0273-2289/93/3940—0427$04.40

Heaps as Bioreactors for Coal Bioprocessing

G. F. ANDREWS,*,[1] C. J. STEVENS,[1] AND S. A. LEEPER[2]

[1]*Biotechnology and Environmental Sciences Group,
Idaho National Engineering Laboratory, PO Box 1625,
Idaho Falls, ID 83415-2203; and* [2]*Eli Lilly Co.,
Clinton Laboratories, PO Box 99, Clinton, IN 47842*

ABSTRACT

The long time required for the microbial removal of pyritic sulfur from coal does not become an economic issue if the coal is treated in heaps over which bacteria and nutrients are trickled. Correct heap design is dictated by the variation of the inherent process rate with coal particle size, the ability of water to trickle through heaps of fine coal without waterlogging owing to capillary forces, and the ability of oxygen and carbon dioxide to diffuse into the heap. A theoretical analysis of oxygen penetration combined with experimental measurements of water holdup suggests an optimum coal particle size in the range 6×30 mesh. This is confirmed by experiments on 4 in×3 ft heaps of Illinois #6 coal ground to 30×100 and 12×30 mesh. The former plugs with biomass and ferric precipitates, whereas the latter shows good depyritization rate with minimal gradients through the heap.

Index Entries: Coal; pyritic sulfur; bioreactors; *Thiobacillus.*

NOMENCLATURE

D	Diffusivity of O_2 in air $= 1.54$ m^2/d
d	Coal particle diameter: mm
L	Penetration depth of O_2 into a coal heap
r	Rate of pyrite oxidation per unit volume of coal: $mol/m^3/d$
U	Superficial liquid velocity

---

*Author to whom all correspondence and reprint requests should be addressed.

V	Heap volume
W	Weight of column plus wetted heap
W_0	Weight of empty column
W_1	Weight of column plus water
W_2	Weight of column plus wet coal plus water
y	Mol fraction O_2 in air = 0.21
Y_0	Mol O_2 consumed/mol pyrite oxidized
ϵ_s	Solid holdup (vol solid/vol heap)
ϵ_l	Liquid holdup (vol liquid/vol heap)
ϵ_g	Gas holdup (vol gas/vol heap)
ρ	Molar density of air = 44.6 mol/m^3
ρ_c	Density of wet coal
ρ_w	Density of water

INTRODUCTION

It has been known for many years (*1–3*) that chemoautotropic bacteria of the genera *Thiobacillus* and *Sulfolobus* can remove the pyritic sulfur from coal. Despite the increased need for low-sulfur coal following the passage of the 1991 Clean Air Act, this discovery has yet to be converted into a viable commercial process. The main difficulty has been the low rate of the bacterial activity: Ten days are typically required for 90% removal of pyrite from coal ground to –100 mesh (150 μm). Yet several investigators (*4–6*) have pointed out that this does not really matter. Utilities keep a large inventory of coal, usually corresponding to several months' supply, in heaps at the power-plant site in order to guard against interruptions in the supply. Trickling a bacteria/nutrient solution over these heaps would convert them into bioreactors in which significant amounts of pyritic sulfur may be removed.

As always in process development, there are only two important questions about the process: What are the main process variables (i.e., those variables that can be fixed by those responsible for process design and control), and what are their optimum values? This article reports the results of the theoretical and experimental work done at the Idaho National Engineering Laboratory to answer these questions.

THE PROCESS VARIABLES

Shape of the Heap

Andrews (*7*) has shown that the optimum bioreactor would be plug-flow for coal and completely mixed for the bacteria. Baier achieved this with a heap in the shape of a doughnut, surrounding a central reservoir (*8*). The bacteria/nutrient solution was sprayed over the entire heap and drained back into the reservoir. Product coal was removed and fresh coal added at a point that rotated continuously around the doughnut. A similar effect can be achieved more simply using several heaps with an arrangement of valves and piping that puts each heap through the necessary sequence of operations. Fresh coal is loaded and soaked with the acidic bacteria/nutrient solution from the reservoir in order to inoculate the coal with bacteria and create the necessary conditions for their metabolism. After this initial inoculation period, the solution from the reservoir is sprayed slowly over the heap in order to bring in fresh nutrients and wash out the metabolic products that may otherwise accumulate to inhibitory levels. After several weeks, the heap is rinsed with fresh acidified water to remove sulfate from the coal. It is then dried and removed for use as needed. If hot-air drying is used, the warm moist air leaving the heap that is being dried can be distributed to the other heaps to maintain their temperature and humidity at the desired levels.

