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Project Title: The use of FBC wastes in the reclamation of
coal slurry solids

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ABSTRACT

Fluidized bed combustion (FBC) is a relatively new technology that is used commercially for the combustion of coal. In Illinois, this technology is valuable because it facilitates the combustion of Illinois high sulfur coal without pollution of the atmosphere with sulfur oxides. In FBC, coal is mixed with limestone or dolomite either before injection into the combustion chamber or in the combustion chamber. As the coal burns, the sulfur in the coal is oxidized to SO_2 which is trapped by reaction with the limestone or dolomite to form anhydrite ($CaSO_4$). Solid by-products from FBC are generally a mixture of calcium oxide, anhydrite, coal ash, and unburned coal. The present research project is designed to provide initial data on one possible use of FBC waste. FBC waste and coal slurry solid (CSS) were mixed together to allow the alkaline components of the FBC waste to neutralize the acid produced by the oxidation of pyrite in the CSS. An objective of this research was to determine the chemical composition of aqueous leachates from such mixtures. These data will be used in future research into the ability of mixtures of CSS and FBC waste to support seed germination and plant growth. The final goal of this and future research is to determine whether mixtures of CSS and FBC waste can be used as a satisfactory growing medium in slurry pond reclamation.

Five fluidized bed combustion (FBC) wastes, one agricultural limestone (Ag LS), and two coal slurry solids (CSS) samples were characterized chemically and mineralogically. Mixtures of the materials (FBC waste or Ag LS and CSS) were prepared and subjected to leaching with deionized water in laboratory experiments and with meteoric water in outdoor weathering experiments. The major cations in the leachates were calcium and sodium, with minor concentrations of magnesium and potassium. The major anions were chloride and sulfate, with minor amounts of fluoride and bicarbonate.

The major minerals in the unleached FBC wastes were calcium oxide and calcium sulfate (anhydrite). The calcium oxide was hydrated upon wetting to calcium hydroxide, which was converted to calcium carbonate (calcite) upon exposure to atmospheric carbon dioxide, or carbon dioxide from the neutralization reaction of acid with calcite. The calcium hydroxide controlled the pH of leachates in the early leaching period, whereas calcite controlled the pH in the later leaching period. The alkaline calcium species in the FBC wastes effectively neutralized the acid generated by pyrite oxidation.

In extracts generated by the Toxicity Characteristic Leaching Procedure (TCLP), selenium was found to be above the U.S. EPA primary drinking water maximum contaminant level (MCL) in extracts from each of the FBC wastes and CSS samples. Mercury was above its MCL in the extract of FBC-2. The other six constituents (As, Ba, Cd, Cr, Pb, and Ag) were below their corresponding MCLs. Hence, these FBC wastes would not be classified as hazardous under the Resource Conservation and Recovery Act (RCRA) if the status of coal combustion wastes were to be revised.

EXECUTIVE SUMMARY

The overall objective of this research is to develop an environmentally acceptable method for utilizing or disposing of fluidized bed combustion (FBC) wastes. The method of disposal being investigated in the present research is the codisposal of FBC waste with coal slurry solids from a coal preparation plant. This disposal scheme would combine two wastes that, individually, would produce objectionable pH in ground water. In combination, the two wastes may attain a near-neutral pH. In so doing, the solubilities of several trace metals, normally somewhat soluble in acidic solutions, could be decreased.

The specific goals for this research year have been to determine the efficacy of FBC wastes in buffering the acidity generated by the oxidation of pyritic coal slurry solids, and to determine the chemical composition of leachates from mixtures of FBC wastes and coal slurry solids.

Samples of FBC wastes were collected from five fluidized bed combustion operators within 200 km of Champaign, IL, samples of coal slurry solids from two coal mining companies, and agricultural limestone from one quarry.

The particle-size distribution of all initial solids were determined. All solids were chemically and mineralogically characterized. The calcium speciation of the FBC wastes was determined and the acid-producing potential of the coal slurry solids was estimated (by means of a hydrogen peroxide oxidation technique). Using these data, the proportion of FBC waste needed to neutralize the potential acidity of the coal slurry solids was estimated. Mixtures of FBC waste or agricultural limestone and coal slurry solid were prepared and tested by laboratory leaching and by outdoor weathering experiments which lasted for several months. All leachates were collected for chemical analysis.

The FBC wastes and coal slurry samples were submitted to an outside laboratory for evaluation according to the U.S. EPA Toxicity Characteristic Leaching Procedure (TCLP) for eight Resource Conservation and Recovery Act (RCRA) inorganic constituents. Selenium occurred at a concentration greater than the Maximum Contaminant Level (MCL) established by the U.S. EPA in leachates from each of the initial solids. Mercury occurred above its MCL in leachate from FBC-2 only. However, neither constituent occurred at concentrations greater than the RCRA limit for hazardous wastes. According to the test results, if byproducts of coal cleaning and coal combustion were subject to the RCRA disposal rules these wastes would not be classified as hazardous on the basis of the selenium concentrations in the leachates.

The major cations in the leachates were calcium and sodium. Magnesium and potassium occurred in minor concentrations. Sulfate and chloride were the major anions in the leachates, and bicarbonate and fluoride occurred at minor concentrations. In the leachates from the early pore volumes, calcium, sodium, chloride, and sulfate occurred at concentrations of thousands of mg/L. Calcium solubility appears to have been controlled by the solubility of gypsum, the product of neutralization of acid and sulfate produced by pyrite oxidation with either calcite or calcium hydroxide.

The calcium oxide that was initially present in the FBC wastes was purposely hydrated to calcium hydroxide prior to packing the leaching vessels. This was done to prevent fracturing of the leaching vessels due to volume expansion of the FBC waste that would accompany the hydration had the wastes been hydrated after packing the vessels. The pH of the

leachates was probably controlled by the solubility of calcium hydroxide in the early leaching period, and by calcium carbonate in the latter leaching period. Comparisons of the chemical and mineralogical data from the unleached and leached solids indicate that calcium hydroxide present in the unleached solids was converted rather rapidly to calcium carbonate by exposure to carbon dioxide, either atmospheric, or that which evolved during the neutralization of calcite by the acid.

Sodium and chloride in the leachates were probably dissolved from soluble salts or minerals contained in the mixtures. Both sodium and chloride were present in the initial leachates of mixtures of coal slurry solids and FBC wastes at concentrations that were higher than were observed in leachates from any of the individual solids (control samples).

These concentrations of sodium and chloride may be toxic to plants, so reclamation of codisposed FBC waste and coal slurry solid may require flushing of the material prior to seeding. Certain trace elements, including B, Co, F, Mn, and Ni may be toxic to plants at the concentrations observed in the early leachates.

FBC waste is effective in neutralizing the acid produced by oxidation of pyrite. Although calcite is the long-term neutralizing agent, initially, the presence of calcium hydroxide provides a more potent alkaline agent. Co-disposal may decrease the solubility (and hence the mobility) of trace cationic groundwater contaminants by maintaining a neutral pH, but may have little effect or a deleterious effect on the mobility of anionic constituents such as As, Se, Mo, and B derived from the tested materials.

OBJECTIVES

The overall objective of this research project was to develop an
environmentally acceptable method for utilization or disposal of coal
fluidized bed combustion (FBC) waste. The disposal method under study is
the codisposal of FBC waste with coal slurry solids from a coal
preparation plant in order to prepare a medium suitable for growing
grasses and/or legumes after the closure of a slurry pond. The overall
objective could not be met in one year of research. It requires a
laboratory study to characterize the materials, of which the present
research is part, then a greenhouse study conducted under the guidance
of a soil ecologist, followed by an agronomic field study at a coal
preparation plant, which will require the cooperation and interest of a
coal mining company.

The scope of the present project was to determine (1) the efficacy of
FBC waste in buffering the acidity generated by the oxidation of pyritic
coal slurry solids, and (2) the nature and chemical composition of
effluent passing through mixtures of FBC waste and coal slurry solids.
Another objective was to provide information on the potential leaching
of groundwater contaminants, and on the chemical composition of the
"soil" solution which, in turn, may determine the types of plants to be
used in future studies for reclamation.

INTRODUCTION AND BACKGROUND

In the fluidized bed combustion of high-sulfur coal, powdered or ground
limestone is injected into the fluidized bed to serve as a "trap" for
sulfur dioxide emitted from the coal as a result of combustion. The
calcium carbonate loses carbon dioxide as a result of heating to
temperatures above 900°C, to form calcium oxide. When the sulfur dioxide
reacts with the calcium oxide and water, it forms gypsum. Typically, the
oxide is not completely converted to gypsum in the process, so much of
the waste material may consist of calcium oxide. However, the waste will
also contain mineral matter residue from the combusted coal, and
possibly some uncombusted coal.

Presently, most of the fluidized bed combustion wastes from central
Illinois are returned to the mine that supplied the coal, presumably for
disposal in the backfill, in the case of a surface mine, or in abandoned
rooms, in the case of an underground mine. This research project was
part of a laboratory study of the suitability of the fluidized bed
combustion waste as a neutralizing or buffering agent in the reclamation
of coal slurry solids. We plan to continue the laboratory studies during
the coming research period.

Coal slurry solids result from the removal of pyrite and rock fragments
in the process of cleaning coal. Fine, pyritic, coaly particles and
clay-rich particles are removed from the coal and are discharged in a
water stream to a slurry pond. The water is drained from the slurry and
is recycled. Eventually, the slurry pond reaches its solids-holding
capacity and its use has to be discontinued. At this point, the mine
operator must reclaim the remains of the pond in some manner.

One possible method for reclamation is to buffer the coal slurry solids
with alkaline fluidized bed combustion wastes and to grow plants on the
amended coal slurry solids to provide some stability against erosion.
Two major concerns in this application are the leaching of potential
groundwater contaminants, and the ability of the fluidized bed
combustion waste to buffer the potential acidity produced by the
oxidation of pyrite in the coal slurry solids. These aspects were
addressed in this research by means of appropriate aqueous leaching

experiments using mixtures of five fluidized bed combustion wastes with two coal slurry solids.

In any proposed waste disposal method, the effect of that waste on the immediate environment should be known. In co-disposing fluidized bed combustion (FBC) waste with coal slurry solids (CSS), the principal environmental effects will be those caused by aqueous leachates from the waste products. As atmospheric precipitation falls on such a waste deposit, snow melt or rain water will either infiltrate the material or run off. The components of the leachate or runoff will affect groundwater, surface water, plants, or animals. One of the first steps in determining the effects of leachate is to determine its composition, which will probably change with time as chemical reactions within the waste deposit occur.

