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Biochemical Removal of HAP Precursors from Coal
DE-AC22-95PC95155

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Executive Summary

Shake flask bioleaching tests were conducted with Pittsburgh No. 8 and Indiana No. 5 coal. Bacteria removed pyritic sulfur from both coals at maximum rates of 5 to 9% per day, which was about 20 times the abiotic rate of pyrite oxidation. Concentrations of inorganic hazardous air pollutant (HAP) precursor elements in starting coal, bioleached coal and in leach solutions were measured. Of the 13 HAP precursors, significant amounts of arsenic, cobalt, cadmium, manganese, and nickel were removed from both coals by bacterial activity and also by the acidic leach solutions in control flasks. Little or no mercury, lead, beryllium, chromium, antimony, fluorine or chlorine was removed from the coals. Selenium was bioleached from both coals as determined by analysis of Se in leach solutions. However, analyses of Se in starting coal and in coal residues remains problematic. With very few exceptions, mass balances for the HAP precursors ranged from 80 to 120%.

Concise Summary of Work Performed

Improved analytical methods were developed for measuring concentrations of Hg, Se, As, and Sb in coal. Shake flask tests with pyrite oxidizing bacteria were conducted on Pittsburgh No. 8 and Indiana No. 5 coal. Concentrations of HAP precursors in the starting coal, leach solutions, and final coal residues were measured. A column leaching-rotating biological contactor (RBC) unit was assembled and a column leach test with Pittsburgh No. 8 coal was begun.

Variances: No major variances to the work plan

Open Items: None

Forecast for Upcoming Quarter: Column-RBC tests with Pittsburgh No. 8 coal will be completed. Shake flask tests on two additional U.S. coals will be conducted. Methods for improved selenium measurement in coal will be investigated. A detailed plan will be finalized for testing HAP precursor removal in the slurry column reactor at the Idaho National Engineering Laboratory. A coal for these tests will be selected and arrangements made for its delivery to INEL.

DISCLAIMER

Technical and Scientific Results

1. Shake Flask Test Work--Pittsburgh No. 8 Coal

An ultimate and short proximate analysis was done on the starting coal (-100 mesh) along with a determination of forms of sulfur and concentration of 13 inorganic HAP precursors (Table 1). Duplicate flasks containing 20% slurries of Pittsburgh No. 8 coal were inoculated with pyrite oxidizing bacteria and incubated at 25°C with shaking at 180 r.p.m. until biooxidation of pyrite was nearly complete. Another set of duplicate flasks were uninoculated controls. An analysis was also done on the recovered product coals (Table 1). Selenium analyses of coals are incomplete (see discussion later in this report). Antimony and mercury analyses are in progress but were not completed as of March 31.

The kinetics of pyrite oxidation were estimated by the concentration of iron and sulfate in solution. The maximum rate of biological pyrite oxidation (Table 2) was determined from the slope of the Fe and sulfate dissolution curves (Figure 1).

Table 2. Maximum daily rate[1] of pyrite oxidation (%) with Pittsburgh No. 8 Coal

	Based on solution Fe	Based on solution $SO^{=}_4$
cells-1	8.4	8.0
cells-2	9.2	8.6
control-1	1.1	1.1
control-2	0.3	0.3

[1]rate for cells based on data from day 4-12, rate for control based on all data (Fig.1)

Despite our attempts to sterilize the coal under argon at 100°C, some growth of pyrite oxidizing bacteria began in control flasks during the time course. This growth was indicated by increasing Fe(III)/Fe(II) ratios and increases in the rate of iron and sulfate dissolution. At this point, 3 ml of a bacteriocidal solution of 2% thymol in methanol was added to control flasks (day 12 in control 2 and day 15 in control 1). This treatment stopped bacterial pyrite oxidation. However, since some limited bacterial growth occurred in controls prior to biocide treatment, the rate of pyrite oxidation in control flasks, especially in control 1, is somewhat higher than the strictly chemical rate of pyrite oxidation.