Recycle Ratio

If water from the reservoir were simply recycled continuously over the heaps, metabolic products (Fe^{3+}, $SO_4^{=}$ and metals leached from the coal) would accumulate to concentrations that would either inhibit bacterial metabolism or allow ferric hydroxysulfate precipitates to form on the coal. To prevent this from happening, some water must be removed and treated by lime precipitation, the liquid volume being made up by the fresh water added to the process to rinse the coal. The flow to the lime tank can be expressed in terms of a recycle ratio that is a critical process variable. The optimum value is coal specific and must be determined by experiment.

pH Control and Nutrient Addition

In any continuous, nonsterile bioprocess, the composition of the microbial culture is not a process variable under the direct control of the process designer. All that he or she can do is control the physicochemical environment (temperature, pH, nutrients), and trust that natural selection in this environment will produce an optimum mixed culture from the microorganisms added to start up the process, those entering on the feed coal, and those drifting in from the atmosphere. The relationship between the physicochemical environment and the composition of the culture constitutes a very difficult control problem. For example, during some of our laboratory experiments, acidophilic protozoa have appeared, grazing on the *Thiobacillus* bacteria. Thereafter, the physicochemical environment included Cu^{2+}, added to inhibit their activity. The pH must be as low as is consistent with microbial metabolism in order to limit the formation of ferric hydroxsulfate precipitates in the coal heap. Other nutrients that must be added to the process are those needed by the bacteria that are not leached out of the coal or added with the wash water. This is coal specific, but usually requires only small amounts of NH_4^+ (*3*).

Heap Depth

The depth is a major process variable in the heap bioprocessing of coal. The possible area of the heap is fixed by space constraints at the site, so the question of whether sufficient heap volume (i.e., residence time) can be provided is reduced to finding the "active depth" of the heap. This active depth is the distance to which oxygen can penetrate by diffusion from the atmosphere while being consumed by the microorganisms for pyrite oxidation (and possibly other processes). A diffusion/consumption analysis based on zero-order kinetics for 0_2 uptake gives an approximation to this distance.

$$L = [(-2D\epsilon_g^{10/3}\rho \ln(1-y) / Y_o r \epsilon_s (1-\epsilon_s)^2)]^{1/2} \tag{1}$$

This equation improves on previous analyses (*5*) in two ways. It is based on the Millington Quirk (*9*) equation $D\epsilon_g^{10/3}/(1-\epsilon_s)^2$ for the effective diffusion coefficient for a gas in a bed of wet solids. The ln (1 - y) term corrects for the air being drawn into the heap owing to the consumption of oxygen. However, the equation still contains sufficient uncertainties so that its predictions can only be treated as a starting point for experimental investigation. The stoichiometry of pyrite oxidation gives $Y_o = 3.75$ if all of the iron leaves the heap in the ferric, Fe^{3+}, state. This underestimates the true active depth, because Fe^{3+} can be used as an electron acceptor in the oxidation of pyrite, either abiotically or biotically in the absence of oxygen. The value is $Y_o = 3.5$ if all the iron emerges in the ferrous, Fe^{2+}, state, and this gives an upper limit for L. Equation (1) lumps all of the factors governing the pyrite oxidation rate, including the types and concentrations of bacteria, into the pseudo-constant r. In fact, the cells near the top of the heap may be in a metabolically active, growing state, because they have access to CO_2. There is an equation identical to (1) for CO_2 but, since $y = 0.0003$ for carbon dioxide in air, the "CO_2 penetration depth" will be smaller than the "O_2 penetration depth." Cells deeper in the heap may oxidize pyrite more slowly, because they are in a nongrowing state. On the other hand, cells may wash down the heap tending to give a higher rate at greater depths. The resulting gradients of cell concentration, pH rate, and so on, are not sufficiently well understood to be modeled at this time. The active depth could be increased by blowing air through the heap, but it does not appear that the energy cost of forced aeration would be worthwhile in most situations (*5*).

Liquid Superficial Velocity

The volume of water sprayed over unit area of the heap per hour, *U*, is another important process variable. It must be large enough to wash out the products of microbial metabolism, or the bacterial activity may be inhibited and ferric hydroxysulfate precipitates may form and cover the pyrite surfaces. At the other extreme, if *U* is too large, the heap will become waterlogged ($\epsilon_g = 0$) stopping microbial activity by preventing oxygen diffusion into the heap. (Oxygen transfer owing to liquid flow and diffusion of dissolved oxygen was not considered in the derivation of Eq. (1), which therefore predicts $L = O$ for a waterlogged heap; in fact, L would be a few millimeters (*5*)).

Coal Particle Size

The coal particle size is the key process variable, because it influences the hydrological and O_2 diffusion problems as well as the inherent process rate. The value of *U* at which the heap waterlogs obviously depends strongly on the coal particle size, becoming zero for very small particles where capillary forces are dominant. With *U* in the practical, trickle-bed range, the particle size dictates the relationship between *U* and the gas holdup ϵ_g, and thus the active depth of the heap (Eq. [1]). The particle size also controls the process rate, *r*. In finely ground coal (the exact meaning of "fine" is coal specific, but is approx 50 mesh), the majority of the pyritic inclusions are exposed to direct bacterial attack somewhere at the particle surface. Sulfur-oxidizing bacteria can attach directly to the exposed surface and help catalyze the oxidation of the pyrite in a few days (*1*). In coarse coal, most of the inclusions are submerged in the coal particle, where they are inaccessible to the bacteria. Sulfur oxidation becomes rate-limiting, because it can only be accomplished chemically by O_2 or Fe^{3+} that has diffused through the coal to the inclusion. This is the particle size regime employed by Hyman et al. (*6*), who found that depyritization takes several months.