This research was designed to characterize (1) the unleached wastes, (2) the leachates from laboratory leaching and outdoor weathering experiments, using mixtures of FBC waste with coal slurry solid, and (3) changes in the mixed wastes as a result of leaching and weathering.

EXPERIMENTAL PROCEDURES

Mixtures of FBC waste with coal slurry solid were prepared based on the calcium carbonate equivalent of the FBC waste and the acid-generating potential of the coal slurry solid. Experiments in which agricultural limestone was used in place of FBC waste were included to provide points of comparison for the behavior of the FBC waste-CSS mixtures. The limestone was prepared so that its particle-size distribution was approximately the same in each case as the FBC waste to which it was compared.

Coal slurry solid contains pyrite, which upon oxidation, produces acid. The FBC waste is high in unreacted calcium oxide from the calcination of calcium carbonate (limestone), which occurs during the combustion process. It is expected that in mixtures of FBC waste with CSS, the acid produced by pyrite oxidation will be buffered by the alkaline components of the FBC waste.

Samples. Samples of FBC waste were collected from five operators within a radius of 200 km of Champaign, IL. Three of the five samples were supplied as composite grab samples of bottom ash and fly ash. The other two samples were supplied as separate fly ash and bottom ash components. Prior to use in the leaching experiments, portions of the fly ash and the corresponding bottom ash were mixed in the proportions of 75% fly ash to 25% bottom ash, according to the operators' estimates of ash production at the plants. In each case, the samples were collected at the outflow of the respective ash silo. We were unable to collect statistically representative samples of any entire ash silo. All samples were collected in plastic buckets and were sealed immediately after collection. The amount of each FBC waste collected is shown in Table 1.

Each FBC waste was passed through a No. 6 (3.36 mm opening) sieve to remove large particles of shale, unburned coal, and limestone that might bias the experiments. The weight percent of each FBC waste that was greater than 3.36 mm is shown in Table 1. The FBC wastes were split into appropriate masses by using a riffle sampler.

A grab sample of coal slurry solid was collected from a "dry" location at each of two coal slurry ponds. Approximately 110 kg of each CSS was shoveled into five five-gallon plastic buckets. The buckets were sealed immediately. The coal slurry solid was spread onto polyethylene film in a laboratory for about two weeks to air dry. The material was mixed

periodically by hand to facilitate drying. The air-dry CSS was also split into appropriate masses by using a riffle sampler. The air-dry percent moisture and bulk density of each CSS are shown in Table 2.

A grab sample of an agricultural limestone was collected at a limestone quarry in east central Illinois. The sample consisted of two five-gallon cans of material. The sample was air-dried prior to dividing it with a riffle sampler into appropriately sized masses.

Particle-size distributions of solids. The particle-size distribution of each of the five FBC samples, two CSS samples, and the agricultural limestone sample was determined by dry sieving to segregate the particles into seven size ranges: >2000, 2000-1000, 1000-500, 500-250, 250-125, 125-62, and <62μm. A portion of the agricultural limestone was divided into the seven particle size ranges for use in preparing limestone samples whose particle-size distributions approximated those of the individual FBC samples.

Bulk and particle densities. The bulk and particle densities of the CSS samples were determined in order to calculate the amount of deionized water to be added each week to the laboratory leaching experiments. The bulk density was determined by packing the solid into a tared 1L graduated cylinder followed by weighing the cylinder plus solid and measuring the volume occupied by the solid. The solid was packed by lightly tamping the graduated cylinder on the laboratory bench top periodically while placing the solid in the cylinder.

The particle density was determined by adding a known volume of water to an empty graduated cylinder. A known weight of hydrated, oven-dried solid was then added to the water in the cylinder, and the volume of water plus solid was determined. The difference in volume was the volume occupied by the solid particles. In each case, the density was calculated by dividing the weight of the solid by the volume it occupied.

Pyrite content of CSS samples. The pyrite content of the CSS samples was estimated by the use of two methods: the hydrogen peroxide oxidation method of Finkelman and Giffen (1986), and the ASTM method for sulfur content in coals (D2492).

Exchangeable acidity of CSS samples. The exchangeable acidity of the two CSS samples was determined according to Method 9-4.2, Potassium Chloride Method (Page, 1982).

Carbonate content of FBC waste and CSS samples. The inorganic carbon content of the FBC waste CSS samples was determined by means of a Coulometrics carbon analyzer.

Cation exchange capacity of CSS samples. The cation exchange capacity (CEC) of the two CSS samples was determined by exchange of K^+ for other exchangeable ions (Page, 1982).

Calcium carbonate equivalent of FBC samples. The calcium carbonate equivalent of each FBC sample and the agricultural limestone sample was determined according to ASTM method C602, Section 14, Procedure for Blast Furnace Slag, Potentiometric Titration Method (ASTM, 1990).

Calcium oxide content of FBC samples. A weighed portion of each air-dried FBC sample was treated with deionized water until the sample was saturated. The sample was then oven dried (with periodic mixing to prevent cementation of the sample), cooled, and weighed. The weight gain

was taken as the amount of water consumed in the hydration of CaO to
$Ca(OH)_2$.

Toxicity Characteristic Leaching Procedure. Portions of each FBC waste
and CSS sample were sent to Environmental Science and Engineering,
Peoria, IL for testing in accordance with the U.S. EPA Toxicity
Characteristic Leaching Procedure (TCLP). Determination of the eight
metals, arsenic, barium, cadmium, chromium, lead, mercury, selenium, and
silver in the test leachate was requested. No organic or pesticide
determinations were requested.

Leaching experiments. A series of laboratory leaching experiments was
prepared in which FBC waste or sized limestone and CSS were mixed
together in proportions calculated to yield a pH of 6.0 to 6.5 if the
mixture reached equilibrium during the time in which water was in
contact with the mixture. Each mixture was placed in a plastic flower
pot that contained a filter paper at the bottom to allow water to
percolate through the pot into a beaker beneath the pot, while
preventing solid from escaping. Approximately one pore volume of water
was added to each mixture weekly and allowed to drain by gravity.
Periodic drying of the FBC-CSS mixture between additions of water was
not prevented. Each FBC waste was mixed with each CSS, each FBC was
simulated by a sized limestone sample and mixed with each CSS, and each
starting solid was leached alone as a set of control samples. In total,
20 mixtures and 8 control samples (Table 3) were leached over a period
of 14 weeks.

A second series of mixtures was prepared using FBC waste and CSS. These
samples included mixtures of each FBC waste or the as-received limestone
with each CSS, to provide a total of 12 mixtures.

The mixtures were placed in individual 9-inch inside diameter
cylindrical containers that were open at the top and closed at the
bottom. The solid mixture was supported by a nylon-mesh-covered
desiccator plate in the bottom. Each container had an opening in the
bottom to which a flexible plastic tube was attached to allow gravity
drainage of leachate into a collection vessel. Each cylinder was covered
by nylon mesh to keep debris out of the samples.

Seven cylinders (6 FBC/CSS mixtures plus one blank) were placed in each
of two plywood cabinets designed and constructed for that purpose. Each
cabinet was open at the top, and had a clear plastic window on its
south-facing side to allow sunlight to shine on the upper surface of
each sample, but to minimize the effects of wind. The blanks were empty
cylinders that were used to determine whether the samples became
contaminated by trace elements in the rain or snow, and to determine the
amount of water that fell upon the mixtures. The mixtures were exposed
to outdoor weathering from February 1 to August 31, 1992.

Leachates that were collected from either the laboratory leaching
experiments or the outdoor weathering experiments were analyzed by
inductively coupled plasma emission spectrometry, inductively coupled
plasma emission-mass spectrometry, and ion chromatography (Table 4). The
pH, Eh, phenolphthalein and total alkalinity were determined for each
leachate.

Chemical and mineralogical analyses of solids and leachates. All
unleached solids were submitted for analysis of major, minor, and trace
elements according to Table 4. All FBC wastes were submitted as
composites of fly ash and bottom ash. The mineralogical composition of
the samples was determined by x-ray diffraction.

RESULTS AND DISCUSSION

Samples. The FBC wastes are designated FBC-1 through FBC-5, the coal slurry solids are designated CSS-1 and CSS-2, and the agricultural limestone is designated Ag LS. As indicated in Table 1, the particle sizes of the feed coals for FBC-3 and FBC-4 were relatively large. This factor appears to have had a significant effect on the nature of the ash, as became evident as the project proceeded. The aqueous leachability and pH behavior of FBC-3 and FBC-4 were different from FBC-1, FBC-2, and FBC-5 when leached in the controls or in mixtures with the CSSs. The feed coals in four of the five FBC operations were Illinois Springfield coal. We are uncertain of the seam of origin of the feed coal used for FBC-1, due to limited available information.

The coal slurry solids were collected from active coal slurry ponds in Illinois. CSS-1 was from Illinois Springfield coal, and CSS-2 was from Illinois Herrin coal. The volumes of the coal slurry ponds were estimated from dimensions given by the operator at the time of our visit.

Particle-size distribution. FBC-1, FBC-2, and FBC-5 were similar in their particle-size distributions (Fig. 1a); 50% or more of the particles in these wastes were smaller than $62\mu m$ (230 mesh). The particle-size distribution of FBC-3 was nearly uniform, and over half the particles in FBC-4 were larger than $500\mu m$ (35 mesh). The particle-size distribution of the Ag LS was similar to that of FBC-4. The cumulative particle-size distributions are shown in Figure 1(b).

Most of the particles in CSS-1 (Fig. 1c and 1d) were smaller than $250\mu m$ (60 mesh), whereas most of the particles in CSS-2 were larger than 250 μm.

The Ag LS was divided into the seven particle size ranges described earlier. Portions of each size fraction were weighed and mixed to approximate the particle-size distributions of the individual FBC wastes. These sized limestones were used as control samples for comparing the behavior of the FBC wastes either alone or in mixtures with the CSSs in the laboratory leaching experiments.

Bulk and particle densities. The bulk densities of CSS-1 and CSS-2 were 0.84 and 1.51 g/cm^3, respectively. The particle densities were 1.35 and 2.46 g/cm^3, respectively, and the porosities were 0.38 and 0.39, respectively. One reason for the higher bulk and particle densities of CSS-2 was that, as shown in the next section, CSS-2 contained significantly more pyrite than did CSS-1.

