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Abstract

The combustion of fossil fuels (eg coal, oil shale) to generate energy results in the production of alkaline solid wastes (fly ash, clean coal technology (CCT) ash, spent shale etc). Reactions involving calcium (Ca) and carbon dioxide (CO_2) usually control the pH and mobility of inorganic contaminants such as Cd, Pb and Se in alkaline solid wastes. Samples of fly ash, spent shale and CCT ash were reacted with CO_2 at different pressures, moisture levels and for various reaction times. Treated and untreated samples were subjected to X-ray diffraction (XRD) and AB-DTPA (ammonium bicarbonate diethylenetriamine pentaacetic acid) extraction studies. Some CO_2 treatment conditions effectively precipitated calcite, and therefore lowered the pH and extractable concentrations of inorganic contaminants (eg Cd, Pb, Zn, Mn, As and Se) in alkaline solid wastes. Thus, the risk of these elements contaminating soils and groundwater resources could be reduced when CO_2 treated alkaline solid wastes are disposed in landfills.

Introduction

The use of coal and oil shale for the production of energy has increased considerably over the past few decades. The combustion of coal and oil shale results in large volumes of solid wastes such as fly ash and spent shale, respectively. For example, in 1988 electric utilities in the USA generated *ca* 90×10^6 t of coal ash. About 62% was fly ash, 23% was bottom ash and boiler slag, and 15% was flue gas desulfurization sludge. More details of coal combustion processes and the production of various solid wastes have been reported by Carlson and Adriano (1993).

About 20-25% of the total amount of the ash produced was used in cement products, road bases and asphalt. The remaining 75-80% was placed in surface impoundments and landfills. One of the main potential adverse impacts of ash disposal on the environment is leaching of potentially toxic elements such as As, Cd, Pb, Se from ash into soils and groundwater (USEPA, 1988). Spent shale also presents similar disposal problems (Stollenwerk and Runnells, 1981).

The pH of fly ash and spent shale can vary from 4.5 to 12.0 depending on the S content of the parent coal and oil shale, with high S (eastern coals and oil shales) generally producing acidic materials, and low S (western coals and oil shales) producing alkaline materials. Several studies have shown that alkaline fly ash and spent shale solids contain dissolved inorganic contaminants (eg Cd, Pb, Se), and therefore land disposal of such materials presents the risk of groundwater contamination (Cherry and Guthrie, 1977; Adriano *et al.*, 1980; Kopsick and Angino, 1981; Humenick *et al.*, 1983; Stark and Redente, 1986; Essington, 1989; Carlson and Adriano, 1993).

New Clean Air legislation enacted by the US Congress mandated the reduction of SO_X emissions from coal burning power plants. As a result, a variety of Clean Coal Technologies (CCTs) are likely to be implemented. In general, the ash produced from CCTs will be alkaline because an alkaline sorbent is used to remove SO_X from flue gas in these processes. However, very little information is available regarding the chemistry of CCT ash.

Calcium is one of the most abundant elements in coal combustion ash and spent shale because it is not volatilized during the combustion process. Additionally, high combustion temperatures drive off CO_2 from the carbonate phases present in coal and oil shale. These conditions increase the pH of aqueous extracts of fly ash, spent shale and CCT ash samples, which affects the solubility and mobility of inorganic contaminants. Therefore, reactions involving Ca and CO_2 are expected to control the pH, solubility and mobility of inorganic contaminants in coal combustion ash and spent shale (Adriano *et al.*, 1982; Reddy *et al.*, 1986; Rai *et al.*, 1987; Schramke, 1992).

A CO_2 pressure treatment process that recarbonates the mineral phases could affect the pH and solubility as well as mobility of inorganic contaminants in alkaline solid wastes (Reddy *et al.*, 1991). Few studies have examined the effects of Ca and CO_2 reactions on the pH and mobility of inorganic contaminants in alkaline solid wastes (Reddy *et al.*, 1986; Essington, 1989; Schramke, 1992). These studies either bubbled CO_2 through ash slurries or aqueous solutions. Such techniques are not practical for field applications and long times (months or years) are required to minimize the mobility of inorganic contaminants. Thus, the objectives of our study were to react alkaline fly ash, spent shale and CCT ash samples in solid forms (with minimum H_2O) under CO_2 gas pressure to determine the effects of recarbonation on the solubility and mobility of inorganic contaminants.

