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TECHNICAL REPORT
March 1, 1992 through May 31, 1992

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 allows the combustion of Illinois high sulfur coal without pollution of the atmosphere with vast quantities of 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, sulfur in the coal is oxidized to SO_2 and this is trapped by reaction with the limestone or dolomite to form gypsum ($CaSO_4 \cdot 2H_2O$). Solid by-products from FBC are generally a mixture of calcium oxide, gypsum, coal ash, and unburned coal. The present research project is designed to provide initial data on one possible use of FBC waste. FBC wastes from five different locations in Illinois are mixed with coal slurry solids (CSS) from two different coal preparation plants at Illinois coal mines. In mixtures of FBC waste and coal slurry solids, the alkaline components of the FBC waste are expected to react with acid produced by the oxidation of pyrite in the coal slurry solid. An objective of this research is to determine the chemical composition of aqueous leachates from mixtures of FBC wastes, generated under various operating conditions, and the coal slurry solids. These data will be used in future research into the ability of such mixtures to support seed germination and plant growth. The final goal of this and future research is to determine whether mixed FBC waste and coal slurry solids can be used as a satisfactory growing medium in slurry pond reclamation.

The chemical analyses of the 8 starting solids (5 FBC wastes, 2 Css samples, and 1 agricultural limestone sample) were completed.

Five composite leachate samples (2 pore volumes of water per composite) were collected from laboratory leaching experiments in which 28 different samples of neat solids (8) or mixtures of CSS samples and FBC wastes or agricultural limestone (20) are leached by deionized water. The pH, Eh, phenolphthalein alkalinity, and total alkalinity were determined for all leachates. Three sets of leachates (pore volumes 3, 5, and 7) were analyzed by inductively coupled plasma spectrometry. At pore volume 11, the pH of each leachate except one was approximately 8.

Two sets of leachates were collected during the quarter from outdoor weathering experiments of 12 samples, mixtures of CSS and FBC wastes or agricultural limestone. The pHs of the first set of leachates ranged from 6.4 to 7.9 for mixtures with CSS-1, and from 2.9 to 11.4 for mixtures with CSS-2. The pHs for the second set of leachates ranged from 7.6 to 8.1 for mixtures with CSS-1, and from 2.9 to 6.4 for mixtures with CSS-2.

MASTER

This project is funded by the U. S. Department of Energy (METC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.

EXECUTIVE SUMMARY

The principal tasks for this quarter were the completion of the chemical analysis of the 8 starting solids (5 FBC wastes, 2 CSS samples, and 1 agricultural limestone sample), and the collection and analysis of leachates from laboratory leaching experiments and outdoor weathering experiments.

Differences between the 8 starting solids were calculated by using a cluster analysis routine. Based on this analysis, FBC-1, FBC-2, and FBC-5 are very similar to each other, FBC-3, FBC-4, and the agricultural limestone are similar to each other. CSS-1 is somewhat similar to FBCs 1, 2, and 5, and CSS-2 is in a group by itself.

Eleven pore volumes of water have been passed through the sample mixtures and neat samples in the laboratory leaching experiments. Every two pore volumes of liquid are composited into one sample. Thus, five composite samples have been collected and analyzed during the quarter for pH, Eh, phenolphthalein alkalinity, and total alkalinity. The first three samples were analyzed by inductively coupled plasma spectrometry.

Based on pH of the leachates, the neat samples CSS-1 and agricultural limestone are similar in pH behavior, with pHs near 8 for each leachate. The leachates from CSS-2 were initially acidic, but quickly approached a pH of 8 in succeeding leachates. The leachates from the five FBC wastes were more alkaline, with pHs in the range 10 to 13. The leachates of mixtures with CSS-1 were also near 8 in all leachate samples.

Leachates from mixtures of CSS-2 and FBC wastes showed evidence of pyrite oxidation. Apparently, the rate of dissolution of alkaline materials in the FBC wastes was not great enough to allow complete neutralization of the produced acid, as the pH values in leachates from four of the five mixtures were acidic.

It is unclear presently whether oxidation is occurring in the laboratory leaching experiments. The solids might not be drying enough between additions of water to allow air to penetrate the intergranular spaces and promote oxidation.

Two leachates were collected from the outdoor weathering experiments during the quarter. The first set of leachates from mixtures of CSS-1 were near neutral, in the range of 7.0 to 7.9. The pH values in the second set of leachates from mixtures with CSS-1 were slightly higher, in the range 7.6 to 8.1. The first set of leachates from mixtures with CSS-2 were acidic (pH 2.9 to 5.8), except for the mixture

CSS-2/FBC-4 (pH 11.4). In the second set of leachates from mixtures with CSS-2, the pHs were in the range 2.9 to 3.9, except that from CSS-2/FBC-4 was 6.4. Oxidation of pyrite has clearly taken place in the outdoor weathering experiments with CSS-2.

OBJECTIVES

The overall objective of this proposed research project is to develop an environmentally acceptable method for disposing of coal fluidized bed combustion (FBC) waste. The disposal method under study is to mix FBC waste with coal preparation plant slurry solids in order to prepare a medium suitable for growing plants after the closure of a slurry pond. The overall objective will not be met in one year of research. It will require a laboratory study to characterize the materials, then a greenhouse study conducted under the guidance of a soil ecologist, followed by an agronomic field study at a coal preparation plant.

The scope of the present project is 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 is 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 used for reclamation in future studies.

INTRODUCTION AND BACKGROUND

In the fluidized bed combustion of high-sulfur coal, powdered limestone is injected into the fluidized bed to serve as a trap for sulfur dioxide emitted from the coal as a result of combustion. When the sulfur dioxide reacts with the calcium carbonate of the limestone, it forms gypsum. Typically, the limestone 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 is 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.

Coal slurry solids arise in the removal of pyrite and rock fragments in the process of cleaning the 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 it 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.