Pyrite content of CSS samples. The oxidation of pyrite by hydrogen peroxide yielded a pyrite content of 3.64% and 12.4% in CSS-1 and CSS-2, respectively. The standard ASTM method for pyritic sulfur in coal yielded pyrite concentrations of 3.01% and 24.70%, respectively. The ASTM results were probably more accurate than the results from the H_2O_2 method. The pyrite content of the CSS samples was calculated based on the concentration of iron in solution as a result of the oxidation of pyrite by H_2O_2. The pyrite content calculated in this manner for CSS-1 was low relative to the result from the later ASTM procedure. One explanation for this is that the solubility of amorphous iron hydroxide may have been exceeded at the pH of the H_2O_2 solution, resulting in iron precipitation

The ASTM results were not available when it was time to prepare the FBC-CSS mixtures, so it was decided to prepare the mixtures based on the H_2O_2

results. The low calculated result for pyrite in CSS-2 did not appear to cause any problem in our leaching experiments over the term of the project, because, as will be discussed later, the pH of all the laboratory leachates reached a desirable pH of 8 at pore volume 15. However, in the long term, a more accurate determination of pyrite content, and hence, acid-generating potential, of the CSS is necessary. In retrospect, the ASTM procedure for pyrite determination would probably have been more accurate for this purpose.

Exchangeable acidity of CSS samples. In an acidic soil, exchangeable acidity can be a major factor in determining the lime requirement for adjusting the pH of the soil. It is thought that much of the exchange complex by which exchangeable hydronium ions and aluminum ions are held is composed of organic matter. Obviously, coal is mostly organic matter. Both exchangeable hydronium and exchangeable aluminum were at low concentrations in the CSS samples. No exchangeable aluminum ion was detected on either CSS sample. The exchangeable hydronium ion concentrations were 0.016 and 0.023 meq/g for CSS-1 and CSS-2, respectively.

Calcium carbonate content of CSS samples. Both CSS samples contained calcium carbonate which, on acidification, would contribute to self-buffering of the produced acid. In calculating the lime requirement of the CSS, its calcium carbonate content must be considered. The calcium carbonate contents of the samples were 4.8% and 15.9% in CSS-1 and CSS-2, respectively.

Cation exchange capacity of CSS samples. The cation exchange capacity (CEC) of the CSS samples indicates the affinity of the wastes to adsorb cations from aqueous solution. The CECs of the CSS samples were 11.6 and 10.4 meq/100g for CSS-1 and CSS-2, respectively. These CEC values are comparable to those for sandy loam soils.

Calcium carbonate equivalent of FBC samples. The CCE indicates the acid-neutralizing ability of a material. In the case of FBC waste samples, the expected acid-neutralizing components are CaO, $Ca(OH)_2$, and MgO. Most, if not all of the $CaCO_3$, $MgCO_3$, and $CaMg(CO_3)_2$ in the feed limestone should have been converted to its corresponding oxide during the combustion process.

Pure limestone would have a CCE of 100%, but it is possible to have a CCE of greater than 100%. For example, 50.04 g of $CaCO_3$ contains one equivalent weight, whereas the same mass contains 1.78 equivalent weights of CaO. Therefore, pure CaO would have a CCE of 178 wt %. None of the FBC wastes had a CCE greater than 100%, however, FBC-4 had a CCE of 93.0% (Table 5).

Carbonate content of FBC samples. The CCE is not necessarily a measure of the calcium carbonate content of the FBC samples. In fact, calcium carbonate played, in four of the five samples, a rather minor part in the acid-neutralizing ability of the FBC wastes. In all but FBC-3, the calcium carbonate content was less than 10% (Table 5). FBC-3 was produced at a facility where the FBC boiler is used for heating purposes only. Therefore, the boiler is idle from about April to October each year. Waste FBC-3 was collected in September 1991. It was taken from a small amount of material that had remained in the ash silo after the silo had been emptied after shutting the boiler down. The boiler temperature was high enough during operation to calcine the limestone used in the process. Some of the calcium oxide produced during combustion was probably recarbonated by atmospheric carbon dioxide during storage of the material in the ash silo.

Calcium oxide content of FBC samples. The amount of CaO contained in each FBC sample was calculated from the weight gain of a known amount of air-dried FBC waste after saturation with deionized water followed by oven drying (Table 5). The weight gain was taken as the amount of water consumed in the hydration of CaO to $Ca(OH)_2$. FBC-3 lost weight during this process. This was an indication that FBC-3 contained no CaO when received, and that any CaO originally in the material had been converted to $Ca(OH)_2$ and $CaCO_3$ during storage in the ash silo.
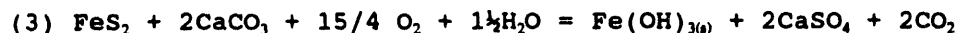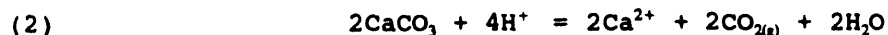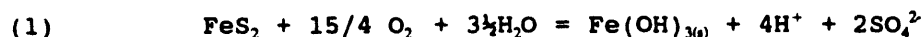
Calcium speciation in FBC samples. The amount of $CaSO_4$ in each FBC sample was calculated from the amount of SO_3 determined by x-ray fluorescence spectrometry. It was assumed in this calculation that all SO_3 in the samples was due to $CaSO_4$.

The calcium speciation in the FBC wastes was calculated from the CCE, the amount of CO_2 evolved upon acidification of the sample, and the amount of water consumed by the sample upon hydration. It was assumed in this calculation that only CaO, $Ca(OH)_2$, and $CaCO_3$ contribute to the CCE.

The $CaCO_3$ content was subtracted from the CCE to determine the amount of CaO plus $Ca(OH)_2$ in terms of $CaCO_3$. This value was then converted to CaO. The actual amount of CaO in the sample (calculated from the amount of water consumed on hydration) was subtracted from the amount of CaO plus $Ca(OH)_2$. This difference represented the amount of $Ca(OH)_2$ in terms of CaO.

Column 7 in Table 5 shows the sum of the wt. % of the Ca species in the FBC samples, calculated as the sum of $CaCO_3$ + CaO + $Ca(OH)_2$ + $CaSO_4$. In the last column is the corresponding value derived from x-ray fluorescence spectrometry. The figures in the last column are the sum of CaO + SO_3 + loss on ignition (LOI) - organic C. (Organic carbon, water, and CO_2 comprise the LOI.) The good agreement between the two columns gives confidence that the calculated Ca speciations are accurate.

Mass of FBC waste added to CSS. The mass of each FBC waste added to each CSS to neutralize the net amount of acid that could be generated by the oxidation of pyrite in the CSS sample was calculated based on the following chemical reactions:

(1) $$FeS_2 + 15/4\ O_2 + 3\tfrac{1}{2}H_2O = Fe(OH)_{3(s)} + 4H^+ + 2SO_4^{2-}$$

(2) $$2CaCO_3 + 4H^+ = 2Ca^{2+} + 2CO_{2(g)} + 2H_2O$$

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(3) $$FeS_2 + 2CaCO_3 + 15/4\ O_2 + 1\tfrac{1}{2}H_2O = Fe(OH)_{3(s)} + 2CaSO_4 + 2CO_2$$

In reaction (1), it is seen that 4 moles of acid is generated for each mole of pyrite oxidized, or the equivalent weight of pyrite in this reaction is one-fourth the formula weight. In reaction (2), one mole of calcium carbonate will react with two moles of acid, or the equivalent weight of calcium carbonate in this reaction is one-half its formula weight.

The amount of FBC waste added to a CSS was calculated by adding the millequivalents of acid possible from the oxidation of pyrite plus the millequivalents of exchangeable acid, less the millequivalents of calcium carbonate in the CSS. The calcium carbonate equivalent of each FBC waste was converted to milliequivalents of calcium carbonate, then the weight of FBC waste required to neutralize one gram of CSS was calculated. These values are shown in Table 6.

Toxicity Characteristic Leaching Procedure. The results of the TCLP (Table 7) show that selenium concentrations were above the U.S. EPA primary drinking water criterion in the extracts from all five FBC samples and the two CSS samples. The drinking water criterion for selenium is 0.01 mg/L. The concentrations of Se in the leachates ranged from 0.13 in CSS-2 to 0.23 mg/L in the leachate from FBC-2. The drinking water criterion for mercury is 2 μg/L. Its concentration was above this value only in the leachate from FBC-2, at 2.3 μg/L. None of the eight constituents listed on the U.S. EPA hazardous substance list was above the limit for hazardous waste classification (100 times the drinking water criterion). Coal combustion by-products are presently exempt from RCRA hazardous waste handling.

Chemical and mineralogical composition of unleached wastes. The FBC waste, Ag LS, and CSS samples were analyzed by instrumental activation analysis, x-ray fluorescence spectrometry, optical emission spectrometry, and atomic absorption spectrometry, according to Table 4. The pyritic sulfur content for CSS-1 and CSS-2 given by the ASTM analysis was 1.61% and 13.20%, respectively.

The mineralogical composition of the unleached solids was determined qualitatively by x-ray diffraction (XRD) spectrometry. The XRD data for calcium species in the FBC wastes was in good agreement with the calcium speciation data given in Table 5. By XRD, the minerals portlandite $[Ca(OH)_2]$, calcite, lime $[CaO]$, and, in one sample (FBC-3), ettringite $[Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26H_2O$ were detected. Zhou and Dayal (1990) reported that free lime in FGD (flue gas desulfurization) waste reacts with water to form portlandite and ettringite, with the aluminum in the ettringite being supplied by mullite in the coal ash that becomes entrained in the FGD waste. It is not unreasonable to expect FBC wastes to exhibit similar mineralogy.

Chemical and mineralogical composition of leached solids. The solids from the laboratory leaching experiments were analyzed in the same manner as the unleached solids. Two prominent changes occurred during leaching: (1) most, if not all, the portlandite present in the unleached solids was converted to calcite by reaction with carbon dioxide, and (2) a new phase, $Na_2Ca_5(SO_4)_6 \cdot 3H_2O$, appeared in both of the leached CSS control samples and four of the five FBC control samples.