Materials and Methods

We used fly ash 1 and 2 (conventional coal combustion processed samples), PPP 6 and Lurgi (oil shale combustion processed samples) and CCT-1, 2 and 3 (CCT combustion processed samples) in this study. Fly ash 1 was collected from the Laramie River Station, Wheatland, Wyoming, USA, while fly ash 2 was collected

Table 1 *Variables and treatment levels for the 2^3 factorial experiment.*

Variable	Low level	Midpoint	High level
Pressure, X_1 (psi)	5	40	75
Moisture, X_2 (%)	5	15	25
Reaction time, X_3 (hours)	0.5	5.25	10

from the Central Energy Plant in Laramie, and spent shale samples were obtained from the Western Research Institute, also in Laramie. CCT-1 (Minnesota, USA) and CCT-2 (Kentucky, USA) samples were from the lime injection process and atmospheric fluidized bed combustion process, respectively. CCT-3 (Colorado, USA) samples were produced by the sodium carbonate injection process. Fly ash and CCT ash samples were collected either directly from the bag-house or electrostatic precipitators. Spent shale samples were collected from pilot processing units of the Western Research Institute. All samples were passed through a 0.25 mm sieve before the experiments.

Initial characterizations of the samples involved determinations of pHs, total elemental compositions, mineral compositions, calcium carbonate contents, as well as the levels of extractable inorganic contaminants. The pHs were measured in a saturated paste with an Orion combination electrode. Samples were digested in nitric plus perchloric acid and total concentrations of Al, S, P, Ca, Fe, Mg, Mn, Cu, Cd, Zn,

Table 2 *Selected properties of the samples used in the study (mg kg^{-1}).*

Property	*Fly ash 1*	*Fly ash 2*	*PPP 6*	*Lurgi*	*CCT-1*	*CCT-2*	*CCT-3*
Al	33.800	400	3,300	2,600	109.500	300	77,400
Na	59,300	10,000	58,200	6,600	47.600	1.500	32,200
S	2.400	16.600	9,400	6.200	3,500	43,100	11,800
P	2.100	4,700	2,300	1.100	1.900	400	10,000
Ca	53,049	51.730	41,116	42.806	56,037	98,037	10,649
Mg	1.000	4,662	9.605	5.240	1.398	6,786	400
K	23.269	20.319	20,461	26,165	5,301	8,613	11,200
Fe	39.217	65,398	37,272	27.950	52.037	73.038	46,046
Mn	2.136	425	361	347	218	124	543
Cu	144	189	80	79	151	39	87
Pb	235	94	170	36	357	4	222
Zn	424	176	130	139	119	187	81
Cd	<10	<10	<10	<10	15	10	13
Mo	38	13	23	43	23	43	23
pH (saturated paste)	12.3	12.8	12.4	12.3	12.5	12.7	11.5

As, Se and Mo were determined by inductively coupled plasma optical emission spectrometry (ICP-OES). Sodium and K were measured by atomic emission spectrometry (AES). The mineral composition of the samples was determined with a Scintag PAD V powder diffractometer using CuKα radiation.

Calcium carbonate content was measured using the method of Soltanpour and Workman (1981), and the %CO_2 absorbed by fly ash, spent shale and CCT ash samples was calculated from this. The chemical extractant AB-DTPA (Soltanpour and Schwab, 1977) was used to predict the extractability of Cd, Pb, Cu, Cr, As, Se, Ni and B. AB-DTPA extracts both soluble (intensity) and potentially soluble (capacity) fractions of inorganic constituents from solid phases. Knowing these fractions is useful in predicting the mobility of a given element and AB-DTPA has been used in a number of studies (Folsom *et al.*, 1981; Schwab *et al.*, 1991; Reddy *et al.*, 1994) to predict the availability and solubility of certain inorganic elements in coal combustion ash.