The above discussion can be summarized as follows. A small coal particle size means a high rate and more water flow needed to wash out the metabolic products. This gives a smaller oxygen penetration depth and a higher probability of waterlogging the heap. Large coal particles give no problems with water flow or oxygen penetration, but a much slower process. The ultimate objective of the work described here was therefore to find the smallest coal size that can realistically be depyritized in a heap bioreactor.

EXPERIMENTAL WORK

The coal used in these experiments was an Illinois #6 supplied by the Monterey Coal Company. This was sieved to different size fractions, and 3 ft high laboratory heaps were created in Plexiglas™ columns of 4-in diameter. The heaps were supported on stainless-steel screens, and the floor beneath the screens was sloped so that water dripping from the heap drained immediately from the column (Fig. 1). Water or bacteria/nutrient

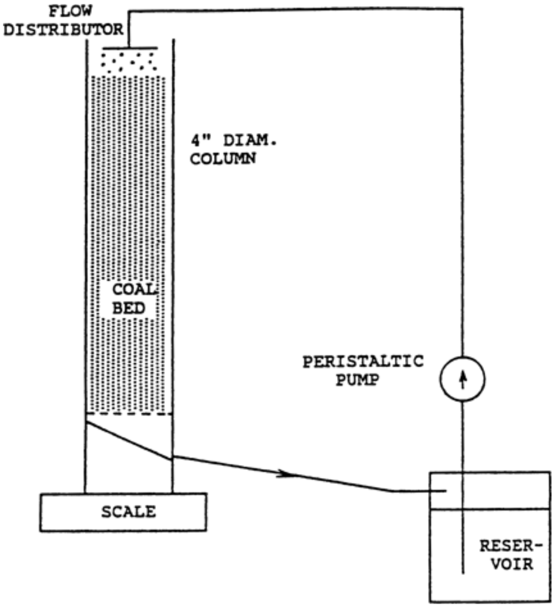

Fig. 1. Experimental apparatus.

solution was trickled over the bed from a flow distributor consisting of a spiral of Tygon tubing in which short lengths of hypodermic needles had been inserted. The entire column rested on a scale that gave a direct indication of the mass of water in the column and, thus, the average liquid holdup in the bed.

Liquid Flow/Holdup Experiments

The objective of these experiments was to measure the hydrodynamics of the heap, that is the gas, liquid, and solid holdups as a function of coal particle size and water flow rate. If the coal were loaded into the column dry, then some of the increase in weight recorded when the water flow was started would be due not to liquid holdup (water on the outside of the coal), but to water soaking into the coal. To avoid this and other errors (coal swelling when wet, effects of fines, settling of the bed during an experiment, and so forth), the coal was first washed to remove fines and any soluble mineral matter. It was then poured as a slurry into a column that was approximately one-quarter full of water. The water level was adjusted to a fixed mark above the heap and the weight of the column (W_2) recorded. The column was then drained and the heap height, and thus its volume, V, recorded. If W_1 is the weight of the column filled to the same mark with no coal heap, the solids holdup is:

$$\epsilon_S = (W_2 - W_1) / V(\rho_c - \rho_w) \tag{2}$$

ρ_c is the density of wet coal. It was measured by keeping a sample of coal in a 100% humid atmosphere for several days and then measuring its density in a pycnometer. A useful check during this procedure was to top up the pycnometer containing the coal and water after a few days and reweigh it. This ensured that the coal had not absorbed more water. This procedure gave $\rho_c = 1.361$ g/cm^3.

Tap water was recirculated over the coal heaps at flow rates between 0.81 and 810 cm^3/min (superficial velocity $0.01 < U < 10$ cm/min). The average liquid holdup at each flow was calculated directly from the column weight W:

$$\epsilon_1 = (W - W_o - \rho_c V \epsilon_s) / \rho_w V \qquad (3)$$

Heap Depyritization Experiments

Experiments were conducted on the microbial depyritization of the 30×100 mesh and 12×30 mesh size fractions of the Illinois #6 coal. The columns were loaded with coal to a depth of 3 ft, and water acidified with H_2SO_4 and supplemented with $(NH_4)_2SO_4$ was trickled over the heap. When the pH stopped increasing, indicating that the basic mineral matter in the coal had been neutralized, the reservoir was inoculated with a mixture of sulfur-grown *Thiobacillus feroooxidans* and a bacterial consortium including *T. thiooxidans*, *Leptospirillium ferrooxidans*, and acidophilic heterotrophs that had been acclimated to this coal in previous experiments.

The reservoir contained a known volume of liquid between 10 and 20 L. Water was added periodically to compensate for evaporation. The reservoir was gently aerated to provide some mixing and to allow aerobic microbial activity. The temperature was kept at 25°C by a Visi-term aquar ium heater. Probes were used to monitor the pH and oxidation/reduction potential (Eh) in the reservoir. The Eh in this system responds mainly to the ratio Fe^{3+}/Fe^{2+}, and thus, is a good indicator of the activity of the iron-oxidizing bacteria. Samples were taken daily from the reservoir for measurements of cell concentration by direct microscope count, and sulfate concentration by the barium chloride turbidimetric method.