Chemical composition of the laboratory leachates. In leaching the mixtures of FBC waste and CSS, the first pore volume of water added did not yield a significant quantity of leachate, because this amount of water was required to saturate the solid. After the first pore volume of water was added, leachate from every two pore volumes was composited so that there would be sufficient volumes for analysis. Overall, seven leachate samples were analyzed for each of the 28 mixtures (represented as pore volumes 3 through 15). As mentioned earlier, the mixtures were alloowed to dry in the periods between additions of water. As a result, desiccation cracks, which could allow preferential flow through the mixtures, developed. Prior to adding the next pore volume of water, each mixture was smoothed to fill the cracks, at least at the surface.

Figures 2 through 5 show the concentrations of Ca, Na, SO_4, Cl, pH, and Se versus pore volume of leachate for the mixtures of CSS/FBC waste and the FBC and CSS control samples. Data from the mixtures involving Ag LS are not included in the figures. The FBC control samples yielded leachates with pH values between approximately 11 and 13 (Fig. 4), as expected, because of the presence of $Ca(OH)_2$ in the matrix. The Ag LS sample yielded leachates of pH approximately 8 throughout the leaching period, with a slight rising trend through the course of the leaching (not shown).

The pH of leachates from the CSS-1 control sample remained at approximately 8 through the leaching period, probably due to the $CaCO_3$ content of the sample. The initial content of pyritic sulfur of moisture-free CSS-1 was 1.61% by weight, whereas the concentration of pyritic sulfur in the leached moisture-free sample was 1.43%, or a loss of approximately 13% of the original pyritic sulfur due to oxidation. However, the $CaCO_3$ content of 5.4% in the material was sufficient to maintain the slightly alkaline pH.

The pH of leachates from the CSS-2 control were acidic at both the beginning and the end of the leaching period. Approximately 12% of the pyrite originally present in the sample was oxidized during the leaching period (13.20% in the unleached moisture-free material, versus 11.54% in the material after leaching). This material contained 16.2% calcite at the beginning of the experiments. The reason for the drop in pH at pore volume 13 is unknown (Fig. 5e), but apparently reaction kinetics or drainage dynamics were unfavorable for neutralization of the acid generated by pyrite oxidation during that period.

The pH of leachates from the mixtures of CSS-1 both with the FBC wastes (Fig. 2e) and the sized limestone samples was similar to that shown by the CSS-1 control sample, that is, the pH remained at approximately 8 in all the leachates. Apparently, because the amount of either FBC waste or Ag LS added to CSS-1 was small (1.4% to 2.8% by weight), the CSS-1 controlled the pH of the leachates.

The pH of the leachates from the mixtures of CSS-2 with FBC wastes was more variable. Mixtures with FBC-1, FBC-2, and FBC-5 behaved similarly (Fig. 3e). Mixtures with FBC-4 behaved similarly to FBC-1, FBC-2, and FBC-5, but the reaction was delayed. The pH of the leachate at pore volume 3 from the mixture with FBC-3 was quite acidic, but in the remainder of the leachates it conformed to the pattern shown by the mixtures with FBC-1, FBC-2, and FBC-5. By pore volume 15, all leachates attained a pH of approximately 8 (Fig. 3e).

The reasons for the different behavior of FBC-3 are not clear. FBC-3 contained the greatest amount of $CaCO_3$ (39.8%) and $Ca(OH)_2$ (28.13%) initially (Table 5). All the other FBC wastes contained less than 10% $CaCO_3$ and less than 8% $Ca(OH)_2$ before hydration of the CaO. The particle-size distribution in FBC-3 was nearly uniform, FBC-4 had an abundance of coarser particles ($\geq 500 \mu m$), and the other three were finer textured ($< 500 \mu m$). The combination of calcium species and particle-size distribution of the solids probably controlled the pH of the leachates after the early pore volumes.

In all cases, at pore volume 15 the pH values were approximately 8, indicative of the influence of calcium carbonate on the solution pH. X-ray diffraction analysis of the solids after the leaching experiments revealed very little portlandite [$Ca(OH)_2$] and more calcite than was present in the unleached solids. Apparently, portlandite reacted with CO_2 in the water added to the mixtures during leaching, or in the air during the periods between additions of water, and formed calcite. In addition, the data of Table 8 show that the concentration of carbonate-carbon in the control samples of FBC waste and the mixtures of FBC waste and CSS after leaching was greater than in the unleached solids in all cases. Calcium carbonate was consumed in the Ag LS control sample, the CSS-2 control sample, and the mixtures prepared with Ag LS and CSS, because there was no $Ca(OH)_2$ in those samples to react with CO_2 in the air or water.

The pH values of leachates from the mixtures of CSS-1 with sized Ag LS were all in the range of 7 to 8. Leachates from mixtures of CSS-2 with

Ag LS had pH values in the range of 6.5 to 8, with the exception of pore volume 3. This set of leachates had pH values near 4, but by pore volume 5 they were approximately 7 and continued to increase slowly after that.

The predominant constituents in solution in all of the leachates were calcium, sodium, sulfate, and chloride. Minor constituents included potassium, magnesium, and carbonate/bicarbonate (as alkalinity).

In comparison with the leachates from the mixtures of CSS and Ag LS, those from mixtures of CSS and FBC waste had higher calcium concentrations in the early pore volumes. However, the calcium concentrations in the last few leachate samples from the mixtures were all in the range of 550 to 650 mg/L. The calcium concentration in these leachates was probably controlled by the solubility of gypsum. Dissolution of gypsum was probably the source of sulfate in the leachates. Gypsum was probably produced by the acid-base reaction of the products of pyrite oxidation (H^+ and SO_4^{2+}) with calcite either during the combustion process or during the leaching experiments. Leachates from mixtures that contained Ag LS had higher concentrations of sulfate in the early pore volumes than those from mixtures that contained FBC waste.

The concentrations of sodium in the initial leachates from mixtures of CSS and either FBC waste or Ag LS were higher than in those from the control samples. At pore volumes 11 and later, sodium concentrations were 600 mg/L or less in leachates from mixtures of CSS-2 and FBC wastes. In all other leachates, the concentrations were 200 mg/L or less. Sodium in the leachates probably did not result from chemical reactions during the leaching, but was probably the result of dissolution of soluble salts. Chloride flushed out of the solids rapidly, and probably also originated from the dissolution of soluble salts.

The concentration of potassium was high in leachates from the control samples of FBC-1, FBC-2, and FBC-5. The concentration of magnesium was higher in leachates from mixtures including CSS-2 than in those including CSS-1, and leachates from mixtures containing Ag LS had higher concentrations of magnesium than those that involved FBC wastes.

Trace element concentrations of note in the leachates from mixtures with both CSS-1 and CSS-2 were molybdenum, boron, and strontium; and selenium and nickel in leachates from mixtures with CSS-2. Molybdenum, which occurs as an anionic species in aqueous solution, correlated strongly with pH. Selenium, another anionic species, correlated mildly with pH in leachates from CSS-1 mixtures. Boron concentrations were independent of pH. Nickel correlated with other chalcophile elements, but not with sulfate. Strontium correlated with calcium and sodium. The observed correlations are not unusual.

While neither the CSS nor FBC wastes are subject to the Federal RCRA regulations for disposal as hazardous wastes, it is informative to compare the concentrations of the RCRA constituents with the U.S. EPA primary drinking water maximum contaminant levels. In July 1992, four elements were added to the list of eight metals originally listed in the regulations. The twelve metals and their maximum contaminant levels (MCL) in mg/L now listed as toxic are antimony (0.006), arsenic (0.05), barium (1.), beryllium (0.004), cadmium (0.010), chromium (0.05), lead (0.005), mercury (0.002), nickel (0.1), selenium (0.01), silver (0.05), and thallium (0.002).

Antimony, lead, mercury, and thallium were, generally, not detected in the leachates by inductively coupled plasma emission spectrometry. Their detection limits by ICP were greater than their respective maximum contaminant levels. Neither barium nor beryllium occurred above the respective MCL in any leachate, and cadmium occurred above the MCL of 0.01 mg/L in only one leachate, pore volume 13 of the CSS-2 control sample.

Arsenic concentrations were greater than the MCL of 0.1 mg/L in 4.5% of the leachates. In each case, the leachate came from a mixture containing CSS-2. Arsenic was below the detection limit of 1 μg/L in 26.6% of the leachates. The concentrations of arsenic in the early pore volume leachates of mixtures were higher than those from any of the control samples. The leachates from the later pore volumes contained about the same concentrations of arsenic as found in the leachates from the control samples. FBC wastes and CSS samples both appeared to contribute As to the leachates. As is often associated with pyrite in coal; this association may be the source of As in the FBC wastes and the CSS samples.

Chromium concentrations exceeded the MCL of 0.05 mg/L in all leachates from FBC-1 and FBC-5 control samples, in the first leachate (pore volume 3) from FBC-2 and FBC-3 control samples, and in the first leachate from the mixture of CSS-1 and FBC-5. The FBC wastes were the principal sources of Cr in the leachates.

Nickel concentrations exceeded the MCL of 0.1 mg/L in leachates from the control samples of FBC-1, FBC-5, and CSS-2, and in all but one leachate from mixtures of CSS-2 and Ag LS. Ni concentrations were also above the MCL in at least the first two leachates collected from each mixture of CSS-2 with FBC waste. The FBC wastes and CSS-2 contributed Ni to the leachates, however, CSS-1 contributed negligible amounts.

Selenium concentrations exceeded the MCL of 0.01 mg/L in 80.5% of the leachates. Selenium was probably associated with pyrite in the CSS samples. As pyrite was oxidized, selenium was released to the leachate solution. The greatest concentrations of selenium, up to 3.4 mg/L in leachates, were detected in mixtures with CSS-2, which had the greater pyrite content of the two coal slurry samples. The selenium concentrations attained a steady-state concentration in the later pore volumes from mixtures containing CSS-1 of <0.05 mg/L, and in mixtures containing CSS-2 of <1 mg/L.

Boron occurred at higher concentrations in leachates from mixtures of CSS and FBC waste than in any of the corresponding control samples, although the leachates from the CSS control samples had higher B concentrations than those from the FBC controls. Fluoride occurred in leachates from mixtures of CSS-2 and FBC waste at much higher concentrations (35 to 177 mg/L) at pore volume 3 than in any leachate from a control sample, either FBC waste or CSS ($\leq$9 mg/L). The CSS materials are the principal contributor of molybdenum to the leachates of FBC/CSS mixtures.