Samples were reacted in a chamber under different CO_2 pressure treatments (at various moisture levels, pressures and reaction times). A two-level by three-variable factorial experiment (Table 1) was used to select the optimum treatment conditions. For each test, water (% moisture) was added to the samples on a weight basis, and the samples were then reacted in a chamber under the different conditions.

A 1:4 (solid:water) suspension of each treated sample was prepared in a plastic centrifuge tube. The pHs of these suspensions were determined within two hours and then monitored on a weekly basis for several months to determine the effects of treatment on the long-term stability of the pHs. Approximately 1 kg of each fly ash and spent samples were reacted at optimum treatment conditions and then analyzed for the main mineral phases, calcium carbonate content and extractable inorganic contaminants.

Additionally, CCT ash samples were spiked with a multi-element standard solution to achieve a level of 50 mg kg^{-1} of Cd, Pb, Cu, Cr, As, Se, Ni and B, and allowed to air dry. Duplicate spiked 100 g samples were each subjected to the CO_2 pressure treatment at optimum treatment conditions. The remaining spiked samples were not subjected to the CO_2 pressure treatment. AB-DTPA was used to predict the extractability of Cd, Pb, Cu, Cr, As, Se, Ni and B in unspiked and untreated, spiked-untreated and spiked-treated CCT ash samples.

Results and Discussion

Selected properties of the samples used in the study showed that fly ash and spent shale samples were enriched in Al, Na, S, P, Ca, K and Fe (Table 2). Fly ash 1 samples contained higher concentrations of Al, Na and Mn and lower concentrations of Mg and Fe when compared with fly ash 2 samples. Similar results were found for PPP 6 and Lurgi samples. Other elements such as Cu, Pb, Zn and Mo were present in minor concentrations. Cadmium, As and Se concentrations in these samples were below 20.0 mg kg^{-1}.

All untreated CCT ash samples were high in Ca, K, Fe and low in Cd, As, Se and Mo (Table 2). Samples produced using lime and sodium carbonate injection processes (ie CCT-1 and 3) also contained more Al, Mn, Cu and Pb than those produced by the 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 3 ash samples. Arsenic and Se concentrations in CCT ash samples were below 20.0 mg kg^{-1}. These characterizations showed that the chemical compositions of fly ash, spent shale and CCT ash samples were different, probably because of the types of parent material (eg coal and oil shale) used in combustion.

XRD analysis suggested that untreated fly ash samples consisted largely of quartz, mullite, amorphous phases together with some anhydrite and calcium oxide, whereas untreated spent shale samples consisted mainly of quartz, periclase, diopside and K-feldspar, and untreated CCT ash samples consisted largely of quartz, silicates, amorphous phases, calcium oxide and anhydrite. The formation of the above phases requires high temperatures (1500 K), which are usually attained during the combustion of coal and oil shale.

Saturated paste pHs of untreated samples ranged between 11.5 and 12.8 (Table 2). During the combustion of coal and oil shale, high temperatures drive off CO_2 from carbonates resulting in the formation of oxide and silicates. These react rapidly with water; the reactions of CaO and $CaSiO_3$ are shown below for example:

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \qquad (1)$$

$$CaSiO_3 + 2H_2O \rightarrow Ca^{2+} + H_3SiO_4^- + OH^- \qquad (2)$$

Thus, the high pHs (approaching 12) of untreated samples of fly ash, spent shale and CCT ash are due to the dissolution of oxides and silicates (Reddy and Lindsay, 1986).

A factorial experiment permitted the maximum amount of information to be obtained from a given number of experiments. Essentially, an analysis of variance technique was employed to decide whether a given variable or interaction of a combination of variables affects the outcome of the experiment. Calculated values of F were compared with the critical F-value ($F_{0.05}(1,3) = 10.10$) to decide which effects or interactions were statistically significant. For example, Table 3 shows mean effects (ME), sum of squares (SSE), degree of freedom (DF), mean squares of effects (MS) and calculated F values based on the pH measurements of treated fly ash samples. An error variance was estimated from the mid-point replications, indicated by an asterisk. The results suggest that high moisture levels and longer reaction times were important to the success of reactions of fly ash and spent shale with CO_2. However, high pressure was not important for the successful treatment of fly ash and spent shale samples. Moisture was a limiting factor for all CCT ash samples, and high pressure was also closely related to the pHs of some CCT ash samples.