A possible means of reclamation is to buffer the coal slurry solids with alkaline fluidized bed combustion wastes and grow plants on it to provide some stability against erosion. The major concerns in this application are the leachability of trace inorganic species from the waste into groundwater 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 will be addressed by means of appropriate aqueous leaching experiments using mixtures of five fluidized bed combustion wastes with two coal slurry solids.

EXPERIMENTAL PROCEDURES

All experiments for this research project were set up during the second quarter. These consist of a series of laboratory leaching experiments and a series of outdoor weathering experiments.

In the laboratory leaching experiments, mixtures of coal slurry solid (CSS) and FBC waste or agricultural limestone were prepared. In addition, samples of the neat solids (5 FBC samples, 2 CSS samples, and 1 agricultural limestone sample) have also been prepared. The mixtures were prepared according to our calculations of the acid generating potential of the CSS and the calcium carbonate equivalent of the FBC or limestone. Our attempt was to prepare each mixture so that any acid generated due to the oxidation of pyrite in the CSS would be neutralized by the calcium hydroxide in the FBC waste.

We prepared a mixture of CSS and crushed limestone to correlate with each mixture of CSS and FBC. In preparing the CSS-limestone mixtures, we attempted to match the particle size composition of each FBC waste in order to have a point of reference for the leaching behavior of the CSS-FBC mixtures.

There are 28 solid samples that are extracted weekly with one pore volume of deionized water. Two consecutive pore volumes of extract are composited for analysis, that is, extracts are collected for two-week periods. To date, five sets of extracts have been collected. All extracts have been analyzed for pH, Eh, phenolphthalein alkalinity, and total alkalinity. The first three extracts from each solid sample have been analyzed by inductively coupled plasma spectrometry (ICP).

Outdoor weathering experiments consisting of mixtures of CSS samples and FBC wastes or as-received limestone were prepared. These mixtures (a total of 12) were placed on the roof of an ISGS building on February 1, 1992 for exposure to weather. Any leachate from these experiments is the result of sufficient rainfall to generate leachate. Since February, two leachates have been collected. One set has been analyzed by ICP. The experiments are presently scheduled to end on June 30.

The solids used as starting materials have been analyzed by atomic absorption spectrometry, neutron activation analysis, optical emission spectrometry, wavelength dispersive x-ray fluorescence spectrometry, energy dispersive x-ray fluorescence spectrometry, carbon analyzer, and standard ASTM methods for varieties of sulfur, ash, and moisture content. The x-ray diffraction analysis of the starting solids is nearing completion.

RESULTS AND DISCUSSION

Analysis of Starting Solids. The results of analysis of the starting solids are listed in Table 1. The data for the major and minor element concentrations were used in cluster analysis to statistically differentiate the samples.

The concentration data for the major and minor elements in the starting solids were standardized statistically to a mean of 0 and a standard deviation of 1 prior to cluster analysis. As shown in Figure 1, FBC-1, FBC-2, and FBC-5 are similar, and FBC-3, FBC-4, and the agricultural limestone are similar. CSS-1 is somewhat similar to FBCs 1, 2, and 5. CSS-2 is in a group by itself. These similarities, however, are not necessarily evident in the leaching experiments.

Laboratory Leaching Experiments. Eleven pore volumes of deionized water have been added to the top of each leaching experiment. The pH of the leachates as a function of pore volume of water leached are shown in Figures 2 through 7. Figures 2 and 3 show the pH behavior of the two CSS samples alone and the five FBC samples plus the agricultural limestone alone, respectively. A comparison of these two figures shows that pH behavior in leachates from the CSS-1 and the Ag LS are similar. The leachates from both the CSS-1 and the Ag LS remained near a value of 8. The pH of CSS-2 began at a low value, about 5, but increased with continued leaching, to a value of about 8.

The pH of the leachates from the five FBC wastes (fig. 3) were between 10 and 13, a result of the presence of high concentrations of CaO or $Ca(OH)_2$ in the samples, as opposed to $CaCO_3$ in the Ag LS. The exception is FBC-3, which contains about 40% $CaCO_3$ and 28% $Ca(OH)_2$. The pH of leachates from FBC-3 alone were generally lower than the others, probably due to the presence of the $CaCO_3$.

Figure 4 shows the pH of leachates from mixtures of CSS-1 and each of the five FBC wastes. Figure 5 shows the pH of leachates from mixtures of CSS-1 and mixtures of Ag LS size-matched to each of the five FBC wastes. Both figures show that the pH of the leachates from the ten mixtures did not vary much from a value of 8, and that these leachates were similar to that from CSS-1 alone. The pH of the mixtures containing Ag LS are slightly lower than those containing FBC wastes.

Figures 6 and 7 show the pH of leachates from mixtures of CSS-2 and FBC waste or size-matched Ag LS, respectively. The pH of the CSS-2/FBC mixtures was somewhat different from those of CSS-2 alone. However, the pH of leachates from the CSS-2/Ag LS mixtures was similar to those from CSS-2 alone.

At pore volume 11, all leachates except CSS-2/FBC-4 had a pH of approximately 8. The pH of CSS-2/FBC-4 was approximately 5 at pore volume 11. The pH behavior indicated in Figure 6 shows that oxidation of pyrite has occurred in these mixtures, and that all the acid produced has leached from the mixtures by pore volume 11, or that dissolution of the alkaline compounds in the FBC wastes was slower than the production of acid from the pyrite in the CSS and the alkalinity of the FBC wastes was initially unable to neutralize the produced acid.

The pH behavior exhibited by the other mixtures is less clear. Leachates from all other mixtures are slightly alkaline. There are two overall possibilities for the exhibited behavior.

(1) Oxidation of pyrite in the CSS has occurred and the produced acid was neutralized by alkaline components of the FBC wastes or the Ag LS.

(2) Pyrite grains are protected from oxidation by the presence of moisture in the mixtures. That is, the mixtures might not be drying sufficiently between additions of water to allow air to come into contact with more than the top surfaces of the CSS/FBC or Ag LS mixtures.

