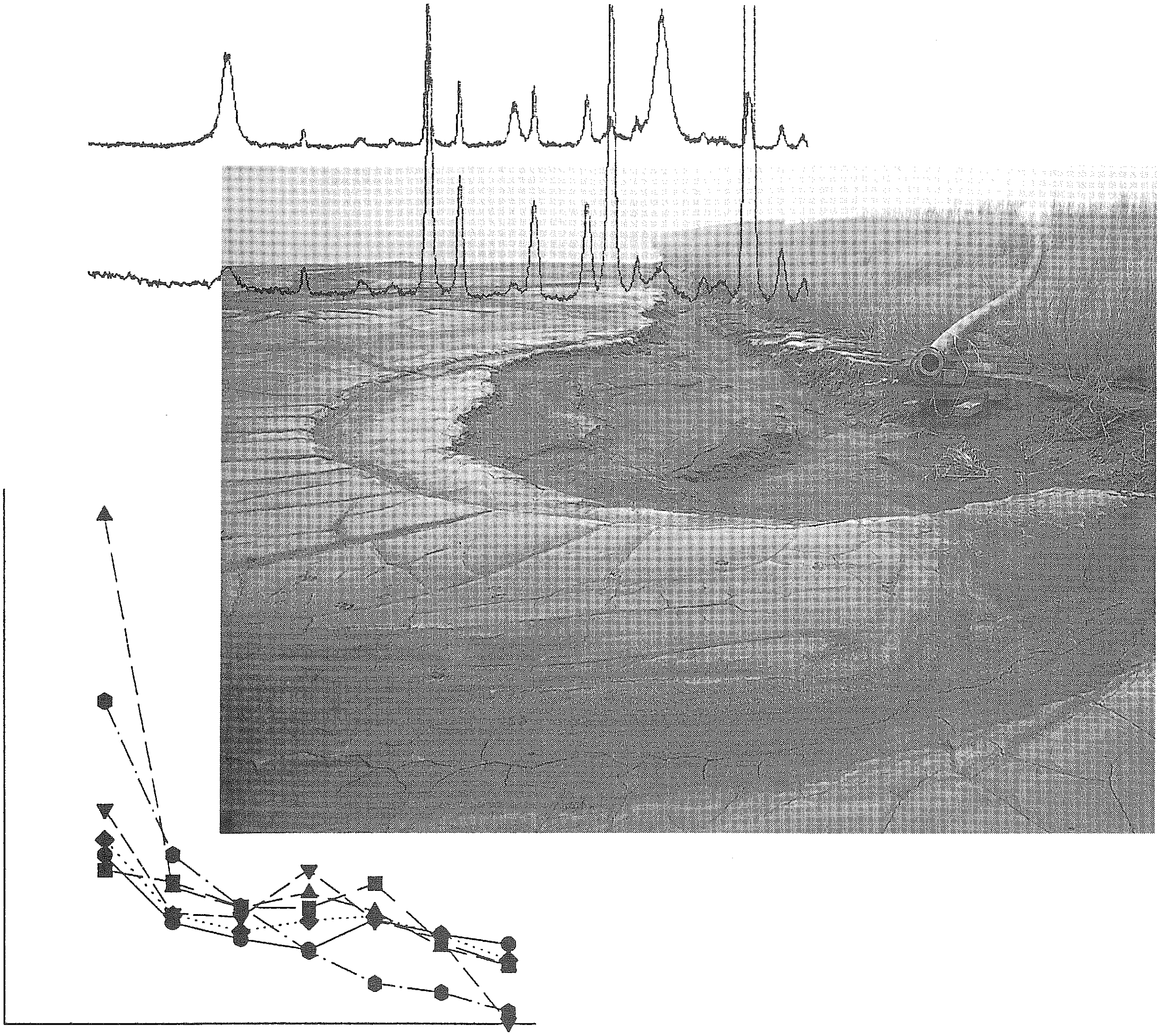
EG 150

Laboratory Studies on the Codisposal of Fluidized-Bed Combustion Residue and Coal Slurry Solid

Gary B. Dreher, William R. Roy, and John D. Steele



Environmental Geology 150 1996

Department of Natural Resources
ILLINOIS STATE GEOLOGICAL SURVEY

Laboratory Studies on the Codisposal of Fluidized-Bed Combustion Residue and Coal Slurry Solid

Gary B. Dreher, William R. Roy, and John D. Steele

Environmental Geology 150 1996

ILLINOIS STATE GEOLOGICAL SURVEY
William W. Shilts, Chief

Natural Resources Building
615 East Peabody Drive
Champaign, Illinois 61820-6964
(217) 333-4747

GLOSSARY OF ABBREVIATIONS

µm	micrometer
AAS	atomic absorption spectrometry
Ag	silver
aglime	agricultural limestone
Al	aluminum
As	arsenic
B	boron
Ba	barium
Ca	calcium
Ca^{2+}	calcium ion
$CaCO_3$	calcite
$Ca(OH)_2$	portlandite
$CaMg(CO_3)_2$	dolomite
CaO	lime
$CaSO_4^0$	calcium sulfate ion pair
$CaSO_4$	anhydrite
$CaSO_4 \bullet 2H_2O$	gypsum
$CaSO_4 \bullet \frac{1}{2}H_2O$	bassanite
Cd	cadmium
Cl	chlorine
Cl^-	chloride ion
Co	cobalt
CO_3^{2-}	carbonate ion
CO_2	carbon dioxide
Cr	chromium
CSS	coal slurry solid
Cu	copper
Eh	oxidation-reduction potential
F	fluorine
F^-	fluoride ion
FBC	fluidized-bed combustion
Fe	iron
FeS_2	pyrite
GF-AAS	graphite furnace atomic absorption spectrometry
H_2SO_4	sulfuric acid
Hg	mercury
IC	ion chromatography
INAA	instrumental neutron activation analysis
In-C	inorganic carbon
ISGS	Illinois State Geological Survey
K	potassium
K^+	potassium ion
L	liter
mg	milligram
Mg	magnesium
Mg^{2+}	magnesium ion
$MgCO_3$	magnesite
MgO	periclase
$MgSO_4^0$	magnesium sulfate ion pair
Mn	manganese
Mn^{2+}	manganese ion
Mo	molybdenum
Na	sodium
Na^+	sodium ion
$Na_2SO_4^0$	sodium sulfate ion pair
Ni	nickel
O_2	oxygen gas
OEP	optical emission (photographic) spectroscopy
Org-C	organic carbon
Org-S	organic sulfur
Pb	lead
Pyr-S	pyritic sulfur
S	sulfur
Se	selenium
SEM-EDS	scanning electron microscopy with energy-dispersive X-ray spectrometric detection
Si	silicon
SiO_2	quartz
SO_4^{2-}	sulfate ion
SO_2	sulfur dioxide
Sul-S	sulfatic sulfur
Tot-C	total carbon
Tot-S	total sulfur
V	vanadium
XRD	X-ray diffraction spectrometry
XRF	X-ray fluorescence spectrometry
Zn	zinc
Zr	zirconium

ILLINOIS
DEPARTMENT OF
NATURAL
RESOURCES

Printed by authority of the State of Illinois/1996/1,000
Printed with soybean ink on recycled paper

CONTENTS

FIGURES

TABLES

Cover Photo Discharge point near the containing berm of a coal slurry impoundment. The sediment is predominantly coaly particles, but it also contains clay, pyrite, and other minerals.

ABSTRACT

The oxidation of pyrite in coal slurry solid, or tailings, from a coal preparation plant produces acidic leachate in the coal slurry impoundment. If left untreated, the acidic leachate may result in local environmental deterioration. The acidic solution could enhance the solubility and mobility of potential groundwater contaminants. If an alkaline material is added to the coal slurry solid, it either prevents or slows pyrite oxidation, or neutralizes the acid produced during the oxidation, and generally decreases the solubility of heavy metals. Therefore, the likelihood of groundwater contamination is diminished. Such codisposal of coal slurry solids with an alkaline material might allow revegetation of coal slurry solids without the soil cover presently required by regulatory agencies.

In this research we investigated the interaction of water with mixtures of fluidized-bed combustion (FBC) residues or agricultural limestone (aglime) and coal slurry solid (CSS) under laboratory conditions. We compared the concentrations of various trace elements in leachates and extracts from the unmixed FBC and CSS materials and from mixtures of FBC residues and CSS materials with the Illinois standards for concentrations of trace elements in general-use water. We also used scanning electron microscopy to study particles of FBC fly and bottom ash.

The major minerals in the unleached CSS were clay minerals and quartz (SiO_2). Also present were minor amounts of pyrite (FeS_2) and calcite ($CaCO_3$). The major minerals in the unleached FBC residues were lime (CaO) and anhydrite ($CaSO_4$). When mixed with water, the lime was hydrated to portlandite [$Ca(OH)_2$], which was converted to calcite during exposure to atmospheric carbon dioxide.

The major ions in the leachates and extracts from the FBC residue-CSS mixtures were calcium (Ca^{2+}), sodium (Na^+), sulfate (SO_4^{2-}), and chloride (Cl^-). The pH of the solutions from the FBC residues initially appeared to be controlled by portlandite, but later in the leaching or extraction period, the pH was probably controlled by the equilibrium between calcite, gypsum, and sulfuric acid. The alkaline species in the FBC residue effectively neutralized any acid produced by the oxidation of pyrite in the CSS.

Constituents that were often observed in the leachates and extracts at concentrations greater than the respective concentrations for Illinois general use water quality were boron (B), chloride (Cl^-), fluoride (F^-), iron (Fe), mercury (Hg), manganese (Mn), nickel (Ni), selenium (Se), and sulfate (SO_4^{2-}). Boron, chloride, cobalt, fluoride, manganese, and nickel were often present in leachates and extracts at concentrations that could be toxic to some plants.

Scanning electron microscopy revealed that some particles of ash were enlarged during the FBC process by accretion of molten ash constituents, and that portions of some limestone particles were inhibited in their reaction with sulfur dioxide (SO_2) in the FBC process, apparently due to the presence of magnesium (Mg).

INTRODUCTION

In the fluidized-bed combustion (FBC) of high-sulfur coal, pulverized limestone is injected simultaneously with the coal to trap SO_2 evolved during the high-temperature oxidation of pyrite in the coal. After combustion of the coal, the resulting residue typically contains substantial amounts of anhydrite ($CaSO_4$), lime (CaO) (Terman et al. 1978), and lesser amounts of coal ash. When mixed with water, the CaO in fresh FBC residue readily reacts with moisture to produce portlandite [$Ca(OH)_2$], which results in a strongly alkaline solution (pH 11.5 to 13). Portlandite, on reaction with CO_2 from the air, is converted to calcite ($CaCO_3$).

Previous researchers found that the alkaline nature of FBC residues makes them useful as substitute liming agents in agricultural practices (Terman et al. 1978, Bennett et al. 1978, Sidle et al. 1979, Korcak 1979, 1980, Stout et al. 1979a, b, Harness et al. 1987). Stout et al. (1982) concluded FBC residue appeared to be a satisfactory substitute for lime in the reclamation of acidic coal mine soils. These previous reports suggested FBC residue could be effective in buffering acid produced during the oxidation of pyrite in coal slurry solid (CSS). Calcite in water yields a solution with a pH of approximately 8. Several species of plants used in reclamation are tolerant to water of this pH.

Coal slurry solid consists of coal, clay minerals, and heavy mineral matter, particularly pyrite, that are all rejected during coal cleaning. The CSS is discharged as an aqueous slurry to an impoundment, where the solids settle out and the water is recycled through the cleaning process.

If CSS and FBC residues can be disposed of together in a manner that allows plants to grow in the mixture, then coal mining companies could save money by avoiding the need to apply the soil cover presently required by state law in reclaiming coal slurry impoundments. Background research to characterize the materials was a necessary first step in the overall research project. The purpose of this study was to provide data on the

(1) physical, chemical, and mineralogical characteristics of five FBC residues, an agricultural limestone (aglime), and two CSS materials;

(2) composition of aqueous leachates and extracts from the as-received solids and mixtures of FBC residues or aglime and CSS;

(3) major mineralogical changes that occurred during the leaching and extraction experiments; and

(4) degree to which pyrite in the CSS would be oxidized in a system buffered by the addition of FBC residue.

Because of time and financial constraints, replicate experiments were not conducted. This report is the result of two funded projects conducted during a 2-year period. During the first year, leaching experiments were conducted under cyclical wet and dry conditions in the laboratory to simulate codisposal of FBC residues and CSS in the unsaturated zone of the subsurface. A series of aqueous batch extractions was conducted during the second year to simulate the disposal of the materials in the saturated zone.

The reported research is part of a larger program, the goal of which is to develop a method to reclaim coal slurry solid. In this reclamation method, FBC residues would be codisposed of with CSS. Two benefits would result from this codisposal: (1) acid generated during the oxidation of pyrite in the CSS would be neutralized by alkaline components of the FBC residue, and (2) the surface of the CSS-FBC deposit would be stabilized by plant growth. If this reclamation method is successful and is accepted by the prevailing regulatory authorities, it could alleviate the need for the thick soil cover. The overall research program is being accomplished in manageable steps, in the field and laboratory, for several years.

Current federal law requires that a coal slurry impoundment be reclaimed after it is no longer used. One purpose of this reclamation is to prevent oxidation of pyrite in the CSS and eventual migration of acidic leachate to underlying groundwater. Illinois state law (Public Act 81-1015, "Surface Coal Mining Land Conservation and Reclamation Act") requires that coal slurry impoundments be revegetated after their use is suspended. If the coal slurry solid cannot support vegetation, it must be covered with a minimum of 4 feet (1.2 m) of soil capable of supporting vegetation. Providing such a soil cover can be costly to the coal mine operator. At \$1.55 yd^{-3} (\$2.03 m^{-3}), it would cost approximately \$10,000 per acre (\$24,700 per hectare) to cover a slurry impoundment with 4 feet of soil.

Other reclamation methods are available and may be permissible from a regulatory standpoint. Nawrot et al. (1985, 1989), for example, converted several coal slurry impoundments in Illinois into wetland habitats, which avoided both the use of soil covers and the production of acidic waters. Limestone was applied to the areas of the impoundment that contained the greatest amounts of pyrite prior to the planting of wetland plants. Our research focuses on the use of FBC residues rather than limestone in the reclamation of CSS, and the establishment of grasses and legumes normally associated with dry land environments. We believe this to be the first reported use of FBC residues in this manner.

MATERIALS AND METHODS

Grab samples of FBC residues (FBC-1–FBC-5) were collected from five Illinois FBC operators. All samples were collected from the outlets of storage silos or, in one case (FBC-4), from a freshly loaded truck. Three samples (FBC-1, FBC-3, and FBC-4) were collected as composites of fly ash and bottom ash. The other two (FBC-2 and FBC-5) were collected as separate fly ash and bottom ash components. Portions of the two separate samples (FBC-2 and FBC-5) were combined prior to experimentation in a ratio of 25% bottom ash to 75% fly ash, according to the operators' estimates of ash production at the plants. The plants from which samples were collected had a relatively wide range of operating conditions (table 1). Each FBC residue was passed through a sieve with 3.36-mm openings (no. 6) prior to further sample preparation and characterization procedures.

A grab sample of fresh CSS was collected from a relatively dry location (i.e., able to support the weight of a person and had no standing water) in an active coal slurry impoundment at two Illinois coal preparation plants. One sample (CSS-1) originated from the Illinois Herrin (No. 6) Coal and the other (CSS-2) originated from the Illinois Springfield (No. 5) Coal.

A grab sample of aglime was collected at a limestone quarry in east-central Illinois. The sample was a slightly dolomitic limestone from the Silurian Racine Formation. The aglime was used as a control material with which to compare the FBC residues.

The CSS materials and the aglime were air-dried by spreading them on polyethylene film and periodically mixing them by hand for about 2 weeks. All materials were split into smaller quantities by riffle sampling prior to their characterization and use.

Characterization of the Unleached Solids

The particle-size distribution of each unleached solid was determined by dry sieving each into seven particle-size fractions: <62, 62–125, 125–250, 250–500, 500–1,000, 1,000–2,000, and >2,000 µm. To use the aglime as a control for the FBC residues, we weighed portions of aglime in each of the particle-size ranges in the same proportions as determined for the corresponding FBC residue. The aglime portions were then combined and mixed, resulting in a material with approximately the same particle-size distribution as the corresponding FBC residue. The aglime portions were mixed so that particle size could be eliminated as a variable in comparing the behavior of the aglime with the behavior of the respective FBC residue. These aglime samples are referred to in this report as sized aglime.

The bulk and particle densities of the CSS materials were determined by simple weight-volume relationships. The porosity of each CSS material was calculated from the bulk and particle densities. The pyrite content of the CSS samples was estimated by two methods: the peroxide oxidation method of Finkelman and Giffin (1986) and American Society for Testing and Materials Method D2492 for sulfur content in coals (ASTM 1990). The exchangeable acidity of the CSS samples was determined according to Method 9-4.2 of Thomas (1982).