Sample pHs reduced significantly immediately after their removal from the treatment chamber. Over time, some samples maintained their low treatment pH values, while others returned to values close to those measured before treatment. The optimum treatment conditions for significantly reducing the pH of samples were different for each sample (Table 4). With CO_2 treatment, PPP 6 samples stabilized at

Table 3 *Results of statistical analysis of the pH measurements for the CO_2 pressure process 2^3 factorial experiment.*

Yates Order	*pH*	*(1)*	*(2)*	*(3)*	*ME*	*SSE*	*DF*	*MS*	
I	10.54	20.82	43.15	81.95	–	–	–	–	
a	10.28	22.33	38.80	−0.23	−0.0575	0.0066	1	0.0066	
b	11.09	19.57	−0.11	1.17	0.2925	0.1711	1	0.1711	
ab	11.24	19.23	−0.12	0.83	0.2075	0.0861	1	0.0861	
c	9.92	−0.26	1.51	−4.35	−1.0875	2.3653	1	2.3653	
ac	9.65	0.15	−0.34	−0.01	−0.0025	1.25×10^{-5}	1	1.25×10^{-5}	4
bc	9.54	−0.27	0.41	−1.85	−0.4625	0.4278	1	0.4278	
abc	9.69	0.15	0.42	0.011	0.0025	1.25×10^{-5}	1	1.25×10^{-5}	4.1
Error	–	–	–	–	–	–	3	3.0067×10^{-2}	

Estimation of error variance from mid-point replication:
$\Sigma x_i = 9.47 + 9.78 + 9.76 + 9.47 = 38.48$
$\Sigma x_i^2 = (9.47)^2 + (9.78)^2 + (9.76)^2 + (9.47)^2 = 370.2678$
No. Replications = n = 4
Degrees of Freedom = r = n − 1 = 4 − 1 = 3.

Table 4 *Optimum CO_2 treatment conditions selected for alkaline fly ash, spent shale and CCT ash samples.*

Sample	*Moisture (%)*	*Pressure (psi)*	*CO_2 (%)*	*Temperature (°C)*	*Time (hr)*	*pH*[a]	*pH*[b]	*pH*[c]
Fly ash 1	20	40	100	25	120	12.3	8.9	9.7
Fly ash 2	20	40	100	25	120	12.8	7.7	9.1
PPP 6	20	40	100	25	120	12.4	8.6	8.7
Lurgi	20	40	100	25	120	12.3	9.3	8.9
CCT 1	20	75	75	25	24	12.5	7.4	7.0
CCT 2	50	100	100	45	24	12.7	8.5	9.3
CCT 3	10	75	75	25	24	11.5	8.7	9.1

[a] initial pH
[b] pH with two hours of treatment
[c] final stable pH

lower pH values than the Lurgi or fly ash samples. Similarly, CCT-1 ash samples stabilized at lower pH values than the CCT-2 and 3 ash samples.

The combustion process appeared to be important in determining the effectiveness of the CO_2 treatment with respect to pH. For example, 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).

The different effects of CO_2 treatment on $CaCO_3$ content and CO_2 uptake are shown in Table 5. Untreated fly ash and CCT ash samples were low in $CaCO_3$ compared to spent shale samples because coal combustion temperatures are generally much higher (1500_K) than those for oil shale combustion. Such high temperatures usually decompose carbonates rapidly. Both %$CaCO_3$ content and %CO_2 uptake increased significantly on CO_2 treatment, suggesting that the CO_2 reaction is effective in precipitating carbonates. However, the degree of precipitation of carbonate phases appears to be related to the chemical composition of the samples (Table 2).

Reacting moist alkaline fly ash, spent shale and CCT ash samples under CO_2 pressure causes the precipitation of calcite and a reduction in pH. These results can be explained by the following reactions:

$$CaO + H_2O \rightarrow Ca^{2+} + 2OH^- \qquad (3)$$

$$Ca^{2+} + CO_2 + H_2O \rightarrow CaCO_3\ \text{(calcite)} + 2H^+ \qquad (4)$$

The Ca ions from the dissolution of CaO (equation 3), combine with added CO_2 and precipitate as calcite. The precipitation of calcite releases protons (equation 4) and restores the system to neutrality.