Many elements are toxic to plants, but at varying concentrations in the nutrient solution, depending on the element and the plant variety. A survey of a publication by Gough et al. (1979) indicated that Al, As, Be, Cd, Cr, Cu, Li, Mo, Se, and Zn are probably not toxic to plants at the concentrations observed in the laboratory leachates. Other elements, namely B, Cl, Co, F, Mn, and Ni are possibly toxic to plants at the observed concentrations. The latter elements were not present at toxic concentrations in all leachates from all solid samples. Sodium was initially present at concentrations that might be toxic to plants. Tests

of the availability of various toxic elements to different types of cover crops or legumes is planned as future research in the overall program on the use of FBC wastes in reclamation.

Chemistry of the outdoor weathering leachates. The outdoor weathering experimental work was incomplete at the time of writing this report, consequently, the discussion of those experiments is brief. A fuller discussion will be given in the Final Technical Report of the research. Leachates in the outdoor weathering experiments were collected from CSS-1/FBC mixtures at approximately 3.2, 4.4, 7.1, 9, 10.2, and 12.9 pore volumes, and from CSS-2/FBC mixtures at approximately 3, 4, 6, 8, 9.8, and 12 pore volumes. The leachabilities of various elements in the outdoor weathering leachates were similar to their behavior in the laboratory leaching experiments. Calcium, potassium, molybdenum, sodium, and strontium were at relatively high concentrations initially, but decreased in successive leachates. The concentrations of boron passed through maxima in the range of 6 to 9 pore volumes. Magnesium and manganese concentrations were higher in the leachates collected after pore volume 6 than in the initial leachates.

As in the laboratory leaching experiments, the calcium concentrations were in the range of 550 to 650 mg/L in all the final leachate samples. Again, the calcium and sulfate concentrations were probably controlled by the solubility of gypsum.

Also, as in the laboratory leaching experiments, the pH values of the final leachates were in the range of 7.5 to 8.5, indicative of pH control by reaction of acid with calcium carbonate.

CONCLUSIONS

Because the peroxide oxidation technique underestimated the amount of pyrite in the CSS-2 samples, the amount of FBC waste or sized Ag LS used in each mixture with CSS-1 were less than necessary to satisfy the stoichiometric amount of acid that could be generated by complete oxidation of the pyrite in the CSS samples. However, the leaching experiments demonstrated that FBC waste is as effective as Ag LS in neutralizing the generated acid, and that the leachate pH would be approximately the same as that from Ag LS/CSS mixtures. In fact, the calcium hydroxide from the original hydrated FBC waste was converted to calcium carbonate in a short period of time, as indicated by chemical and mineralogical data.

If the laboratory leaching experiments had continued for a long enough term, the alkaline materials present either in the unleached CSS-2, or added to the FBC wastes would have been consumed before all the pyrite had been oxidized, because of the deficiency of FBC waste in the mixtures.

There is some concern, because of the concentrations of sodium and chloride in the initial leachates, over the toxicity of the leachates to plants. Although both these solutes were flushed quickly from the laboratory and outdoor weathering solids, this might not be the case in a coal slurry pond. Therefore, salt-tolerant plants might have to be selected for revegetation of the amended coal slurry solids.

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TABLE 1
Operating characteristics of fluidized bed combustion plants

Operating Characteristics	FBC-1	FBC-2	FBC-3	FBC-4	FBC-5
FBC Type	circulating	circulating	forced air	AFBC	circulating
Coal	Ill. No. 6?	Ill. No. 5	Ill. No. 5	Ill. No. 5	Ill. No. 5
Sorbent	Limestone	Limestone	Limestone	Limestone	Limestone
Particle Size					
Coal	--*	0 to 13 mm	6 to 32 mm	13 to 25 mm	<2 mm
Sorbent	--	<0.59 mm		0.84 to 2.4 mm	<2 mm
Nominal Ca/S Mole Ratio	--	2.4-2.7	2.5	7.6	2.5
Feed Rate					
Coal	590 T/d per unit	1.8 T/hr	--	4.5 T/hr	10 T/hr
Sorbent	--	14 T/hr		1.8 T/hr	6-6.5 T/hr
Combustion Temperature (°F)	--	1550-1650	1500-1700	1510-1530	1700
Operating Pressure (psig)	--	400	50	685	1300-1400
Air Input (lbs/hr)	--	1°:88,000 2°:55,000	--	85,000-86,000	350,000-400,000
% O_2 in Stack Gas	--	3.75-6.5	--	3.5-4.5	4
Size of FBC	425,000 lbs steam per hr per unit 24.6 MW	125,000 lbs steam per hr	--	120,000 lbs steam/hr 3500kW	30 MW par unit
Manufacturer/Model of FBC		Alstrom/ Pyro Power	Stone-Johnson/ Fluid Fire	Foster-Wheeler	Riley Stoker
Ash Collection Points	--	•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	700-800 T (75% fly ash, 25% bottom ash)	70 T flyash 50 T bottom ash	--	82 T	435 T
Current Ash Disposal Method	back to coal mine	back to coal mine	local ash heap	back to coal mine	back to coal mine

TABLE 1
Operating characteristics of fluidized bed combustion plants

Amount Collected (kg)	flyash: 13.4 bottom ash: 30.2	flyash: 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

*unavailable

TABLE 2
Characteristics of coal slurry ponds

Slurry Pond Characteristic	Coal Mine Preparation Plant	
	CSS-1	CSS-2
Coal Seam	Ill. No. 6	Ill. No. 5
Slurry Pond Volume(10^6 yd^3)	23	8-9
Remaining Useful Life of Pond (yrs)	8-9	10
Reclamation Plan	soil cover, revegetation	thin soil cover, revegetation
% of Coal Stream Represented by Slurry Stream	20-30	--
% Moisture, as received	--[*]	15
Dry Bulk Density (g/cm^3)	0.83	1.45

[*]unknown

Table 3. Sample mixtures prepared for
laboratory leaching experiments

FBC waste or agricultural limestone	CSS-1	CSS-2	Control
FBC-1	X	X	X
FBC-2	X	X	X
FBC-3	X	X	X
FBC-4	X	X	X
FBC-5	X	X	X
Ag LS			X
Ag LS/FBC-1	X	X	
Ag LS/FBC-2	X	X	
Ag LS/FBC-3	X	X	
Ag LS/FBC-4	X	X	
Ag LS/FBC-5	X	X	
Control	X	X	

Table 4. Methods for analysis of limestone, coal slurry solids, FBC wastes, (XRF, AAS, OEP, INAA) and extracts (ICP, IC, ICP/MS)

Element	SOLID PHASES				EXTRACTS		
	XRF	AAS	OEP	INAA	ICP	IC	ICP/MS
Ag			X				
Al	X				X		
As				X			X
B			X		X		
Ba	X				X		
Be			X		X		
Ca	X				X		
Cd		X			X		
Co				X	X		
Cr				X	X		
Cu		X			X		
Fe	X			X	X		
Hg					X		
K	X			X	X		
La				X	X		
Mg	X				X		
Mn				X	X		
Na	X			X	X		
Ni		X			X		
Pb		X			X		
S	X						
Sc				X	X		
Se				X			X
Si	X				X		
Sr	X				X		
Ti	X				X		
V			X		X		
Zn				X	X		
Zr					X		
Cl$^-$						X	
F$^-$						X	
NO$_3^-$						X	
SO$_4^{2-}$						X	

Table 5
Speciation of calcium in FBC wastes (wt. %)

Sample	CCE	CaCO₃	CaO	Ca(OH)₂	CaSO₄	Total Ca*	XRF Ca**
FBC-1	65.1	3.58	28.61	7.73	29.58	69.5	64.8
FBC-2	48.2	4.00	23.44	1.74	28.42	57.6	54.4
FBC-3	77.8	39.8	0.0	28.13	13.23	81.2	79.6
FBC-4	93.0	9.75	45.60	1.36	27.73	84.4	82.2
FBC-5	50.2	3.67	22.72	4.41	23.24	54.0	58.6

*Total Ca = $CaCO_3$ + CaO + $Ca(OH)_2$ + $CaSO_4$.
**XRF Ca = CaO + SO_3 + LOI - org C

Table 6
Amount of each FBC waste or agricultural limestone required to
neutralize the total potential acidity from one gram of coal slurry
solid (g/g)

FBC waste or agricultural limestone	CSS-1	CSS-2
FBC-1	0.021	0.076
FBC-2	0.028	0.10
FBC-3	0.017	0.064
FBC-4	0.014	0.053
FBC-5	0.027	0.099
agricultural limestone	0.014	0.052

Table 7
Concentrations of RCRA constituents in TCLP extracts

Sample	As	Ba	Cd	Cr	Pb	Se	Ag	Hg
FBC-1	<0.05	0.40	<0.005	0.03	<0.05	0.18	<0.01	<0.0005
FBC-2	<0.05	0.18	<0.005	<0.01	<0.05	0.23	<0.01	0.0023
FBC-3	<0.05	0.22	<0.005	0.05	<0.05	0.18	<0.01	<0.0005
FBC-4	<0.05	0.19	<0.005	<0.01	<0.05	0.22	<0.01	<0.0005
FBC-5	<0.05	0.39	<0.005	<0.01	<0.05	0.21	<0.01	<0.0005
CSS-1	<0.05	0.17	<0.005	<0.01	<0.05	0.16	<0.01	<0.0005
CSS-2	<0.05	0.20	<0.005	<0.01	<0.05	0.13	<0.01	<0.0005
PDWC*	0.05	1.	0.010	0.05	0.005	0.01	0.05	0.002

*Primary drinking water criteria

Table 8
Calcium carbonate content of unleached and leached mixtures of FBC waste or Ag LS and CSS

Sample	$CaCO_3$ in unleached solid (%)	$CaCO_3$ in leached solid (%)
Controls		
FBC-1	3.58	23.75
FBC-2	4.00	22.58
FBC-3	39.8	51.75
FBC-4	9.75	29.83
FBC-5	3.67	19.92
Ag LS	94.8	91.91
CSS-1	5.4	6.75
CSS-2	16.2	12.42
Mixtures		
CSS-1/FBC-1	5.36	7.83
CSS-1/FBC-2	5.36	7.50
CSS-1/FBC-3	5.99	7.17
CSS-1/FBC-4	5.46	7.33
CSS-1/FBC-5	5.35	5.58
CSS-1/LS/FBC-1	6.65	5.58
CSS-1/LS/FBC-2	6.65	6.58
CSS-1/LS/FBC-3	6.65	5.58
CSS-1/LS/FBC-4	6.65	5.25
CSS-1/LS/FBC-5	6.65	6.65
CSS-2/FBC-1	15.24	16.92
CSS-2/FBC-2	14.98	17.58
CSS-2/FBC-3	17.71	18.67
CSS-2/FBC-4	15.86	18.25
CSS-2/FBC-5	14.96	18.25
CSS-2/LS/FBC-1	20.29	18.33
CSS-2/LS/FBC-2	20.29	18.08
CSS-2/LS/FBC-3	20.29	17.92
CSS-2/LS/FBC-4	20.29	16.67
CSS-2/LS/FBC-5	20.29	17.83

The initial concentrations of $CaCO_3$ in the mixtures were calculated from the concentrations of $CaCO_3$ in the unleached solids and the amounts of each in the mixtures. The final concentrations of $CaCO_3$ were calculated from the measured concentrations of carbonate-carbon.

