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Illinois coal ground to 80-200 mesh was leached with a low phosphate, high nitrogen medium containing a mixture of Thiobacillus ferrooxidans and thiooxidans in a fluidized bed. Coal slurries of 20-160 g/L were treated in a 5 cm ID, 9.5 m high continuous loop bioreactor with crossovers at top and bottom, and a volume of 41.3 L (11 gal). Air introduced into the bottom of one side at 1500 cm^3/min oxygenated the system and caused a rapid continuous circulation. Fresh medium was added to the top of the reactor at the same place air was vented, while coal-free leachate was continuously removed from the bottom of the reactor; the flowrate being 1.9 cm^3/min with a liquid residence time of 15.2 days. This produced about 20 gal of drained leachate plus what was still in the column at the end of a 28 day run.

Temperature, pH and dissolved oxygen concentration were monitored. Atomic absorption spectrophotometer (AAS) analyses of the leachate (drained and in column)

plus leached and unleached coal indicated significant leaching of sulfur, iron, calcium, lead, magnesium, sodium, chromium, nickel and gold (0.4 ppm in leachate). AAS readings for silicon, titanium, platinum and arsenic (column samples only) suffered from high detection limits due to noise or other difficulties with the atomic absorption unit used and, consequently were not detected. A significant level of Arsenic was detected in the concentrated coal extracts, which indicated that leaching had occurred; however, data scatter was large. A small amount of aluminum was also leached.

Shake flask experiments were also carried out to compare surfactant levels, coal type, the effect of a filtered inoculum (ferric sulfate but no bacterium), and the controls. These results were related to the reactor data to develope parameters describing the effect on leaching of variation in coal type and slurry concentration for various elements. The efficiency of the reactor compared to shake flask work was also determined.

Bioleaching of Coal in a Fluidized Bed

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BIOLEACHING OF COAL IN A FLUIDIZED BED

1. INTRODUCTION

1.1. BACKGROUND

1.1.1. Problems With Coal

Coal is an important fossil fuel used to provide heating, steam and power generation capability in industry.

Coal contains many impurities including sulfur, iron, calcium, magnesium, silicon, lead and arsenic and trace amounts of more valuable metals like chromium, nickel, titanium and possibly precious metals as well. The combustion of coal containing large amounts of metallic impurities results in significant amounts of waste ash being produced which can foul heat exchange surfaces or contain toxic elements such as lead or arsenic. The combustion of coal containing sulfur will generate sulfur dioxide gasses which have been implicated in the formation of acid rain.

Reduction of the sulfur content in coal reduces the sulfur dioxide emissions from the combustion of coal. This would enable higher sulfur content coals, which are cheaper to obtain, to be used with less treatment of emissions to scrub the acid rain producing sulfur dioxide

gasses.

Reduction of the metal content in coal reduces the amount of ash generated and lessens the fouling of heat exchange surfaces in the combustor (Olsen et al., 1986) plus other potentially harmful effects.

1.1.2. Bioleaching

The desulfurization and demineralization of coal is a desireable process that can be effectively catalyzed by acidophilic aerobic bacteria of the genus *Thiobacillus*. This process is known as bioleaching and involves using a suitable bacteria laden growth media to form a slurry with ground coal and then providing correct ambient conditions. Over time, the inorganic sulfur (which is a significant part of the total sulfur in many coals) and metal impurities will be removed by the bacteria and solubilized into the media. The bacterium *Thiobacillus ferrooxidans* is particularly effective at accomplishing this.

Most iron and inorganic sulfur in coal exists as iron pyrite. Most metal impurities exist as sulfides or easily soluble (in acidic water) sulfates. Pyrite and other metal sulfides can be effectively leached from coal and other metal ore with the bacterium *Thiobacillus ferrooxidans* (Olson and Kelly, 1986). Bioleaching of low

grade ore is responsible for 10-20% of U.S. copper production and is also used successfully in the recovery of uranium from ore (Olson and Kelly, 1986). In addition, dump heap bioleaching with Thiobacillus ferrooxidans may also improve extraction of gold from pyritic ore. A commercial bioleaching assisted gold extraction plant is being built in Nevada (Cook, 1989). Bioleaching of galena, nickel sulfide and arsenic sulfides have also been studied (Brierly, 1978). The recovery of precious or valuable metals from the leachate would add an additional economic benefit to a coal bioleaching process.

Because of the complementary contribution of Thiobacillus thiooxidans to the pyritic leaching mechanism, mixed cultures of both strains may be more effective for the oxidation and solubilization of pyrite in coal. Wakao et al. (1983) reportedly found that mixed cultures did increase pyritic oxidation, but Hoffmann et al. (1981) indicated the opposite.

Bacteria of the genus Thiobacillus have been reported to secrete a surface active compound (Tributsch and Bennett, 1981), which apparently increases the activity of the microorganism. Chandra et al. (1980) have found that the use of 100 ppm of Tween-80, a surfactant, significantly improved the desulfurization of

Jeypore, an Indian coal. Wakao et al. (1983) found a similar improvement in pyrite oxidation when using a surfactant.

1.1.3. Bioleaching Reactor Design

Coal bioleaching studies with Thiobacillus ferrooxidans and thiooxidans have predominantly been done in shake flasks or small batch reactors (volume less than one liter). Presently, commercial low grade ore leaching is performed in-situ on heaps of ore (no reactor). Although many commercial bioreactor configurations have been proposed and discussed (Olson and Kelly, 1986), only two coal bioleaching studies conducted with larger scale designs were located: (1) Tillet and Myerson (1987) used a packed bed reactor and (2) Rai (1985) used a slurry pipeline loop, circulated with a mechanical pump. A fluidized bed would provide an effective three-phase contacting pattern, but a slurry pipeline reactor would be useful for desulfurization of coal during transport providing that sufficient aeration (a problem) could be provided (Olson and Kelly, 1986)

In the biological pre-oxidation of pyritic ore concentrates for gold recovery, the leaching solution containing high ferric iron levels at a low pH must be replaced periodically for optimal conditions. High

levels of ferric iron, which is the primary form of iron in coal leachates, inhibits the oxidation of pyrite. The inhibitory level varies widely with the reference cited (Brierly, 1978). It is also desireable to remove trace metals that are toxic to the organisms, such as silver, and control the pH to a level of between 2-3, which is the optimum growth level (Olson and Kelly, 1986). An effective way of controlling the levels of inhibiting compounds and supplying nutrients could be a continuous flow of clean media at optimum pH into the reactor with a subsequent withdrawal of leachate for further treatment.

The effective contacting and aeration of the fluidized bed reactor could be combined with the practicality of a pipeline reactor and the steady-state characteristics of a continuous stirred tank reactor. The aeration from air introduced in the vertical sections of the pipe would provide the fluidizing circulation which would travel in a continuous loop and, thereby, operate as a mixed flow system. Thus, the resulting fluidized bed mixed flow pipeline reactor would be simple in design, require no mechanically induced circulation (no pump corrosion), and be well mixed.

1.1.4. Economic Justification for Coal Bioleaching

Detz and Barvinchak (1979) presented a cost analysis for a proposed 8000 tons/day coal bioleaching facility to treat 200 mesh coal with Thiobacillus ferrooxidans. Leaching was to be conducted in 25 acres of aerated open air lagoons which were continuously fed with 20% coal slurry. The slurry was also to be continuously withdrawn and solidified for use. Residence time and other operational factors used in the analysis were based on kinetic data developed from shake flask and bench scale continuous stirred tank reactor experiments. Illinois, Ohio, Kentucky and W. Virginia coals were used. Calculated residence time for 90% removal of pyritic sulfur varied from 14-36 days depending on coal type and origin.

The cost analysis presented was based on a 16-day residence time and indicated a unit bioleaching cost of $10.5/ton of previously ground coal. The cost of grinding the feed coal to 200 mesh and pelletizing the dried leached coal after treatment would add $3.4/ton coal but could be offset by a $1./ton heat recovery credit from the system. The overall unit cost would then be $10-14/ton coal, which compares favorably to the unit costs of four other experimental coal desulfurization processes under study. These other processes (TRW-

ferric, Battelle-hydrothermal, Kennecott-oxygen and solvent refining) are chemical in nature with unit costs of $20-30/ton coal (Detz and Barvinchak, 1979).

A later study by Olson et al. (1986) presented a cost analysis of a similar lagoon bioleaching process utilizing the same bacterium and coal size again based on shake flask experimental work. A bioleaching unit cost of $7-12/ton coal was calculated as compared to other processes discussed (ARCO-oxydesulfurization, Battelle-hydrothermal and TRW-ferric) with unit costs of $43-58/ton coal. The bioleaching unit cost neglected costs of agitation and heating of the lagoons, which was assumed to be obtainable from waste heat recovered elsewhere. Detz and Barvinchak (1979) included heating and agitation costs in their study.

In both studies, particularly the most recent which represents the effects of inflation on chemical process costs, bioleaching with Thiobacilli is an economically favorable option compared to other coal treatment processes. Even if additional bioleaching costs arise or if other chemical processes are made cheaper, the recovery of valuable or precious metals from the bioleaching leachate could provide additional cost protection.

No cost studies were found based on other reactor designs (slurry pipeline, fluidized bed, etc.). A fluidized bed bio-reactor would require much less land and excavation work than 25 acres of lagoons but material costs would probably be higher. Coal drying and pulverizing costs would be similar but agitation in the fluidized bed would be a product of aeration and these costs might be lower.

1.2. OBJECTIVES

The objective of this study was to determine the effectiveness of microbial leaching with the two strains of Thiobacillus in a fluidized bed bioreactor. The coal was to be leached in batches with only continuous flow of the leachate; although the possibility of continuous flow of coal was taken into account in the design of the fluidized bioreactor. The effects of various conditions involving slurry concentration, surfactant levels and coal type were studied in both the reactor and a set of batch shake flask experiments. Comparisons were generated to characterize leaching behavior in both systems.

1.3. BIOLEACHING MECHANISM

The bacterium Thiobacillus ferrooxidans (Tf) catalyzes the solubilization of inorganic sulfur compounds, mainly pyrite (Silverman, 1967). Thiobacillus ferrooxidans flourishes in aerobic, acidic environments at ambient temperatures. They obtain energy by oxidizing ferrous iron to ferric (Olson and Brinckman, 1986).

$$4\ Fe^{2+} + O_2 + 4\ H^+ \xrightarrow{Tf} 4\ Fe^{3+} + 2\ H_2O \qquad (1)$$

Ferric ions (either introduced independently or by the above reaction) solubilize pyrite (Olson and Brinckman, 1986).

$$FeS_2 + 2Fe^{3+} \longrightarrow 3\ Fe^{2+} + 2\ S^{\circ} \qquad (2)$$

Other metal sulfides are also attacked by ferric solutions yielding soluble metal ions and elemental sulfur (Olson and Kelly, 1986).

$$MS + 2\ Fe^{3+} \longrightarrow M^{2+} + 2\ Fe^{2+} + S^{\circ} \qquad (3)$$

Leaching by ferric solution attack is known as the indirect leaching mechanism.

Direct leaching of the pyrite and other metal sulfides by bacterium attached to the substrate has also been postulated (Monticello and Finnerty, 1985).

$$FeS_2 + 3.5\ O_2 + H_2O \xrightarrow{Tf} FeSO_4 + H_2SO_4 \qquad (4)$$

$$2\ FeSO_4 + 0.5\ O_2 + H_2SO_4 \xrightarrow{Tf} Fe_2(SO_4)_3 + H_2O \qquad (5)$$

Evidence seems to indicate that both mechanisms are probably present and complementary, but to an unknown degree of balance (Olson and Kelly, 1986).

Thiobacillus thiooxidans (Tt) and Thiobacillus ferrooxidans, which have similar environmental preferences, both oxidize elemental sulfur to sulfuric acid; thus preventing a layer of elemental sulfur from coating the coal surface and inhibiting further leaching (Olson et al., 1986; Monticello and Finnerty, 1985).

$$S^\circ + H_2O + 3/2\ O_2 \xrightarrow{Tt,Tf} SO_4^{2-} + 2\ H^+ \qquad (6)$$

In the direct leaching mechanism, pyritic sulfur may be preferentially oxidized. Diffusion of the sulfur out of the pyrite matrix and along grain boundaries to the particle surface may account for this. This preferential oxidation of pyritic sulfur yields almost 24 times the energy to the bacteria as oxidation of ferrous iron provides (Monticello and Finnerty, 1985). Because some iron is left behind as the sulfur diffuses out and is oxidized, the molar ratio of sulfur to iron leached would be greater than the stoichiometric value of two.

2. APPARATUS AND PROCEDURES

2.1. DESCRIPTION OF APPARATUS

The fluidized bed bioreactor (Figure 1) was constructed of two parallel, vertical, 5 cm ID PVC pipes with short crossovers at the top and bottom to provide a loop for continuous circulation. The overall height of the reactor is 9.5 meters (a 4 m section is wrapped in heat tape) and its volume is 41.3 L (11 gal). Air can be introduced into the bottom of one side of the reactor through three sintered bubblers and can exit the column at the air vent. Rotameters are located at the air vent and at the 45° elbow. A drain is located under the sintered air bubblers (Figure 1).

An orbital shaker (Orbit #3527) was used for shake flask work. The shaker is equipped with a plastic hood which coveres the rotating flask bed. This hood permits precise temperature control by the thermostatically controlled heater in the unit. The rotating flask bed is configured for 250-ml erlenmeyer flasks.

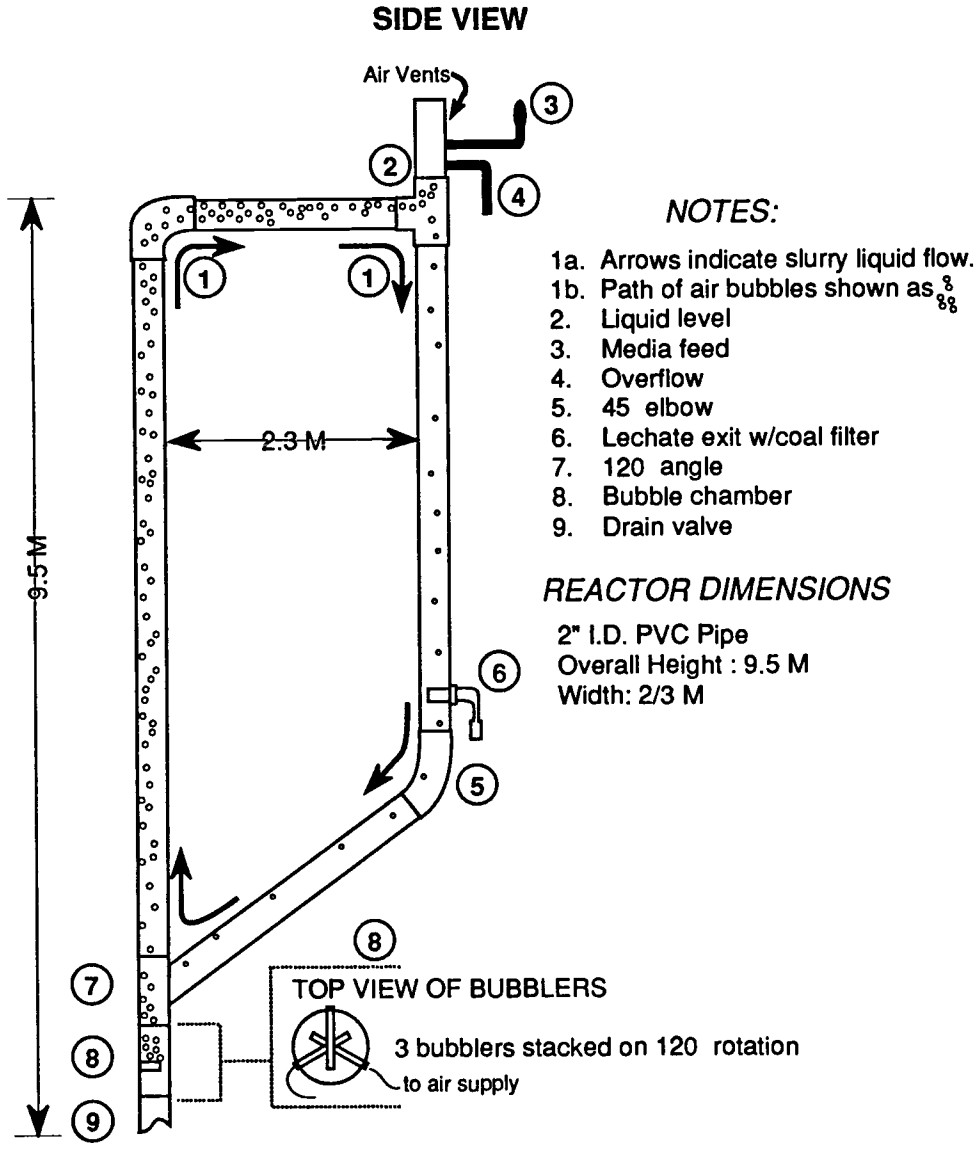

FIGURE 1. Schematic of Fluidized Bioreactor

2.2. MATERIALS

2.2.1. Coal

The coal used was 80-200 mesh (75-180 um) Illinois #6 supplied by the Illinois Geological Survey. The given mesh range allowed for 82 % of a 20 lb sample of roller milled coal to be usable, thus minimizing waste. The size distribution of the ground coal, within the 80-200 mesh range was skewed to the high mesh or smaller particle size end (Figure 2).

Three distinct types of coal (pretreated-old, raw-old, pretreated-new) were used (Table 1). Data from Table 1 was supplied by the Illinois Geological Survey. The highly mineralized raw-old coal was a very dark brown in color.

2.2.2. Bacteria and Chemicals

The bacteria in this study were obtained from the American Type Culture Collection (ATCC). *Thiobacillus ferrooxidans* ATCC culture number 19859 and *Thiobacillus thiooxidans* ATCC culture number 19377 were obtained.