The calcium carbonate equivalent of the FBC residues was determined according to American Society for Testing and Materials Method C602 (ASTM 1990). The CaO content of the FBC residues was estimated as follows. A weighed sample of the FBC residue was treated with deionized water until the sample was saturated. The sample was oven-dried at 110°C and mixed periodically to prevent cementation, then it was cooled and weighed. We assumed the weight gain to be equal to the amount of water absorbed in the hydration of CaO to $Ca(OH)_2$. This assumption allowed for a back calculation of the amount of CaO in the fresh FBC residue. The assumption was believed to be valid because (1) no gypsum was observed by X-ray diffraction spectrometry (XRD) in two FBC residue samples after storage for 5 months; hence, anhydrite was not easily hydrated; and (2) the content of other potentially hydratable minerals, such as clay minerals, was low. An estimate of the proportion of Ca-containing species in each unleached FBC residue was calculated from the calcium carbonate equivalent, total Ca, sulfate-S, the carbonate-carbon content, and the amount of water consumed upon hydration. In making these estimates, we assumed that only CaO, $Ca(OH)_2$, and $CaCO_3$ contributed to the observed calcium carbonate equivalent, all SO_4^{2-} occurred as $CaSO_4$, and all CO_3^{2-} occurred as $CaCO_3$. We also assumed that all lime was hydrated to portlandite during leaching or extraction, because no lime was detected by XRD in the leached or extracted residues.

Each unleached and leached solid was analyzed by instrumental neutron activation analysis (INAA) for arsenic (As), cobalt (Co), chromiun (Cr), manganese (Mn), and selenium (Se) (Harvey et al. 1983); by optical emission spectrometry (OEP) for silver (Ag), boron (B), beryllium (Be), and vanadium (V) (Harvey et al. 1983); and by atomic absorption spectrometry (AAS) for cadmium (Cd), copper (Cu), nickel (Ni), lead (Pb), and zinc (Zn) according to ASTM Method 3683. Major and minor elements in coal and coke ash were analyzed by wavelength-dispersive X-ray fluorescence spectrometry (XRF) for aluminum (Al), barium (Ba), calcium (Ca), iron (Fe), potassium (K), magnesium (Mg), sodium (Na), sulfur (S), and silicon (Si). In the XRF method, a 125-mg aliquot of an ashed sample of solid was fused with 1 g of a 50:50 mixture of lithium metaborate and lithium tetraborate in a platinum crucible for 15 minutes at 1,000°C. The fused mixture was pulverized with 2% Somar

Table 1 Operating characteristics of the FBC plants.

Operating characteristics	FBC-1	FBC-2	FBC-3	FBC-4	FBC-5
Type FBC	Circulating (5 units)	Circulating	Forced air	AFBC	Circulating (2 units)
Coal	Herrin? (Ill. No. 6)	Springfield (Ill. No. 5)	Springfield (Ill. No. 5)	Springfield (Ill. No. 5)	Springfield (Ill. No. 5)
Sorbent	Limestone	Limestone	Limestone	Limestone	Limestone
Particle size					
Coal	nr*	≤1.27 cm	0.64–3.18cm	1.27–2.54cm	<2 mm
Sorbent	nr	<0.59 mm	nr	<0.84mm	<2 mm
Calcium/sulfur mole ratio	nr	2.4–2.7	1.4	2.5	4
Feed rate					
Coal	0.93 t hr^{-1} per unit	0.91 t hr^{-1}	nr	4.1 t hr^{-1}	9.1 t hr^{-1}
Sorbent	nr	12.7 t hr^{-1}	nr	0.91 t hr^{-1}	5.4-5.9 t hr^{-1}
Combustion temperature (°C)	nr	843–899	816–927	821–832	927
Operating pressure (Mpa)	nr	2.76	0.34	4.72	8.96–9.65
Air input (kg hr^{-1})	nr	Primary: 40,000 Secondary: 25,000	nr	38,600–39,000	159,000–181,000
% O_2 in stack gas	nr	3.75–6.5	nr	3.5–4.5	4
Size of FBC	193,000 kg steam per hr per unit 24.6 MW	56,700 kg steam per hr	nr	54,400 lbs steam per hr 3.5 MW	30 MW per unit
Manufacturer/model of FBC	nr	Alstrom/Pyro Power	Stone-Johnson/ Fluid Fire	Foster-Wheeler	Riley Stoker
Available ash collection points	nr	Baghouse Bottom ash Economizer Boiler banks	Baghouse Bottom ash	Baghouse Economizer Surge hopper Multiclones Superheater hoppers	Baghouse Air heater hoppers Ash coolers
Total daily ash amount	635–726 t (75% fly ash, 25% bottom ash)	63 t fly ash 45 t bottom ash	nr	72 t	394 t
Current ash disposal method	Back to coal mine	Back to coal mine	Local ash heap	Back to coal mine	Back to coal mine
Amount collected (kg)	Fly ash: 13.4 bottom ash: 30.2	Fly ash: 16.3 bottom ash: 26.3	19.7	14.5	13.8
% ≥3.36 mm	0.86	5.0	6.7	1.5	0.07

*nr = not reported

mix in a tungsten carbide grinding vial on a No. 6 Wig-L-Bug®[1]. The ground sample was pressed into a disk, 1 inch in diameter, at 40,000 psi. The pressed disk was then analyzed quantitatively on a Rigaku Model 3371 X-ray fluorescence spectrometer.

The carbonate-carbon content of each sample was determined by using a UIC® carbon analyzer (Cahill and Autrey 1988). The solids were analyzed for bulk mineralogical composition by XRD (Hughes et al. 1994). In addition, samples of unleached FBC fly ash and bottom ash were examined by scanning electron microscopy with energy-dispersive X-ray spectrometric (SEM-EDS) detection.

Preparation of Mixtures

The amount of each FBC residue added to each CSS material was calculated according to the acid-neutralizing ability of the FBC residue and the net acid-generating potential of the CSS material. (For the wet-dry leaching experiments, the net acid-generating potential of the CSS material was derived from the Finkelman and Giffin [1986] method, which probably underestimated the amount of FBC residue required to stoichiometrically match the amount of pyritic sulfur in the CSS. Because calcite was not fully consumed in the wet-dry leaching experiments, the underestimation did not create a serious deficiency). The calculation was based on the reaction between $CaCO_3$ and the acid produced during pyrite oxidation. Four moles of $CaCO_3$ are consumed for each mole of FeS_2 oxidized, according to the following reaction:

$$FeS_2 + 3.75O_2 + 3.5H_2O + 4CaCO_3 = Fe(OH)_3 + 2CaSO_4 + 2Ca(HCO_3)_2 \qquad (1)$$

Wet-Dry Leaching Experiments

Laboratory leaching experiments were prepared by mixing FBC residue or sized aglime and CSS in the proportions calculated as described (table 2). Each of 20 mixtures was placed into a plastic flower pot, 17.8 cm in diameter. The bottoms of the pots were lined with filter paper to prevent the elution of fines. The eight unmixed samples (five FBC residues, one aglime, and two CSS materials) were also leached. Each flower pot was nested into a polypropylene beaker. We added approximately one pore volume (200–500 mL) of deionized water weekly to each mixture for 15 weeks. This interval allowed for at least partial drying of the solids and oxidation of pyrite, yet allowed the research to proceed at a reasonable pace. The water was allowed to flow through the mixture by gravity, and leachate was collected in the plastic beaker. The first pore volume of water produced no leachate because this amount was required to initially saturate the solid. Leachates from each two pore volumes of water were composited to accumulate sufficient volume for the desired analyses. No attempt was made to prevent drying of the solids between additions of water.

Table 2 Percentage of FBC residue or aglime mixed with balance of CSS in wet-dry leaching experiments.

FBC residue or aglime mixed with CSS-1	
FBC-1[‡]	2.1
FBC-2	2.8
FBC-3	1.7
FBC-4	1.4
FBC-5	2.7
FBC residue or aglime mixed with CSS-2	
FBC-1	7.6
FBC-2	10.0
FBC-3	6.4
FBC-4	5.3
FBC-5	9.9

[‡] Or aglime with size composition adjusted to approximate that of the corresponding FBC residue

Batch Extraction Experiments

Each of three FBC residues (FBC-3, FBC-4, and FBC-5) or sized aglime was mixed with each CSS in the percentages shown in table 3. Only FBC-3, FBC-4, and FBC-5 were used in the batch extraction experiments because FBC-1 and FBC-2 appeared to be similar to FBC-5. Extractions from these mixtures were conducted for 3, 10, 30, 90, and 180 days.

One part by weight of solid was mixed with four parts by weight of deionized water. The mixtures were agitated briefly and aerated by flowing air into the solution through a frit

---

[1] The use of trade names in this report is for descriptive purposes only and does not constitute endorsement by the Illinois State Geological Survey.

for 4 hours per workday to encourage pyrite oxidation. Water that evaporated during the experiments was replenished weekly. The pH of each solution was determined prior to filtration at the end of each extraction period. Each filtrate was analyzed chemically; each extracted solid was air-dried and analyzed chemically and mineralogically.

Table 3 Percentage of FBC residue or aglime mixed with balance of CSS in batch extraction experiments.

FBC residue or aglime mixed with CSS-1	
FBC-3	0.35
FBC-4	0.29
FBC-5	0.54
aglime	0.29
FBC residue or aglime mixed with CSS-2	
FBC-3	32.67
FBC-4	27.33
FBC-5	50.64
aglime	26.81

Analysis of Leachates and Extracts

The leachates and extracts were analyzed by inductively coupled plasma emission spectrometry (ICP) for aluminum (Al), boron (B), barium (Ba), calcium (Ca), cadmium (Cd), chromium (Cr), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb), vanadium (V), zinc (Zn), and zirconium (Zr). Inductively coupled plasma-mass spectrometry (ICP-MS) was used to determine As and Se in the wet-dry leachates. Graphite furnace atomic absorption spectrometry (GF-AAS) was used to determine As and Se in the batch extracts. Both sets of analyses for As and Se were conducted by the Illinois Hazardous Waste Research and Information Center (HWRIC). Chloride, fluoride, and sulfate were determined by ion chromatography (IC), and alkalinity was detemined by titration using standardized dilute hydrochloric acid. The Eh and pH were determined by conventional electrode methods. The platinum electrode-reference electrode pair used for Eh measurement was calibrated against a standard ZoBell solution (ZoBell 1946).

RESULTS AND DISCUSSION

Physical, Chemical, and Mineralogical Characteristics of FBC Residues and CSS

Particle size The particle-size distributions of FBC-1, FBC-2, and FBC-5 were similar (fig. 1); 50% or more of the particles in these residues was smaller than 62 µm. The particle-size distribution of FBC-3 was nearly uniform; about 50% of the particles was smaller than 250 µm. More than half the particles in FBC-4 was smaller than 500 µm. The particle-size distribution of the aglime was similar to that of FBC-4. Approximately 50% of the particles in CSS-1 was smaller than 125 µm, and about 50% of the particles in CSS-2 was smaller than 500 µm. It is expected that the smaller the average particle size of an FBC residue, the more quickly it will dissolve on exposure to moisture. In codisposal, small particle sizes will allow the FBC residue to respond quickly to an acidic leachate, but it might then be necessary to replenish the FBC residue every few years.

Chemical composition The chemical composition of each of the five FBC residues in this study appeared to be comparable with those of previous studies (table 4). The ranges of constituent concentrations reported by others for FBC residues are listed for comparison (Bennett et al. 1978, Sidle et al. 1979, Harness et al. 1987, Fennelly et al. 1987, and Tavoulareas et al. 1987). The concentrations reported by others for elements in Illinois coal ash (Gluskoter et al. 1977) and in limestones (in general) (Brownlow 1979) are also listed for comparison. The concentrations of several elements, for example boron, in the FBC residues were higher than the concentrations of those elements reported for limestone. Coal ash, with its typically higher concentrations of trace elements, probably contributed to the increased concentrations observed in the FBC residues.

Mineralogical composition The dominant crystalline phases in most of the FBC samples were portlandite [$Ca(OH)_2$], anhydrite ($CaSO_4$), lime (CaO), and to a lesser extent quartz (SiO_2; table 5). In the case of FBC-3, the fluidized-bed combustion boiler was used to supply heat to a complex of buildings from October 1991 through April 1992. After April, the ash silo was emptied, but a small amount of ash clung to the walls of the silo. A portion of this remainder was collected in September 1992. Hence, it had been exposed to the atmosphere for approximately 4 to 5 months. As a result, FBC-3 consisted largely of $CaCO_3$ and $Ca(OH)_2$ (table 5).

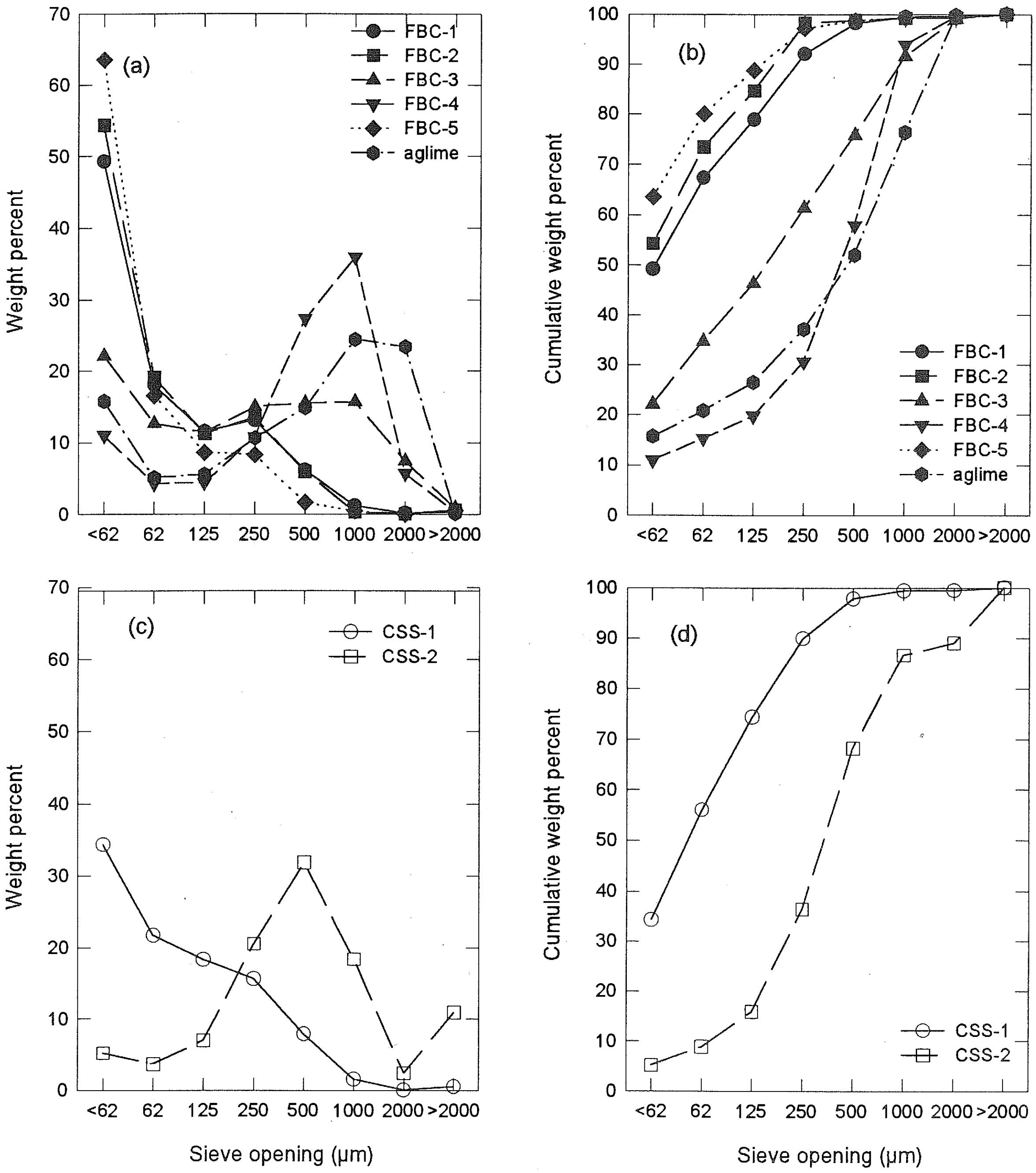


Figure 1 Particle-size distribution of FBC residues, aglime, and CSS materials.

On the basis of the calculated results, the FBC residues (except for FBC-3) consisted largely of $CaSO_4$ and unreacted CaO (table 5). On exposure to atmospheric moisture, CaO is easily hydrated to $Ca(OH)_2$ (Sisler et al. 1961, Hurlbut 1961). Evidence of such hydration during the 5-month storage of a sample in the laboratory is illustrated in figure 2 by the decrease in the peak area of lime and the increase in the peak area for portlandite. Portlandite readily reacts with CO_2 to form $CaCO_3$ (Sisler et al. 1961). The FBC residues also contained coal ash, which typically contains large amounts of SiO_2 and Al_2O_3. Whereas others (Graham and Hower 1994, Bland et al. 1995) have observed the presence of ettringite $[Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O]$ in FBC residues, we detected it only in FBC-3. The CSS materials contained varying amounts of pyrite and ash-forming minerals. By inference from chemical analysis, the aglime consisted principally of calcite ($CaCO_3$) and dolomite $[CaMg(CO_3)_2]$, but it also contained quartz (SiO_2; $\leq 7.0\%$), hematite (Fe_2O_3; $\leq 0.62\%$), and minor amounts of clay minerals. Both CSS materials contained calcite (table 5) and, therefore, had

Table 4 Chemical composition of the FBC residues and coal slurry solids.

