θ _ω	Pressure (psi)	%CO ₂	Temperature (°C)	Time (hr.)	pH-A	pH-F	pH-B	∆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†	50	100	100	45	24	8.55	9.34	+0.79	3.40

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OPTIMUM TREATMENT VARIABLES FOR CCT-2 ASH SAMPLES

The pH before treatment = 12.74. A = pH within two hours after treatment. F = final stable pH. B = difference in pH between A and F. $\triangle pH$ = net change in pH.[†] = final treatment

Treatments 1 through 4 (Table 6) produced an average \triangle pH of 2.30 for CCT-3 ash samples. Initial pH values around 8.50 were obtained by different optimum treatment conditions. However, these initial pH values stabilized near 9.20 in most treatments, and therefore treatment 2 was selected for CCT-3 ash samples. The high buffering capacity and the apparent slow dissolution of silicate minerals, as well as the relatively low concentration of Ca as compared to percent Na, might have prevented attainment of a larger drop in the pH of CCT-3 ash samples.

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No	%θ	Pressure (psi)	%CO ₂	Temperature (°C)	Time (hr.)	pH-A	pH-F	pH-B	⊿рН
1	10	100	20	25	48	8.72	9.14	+0.42	2.36
2^{\dagger}	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

OPTIMUM TREATMENT VARIABLES FOR CCT-3 ASH SAMPLES

The pH before treatment = 11.50. A = pH within two hours after treatment. F = final stable pH. B = difference in pH between A and F. $\triangle pH$ = net change in pH.[†] = final treatment.

Treatment Effects on Calcium Carbonate Content - The percent $CaCO_3$ equivalent and percent CO_2 absorbed (Table 7) were increased significantly after the CO_2 pressure treatment. $CaCO_3$ and CO_2 were not detected in untreated samples of CCT-1 and CCT-2 ash samples, but both were detected upon CO_2 pressure treatment. This increase in carbonate content suggests the precipitation of calcium carbonate nfineral phase, which was confirmed in XRD analyses by the presence of calcite peaks in treated CCT ash samples (Table 7). These results suggest that reacting moist alkaline CCT ash samples under CO_2 pressure causes the precipitation of calcite.

TABLE 7

EFFECT OF FINAL CO₂ PRESSURE TREATMENT CONDITIONS ON PERCENT CaCO₃ EQUIVALENT, PERCENT CO₂ AND MINERAL TRANSFORMATION

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

N.D. = not detected

Solubility Studies - The pH of CCT ash leachates dropped dramatically upon the application of optimum treatment levels of CO_2 to CCT ash samples. The degree of fluctuation over time to reach pH stability after treatment varied significantly among the three samples (Figures 4,5,6). pH measurements of prepared suspensions within 2 hours from removing the solids from the pressure chamber recorded a significant drop in the pH of the three fly ash samples.

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EFFECT OF CO₂ PRESSURE TREATMENT ON THE pH OF CCT-1 ASH SAMPLES



EFFECT OF CO₂ PRESSURE TREATMENT ON THE pH OF CCT-2 ASH SAMPLES



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EFFECT OF CO₂ PRESSURE TREATMENT ON THE pH OF CCT-3 ASH SAMPLES



Over time, fly ash No. 1 (CCT-1) maintained the initial low pH values with small fluctuations (Figure 4). Monitoring the pH fluctuation in fly ash No. 1 suspensions, showed that an average of 96 hours was required to attain pH stability without significant variation. A stable pH drop between 3.89 to 5.42 ± 0.10 was maintained by different optimum treatments in fly ash No. 1. The pH of the suspensions of treated fly ash Nos. 2 and 3 (CCT-2 and CCT-3) showed a high degree of fluctuation, even though a significant pH drop was measured within 2 hours of the treatment. The pH of fly ash No. 2 exceeded 12 within 48 hours of the treatment before starting to decline again (Figure 5). A stable pH drop was obtained after 504 hours by different treatments and ranged from 3.16 to 3.40 with an average $\triangle pH = 3.25$. The pH of fly ash No. 3 also started to increase within 24 hours of the treatment and reached values around 9.5 after 96 h before declining (Fig. 6). A stable pH < 9.4 was obtained after 168 h, with an average $\triangle pH = 2.5$ by various treatments.