The fact that the pH of leachates from all CSS-1 experiments, including CSS-1 alone, has remained near 8 through pore volume 11, and that all these leachates appear similar in terms of pH, suggests that oxidation has not occurred in CSS-1 mixtures. Evidently, some alkaline components have dissolved with the passage of water through the samples, and have done so rather uniformly and consistently, in order to maintain the pH so nearly constant.

With CSS-2, at least some initial oxidation of pyrite appears to have occurred, based on the low pH of leachates from pore volume 3.

Outdoor Weathering Experiments. Two sets of leachates have been collected to date from the outdoor weathering experiments. The first set was collected on April 20, 1992, and the second set was collected on May 26, 1992.

We have attempted to measure the amount of rainfall collected by each of the outdoor weathering experiments by setting up two parallel empty sample holders, one in each weathering cabinet. Our attempt is to collect all the precipitation and only the precipitation that falls into a nine-inch inside diameter tube, identical in length to those used to contain the sample mixtures. The two blank sample holders are approximately 6 feet apart. By our measure, the outdoor weathering samples received between 3.46 and 3.72 inches of rainfall during the period February 1 and April 15, 1992. The volumes of water collected on the two occasions consist of precipitation from more than one rainfall event, however, the events occurred over a short duration, no more than two to three days.

The official rainfall totals from the Illinois State Water Survey for Champaign during the months February through May 26, 1992 are:

February	1.35"
March	2.00"
April	3.30"
May	2.96"

The data in Table 2 show the volume of water collected from each sample mixture and the pH of the water. The volumes of water collected on the second occasion are somewhat lower than on the first occasion. The probable cause for this is not that less water fell on the sample, but that before water will flow into the collection vessel beneath a sample, the sample must be saturated to its water-holding capacity. It took almost three months for the samples to maintain enough water to allow flow into the collection vessel. The reason for this is that a certain amount of drying occurs between rainfalls, depending on the air temperature, the relative humidity, the intensity of the sunlight falling on the surface of the sample, and the wind velocity.

The amount of water collected in the second set of leachates was smaller than in the first set, because the samples had dried considerably in the month between collections, due to the above mentioned factors.

The two sets of leachates from CSS-1 mixtures are similar to those collected during the laboratory leaching experiments. It cannot yet be determined whether pyrite oxidation has occurred in the mixtures containing CSS-1.

However, it is obvious that pyrite oxidation has occurred in the mixtures containing CSS-2. The pH value for each leachate in the first set is acidic, in the range 2.90 to 5.86, except for the leachate from CSS-2/FBC-4. The leachate pH from this mixture was 11.39. The pH of the second set of leachates from mixtures with CSS-2 were lower than in the first set, pH 2.93 to 3.94, except for that from CSS-2/FBC-4. The pH in the second leachate from this mixture was lower than in the first leachate, but it was higher than in leachates from the other five mixtures, 6.43. Of the five FBC wastes, FBC-4 has the greatest amount of total Ca and the greatest amount of $CaO + Ca(OH)_2$. Curiously, the pH is lowest in both leachates from the CSS-1/FBC-4 mixture.

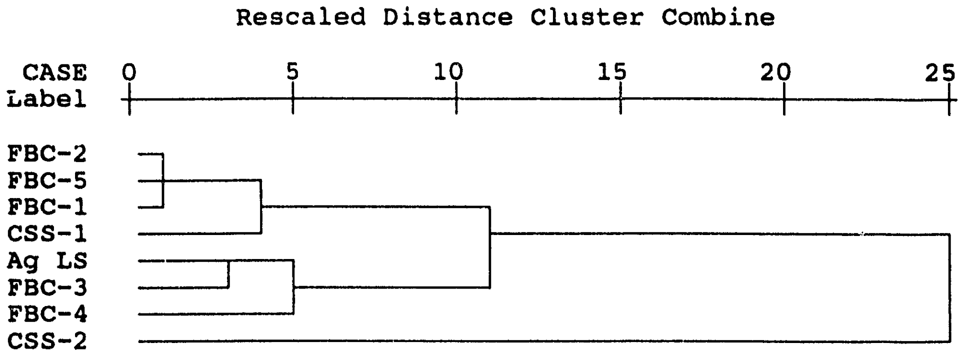


Figure 1. Cluster analysis dendogram of FBC wastes, agricultural limestone sample, and CSS samples, based on standardized data of major and minor element concentrations.