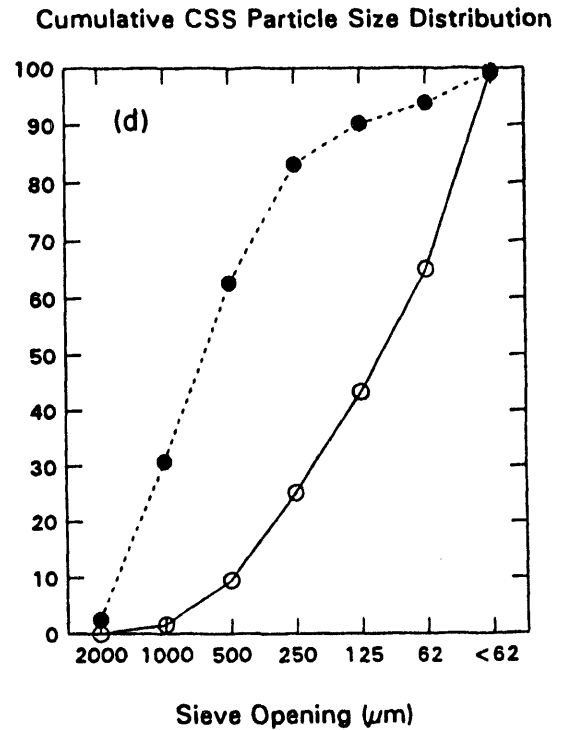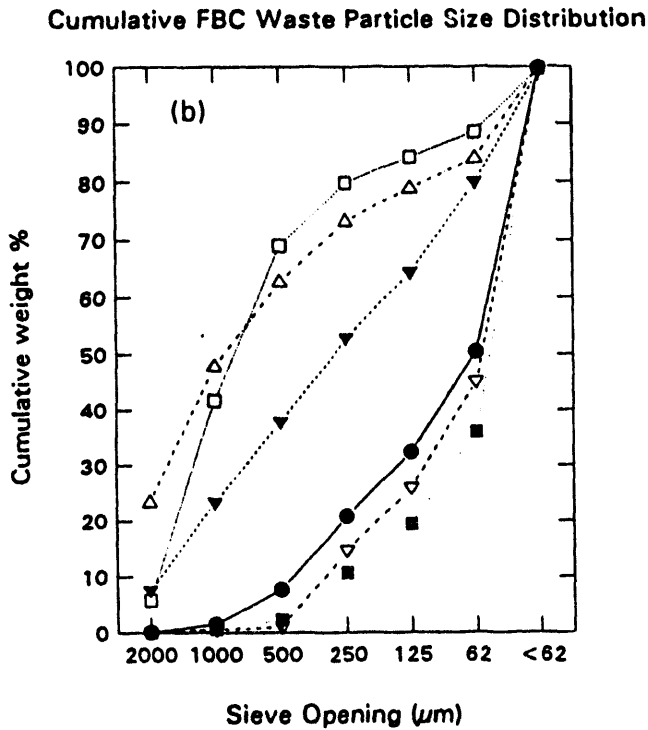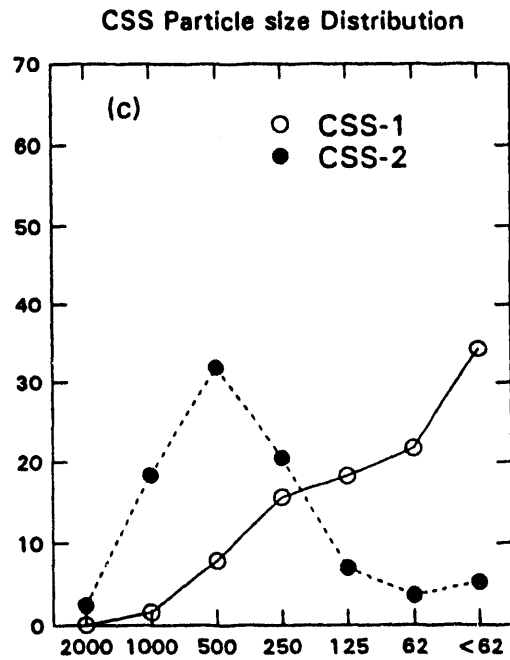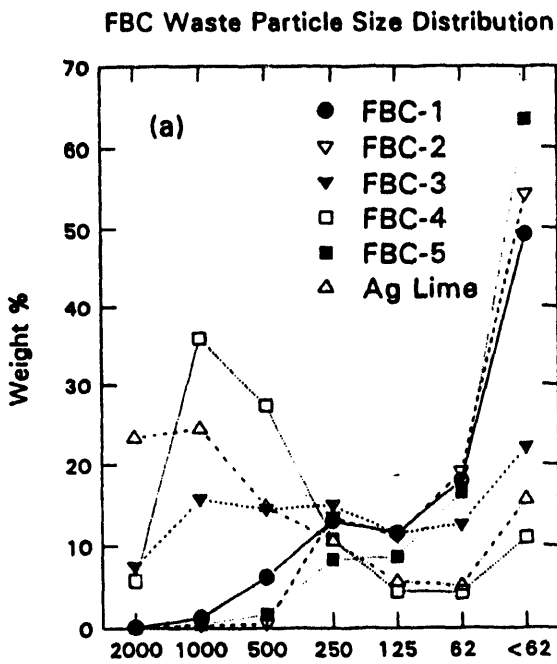# Figure 1. Particle Size Distributions of Five FBC Wastes

FBC Waste Particle Size Distribution

CSS Particle size Distribution

Cumulative FBC Waste Particle Size Distribution

Cumulative CSS Particle Size Distribution

Figure 2. Concentrations of Ca, Na, SO$_4$, Cl, pH and Se
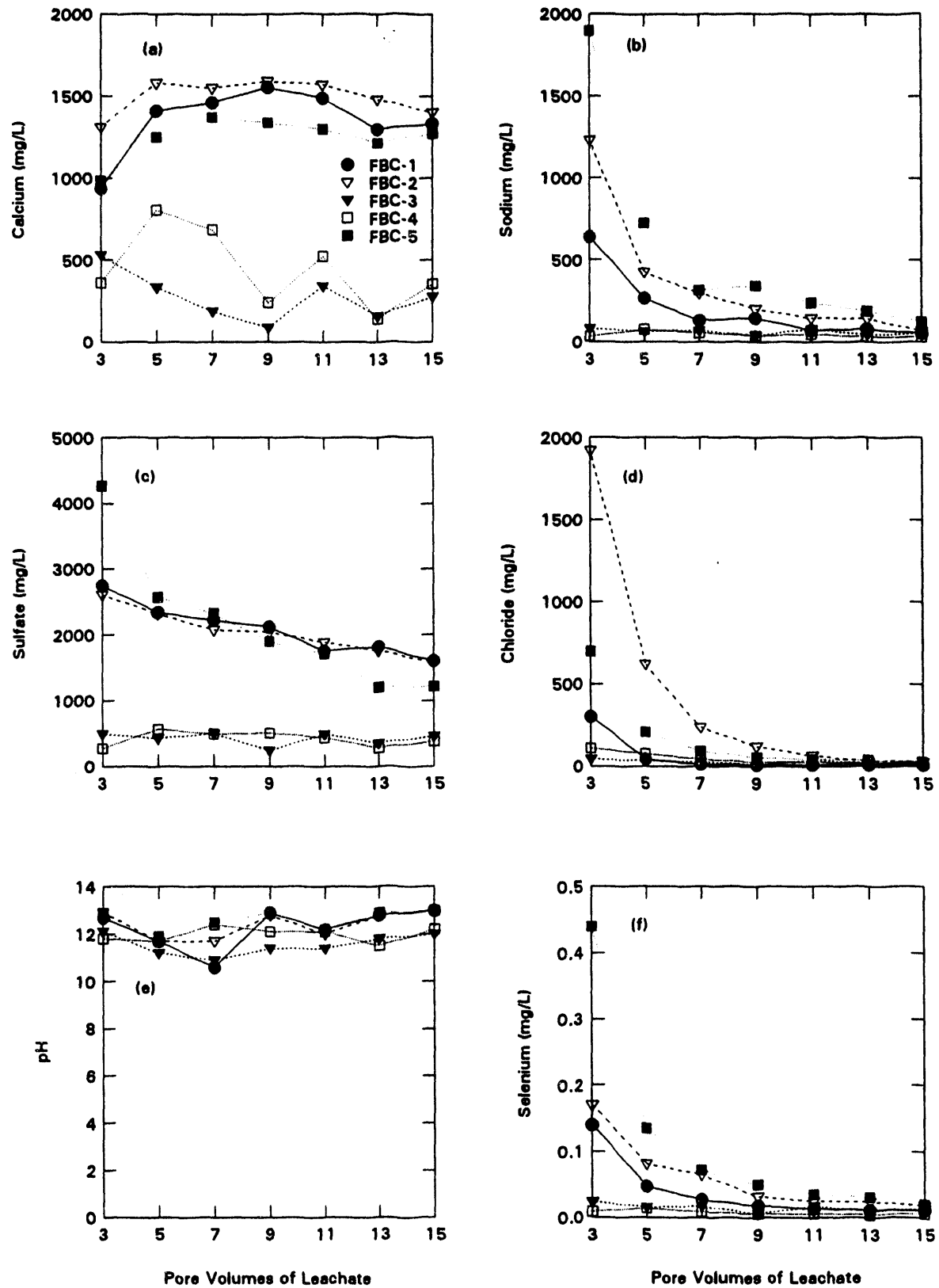in leachates from FBC controls