Coal samples were analyzed for pyritic and sulfate sulfur at the beginning and end of experiment. Core samples from the 12×30 mesh heap were also analyzed. It was found that the presence of ferric hydroxysulfate precipitates on many of these samples necessitated a modification of the ASTM procedure for these measurements. Boiling the samples in 4.8*N* HCl, as in the standard procedure, did not remove all of the nonpyritic iron and sulfate from the coal. The 5-gm coal samples were therefore given a preliminary room temperature wash in 100 mL of 4.8*N* HCl. This acid was then mixed with that from the boiling step for measurement of the sulfate sulfur.

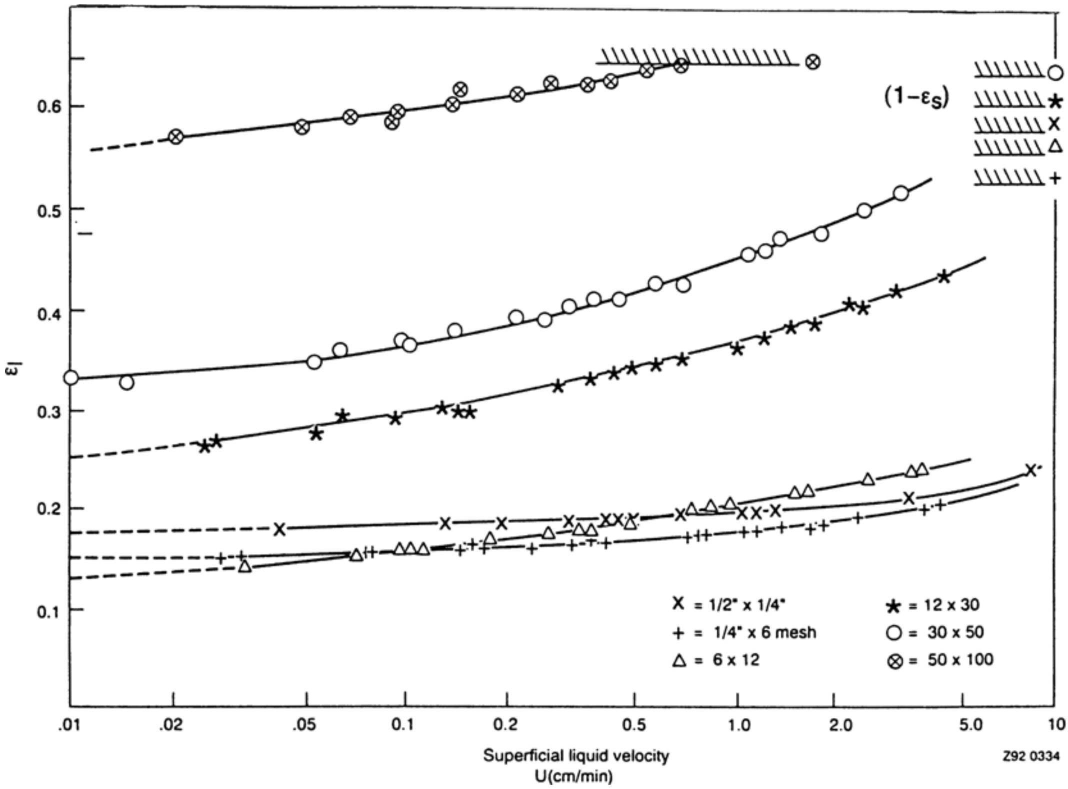

Fig. 2. Total porosity and average liquid holdup in coal heaps.

RESULTS AND DISCUSSION

Gas Holdup and the Active Depth

The values of the total bed porosity $(1-\epsilon_s)$ calculated from the data and Eq. (2) are shown as the upper limits in Fig. 2. The porosity decreased with increasing coal particle size, except for the anomalous behavior of the 1/4×1/2 in size fraction, which is probably owing to the effect of the column walls preventing these large particles from settling properly.

Figure 2 also shows the average liquid holdup in the heap calculated from the data using Eq. (3). It must be emphasized that this is the average value, i.e. (total water volume in heap)/(heap volume). The flow of water through the heap is determined by a combination of gravity and capillary forces, the latter being dominant in heaps of finely ground coal. When capillary forces are significant (coal smaller than approx 6×12 mesh), the support screen acts as a capillary barrier, and the heap just above the screen approaches 100% water saturation. This effect not only distributes the water nonuniformly through the heap, but it also cuts off diffusion of oxygen into the heap from below. This is a major source of uncertainty in