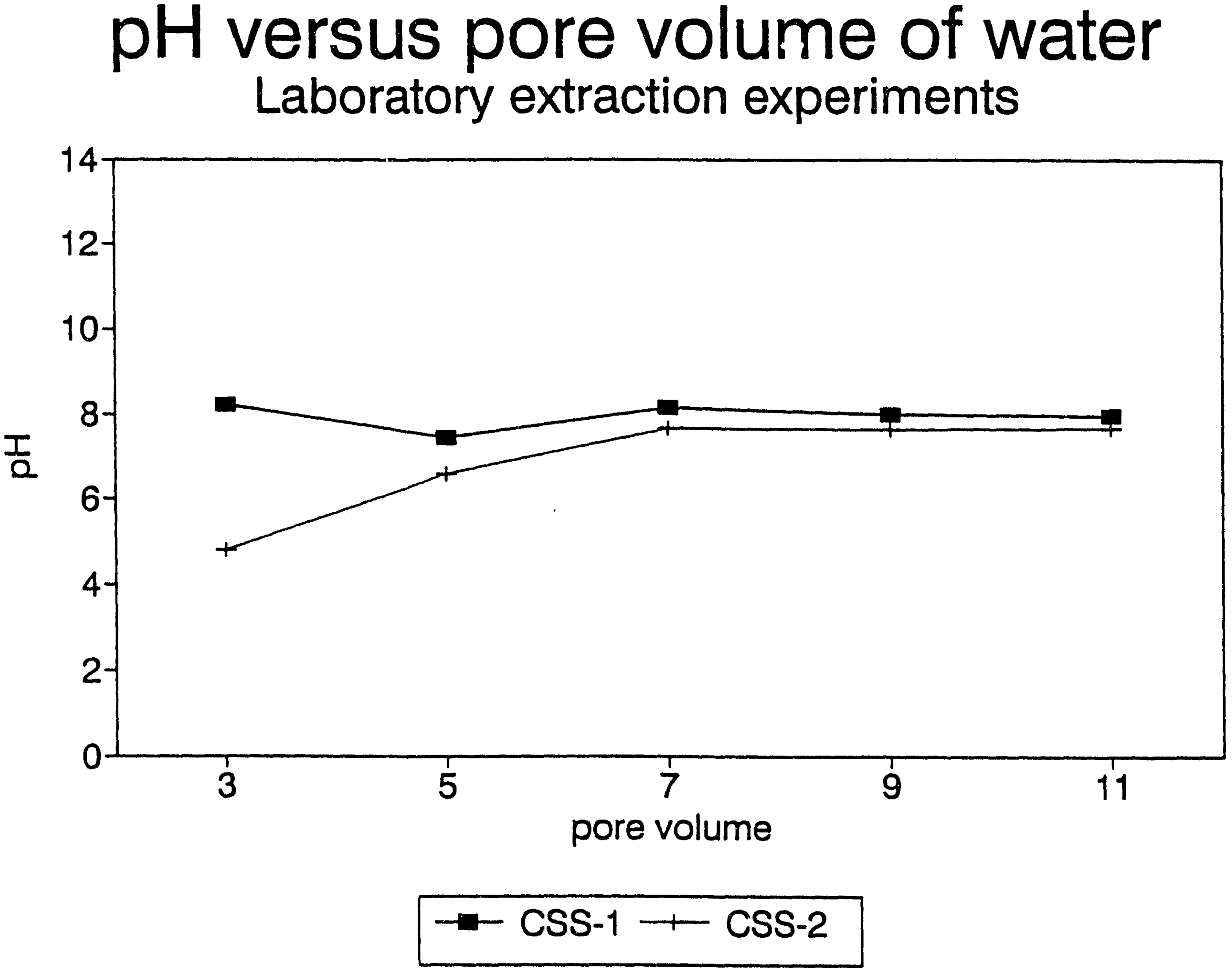


Figure 2. pH versus pore volume of water in laboratory leaching experiments: neat CSS samples

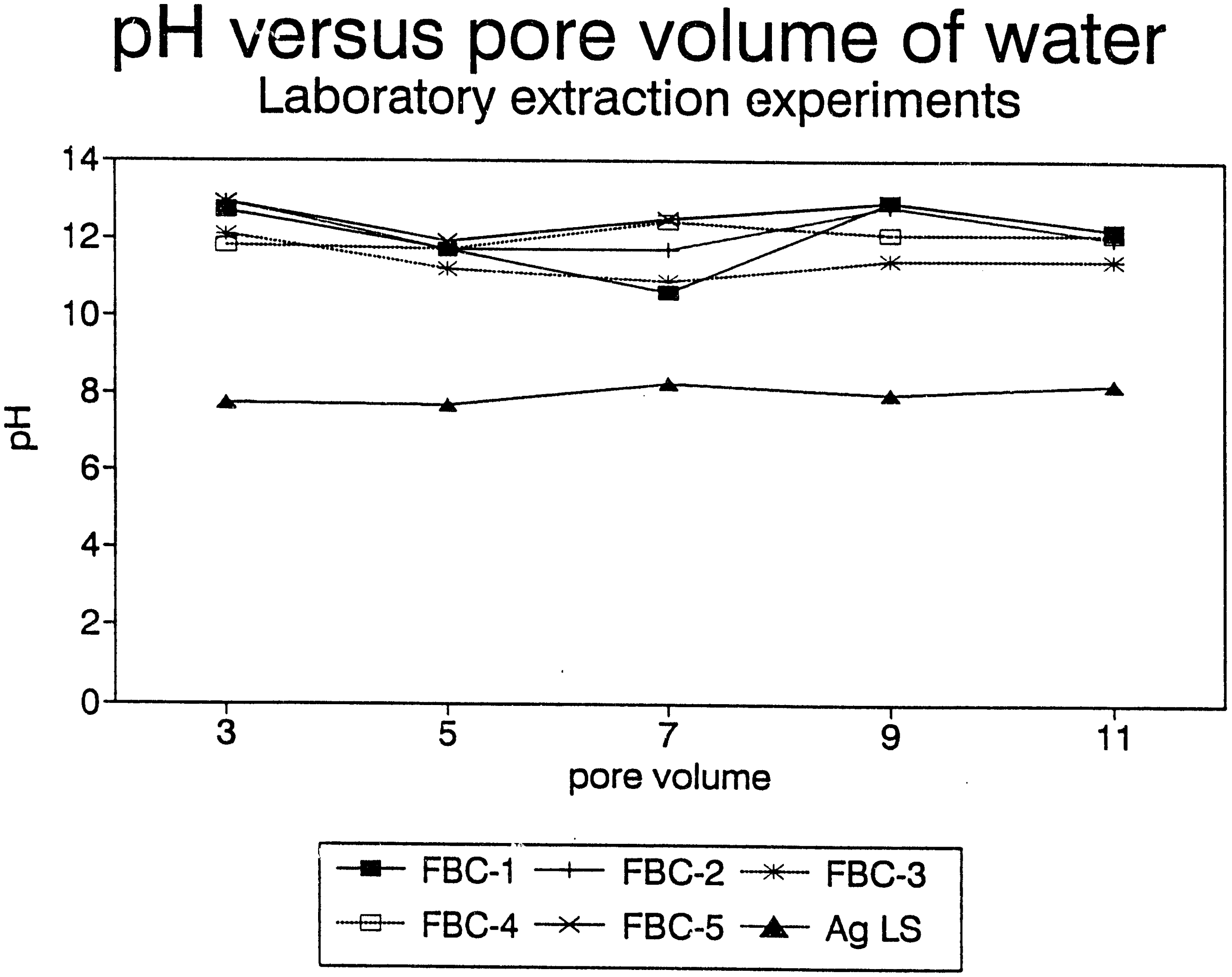


Figure 3. pH versus pore volume of water in laboratory leaching experiments: neat FBC samples and agricultural limestone sample