Solid compounds and liquid chemicals used for media formulation or sample analysis were standard reagent grade obtained from E.M. Science of New Jersey. Atomic absorption spectrophotometer (AAS) standards were

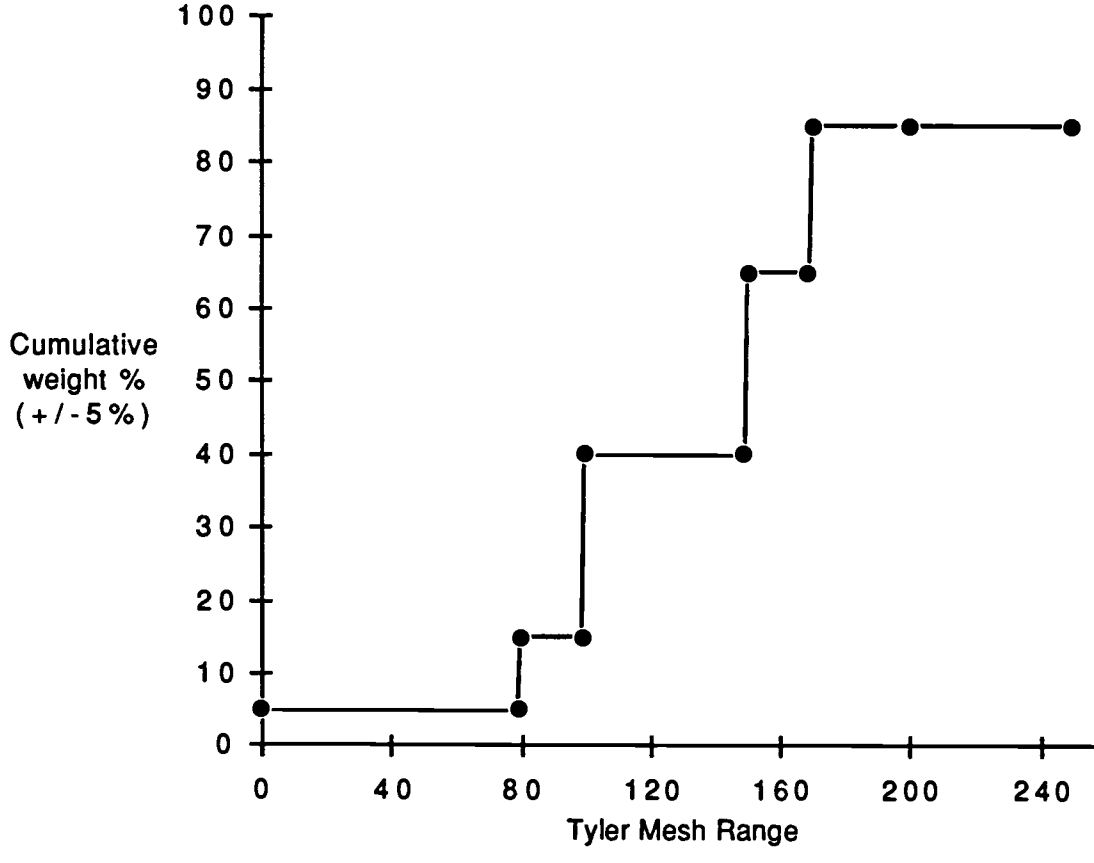

FIGURE 2. Coal Particle Size Distribution of Pretreated-Old Coal

TABLE 1. Minerals in the Illinois #6 Coals Used
(data provided by Illinois Geological Survey)

Coal Type	wt% minerals				
	FeS_2	$CaCO_3$	Clay	Quartz	Total Minerals
Pretreated-Old[1]	2.2	0.5	7.7	2.6	13.0
Pretreated-New[2]	2.2	0.5	7.7	2.6	13.0
Raw-Old[3]	4.6	1.6	28.8	8.0	43.0

[1] Product of a pretreatment wash; pulverized to 80-200 mesh (75-180 um) and stored for over one year in dry air.

[2] Product of a pretreatment wash plant; pulverized to 80-200 mesh (75-180 um) upon delivery and stored for less than one week in dry air.

[3] Raw "mine run" coal with no treatment; pulverized to 80-200 mesh (75-180 um) and stored for over one year in dry air.

prepared from standard reagent grade compounds or were purchased in liquid form premixed to the desired concentration. All AAS standards also originated from E.M. Science products. The surfactant used was Triton X-100, an alkyl aryl polyether alcohol obtained from J.T. Baker Co.

2.3. GROWTH AND MAINTENANCE OF BACTERIUM

Thiobacillus ferrooxidans ATCC culture 19859 and *Thiobacillus thiooxidans* ATCC culture 19377 were grown and processed into their respective inoculums in similar manner for all experiments conducted.

A modified version of the 9K media used by Silverman et al. (1963) was used for *Thiobacillus ferrooxidans* growth (see column 1 of Table 2). Each culture flask contained 150 ml of the growth media and 3.75 ml (2.5% volume/volume) of a previous inoculum (stored "as grown" for one month at 15 °C in the dark).

The culture flasks were covered, but not air tight, and shaken at 100 rpm for 96 hr at 28 °C. According to Silverman and Lundgren (1958), this was a sufficient time to produce cultures of approximately 10^8 cells/ml. The culture flasks were then stored for an additional 3 days until needed for the reactor or shaker.

TABLE 2. Media Composition (diluted in tap water)

Compound	Ferrooxidans culture	Thiooxidans culture	Reactor Leaching
$FeSO_4 7H_2O$ (g/L)	44.20	0.50	--
$(NH_4)_2SO_4$ "	3.00	0.20	--
$MgSO_4 7H_2O$ "	0.50	0.50	--
K_2HPO_4 "	0.50	3.00	--
$Ca(NO_3)_2$ "	0.010	--	--
$CaCl_2$ "	--	0.25	0.0008
$MgCl_2$ "	--	--	0.085
NaCl "	--	--	0.010
NH_4Cl "	--	--	0.276
S (g/culture flask)	--	.15	--
pH	2.5	2.5	1.9-2.2

This procedure was duplicated for Thiobacillus thiooxidans, except a different formula of growth media, adapted from that used by Hoffmann et. al (1981), was used (see column 2 of Table 2).

The inoculum used for the reactor runs and shake flask work was 2.5 percent volume/volume for each of the two strains of Thiobacillus. Each reactor run required seven culture flasks of each strain. Extra flasks were grown at the same time and stored for a month to provide inoculums for renewing the cultures.

Leaching media for the reactor and shake flasks was a low phosphate, low sulfate, high nitrogen media (see column 3 of Table 2). This media was a 90:1 molar ratio (NH_4^+/PO_4^{3-}) version of a 1/10th dilution of Hoffmann's LOPOSO medium. The 90:1 ratio and the 1/10th dilution exhibited optimal initial leaching properties in the source study by Hoffmann et al. (1981).

2.4. EXPERIMENTAL PROCEDURE

2.4.1. Fluidized Bed Bioreactor

The reactor was filled with leaching media containing the surfactant (Triton X-100) at a desired concentration. Air was introduced through the three sintered bubblers at the bottom of the left column to initiate liquid circulation. Both Thiobacillus inoculums

were added and allowed to uniformly disperse into the media. The inoculums were not centrifuged, hence, ferric sulfate was introduced into the reactor with the ferrooxidans culture. Coal was then dry loaded through the air vent. All three types of the Illinois #6 coal presented in Table 1 were used in the experimental work. Finally, continuous flow of fresh media and coal-free leachate were initiated and the operation was underway.

Air was introduced at 1500 cm^3/min with a supply pressure of 40 psig. The liquid circulated rapidly and with stable flow patterns. Measurement of the velocity of entrained air bubbles in the downward flowing leg of the reactor in conjunction with a terminal velocity correlation from Treybal (1980) permitted the calculation of the liquid circulation rate (see A.1 in the Appendix), which was 0.50 m/s (plug) or 16 GPM. The velocity of the small amount of entrained bubbles in the downward flowing leg was determined by a digital stopwatch timing across a carefully measured section of reactor pipe.

Flow within the clear and smooth walled PVC was observed to have minimal visible turbulence except at elbows and obstructions (e.g., sample ports), where strong churning turbulence occurred but dampened out approximately 2 ft downstream. The average Reynolds number in the pipe is estimated at 30,000. The turbulent

areas had defined flow patterns (Figure 3). At the lower 45° elbow, the downward flowing slurry separated from the inner side of the pipe and accelerated into the 120° angle and the rising bubble stream. The reactor recycle rate, which is defined as (recirculation flow rate)/ (liquid feed rate), was over 30,000. At such a high recycle rate, the fluidized bed bioreactor is effectively operating as a mixed flow or continuous stirred tank reactor (Figure 6-16 of Levenspiel, 1972).

For the 16% slurries, hydrochloric acid was added after loading the coal to reduce the pH in the reactor to below three.

Fresh media was fed into the system at the air vent and coal free leachate was withdrawn at the bottom near the 45° elbow (Figure 1). At a feed rate of 1.9 cm^3/ min, 20 gal of leachate were drained in 28 days resulting in a 15.2-day residence time.

Run duration was approximately 28 days with a controlled temperature of 25°C (an easily maintained ambient temperature near the optimum for Thiobacillus activity (Detz and Barvinchak, 1979)).

Samples of the reactor and shake flask media, before and after the inoculums were added and well mixed, were taken to account for introduced metals and sulfur. At regular intervals during a leaching run, reactor and

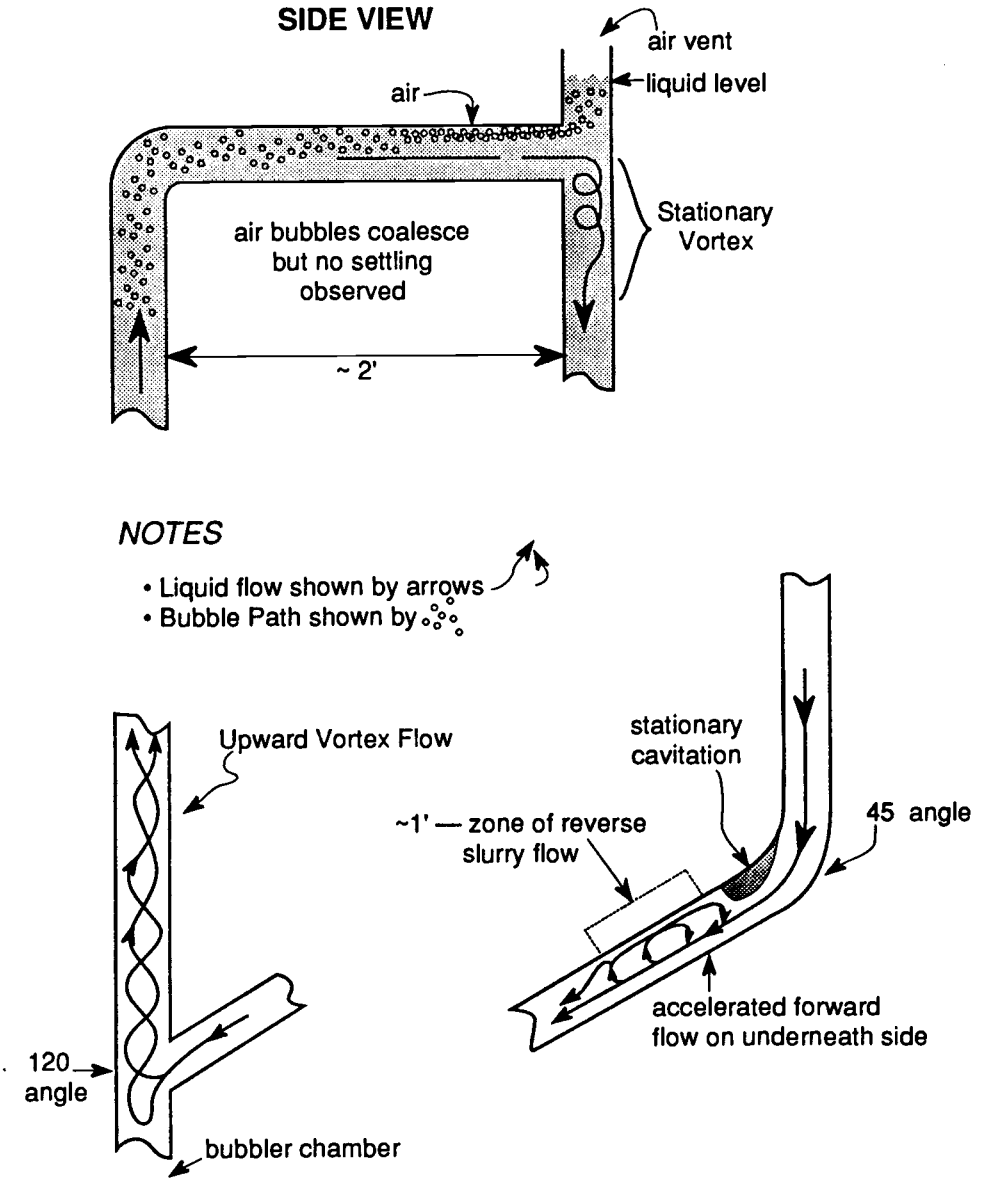

FIGURE 3. Turbulent Flow Patterns in the Reactor

shake flask (if applicable) leachate samples were withdrawn. The temperature of the reactor or shaker was checked with a VWR digital thermometer as the sample was being taken. Immediately upon withdrawal of the sample, the dissolved oxygen content (in the sample) was determined using a YSI model 54A oxygen meter. At the end of the leaching run, a final leachate sample was withdrawn and for the reactor only, a sample of the approximately 20 gal (almost twice the reactor volume) of accumulated exit flow leachate was taken. This accumulated leachate passed out of the reactor through the exit flow rotameter and was collected in a barrel over the course of the run. It is referred to as the composite. All leachate samples were passed through a syringe filter using a 0.22 um Gelman membrane to remove bacterium and fine coal. The pH was then taken using a Beckman 21 pH meter with Corning #476530 electrode and the sample acidified (hydrochloric) to a pH of 2 for storage. All samples were stored in glassware, except for those from reactor Runs #2 and 4, which were stored in polyethylene bottles.

At the end of the run, the leached coal slurry was drained into a barrel through the drain valve located under the sintered bubbler. The leached coal was allowed to settle to the bottom of this barrel and a sample of

this leached coal taken for analysis and comparison to the unleached feed coal samples being analyzed. The leached coal had to be treated to remove surface biomass and any precipitated matter for elemental analysis. One hundred ml of the leached coal sludge was diluted to 400 ml by addition of 1/3 wt% hydrochloric acid in distilled water and stirred vigorously for 10 min at 50°C. The liquid was then decanted after 5 min of settling and the wash repeated with only DI water.

2.4.2. Shake Flask Experiments

Each 250-ml erlenmeyer shake flask was filled with 95 ml of the same leaching media used in the reactor. Varying amounts of the surfactant Triton X-100 were added to give concentrations from 0-10 ppm depending on the desired level. The inoculum was 2.5% volume/volume (2.5 ml) each of the Thiobacillus ferrooxidans and thiooxidans cultures. The inoculum was not centrifuged thus allowing ferric sulfate to be introduced. After inoculation, 8 g of dry coal was added to give an 8% slurry and the flasks covered loosely and agitated at 150 rpm. The coal types used were pretreated-old and pretreated-new 80-200 mesh Illinois #6 (same types used in the reactor and described in Table 1). The shake flask study ran for 24 days at a controlled temperature of 25 $\pm$ 1 °C.

2.5. ANALYTICAL METHODS

2.5.1. Coal Sample Processing

Samples of the three types of feed (unleached) coal used (Table 1) were dried for 8 hr at 90°C. The ashing method was adapted from that used by Olson et al. (1986). Crucibles (Coors #60103) containing 2 g of coal each were placed in a Hevi-Duty Mk-70 tube furnace and ashed at 790-840 °C for 2.5 hr after a 20 min run-up to the operating temperature. The unburnt coal was then mixed with the surface ash layer and the crucibles ashed for an additional 2.5 hr at the same temperature. The ash weight was compared to the dry coal weight to generate ash percent data.

The leached coal samples were dried in a 90 °C water bath until visible moisture was gone and then dried by the method described for the unleached coal. The leached coal was ashed by the same ashing procedure described for unleached coal to generate ash percent data.

Ashed coal was digested to permit analysis of the element content of the coal. This allowed leaching based on the coal data to be compared to leaching based on the reactor leachate sample data and the leached amount to be compared with the coal content. The original digestion

method was adapted from that of Olson et al. (1986) but was revised the second time it was done. The revised digestion method involved placing a 0.3 g (weight accurate to 0.0001 g) ash sample into a cleaned (boiling hydrochloric) crucible (Coors #60103), mixing the ash with 0.8 g Lithium Tetraborate and layering another 0.2 g Lithium Tetraborate on top (exact weight not needed). Three crucibles were prepared in this manner for each type of ash being digested. The crucibles were heated at 900-950 °C for 30 min in the same tube furnace used for ashing, and then allowed to cool down overnight. The fused crystalline mass was solubilized by placing the triplicate crucibles in 160 ml of near boiling 5% hydrochloric. The coal "extract" was diluted to 250 ml with distilled water after addition of 1 ml each of saturated potassium chloride (for sodium analysis), 2% ammonium chloride (for chromium analysis), 52% hydrofluoric acid (for silicon analysis) and 7 ml of a 2% lanthanum solution (for calcium analysis). These added chemicals are necessary for proper elemental analysis of the extract.

2.5.2. Elemental Analyses by Atomic Absorption Spectrophotometry

Selected leachate samples (for both reactor and shake flask work) and the coal extracts were analyzed for iron, nickel, chromium, gold, silver, arsenic, platinum, lead, magnesium, sodium, calcium, titanium and silicon by atomic absorption (Perkin Elmer model 5000). Appropriate dilutions (tabulated with the Reactor Run Leachate Data in A.2 of the Appendix) were made to keep samples in the linear range of the element at the wavelength used. Dilutions were performed with a micro pipet (Eppendorf #4710). Listed accuracy error for the 10-100 *u*L cartridge used is less than one percent.

Standard atomic absorption spectrophotometer (AAS) analysis conditions were used for each element (Table 3). The common method of AA analysis was to autozero the unit with a distilled blank followed by calibration with the standard and reading of the samples. For some elements that were present in amounts close to their detection limits and/or plagued with noisy, drifting absorption signals, an alternative analysis method was used. This involved reading the blank and standard before and after reading each sample and averaging the two blank and standard readings with the sample determined from a linear interpolation between them. The deuterium

TABLE 3. Atomic Absorption Conditions

element	slit (nm)	wave length (nm)	fuel[a] flow (L/min)	oxidant[b] flow (L/min)	linear range (mg/L)	standard conc. (mg/L)
Iron	.2	248.3	3.1	19.6	0- 5	5.000
Calcium	.2	422.7	3.1	19.6	0- 5	5.000
Magnesium	.7	285.2	3.1	19.6	0- 0.5	0.500
Sodium	.2	589.0	3.1	19.6	0- 1	1.000
Nickel	.2	232.0	3.1	23.6	0- 2	2.000
Chromium	.7	357.9	3.1	15.5	0- 5	5.000
Lead	.7	283.3	3.1	19.6	0- 20	20.7
Arsenic	.7	193.7	3.1	19.6	0-100	73.5
Silver	.7	338.3	3.1	19.6	0- 10	10.00
Gold	.7	242.8	3.1	19.6	0- 15	10.00[d]
Platinum	.7	265.9	3.1	19.6	0- 60	100.0[e]
Aluminum	.7	309.3	4.8	8.0[c]	0-100	100.0
Titanium	.2	364.3	4.8	8.0[c]	0-100	50.0
Silicon	.2	251.6	4.8	8.0[c]	0-150	100.0

[a] Fuel was acetylene.
[b] Oxidant was air except for where indicated otherwise.
[e] Oxidant was nitrous oxide.
[c] Original data was verified with a 1.00 mg/L standard.
[d] A 10.0 mg/l standard was also used for calibration.

element	lamp	lamp current (ma-dc)	sensitivity[f] (mg/L)	additions (per 20-ml sample)
Iron	Fe	30	.18	
Calcium	Ca-Mg	15	.1	.2 ml satd KCl
Magnesium	Ca-Mg	15	.01	
Sodium	Na	8	.012	.2 ml satd KC
Nickel	Ni	18	.14	
Chromium	Cr	14	.078	.2 ml 2% NH_4Cl
Lead	Pb	12	.45	
Arsenic[g]	As	14	1.0	
Silver	Ag	16	.11	
Gold	Au	16	.33	
Platinum	Pt	16	2.2	.2 ml 2% La
Aluminum	Al	20	1.1	.2 ml satd KCl
Titanium	Ti	18	1.8	.2 ml satd KCL
Silicon	Si	40	2.1	.2 ml satd KCL

[f] Sensitivity is the conc. giving a 1% absorbance. At optimum analysis conditions the detection limit should not be above this level.
[g] Lamp current with and without D_2O background.

background corrector was used for some arsenic measurements. All readings of blanks, standards or samples were taken with a 5-sec integration time. Since the AAS normally reads the absorption signal every 0.5 sec, this would be the time averaged equivalent of ten normal readings and is displayed as a single value. A minimum 0.2% coefficient of variation on the time averaged reading can be achieved with this integration time, which is a compromise between time and accuracy. The Perkin Elmer AAS will only display the concentration readings to the number of significant digits justified by the machine when calibrating on the standard and reading the noise on the blank. As an additional check, data was only used to the number of significant digits of the calculated detection limits which represent a signal to noise ratio of two.