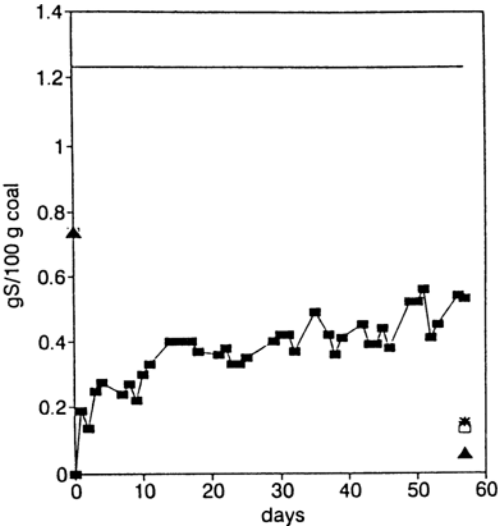

Fig. 3. Sulfur balance: 30×100 mesh heap. —■— S solubilized, —□— top: PyS if Fe=2S, —▲— middle: PyS if Fe=2S, —*— bottom: PyS if Fe=2S.

the design of heap bioreactors, particularly since the surfactants produced by *Thiobacillus* bacteria greatly reduce the interfacial tension and thus the magnitude of the capillary forces. Further investigation is needed using the methods of soil hydrology.

The gap between the "liquid holdup" and "total porosity" lines in Fig. 3 gives the fraction of the bed volume occupied by air, ϵ_g. As expected, ϵ_g is very small in heaps of 50×100 mesh coal, the heap becoming totally waterlogged when the superficial water velocity is above 0.7 cm/min. With larger particles, the heap approaches "trickle-bed" behavior with larger gas holdup that decreases far more slowly with increased water flow.

The flow data in Fig. 2 can be combined with Eq. (1) to give a preliminary answer to the question of the smallest coal particles that should be put in a heap bioreactor. In a well-designed bioprocess (one in which liquid recycle and nutrient addition are controlled to give an excess of bacteria), the initial rate of pyrite degradation depends on the exposed surface area of pyrite, which, to a first approximation, is inversely proportional to coal size (*10*). Knowing that 90% of the pyrite in 100×140 mesh fraction of a 2% pyrite coal can be degraded in 10 days (*1*) allows the calculation of $r=2.55/d$ mol/m^3 d, where d=coal particle size in mm. Since the water flow exists to bring in fresh nutrients and wash out metabolic products, the velocity, U, should be proportional to r. The optimum value for the water velocity is unknown, but is not critical since ϵ_g is only a weak function of U (Fig. 2). Estimating $U=0.02r$ cm/min allows the active depth of heaps of different coal particle sizes to be calculated from Eq. (1), using the experimentally determined values for ϵ_g and the average value $Y_o=3.625$. The results (Table 1) show a rapid decrease in the active depth

Table 1

Calculated Values of Oxygen Penetration Depth and Total Depyritization Rate as a Function of Coal Particle Size

Coal size		Depyritization rate per unit cal volume r mol/m^3 d = 2.55/d	Superficial water velocity $U = 0.02r$ cm/min	ϵ_g Fig. 2	Active depth, Eq. 1, L m	Depyritization rate per unit area of heap $r\epsilon_s L$ mol/m^2 d
Mesh	d mm					
50×100	0.21	12.1	0.242	0.026	0.005	0.021
30×50	0.42	6.07	0.121	0.161	0.151	0.338
12×30	1.01	2.52	0.050	0.318	0.735	0.741
6×12	2.39	1.07	0.021	0.413	1.79	0.859
1/4 in.×6	4.61	0.55	0.011	0.371	2.14	0.564
1/2 in.×1/4 in.	8.98	0.28	0.006	0.406	3.35	0.395

from over 3 meters for 1/4×1/2 in coal to <1 cm for the 50×100 mesh heap, which is almost waterlogged at the proposed water flow rate. Also shown in Table 1 is the rate at which pyrite can be oxidized per unit area of heap ($=r\epsilon_s L$). This shows a definite maximum for coal in the 6×30 mesh size range. With smaller coal, oxygen has difficulty penetrating the heap, and the rate is low because the active depth is small. This is the operating regime of the "tray bioreactor" (*5*), in which coal is kept in a relatively thin layer on a long conveyor belt. For coal larger than 6×30 mesh, oxygen transfer is not a problem. The numbers in Table 1 actually underestimate the true "active depth," which will be increased in practice by flow of air through the heap (because of wind and natural convection) and the much lower rate of oxygen consumption once the immediately accessible pyrite has been degraded. This is the operating regime studied by Hyman et al. (*6*).

Column Depyritization: 30 × 100 Mesh Coal

Data on the forms of sulfur in the column containing 5.26 kg (height = 99 cm) of 30×100 mesh coal are shown in Fig. 3. This coal was quite oxidized, and contained 0.74% pyritic sulfur and 0.50% sulfate sulfur. The upper horizontal line in Fig. 3 therefore represents the total amount of inorganic sulfur in each 100 gm of coal. The lower line shows the amount of sulfur that has been solubilized and has appeared in the liquid as sulfate (converted to the same basis of grams of sulfur per 100 gram of coal). This shows a sharp rise in the first few days as some of the sulfate sulfur is washed out of the coal by the acidic water being recirculated over it. The pH in the reservoir rose from 1.36 to 1.60 during this period because of the basic minerals in the coal. On day 7, 1 L of a concentrated mixed microbial culture acclimated to this coal during previous experiments was added to the reservoir. The pH stayed in the range 1.6 to 1.9 for the rest of the experiment. After inoculation, the sulfate in the liquid rose slowly, accounting for 0.5 g/100 g of the 1.24 g/100 g inorganic sulfur in the coal when the experiment was stopped after 58 d. When the product coal was analyzed, it was found to contain between 0.05 and 0.15% pyritic sulfur with an average of 0.12%, corresponding to 84% removal in the 51 d after inoculation of the heap. Note, however, that the ASTM procedure actually measures pyritic iron, so these numbers are based on the assumption that pyrite degradation proceeds stoichiometrically.