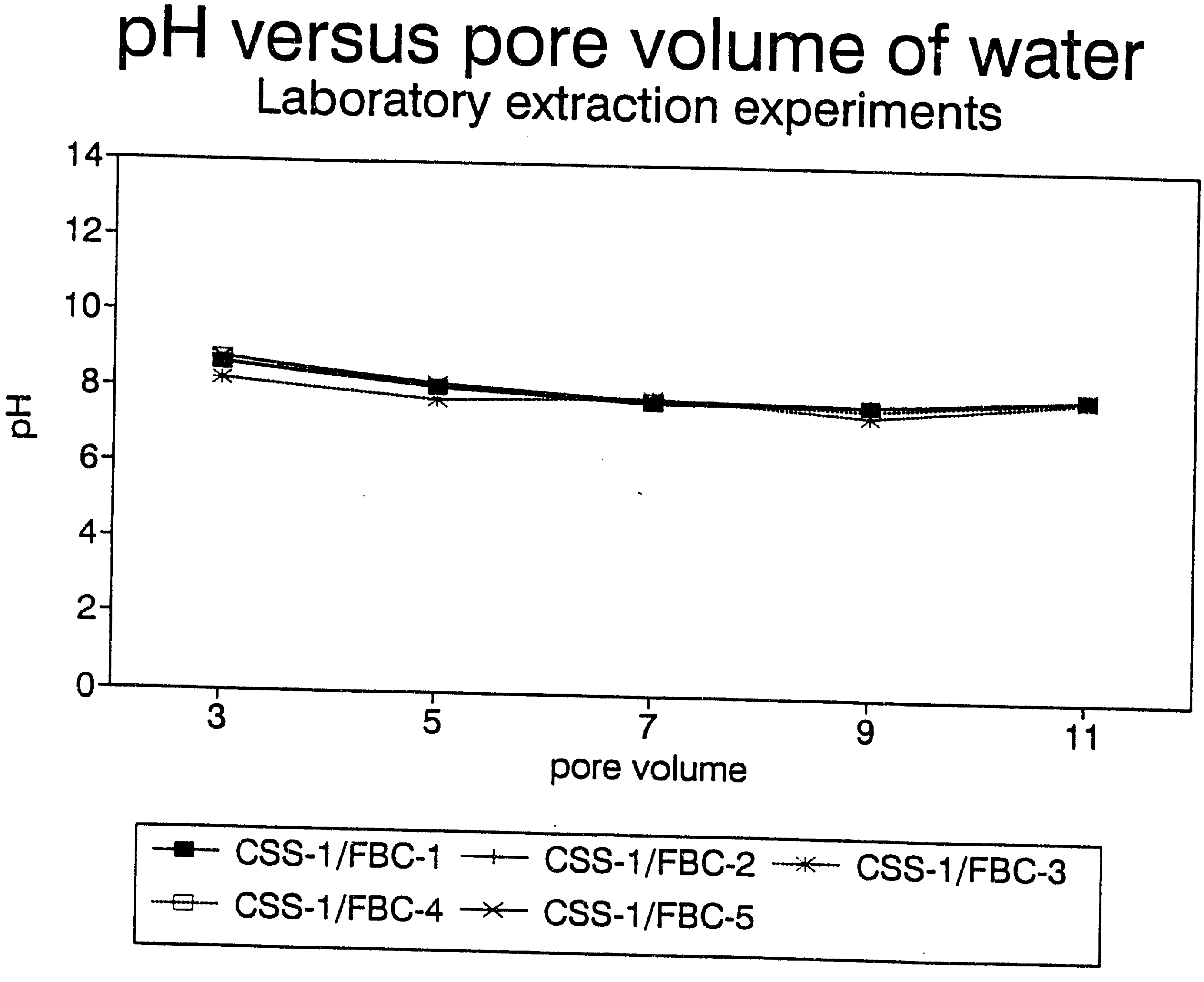


Figure 4. pH versus pore volume of water in laboratory leaching experiments: mixtures of CSS-1 and FBC wastes