Detection limits were calculated based on the method recommended by Perkin Elmer. The unit was calibrated with the element standard then auto zeroed with the blank. The standard was then read again and the unit zeroed again with the blank. This was repeated five times (all readings are 5-sec integrated) and the mean and standard deviation (s) of the standard readings calculated. The detection limit (dl) is the product of the known standard concentration and twice the standard deviation divided by the mean of the standard readings.

$$\text{detection limit} = (2\ c\ s)/ \bar{y} \qquad (7)$$

c = known concentration of standard

s = standard deviation of standard readings

$\bar{y}$ = mean of standard readings

Detection limits, calculated for all elements analyzed by atomic absorption, are tabulated along with the absorption readings for the standards used, quoted sensitivity check values (a concentration giving an absorbance value of 0.2 at optimal conditions) and quoted sensitivity values (a concentration that should be greater than or equal to the detection limit at optimal conditions) in Table 4. By monitoring standard absorbance, the integrity of the standard can be assured. If absorbance is abnormally low compared to the sensitivity check, either the standard has decayed or the analysis conditions are not optimal. In an ideal situation, the sensitivity should be greater than the detection limit; this was the case for many elements.

2.5.3. Sulfur Analysis

In the reactor and shake flask leachates, sulfur was determined as sulfate by titration with a standardized concentration of lead perchlorate. The perchlorate anion oxidizes any sulfur species present to

TABLE 4. Detection Limits and Associated Parameters

element	sens.[a] check (mg/L)	standard conc. (mg/L)	absorbance on standard (abs. units)	sens.[b] (mg/L)	detection limit (mg/L)
Iron	5	5.000	0.114	0.18	0.06
Calcium	4	5.000	0.192	0.1	0.05
Magnesium	0.3	0.500	0.172	0.01	0.002
Sodium	0.5	1.000	0.460	0.012	0.013
Nickel	7	2.000	0.061	0.14	0.055
Chromium	4	5.000	0.276	0.078	0.027
Lead	20	20.7	0.033	0.45	0.65
Arsenic	45	73.5	0.089	1.0	5.0 0.9[c]
Silver	5	10.00	0.215	0.11	0.03
Gold	15	10.00	0.081	0.33	0.07[d]
Platinum	100	100.0	0.086	2.2	1.9
Aluminum	100	100.0	0.153	1.1	0.5
Titanium	100	50.0	0.022	1.8	6
Silicon	100	100.0	0.037	2.1	15

[a] Sensitivity check is the concentration of element that would produce an absorbance of 0.2 under optimum conditions (flame, lamp, machinery). It does not take into account the noise in the signal, which has a much greater effect on the detection limit.

[b] Sensitivity is the concentration of element that would produce an 1% absorbance (0.0044) signal. If signal noise is low, the detection limit can be well below this; however, if conditions are not optimal (noisy or low standard absorbance), then the detection limit can be much higher.

[c] This lower detection limit of 0.9 mg/L for arsenic was achieved with the D_2O background corrector.

[d] The detection limit for gold was recalculated with a 1.00 mg/L standard to be 0.08 mg/L or basically the same as the indicated value.

sulfate, which precipitates as insoluble lead sulfate upon interaction with the lead cations in the solution. A Corning #250 ion analyzer (for readout) with an Orion #942200 lead cation electrode (for actual detection) were used to monitor the lead cation levels in solution (electrode is insensitive to precipitate). Since most of the lead precipitates initially with sulfate, the lead concentration in solution will initially be very dilute. When all the sulfate has precipitated, the lead cation concentration in solution will increase rapidly to a high level. When the output of the ion analyzer is plotted as mV versus ml of titrant added, it shows a distinct inflection point from which sulfate concentration can be calculated. This endpoint is not affected by the calibration of the ion analyzer, which may change the shape of the plot but not the endpoint position.

The pH of the sample to be tested must be adjusted with a non-sulfate anion acid/base to 4-7 in order to precipitate interfering ferric iron as ferric hydroxide. Calcium (according to Orion) is also an interferant, but was only a problem when the calcium concentration in the solution was greater than the sulfate concentration present. Standardization of the lead perchlorate titrant is done by titrating a 0.0100 M sodium sulfate solution.

2.5.4. Ferric Iron Analysis

Ferric (Fe^{3+}) iron in solution was determined by difference between the total sample iron measured by atomic absorption and the ferrous iron (Fe^{2+}) in solution determined by titration of the sample with 0.002 M potassium permanganate solution standardized with sodium oxalate as described by Tillet and Myerson (1987). This method is also used in Oregon State University's general chemistry laboratory. The endpoint is detected by the first visible tinge of purple color (characteristic of permanganate) in the sample and is quite sharp.

After determining ferrous iron concentration by this method and ferric iron concentration by difference, ferric/ferrous iron ratios could then be calculated. This analysis was performed on the data for one reactor run.

3. RESULTS AND DISCUSSION

3.1. OPERATIONAL COMMENTS

3.1.1. Reactor

Five reactor runs were conducted at varying slurry concentration, surfactant levels and coal types (Table 5) Temperatures remained fairly uniform and centered around 25 °C.

Thiobacillus ferrooxidans and, to a lesser extent, thiooxidans colonize readily on the walls of a glass culture flask but the clear, smooth PVC reactor piping showed no visible biological film or residue either during or after any run. This indicates that the bacterium did not colonize on the reactor walls, and either remained in solution or attached to the coal. A biological film was present on the slurry surface at the air vent (only observable when the air flow to the bubblers was shut off). A modification after Run #1 significantly decreased coal settling (Table 5).

Dissolved oxygen levels varied from 73-127% of saturation at 1 atm. Dissolved oxygen in the leachate sampled can be greater than saturation at one atm because the sampling outlet for the leachate is located near the bottom of the reactor where static liquid pressure is almost 2 atm absolute (the liquid level being

TABLE 5. Fluidized Bed Bioreactor Run Conditions

	Run Number				
	1	2	3	4	5
Temp. (°C)	25-27	24-25	24-26	24-26	25-26
pH	2.1-2.5	2.0-2.6	2.0-2.5	1.9-2.8[b]	1.9-3.0[c]
Surfactant	none	none	1 ppm	1 ppm	1 ppm
Slurry (% w/v)	2	8	8	16	16
Coal Type[a]	1	1	1	2	3
Coal Settling (wt%)	30-40	3-4	3-4	2	2

[a] Coal type explained in Table 1.

1 = pretreated-old Illinois #6 coal.

2 = pretreated-new Illinois #6 coal.

3 = raw-old Illinois #6 coal.

[b] An initial pH spike of 6.4 occurred on the first day of leaching, but was adjusted to below 3 by second day.

[c] An initial pH spike of 4.5 occurred on the first day of leaching, but was adjusted to below 3 by second day.

approximately 8.5 m above the sample point (Figure 1)). The lowest levels (those below saturation) occurred during peak bacterial leaching activity, around the 14th day of leaching, with an overall downward trend as the slurry concentration increased. Representative oxygen profiles are shown in Figure 4. The leaching mechanism requires significant amounts of oxygen both for the slurry reactions and bacterial growth. As the slurry concentration increases, more oxygen will be consumed. Even at 16% coal slurry, dissolved oxygen was at or above saturation for most of the run.

The pH rose after addition of coal but not to above 2.6 for the 2 and 8% slurries. For the 16% slurries, the added effects of increased concentration and the raw-old coal (Run #4) caused a pH spike to 6.4 for Run #4 and 4.5 for Run #5 on the first day of leaching (Figure 5). Additional hydrochloric acid was added on the first day of leaching for these runs to lower the pH below three. The raw-old coal has the highest neutralization capacity with the pretreated-new coal neutralizing more than the pretreated-old coal. Oxidation of the coal particle surfaces of the pretreated-old coal (not being freshly ground) probably affected this. In Run #5, additional HCl was added on the 5th day because the amount added on the 1st day only

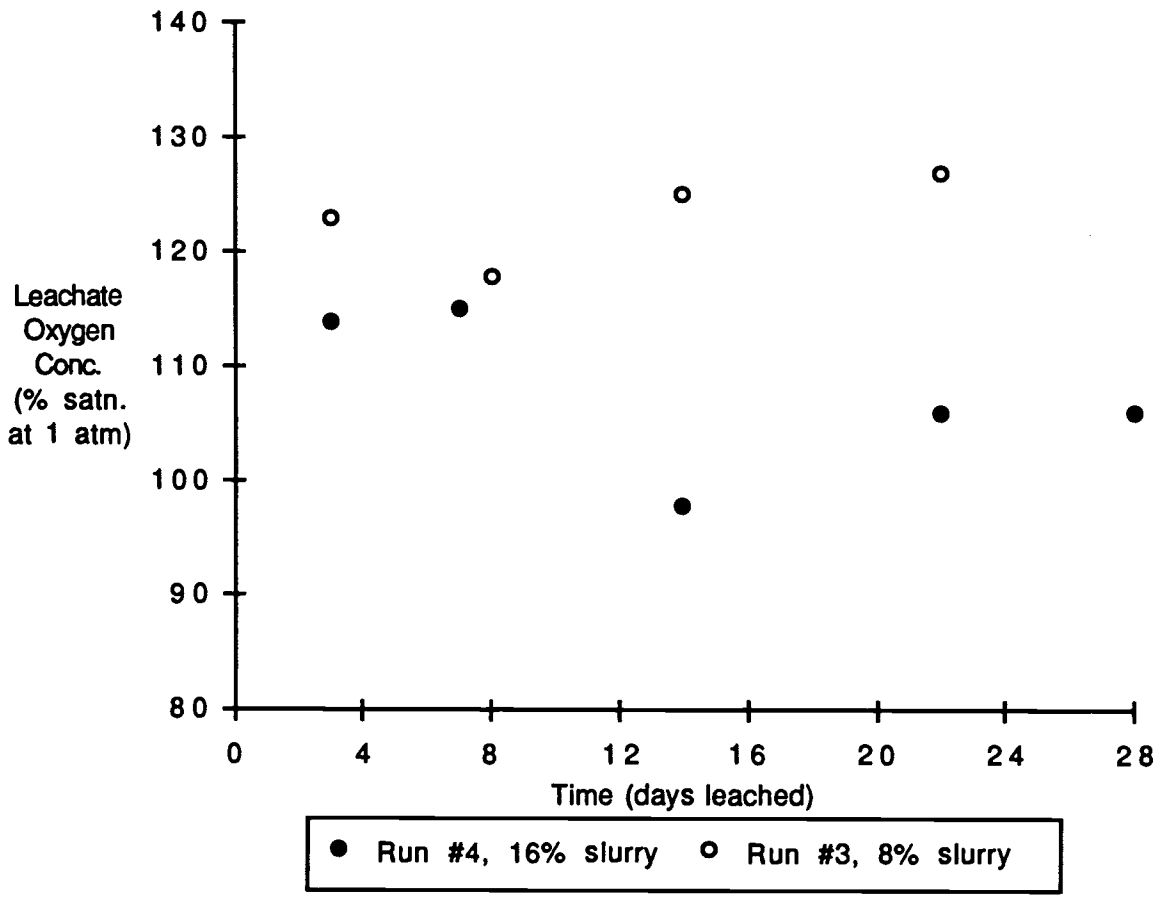

FIGURE 4. Profiles of Dissolved Oxygen in the Reactor (Runs #3 and 4)

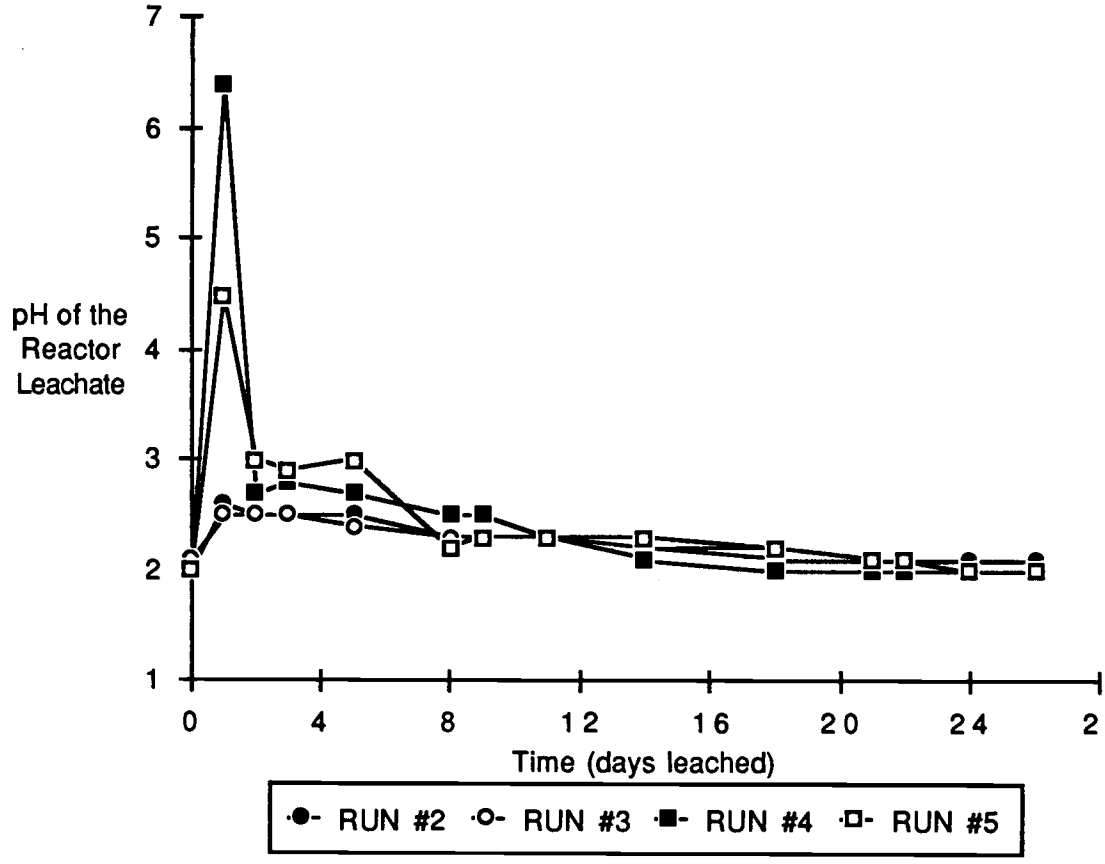

FIGURE 5. Profiles of pH in the Reactor (Runs #2, 3, 4 and 5)

decreased the pH to 3.0 as opposed to 2.7 for Run #4. The pH fell rapidly and naturally from the 10th day onward, due to the bacterial activity.

3.1.2. Shake Flask

A shake flask run was conducted using 24 flasks in groups of four. Each group represented a specific set of operating conditions (Table 6). The run was conducted at 25 °C and for 24 days. Groups s-1, s-2 and s-3 compare surfactant level. Groups s-2 and s-6 compare the pretreated-new coal with the pretreated-old coal. Groups s-2, s-4 and s-5 compare the effects of the inoculum.

The pH levels in the samples from each group are tabulated in Table 7. As in the fluidized bed bioreactor, additional hydrochloric acid had to be added to control the initial pH spike occurring on the first day of leaching. This was not necessary for s-6, which contained the pretreated-old coal. As was shown in the fluidized bed, the pretreated-new coal had a higher neutralization capacity. Surfactant level had little effect on the pH; the final pH at day 24 was 1.9-2.0 for both types of coal and various surfactant levels. The drop in pH indicates that bacterial leaching occured. However, when the pH drops to less than 2, the rate of bacterial leaching tends to decline. Leaching behavior

TABLE 6. Shake Flask Group Conditions

	Group Number					
	s-1	s-2	s-3	s-4	s-5	s-6
Coal Type	P-N[a]	P-N	P-N	P-N	P-N	P-O[b]
Slurry (% w/v)	8	8	8	8	8	8
Surfactant (ppm)	10	1	0.1	1	1	1
Inoculum	N[c]	N	N	none[d]	F[e]	N
Run Time (days)	24	24	24	24	24	24
Temp. (°C)	25	25	25	25	25	25
Agitation (rpm)	150	150	150	150	150	150

[a] P-N = pretreated-new coal (Table 2).

[b] P-O = pretreated-old coal (Table 2).

[c] N = normal inoculums containing both bacteria and ferric sulfate from the *ferrooxidans* culture media.

[d] No inoculum, i.e., s-4 was the control group.

[e] F = filtered inoculum containing ferric sulfate from the *ferrooxidans* culture media but no bacteria.

TABLE 7. pH Changes in the Shake Flask Groups

	Group Number					
days leached	s-1	s-2	s-3	s-4	s-5	s-6
0	2.0	2.0	2.0	2.0	2.0	2.0
1	3.3	3.4	3.3	5.1	3.4	2.5
1[a]	2.5	2.5	2.5	2.4	2.4	
7	2.6	2.7	2.7	3.4	2.7	2.3
7[a]				2.5		
14	2.3	2.3	2.3	2.6	2.5	2.2
24	1.9	2.0	2.0	2.7	2.5	1.9

[a] pH after HCL added to compensate for neutralization of acidity by basic components in coal (where there is no value listed indicates that no HCl was added).

was significantly different for the various groups. The control group (s-4), which contained no bacteria, needed additional hydrochloric acid again on the 7th day as it exhibited no naturally occurring drop in pH. This is not surprising since little or no bacterially catalyzed presumably occurred.

Group s-5, containing the filtered inoculum, exhibited similar behavior as s-4. The filtered inoculum contained ferric sulfate but not the Thiobacillus bacteria. The ferric sulfate in group s-5 (not present in the control) seemed to provide some neutralization capacity, probably as an acid/base reaction between ferric iron and carbonates in the coal. Leaching behavior was significantly different for these groups.

3.2. OVERALL LEACHING IN THE REACTOR

The amounts of various elements leached from coal in the fluidized bioreactor were determined from the analyzed leachate samples as mg element leached/kg feed coal and % coal content leached.

The calculation of the mg element leached/kg feed coal values involves many steps which are discussed in detail in Section A.3 of the Appendix. The first step in this calculation is to correct the analyzed element concentration of a leachate sample (in mg/L) so this

concentration represents only the effects of leaching and not of the media or the inoculum added initially. This is done by subtracting the influence of the media and the inoculum from the leachate sample element concentration (in mg/L). The media continuously added elements to the leachate at a constant concentration. The concentration of elements added with the inoculums decayed exponentially over time as fresh media was fed to the reactor. An exponential decay factor, multiplied by the initial concentration of elements added with the inoculums, accounted for the influence of the inoculums. Subtraction of both influences (media and inoculum) results in a corrected leachate element concentration.