If the pyritic sulfur at the end of the experiment is added to what had appeared in the liquid, almost 0.6 g S/100 g remains unaccounted for. The probable location of this sulfur was shown by the liquid holdup, calculated from the measurements of the column weight and shown in Fig. 4. Initially, the liquid superficial velocity was set at 0.14 cm/min, and the

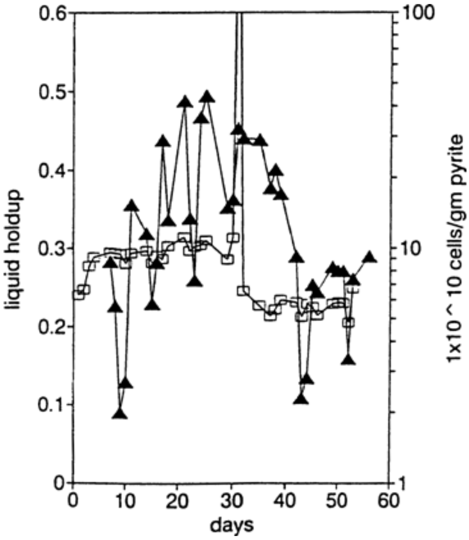

Fig. 4. ▲ Cell concentration and ☐ liquid holdup: 30×100 mesh heap.

liquid holdup fluctuated in the range $0.28<\epsilon_l<0.30$. This is less than expected from Fig. 2 for a mixture of 30×50 and 50×100 mesh coal, a consequence of either local channeling in the heap or the reduction of interfacial tension owing to the biosurfactants produced by the bacteria. However after 31 days, the flow resistance of the heap suddenly increased to the point where a 30-cm column of water formed on top of it. This plugging was caused by a mixture of biomass and the ferric hydroxysulfate precipitates (geothite, jarosites, and so forth) created by their activity. Turning the liquid velocity down to 0.02 cm/min eliminated the waterlogging of the heap and reduced the liquid holdup to the range 0.21 to 0.23 (again lower than expected from Fig. 2) for the rest of the experiment. These hydroxysulfate precipitates are undesirable in several ways. Besides plugging the heap, they may cover the pyrite surface and reduce the biooxidation rate. They also account for the missing sulfur and make it essential that they be removed from the product coal by washing the heap. An attempt to flood the heap with dilute acid from below at the end of the experiment was unsuccessful; the entire heap rose up the column as a solid plug.

Figure 4 also shows the number of cells in the liquid, measured by direct microscope counts of samples from the reservoir and expressed as number per gram of pyrite in the feed coal. The inoculum added on day 7 contained 10^{10} cells/g, which was found to be sufficient to give a high rate in shake-flask studies (*1*). Over the next two days the number dropped as the cells attached to the coal. Days 12 to 25 were the period of maximum microbial activity as shown by the increased cell numbers and an increase in the Eh of the liquid from 460 to 580 mV. Reducing the liquid

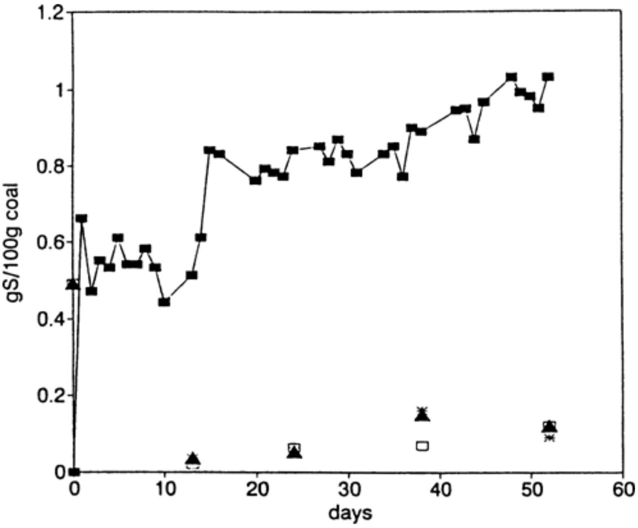

Fig. 5. Sulfur solubilized and precipitated: 12×30 mesh. ■ S solubilized, □ top: ppt. S, ▲ middle: ppt. S, * bottom: ppt. S.

velocity after day 32 caused the number of cells in the liquid to drop, presumably because fewer cells were being washed out of the heap.

Column Depyritization: 12 × 30 Mesh

Several changes were made in order to minimize and monitor the formation of precipitates during the experiments with 12×30 mesh coal. The experiment was run at the lowest pH at which the microorganisms can function (1.2 ~ 1.35) and the liquid velocity was increased to 0.41 cm/min. Also, ports were added to the bottom, middle, and top of the column, so that core samples could be taken periodically from the heap.