Species	Concentrations determined in this study								Concentration range in FBC residues[†]	Average concentration in IL coal ash[¶]	Range of concentrations in	
	FBC-1	FBC-2	FBC-3	FBC-4	FBC-5	aglime	CSS-1	CSS-2			soil[§]	limestone[§]
SiO_2 (%)	18.01	20.67	8.54	6.75	17.87	7.00	19.69	29.91	0.024–15	47.11	<0.12–66	15–94
Al_2O_3 (%)	5.80	5.90	1.99	1.84	4.56	1.34	5.80	7.59	1.4–7.5	20.55	2.1–12.3	0.32–3.8
Fe_2O_3 (%)	5.39	10.95	3.18	2.87	5.41	0.62	3.02	19.73	2.4–21	23.89	0.67–6.15	0.16–3.00
MgO (%)	1.05	0.83	0.62	1.00	0.83	4.20	0.40	0.80	0.47–1.8	0.65	0.05–1.39	nr[‡]
CaO (%)	45.17	34.99	47.22	61.91	29.85	45.68	3.17	9.53	16–45	8.22	0.01–0.24	nr
Na_2O (%)	0.32	0.44	0.12	0.13	0.40	0.027	0.36	0.47	0.022–.26	0.85	0.03–0.84	0.01–0.23
K_2O (%)	0.80	0.55	0.24	0.16	0.60	5.3	0.90	1.37	0.005–3.4	1.89	0.08–3.1	0.14–0.67
MnO (%)	0.09	0.06	0.018	0.11	0.075	0.035	0.025	0.098	0.011–0.027	0.061	0.008–0.14	0.011–0.12
Ash (%)	93.3	92.3	70.1	91.8	87.8	99.9	37.7	81.1	nr	0.12	nr	nr
Pyr-S (%)	0.03	0.04	0.04	0.04	0.04	nd*	1.61	13.2	nr	nr	nr	nr
Sul-S (%)	6.44	6.05	3.03	6.26	5.81	nd	0.35	0.46	nr	nr	nr	nr
Org-S (%)	0.41	0.61	0.01	0.36	0.37	nd	1.68	1.05	nr	nr	nr	nr
Tot-S (%)	6.88	6.70	3.08	6.66	6.22	nd	3.64	14.7	nr	30	nr	nr
In-C (%)	0.43	0.48	4.78	1.17	0.44	11.2	0.65	1.95	nr	nr	0.046–0.055	nr
Org-C (%)	2.82	5.67	5.55	4.47	11.1	<0.01	46.7	8.14	nr	nr	0.70-2.8	0.10–0.28
Tot-C (%)	3.25	6.15	10.3	5.64	11.6	11.2	47.4	10.1	nr	nr	nr	nr
As (mg kg^{-1})	9.5	9.8	4.5	8.5	11	1.4	2.7	81	<12–53	95	6.7–13.0	0.74–2.5
B (mg kg^{-1})	218	281	118	145	316	<10	175	62	<10–500	1000	18–63	29–31
Ba (mg kg^{-1})	316	187	101	89	328	61	165	366	50–200	1200	86–740	5.6–160
Cd (mg kg^{-1})	<3	<3	<3	<3	<3	<3	<1	21	<0.5–7.0	13	nr	nr
Cr (mg kg^{-1})	44	67	25	22	55	6.5	35	73	<0.6–62	150	11–78	2.7–29
Cu (mg kg^{-1})	32	28	12	19	30	9	17	45	nr	110	8.7–33	0.84–12
Mo (mg kg^{-1})	16	18	<10	12	15	<10	<10	46	0.4–26	80	nr	0.79
Ni (mg kg^{-1})	36	51	<16	14	40	<17	21	74	<3–81	155	4.4–23	2.3–16
Se (mg kg^{-1})	4.9	9.3	1.8	2.8	6.5	<0.5	3.3	14	0.29–160	20	0.27–0.73	0.16–0.31
V (mg kg^{-1})	61	76	26	40	94	14	46	64	64–150	270	15–110	3.9–40
Zn (mg kg^{-1})	452	212	127	97	138	19	80	937	55–435	2200	25–67	6.3–24

[†] Concentration ranges for FBC residues compiled from Bennett et al. (1978), Sidle et al. (1979), Harness et al. (1987), Fennelly et al. (1987), and Tavoulareas et al. (1987)
[¶] Average concentrations of elements in Illinois coal ash calculated from Gluskoter et al. (1977) and Harvey et al. (1983)
[§] Ranges of concentrations in limestones and uncultivated soils from Brownlow (1979)
[‡] nr = not reported
*nd = not detected (sought but not observed)

Table 5 Physical, chemical, and mineralogical properties of unleached FBC, aglime, and CSS samples.

	FBC-1	FBC-2	FBC-3	FBC-4	FBC-5	Aglime	CSS-1	CSS-2
Physical and chemical properties								
Bulk density (g cm^{-3})	—[*]	—	—	—	—	—	0.84	1.51
Particle density (g cm^{-3})	—	—	—	—	—	—	1.35	2.46
Porosity	—	—	—	—	—	—	0.38	0.39
Pyrite (%)[†]	—	—	—	—	—	—	3.66	12.4
Pyrite (%)[‡]	—	—	—	—	—	—	3.01	24.7
Exchangeable acidity (meq kg^{-1})	—	—	—	—	—	—	16	23
CCE (%)	65.1	48.2	77.8	93.0	50.2	94.8	—	—
$CaCO_3$ (%)	3.58	4.00	39.8	9.75	3.67	93.1	4.83	15.9
Calculated proportions of calcium compounds (%)								
CaO	28.6	23.4	<0.1	45.6	22.7	—	—	—
$Ca(OH)_2$	7.73	1.74	28.1	1.36	4.41	—	—	—
$CaSO_4$[§]	27.4	25.7	12.9	26.6	24.7	—	—	—
$CaMg(CO_3)_2$	—	—	—	—	—	19.2	—	—
Minerals detected by XRD								
Portlandite	M	M	M	M	M	nd[**]	nd	nd
Quartz	M	M	t	m	M	m	M	M
Anhydrite	M	M	M	M	M	nd	nd	nd
Calcite	m	m	M	m	m	M	m	M
Lime	M	M	nd	M	M	nd	nd	nd
Ettringite	nd	nd	t	nd	nd	nd	nd	nd
Hematite	m	M	m	m	m	nd	nd	nd
Illite/smectite	nd	nd	nd	nd	nd	nd	m	m
Illite	nd	nd	nd	nd	nd	m	m	m
Kaolinite	nd	nd	nd	nd	nd	nd	m	m
Gibbsite	nd	nd	nd	nd	nd	nd	t	t
Plagioclase feldspar	nd	nd	nd	nd	nd	nd	m	m
Pyrite	nd	nd	nd	nd	nd	nd	m	M
Dolomite	nd	nd	nd	nd	nd	M	nd	nd

[†] Method of Finkelman and Giffin (1986)

[‡] ASTM Method D2492

[§] The amount of $CaSO_4$ in each FBC residue was calculated from the value for Sul-S (table 4)

[¶] M = major component (10–100%), m = minor component (0.5–10%), t = trace component (<0.5%)

[*] — = not determined (not sought)

[**] nd = not detected (sought but not observed)

some natural buffering capacity toward acid. On the basis of the number of chemical equivalents of calcite and pyrite present, and considering that the oxidation of 1 mole of pyrite will consume 4 moles of calcite (Eq. 1), there was enough calcite in CSS-1 to neutralize one-half the acid-generating potential of the pyrite present, and enough calcite in CSS-2 to neutralize one-fifth of the acid-generating potential of the pyrite present.

The major changes in the mineralogy of the FBC residues during either the leaching experiments or the batch extractions, as revealed by X-ray diffraction spectrometry, were the general decrease in lime (CaO) and portlandite [$Ca(OH)_2$)] content and the increase in calcite ($CaCO_3$) content. The relative height of the primary peak in the X-ray diffractogram for portlandite increased on storage of the FBC residues. Figure 2b shows the X-ray diffraction spectra for unleached FBC-4 at 4 months (January 31, 1992) and 7 months (July 2, 1992) after collection, and for leached FBC-4. The peak height (relative to quartz at 20.85° 2θ) for portlandite at approximately 18° and 34° 2θ became progressively greater through time, whereas the peaks for lime collapsed. Note also that the portlandite peaks in the spectrum from July 2, 1992, were rather broad, an indication that the portlandite crystals

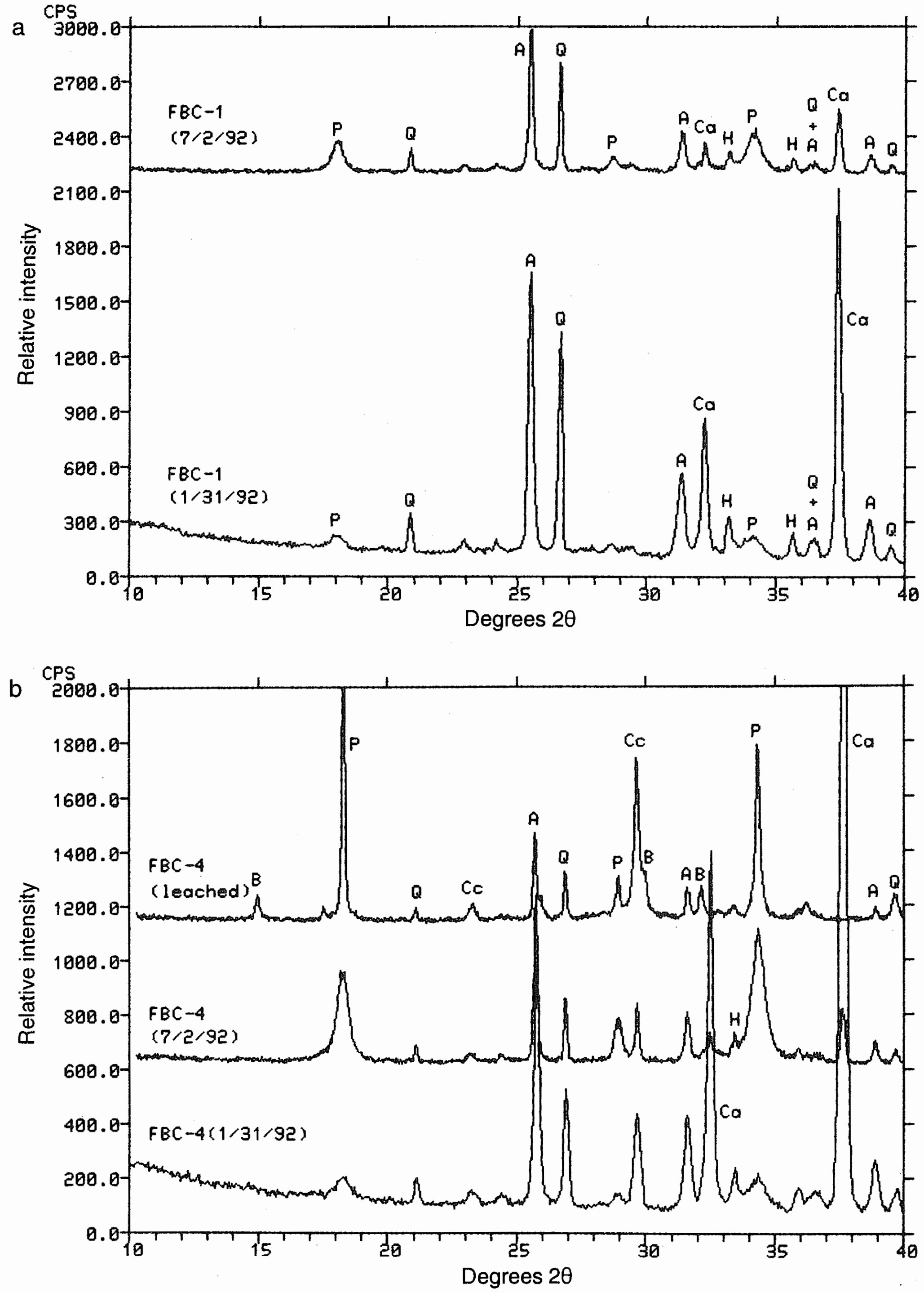


Figure 2 X-ray diffraction spectra of FBC-1 and FBC-4. (a) X-ray diffraction spectra show the decrease in lime (Ca) content and the increase in portlandite (P) content of FBC-1 after storage for 5 months. (b) X-ray diffraction spectra show the decrease in lime content and the increase in portlandite content of FBC-4 after storage for 5 months, and the refinement of the crystallinity of portlandite, the disappearance of anhydrite (A), and the appearance of bassanite (B) during leaching. Calcite (Cc), iron oxides/hydroxides (H), and quartz (Q).

in the specimen were small and/or disordered. By comparison, the portlandite peaks in the spectrum for the leached FBC-4 were narrower and showed increased relative peak height, which is indicative of larger crystal size as a result of the wet-dry leaching.

The calcium carbonate equivalent of a lime-based material is an indicator of its acid-neutralizing ability. The calcium carbonate equivalent values of the FBC residues indicated they had relatively large acid-neutralizing capabilities (table 5). The acid-neutralizing components expected to be present in the fresh FBC residues were CaO, $Ca(OH)_2$, and MgO. Most of the $CaCO_3$ in the feed limestone was calcined during fluidized-bed combustion. If $MgCO_3$ and $CaMg(CO_3)_2$ were present in the feed limestone, they too would have been calcined. The calcium carbonate content in all the as-received FBC residues, except FBC-3, was less than 10% (table 5), indicating little exposure to atmospheric carbon dioxide had been allowed prior to sample collection.

Effects of Leaching

The major changes in the mineralogy of the FBC residues during either the leaching experiments or the batch extractions, as revealed by XRD, were the general decrease of lime and portlandite content and the increase of calcite content. The relative peak areas for various minerals in the FBC residues and aglime before and after wet-dry leaching are given in table 6. In each of the FBC residues in which lime was initially present, none was detected after leaching. For FBC-2, FBC-3, and FBC-5, the relative peak height for portlandite was substantially decreased after leaching, and in every case, the peak area for calcite was significantly greater after leaching than before. As discussed earlier, the increase in the relative peak height for portlandite during the leaching of FBC-1 and FBC-4 was apparently the result of improved crystallinity, rather than increased portlandite content. On the basis of the data in table 6 for lime, portlandite, and calcite, and in tables 4 and 8 for inorganic carbon, the lime or portlandite in the FBC residues appeared to have reacted with carbon dioxide from the air to form calcite. Mineralogical changes in the residues from the batch extractions were minor and nonsystematic. The chemical composition of the FBC, CSS, and aglime samples after 180 days of extraction (table 7) was similar to the chemical composition of the wet-dry leached samples (table 8). In most of the leaching experiments (table 9), the calcium carbonate content increased, whereas in the batch extractions it decreased. Iron oxides and hydroxides were present in all the FBC residues as a result of the incorporation of coal ash during the combustion cycle.

Chemical analyses indicated the pyrite content of CSS-1 was approximately 3.01%, whereas that of CSS-2 was 24.7% (table 5). The greater density of pyrite (5.00 g cm^{-3}) compared with that of coal (approximately 1.3 g cm^{-3}) and the greater content of pyrite in CSS-2 than in CSS-1 were responsible for the higher bulk and particle densities of CSS-2. The fractional porosities of the materials, as packed in the leaching containers, were approximately equal, 0.38 for CSS-1 and 0.39 for CSS-2.

In the presence of certain bacteria, pyrite can be oxidized rapidly under acidic conditions. A goal of this research was to determine whether pyrite would be oxidized under the buffered conditions presented by the admixture of FBC residue to CSS. We observed the pyritic sulfur content decreased from 1.61% to 1.43% in CSS-1 and from 13.2% to 11.5% in CSS-2 during the wet-dry leaching experiments. These percentages amount to relative decreases in pyritic sulfur content of 11.2% and 12.9%, respectively. In the mixtures of CSS and FBC residue or aglime, the relative decrease in pyritic sulfur during the wet-dry leaching experiments ranged from 7.8% to 19.6%. These data gave a clear indication that pyrite in the solids was oxidized during the wet-dry leaching experiments under the pH-buffered conditions provided by the FBC residue.