At the termination of a run, the corrected leachate element concentration values for the composite sample (leachate collected over the course of the entire run) and the final leachate sample are used to directly calculate the mg of each element leached for the entire run. Division by the kg of coal used in the run completes the calculation. For calculation of mg element leached during the course of the run, a plot of corrected leachate element concentration (mg/L) as a function of time must be integrated. Division by the kg of coal used in the run completes the calculation.

The % coal content leached values were calculated from comparison of the unleached coal element content and the mg element leached/kg feed coal values.

3.2.1. Leaching of Gold

Gold was leached in significant quantities (Table 8). In Run #4, 7.0 mg of gold/kg coal (± 13%) was leached from the raw-old coal used. Around 23 ± 6% of the gold in the feed (unleached) coal for run #4 was removed. The value of this leached gold is roughly $100 per metric ton feed coal based on a $400 per ounce gold value. The average concentration of gold in the leachate was 0.4 ppm versus a detection limit of 0.07 ppm calculated from a 10.00 ppm standard and a detection limit of 0.08 ppm calculated from a 1.00 ppm standard (standards were dilutions of a purchased standard) (Table 4). Raw data for gold in the leachate is tabulated in A.2 of the Appendix.

The presence of gold in the raw-old coal was further verified by resampling the unleached coal extract with a 1.00 ppm gold standard as opposed to the original 10.00 ppm standard used. Initial data for the extract was a mean of 0.31 mg/L gold with the resampling yielding a mean of 0.34 mg/L. The extract absorbance fell along a linear plot formed by the absorbance of the blank, and

TABLE 8. Overall Leaching in the Reactor[a]

mg element leached/kg feed coal
(% leached of total element in unleached coal)

element	Run Number 1	2	3	4	5	error[b] (%)
Iron	4200	4450	4990	7730	5250	1.8
	(30)	(31)	(35)	(24)	(37)	2.6
Inorganic Sulfur	4600	4700	6400	9820	6630	2
	(36)	(39)	(51)	(40)	(53)	2
Magnesium	54	72	70	304	96	0.5
	(24)	(31)	(31)	(32)	(42)	0.6
Calcium	2330	1470	1490	7780	2040	1.7
	(64)	(40)	(41)	(61)	(56)	4.3
Sodium	1000	790	650	1700	1100	1.7
	(71)	(56)	(46)	(81)	(79)	6.4
Nickel	34	29	32	17	9	4.2
	(60)	(53)	(56)	(27)	(14)	9.7
Chromium	11	3.3	3.8	1.9	2.9	14
	(18)	(5)	(6)	(3)	(5)	15
Lead	nd	30	nd	27[90]	nd	31[90]
				(10)[(33)]		39[93]
Gold		9	10	7	6	13
				(20)		26
Arsenic				nd[40]		[100+]
				[(30)]		[100+]
S:Fe Ratio[c]	1.9	1.9	2.2	2.2	2.2	3

[a] Based on reactor leachate compared to unleached coal except where noted by [].

[b] Based on Run #4 data. Error is ± percent of (mg/kg) value and ± percent of (% leached) value.

[c] Molar stoichiometry of inorganic sulfur to iron leaching.

[] Based on leached versus unleached coal instead of column sample versus unleached coal (all other entries). The usual good correlation between the two basis did not occur with lead and arsenic.

nd Indicates a non-detectable quantity.

0.33, 1.00 and 10.00 ppm standards (within the accuracy limits of the machine readout which does not display the 0.0001 absorbance digit corresponding to a concentration in the 0.01 ppm magnitude, but does record and carry this digit along in the calculation of the sample concentration from a calibrated standard). The gold measurement errors come from data 4-5 times the detection limit. The presence of gold in the raw-old coal used in Run #4 was also verified by comparison of the analyses of the digested leached and unleached coal. The unleached coal contained 31 ppm ($\pm$ 23%) of gold (Table 9), which is a commercially exploitable amount.

All types of coal used contained quartz in the 2.6-8.0% range (highest was the raw-old coal)(Table 1). Gold is sometimes found in association with quartz. Brierly (1978) indicates that gold is associated also with arsenopyrite (FeAsS), which is a minor constituent of pyrite. A commercial operation in Nevada is currently being built to extract gold from rock ore containing pyrite by cyanide leaching after batch tank treatment with Thiobacillus ferrooxidans (Cook, April 1989).

TABLE 9. Coal Content

element	Pretreated-Old[a] (wt% or ppm)	Error[b] (%)	Raw-Old (wt% or ppm)	Error[b] (%)
Silicon	2.7 wt%	14		
Total Sulfur	4.26 wt%		4.19 wt%	
Inorganic Sulfur	1.26 wt%		2.43 wt%	
Iron	1.42 wt%	2.1	3.22 wt%	1.8
Aluminum	0.9 wt%	1.3	1.4 wt%	0.7
Calcium	0.37 wt%	1.4	1.27 wt%	4.0
Titanium	0.23 wt%	65		
Sodium	0.14 wt%	4.6	.21 wt%	6.2
Magnesium	229 ppm	0.4	961 ppm	0.4
Lead			270 ppm	24
Arsenic			130 ppm	70
Chromium	61 ppm	11	58 ppm	4.6
Nickel	57 ppm	24	63 ppm	8.7
Gold			31 ppm	23

[a] Content of pretreated-new coal is identical.

[b] Error is percent of given value (ppm or % content); i.e., iron content in the pretreated-old coal is (1.42 wt%) $\pm$ (1.8% of 1.42 wt%), which is equivalent to (1.42 $\pm$ 0.03) wt%. Error analysis is discussed further in the Appendix.

Note: sulfur data supplied by Illinois Geological Survey.

3.2.2. Other Elements Leached in Significant Quantities

Significant leaching of iron, sulfur, magnesium, sodium, calcium, chromium, nickel and lead was detected in all of the reactor runs (Table 8).

As discussed in the introductory paragraph for Section 3.2, the percentages of total coal content leached (given in Table 8) are based on the analysis of the digested unleached pretreated-old coal (Table 9). The elemental content of pretreated-new coal was assumed to be the same as for pretreated-old coal as they are the same coal, just differing in age only. The mineral content and ash yield of these two types of coal are identical within error (Tables 1 and 10).

All of the leached sulfur (indicated in Table 8) is presumed to be inorganic. Conclusive evidence that Thiobacilli can oxidize organic sulfur is not present in the literature.

Sodium and calcium were almost completely leached within the first 3 days. In Run #1 (2% slurry), nickel was also almost completely leached within the first 3 days. Most of this initial leaching for all three elements discussed actually occurred in the first day. Nickel leaching was delayed for the 8 and 16% slurries. Iron, chromium, lead and sulfur exhibited delayed leaching 7-10 days after the initial leaching of 20-50%

TABLE 10. Ash Yield

Coal type	wt % ash	Unleached	Leached
Pretreated-New	9.4	X	
Pretreated-Old	9.5	X	
Pretreated-Old	8.8		X
Raw-Old	36.2	X	
Raw-Old	27.1		X

of the total amount leached during the run.

Profiles from run #3 of measured and corrected leachate iron concentration (mg/L) versus time and total iron leached (mg leached/kg feed coal) versus time are shown in Figures 6 and 7. The iron profiles are similar in shape to those of sulfur and magnesium although more magnesium was leached initially (for reference, the corrected leachate element concentration was discussed in the introductory paragraph of Section 3.2).

Profiles (from Run #3) of leached element (mg leached/kg feed coal) versus time for calcium and nickel are shown in Figures 8 and 9, respectively. These profiles are typical of those seen in other runs. The calcium profile (Figure 8) is similar in shape to those of sodium and, for the 2% slurry run, nickel. The nickel profile (Figure 9) from Run #3 (8% slurry) would be similar in shape to those of chromium and aluminum if it were more linear.

The 7 to 10-day delay in bacterially catalyzed leaching (Figure 7) is referred to as the lag time; as it is thought that the bacterium take time to adjust to a substrate (coal-pyrite) different than that upon which they were cultured (ferrous sulfate). This could lend credence to the direct leaching mechanism (attachment of the bacterium to the substrate) being dominant for pyrite

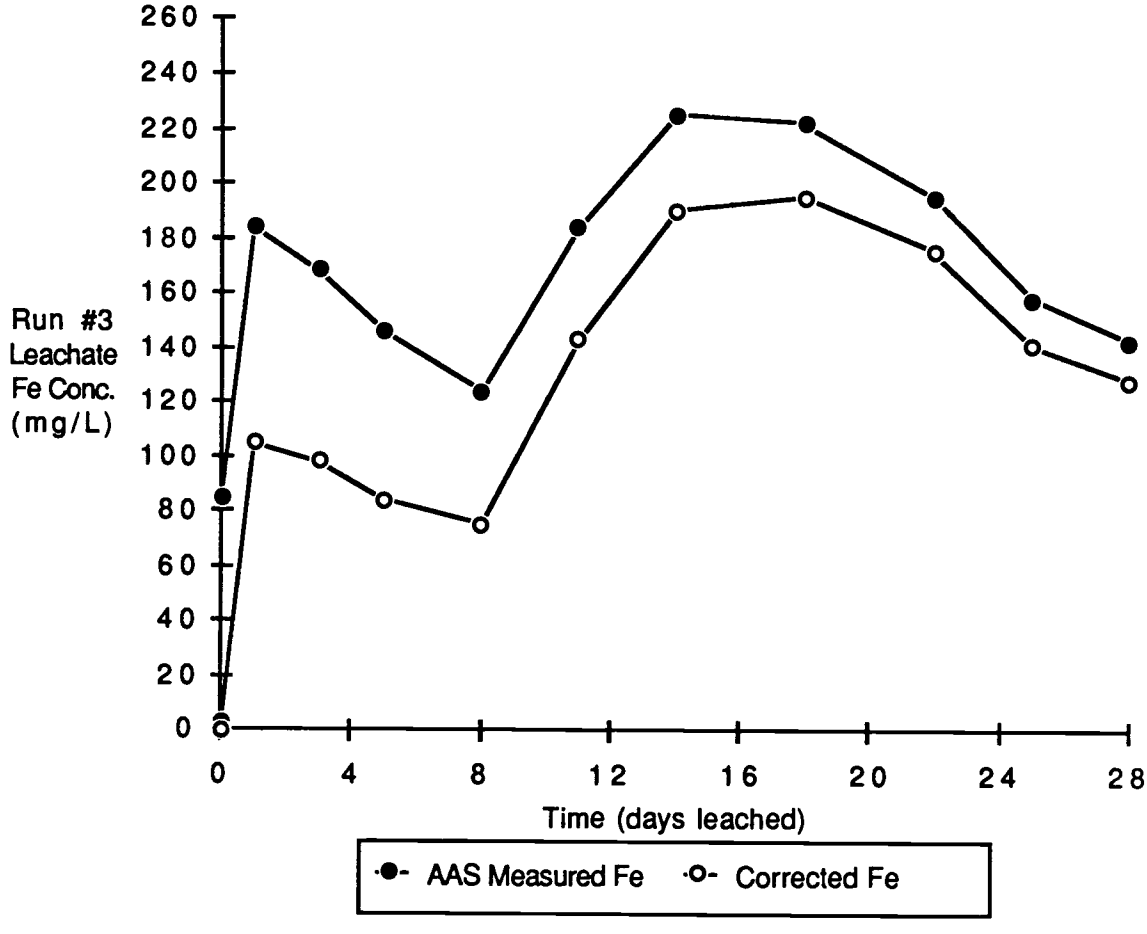

FIGURE 6. Typical Profile of Measured and Corrected Iron Concentrations in the Reactor (Run #3)

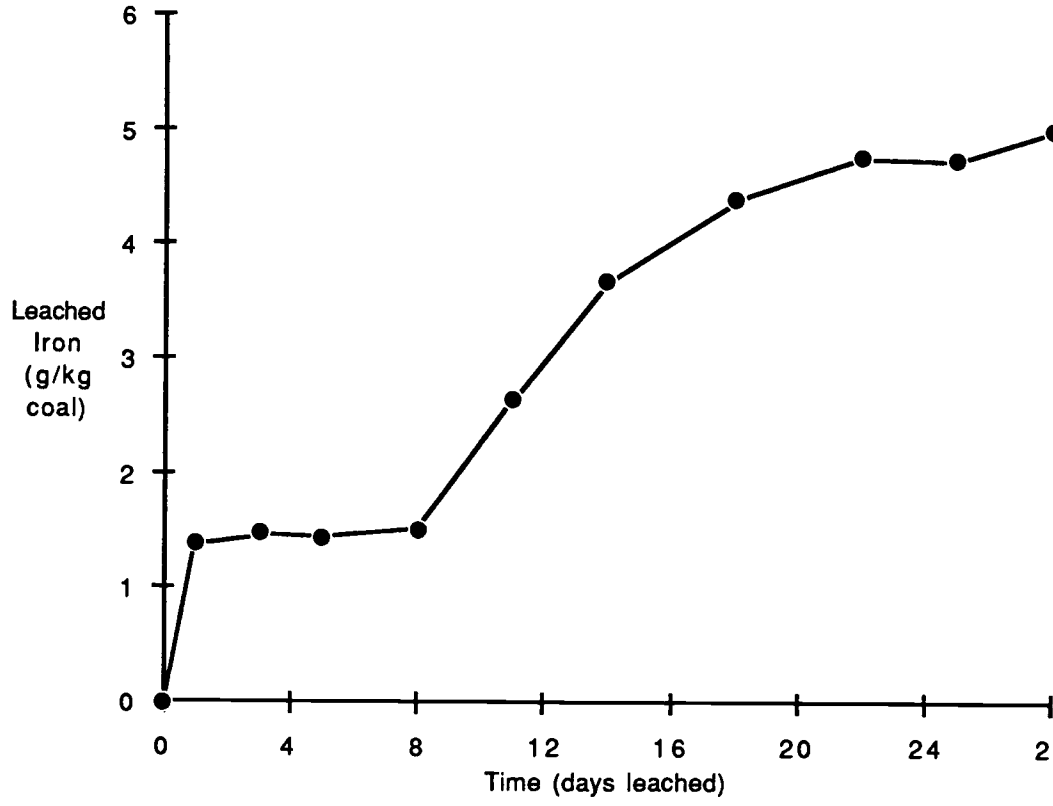

FIGURE 7. Typical Profile of Iron Leaching in the Reactor (Run #3)

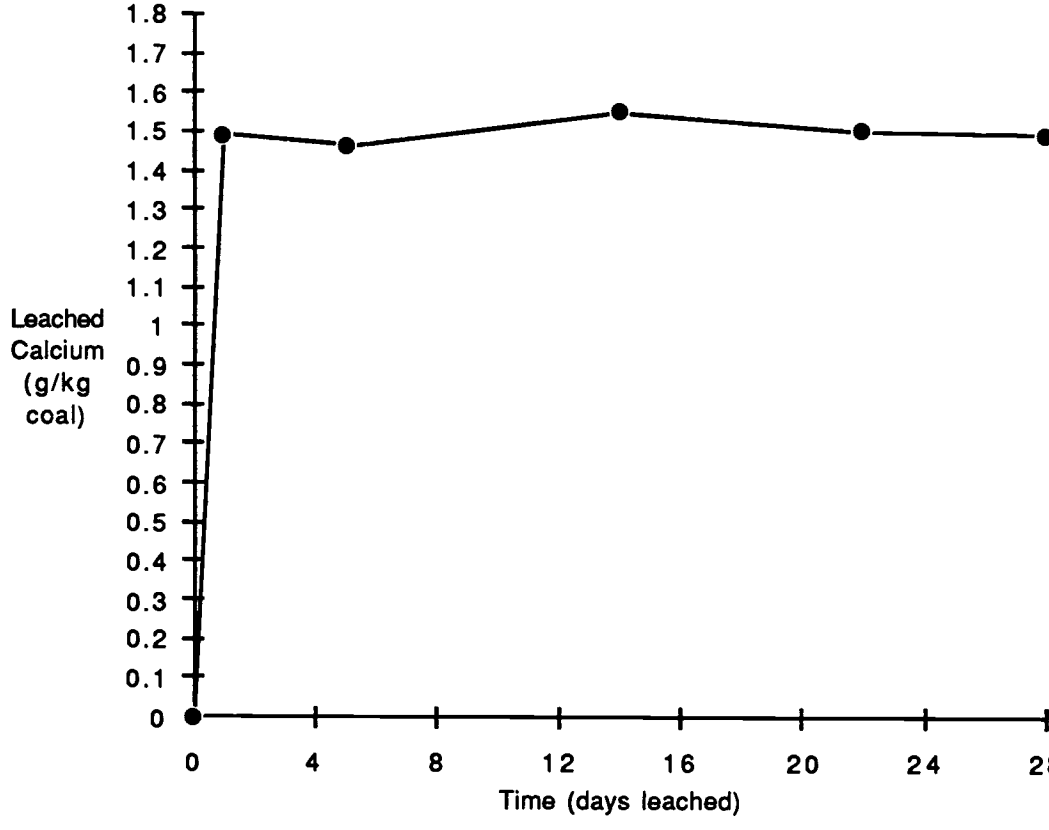

FIGURE 8. Typical Profile of Calcium Leaching in the Reactor (Run #3)

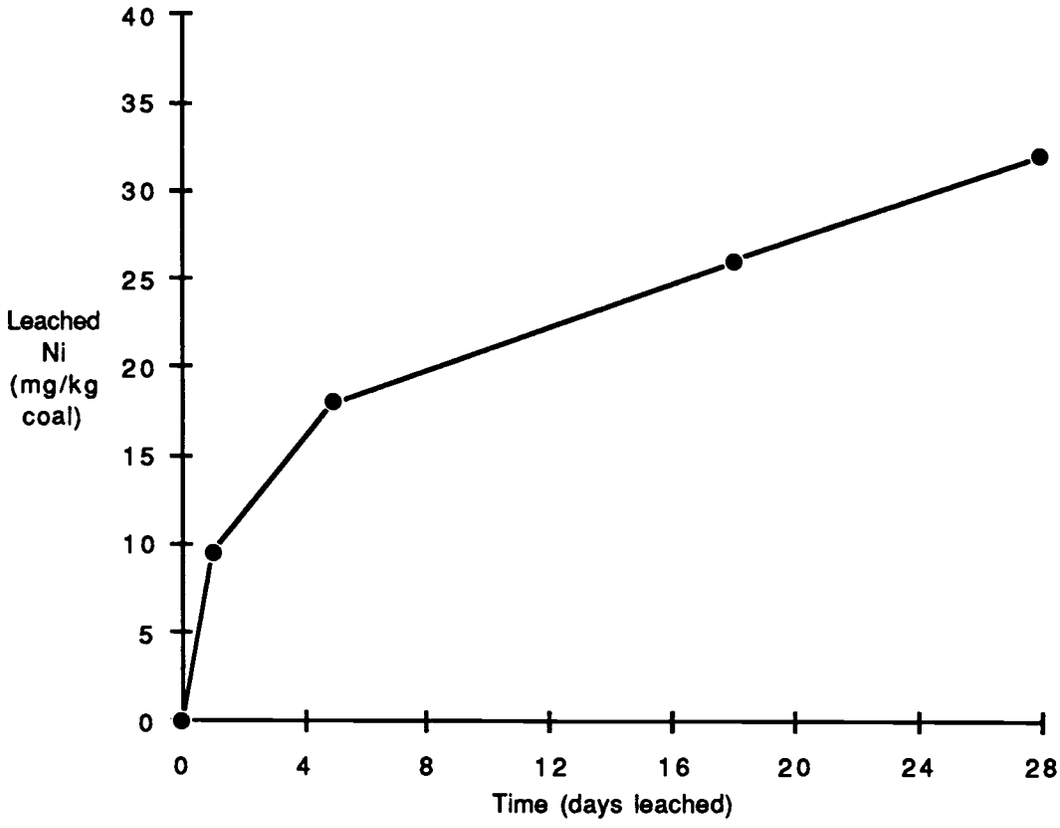

FIGURE 9. Typical Profile of Nickel Leaching in the Reactor (Run #3)

oxidation because of the delayed leaching, but could also be explained by the need for the bacterium to grow in the reactor to reach a critical level or by inhibitory agents present in the coal. Besides substrate adjustment, other factors can contribute to lag time. In the presence of metals, Thiobacillus ferrooxidans exhibits a lag period before iron oxidation proceeds (Brierly, 1978). Calcite can reduce or inhibit iron oxidation by Thiobacillus ferrooxidans until it is neutralized (Chandra et al., 1980; Silverman et al., 1963). In addition, silver at 0.05 ppm was shown to induce a significant lag (5 days) in initiating bacterial oxidation of pyritic iron and associated exponential growth (Roy and Mishra, 1981). All of the inhibitory conditions previously discussed were present in the reactor for all runs conducted (particularly Run #4 using the raw-old coal). Silver concentration in the reactor leachate is given in Tables A.1-A.5 in the Appendix.