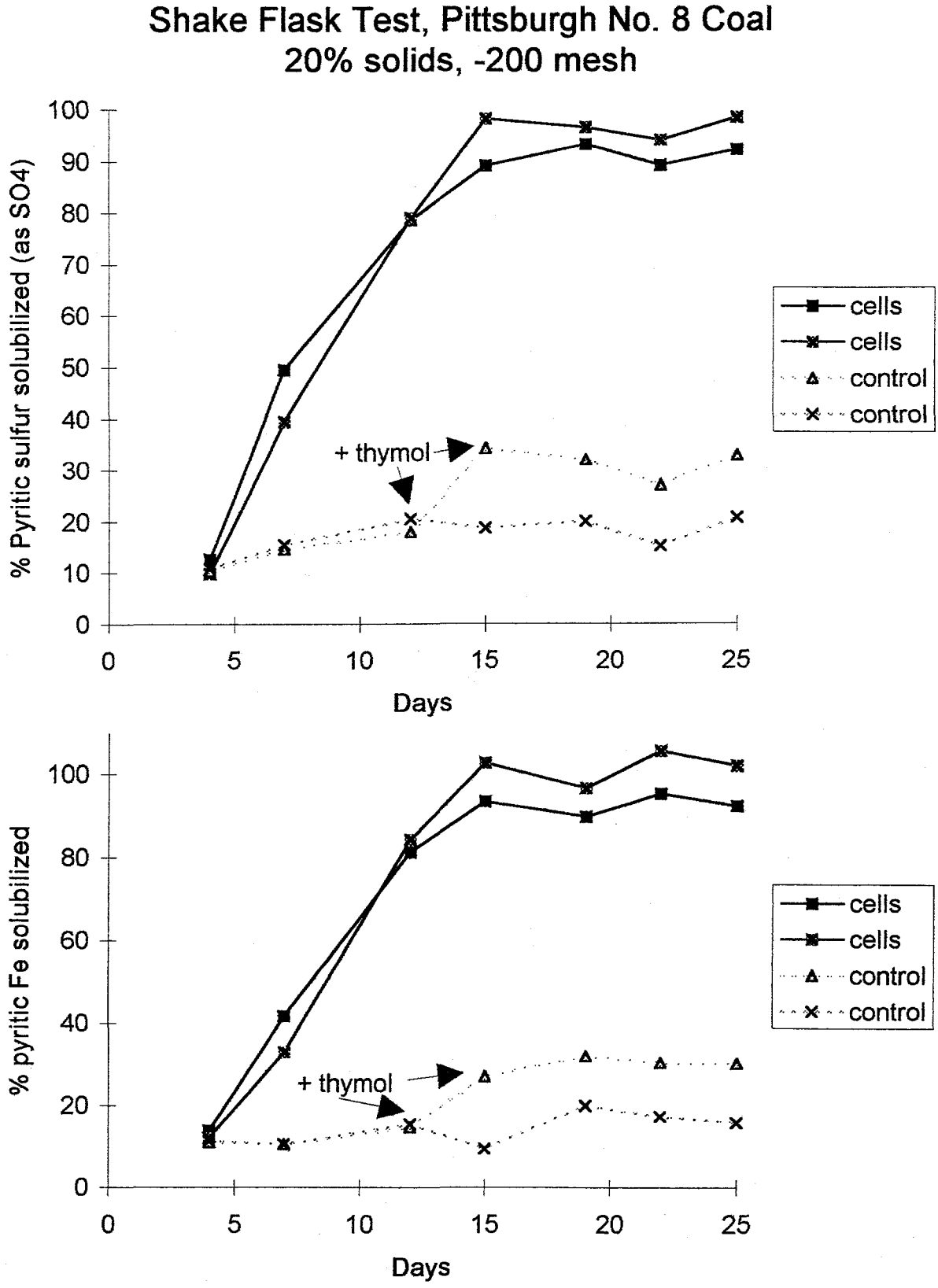
Over one third of the arsenic, cadmium, cobalt, manganese, and nickel were removed from Pittsburgh coal following biooxidation, based on analyses of the starting coal and biotreated and control coal residues (Table 1). With the exception of arsenic, over 20% of each of these elements was also removed from coal in control flasks. Chromium removal was 12 to 15% in biotreated coal and 4% in controls.