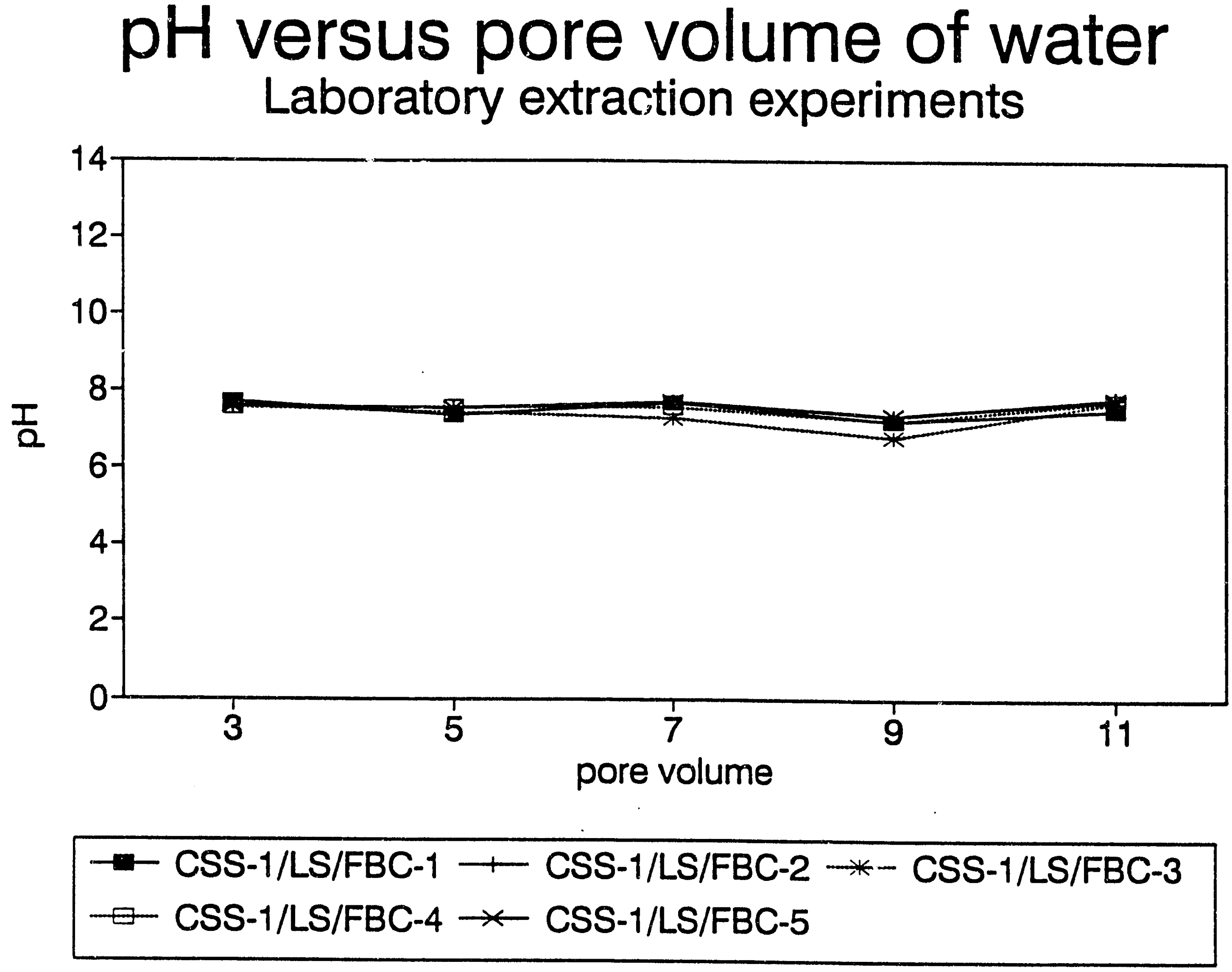


Figure 5. pH versus pore volume of water in laboratory leaching experiments: mixtures of CSS-1 and size-matched agricultural limestone

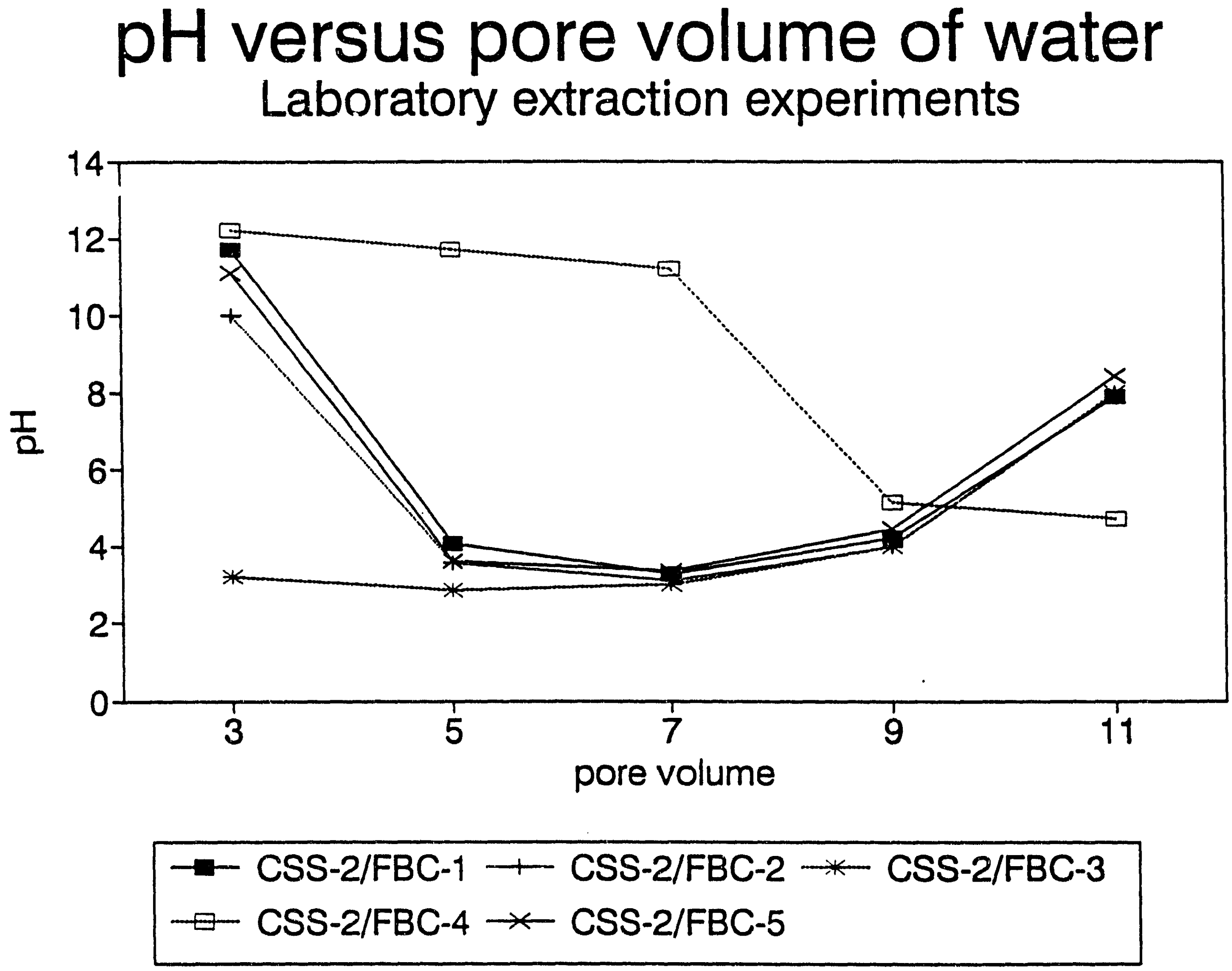


Figure 6. pH versus pore volume of water in laboratory leaching experiments: mixtures of CSS-2 and FBC wastes