Gypsum ($CaSO_4 \cdot 2H_2O$), the product of reaction between calcite and sulfuric acid, was observed by XRD analysis of CSS-2 (fig. 3). Anhydrite ($CaSO_4$), the high-temperature reaction product of SO_2, CaO, and O_2, was observed in the unleached FBC residues (fig. 3), but gypsum was not. We expected gypsum would form in mixtures of CSS-2 and FBC residues during leaching, from the reaction of the alkaline, calcium-containing constituents of FBC residues with the sulfuric acid generated during the oxidation of pyrite in the CSS. After leaching, however, neither gypsum nor anhydrite was detected in the mixtures. Rather, bassanite ($CaSO_4 \cdot \frac{1}{2}H_2O$) was detected in all mixtures that contained CSS-2 (figs. 2b, 3).

It is unlikely that anhydrite was partially hydrated to bassanite during the leaching experiments because this reaction proceeds very slowly, if at all (Hardie 1967). The hydration of anhydrite to gypsum is also slow. Therefore, we attributed the disappearance of anhydrite from the mixtures to dissolution during the leaching experiments.

Table 6 Peak areas from x-ray diffraction spectrometry for the major minerals relative to quartz at 20.85°2θ, before and after wet-dry leaching.

Sample	Portlandite	Anhydrite	Calcite	Lime	Ettringite	Hematite	Bassanite
Before leaching							
FBC-1	0.23	1.50	nd*	2.17	nd	0.23	nd
FBC-2	0.13	0.60	0.06	0.76	nd	0.40	nd
FBC-3	1.93	1.53	5.51	nd	0.20	0.26	nd
FBC-4	0.52	2.58	0.98	9.80	nd	0.36	nd
FBC-5	0.13	0.85	nd	0.99	nd	0.19	nd
Aglime	nd	nd	12.12	nd	nd	nd	nd
After leaching							
FBC-1	0.65	0.06	1.32	nd	nd	0.26	0.23
FBC-2	nd	0.07	0.92	nd	nd	0.53	0.24
FBC-3	0.57	0.08	6.03	nd	nd	0.30	0.19
FBC-4	4.74	1.80	5.39	nd	nd	0.49	0.69
FBC-5	0.03	0.03	0.81	nd	nd	0.21	0.15
Aglime	nd	nd	10.35	nd	nd	0.51	nd

*nd = not detected

Table 7 Chemical composition of solids after the 180-day batch extraction experiments.

	Concentrations determined in this study					
Species	FBC-3	FBC-4	FBC-5	Aglime	CSS-1	CSS-2
SiO_2 (%)	7.96	5.61	18.91	7.02	20.06	29.10
Al_2O_3 (%)	1.81	1.54	4.76	1.30	5.84	7.29
Fe_2O_3 (%)	2.96	2.38	5.56	0.64	2.99	21.34
MgO (%)	0.58	0.87	0.91	4.28	0.40	0.76
CaO (%)	43.36	49.19	30.16	45.42	2.73	9.42
Na_2O (%)	0.06	0.06	0.19	0.04	0.12	0.34
K_2O (%)	0.16	0.10	0.34	0.52	0.88	1.27
MnO (%)	0.17	0.84	0.65	0.35	0.26	0.99
As (mg kg^{-1})	4.5	7.3	10	2.0	2.7	85
B (mg kg^{-1})	85	114	300	<10	113	71
Ba (mg kg^{-1})	40	<10	230	30	145	315
Cd (mg kg^{-1})	<3	<4	<3	<3	<1	28
Cr (mg kg^{-1})	22	17	47	5.8	36	67
Cu (mg kg^{-1})	16	20	25	11	17	38
Mo (mg kg^{-1})	<10	<10	14	<10	5	18
Ni (mg kg^{-1})	21	25	34	17	28	72
Se (mg kg^{-1})	1.4	2.8	5.1	<0.5	2.8	14
V (mg kg^{-1})	41	54	125	16	33	54
Zn (mg kg^{-1})	122	79	110	<17	52	1276
Ash (%)	64.71	74.05	74.90	59.61	36.37	80.46
Pyr-S (%)	—*	—	—	—	1.37	12.52
Sul-S (%)	2.59	3.88	4.66	—	0.21	1.35
Org-S (%)	—	—	—	—	1.96	1.86
Tot-S (%)	2.84	5.10	4.99	0.03	3.54	15.73
In-C (%)	7.17	3.35	2.48	11.15	0.46	1.76

*— = not determined

Table 8 Chemical composition of solids after the wet-dry leaching experiments (15 pore volumes).

	Concentrations determined in this study							
Species	FBC-1	FBC-2	FBC-3	FBC-4	FBC-5	Aglime	CSS-1	CSS-2
SiO_2 (%)	15.92	19.07	8.30	5.27	19.08	6.93	20.08	29.58
Al_2O_3 (%)	5.16	5.40	1.87	1.37	4.89	1.20	5.98	7.54
Fe_2O_3 (%)	4.77	10.22	3.20	2.27	5.81	0.61	2.98	20.58
MgO (%)	0.91	0.76	0.57	0.83	0.88	4.04	0.36	0.68
CaO (%)	28.66	30.58	44.82	50.76	30.62	45.39	2.42	9.02
Na_2O (%)	0.36	0.15	0.16	0.07	0.07	0.16	0.10	0.36
K_2O (%)	0.35	0.35	0.16	0.11	0.35	0.53	0.89	1.30
MnO (%)	0.08	0.06	0.02	0.09	0.07	0.04	0.03	0.09
As (mg kg^{-1})	8.9	9.3	5.1	7.3	10	2.0	2.7	78
B (mg kg^{-1})	312	373	153	191	433	<10	135	48
Ba (mg kg^{-1})	85	108	40	49	81	10	39	58
Cd (mg kg^{-1})	<2.2	<2.2	<2.2	<2.4	<2.0	<2.3	<0.9	15.6
Cr (mg kg^{-1})	36	63	24	17	49	6.7	37	69
Cu (mg kg^{-1})	23	17	6	11	21	<7	15	37
Mo (mg kg^{-1})	nd*	9	nd	nd	7	nd	nd	29
Ni (mg kg^{-1})	23	43	<19	<20	38	<20	20	56
Se (mg kg^{-1})	3.9	8.7	1.3	2.2	5.3	<0.5	2.1	11
V (mg kg^{-1})	85	108	40	49	81	10	39	58
Zn (mg kg^{-1})	405	182	97	86	125	32	74	1060
Ash (%)	81.35	81.33	67.60	74.83	76.11	59.82	36.43	80.66
Pyr-S (%)	0.01	0.01	0.03	0.01	0.02	<0.01	1.43	11.54
Sul-S (%)	5.55	5.20	2.62	4.90	5.12	<0.01	0.07	2.36
Org-S (%)	0.41	0.55	0.02	0.51	0.47	<0.01	1.73	0.75
Tot-S (%)	5.97	5.76	2.67	5.42	5.61	<0.01	3.23	14.65
In-C (%)	2.85	2.71	6.21	3.58	2.39	11.03	0.81	1.49
Org-C (%)	2.46	4.86	5.46	3.66	10.05	0.23	47	7.58
Tot-C (%)	5.31	7.57	11.67	7.24	12.44	11.26	48	9.07

* nd = not detected

Table 9 Change in the calcium carbonate content of the FBC residue, aglime, and CSS resulting from leaching or extraction.

Sample	Change in $CaCO_3$ content (%)	
	Wet-dry leaching	Batch extractions (180 days)
Unmixed		
FBC residue	+12.0 to +20.2	+10.19 to +11.94
Aglime	−2.90	−0.95
CSS-1	+1.40	−0.95
CSS-2	−3.80	−0.10
Mixtures		
CSS-1 + FBC residue	+0.23 to +2.47	−0.65 to −0.70
CSS-1 + aglime	0.00 to −1.40	−0.85
CSS-2 + FBC residue	+1.00 to +2.60	+3.10 to +6.40
CSS-2 + aglime	−2.00 to −3.60	−0.49

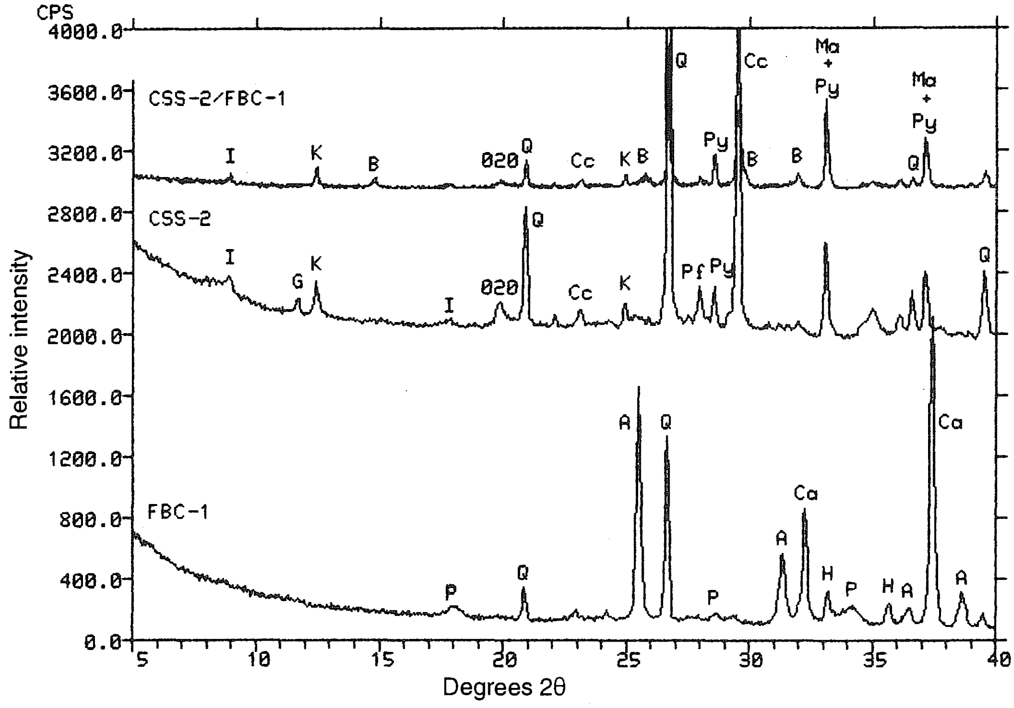


Figure 3 X-ray diffraction spectra of FBC-1 and CSS-2 before wet-dry leaching and CSS-2/FBC-1 after 15 pore volumes of water were leached through the mixture. Anhydrite (A), bassanite (B), calcite (Cc), clay (020), gypsum (G), illite (I), iron oxides/hydroxides (H), kaolinite (K), lime (Ca), marcasite (Ma), plagioclase feldspar (Pf), portlandite (P), pyrite (Py), and quartz (Q).

Gypsum probably precipitated during the leaching experiments, but it was partially dehydrated to bassanite during low temperature drying of the samples at 70°C in preparation for XRD analysis. Deer et al. (1962) indicated that gypsum is dehydrated to bassanite, beginning at a temperature of about 70°C. Bassanite was observed only in mixtures that contained CSS-2, probably because the bassanite content was above the detection limit only in those mixtures. The amounts of FBC residue added to CSS-1 were 1.4% to 2.8% and the amounts added to CSS-2 were 5.3% to 10.0%. The greater the amounts of pyrite and FBC residue in the mixture, the greater the probability of gypsum formation during the wet-dry leaching, and hence the greater the amount of bassanite on drying of the sample.

pH of Leachates and Extracts

Lindsay (1979) indicated that in a soil containing both gypsum and calcite at equilibrium under a fixed partial pressure of CO_2, the addition of sulfuric acid will cause calcite to dissolve and gypsum to precipitate, according to the following reaction:

$$H_2SO_4 + CaCO_3 + H_2O \Rightarrow CaSO_4{\bullet}2H_2O + CO_2\Uparrow. \qquad (2)$$

As long as there is a supply of $CaCO_3$, the composition of the solution phase will not change with the addition of sulfuric acid, and the pH of the solution will be approximately 7.8 at a CO_2 partial pressure of 0.0003 atmosphere, the partial pressure of CO_2 in the atmosphere (Lindsay 1979). This stoichiometric equation above represents the probable reaction in the neutralization by calcium carbonate of sulfuric acid generated during pyrite oxidation.

The pH of the wet-dry leachates from the unmixed FBC residues ranged from 10.5 to 13.0 (fig. 4a), and that of the batch extracts ranged from 11.9 to 12.6 (fig. 4b). The range of pH values in the solutions from the unmixed aglime was 7.7 to 8.4 in the wet-dry leachates and 7.5 to 8.4 in the batch extracts (fig. 4). The high pH of the solutions from the unmixed FBC residues was characteristic of portlandite dissolution, which would produce a solution with a pH of approximately 12.4. The pH of the solutions from the unmixed aglime was characteristic of a solution in equilibrium with calcite.

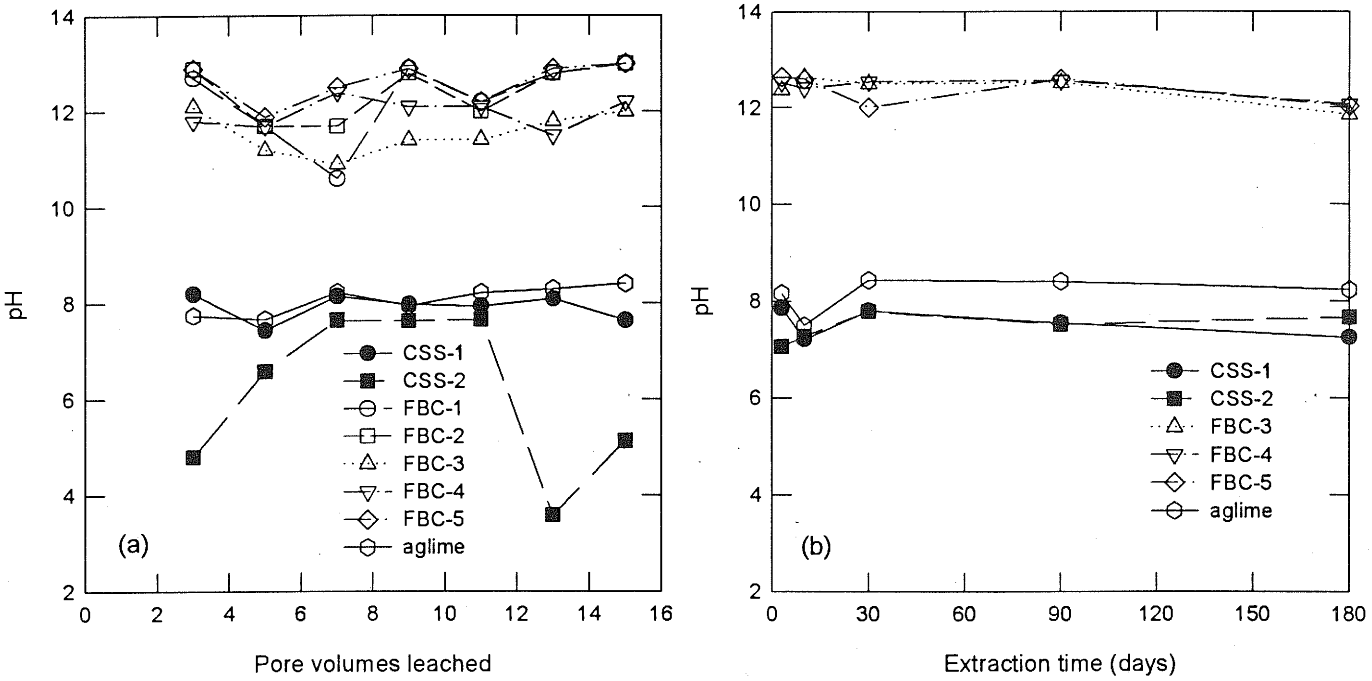


Figure 4 pH in leachates and extracts from unmixed FBC residues and CSS.

Unmixed CSS-1 initially contained 4.83% $CaCO_3$, which buffered the pH of leachates to about 8 (fig. 4a) throughout the wet-dry leaching period. The pH of 8 indicates the CSS-1–water system was probably buffered by calcite.

Leachates from unmixed CSS-2 (fig. 4a) were acidic at the beginning and the end of the leaching period. This material contained 15.9% calcite at the beginning of the experiments. The reason for the decrease in pH at pore volume 13 (fig. 4a) is unknown, but the decrease may have been the result of differences in the kinetics of pyrite oxidation versus calcite dissolution, or a decrease in the availability of calcite particles due to a possible coating of iron oxides and/or hydroxides (products of pyrite oxidation) during the leaching experiments.

The pH of all leachates from the mixtures of CSS-1 and FBC residues and mixtures of CSS-1 and sized aglime was approximately 8 (fig. 5). The pH of these leachates was apparently controlled by calcite. In the mixtures, the amount of FBC residues was small, so the conversion of portlandite to calcite was nearly complete, in contrast to the unmixed residues, in which the amount of calcite produced was relatively small compared with the large amounts of portlandite. The data point for the CSS-1–FBC-4 mixture at 90 days extraction time (fig. 5b) appears to be an outlier. The 180-day extract for this mixture was spilled and was unsalvageable.