Pore Volumes of Leachate

Figure 3. Concentrations of Ca, Na, SO_4, Cl, pH and Se in leachates from CSS controls

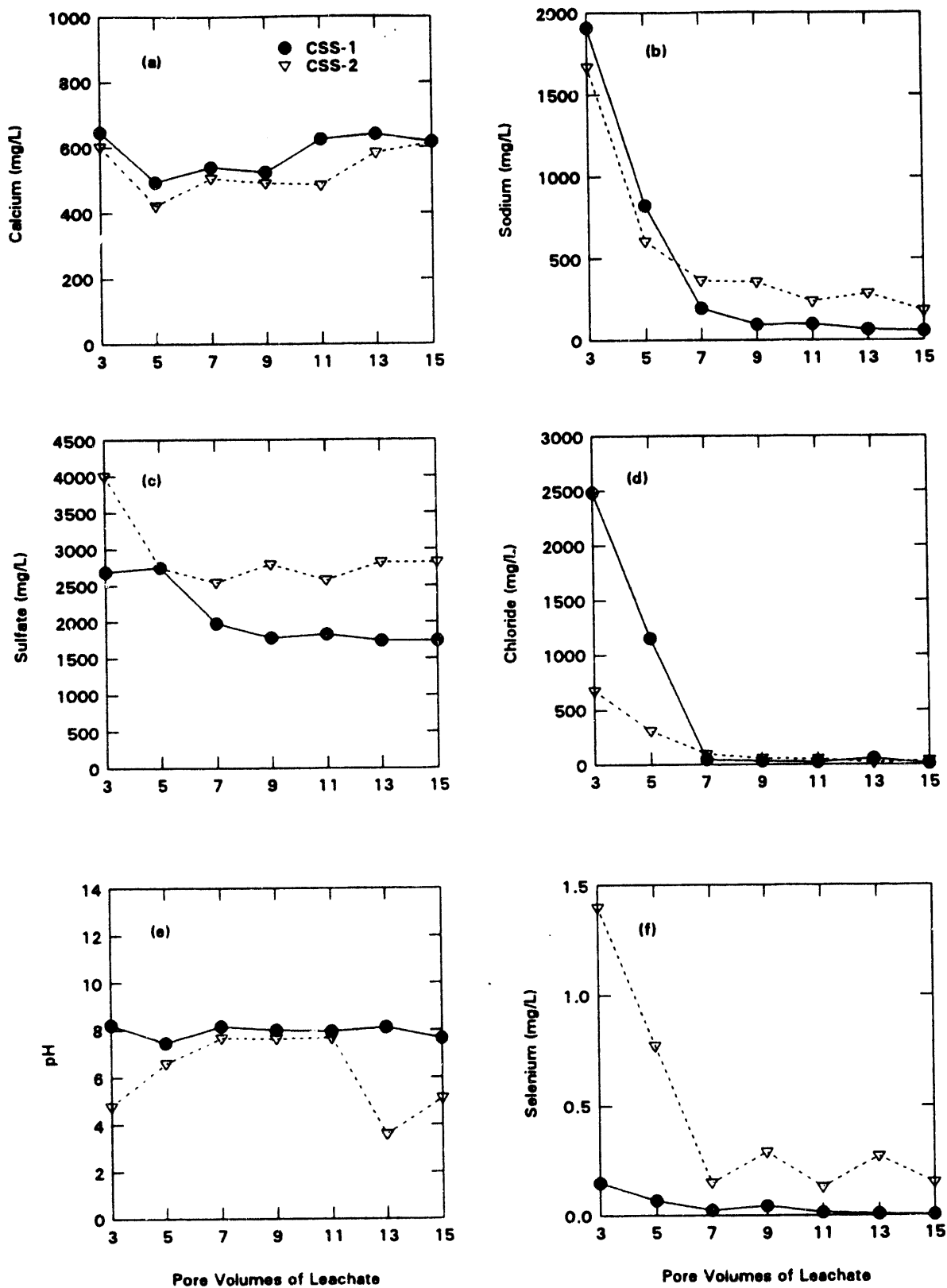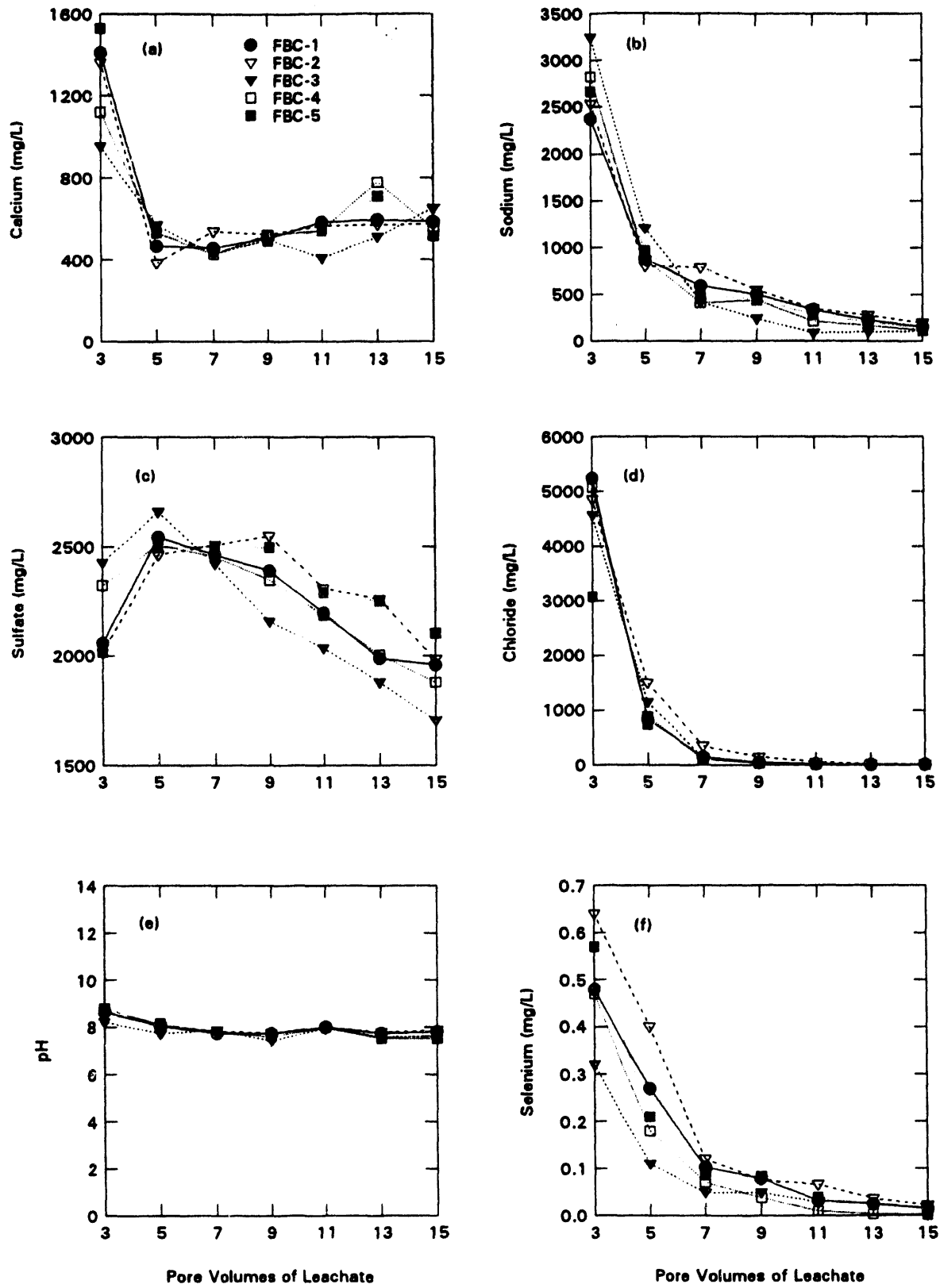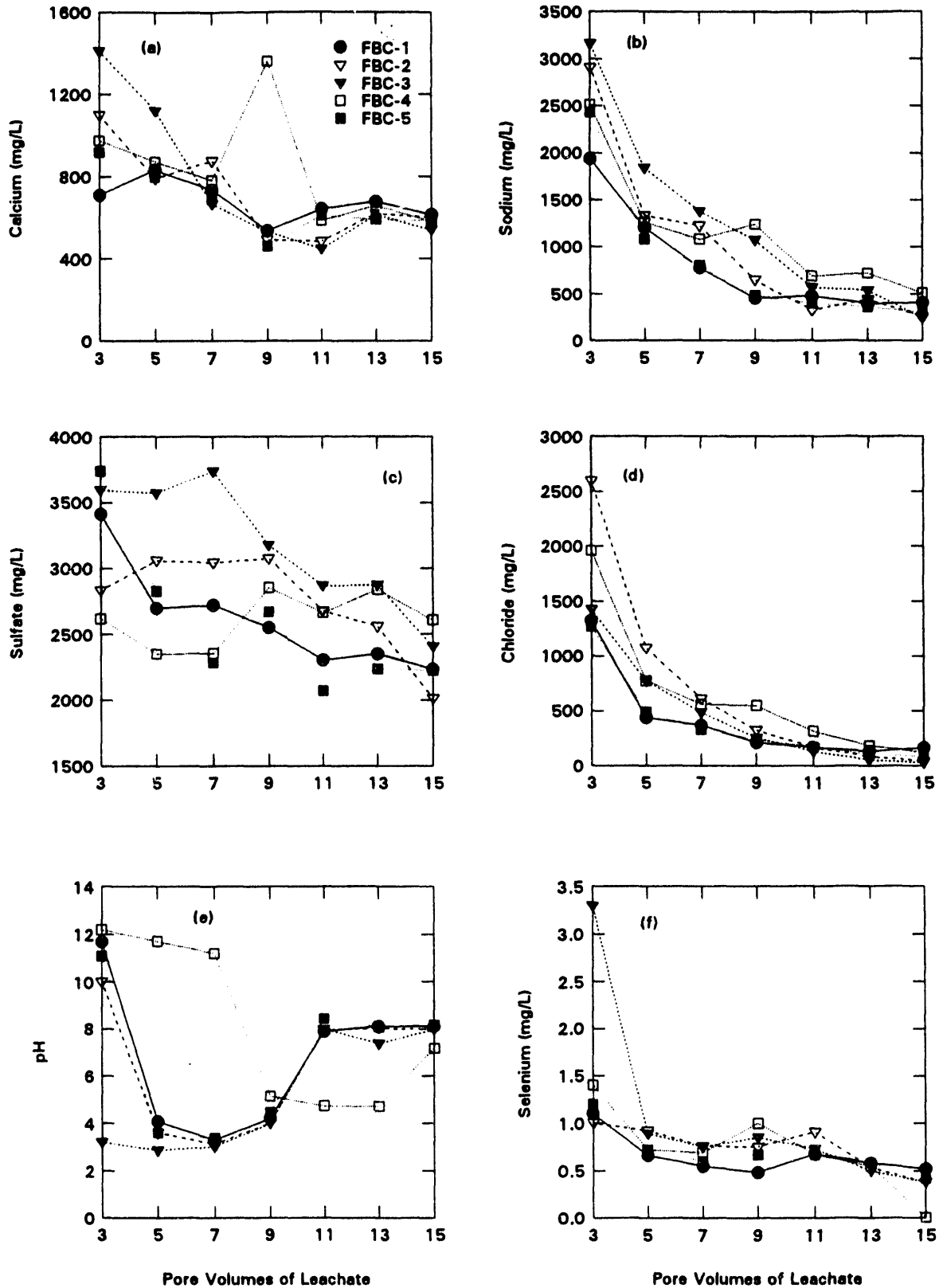# Figure 4. Concentrations of Ca, Na, SO₄, Cl, pH and Se in leachates from mixtures of CSS-1/FBC