As indicated by a 7 to 10-day lag time after an initial leaching period, magnesium is affected in some way by bacterial action and is not solubilized completely in the initial leaching phase (Figure 10). This is contrary to a discussion by L.J. Olson et al. (1986). Some iron and sulfur, and much calcium and sodium are present in coal as easily solubilized sulfate or

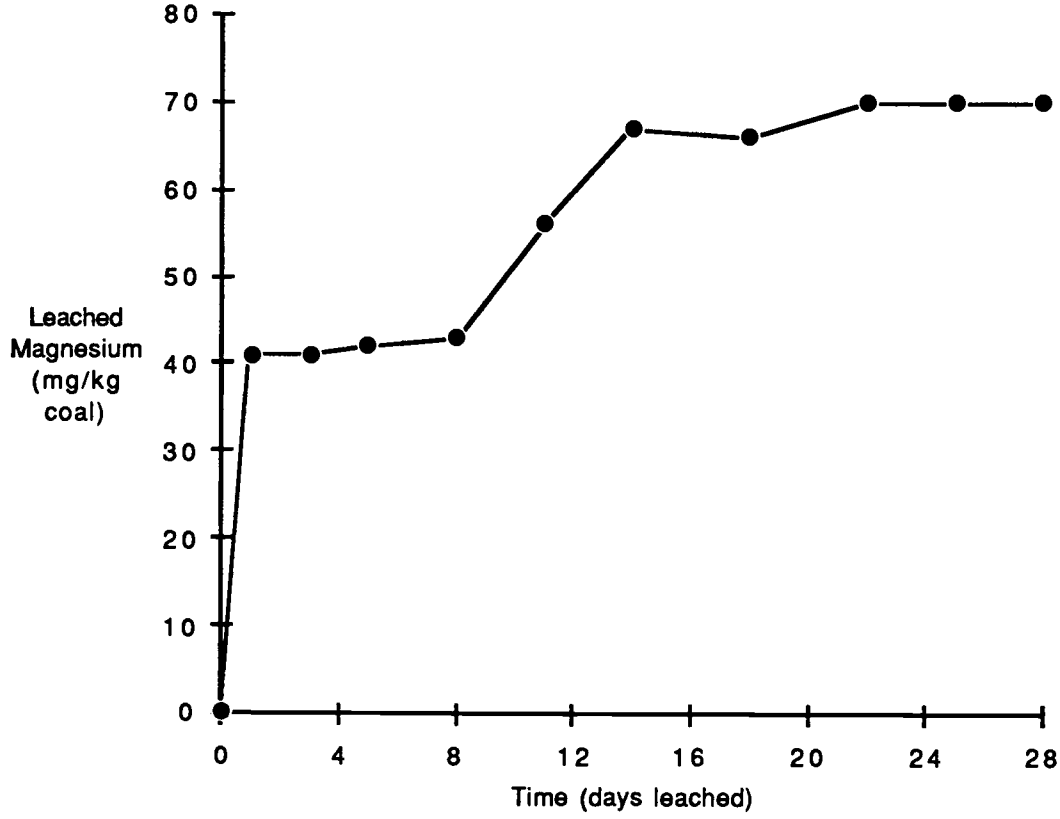

FIGURE 10. Typical Profile of Magnesium Leaching in the Reactor (Run #3)

carbonate, which is removed quickly by the acidic ferric sulfate inoculum and media (the initial leach). Initial leaching (first 3 days) is then a chemical attack on the more easily solubilized components.

Profiles of leached element (mg leached/kg coal) versus time indicate a strong bacterial influence on iron and sulfur leaching with some influence on lead, magnesium and gold leaching. This bacterial influence was indicated by an initial leaching (1st to 3rd-day) followed by an almost complete cessation of leaching (lag time) until the 7 to 10th-day when significant leaching was again noted. From Run #3, 70% of the iron leaching occurred after the lag time (Figure 7) and 42% of the magnesium leaching occurred after the lag time (Figure 10). Calcium and sodium showed no bacterial influence; over 90 % of the leaching occurred in the first 3 days with no recognizable secondary leach phase after the lag (Figure 8). Chromium, aluminum and nickel leaching (8% slurry) was somewhat linear after an initial jump. The linearity indicates a constant rate chemical process (Figure 9).

3.2.3. Effect of pH Spikes on the Determination of Iron and Sulfur Leaching in Runs #4 and 5

The pH spikes that occurred at the initiation of Runs #4 and 5 apparently caused the precipitation of the ferric iron introduced in the ferrooxidans inoculum. Most of the iron in the inoculum is ferric (80% for Run #4), which tends to precipitate as a brown colloidal ferric hydroxide, $Fe(OH)_3$, at a pH of above 3.5. This was observed during sulfate analysis when the ferric iron had to be precipitated out to avoid interference in the sulfate titrations. Precipitated $Fe(OH)_3$ is easily resolubilized by the addition of acid. The sulfate remained in solution as verified by sulfate titration. Also, for Runs #4 and 5, the addition of barium chloride to precipitate barium sulfate (an alternative method of sulfur analysis) indicated the presence of a large amount of sulfate in solution. This means that the irreversibly precipitated jarosite species $M^{+}Fe_x(SO_4)_y(OH)_z$ is not being formed and that precipitated iron resolubilizes as the ferric hydroxide.

The resolubilization of the inoculum ferric iron is complete when the amount that precipitated by the end of the first day (found from comparing the measured leachate iron concentration data at time zero and at the end of the first day) is equal to the amount that

resolubilized (calculated from summing the daily increase in the corrected leachate iron concentration in the reactor after the first day).

$$C_0 \exp(-1/T) - C_1 = \sum_{t=2}^{t_s} \{C_t - C_{t-1} [1-\exp(-1/T)]\} \qquad (8)$$

t = leaching time (days)

C_t = leachate iron concentration at time t that has been corrected for the media ONLY (mg/L)

t_s = time required to resolubilize precipitated iron (days)

T = reactor residence time defined as media flow rate/ reactor volume (days)

The time t_s, at which the amount of precipitated iron (time zero to end of first day) equals the amount of resolubilized iron (second day to time t_s), is found from the equality described in Eqn (8). When this equality is met (at time t_s), all iron precipitate has resolubilized and any further solubilization of iron is from pyrite leaching. The amount of iron leached as time proceeds forward from t_s is calculated, as discussed in Section A.3, from a corrected leachate element concentration. This corrected concentration accounts for the exponential decay in the reactor of the concentration of resolubilized iron initially present at t_s.

$$CC_{ts+y} = C_{ts+y} - [C_{ts} \exp(y/T)] \quad (9)$$

$_y$ and y = an increment of time (days)

CC_{ts+y} = corrected leachate element concentration at time t_{s+y} (mg/L)

All other symbols and subscripts are defined in eqn (8).

The composite leachate sample can be corrected for the influence of the resolubilized iron by subtracting the following summation from the right side of Eqn (9):

$$\sum_{t=1}^{t_s} \{C_{t-1} [1-\exp(-1/T)]\} (V/V_c) \quad (10)$$

V = reactor volume = 41.3 L

V_c = composite volume at end of run (76.3 L for Run #4)

This additional term accounts for resolubilized iron that exited the reactor into the composite before time t_s was reached.

For Runs #4 and 5, about the same amount of iron precipitated (143-155 mg/L); also the time t_s required to resolubilize the iron was 6.5 days for both runs. In Run #4, all resolubilized iron from t = 1 day to t = 6.5 days was ferric, which suggests that no leaching of pyrite occurred during this time (pyrite solubilization yields ferrous not ferric iron). It is assumed that in light of the lag time discussion, the bacterium could not be

active at this time, especially with the swings in pH. Oxidation of ferrous iron without bacterial catalysis is too slow to account for all returning iron to be ferric. The conclusion left is that the resolubilization model is correct. Sulfur did not precipitate and was not treated in this way.

The sulfur to iron leached molar ratio remained at 2.2 for Runs #3, 4 and 5 (Table 8), even though the resolubilization model was not applied to Run #3 (no precipitation) and the total iron leached in Run #4 is 1.4 times that of Run #5. No reference was found which indicates that leaching stoichiometry is affected by pH. The stoichiometry of leaching is expected to remain the same during each of these runs. The effect of surfactant is different because surfactant may change the leaching mechanism; while pH will just effect the rate of leaching. Because the molar ratio did not change, the resolubilization model evidently works well.

In Run #4, less inoculum iron precipitated (143 mg/L) than in Run #5 (155 mg/L), yet more of the coal iron content was removed in Run #5 i.e., 37% as compared to 24% for Run #4. Evidently the overall leaching of iron by the end of the run is not effected by the pH spike that occurred on the first day. Since the iron that leaches initially is likely an easily soluble

sulfate of surface weathered pyrite, this leaching will progress quickly once the pH is brought down and the ferric hydroxide coating the coal particles is solubilized off. It is likely that some leaching occurred during inoculum resolubilization, but this could not be accounted for experimentally or analytically. Calcium, sodium, chromium and nickel leaching is not affected by the pH spikes.

3.2.4. Leaching of Lead

Glassware adsorption of lead ions apparently affected the amount of solubilized lead as measured by AAS. The only leachate samples that lead was detected in were those of Runs #2 and 4 (Table 8). These samples were the only leachate samples stored in plastic bottles as opposed to glassware. Precipitation of lead, with sulfate, may have occurred in the reactor; thereby, reducing the apparent leaching of lead (based on the leachate sample data) as compared to results based on comparison of the analyses of the digested leached and unleached coal.

3.2.5. Elements that were Not Detected in the Leachate

Arsenic was not detected in any of the reactor leachate samples. A combination of an improved technique

for arsenic measurement (use of the deuterium lamp background corrector to compensate for absorption of the signal by the flame) and a sufficiently concentrated digested coal extract allowed for arsenic to be roughly determined in coal. For Run #4, arsenic in the unleached coal was 130 ppm with leached coal containing 90 ppm. Data scatter and associated error were severe for these measurements. A discussion of the mechanism for and work done on the bioleaching of arsenopyrite can be found in Brierly (1978). Since ferric arsenates that are formed by the proposed leaching mechanism will precipitate (Brierly, 1978), it is possible that arsenic leached from the coal but did not remain in the leachate, and thus, was not detected.

No platinum, titanium or silicon were detected in the leachate. These three elements exhibited unusually high detection limits due to noise and other difficulties (Table 4). A small amount of titanium was found in the unleached pretreated-old coal (Table 9). The quantity was consistent with reported titanium concentration in coal.

3.2.6. Effect on Ash Yield

Ash yield of the leached coal was significantly lower than that of the unleached coal (Table 10).

Unleached coal ash tended to be chunky and molded to the crucible sides while leached ash was a finer powder not fused into chunks. Under bright light, the leached coal was black and almost crystalline in appearance, while the unleached coal was a duller shade of dark brown. This was noted for all types of coal leached.

3.3. FACTORS CHARACTERIZING EFFECT OF OPERATING CONDITIONS

Analysis of sulfur, calcium, nickel and chromium was performed on the shake flask groups. The leaching behavior of these four elements is representative of all other elements studied. Leaching of these elements (mg leached per kg feed coal) is presented in Table 11. Information from this table can be used with that from Table 8 to develop factors that characterize the effect of the coal types, the slurry concentration and the efficiency of the reactor compared to the shake flasks. These factors can be multiplied together to characterize the effect on total leaching of a combination of operational condition changes. With one exception (the factor developed in section 3.3.4) these factors are not based on percent leached but rather are based on total mg leached/kg feed coal and are valid for sulfur, calcium, nickel and chromium. The magnitude and trend for the iron factors should be similar to those calculated for

TABLE 11. Leaching in the Shake Flask Groups

Group (#)	Days Leached (days)	Inorganic Sulfur (mg/kg)	Calcium (mg/kg)	Nickel (mg/kg)	Chromium (mg/kg)
S-1	24	6130	1700	10	1.6
S-2	7	1960	1600	6	.8
S-2	24	5790	1690	9	1.6
S-3	24	4710	1650	10	1.4
S-4	7	80			
S-4	24	380	1730	7	1.0
S-5	7	1380			
S-5	24	1880	1630	8	1.1
S-6	24	5250	1260	12	1.8
Error[a] (%)		1-2	1.7-2.4	5-12	19-45

[a] Error is in percent of mg/kg value given. The error increases linearly with decreasing mg/kg value. The low end of the error range corresponds to the high mg/kg values. The high end corresponds to the low mg/kg values. Error is discussed further in the Appendix.

sulfur as iron leaching tends to be a mirror image of sulfur leaching in behavior. Similarly, the calcium factors will behave as sodium would. As previously discussed in Section 3.2.3, overall leaching of iron was unaffected by the pH spikes that occurred at the start of Runs #4 and 5 (Table 8).

3.3.1. Effect of Reactor Type: Comparison of Fluidized Bed Bioreactor to Shake Flask

Reactor Run #3 and shake flask Group s-6 were run at the same operating conditions. Both used pretreated-old coal at an 8% slurry with 1 ppm surfactant. Run #3 data must be corrected to 24 days of leaching by interpolation along the constructed leached element (mg leached/kg feed coal) versus time (days leached) curves because the shake flasks ran for 24 days (all other conditions being equal including inoculum and temperature).

From the constructed leached element (mg leached/kg feed coal) versus time (days leached) plot for sulfur, sulfur leaching after 24 days in Run #3 amounted to 6100 mg S/kg feed coal. From Table 11, sulfur leaching after 24 days in s-6 amounted to 5250 mg S/kg feed coal. The quotient of these two values gives a reactor/shaker leaching factor $F_{r/s}$ = 1.16 for sulfur. The $F_{r/s}$ factors for sulfur, calcium, nickel and chromium are given in

Table 12. The factors were highest for the sulfide elements (nickel and chromium) not directly oxidized by the bacterium, but released either through the breakup of the pyrite matrix or by ferric solution leaching.

For all four elements the reactor is clearly superior to the shake flask in leaching capability ($F_{r/s}$ ranges from 1.16 for sulfur to 2.42 for nickel). Both leaching by acidic ferric solution attack and by bacterial catalysis are improved by the vigorous aerobic agitation in the fluidized bed bioreactor.

3.3.2. Effect of Coal Age: Comparison of Pretreated-New Coal to Pretreated-Old Coal

Shake flask Groups s-2 and s-6 were run at identical operating conditions except for the age of coal used. Group s-2 used the pretreated-new coal and s-6 used the pretreated-old coal. Before leaching, the pretreated-new coal and the pretreated-old coal have essentially the same mineral content (Table 1) and percent ash (Table 10). The minor pH spike (up to 3.4) for s-2 had no effect on the sulfate introduced by the inoculum (same as for the reactor). From Table 11, total sulfur leaching in groups s-2 and s-6 amounted to 5790 mg S/kg feed coal and 5250 mgS/kg feed coal, respectively. The quotient of these two values gives a new coal/old coal leaching factor $F_{new/old}$ equal to 1.10 for sulfur.

TABLE 12. Factors Characterizing Effect of Operating Conditions on Coal Bioleaching

Element	$F_{reactor/shaker}$	$F_{new/old}$	$F_{16\%/8\%}$	$F_{raw-old/pre-old}$	Error[c]
Inorganic Sulfur[a]	1.16	1.10	0.94	0.85	3-4%
Calcium[b]	1.18	1.34	1.02	1.47	3-6%
Nickel	2.42	0.75	0.36	1.33	11-26%
Chromium	1.9	0.9	0.8	0.6	35-54%

[a] Similar magnitude and trend implied for iron.

[b] Similar magnitude and trend implied for sodium.

[c] The error on the first two factors (left to right) is the lower end of the given error range while the third factor error is in the mid to upper part of the error range, and the fourth factor ($F_{raw-old/pre-old}$) error is the upper end of the error range. Data and calculation errors are discussed in the Appendix.

The value greater than unity could be due to native microorganisms that are still active in the new coal (being of less age). The factors for sulfur, calcium, nickel and chromium are given in Table 12.

For calcium and sulfur, the $F_{new/old}$ factors are greater than one, which indicates that the leaching from the old coal is less than from the new. This could be due to greater oxidation of the surface of the gangue minerals, which probably inhibits leaching.

The chromium and nickel $F_{new/old}$ factors are less than one indicating less leaching (0.75 for Ni) with the new coal versus the old coal. This could be due to the same weathering (surface oxidation) discussed above. Here, the weathering of the old coal surface may oxidize the nickel sulfide or chromium complex to a more soluble form. Some other inhibition resulting from the increased leaching of calcium and other species, from the new coal, may also occur. It should be noted that the large error on the chromium factor (0.9 $\pm$ 35%) results from near detection limit analysis and from accumulated calculation error. This error could cause the factor to be either above or below one. The other factors do not share this level of uncertainty and definite conclusions can be made (Refer to the % error data given in Table 11).