Long-term leaching experiments (Dudas, 1981) with coal combustion ash have suggested that calcite will precipitate in weathered fly ash samples. On the basis of

Table 5 *Effects of optimum CO_2 treatment conditions on % $CaCO_3$, % CO_2 uptake, and mineral phases in fly ash, spent shale and CCT ash samples, quoted as the mean of duplicate analyses.*

Sample	pH	%$CaCO_3$	%CO_2	Mineral phases
Fly ash 1 before treatment	12.3	4.8	-	quartz, mullite, amorphous phases
Fly ash 1 after treatment	9.7	15.0	4.0	quartz, silicates, gypsum, calcite
Fly ash 2 before treatment	12.8	10.7	-	quartz, calcium oxide amorphous phases
Fly ash 2 after treatment	9.1	47.3	15.0	quartz, calcite, silicates, gypsum
PPP 6 before treatment	12.4	17.6	-	quartz, calcite, periclase
PPP 6 after treatment	8.7	33.7	8.0	quartz, calcite gypsum, gehlenite
Lurgi before treatment	12.3	39.4	-	quartz, calcite, k-fieldspar
Lurgi after treatment	8.9	53.4	4.0	calcite, quartz dolomite
CCT 1 before treatment	12.5	Nn	ND	quartz, silicates, amorphous phases
CCT 1 after treatment	7.0	2.82	0.62	calcite, gypsum, anhydrite, mullite
CCT 2 before treatment	12.7	ND	ND	quartz, calcium oxide
CCT 2 after treatment	9.3	4.48	0.99	calcite, anhydrite, gypsum
CCT 3 before treatment	11.5	3.38	0.74	quartz, amorphous phases
CCT 3 after treatment	9.1	4.57	1.01	anhydrite, quartz, calcite

ND = not detected.

Table 6 *Effects of optimum CO_2 treatment conditions on extractability of contaminants in fly ash and spent shale samples, quoted as the mean of duplicate analyses (mg kg^{-1}).*

Sample	Cd	Pb	Zn	Mn	Ni	Cu	As	Se
Fly ash 1 before treatment	0.1	BD	0.8	2.2	0.2	1.3	BD	BD
Fly ash 1 after treatment	0.05	BD	0.3	0.8	0.1	0.6	BD	BD
Fly ash 2 before treatment	1.8	19.0	35	15.5	5.5	31	BD	0.4
Fly ash 2 after treatment	0.3	2.9	5	2.7	0.9	9	BD	0.1
PPP 6 before treatment	BD	0.85	1.9	12	0.3	0.4	BD	BD
PPP 6 after treatment	BD	0.2	2.6	1.3	0.5	2.0	BD	BD
Lurgi before treatment	BD	BD	4.6	20	0.6	1.4	1.0	BD
Lurgi after treatment	BD	BD	2.8	2.2	0.6	1.5	BD	BD

thermodynamic evaluations, Rai *et al.* (1987) suggested that dissolved Ca concentrations in unweathered fly ash samples are controlled by CaO and/or $Ca(OH)_2$. However, in weathered samples (ie samples reacted with CO_2), the dissolved Ca concentrations would be controlled by calcite.

Reddy *et al.* (1986) and Essington (1989) have reported that continuous bubbling of CO_2 through aqueous extracts of spent shales, for six to nine months, causes dissolution of silicates, precipitation of calcite, and a reduction in the pH from 12.0 to *ca* 8.0. In our experiments, reacting moist alkaline fly ash, spent shale and CCT ash samples under elevated CO_2 pressures probably accelerated the precipitation of calcite, which effectively lowered the pH in a relatively short time.