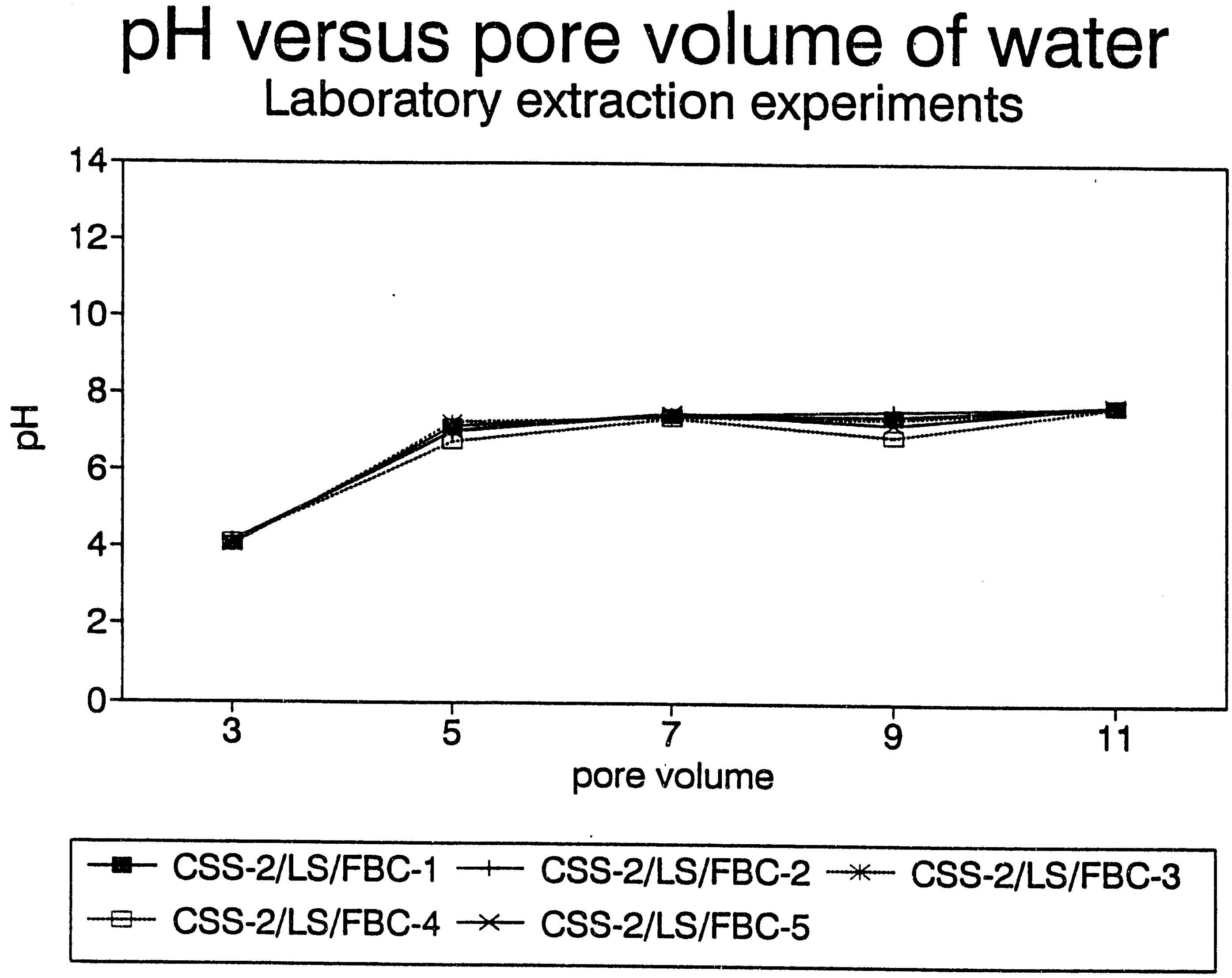


Figure 7. pH versus pore volume of water in laboratory leaching experiments: mixtures of CSS-2 and size-matched agricultural limestone

Table 1. Inorganic composition of starting solids

Major and minor elements (%)