The value of the pH drop obtained in fly ash leachates as well as the time required to attain pH stability, appear to be controlled by calcite precipitation. The results of calculated Ca^{2+} activities in untreated and treated fly ash leachates by application of the MINTEQA2 model are shown in Figure 7. These results show that the activity of Ca^{2+} , in treated fly ash No. 1, has approached that of pure calcite, however, the SI value calculated by MINTEQA2 indicated a 0.75 log units oversaturation. Activities calculated for fly ash No. 2 and 3 indicated an oversaturation with respect to calcite. Nevertheless, calcite peaks clearly were determined in the three samples by XRD. The pH monitoring results discussed previously explain the apparent contradiction between speciation results and XRD analysis done on treated solid fly ash samples, in which the pH of fly ash No. 1 stabilized faster than the other two indicating faster rate of calcite precipitation.

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EFFECT OF CO₂ PRESSURE TREATMENT ON Ca²⁺ ACTIVITY WITH RESPECT TO CALCITE AND LIME



Upon water additions to treated solids the pH of leachates increased and dissolution-precipitation of solids started following the steps discussed by Schramke (1992). Solution concentrations of SO_4^{2-} and Mg^{2+} increased in the three samples (Figure 8), but were more dramatic in fly ash No. 1. The data consistently showed that solutions of high SO_4^{2-} and Mg^{2+} concentrations approached calcite solubility faster than the others. Gypsum and anhydrite solid phases were presented in higher quantities in fly ash No. 2 and 3 than in fly ash No. 1. The precipitation of different sulfate solid phases prior to their dissolution slowed down the rate of calcite precipitation and consequently pH stability in CCT-2 and 3.

Leachability Studies - No differences in metal concentrations between treated and untreated samples were found by the EPA-TCLP test (Table 8). Levels of As, Ba, Cr, Cd, Pb, Hg, Se, and Ag were all below the EPA standards in both CO₂ pressure treated and the untreated samples. However, the TCLP technique extracts samples under acidic conditions. The procedure requires the preparation of two low pH extraction fluids. Extraction fluid #1 is prepared from glacial acetic acid (CH₃CH₂OOH) and 1.0 <u>N</u> NaOH and its final pH = 4.93 ± 0.05 . The #2 fluid is obtained through the dilution of CH₃CH₂OOH in water and the pH = 2.88 ± 0.05 . These acidic extractants probably prohibited the determination of the effects of the pH reduction obtained by the CO₂ pressure treatment on leachable metal concentrations.

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Treatment	As	Ba	Cd	Cr mg/L	Pb	Hg	Se	Ag
CCT-1 Untreated	<0.5	<10	<0.1	<0.5	<0.5	<0.002	<0.1	<0.5
CCT-1 Treated	<0.5	<10	<0.1	<0.5	<0.5	<0.002	<0.1	<0.5
CCT-2 Untreated	<0.5	<10	<0.1	<0.5	<0.5 *	<0.002	<0.1	<0.5
CCT-2 Treated	<0.5	<10	<0.1	<0.5	<0.5	<0.002	<0.1	<0.5
CCT-3 Untreated	<0.5	<10	<0.1	<0.5	<0.5	<0.002	0.3	<0.5
CCT-3 Treated	<0.5	<10	<0.1	<0.5	<0.5	<0.002	0.4	<0.5

EFFECT OF FINAL CO $_2$ TREATMENT CONDITIONS ON THE SOLUBILITY OF TRACE ELEMENTS WITH THE TCLP

The CO₂ treatment effects on the leachability of trace elements were clearly observed from the results of the AB-DTPA extraction procedure (Table 9). A significant drop in the concentrations of leachable trace elements was obtained in all spiked plus CO₂ treated CCT ash samples. For instance, in spiked plus CO₂ treated samples, arsenic concentrations decreased from 3.40 to 0.10 mg/L for CCT-1 ash samples, from 0.35 to 0.10 mg/L for CCT-2 ash samples and from 3.70 to 1.15 mg/L for CCT-3 ash samples. Similar results were observed for other trace elements.