Coal and oil shale solid wastes may contain different inorganic constituents, some of which may become mobile (Adriano *et al.*, 1980; Carlson and Adriano, 1983; Essingtton, 1989), therefore, it is important to predict their mobility from waste disposal facilities. The effects of CO_2 treatment on the extractability of inorganic contaminants suggest that treatment was effective in reducing the solubility of certain contaminants in fly ash and spent shale samples (Table 6). For example, extractable Mn concentrations decreased from 2.2 to 0.8 mg kg^{-1} for fly ash 1 and from 15.5 to 2.7 mg kg^{-1} for fly ash 2. Treatment decreased extractable Mn concentrations in spent shales from 12.0 to 1.3 mg kg^{-1} for PPP 6, and from 20 to 2.2 mg kg^{-1} for Lurgi. Similar effects were observed for Cd, Pb and Zn.

A significant drop in the concentrations of extractable inorganic contaminants was obtained in all spiked plus CO_2 treated CCT ash samples (Table 7). For

Table 7 *Effects of optimum CO_2 treatment conditions on extractability of contaminants in CCT ash samples, quoted as the mean of duplicate analyses (mg kg^{-1}).*

	mg kg^{-1}							
I.D[1]	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	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

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 kg^{-1}.

example, in spiked CO_2 treated samples, extractable As concentrations decreased from 3.4 to 0.1 mg kg^{-1} for CCT-1 ash samples, from 0.35 to 0.1 mg kg^{-1} for CCT-2 ash samples and from 3.7 to 1.15 mg kg^{-1} for CCT-3 ash samples. However, CO_2 treatment was most effective in reducing the extractable concentrations of inorganic contaminants in CCT-1, and then in CCT-2 ash samples.

Reacting alkaline fly ash, spent shale and CCT ash samples at elevated CO_2 pressures caused the precipitation of calcite. This effectively reduced the pH as well as extractable concentrations of inorganic contaminants. A possible reason for the decrease in the concentration of extractable metal contaminants (eg Cd, Pb, Zn and Mn) is due to the precipitation of metal carbonates. In alkaline fly ash, spent shale and CCT ash samples, these metals could be present in the form of oxides and/or hydroxides (eg CdO, $Pb(OH)_2$) due to combustion. However, when these samples were reacted under CO_2 pressure, oxides and/or hydroxides were probably converted to carbonates (eg $CdCO_3$, $PbCO_3$) as well as co-precipitated with calcite (McBride, 1980), which are much less soluble (Rai *et al.*, 1987).

A reduction in the amounts of extractable As, Cr, B and Se is probably attributable to an increased sorption of these elements by iron oxides at lower pH, because fly ash, spent shale and CCT ash samples commonly contain iron oxides (Theis and Wirth, 1977). It is well established that by decreasing the extractable concentration of a given contaminant, the mobility of that contaminant will also be reduced. The process described here for alkaline solid wastes has, under laboratory conditions, demonstrated its potential to reduce the concentration of extratable harmful inorganic elements, thereby reducing the risk of these elements contaminating various aspects of the environment, including groundwater. Further research to evaluate the cost and economic viability of the CO_2 process under field conditions is needed.

The CO_2 process described in this study involves the treatment of alkaline solid wastes in a solid form containing small amounts of moisture, and requires a much shorter reaction time (under pressure) than reported for aqueous slurries (Schramke, 1992; Essington, 1989; Reddy *et al.*, 1986) to effectively lower the pH and the solubilities of different inorganic contaminants. Since this process uses CO_2, which can be obtained from the combustion process itself (ie from flue gas), it has the potential to concomitantly reduce emissions of CO_2 - the so-called greenhouse gas.

Conclusions

The CO_2 pressure treatment reduced the pH of alkaline solid wastes approximately from 12 to 9. This pH drop was principally due to the precipitation of calcite, as confirmed by XRD analysis. The presence of gypsum and anhydrite was also confirmed by the XRD analysis.The CO_2 pressure treatment caused the dissolution of oxides and silicates and the precipitation of $CaCO_3$, $CaSO_4.2H_2O$ and $CaSO_4$. The process used for the combustion of coal and oil shale was important in determining the optimum levels of the treatment variables (moisture, pressure and reaction time). For example, the lime injection process played a key role in supplying Ca needed to enhance the rapid precipitation of $CaCO_3$ and $CaSO_4$ in some CCT ash samples. Moisture levels correlated very well with the treatment effect on the pHs of all samples. The CO_2 pressure treatment effectively decreased the concentrations of extractable inorganic contaminants in alkaline solid wastes.

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