The pH of leachates from the mixtures of CSS-2 and FBC residues was more variable than the pH of leachates from mixtures of CSS-1 and FBC. Mixtures of CSS-2 and FBC-1, FBC-2, or FBC-5 behaved similarly (fig. 6a). The graph of pH versus time for CSS-2/FBC-4 was similar to those for the other mixtures, but the low-pH portion of the leaching response was delayed, again, possibly because of a coating of iron oxides and/or hydroxides on the calcite particles. The pH of the leachate from the mixture of CSS-2 and FBC-3 at pore volume 3 was acidic, but the pH in the remainder of the leachate samples conformed to the pattern shown by the mixtures of CSS-2 with FBC-1, FBC-2, and FBC-5. Each leachate from pore volume 15 attained a pH of approximately 8, which suggested a system buffered by calcite.

In the batch extraction experiments, the pH of extracts from mixtures of CSS-1 and FBC residues was between 7 and 8 after 30 days of extraction, and the pH remained in that interval for the balance of the extraction periods (fig. 5b). The pH of extracts from mixtures that contained CSS-2 and FBC residue was initially between 12 and 13, but the pH decreased as the extraction period progressed (fig. 6b). The gradual change in pH was indicative of the initial presence of portlandite, followed by its slow conversion to calcite. The slower transition of portlandite to calcite in the batch extraction experiments, compared with the transition of portlandite in the leaching experiments, can be attributed to decreased exposure of the portlandite to carbon dioxide.

Major Solutes in Leachates and Extracts

The predominant solutes in the leachates and extracts from mixtures of CSS and FBC residue or aglime were Ca^{2+}, Na^{+}, SO_4^{2-}, and Cl^{-}. Sodium and chloride were quickly flushed during the wet-dry leaching experiments. Their maximum concentrations were generally attained within 3 to 10 days during the batch extractions, owing to their solubility.

In comparison with the leachates from the mixtures of CSS and aglime, those from mixtures of CSS and FBC residue had greater Ca^{2+} concentrations in the early pore volumes (figs. 7a, 8a). The Ca^{2+} concentrations in the last few leachate samples from the mixtures, however, ranged from 400 to 800 mg L^{-1}. We attributed the presence of Ca^{2+} in the solution to the dissolution of calcite, anhydrite, or gypsum.

Sulfate in all the leachates (figs. 9a,10a) was attributed to the oxidation of pyrite and/or the dissolution of anhydrite. The Ca^{2+} and SO_4^{2-} concentrations in the 180-day batch extracts (figs. 7–10) were apparently the result of thermodynamic equilibrium with calcite and gypsum (see below). If pyrite oxidation did occur in the batch extractions, the reaction products would have supplied SO_4^{2-} and Ca^{2+} ions to the solution, and the acid produced would have been neutralized by carbonate.

The observed changes in the Ca^{2+} and SO_4^{2-} concentrations in the batch extracts were important to understanding the major chemical reactions that occurred in the FBC residue-CSS mixtures. The mean Ca^{2+} concentration in all 180-day batch extracts was 566 ± 18 mg L^{-1}. The Ca^{2+} concentrations (fig. 8b) in the extracts from mixtures that contained CSS-2 were initially high because of the solubility of portlandite (1,590 mg L^{-1} at 25°C). With increasing extraction time, the concentration of Ca^{2+} in the extracts decreased to a relatively constant value, reflecting the lower solubility of calcite (14 mg L^{-1} at 25°C) when compared with that of portlandite.

The possible sources of SO_4^{2-} in the extracts were the dissolution of anhydrite that was initially present in the solids and the oxidation, if any, of pyrite during the extraction period (figs. 9b,10b).

In general, the concentrations of Ca^{2+} and SO_4^{2-} in the leachates and extracts were controlled by the solubility of gypsum, as indicated in the solubility diagrams in figures 11 and 12. In calculating the solubility boundaries, we assumed the gypsum dissolved into a pure aqueous solution. The solutions in this study, however, contained other ions, in particular, sodium and chloride. The presence of other ions increased the ionic strength of the solutions, which increased the solubility of gypsum (and other minerals) relative to its solubility in a solution of low ionic strength. The leachates and extracts were relatively dilute solutions that had ionic strengths of approximately 0.1 (for comparison, seawater has an ionic strength of approximately 0.7). Ionic interactions, however, would have had some effect on the solubilities of the salts. For example, sulfate ions will interact in solution with cations, such as Ca^{2+}, Mg^{2+}, and Na^{+}, to form ion pairs, such as $CaSO_4^{0}$, $MgSO_4^{0}$, and $Na_2SO_4^{0}$. The concentration of these ion pairs and others would be relatively low when compared with the concentrations of Ca^{2+} and SO_4^{2-}, but they will, nevertheless, increase the solubility of sulfate salts. This ionic strength effect would displace the gypsum solubility boundary upward so that it would lie closer to the points representing the concentration of sulfate on the graphs (figs. 11b, 12b). Consideration of the ionic strength effect makes equilibrium with gypsum more reasonable than it appears on the graphs for sulfate ion. As indicated in figures 7 to 10, the concentrations of Ca^{2+} and SO_4^{2-} each converged on or tended to converge on common concentrations for the two ions, another indication of an approach to equilibrium.

When the total dissolved concentrations of Ca^{2+}, Na^{+}, Cl^{-}, and SO_4^{2-}, alkalinity, and pH and Eh values were input to the thermodynamic equilibrium model, MINTEQA2 (U.S. EPA 1990), the calculated results confirmed that after 15 pore volumes were leached, the leachates from the wet-dry column experiments would be in equilibrium with both calcite and gypsum. The model was also used to calculate the equilibrated systems for the 180-day extracts. In the case of the batch extracts, however, alkalinity data were lacking. Because the batch solutions were periodically aerated, a constant carbon dioxide partial pressure of 0.0003 atmosphere (the approximate partial pressure of carbon dioxide in air) was used in the model. The modeling results indicated the extracts from the mixtures containing CSS-1 would be in equilibrium with gypsum, and the extracts from the mixtures containing CSS-2 would be in equilibrium with calcite. The latter results are contrary to the results shown by the open triangle symbols for mixtures with CSS-1 (the points between pH 9 and 11) in

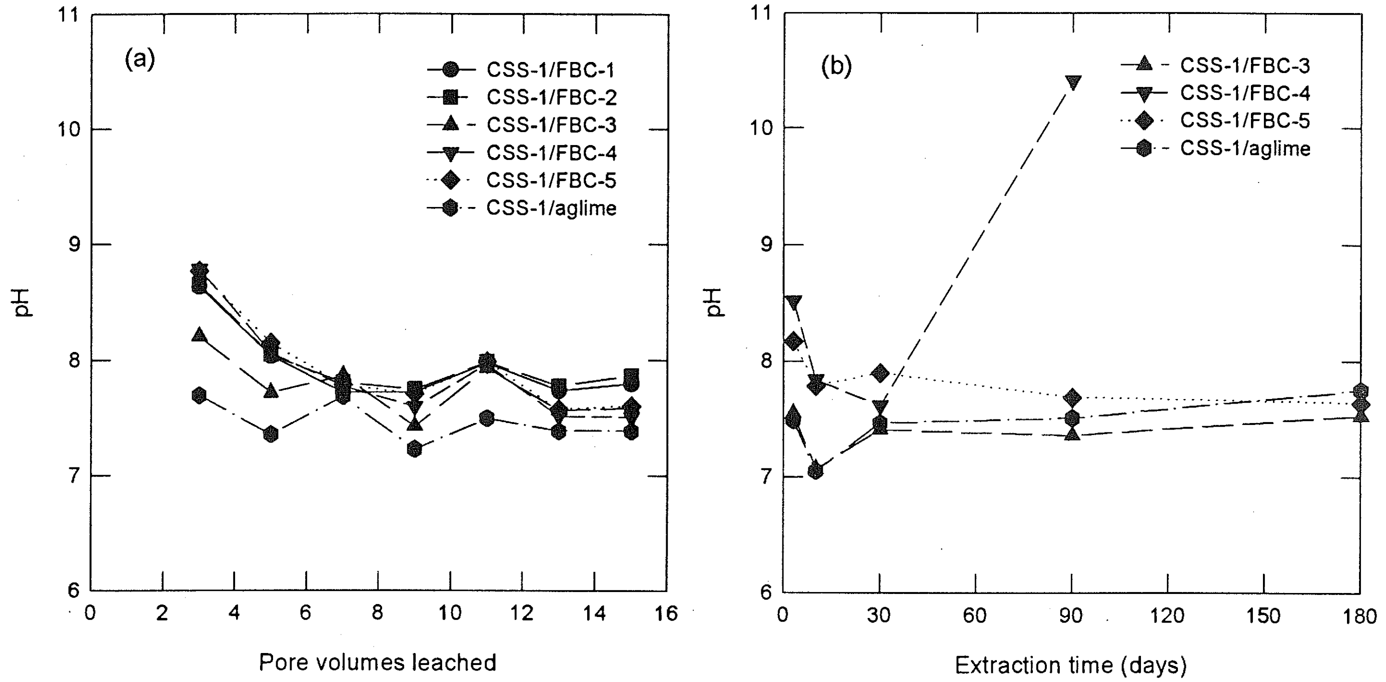


Figure 5 pH of leachates and extracts from mixtures of FBC residues and CSS-1.

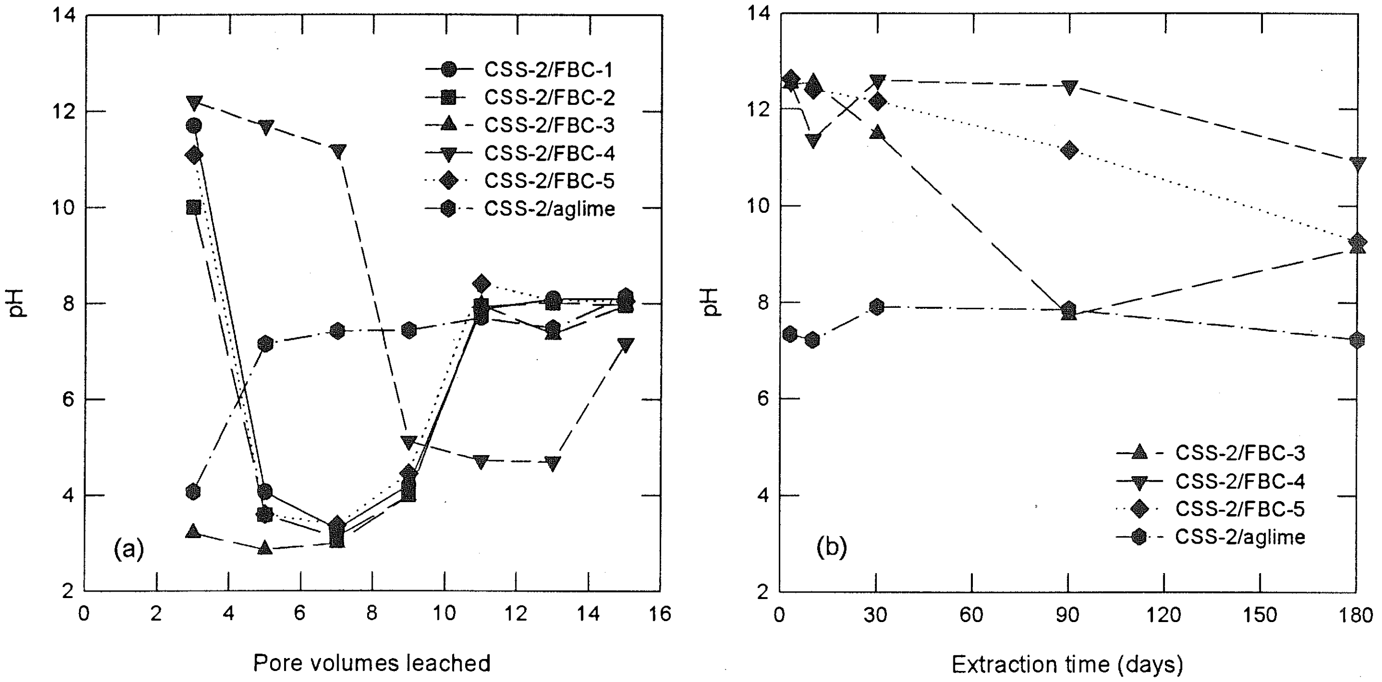


Figure 6 pH of leachates and extracts from mixtures of FBC residues and CSS-2.

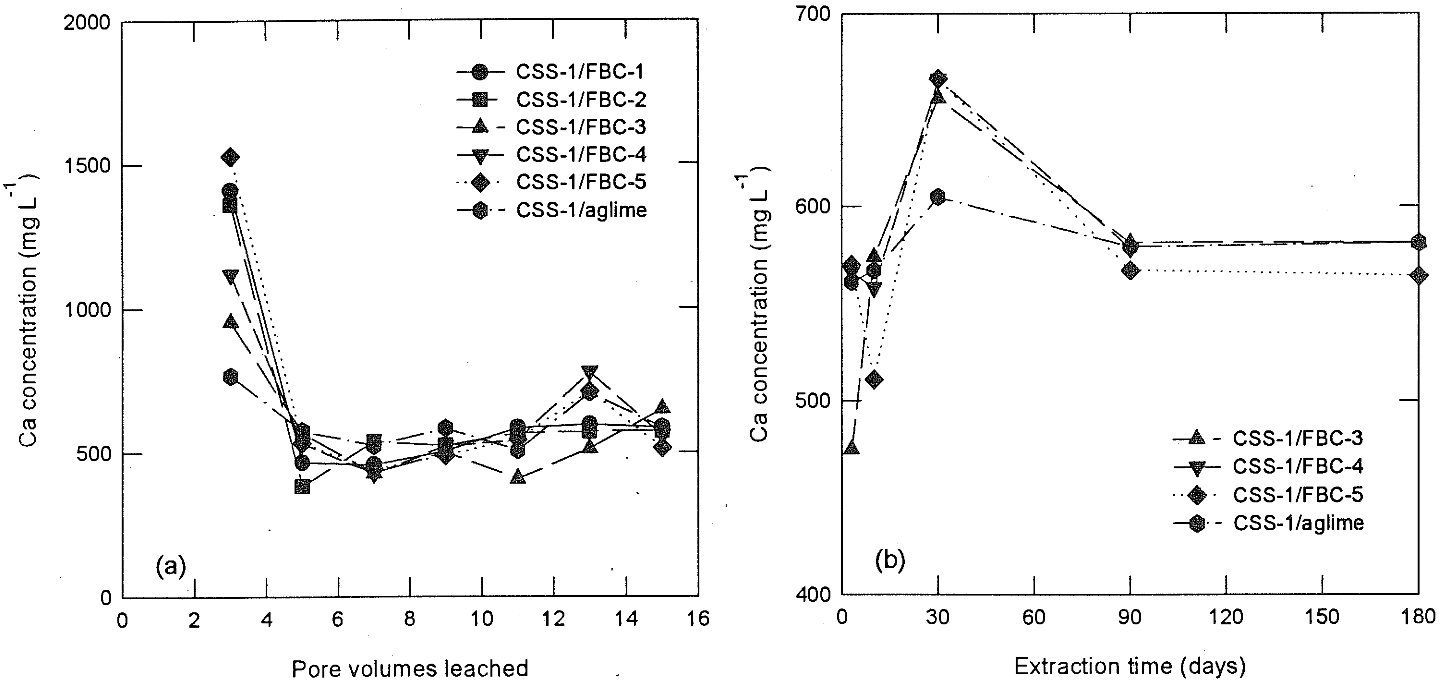


Figure 7 Calcium concentration in leachates and extracts from mixtures of FBC residues and CSS-1.