3.3.3. Effect of Increase in Slurry Concentration

Reactor Runs #3 and #5 were conducted at 8 and 16% slurries, respectively, of pretreated-old and pretreated-new coal, respectively. All other operating conditions were identical. The pH spike in Run #5 did not effect sulfate in solution or other elements and as discussed earlier in Section 3.2.1, overall iron leaching was not affected either after compensation for inoculum resolubilization. The 16%/8% slurry factor ($F_{16\%/8\%}$) can be calculated as follows:

$$F_{16\%/8\%} = \frac{L_{Run\ \#5}/L_{Run\ \#3}}{F_{new/old}} \qquad (11)$$

L = leached element (mg element/kg feed coal)

The leached element total from Run #5 is divided by that of Run #3 (totals from Table 8) and the quotient corrected for the shift to new coal in Run #5 by division with the $F_{new/old}$ factor from Table 12. From Table 8, the total sulfur leached in Run #5 (6630 mg S/kg coal) divided by the total sulfur leached in Run #3 (6400 mg S/kg coal) divided again by $F_{new/old}$ = 1.10 for sulfur (from Table 12) gives an $F_{16\%/8\%}$ of 0.94 for sulfur. The $F_{16\%/8\%}$ factors for sulfur, calcium, nickel and chromium are given in Table 12.

Calcium does not show a slurry concentration dependence from 8 to 16% slurry ($F_{16\%/8\%}$ factor is nearly 1 within error), while sulfur shows a weak decrease in leaching as slurry concentration increases in this range. From 2 to 8% slurry (Run #1 to Run #2 from Table 8), Calcium does show a strong dependance on slurry concentration even with the reduction in settling of coal. Sulfur leaching increases slightly from 2 to 8% leaching (Table 8), but the reduction on coal settling may have counteracted a weak slurry concentration effect. This is why the slurry factor $F_{16\%/8\%}$ is not valid for 2% slurry. Nickel shows a strong decrease in leaching (slurry factor is 0.36) as slurry concentration is doubled from 8 to 16% (a decrease also appears from the 2% to the 8% slurry, but the coal settling differential (Table 5) cannot be factored out. Again, the chromium $F_{16\%/8\%}$ factor is compensated by error (0.8 $\pm$ 45%), but seems to indicate a decrease which is also apparent from 2 to 8% slurry (Table 8). Reactor results from Table 8 also trend this way.

3.3.4. Effect of Coal Mineral Content: Comparison of Raw-old Coal to Pretreated-old Coal

Reactor Runs #3 and 4 were conducted under identical operating conditions with the exception of coal type used and slurry concentration. The pH spike that

occurred initially in Run #4 had no effect on sulfate or other elements in solution except iron and possibly lead. As discussed in Section 3.2.3, the overall iron leaching appeared to be unaffected by this phenomena. The raw-old coal used in Run #4 has considerably more mineral content (Table 1) and silicon, iron, aluminum, sodium, calcium and magnesium (Table 9) than the pretreated coals used.

The ratio of leaching in Run #4 to Run #3 can be corrected for the slurry concentration difference and the mineral content difference to give the factor characterizing the effect of coal mineral content on leaching (defined as percentage of the element in the coal that was leached) for two coals of the same age (these percentages are also given in Table 8). This is a different basis than total leached element (mg element/kg coal) values also used, which do not take into account the difference in coal content for the raw-old coal versus the pretreated coals. Since the coals used in Runs #1, 2, 3 and 5 have the same mineral content, the basis for calculation of element leaching, defined as a percentage or as mg element/kg coal, are the same and this distinction does not exist.

$$F_{raw\text{-}old/pre\text{-}old} = \frac{L_{run\ \#4} / L_{run\ \#3}}{(F_{16\%/8\%})\ (ER)} \qquad (12)$$

ER = the ratio of element concentration in raw-old coal to pretreated-old coal

L = total element leached (mg element/kg feed coal)

In run #3, total sulfur leaching amounted to 6400 mg S/kg feed coal while in run #4, total sulfur leaching amounted to 9820 mg S/kg feed coal (Table 8). The quotient of $L_{run\ \#4}/L_{run\ \#3}$ divided by $F_{16\%/8\%}$ for sulfur (equal to 0.94) gives a value of 1.63. The element ratio for inorganic sulfur is (2.43/1.26) which equals 1.93 (from Table 9). Division of these two values yields the $F_{raw-old/pre-old}$ factor of 0.85. $F_{raw-old/pre-old}$ factors for sulfur, calcium, chromium and nickel are given in Table 12.

Sulfur leaching (on a percent basis) decreases with a highly mineralized raw coal (factor = 0.85). This is consistent with the calcite/metal inhibitions discussed earlier and reports from the literature of acid pretreatment to remove calcite being beneficial to microbial leaching (Chandra et al., 1980).

Calcium and nickel leaching were enhanced, while chromium leaching was depressed. The errors for the calcium and sulfur factors are only 4-6% but 26% for nickel and 54% for chromium due to near detection limit work. Nevertheless, the nickel factor is still greater than 1 and the chromium factor is still less than 1, even within the full error ranges. The pretreatment washing

process may be beneficial for the removal of chromium.

3.3.5. Comparison of Factors

The products of the $F_{new/old}$ and $F_{16\%/8\%}$ factors, the $F_{new/old}$ and $F_{raw\text{-}old/pre\text{-}old}$ factors and all three factors together (Table 12) all are approximately 1.0 (0.88-1.04 for sulfur, with all three factors being within 25% of each other). The positive or negative effects on leaching that result from varying slurry concentration or coal age or coal mineral content are all fairly balanced. This behavior can be implied for iron also.

The products for calcium factors (Table 12) are all well above 1.0 but the slurry factor has a negligible contribution. Coal type (age or mineral content) is clearly the dominant factor that would effect leaching in the 8-16% slurry range for calcium, and for sodium by implication.

For nickel, the slurry concentration factor (0.36) indicates a greater effect on leaching than coal type ($F_{new/old}$ and $F_{raw\text{-}old/pre\text{-}old}$ factors of 0.75 and 1.33, respectively). The product of the slurry concentration factor and either coal type factor will be significantly less than 1.0, which indicates that slurry concentration is the dominant factor influencing nickel leaching.

The chromium factors are all less than 1.0 with the mineral content factor being the farthest from unity, indicating that it has the greatest effect. The age of the coal (new coal versus old) and slurry concentration (16%/8%) both effect leaching equally in a negative manner. The product of the $F_{16\%/8\%}$ factor and the $F_{raw\text{-}old/pre\text{-}old}$ factor is 0.48, while the product of the $F_{16\%/8\%}$ factor and the $F_{new/old}$ factor is 0.72, and the ratio of these products is 1.5. This predicts that the decrease in chromium leaching from Run #3 to Run #4 would be 1.5 times the decrease in chromium leaching from Run #3 to Run #5. Note from Table 8 that the decrease in chromium leaching from Run#3 to Run #4 is about twice that from Run #3 to Run #5 (chromium content of all coals is similar). This difference (25-33%) is within the error of the factors involved in the calculation. For the other elements, the factors account for the leaching behavior, under the different operating conditions analyzed, to within the experimental error of the factors.

3.4. EFFECT OF SURFACTANT

The addition of 1 ppm of the surfactant Triton X-100 (liquid) to the leaching media improved leaching of iron and sulfur significantly, and had smaller effects on the leaching of chromium and nickel. This is in agreement with Chandra et al. (1980). An additional 13% of the inorganic sulfur in the feed coal was removed in the reactor (comparing Run #3 to Run #2 from Table 8), with 50.8% of the total inorganic sulfur content being leached in Run #3. The operating conditions in these two runs were identical except for addition of surfactant. Even with the doubling of slurry concentration from 8 to 16% ($F_{16\%/8\%}$ = 0.94) and the use of highly mineralized coal in Run #4 ($F_{raw\text{-}old/pre\text{-}old}$ = 0.85), more sulfur was leached in Runs #4 and #5 than in Run #2 which used an 8% slurry with no surfactant (Table 8). No organic sulfur was assumed to have leached. While the presence of surfactant only increased the initial leaching of sulfur slightly (by 400 mgS/kg feed coal), it had a profound effect on the bacterial phase of leaching, which was accelerated, resulting in an additional 1.7 g S/kg feed coal being leached within a 27-day period (Figure 11).

Inorganic sulfur and iron leached in a molar ratio of 1.9 to 1 for Runs #1 and 2, which strongly suggests the leaching of FeS_2 (pyrite). Upon addition of

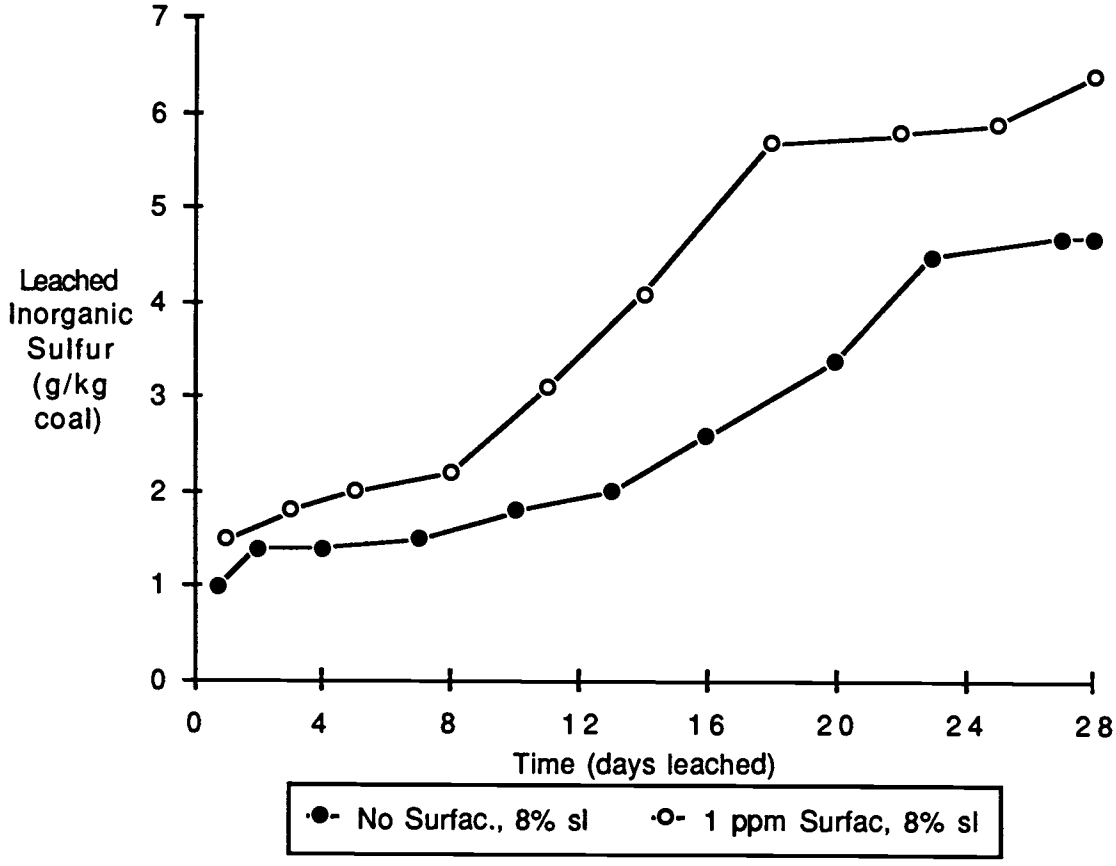

FIGURE 11. Effect of Surfactant on Profiles of Inorganic Sulfur Leaching in the Reactor (Run #2 and 3)

surfactant, the sulfur to iron leached molar ratio increased to 2.2 to 1 for Runs #3, 4 and 5. This indicates a preference for sulfur removal from pyrite. Monticello and Finnerty (1985) and Miller (1987) site and discusses references that point to preferential solubilization of sulfur from pyrite, possibly by diffusion of sulfur through grain boundaries. This would result in non stoichiometric leaching favoring sulfur.

A correlation between mg sulfur leached/kg coal and surfactant level is given in Figure 12 for both the shake flask Groups s-1, s-2 and s-3 (10, 1 and 0.1 ppm surfactant, respectively) and the reactor Runs #2 and 3 (0 and 1 ppm surfactant, respectively). Surfactant levels of 1 ppm are clearly superior to 0 or 0.1 ppm, but levels of 10 ppm appeare to be approaching a maximum leaching limit. Brierly (1978) indicated that small amounts of surfactant (Tween was used in his work) may enhance leaching, but thst excessive amounts could be detrimental. When the surfactant was added to the fluidized bed leaching media, foaming occurred at start up, prior to loading the coal, but was suppressed once the coal was loaded. The coal slurry did not foam.

Foaming, at start up, appeared to be tolerable at a 1 ppm surfactant concentration, but levels greater than 10 ppm surfactant may not be feasible (or even desired)

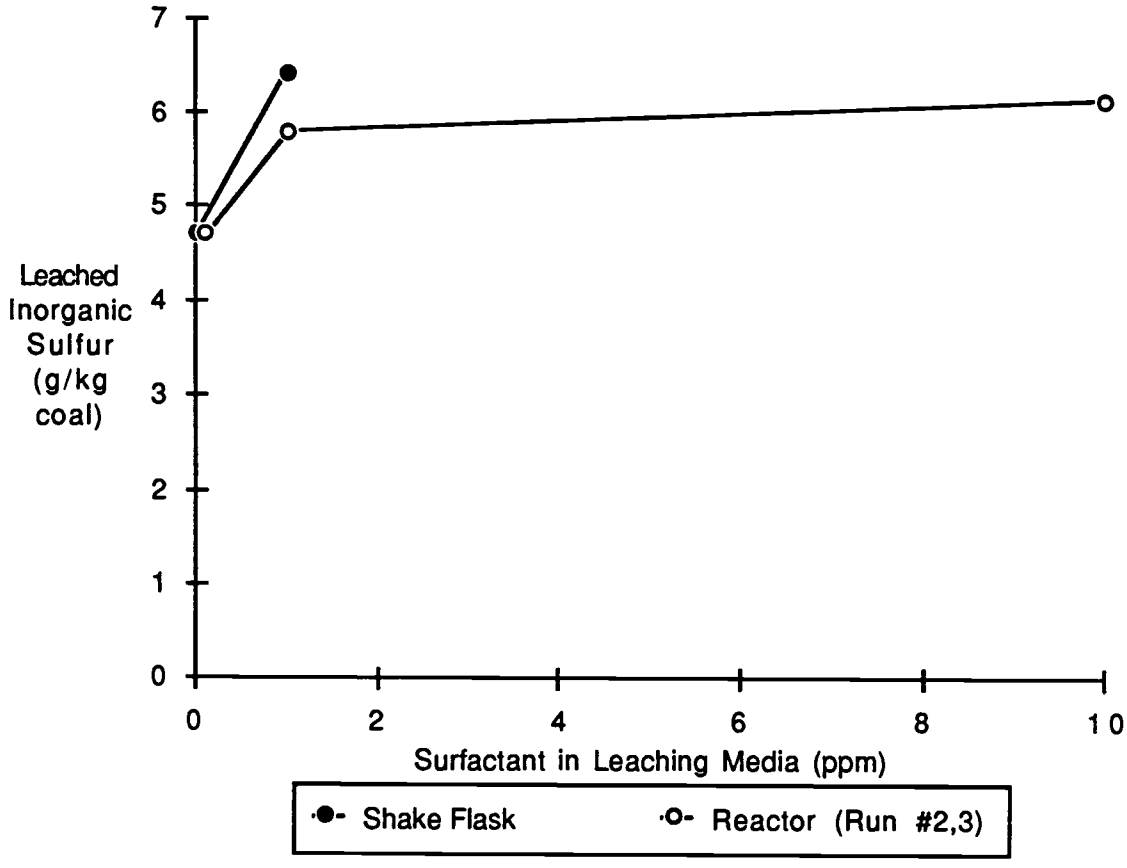

FIGURE 12. Effect of Surfactant on Inorganic Sulfur Leaching

given the diminishing returns. In addition, excessive surfactant concentration would impare the circulation in the reactor due to excessive entrained air (not disengaging at the vent) and the generation of bubbles that are too small to provide effective lift in the upflow side of the reactor.

3.5. EFFECT OF FERRIC IRON/ FERRIC SULFATE

3.5.1. Shake Flask Experiments

Shake flask group s-5 used an 8% slurry of pretreated-new coal, 1 ppm surfactant but with a 0.22 um. filtered inoculum (138 mg/L ferric ion as ferric sulfate but no bacterium). Shake flask Groups s-4 and s-2 were run under similar conditions except no inoculum was used for s-4; whereas, a normal unfiltered inoculum (ferric and bacterium) was used for s-2. In s-2, sulfur leaching during the first 7 days amounted to 1960 mg S/kg feed coal or 34% of the total amount leached in the 24-day run (similar to reactor Run #3). In s-4, sulfur leaching in the first seven days amounted to only 80 mg S/kg feed coal compared to sulfur leaching of 1380 mg S/kg feed coal from s-5 in the same time period. The initial leaching of sulfur (and iron because pyrite is being solubilized) is clearly promoted by the ferric sulfate added in the inoculum. The ferric iron introduced in the

inoculum (138 mg/L or 84% of the total iron in the inoculum) could theoretically account for 990 mg sulfur leached/kg coal in s-2 or s-5.

Oxidation of ferrous iron to ferric by dissolved oxygen in acid solutions does occur but at a rate much slower than for bacterially catalyzed oxidation. It is possible that either the mechanism is more complicated, a naturally occurring biological species is contributing, or the Thiobacillus ferrooxidans not attached to the coal are oxidizing some ferrous iron (initially leached by the ferric) to produce more ferric iron in solution. The bacteria in solution would not need to adjust to the leachate as it is chemically similar to the culture media, while those attached to the coal would have to adjust to the pyrite substrate (producing the lag time). This would suggest that the direct leaching mechanism predominates as most sulfur and iron leaching occurs after the lag period. The presence or lack of an inoculum, either filtered or not, has no effect on calcium leaching. Therefore, we can conclude that the acid media alone is sufficient for solubilizing calcium and bacterial action or ferric iron is not required (Table 11).

The presence of ferric sulfate has no effect on the leaching of nickel or chromium (control versus

filtered inoculum), but the presence of bacterium in the inoculum increases nickel leaching by a factor of 1.22 times and increases chromium leaching by a factor of 1.53 times (comparing s-5 to s-2).

3.5.2. Reactor

For reactor Run #4, ferric iron comprised 90-98% of the total iron in the system once leaching had begun (raw-old coal, 1 ppm surfactant, 16% slurry). This suggests that the oxidation of pyrite by ferric iron (part of the indirect leaching mechanism) is probably the rate limiting step (Miller, 1987).