Table 1. Analysis of Pittsburgh 8 Coal: Shake Flask Test (-100 mesh, dry basis)

	Raw coal	Biotreated	Control	%loss-microbial	% loss-control
% carbon	67.95	70.35 70.49	69.43 69.50		
% hydrogen	4.59	4.53 4.51	4.52 4.49		
% nitrogen	1.38	1.37 1.36	1.33 1.33		
% sulfur	2.69	1.50 1.53	2.17 2.29	44 43	19 15
% ash	16.66	14.82 15.27	16.03 15.97	11 8	4 4
% oxygen (diff)	6.73	7.43 6.84	6.52 6.42		
Btu/lb	12120	12446 12433	12314 12307		
% pyritic sulfur	1.17	0.12 0.12	0.80 0.87	90 90	32 26
% sulfate sulfur	0.32	0.24 0.27	0.22 0.21		
% org. S (diff)	1.20	1.14 1.14	1.15 1.21		
HAPS, ug/g coal					
mercury	0.19 0.16				
arsenic	8.9 8.4	4.9 4.4	7.6 8.8	43 49	12 0
cadmium	1.0 1.1	0.5 0.6	0.7 0.7	53 46	32 30
chromium	29.1 29.6	25.1 25.9	28.1 28.3	15 12	4 4
selenium					
antimony	0.6 0.5				
beryllium	<0.2 <0.2	<0.2 <0.2	<0.2 <0.2		
cobalt	7.6 7.3	4.7 4.7	5.2 5.3	37 37	30 29
lead	12.3 14.3	13.9 13.2	13.1 12.3	0 1	2 8
manganese	63.5 59.6	22.6 24.6	29.0 30.5	63 60	53 50
nickel	17.3 17.4	10.9 11.3	13.6 13.6	37 35	22 22
chlorine (%)	0.08	0.08 0.08	0.08 0.07	0 0	0 12
fluorine	120	109 133	151 138	9 0	0 0

Duplicate values are for duplicate flasks, except for raw coal HAPs determinations which represent duplicate digestions. Some analyses on residues are not yet completed (Se, Sb, Hg).

Figure 1. Kinetics of Pyrite Oxidation in Pittsburgh No. 8 Coal



Less than 10% of fluorine, chlorine, and lead was removed from coal following biooxidation of the coal pyrite. Beryllium was not detected in the starting coal or in coal residues. Analyses of mercury, selenium and antimony in coal residues has yet to be completed.

HAP precursors were also measured in shake flask solutions at two time points during the test (after 11 and 15 days) and at the conclusion of the shake flask test. These solution measurements provided information for mass balances and for correlating pyrite oxidation with HAP precursor leaching. However, the two time point samples were taken after comparatively large amounts of pyrite had been biooxidized. Table 3 shows the extent of removal of HAP precursors in intermediate time point samples for the five elements which were significantly removed from coal in shake flask tests (As, Cd, Co, Mn, Ni). Note that most of the microbially catalyzed removal had occurred by the first time point sample when about 70% of the pyrite had been biooxidized. In some cases, the amount of metal in solubilized at the conclusion of the test was less than that shown for day 11 or day 15. Possibly adsorption of metal to the coal occurred.