The forms-of-sulfur results are shown in Fig. 5 (sulfate sulfur on coal and in liquid) and 6 (pyritic and total inorganic sulfur), all data having been converted to the common basis of gS/100 g coal. This size fraction was even more oxidized than the 30×100 mesh, containing 0.655% pyritic sulfur and 0.49% sulfate sulfur. Almost all of the sulfate sulfur washed out into the liquid before the reservoir was inoculated with microorganisms on day 3. The sulfate on the coal was still almost zero on day 13, when the first core samples were taken, and it increased slowly thereafter as microbial activity generated precipitates. Note, however, that the amount of precipitate shown in Fig. 5 is much less than was deduced from Fig. 3. There was no heap plugging with this coal size, although the liquid holdup (Fig. 7) showed some interesting variations. There was a definite decline from 0.23 on day 4 when the bacteria were added to an operating value close to 0.17. This gives some idea of the effect of the

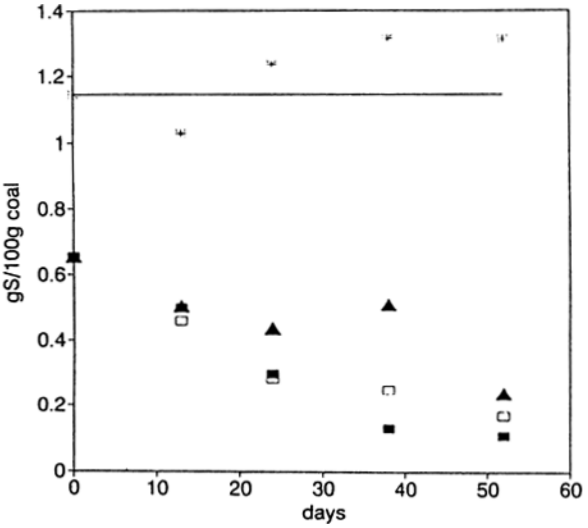

Fig. 6. Pyritic and total inorganic sulfur: 12×30 mesh. —■— top: PyS if Fe=2S, —□— middle: PyS if Fe=2S, —▲— bottom: PyS if Fe=2S, —*— total S measured, ____ initial S. conc.

biosurfactants on the capillary forces keeping water in the heap. The subsequent increase to over 0.4 at day 15 suggests an accumulation of cells plugging sections of the heap. Cells must be growing, because this is the period when the oxidation rates of sulfur (Fig. 5) and iron (from Eh data) were the highest. However, these cells did not wash out into the liquid in large numbers until a few days later (Fig. 7).

Figure 6 shows that the pyritic sulfur decreased continuously over the 48 d after inoculation, finishing with an average value for the heap of 0.13%. This represents 80% removal, which is excellent for fairly large particles of a coal known to contain considerable micropyrite. Adding the sulfate sulfur on the coal and in the liquid to the average pyritic sulfur value in the heap should give a constant value equal to the inorganic sulfur content of the raw coal. This check on the sulfur balance over the experiment gives reasonable results, although the data fall below the horizontal line in Fig. 6 at small times and above it later. There are two possible reasons for this. The ASTM procedure actually measures pyritic iron and only gives a pyritic sulfur number of assuming a composition of exactly FeS_2. In fact, it is known that coal pyrite, a far more amorphous material than pure crystalline pyrite, does not necessarily biodegrade stoichiometrically (*1*). Iron can be preferentially removed by the (chemical) reaction:

$$FeS_2 + 2Fe^{3+} \rightarrow 3Fe^{2+} + 2S \qquad (4)$$

This is particularly likely to occur on inclusions submerged in the coal particles, because Fe^{3+} and Fe^{2+} are soluble and can diffuse through the

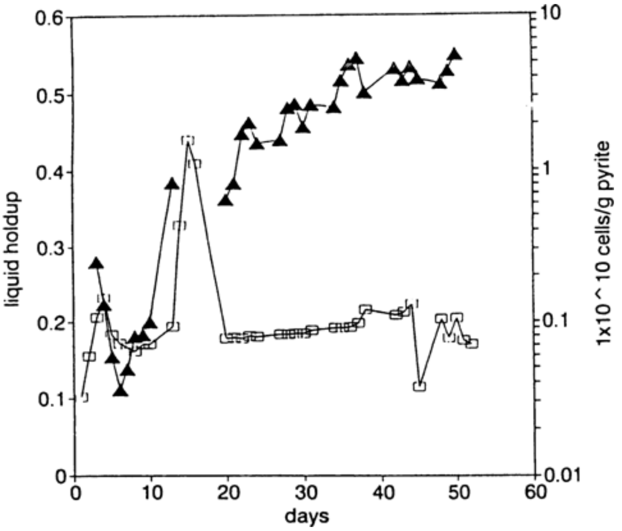

Fig. 7. Liquid holdup and cell concentration: 12×30 mesh. —□— Liquid holdup, —▲— cells.