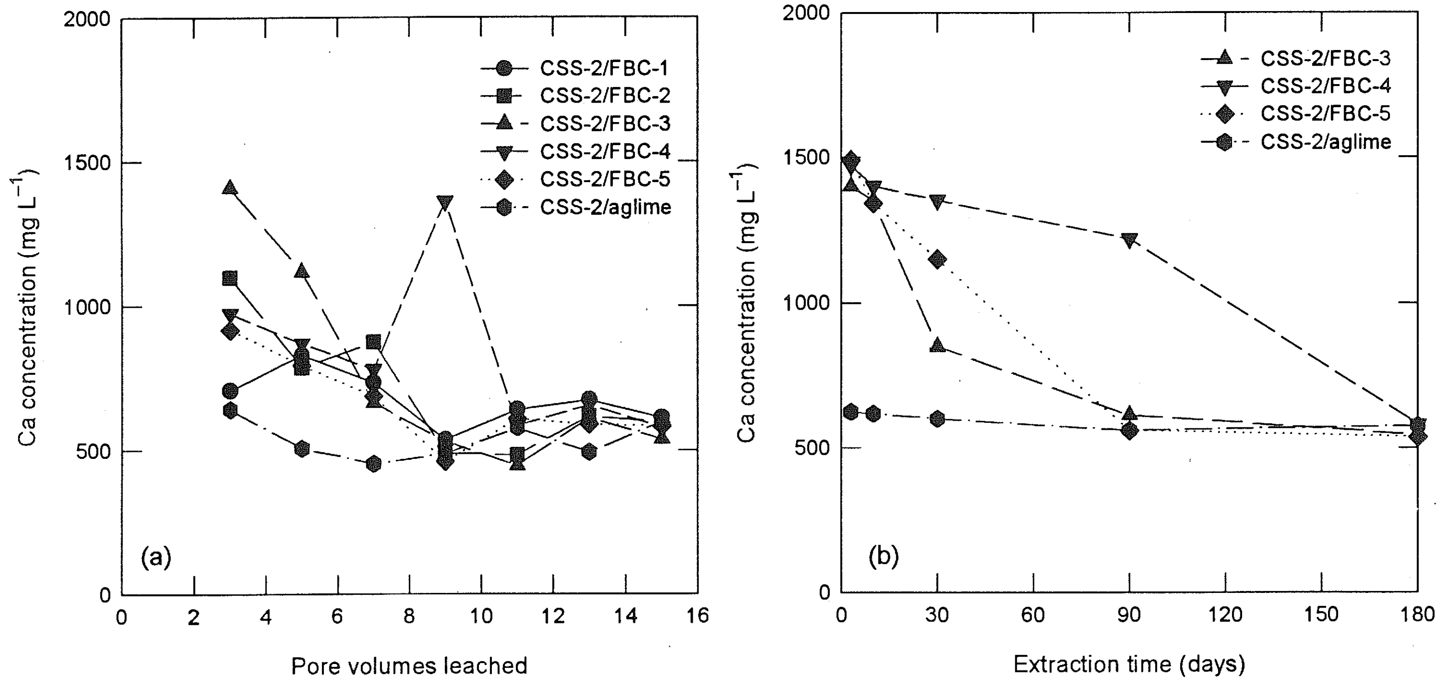


Figure 8 Calcium concentration in leachates and extracts from mixtures of FBC residues and CSS-2.

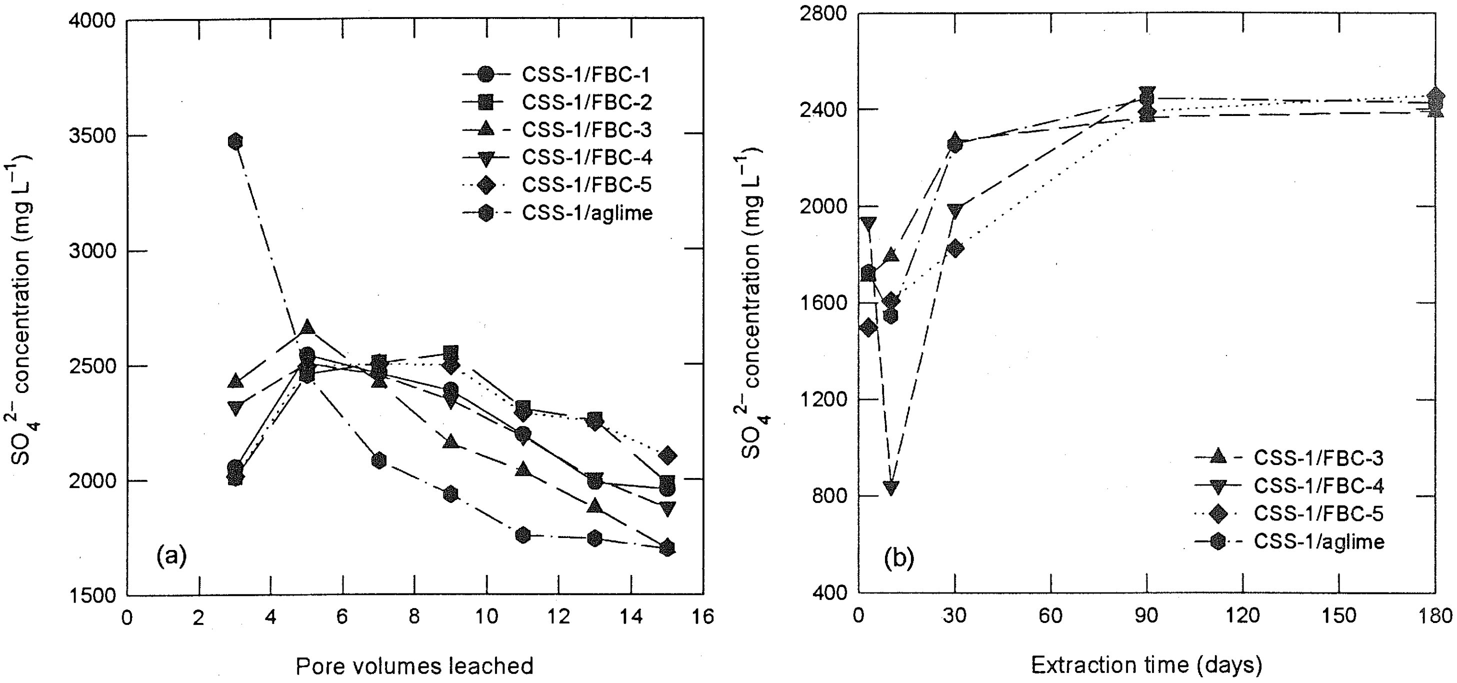


Figure 9 Sulfate concentration in leachates and extracts from mixtures of FBC residues and CSS-1.

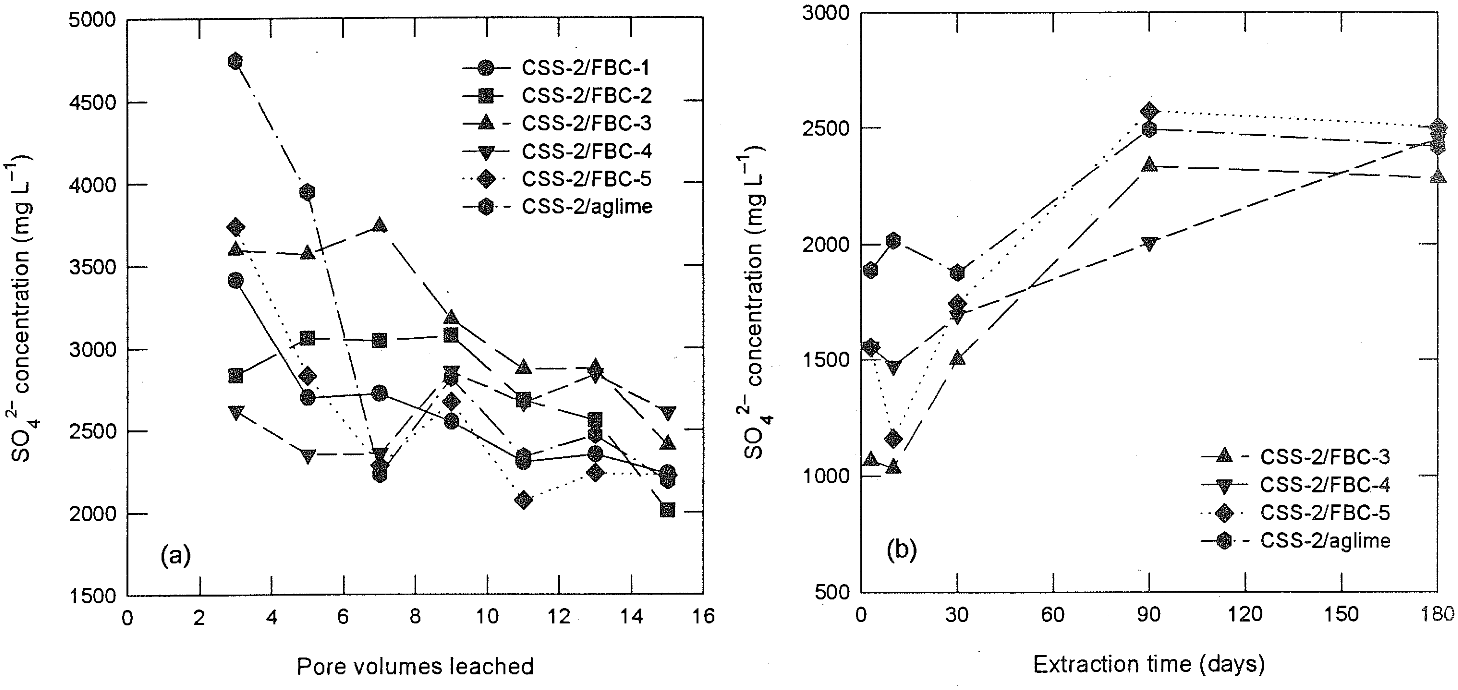


Figure 10 Sulfate concentration in leachates and extracts from mixtures of FBC residues and CSS-2.

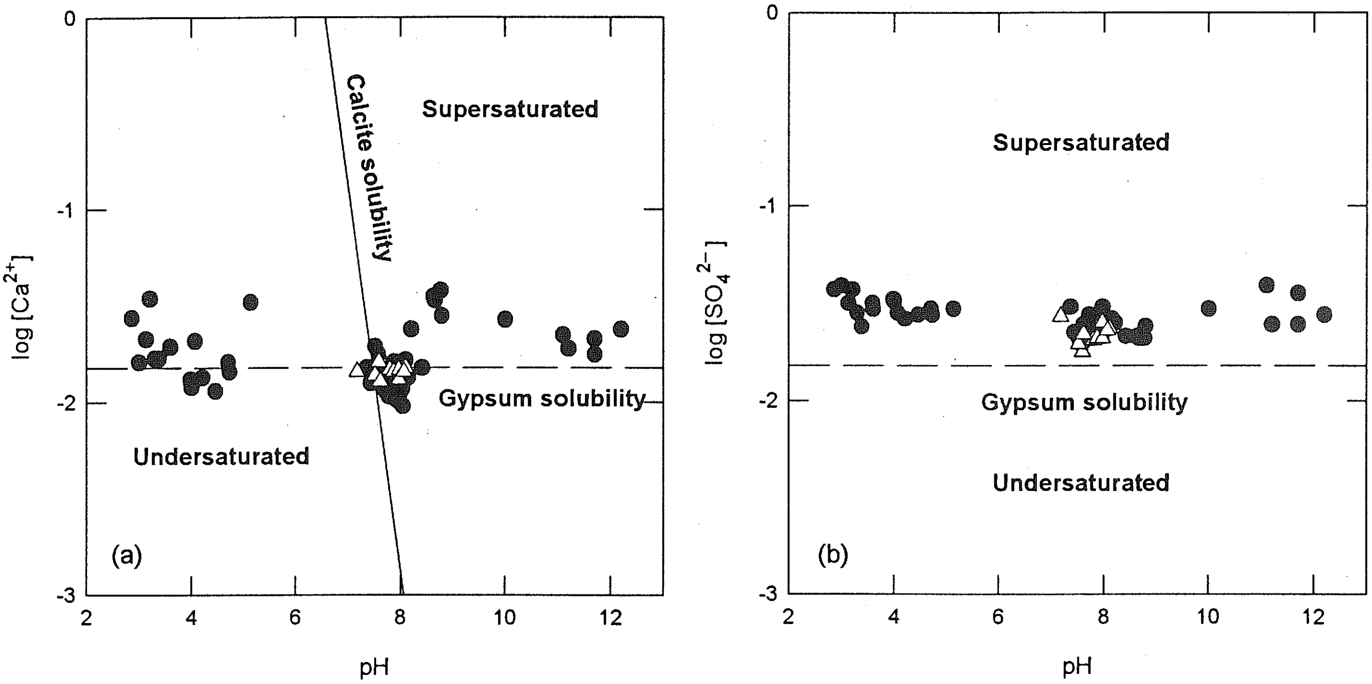


Figure 11 Molar concentrations of calcium and sulfate versus pH in leachates from mixtures of FBC residues and CSS. The filled circles represent leachates from pore volumes 3 through 13. The open triangles represent leachates from pore volume 15. The lines representing the solubilities of calcite and gypsum were calculated from data by Dean (1985).

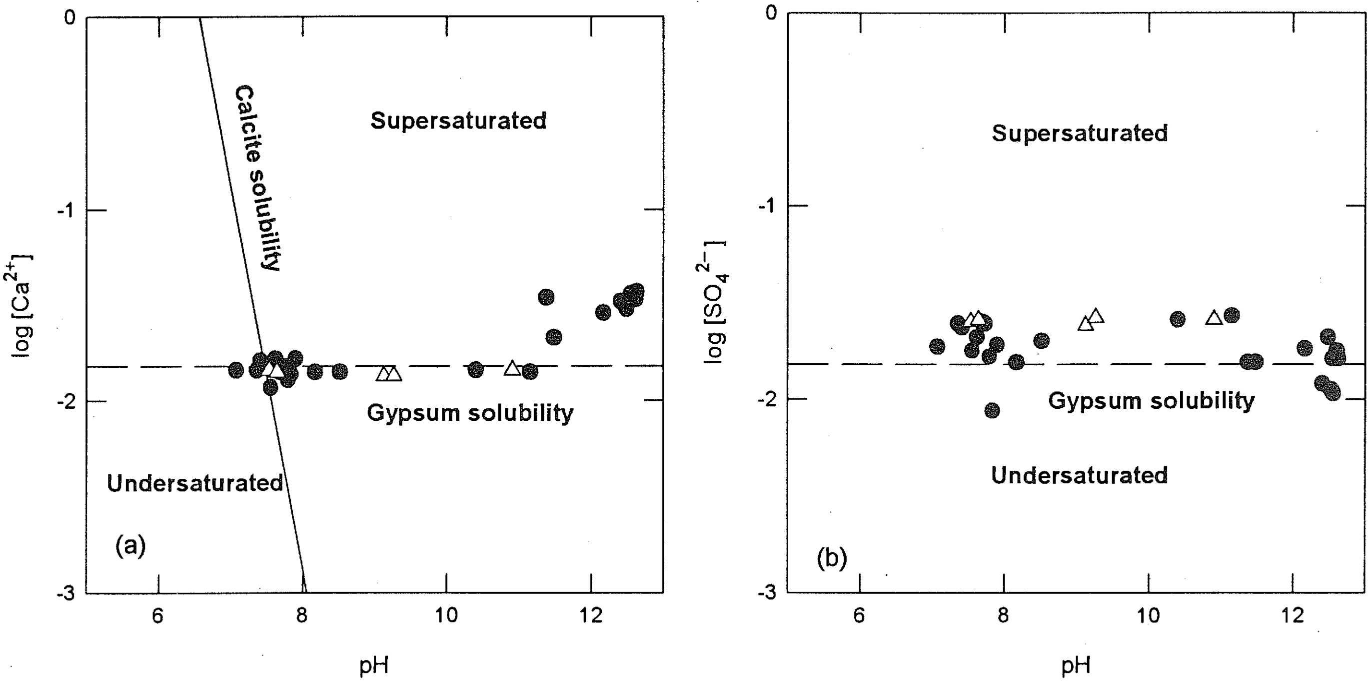


Figure 12 Molar concentrations of calcium and sulfate versus pH in extracts from mixtures of FBC residues and CSS. The filled circles represent extracts from 3 through 90 days extraction time. The open triangles represent extracts from 180 days. The lines representing the solubilities of calcite and gypsum were calculated from data by Dean (1985).

Table 10 State of Illinois General Use Water Quality Standards and ranges of concentrations of various inorganic chemicals in leachates and extracts from mixtures of CSS and FBC residues.

Constituent	Illinois Standard* (mg L^{-1})	Range of concentrations in leachates and extracts from mixtures (mg L^{-1}) CSS-1	CSS-2
pH	6.5–9.0	6.77–8.79	2.86–12.6
Ag	0.005	—[†]	—
As	0.36	<0.001–0.04	<0.001–0.08
B	5.0	1.7–12	0.03–20
Ba	5.0	0.01–0.07	0.01–0.20
Cd	0.05	<0.01	<0.01
Cl	500	4.21–5243	12.0–2598
Cr^{3+}	31	<0.01–0.06	<0.01–0.05
Cu	0.5	<0.01–0.01	<0.01–0.25
F	1.4	1.00–11.7	0.99–177
Fe	1.0	<0.01–0.03	<0.01–2.08
Hg	0.0005	<0.02–0.03	<0.02–0.03
Mn	1.0	<0.004–0.83	<0.004–13.5
Ni	1.0	<0.03–0.07	<0.03–2.90
Pb	0.1	<0.08	<0.08
Se	1.0	<0.01–1.4	<0.01–3.3
SO_4^{2-}	500	840–4211	1030–4746
Zn	1.0	<0.004–0.057	<0.004–0.12

*From State of Illinois Rules and Regulations (1995)

[†] — = not determined

figure 12a. The contradiction between the modeling results and the graphical results might have been caused by the use of carbon dioxide partial pressure in modeling rather than alkalinity values.

Table 10 compares the concentrations of various constituents in the leachates and extracts from mixtures of FBC residues and CSS with the Illinois General Use Water Quality Standards (State of Illinois 1995). Several constituents were present at concentrations below the respective standard in all leachates and extracts, but most were present at concentrations above the respective standard in some of the leachates and/or extracts. Only SO_4^{2-} was present at concentrations above its standard in all leachates and extracts. The leachates from mixtures of CSS and FBC residue or aglime had higher concentrations of both Na^+ and Cl^- than those from unmixed samples. At pore volumes 9 through 15, Na^+ concentrations were 700 mg L^{-1} or less and Cl^- concentrations were less than 400 mg L^{-1} in leachates from mixtures of CSS-2 and FBC residues. In all other leachates, the concentrations of Na^+ were 200 mg L^{-1} or less, and Cl^- concentrations were 65 mg L^{-1} or less.