Table 3. % of Coal HAP Precursors in Leach Solutions--Pittsburgh No. 8 Coal

	Day 11	Day 15	Final
% pyrite biooxidation (based on solution sulfate concentration)	73 (cells) 71 (cells) 17 (control) 19 (control)	89 98 18 10	92 98 33 21
Arsenic	60% 55 1 2	62% 59 16 2	47% 43 11 2
Cadmium	31 33 17 18	30 35 20 17	31 31 19 19
Cobalt	35 37 30 30	33 37 29 29	28 28 25 24
Manganese	57 61 45 44	61 57 46 45	47 47 41 40
Nickel	35 38 26 26	33 37 26 26	29 30 23 22

Values in above boxes are for duplicate inoculated (first two values) and control (second two values) flasks. Values are % of HAP precursor in coal that has been solubilized.

Mass balances were calculated for each HAP precursor (Table 4). The total mass of each HAP precursor was determined by multiplying its concentration in starting coal by the weight of starting coal. This mass was compared to the amount recovered in residue plus leach solutions. Mass balances were 82 to 113%, with the exception of cadmium in one biotreated flask (75%), and fluorine in 3 of the 4 flasks (127-138%). The % loss of metal (by solution) generally agreed well with the % loss of metal determined by starting coal and residue coal analysis.

It was surprising that a greater extent of metal removal from coal was not achieved, since many of the HAP precursors are thought to be associated primarily with pyrite or as sulfides, and given that 90% of the pyrite was removed from the coal. Perhaps some readsorption of solubilized metal occurred (see discussion above related to table 3). It is worthwhile to determine whether coals can adsorb HAP precursors from solution. A experiment will be conducted in the coming quarter with Pittsburgh coal and acidic bioleach solutions to test this hypothesis. Should significant adsorption occur, it will be worthwhile to consider process steps to minimize adsorption or to strip metals with an improved washing step.

Table 4. Mass Balances for Pittsburgh 8 Shake Flask Test*

	starting coal mg	solution mg	final coal mg	% recovery	% loss (by solution)
Hg cells	0.0060	<0.0001			
cells	0.0060	<0.0001			
control	0.0060	<0.0001			
control	0.0060	<0.0001			
arsenic	0.259	0.120	0.143	102	46
	0.260	0.111	0.127	92	43
	0.259	0.028	0.225	98	11
	0.259	0.004	0.262	103	2
cadmium	0.032	0.010	0.014	75	31
	0.032	0.010	0.017	84	31
	0.032	0.006	0.021	84	19
	0.032	0.006	0.022	88	19
chromium	0.882	0.035	0.729	87	4
	0.884	0.034	0.754	89	4
	0.882	0.019	0.833	97	2
	0.882	0.015	0.846	98	2
selenium		0.005			
		0.005			
		<0.001			
		<0.001			
antimony	0.017	<0.001			
	0.017	<0.001			
	0.017	<0.001			
	0.017	<0.001			
beryllium	<0.006	0.002	<0.006		
	<0.006	0.002	<0.006		
	<0.006	0.002	<0.006		
	<0.006	0.002	<0.006		
cobalt	0.225	0.063	0.135	88	28
	0.225	0.064	0.136	89	28
	0.225	0.056	0.153	93	25
	0.225	0.055	0.159	95	24
lead	0.399	0.025	0.404	108	6
	0.399	0.025	0.384	103	6
	0.399	0.016	0.388	101	4
	0.399	0.013	0.367	95	3
manganese	1.848	0.863	0.657	82	47
	1.853	0.874	0.715	86	47
	1.848	0.761	0.859	88	41
	1.848	0.737	0.911	89	40
nickel	0.523	0.153	0.317	90	29
	0.524	0.156	0.328	92	30
	0.523	0.120	0.403	100	23
	0.523	0.117	0.406	100	22
chlorine	24	2	23	104	8
	24	4	23	113	17
	24	0	24	100	0
	24	3	21	113	13
fluorine	3.60	0.83	3.17	111	23
	3.60	0.77	3.87	129	21
	3.60	0.51	4.47	138	14
	3.60	0.45	4.12	127	13

*Four values are shown for each HAP precursor. As shown for Hg above, the first two rows are for the two inoculated flasks, the last two rows are for control flasks

2. Shake Flask Test Work--Indiana No. 5 Coal

As with Pittsburgh coal, an ultimate analysis was done on the starting coal (-100 mesh) along with a determination of forms of sulfur and concentration of HAP precursors (Table 5). Some analyses were not yet available at the end of the quarter (empty boxes below).