coal particle, whereas S is insoluble and cannot. Accumulation of elemental sulfur would keep the total measured sulfur below the expected value at small times. The subsequent oxidation of this sulfur, along with elemental sulfur formed by weathering of the coal before the start of the experiment (which does not register in the ASTM procedures for inorganic sulfur) would put the total measured sulfur above the expected value later in th experiment. The data provide further support for this interpretation of Fig. 6. The oxidation/reduction potential of the liquid rose rapidly from 450 mV (roughly equal amounts of the two forms of iron) to 700 mV (virtually all Fe^{3+}) between days 9 and 13, indicating that reaction (4) was virtually complete by day 13. The pyrite surfaces were passivated with a layer of the sulfur, so ferric ion was no longer being reduced as rapidly by the reaction, and the bacteria could oxidize the ferrous ion back to ferric as fast as it was produced. Only later, at day 15, did the sulfur oxidation rate reach a maximum (Fig. 5).

The cell concentration measurements (Fig. 7) show a similar pattern as in the previous experiment with an initial drop (days 3–6) owing to attachment of bacteria to the coal, followed by a rapid rise through the period of maximum microbial activity (days 6 to 16) and a slower increase thereafter. The inoculum in this experiment was only 2.5×10^9 cells/g pyrite, significantly less than the optimum number. Coupled with the low pyrite content of the coal, this means that the r value calculated from the data is about nine times smaller than the value used in the calculation of the theoretical values in Table 1. The actual oxygen penetration depth in the coal heap should therefore be three ($9^{1/2}$) times larger or about 2 meters. It is interesting that the 1.02-meter experimental heap exhibits gradients in the depyritization rate. The data in Fig. 6 show that the depyritization rate at the top of the heap is consistently higher than at the bottom. This is probably because of CO_2 transfer limitations discussed in the Introduction. The alternative explanation that precipitates are washing down the heap and occluding the surface of the pyrite lower down is belied by the data in Fig. 5, which show only a slight variation in precipitates through the heap.

CONCLUSIONS

In heap bioreactors for the removal of pyrite from coal, there exists an optimum coal particle size that gives a maximum rate of pyrite removal per unit area of the heap. With larger particles, the rate is limited by the inaccessibility of pyritic inclusions to direct microbial attack, and with smaller particles, it is limited by oxygen (and CO_2) diffusion into the heap. The exact coal size and magnitude of this maximum rate depend to some extent on the operating conditions, but its existence seems intuitively reasonable. It is confirmed by experiments with laboratory-scale heaps of 30×100 and 12×30 mesh coal. The 30×100 mesh heap became waterlogged because of plugging with biomass and ferric hydroxysulfate precipitates generated by the process. Washing these precipitates out of the heap would be difficult. The 12×30 mesh heap showed similar rates of pyrite removal. It came close to plugging at one point and showed definite gradients of depyritization rate through the heap, probably owing to CO_2 transfer limitation. There was some indirect evidence for the production, and subsequent oxidation, of elemental sulfur, but this is expected during the microbial depyritization of larger coal particles. It is safe to conclude that 30 mesh is the smallest desirable particle size in a heap bioreactor. The largest is fixed by rate considerations, and 1/2 in is recommended based on the theoretical and experimental work reported here. More detailed design work for the heap bioreactor is continuing.

ACKNOWLEDGMENTS

This work was supported under contract no. DE-AC07-76ID01570 from the US Department of Energy, Office of Advanced Research and Technology Development, Office of Fossil Energy to the Idaho National Engineering Laboratory/EG&G Idaho, Inc.

REFERENCES

1. Andrews, G. F. and Maczuga, J. (1982), *Biotech. Bioeng. Symposium Series* **12,** 337.
2. Detz, C. M. and Barvinchak (1979), *Mining Congress J.* **65,** 75.
3. Dugan, P. R. and Apel, W. A. (1978), in *Metallurgical Applications of Bacterial Leaching and Related Microbial Phenomena,* Murr, L. E., Torma, A. E., and Brierley, J. A., eds., Academic Press, New York, Chap. 12.
4. Tillet, D. M. and Myerson, A. S. (1987), *Biotech. Bioeng.* **29,** 146.
5. Andrews, G. F., Stevens, C. J., Quintana, J., and Dugan, P. R. (1990), Proceedings 7th Pittsburgh Coal Conference, University of Pittsburgh, p. 358.
6. Hyman, D., Hammack, R., Finseth, D., and Rhee, K. (1990), Proc. 1st Int. Symp. on the Biological Processing of Coal, EPRI GS 6970, pp. 3-101.
7. Andrews, G. F. (1990), *Resources Conservation and Recycling* **3,** 137.
8. Baier, E. (1990), Proceedings of the DOE Workshop on the Biological Treatment of Coal, Vienna, VA, July.
9. Millington, R. J. and Quirk, J. M. (1961), *Transactions of the Faraday Society,* **57,** 1200.
10. Andrews, G. F., Stevens, C. J., and Wey, J. (1992), Proc. 3rd Int. Symposium on the Biological Processing of Coal, Clearwater, FL, May, in press.