Pore Volumes of Leachate

Figure 5. Concentrations of Ca, Na, SO$_4$, Cl, pH, and Se in leachates from mixtures of CSS-2/FBC

PROJECT MANAGEMENT REPORT
September 1, 1991 through August 31, 1992

Project Title: The use of FBC wastes in the reclamation of
coal slurry solids

Principal Investigator: Gary B. Dreher, ISGS
Other Investigators: William R. Roy, ISGS
                        John D. Steele, ISGS
Project Monitor: Dan Banerjee, CRSC

COMMENTS

The fourth quarter budget line reflects a transfer of $425 from Major Equipment to Materials and Supplies. We have requested a no-cost extension of the contract until December 31, 1992 in order to complete the analyses of solids from the series of outdoor weathering experiments. This will involve expenditure of $6,012 in Other Direct Costs and $601 in Indirect Costs, a total of $6,613.

Milestones D, E, and F were completed during the quarter. Milestone G is in progress.

Projected and Estimated Actual Expenditures by Quarter

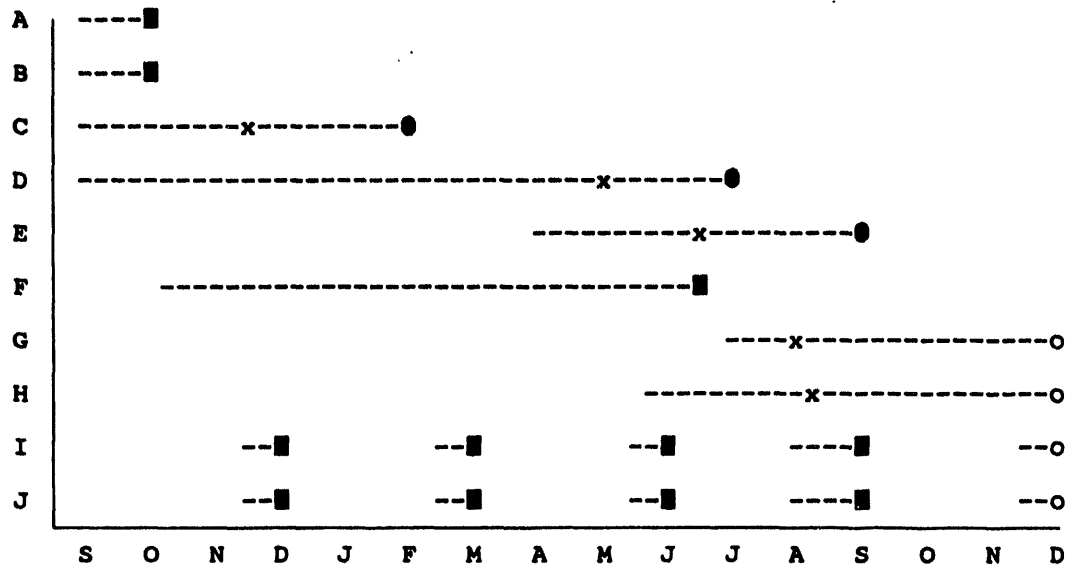| Quarter*	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1991 to Nov. 30, 1991	Projected	791	1,700	400	425	10,717	1,403	15,436
	Estimated Actual	283	1,544	260	0		209	2,296
Sept. 1, 1991 to Feb. 29, 1992	Projected	1,583	1,900	400	425	29,042	3,335	36,685
	Estimated Actual	514	1,950	297	0	2,500	526	5,787
Sept. 1, 1991 to May 31, 1992	Projected	2,374	2,075	400	425	37,144	4,242	46,460
	Estimated Actual	1,532	2,168	297	0	8,673	943	13,613
Sept. 1, 1991 to Aug. 31, 1992	Projected	3,166	2,675	400	0	44,389	5,063	55,693
	Estimated Actual	2,840	2,522	297	0	35,970	4,163	45,792

* Cumulative by quarter

COSTS BY QUARTER – EXHIBIT C
THE USE OF FBC WASTES IN THE RECLAMATION
OF COAL SLURRY SOLIDS
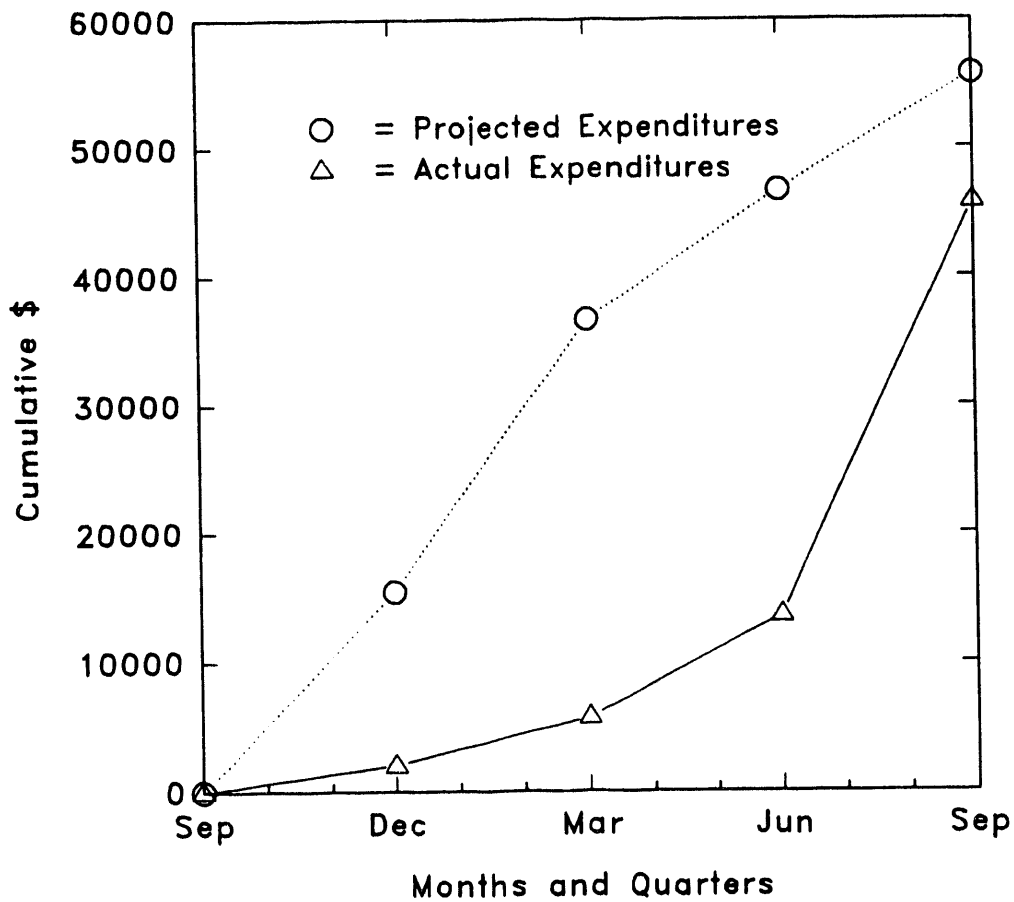
Total CRSC Award $ 55,693

SCHEDULE OF PROJECT MILESTONES

```
A  |  ----■
B  |  ----■
C  |  ----------x---------●
D  |  --------------------------------x-------●
E  |                    ---------x---------●
F  |         -------------------------------■
G  |                                    ----x---------------o
H  |                                  ---------x--------------o
I  |         --■        --■        --■        ----■        --o
J  |         --■        --■        --■        ----■        --o
   |_____
      S   O   N   D   J   F   M   A   M   J   J   A   S   O   N   D
```

Begin September 1, 1991

Milestones:
 A. Write and submit QA plan (Task 1)
 B. Collect FBC waste, coal slurry solid, and limestone (Task 2)
 C. Characterize starting materials (Task 2)
 D. Prepare waste solid mixtures and conduct leaching experiments
    (Task 3)
 E. Analyze leachates, extracts, and solids from
    leaching experiments (Task 3)
 F. Prepare waste solid mixtures and conduct outdoor
    weathering experiments (Task 4)
 G. Analyze leachates and solids from outdoor weathering
    experiments (Task 4)
 H. Interpret data
 I. Technical reports prepared and submitted
 J. Project management reports prepared and submitted

 Comments: Milestones C, D, and E slipped because of the
             unexpected need to obtain a second coal slurry solids
             sample. Milestone G slipped because of unexpectedly
             dry weather during the spring. All outdoor weathering
             leachates have been collected and analyzed. The solids
             remain to be analyzed.

END

DATE FILMED

2 / 24 / 94