TABLE 9

I.D ¹	Cd	РЪ	Cu	Cr mg/L	As	Se	Ni	В
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
<u>1-A</u>	0.04	0.50	2.65	0.02	0.10	0.65	0.20	19
*% Drop	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
<u>2-A</u>	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
<u>3-A</u>	3.10	3.30	3.91	0.08	1.15	8.20	1.81	158
% Drop	21	43	24	75	68	34	15	17

EFFECTS OF FINAL CO $_{\rm 2}$ TREATMENT CONDITIONS ON SOLUBLE TRACE ELEMENTS WITH AB-DTPA

I.D. = sample identification. C = control, B = spiked-untreated, and A = spiked-treated. * %Drop = $100 - \{(A/B) \ 100\}$. N.A.* = not available. BD = below detection limit of 0.01 mg/L

The results of this study suggest that reacting moist CCT ash samples under CO_2 pressure causes the precipitation of calcite and a concomitant reduction in the pH. This reduction in the pH effectively reduces the leachable concentrations of trace elements (e.g., Cd, Ni, Pb, As and Se) in CCT ash samples.

A possible explanation for the decrease in the concentration of trace metal concentrations is the precipitation of metal carbonates. In CCT ash samples, these metals are present in the form of oxides and/or hydroxides (e.g., CdO, $Pb(OH)_2$) due to the combustion process. However, when

CCT ash samples are reacted under CO_2 pressure, soluble oxides and/or hydroxides were probably converted to less soluble carbonates (e.g., CdCO₃, PbCO₃). A reduction in the concentrations of leachable As, B, Cr and Se is probably attributable to an increased sorption of these elements by iron oxides at lower pH values.

Rai et al. (1987) predicted, based on thermodynamic evaluations, that pH will play an important role in controlling the solubility of metals in fly ash, and therefore the leaching properties of fly ash. Furthermore, these researchers suggested that dissolved metal concentrations in alkaline fly ash leachates (i.e. unweathered fly ash) are controlled by oxides and/or hydroxides. In low pH fly ash leachates (i.e. weathered fly ash), dissolved metal concentrations are controlled by metal carbonates.

Theis and Wirth (1977) reported that release of trace elements from coal combustion ash is strongly related to the pH. Results from these studies also suggest that as pH decreases from 12 to around 9 trace elements become less soluble in fly ash due to sorption and precipitation processes. Several other studies have also predicted similar results for coal combustion ash. Thus, observed reduction in the concentrations of trace elements in treated CCT ash samples is probably due to the decrease in the pH, which in turn enhanced both precipitation and sorption processes of trace elements.

The CO_2 pressure process described here has, under laboratory conditions, demonstrated its potential to reduce the leachability of harmful trace elements thereby reducing the risk of these elements contaminating soils and groundwaters. Since this process uses CO_2 , which can be obtained from the combustion process itself (i.e., flue gas), it has the potential to concomitantly reduce CO_2 emissions from the coal combustion process. Further research is needed to evaluate the cost and economic viability of CO_2 pressure process under field conditions.

CONCLUSIONS

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The CO_2 pressure treatment process produced a significant drop in the pH of CCT treated ash samples. This pH drop principally was due to the precipitation of calcite, which was confirmed by the XRD analysis. The presence of gypsum and anhydrite were also confirmed by the XRD analysis. The CO_2 pressure treatment process caused the dissolution of oxides and silicates mineral phases and precipitation of $CaCO_3$, $CaSO_4.2H_2O$ and $CaSO_4$ phases. CCT processes used in each power plant were an important factors in determining the optimum levels of the different variables for each treatment. Lime injection played a key role by supplying the Ca needed to enhance the rapid precipitation of $CaCO_3$ and $CaSO_4$ phases in CCT ash samples. Moisture level was highly correlated with the treatment effect on pH in all samples. The CO_2 pressure treatment effectively decreased the concentrations of leachable trace elements in CCT ash samples. Concentrations of trace elements in spiked plus CO_2 pressure treated samples were less than in spiked-untreated samples, and in most cases were less than in control treatments.

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