Table 5. Analysis of Indiana 5 coal: Shake Flask Test (-100 mesh, dry basis)

	Raw coal	Biotreated	Control	%loss-microbial	% loss-control
% carbon	70.67				
% hydrogen	4.21				
% nitrogen	1.44				
% sulfur	4.09				
% ash	12.4				
% oxygen (difference)	7.19				
Btu/lb	12519				
% pyritic sulfur	2.21				
% sulfate sulfur	0.14				
% organic S (difference)	1.74				
HAPS, ug/g coal					
mercury	0.11 0.12	0.13 0.11	0.11 0.13	0 0	0 0
arsenic	5.5 5.7				
cadmium	1.2 1.2	0.4 0.7	0.5 0.8	66 45	59 32
chromium	12.2 11.6	11.9 12.8	12.6 12.8	0 0	0 0
selenium					
antimony	0.6 0.7				
beryllium	0.8 0.8	0.8 0.7	0.9 0.7	6 12	0 17
cobalt	4.8 4.4	2.6 3.4	3.3 2.6	44 27	28 44
lead	9.7 9.4	9.1 9.2	10.7 9.6	6 2	0 0
manganese	39.1 43.1	14.8 21.0	17.3 19.0	64 49	58 54
nickel	16.0 15.6	10.8 14.7	15.6 10.9	32 7	1 31
chlorine (%)	0.01				
fluorine	70				

Duplicate inoculated and uninoculated flasks containing 20% slurries (40 g coal, 160 ml of modified Kelly medium) of minus 100 mesh Indiana No. 5 coal were incubated at 25°C with shaking at 180 r.p.m. until biooxidation of pyrite was nearly complete. Uninoculated flasks were treated with 3 ml of 2% thymol in methanol at the beginning of the test. An analysis was also done on the recovered product coals (Table 5).

The kinetics of pyrite oxidation were somewhat slower than with Pittsburgh coal and are shown Table 6 and Figure 2.

Table 6. Maximum daily rate[1] of pyrite oxidation (%) with Indiana No. 5 Coal

	Based on solution Fe	Based on solution $SO^{=}_4$
cells-1	6.1	5.0
cells-2	5.2	4.6
control-1	0.3	0.5
control-2	0.5	0.3

[1] rate for cells based on data from day 6-18 (day 15 omitted), rate for control based on all data (see Fig. 2)

As with Pittsburgh coal, significant amounts of cadmium, cobalt, manganese and nickel were removed in biotreated coal (although the agreement of duplicates was poor with respect to nickel content of bioprocessed and control coal). To a lesser extent these elements were also leached from coal in control flasks. Little or no mercury, chromium, beryllium or lead was removed from coal. Coal residue analyses for F, Cl, As, Se and Sb were not yet completed, although solution arsenic measurements indicate biooxidation significantly increased arsenic removal compared to controls.

Time point samples were taken for Indiana No. 5 coal as they were for Pittsburgh No. 8 coal. Results for the five HAP precursors that were significantly leached are shown in Table 7. Again, the time points were taken after considerable pyrite oxidation occurred. Most of the HAPs were leached at the first time point. The first flask shown on day 18 has an anomalously high Mn value. The data were reexamined, but no explanation is obvious for the elevated value.

Mass balances (Table 8) were generally between 80% and 120%. Two cadmium flasks had low values (60%, 63%).