At low concentrations, chloride is an essential nutrient for plants, but at 500 mg L^{-1} Cl^- is toxic to most sensitive plants (Severson and Shacklette 1988), and it would probably be toxic to plants used in revegetation (Gough et al. 1979). Excess Cl^- will cause yellowing and burning in leaves. Sodium interferes with a plant's ability to absorb water through the roots. In addition, sodium required five to seven pore volumes of leaching to decrease its concentration to less than 500 mg L^{-1}. The presence of these ions in the pore water of a codisposed mixture of FBC residue and CSS is a cause for concern and will need to be monitored during the early phases of revegetation.

The concentration of K^+ was high (up to 2700 mg L^{-1}) in leachates from the unmixed samples of FBC-1, FBC-2, and FBC-5, whereas in the extracts, the highest concentration was 220 mg L^{-1}. The concentration of Mg^{2+} was generally higher in leachates from mixtures containing CSS-2 (≤230 mg L^{-1}) than in those containing CSS-1 (≤70 mg L^{-1}), and leachates from mixtures that contained aglime had higher concentrations of Mg^{2+} than those that contained FBC residues. In the batch extracts, the Mg^{2+} concentrations from mixtures that contained CSS-1 were higher than in those from mixtures that had CSS-2. The unmixed CSS-2 contained twice the concentration of Mg (0.8% as MgO) as the unmixed CSS-1 (0.4% as MgO). Unmixed FBC residues contained concentrations of Mg (as MgO) between 0.62% and 1.05%. Neither K^+ nor Mg^{2+} appeared to be present in the leachates or extracts of the mixtures at concentrations that would be toxic to plants.

The trace elements of note in the leachates from mixtures with either CSS-1 or CSS-2 were B, Se, Ni, and Mo (table 10). Boron concentrations were independent of pH and were higher in leachates from the unmixed aglime sample (0.20–0.36 mg L^{-1}) than in those from the unmixed FBC residues (0.03–0.18 mg L^{-1}), but they were highest in the leachates from the unmixed CSS materials (0.66–3.9 mg L^{-1}). The concentration of B in the extracts ranged from 0.03 to 3.2 mg L^{-1}. Severson and Shacklette (1988) indicated that sensitive plants may show symptoms of toxicity to B when the concentration in water used for irrigation is greater than 0.75 mg L^{-1}. Boron may be removed by adsorption on $Al(OH_3)$, and the liming of acidic soils increases the adsorption. Boron in the codisposal situation could quite possibly occur at subtoxic concentrations. Selenium and nickel occurred at elevated concentrations in leachates from mixtures with CSS-2. Selenium, which occurs as an anion in aqueous solution, was mildly correlated with pH ($r^2 = 0.68$) in leachates from CSS-1 mixtures. Nickel was correlated with other chalcophile elements, such as selenium and copper, but not with SO_4^{2-}. These findings for nickel may indicate that pyrite oxidation was not the sole source of sulfate in the leachates, but that anhydrite was also a contributor. Molybdenum, which also occurs as an anionic species in aqueous solution, was moderately correlated with pH ($r^2 = 0.77$). For those solutes that displayed a correlation with pH, one can expect that the concentration of such a solute will change if the pH of the leachate changes in a codisposal situation.

The concentration of F^- in the leachates after about the seventh pore volume generally ranged from 2 to 4 mg L^{-1}. The concentration of F^- in the extracts ranged from 1 to 5 mg L^{-1}. If the codisposed mixture of CSS and FBC residue is not allowed to leach prior to sowing seeds, toxic concentrations of F^- could be present.

Manganese is not expected to be toxic to plants used in revegetation, especially if the growth medium is maintained in a slightly alkaline condition. Of the various aqueous species of Mn, only Mn^{2+} is absorbed by plants (Severson and Shacklette 1988). At alkaline pH, Mn is effectively removed from the soil solution by precipitation as oxyhydroxides.

Selenium was found to substitute for S in pyrite (Finkelman 1981). If Se was associated with the pyrite in the CSS materials, then as pyrite oxidation proceeded, Se would have been released to the leachate solution. Selenium in the FBC residues was probably associated with the coal ash portion of the residues. The greatest concentrations of Se (fig. 13) were detected in leachates from mixtures with CSS-2, which had the greater pyrite content of the two coal slurry samples. Selenium attained steady-state concentrations of <1 mg L^{-1} in mixtures containing CSS-2 and <0.05 mg L^{-1} in the later pore volumes from mixtures containing CSS-1.

Sulfate is probably the only form of sulfur absorbed by plants (Severson and Shacklette 1988), and it is used in metabolic functions, such as in the production of chlorophyll and the synthesis of amino acids. The presence of SO_4^{2-} at the observed concentrations in the pore water of a codisposed mixture of FBC residue and CSS is not expected to be deleterious to the plants used in reclamation of the site (Gough et al. 1979).

The concentrations of Al, As, Be, Cd, Cr, Cu, Hg, Mo, Se, and Zn in the leachates were less than the levels indicated by Gough et al. (1979) as being toxic to plants. B, Cl^-, Co, F^-, Mn, and Ni at their highest observed concentrations could be toxic to some plants, depending on the sensitivity of the plant to the element and the ability of the plant to absorb that element. The latter constituents were present at potentially toxic concentrations in some leachates from some solid samples, and in these cases, the mixture usually contained CSS-2. Sodium, another element potentially toxic to plants, was present in the initial leachates at concentrations that might inhibit the ability of plants to absorb water through the roots.

SUMMARY

The particle-size distribution of FBC residues varies between residues. Those residues with a predominance of smaller particles (FBC-1, FBC-2, and FBC-5) are expected to dissolve more quickly than the others upon weathering. Therefore, application of an FBC residue having small particles to CSS may be required more frequently than those with larger particles. The use of only bed ash rather than a mixture of fly ash and bed ash may be advisable in codisposal because bed ash particles are typically about 1 to 2 mm or larger in diameter.

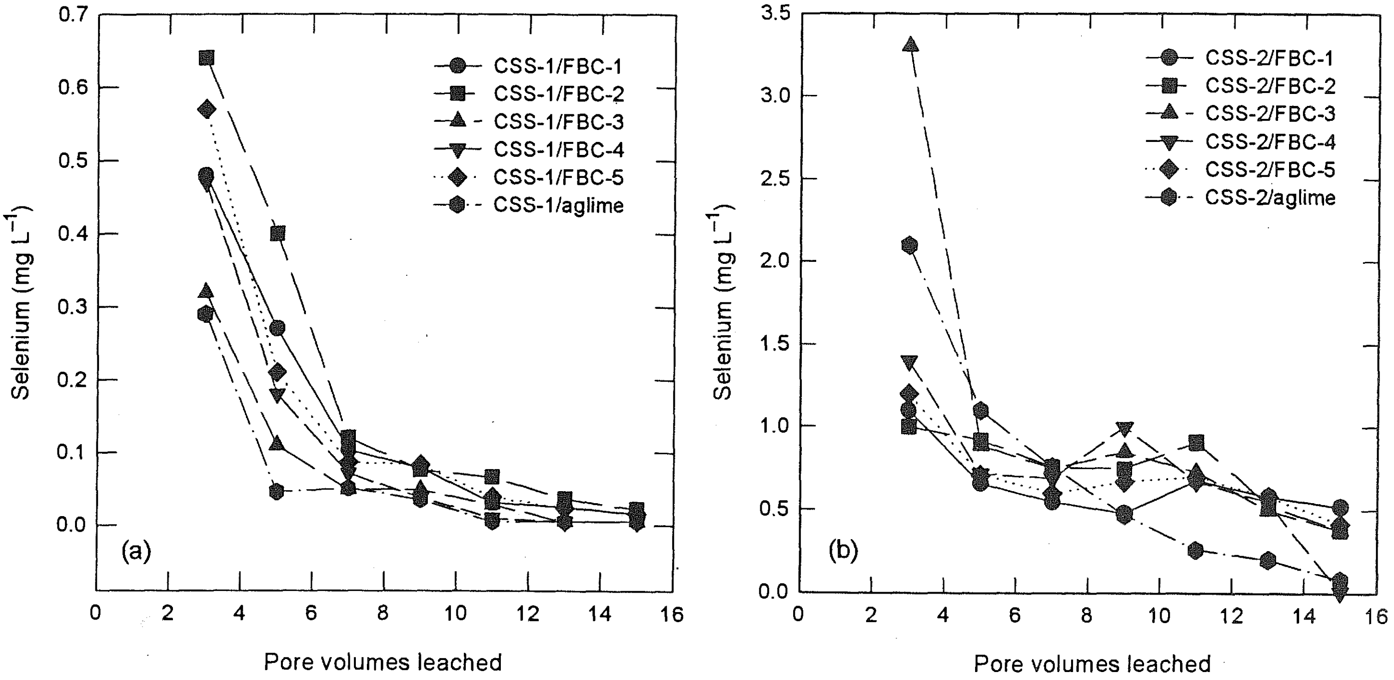


Figure 13 Concentrations of selenium in leachates from mixtures of FBC residues and CSS.

The major minerals in the FBC residues were calcium oxide and calcium sulfate. On exposure to atmospheric moisture and carbon dioxide, the calcium oxide was sequentially converted to calcium hydroxide and calcium carbonate. The presence of calcium carbonate is preferable to calcium oxide or hydroxide in reclamation because a solution of calcium carbonate has a pH that is more tolerable to plants. The major minerals in the coal slurry solid were quartz and clay minerals, with lower amounts of pyrite and calcite.

Pyrite in coal slurry solid was oxidized in laboratory wet-dry leaching experiments in the presence of alkaline fluidized-bed combustion residues. Similar oxidation under saturated conditions was not obvious from the batch extraction data, even with periodic aeration of the extraction solution. In addition, FBC residue can be as effective as aglime of similar particle-size distribution in neutralizing the acid generated during pyrite oxidation, and the pH of leachate from FBC residue is approximately the same as that from aglime-CSS mixtures. The portlandite from the original hydrated FBC residue was largely converted to calcium carbonate in a short time in the FBC residue-CSS mixtures. Solutions from either the wet-dry leaching or the batch extraction experiments attained a pH of between 7 and 8, which is indicative of equilibrium between calcite and gypsum. Bassanite was detected by XRD in the leached solids that contained CSS-2, but it was probably an experimental artifact created by the dehydration of gypsum during sample preparation.

The most abundant ions in the leachates and extracts from FBC residues-CSS mixtures were Ca^{2+}, Na^+, SO_4^{2-}, and Cl^-. The solutions appeared to be in equilibrium with gypsum or calcite. The trace constituents that occurred at notable concentrations in the leachates and extracts and were of environmental interest were B, Se, Ni, and Mo. The extracts from the mixtures generally had lower concentrations of the trace constituents than the leachates, which may indicate that trace constituent concentrations would be decreased in the saturated zone of coal slurry solid when codisposed with FBC residue. At the observed concentrations, B, Cl^-, Co, F^-, Mn, and Ni could be toxic to plants used in the revegetation of codisposed FBC residue and CSS.

Scanning electron microscopy (see appendix) of particles of FBC bottom ash and fly ash showed that particles of CaO react with SO_2 in the fluidized-bed combustor from the outside of the particle toward the center. The presence of an elevated concentration of magnesium in the particles appears to inhibit reaction with SO_2.

ACKNOWLEDGMENTS

We thank Randall E. Hughes and Duane M. Moore, Illinois State Geological Survey, for XRD analyses and helpful discussions on mineralogical changes that occurred during the leaching and extraction experiments. Richard D. Harvey, ISGS, provided helpful discussions related to the SEM analyses of the FBC residues. In addition, we thank the following ISGS staff members for conducting the analyses, as indicated: Robert R. Frost (XRF); Joyce K. Frost (INAA); L. R. Henderson (OEP); and Donald J. Lowry (SEM). Aaron D. Weiss, Illinois Hazardous Waste Research and Information Center, performed the ICP-MS analysis. This study was partially funded by the Illinois Department of Energy and Natural Resources (ENR) through its Coal Development Board and the Illinois Clean Coal Institute (ICCI), and the U.S. Department of Energy (DOE) (Grant Numbers DE-FG22-91PC91334 and DE-FG22-92PC92521). Any opinions, findings, conclusions, or recommendations expressed herein are those of the authors and do not necessarily reflect the views of the ENR, ICCI, or DOE. Daniel D. Banerjee, Illinois Clean Coal Institute, served as project manager.

REFERENCES

American Society for Testing and Materials, 1990, Annual Book of ASTM Standards, Methods D2492 and D3683, Volume 05.05; and Method C602, Volume 04.01, Philadelphia, PA.

Bennett, O.L., W.L. Stout, J.L. Hern, and R.C. Sidle, 1978, Potential agricultural uses of fluidized bed combustion wastes, *in* Proceedings of the 5th National Conference on Energy and the Environment, Dayton, OH, October 31–November 3, 1977: American Institute of Chemical Engineers, p. 84–89.

Bland, A.E., T.H. Brown, L.-J. Young, and J.M. Wheeldon, 1995, Hydration reaction chemistry associated with management of pressurized fluidized bed combustion ash, *in* 1995 International Ash Utilization Symposium Proceedings, Lexington, KY, October 23–25, 1995.

Borgwardt, R.H., and R.D. Harvey, 1972, Properties of carbonate rocks related to SO_2 reactivity: Environmental Science Technology, v. 6, p. 350–360.

Brownlow, A.H., 1979, Geochemistry: Prentice-Hall, Inc., Englewood Cliffs, NJ, p. 294–295.

Cahill, R.A., and A. D. Autrey, 1988, Total and inorganic carbon content of eighteen National Bureau of Standards and four Canadian Certified Reference Materials: Geostandards Newsletter, Vol. XII, p. 39–42.

Dean, J.A., editor, 1985, Lange's Handbook of Chemistry: McGraw-Hill, New York, NY, various pages.

Deer, W.A., R.A. Howie, and J. Zussman, 1962, Rock-forming minerals, Volume 5, Non-silicates: John Wiley and Sons Inc., New York, NY, p. 202–218.

Fennelly, P.F., J.O. Milliken, T. Grimshaw, R.A. Minear, L.J. Minnick, and O.L. Bennett, 1987, Environmental aspects of AFBC, *in* S. Tung and G.C. Williams, editors, Atmospheric Fluidized Bed Combustion—A Technical Source Book: U.S. Department of Energy Report no. DOE/MC/14536-2544, Washington, DC., p. 11-1–11-94.

Finkelman, R.B., 1981, Modes of Occurrence of Trace Elements in Coal: U.S. Geological Survey Open-File Report 81-99. Reston, VA, p. 203.

Finkelman, R.B., and D.E. Giffin, 1986, Hydrogen peroxide oxidation—An improved method for rapidly assessing acid-generating potential of sediments and sedimentary rocks: Reclamation Revegetation Research, v. 5, p. 521–534.

Gluskoter, H.J., R.R. Ruch, W.G. Miller, R.A. Cahill, G.B. Dreher, and J.K. Kuhn, 1977, Trace Elements in Coal—Occurrence and Distribution: Illinois State Geological Survey Circular 499, p. 44–45.

Gough, L.P., H.T. Shacklette, and A.A. Case, 1979, Element Concentrations Toxic to Plants, Animals, and Man: U.S. Geological Survey Bulletin 1466, Washington, DC., 80 p.

Graham, U.M., and J.C. Hower, 1994, Mineralogy and petrology of coal combustion by-products at Kentucky generating stations burning southern Illinois Basin coal: Conference Proceedings, Management of High Sulfur Coal Combustion Residues—Issues and Practices, Springfield, IL, April 5–7, 1994, p. 80–90.

Hardie, L.A., 1967, The gypsum-anhydrite equilibrium at one atmosphere pressure: American Mineralogist, v. 52, p. 171–200.

Harness, J.L., Y.C. Chung, and D.A. Mays, 1987, Shawnee AFBC demonstration project ash utilization program, *in* J.P. Mustonen, editor, Proceedings of the 1987 International Conference on Fluidized Bed Combustion, Boston, MA, May 3–7: American Society of Mechanical Engineers, v. 2, p. 927–934.

Harvey, R.D., R.A. Cahill, C.-L. Chou, and J.D. Steele, 1983, Mineral Matter and Trace Elements in the Herrin and Springfield Coals, Illinois Basin Coal Field: Illinois State Geological Survey Contract/Grant Report 1983-4, p. 65, 80.

Hughes, R.E., D.M. Moore, and H.D. Glass, 1994, Qualitative and quantitative analysis of clay minerals in soil, *in* J.E. Amonette and L.W. Zelazny, editors, Quantitative Methods in Soil Mineralogy: Soil Science Society of America Miscellaneous Publication, Madison, WI, p. 330–359.