There were two leachate ferrous iron concentration peaks during the course of Run #4 (Figure 13). One peak occurred near the end of the steepest (positive slope) part of the leached iron versus time profile at around 14 days of leaching (Figure 14). This is a zone of maximum bacterial leaching rate (Figure 15). The other peak occurred at the end of the run (28th day) as the iron leaching rate decreased substantially to a linear rate (Figure 15). The ferrous iron peak occurring at about the 14th day, during maximum bacterial leaching, produced a correspondingly low ferric to ferrous ratio of 9:1 as compared to the 22:1 ratio present at the end of the lag period, i.e. the 7th day (Figure 16). Figure 15 gives

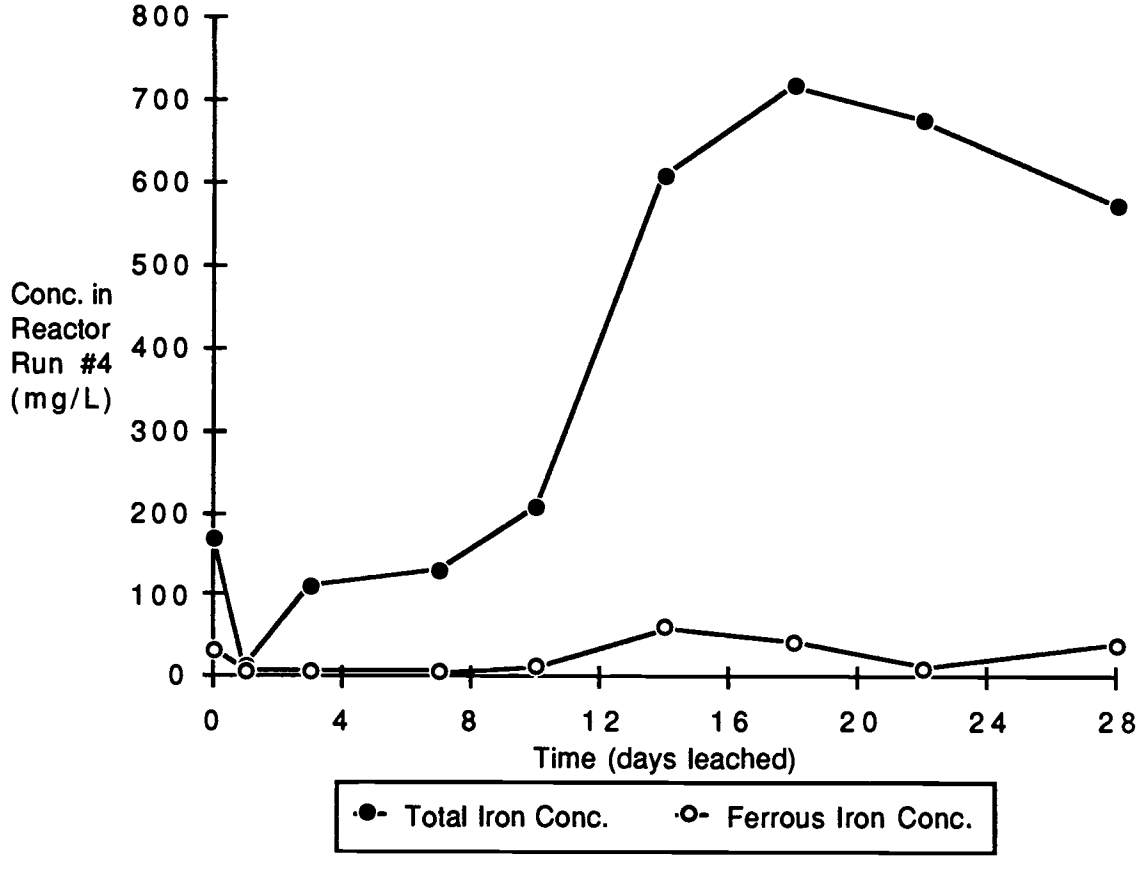

FIGURE 13. Profiles of Ferrous and Total Iron Concentration in the Reactor (Run #4)

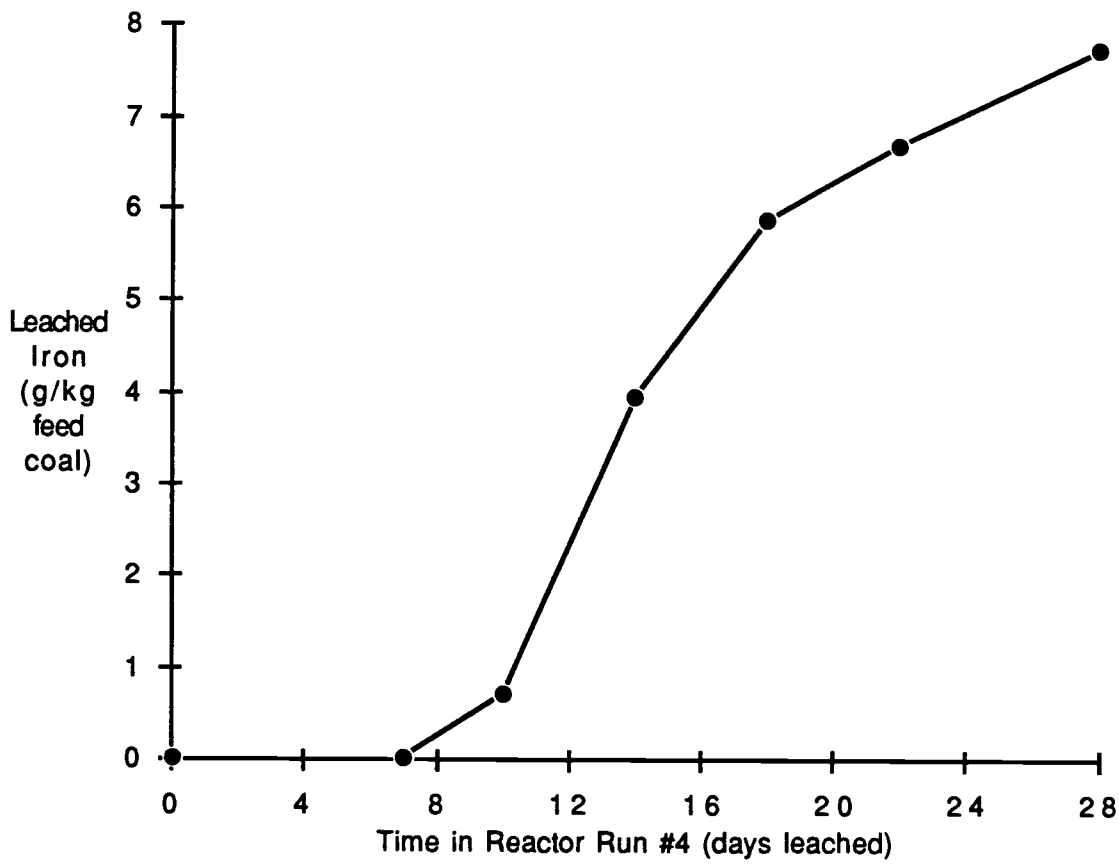

FIGURE 14. Profile of Iron Leaching in the Reactor (Run #4)

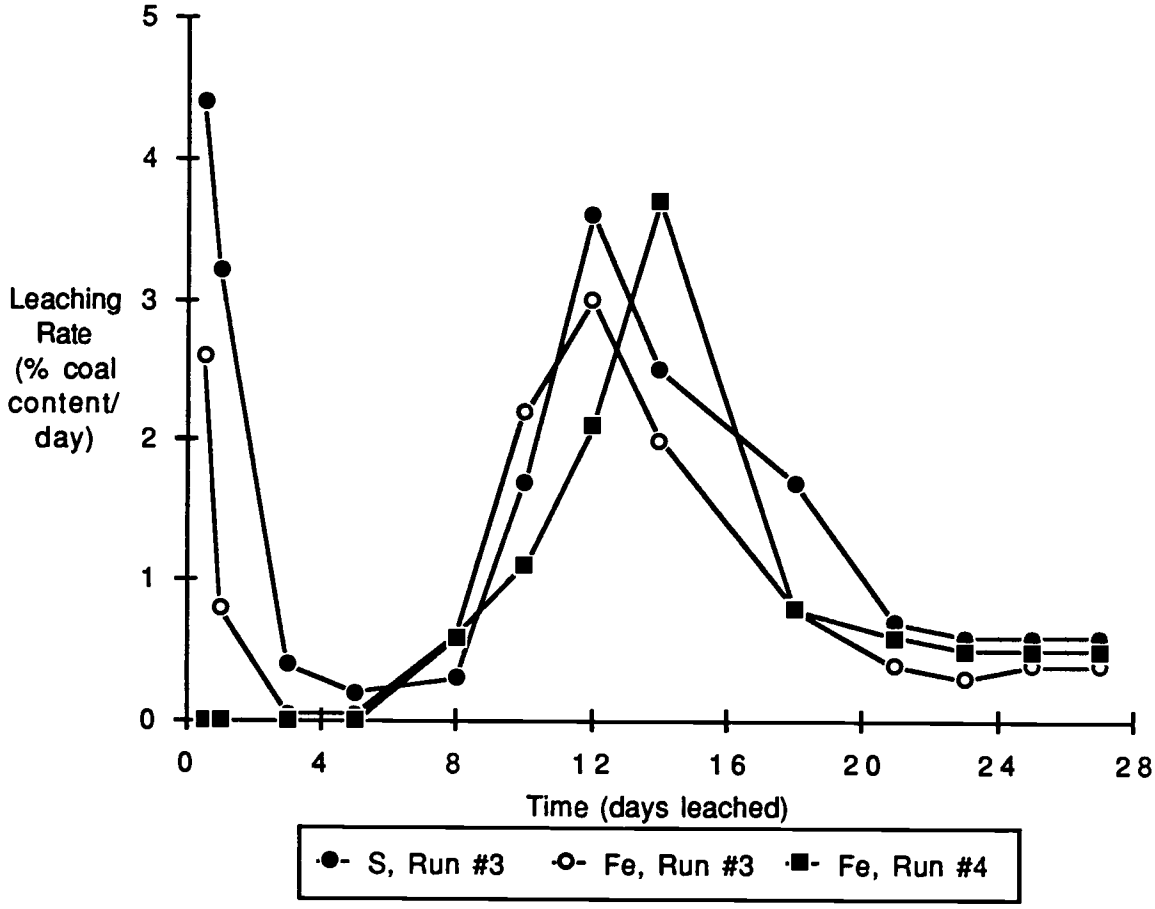

FIGURE 15. Profiles of Iron and Sulfur Leaching Rates in the Reactor (Runs #3 and 4)

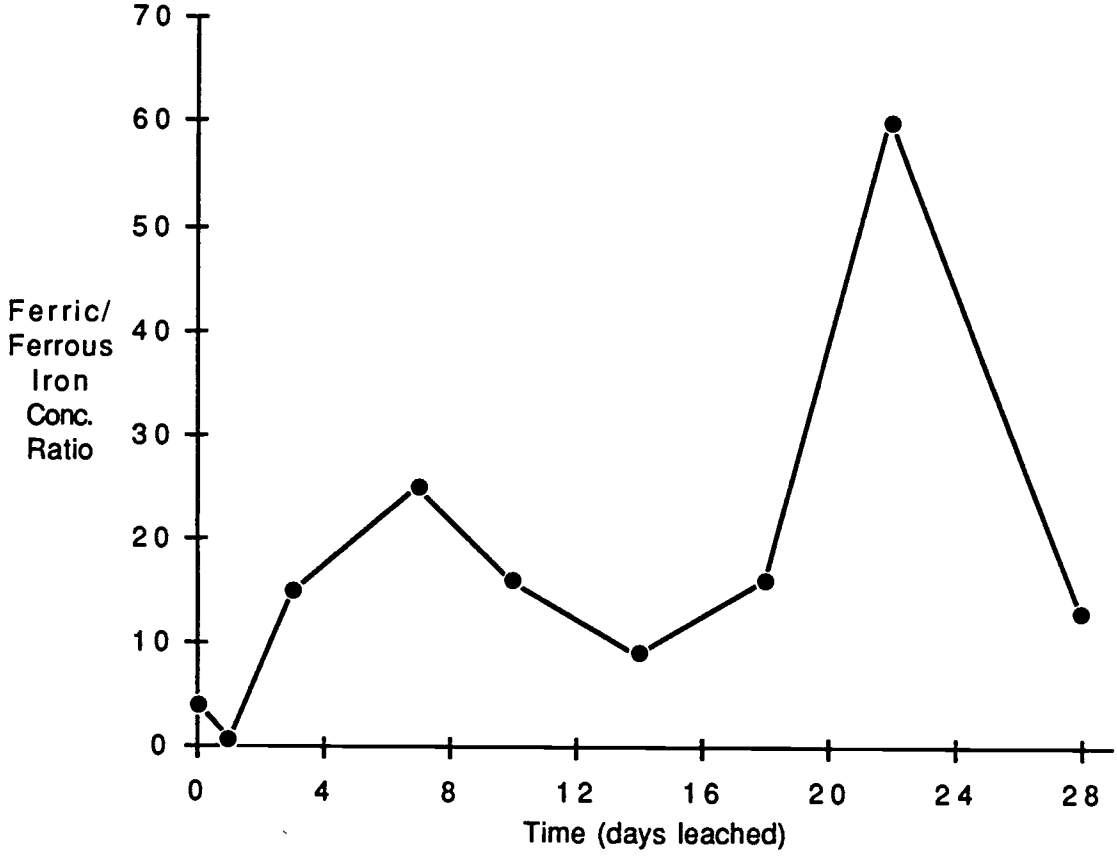

FIGURE 16. Profile of Ferric/Ferrous Iron Concentration Ratio in the Reactor (Run #4)

rates in % total coal content leached per day to compensate for the increased iron content in the raw-old coal from Run #4. To convert to (mg iron leached/kg feed coal/day) simply multiply Figure 15 rates by the total ppm iron in the coal.

The leaching rate of iron drops drastically during the 14th-21st days of leaching in conjunction with a rapid increase in the ferric to ferrous iron ratio from 9:1 to 60:1 during this period. Such an increase in the relative amount of ferric iron results from the bacterial leaching of iron. The ferric to ferrous iron ratio peaked at 60:1 around the 21st day of leaching and then fell to 13:1 at the 28th day (Figure 16). During this time period, the leaching rate was approximately constant. A similar effect was also noted for both sulfur and iron in Run #3 (Figure 15). The zone of linear leaching present after the peak ferric to ferrous ratio may indicate that bacterial growth stopped while bacterial oxidation of pyrite continued. The bacterium may have ceased growing due to some toxic or inhibitory factor in the media but are still oxidizing pyrite. Roy and Mishra (1981) have reported that this can occur at below the minimum inhibitory levels. The relationship between the ferric to ferrous peak and the zone of linear leaching suggests that the high ferric ratio is the

inhibiting factor. In Run #3 about 10% of the total iron removed was leached after the 20th day with 60% of the total iron removed being leached between the 7th and 20th day.

The peak ferric iron concentration measured in Run #4 was 0.614 g/L at a pH of 2.0 (measured on the 18th day). Brierly (1978) has discussed references and work done on ferric iron interference in the oxidation of ferrous iron by Thiobacilli. A reduction in the organisms affinity to bind with ferrous iron is a logical explanation. Inhibiting values of ferric iron cited vary from a high of 11 g/L (Kelly et al.,1977) to a low value of 0.14-0.84 g/L (Wong et al., 1973). The peak ferric level in Run #4 falls within the range set by Wong.

The profiles of inorganic sulfur and iron leaching rates in the reactor appear almost identical in shape and magnitude. The magnitudes of the inorganic sulfur rates are generally slightly higher than those of iron, indicating the non-stoichiometric leaching which favors sulfur (Figure 15).

4. RECOMMENDATIONS

Leaching of coal slurries with concentration higher than 16% and/or continuous coal flow leaching could be effectively performed after modification of the experimental fluidized reactor. These modifications would include a pH control system and flow control for the media/leachate. Work should be continued on investigating the feasibility of coal bioleaching at both higher concentration slurries and, more importantly, with continuous coal slurry flow.

In addition, thermophilic Sulfolobus bacteria should be utilized in further bioleaching studies, as these bacteria have shown promising results in bioleaching studies including an accelerated desulfurization rate over that produced by the Thiobacilli and the ability to remove organic sulfur from coal. The bioleaching fluidized reactor would have to be insulated and heated to accommodate these bacteria which would require the use of high temperature CPVC as a material of construction (normal PVC not being able to handle the 50-70 °C temperatures required).

5. CONCLUSIONS

1. A fluidized bed can be used to leach inorganic sulfur and other elements from Illinois #6 coal.

   A. Use of a mixed culture of Thiobacillus ferrooxidans and thiooxidans significantly enhances the leaching of inorganic sulfur, iron and chromium. Magnesium leaching follows a pattern similar to that of iron and inorganic sulfur leaching which indicates a bacterial influence.

   B. Use of mixed cultures of Thiobacillus ferrooxidans and thiooxidans has a minor enhancing effect on nickel leaching but has no effect on calcium or sodium leaching.

   C. Gold can be leached in a significant quantity with a value of about $100/metric ton feed coal. The raw-old Illinois #6 coal used in this study may contain commercially exploitable quantities of gold.

2. A pH of 2 to 2.5 should be maintained. This would prevent an initial pH spike, which causes the initial precipitation of ferric compounds and the associated difficulty in accounting for the resulting

precipitation of elements. A low pH would also keep leached arsenate compounds in solution until their precipitation is desired.

3. The use of a surfactant significantly enhances leaching of iron and inorganic sulfur. Leaching of chromium is slightly enhanced by use of a surfactant but leaching of nickel is unaffected.

4. For sodium and calcium, leaching appears to decrease with increasing slurry concentration in the range of 2 to 8% but is unaffected by increases in slurry concentration between 8 to 16%. In the 8 to 16% range, the leaching is affected primarily (increased) by the coal type used (both age and mineral content).

5. Changes in slurry concentration and coal type (both age and mineral content) have an equal and balanced effect on leaching of iron and inorganic sulfur with no condition having a dominant effect. Iron and inorganic sulfur leaching is only weakly slurry concentration dependant (weakly decreasing with increasing slurry).

6. Slurry concentration change has the dominant (decreasing) effect on leaching of nickel with coal type having a lesser effect. Nickel leaching decreases sharply with increasing slurry concentration from 2 to 16%. Chromium leaching is most affected (decreased) by use of a highly mineralized coal.

7. Suppression of bacterial growth in the reactor is related to a high ferric to ferrous iron ratio. Oxidation of pyrite by ferric iron produced by the indirect leaching mechanism may be the rate-limiting step in bacterially-catalyzed pyrite oxidation because most of the iron in the reactor (90% plus) was ferric at all times.

8. Fresh, newly pulverized coal that has been acid pretreated to remove calcite should be utilized to optimize bioleaching, but significant leaching will occur regardless of coal age or acid treatment.

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APPENDICES

A.1. Liquid Recirculation Rate in the Reactor

At 1500 ml/min air flow, hemispherical air bubbles of 0.125 to 0.25-inch diameter were observed (in the downflow leg of the reactor) being carried downward in helical paths at 0.51 m/s $\pm$ 5%. These bubbles exhibited the flow characteristics of bubbles in this diameter range as described by Treybal (1980) who has presented a method (Treybal Eq. 6.7) for calculation of the terminal velocity.

$$V_t = [\{(2\ o\ g_c)/(d_p\ p)\} + \{(g\ d_p)/2\}]^{0.5} \qquad (A.1)$$

V_t = terminal velocity of gas bubble in liquid (m/sec)

o = surface tension of liquid (N/m)

g_c = gravitational conversion factor (= 1 in SI)

d_p = average diameter of gas bubble (m)

p = density of liquid (kg/m^3)

g = acceleration of gravity (= 9.8 [kg m]/sec^2 in SI)

A surface tension value of 0.070 N/m was used. This was based on water at 25 °C.

For the bubble size range described, the terminal velocity is insensitive to bubble size and is calculated as 0.23-0.24 m/s (or 0.235 $\pm$ 2%). The circulation rate is based on a plug flow assumption, where average pipe velocity is 2/3 the core or maximum velocity. This core

velocity is the vector difference between the upwards terminal velocity and the measured downward velocity and has a magnitude of 0.75 m/s ($\pm$ 3%). Both the bubble size and flow measurements were taken at the core or center of the clear PVC piping.