Analyte	FBC-1	FBC-2	FBC-3	FBC-4	FBC-5	Ag LS	CSS-1	CSS-2
Al_2O_3	5.80	5.90	1.99	1.84	4.56	1.34	5.80	7.89
BaO	0.04	0.02	0.01	0.01	0.03	<0.01	0.02	0.04
CaO	45.17	34.99	47.22	61.91	29.85	45.68	3.17	9.53
Fe_2O_3	5.39	10.95	3.18	2.87	5.41	0.62	3.02	19.73
K_2O	0.80	0.55	0.24	0.16	0.60	0.53	0.90	1.37
MgO	1.05	0.83	0.62	1.00	0.83	4.20	0.40	0.80
MnO	0.09	0.06	0.02	0.11	0.07	0.04	0.03	0.10
Na_2O	0.34	0.44	0.18	0.14	0.35	0.10	0.35	0.47
P_2O_5	0.17	0.10	0.06	0.06	0.13	0.03	0.14	0.45
SO_3	17.40	16.72	7.78	16.31	13.67	0.10	----*	----
SiO_2	18.01	20.67	8.54	6.75	17.87	7.00	19.69	29.91
SrO	0.07	0.02	0.04	0.04	0.06	0.02	0.01	0.01
TiO_2	0.29	0.28	0.09	0.08	0.24	0.08	0.29	0.34
Trace elements (mg/kg)								
Ag	<1	<1	<1	<1	<1	<1	<1	<1
As	9.5	9.8	4.5	8.5	11	1.4	2.7	81
B	218	281	118	145	316	<10	175	62
Be	1.2	3.0	1.1	<1	2.4	1.2	<1	<1
Br	13	36	4	9.4	27	<2	13	3
Ce	32	21	9.6	10	22	11	26	43
Co	9.1	7.9	2.3	3.0	6.9	1.7	6.3	19
Cr	44	67	25	22	55	6.5	35	73
Cs	3.4	2.8	0.98	0.88	2.6	0.6	3.1	3.6
Dy	2.6	2.1	1.1	0.92	2.1	0.96	1.7	3.3
Eu	0.65	0.51	0.21	0.23	0.49	0.24	0.47	0.97
Ga	8.9	8.3	2.7	2.7	8.9	1.8	6.7	7.9
Ge	9	7	11	12	7	11	<5	<5
Hf	1.7	1.4	0.88	0.46	1.4	0.7	1.5	2.0
La	16	11	6.3	5.3	12	8.4	14	24
Lu	0.26	0.24	0.12	0.12	0.21	0.1	0.18	0.34
Mo	16	18	<10	12	15	<10	<10	46
Pb	42	14	<10	<10	12	12	10	52
Rb	49	37	13	12	37	16	47	88
Sb	1.5	3.6	0.8	1.4	2.2	<0.2	0.5	4.1
Sc	6.9	6.5	2.1	2.2	6.1	1.5	6.1	8.7
Se	4.9	9.3	1.8	2.8	6.5	<0.5	3.3	14
Sm	2.8	1.9	0.95	0.95	2.1	1.1	2.3	4.1
Sn	<5	6	<5	<5	<5	<5	<5	12
Ta	0.35	0.4	0.12	0.11	0.35	0.1	0.35	0.43
Tb	0.47	0.38	0.19	0.15	0.37	0.54	0.28	0.51
Th	4.6	4.1	1.5	1.4	3.9	1.2	4.1	5.4
U	6	9	4	4	7	<1	2.5	7
V	61	76	26	40	94	14	46	64
Yb	1.4	1.3	0.56	0.49	1.3	0.54	0.95	2.0
Zn	500	240	110	120	150	----	91	1400
Zr	68	73	32	26	68	27	64	96

*Not Detected

Table 2. Volume and pH of water collected from outdoor weathering experiments after two different rainfall events.

Sample	April 20, 1992		May 26, 1992	
	Volume (mL)	pH	Volume (mL)	pH
CSS-1/FBC-1	1089	7.04	104	7.74
CSS-1/FBC-2	1071	7.42	143	7.67
CSS-1/FBC-3	1196	7.86	128	8.11
CSS-1/FBC-4	1071	6.42	98	7.64
CSS-1/FBC-5	1018	7.25	122	7.72
CSS-1/Ag LS	1107	7.83	128	7.97
CSS-2/FBC-1	964	5.16	202	3.90
CSS-2/FBC-2	893	4.97	167	3.39
CSS-2/FBC-3	1054	2.90	88	3.94
CSS-2/FBC-4	1179	11.39	246	6.43
CSS-2/FBC-5	875	3.88	105	2.93
CSS-2/Ag LS	1304	5.86	119	3.88

PROJECT MANAGEMENT REPORT
March 1, 1992 through May 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

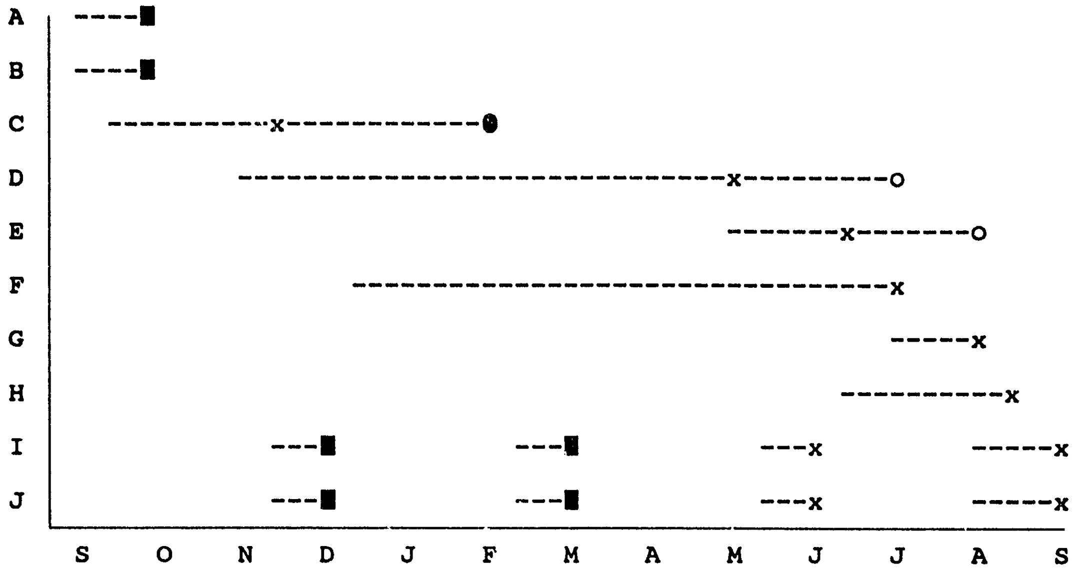
COMMENTS

The Projected Expenditures shown on "EXPENDITURES - EXHIBIT B: Projected and Estimated Actual Expenditures by Quarter" were in error in the reports for the first quarter. They have been corrected this quarter and are now in agreement with the figures shown in the proposal.

Milestones C was completed during the quarter. Milestones D, E, F, G, and H are underway.

This project is funded by the U. S. Department of Energy (METC) and by the Illinois Department of Energy and Natural Resources as part of their cost-shared program.

SCHEDULE OF PROJECT MILESTONES



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. There is sufficient time in the schedule so that meeting the requirements of the research project will be met.

END

DATE FILMED

12 / 14 / 92