Hurlbut, C.S., Jr., 1961, Dana's Manual of Mineralogy: John Wiley & Sons, Inc., New York, NY, 338 p.

Korcak, R.F., 1979, Fluidized bed material as a calcium source for apples: HortScience, v. 14, p. 163–164.

Korcak, R.F., 1980, Fluidized bed material as a lime substitute and calcium source for apple seedlings: Journal of Environmental Quality, v. 9, p. 147–151.

Lindsay, W.L., 1979, Chemical Equilibria in Soils: John Wiley & Sons, New York, 449 p.

Nawrot, J.R., S.C. Yaich, and W.D. Klimstra, 1985, Enhancing reclamation through selective slurry disposal, *in* Proceedings of the Illinois Mining Institute Annual Meeting, Springfield, IL, October 4–5, 1984, p. 48–9.

Nawrot, J.R., W.D. Klimstra, J. Sandusky, and R.W. Holloway, 1989, Wetland reclamation—Meeting needs and mitigating losses, *in* Proceedings of the Illinois Mining Institute Annual Meeting, Mount Vernon, IL, September 29–30, 1988, p. 87–101.

Severson, R.C., and H.T. Shacklette, 1988, Essential Elements and Soil Amendments for Plants—Sources and Use for Agriculture: U. S. Geological Survey Circular 1017, Washington, DC, 48 p.

Sidle, R.C., W.L. Stout, J.L. Hern, and O.L. Bennett, 1979, Solute movement from fluidized bed combustion waste in acid soil and mine spoil columns: Journal of Environmental Quality, v. 8, p. 236–241.

Sisler, H.H., C.A. VanderWerf, and A.W. Davidson, 1961, College Chemistry: Macmillan, New York, NY, 546 p.

State of Illinois, 1995, Rules and Regulations, Title 35, Environmental Protection; Subtitle C: Water Pollution; Chapter I: Pollution Control Board; Part 302: Water Quality Standard; Subpart B: General Use Water Quality Standards, p. 9–13.

Stout, W.L., H.A. Menser, J.L. Hern, and O.L. Bennett, 1979a, Fluidized bed combustion waste in food production, *in* Proceedings of American Society of Civil Engineers/Power Research Council-Electric Power Research Institute Workshop on Solid Waste Research and Development Needs for Emerging Coal Technologies, San Diego, CA, April 23–25, 1979: Society of Civil Engineers, p. 170–184.

Stout, W.L., R.C. Sidle, J.L. Hern, and O.L. Bennett, 1979b, Effects of fluidized bed combustion waste on the Ca, Mg, S, and Zn levels in red clover, tall fescue, oat, and buckwheat: Agronomy Journal, v. 71, p. 662–665.

Stout, W.C., H.A. Menser, O.L. Bennett, and W.M. Winant, 1982, Cover establishment on an acid mine soil using composted garbage mulch and fluidized bed combustion waste: Reclamation Revegetation Research, v. 1, p. 203–211.

Tavoulareas, S., W. Howe, D. Golden, and G. Eklund, 1987, Research on AFBC byproduct management, *in* J. P. Mustonen, editors, Proceedings of the 1987 International Conference on Fluidized Bed Combustion, Boston, MA, May 3–7: American Society of Mechanical Engineers, v. 2, p. 916–926.

Terman, G.L., V.J. Kilmer, C.M. Hunt, and W. Buchanan, 1978, Fluidized bed boiler waste as a source of nutrients and lime: Journal of Environmental Quality, v. 7, p. 147–150.

Thomas, G.W., 1982, Exchangeable cations, *in* A.L. Page, R.H. Miller, and D.R. Keeney, editors, Methods of Soil Analysis, Part 2, 2nd edition: American Society of Agronomy and Soil Science Society of America, Agronomy Monogram 9, Madison, WI, p. 159–165.

U.S. Environmental Protection Agency, 1990, Geochemical assessment model for environmental systems, version 3.0: Environmental Research Laboratory, Office of Research and Development, Athens, GA, MINTEQA2/PRODEFA2, 110 p.

Williamson, M.A., and J.D. Rimstidt, 1994, The kinetics and rate-determining step of aqueous pyrite oxidation: Geochimica Cosmochimica Acta, v. 58, p. 5443–5454.

ZoBell, C.E. 1946, Studies on redox potentials of marine sediments: American Association of Petroleum Geology Bulletin 30, p. 477–513.

APPENDIX Scanning Electron Microscopy of FBC Residue

SEM-EDS analyses indicated some particles in the bottom ash were enlarged by accretion of molten material during combustion (fig. 14a). The outer portion of a particle of bottom ash from FBC-1 (fig. 14a) contained relatively high concentrations of Si, Al, and Ca but very little S, and the core was quartz. A more detailed examination of the particle (fig. 14b) revealed that the porosity of the outer material was low, although some radial fractures were evident at the interface with the core. The circular cross section of the particle, its apparent low porosity, chemical composition, and a faint hint of concentric structure in its outer layer suggested that the particle was enlarged by accretion of molten coal ash to the quartz core during the combustion process. A similarly shaped particle (fig. 15a) that had a $CaSO_4$ core and an outer surface of Si, Al, and Ca was found in the same sample of bottom ash. The sample also contained particles of $CaSO_4$ that had no accretions of molten coal ash. Most fly ash particles in FBC-1 had angular morphologies (fig. 15b) and consisted of $CaSO_4$ or unreacted lime. Only a few spherical particles were found.

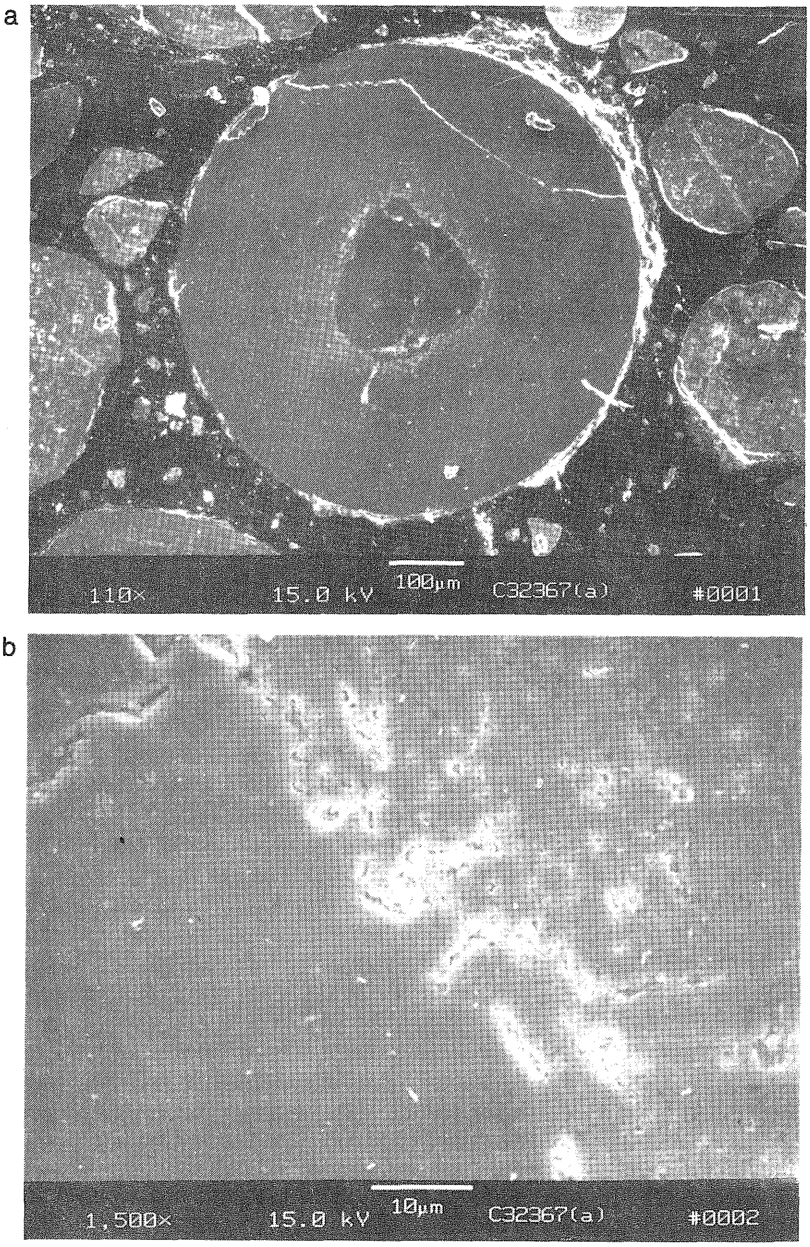


Figure 14 Scanning electron micrographs of particles of bottom ash in an FBC residue. (a) Quartz core surrounded by apparently accreted Si-Al-Ca coating. (b) Enlarged view of the interface between the quartz core (left) and the Si-Al-Ca coating.

Other calcium-containing bottom ash particles had reacted with SO_2 from the outside of the particle inward (fig. 16a); high Mg content in another particle of bottom ash appeared to inhibit the reaction of the sorbent with SO_2 (fig. 16b). Examination of the particle of bottom ash from FBC-2 (fig. 16a) showed that the particle contained almost exclusively Ca, S, and O. The light colored surface layer of the particle was the result of more extensive reaction of CaO with SO_2 than in the dark-colored core. The particle of bottom ash from FBC-2 (fig. 16b) had three distinct areas. The core and the outermost ring showed extensive reaction with SO_2, whereas the central ring showed no reaction with SO_2. All three areas contained Mg and Ca, but the central ring contained approximately 2.5 times more Mg than either the outer ring or the core. The core of the particle was subject to reaction with SO_2, evidently because of breaches similar to that visible in the photomicrograph at the top of the less reactive center ring, which may have allowed SO_2 gas to penetrate. The observations suggest that a high ratio of Mg to Ca inhibits the reaction of Ca with SO_2. Borgwardt and Harvey (1972) found that magnesite ($MgCO_3$) did not react readily on exposure to SO_2 at temperatures between 540° and 980°C.

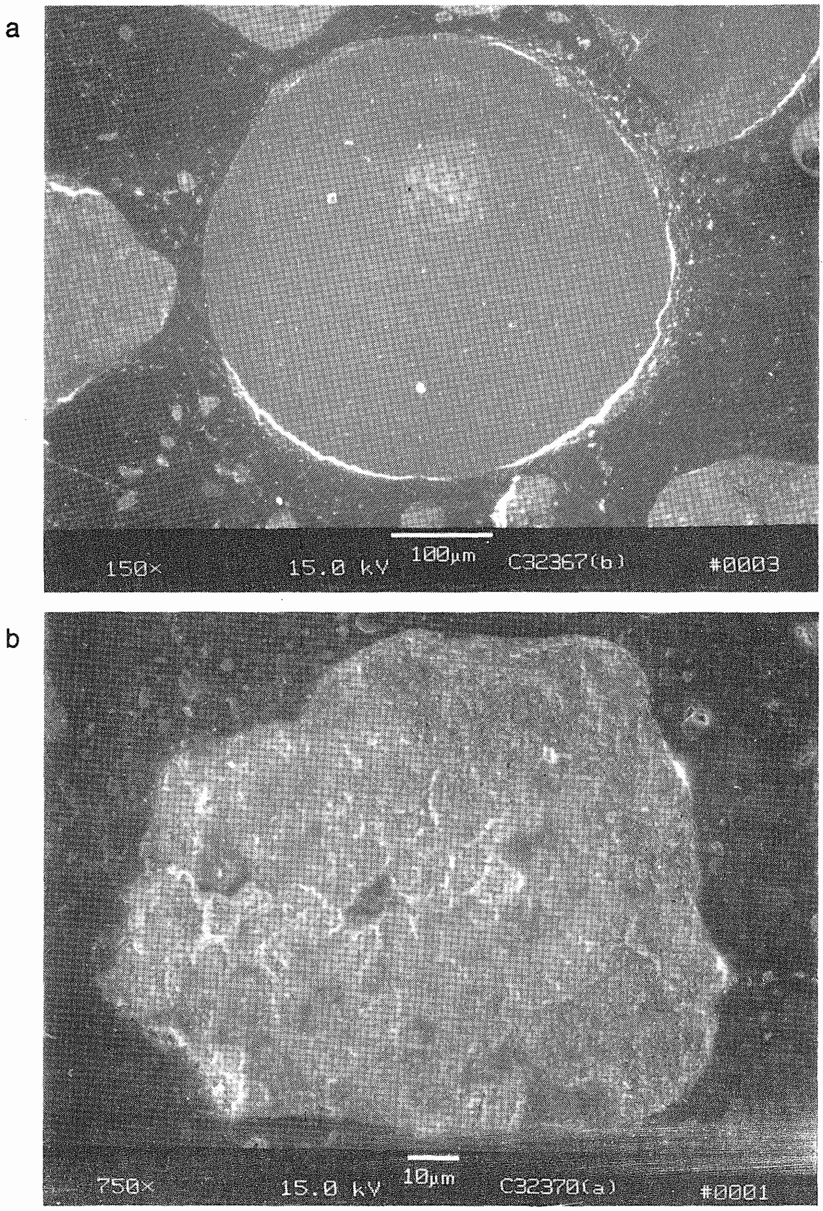


Figure 15 Scanning electron micrographs show the morphology of spherical and angular particles of fly ash from an FBC residue. (a) A particle of fly ash with a center (light colored area) of probably $CaSO_4$ and a Si-Al-Ca coating. (b) An angular particle of fly ash, predominantly of calcium sulfate.

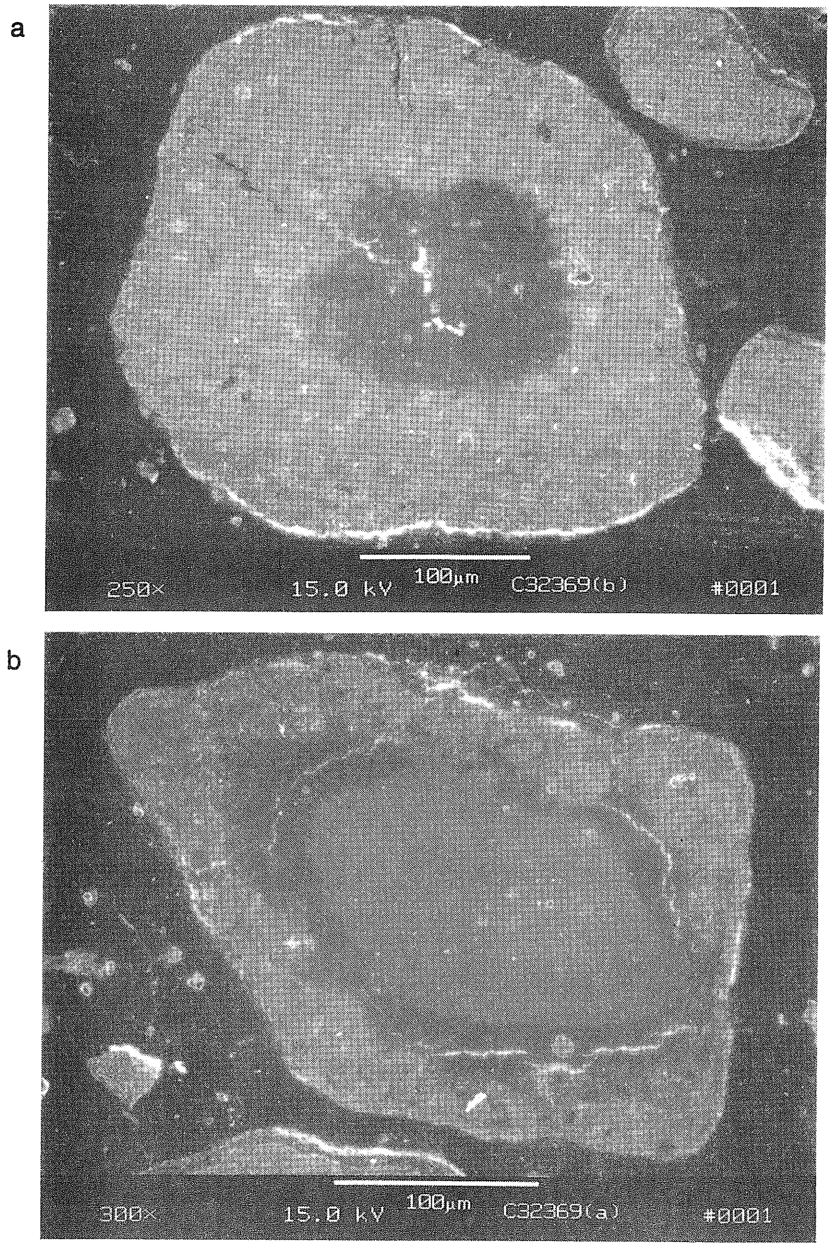


Figure 16 Scanning electron micrographs of bottom ash particles from FBC residues. (a) Light outer ring is the product of the reaction of CaO with SO_2 and H_2O to form $CaSO_4$. The dark core is unreacted CaO. (b) Similar to a, except the dark middle region is high in magnesium. Reaction with SO_2 in this region was inhibited.