A.2. Reactor Leachate Data

Reactor leachate data for Runs #1, 2, 3, 4 and 5 are given in Tables A-1, A-2, A-3, A-4 and A-5, respectively. The dilution factors for the measured samples are also given. To keep the samples within the linear range of the element being measured by atomic absorption, it was necessary to dilute the samples by a specific amount. A dilution factor of 0.01 indicates that the sample measured was diluted to 1% of its original strength. The true sample concentration is then 100 times the measured concentration given in the table.

TABLE A-1. Reactor Run #1 Leachate Sample Data

Element concentration, mg/L and [dilution factor][a]

run time (days)	Fe	Mg	Ca	Na	Ni	Cr	Al	S[e]
0[b]	0.24[.1]	.47[.05]	.51[.05]	.30[.01]	.30	nd	.7	17
0[c]	2.78[.05]	.50[.05]	.61[.05]	.31[.01]	.31	nd	.7	260
1	4.31[.05]	.52[.05]	1.59[.05]			.08		390
3	3.98[.05]	.52[.05]	1.56[.05]					320
5	3.51[.05]	.51[.05]	1.54[.05]	.51[.01]	.54	.10	.7	310
7	3.03[.05]	.50[.05]	1.53[.05]			.09		260
9	2.89[.05]	.50[.05]	1.47[.05]					260
11	2.86[.05]	.50[.05]	1.43[.05]					250
14	2.73[.05]	.50[.05]	1.38[.05]			.80		230
18	2.30[.05]	.51[.05]	1.31[.05]					210
21	2.10[.05]	.51[.05]	1.28[.05]					220
24	1.98[.05]	.50[.05]	1.24[.05]					150
26	1.89[.05]	.50[.05]	1.22[.05]	.33[.01]	.37	.08	1.0	130
26[d]	2.92[.05]	.51[.05]	1.44[.05]	.40[.01]	.44	.09	.9	250

[a] If not given, the dilution factor is one. The dilution factor does not apply to sulfur measurement.

[b] Media sample.

[c] Reactor sample after inoculum has been added and mixed.

[d] Composite sample.

[e] Inorganic sulfur as sulfate.

nd Not detectable.

Note: Ti, Si, As and Pb were not detected.

TABLE A-2. Reactor Run #2 Leachate Sample Data

Element concentration, mg/L and [dilution factor][a]

run time (days)	Fe	Mg	Ca	Na	Ni	Cr
0[b]	.62[.05]	.112[.01]	4.11[.5]	.31[.01]	.13[.5]	.05
0[c]	1.01[.01]	.145[.01]	4.86[.5]	.31[.01]	.15[.5]	.06
1	1.46[.01]	.170[.01]	5.07[.05]	.83[.01]	.28[.2]	.09
2	1.54[.01]	.166[.01]	5.03[.05]		.29[.2]	.11
4	1.36[.01]	.161[.01]	4.28[.05]		.30[.2]	.12
7	1.18[.01]	.155[.01]	3.64[.05]	.69[.01]		
10	1.17[.01]	.149[.01]	3.05[.05]	.60[.01]		.12
13	1.25[.01]	.144[.01]	2.48[.05]	.52[.01]	.25[.2]	
16	1.66[.01]	.141[.01]	2.15[.05]	.47[.01]	.23[.2]	
20	2.06[.01]	.143[.01]	1.77[.05]	.46[.01]	.23[.2]	.15
23	1.89[.01]	.144[.01]		.43[.01]	.21[.2]	
27	1.84[.01]					
30	1.96[.01]	.134[.01]	1.44[.05]	.40[.01]	.17[.2]	.17
30[d]	1.62[.01]	.147[.01]	3.00[.05]	.61[.01]	.23[.2]	.14

Element concentration, mg/L [dilution factor][a]

run time (days)	Pb	Al	Ag	Au	S[e]
0[b]	nd	.6	nd	nd	18
0[c]	nd	.8	nd	nd	440
1	1.2				650
2	1.0		.05	.45	680
4					600
7					520
10	.8				490
13		1.3			480
16					480
20					550
23					680
27					570
30	.7	2.2	.03	.21	500
30[d]	.8	1.5	.05	.26	570

[a] If not given, the dilution factor is one. The dilution factor does not apply to sulfate data.
[b] Media sample.
[c] Reactor sample after inoculum has been added.
[d] Composite sample.
[e] Inorganic sulfur as sulfate.
nd Not Detectable.

Note: Ti, Si, As and Pt were not detected.

TABLE A-3. Reactor Run #3 Leachate Sample Data

run time (days)	Element concentration , mg/L [dilution factor][a] Fe	Mg	Ca	Na	Ni	Cr
0[b]	.16[.05]	1.014[.01]	3.6[.5]	.172[.01]	nd	nd
0[c]	.85[.01]	1.286[.01]	5.4[.5]	.162[.01]	nd	nd
1	1.85[.01]	1.579[.01]	5.99[.05]	.679[.01]	.76	.08
3	1.67[.01]	1.509[.01]				
5	1.46[.01]	1.451[.01]	4.53[.05]	.553[.01]	1.20	.11
8	1.24[.01]	1.385[.01]				
11	1.84[.01]	1.409[.01]				.12
14	2.25[.01]	1.419[.01]	2.89[.05]	.385[.01]		
18	2.22[.01]	1.313[.01]			.90	.14
22	1.95[.01]	1.275[.01]	1.71[.05]	.251[.01]		
25	1.58[.01]	1.222[.01		.235[.01]		
28	1.42[.01]	1.192[.01]	1.24[.05]	.238[.01]	.69	.14
28[d]	1.86[.01]	1.370[.01]	3.32[.05]	.421[.01]	.94	.12

run time (days)	Element concentration, mg/L [dilution factor][a] Al	Ag	Au	S[e]
0[b]	1.3	nd	nd	12
0[c]	1.6	nd	nd	350
1		.06	.31	660
3	2.1			660
5		.05	.35	610
8				560
11		.03	.23	630
14	2.3			750
18		.03	.26	890
22				720
25				620
28	2.6	.03	.30	610
28[d]	2.4	.04	.29	700

[a] If not given, the dilution factor is one. The dilution factor does not apply to sulfate data.
[b] Media sample.
[c] Reactor sample after inoculum has been added.
[d] Composite sample.
[e] Inorganic sulfur as sulfate.
nd Not detectable.

Note: Ti, Si, As, Pb and Pt were not detected.

TABLE A-4. Reactor Run #4 Leachate Sample Data

Element concentration, mg/L [dilution factor][a]

run time (days)	Fe	Mg	Ca	Na	Ni
0[b]	.12[.05]	.103[.01]	.44[.05]	.12[.01]	nd
0[c]	1.68[.01]	.146[.01]	.56[.05]	.13[.01]	nd
1	.14[.01]	.383[.01]	3.76[.005]	1.21[.005]	1.12
3	.55[.005]	.436[.01]	4.08[.005]	1.14[.005]	1.07
7	.65[.005]	.342[.01]	3.83[.005]	.78[.005]	.96
10	1.03[.005]	.330[.01]	3.36[.005]		
14	3.04[.005]	.298[.01]	2.74[.005]	.62[.005]	.96
18	3.58[.005]	.266[.01]	2.08[.005]		
22	3.37[.005]	.243[.01]	1.67[.005]	.43[.005	
28	2.86[.005]	.204[.01]	1.14[.005]	.29[.005]	.93
28[d]	2.32[.005]	.334[.01]	2.81[.005]	.69[.005]	.97

Element concentration, mg/L [dilution factor][a]

run time (days)	Cr	Pb	Al	Ag	Au	S[e]
0[b]	.03	nd	1.4	nd	nd	7
0[c]	.04	nd	1.4	nd	nd	350
1		nd	1.7			
3	.11	2.8	5.3			
7						
10			5.8			
14	.11					
18			8.8			
22	.15					
25						
28	.16	1.6	6.9	.04	.30	1740
28[d]	.13	1.5	6.6	.04	.44	1790

[a] If not given, the dilution factor is one. The dilution factor does not apply to sulfate data.
[b] Media sample.
[c] Reactor sample after inoculum has been added.
[d] Composite sample.
[e] Inorganic sulfur as sulfate.
nd Not detectable.

Note: Ti, Si, As and Pt were not detected.

TABLE A-5. Reactor Run #5 Leachate Sample Data

Element concentration, mg/L [dilution factor][a]

run time (days)	Fe	Mg	Ca	Na	Ni	Cr
0[b]	.17[.05]	.113[.01]	.42[.05]	.11[.01]	nd	.03
0[c]	1.84[.01]	.171[.01]	.47[.05]	.17[.01]	nd	.04
1	.20[.01]	.253[.01]	2.59[.01]	.75[.01]	.35	.04
3	.46[.005]	.239[.01]	2.40[.01]	.66[.01]	.45	.05
7	.75[.005]	.254[.01]	2.10[.01]	.51[.01]	.50	.09
11	.78[.005]	.229[.01]	1.65[.01]	.47[.01]		
17	.79[.005]	.198[.01]	1.04[.01]	.33[.01]		.10
22	2.39[.005]	.181[.01]	4.40[.05]			
28	2.92[.005]	.163[.01]	3.16[.05]	.23[.01]	.60	.27
28[d]	1.29[.005]	.201[.01]	1.56[.01]	.45[.01]	.49	.15

Element concentration, mg/L [dilution factor][a]

run time (days)	Al	Ag	Au	S[e]
0[b]	1.0	nd	nd	4
0[c]	1.6	nd	nd	340
1				
3				
7				
11				
17				
22				
28	4.5	.04	.35	1500
28[d]	4.3	.03	.34	1100

[a] If not given, the dilution factor is one. The dilution factor does not apply to sulfate data.
[b] Media sample.
[c] Reactor sample after inoculum has been added.
[d] Composite sample.
[e] Inorganic sulfur as sulfate.
nd Not detectable.

Note: Ti, Si, As, Pb and Pt were not detected.

A.3. Calculation of the Amounts of Elements Leached from Raw Data

A.3.1. Calculation of the Amounts of Elements Leached from Raw Data in the Shake Flasks

For the batch shake flasks, the total amount of each element leached after a given time period can easily be determined by the difference between the leachate element concentration data (in mg/L) at the beginning and end of the time period multiplied by the flask liquid volume.

$$(C_t - C_0)\ V = \text{mg leached at time t} \qquad (A.2)$$

C_o = element leachate concentration at time zero (mg/L)

C_t = element leachate concentration at time t (mg/L)

V = volume of leachate in shake flask (L)

A.3.2. Calculation of the Amounts of Elements Leached from Raw Data in the Reactor

Equation (A.2) is not valid for the fluidized bioreactor because leachate is replaced by fresh media at a constant rate. The concentration of element present at time zero, which was introduced by the inoculum, will decay over time in an exponential fashion; while the effect of the media will remain constant and not decay. At time t days the decayed inoculum concentration plus

the full media concentration will have to be subtracted from the analyzed sample concentration to get the true level of element present from actual leaching. This true level is referred to as the corrected leachate element concentration.

$$CC_t = C_t - C_{media} - [(C_0 - C_{media})\ F_{decay}] \qquad (A.3)$$

For the reactor leachate:

C_t = actual reactor leachate concentration at time t (mg/L)

CC_t = corrected reactor leachate element concentration at time t (mg/L)

C_0 = reactor leachate concentration after the inoculum has been added and well mixed (mg/L)

For the composite leachate:

C_t = actual composite leachate concentration at time t (mg/L)

CC_t = corrected composite leachate element concentration at time t (mg/L)

C_0 = reactor leachate concentration after the inoculum has been added and well mixed (mg/L)

F_{decay} is an exponential decay factor, which takes the following forms: (A.4a) for all reactor leachate samples and (A.4b) for the composite leachate sample only.

$$F_{decay} = \exp(-t/T) \quad (A.4a)$$

$$F_{decay} = (T/t)[1-\exp(-t/T)] \quad (A.4b)$$

t = time (days)

T = reactor residence time (days)

Reactor residence time is defined as (media flow/reactor volume). T for the reactor is 15.2 days except, where local inlet/outlet flow variation forced the calculated time averaged T to deviate slightly. The deviation is almost insignificant in its effect on T. Because the composite is collected over the entire course of the run, the composite exponential decay factor, defined in eqn. (A.4b), must be a time average of all of the leachate sample exponential decay factors, defined in eqn. (A.4a), from time zero to the end of the run. Consequentially, eqn. (A.4a) is integrated from time zero to time t and the result is divided by the elapsed time interval t to produce eqn (A.4b).

The total amount of element leached at time t (days), can be calculated by integrating a plot of the corrected leachate element concentration (mg/L) vs time (days leached) up to time t, multiplying the integral by the time averaged flow through the reactor, and adding the product to a product of the corrected leachate element concentration (mg/L) for the leachate sample taken at time t and the reactor volume.

$$L_t = (CC_t\ V) + (I\ v_o) \qquad (A.5)$$

L_t = total amount of element leached at time t (mg)

CC_t is defined in eqn (A.3)

I = integral of plot of CC_t versus time evaluated from time 0 to time t [(mg/L)days]

v_o = time averaged outlet flow = 2.72 L/day

V = reactor volume = 41.3 L

If I is evaluated at the time of run termination, the product of I and v_o should equal the product of the composite CC_t and the composite volume. This provides a check on integration accuracy and allows for the total mg of element leached during the run to be calculated quickly using the corrected composite concentration, thus bypassing the need for integration. Integration is needed to determine the progress of leaching within the run. Dividing by the kg of feed coal used yields a useful term for characterizing element leaching (mg element leached/kg feed coal). This term can be plotted against time with the slope of the plot determining the leaching rate. Leaching rate cannot be calculated directly from corrected leachate concentration data as mixed flow reactor theory suggests. The actual leaching reactions take place on the coal surface, which is a quasi batch system. These reactions are catalyzed by

microorganisms through two different mechanisms of unknown balance. In one mechanism (indirect leaching) the catalyst, which is multiplying, is also in mixed flow (decaying concentration) and in the other mechanism (direct) the catalyst is on the coal and in a batch system but with growth affected by the mixed flow conditions. With complexity such as this, direct analytical analysis to determine the leaching rate without resorting to integration and slope taking was beyond the scope of this study.

A.4. Error in Analysis and Calculation

Error generated in the analysis of the leachate samples is carried through and magnified in the calculation of element leaching. The overall error of a result calculated from values with their own intrinsic errors is determined in the following manner.

$$s_{(y=a+/-b)} = [(s_a)^2 + (s_b)^2]^{0.5} \quad (A.6)$$

$$s_{(y=a/b \text{ or } axb)} = [(s_a/a)^2 + (s_b/b)^2]^{0.5} \quad (A.7)$$

$$\%\ \text{error}_{(y=a/b \text{ or } axb)} = [(\%\ \text{error}_a)^2 + (\%\ \text{error}_b)^2]^{0.5} \quad (A.8)$$

s = standard deviation.

$_{a,b}$ = mathematical values operated on as indicated

The primary source of error in the leaching calculations is the reproducibility of the measurements. The standard deviation or variance on the atomic absorption measurements is primarily the detection limit for the element measured. The detection limit is the smallest concentration of element that can be determined above noise generated by interferences; it represents a signal to noise ratio of two (Table 4). Eqn (A.6) can be applied to calculate the error in the element leaching (mg leached/kg feed coal) values calculated for the reactor.

$$\% \text{ error} = 100 \left\{ \frac{[(dl\ V_c)^2 + (dl\ V)^2]^{0.5}}{[C_c\ V_c] + [C_t\ V]} \right\} \qquad (A.9)$$

V = reactor volume (L)

V_c = composite volume (L)

C_c = diluted composite sample concentration (mg/L)

C_t = diluted leachate sample concentration (mg/L) at time t

dl = Atomic Absorption analysis detection limit

The end of run leachate sample and the composite sample exert the primary influence on the calculated leached values.

For the coal content calculated values (% or ppm) and the shake flask mg leached/kg coal calculated values, Eqn (A.7) can be applied.

$$\% \text{ error} = 100\ (dl/C_{\text{diluted coal extract sample}}) \qquad (A.10)$$

$$\% \text{ error} = 100\ (dl/C_{\text{diluted end of shaker run sample}}) \qquad (A.11)$$

where C is the concentration of the sample (mg/L).

In all three equations, the diluted sample data is compared directly to the detection limit. Recall that the samples for many elements must be diluted to bring them into the linear range of the element measured. The reproducible dilution error (0.2% precision for a micropipet) and other errors are not significant when

compared to the detection limit introduced errors, which range from 1.8% for iron to nearly 100% for arsenic (Table 8).

For the reactor % leached calculated values, Eqn (A.8) can be applied.

$$\% \text{ error} = 100 \left[(\% \text{ error}_{\text{reactor mg leached/kg coal}})^2 + (\% \text{ error}_{\text{coal content}})^2 \right]^{0.5} \qquad \text{(A.13)}$$

Percent errors for the calculated reactor leaching results for the primary elements of interest are given in table A-6. These errors are based on Run #4 data, which has typically representative errors. As an example, from Table A-4, the composite sample and end of run leachate sample for gold in Run #4 were 0.44 and 0.30 mg/L respectively. Applying Eqn (A.9) with V_c = 76.3 L, V = 41.3 L (Run #4 values) and detection limit = 0.07 mg/L (Table 4) gives a % error of 13% for the calculated mg leached/kg coal results (Table A-6). The unleached raw coal extract (diluted sample) measured 0.31 mg/L gold. Applying Eqn (A.10) with the gold detection limit (0.07 mg/L) gives an error of 23% for the coal content ppm result. The % error for the % leached result is calculated from Eqn (A.11) using the two % error values just calculated.

Sulfur mg leached/kg coal values have a minimum error of 2% with the error growing larger as the ratio of minimum detectable endpoint (which is 0.1 mL of lead perchlorate titrant used) divided by mL lead perchlorate titrant used at endpoint decreases in value (this is like a detection limit). The minimum ratio (which is the typical value for the samples that primarily influence the calculated result) is approximately 1% with dilution and sample preparation error adding the other 1%.

TABLE A-6. Percent Errors for Calculated Coal Content and Amounts of Elements Leached in the Reactor

element	% error for indicated values[a]		
	mg leached per kg feed coal	coal content: wt% or ppm[b]	% leached
Fe	1.8	1.9	2.6
Mg	0.5	0.4	0.6
Ca	1.7	4.0	4.3
Na	1.7	6.2	6.4
Pb	31	24	39
Cr	14	4.6	15
Ni	4.2	8.7	9.7
Au	13	23	26

[a] The indicated % error is a ± % error of a calculated leaching result in one of the calculated forms shown. For Fe leaching results calculated as (x) mg leached per kg coal, the error would be (x ± 0.018x) mg leached per kg coal. For Fe leaching results calculated as (x) % leached, the error would be (x ± 0.026x) % leached.

[b] The % error given applies to the applicable coal content value that is given in Table 9 either as wt% or ppm. For an element content in coal calculated as (x) wt%, such as for Fe, the error would be (x ± 0.019x) wt% Fe in coal. For an element content in coal calculated as (x) ppm, such as for Au, the error would be (x ± 0.23x) ppm Au in coal.