Figure 2. Kinetics of Pyrite Biooxidation in Indiana No. 5 Coal

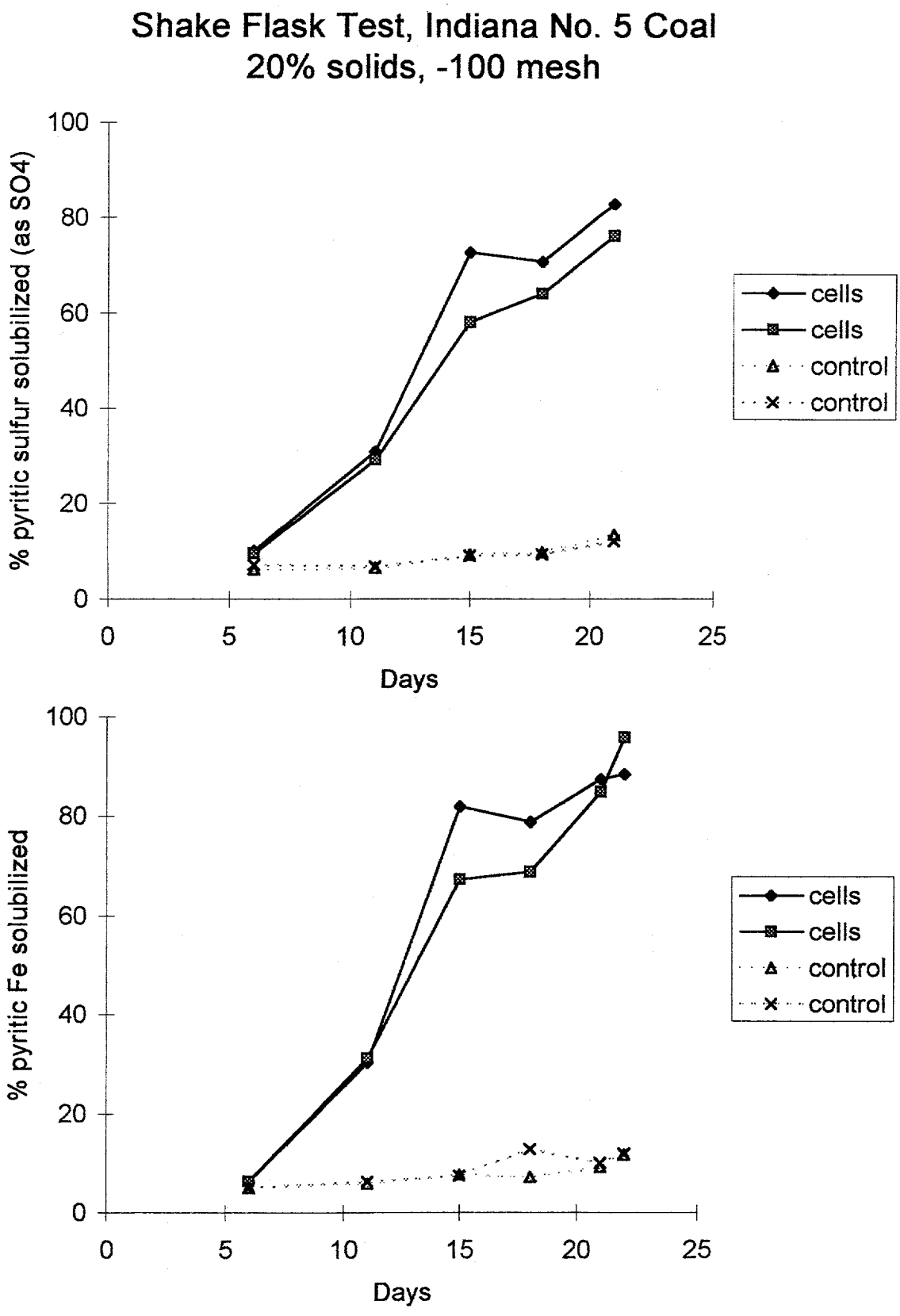


Table 7. % of Coal HAP Precursors in Leach Solutions--Indiana No. 5 Coal

	Day 16	Day 18	Final
% pyrite biooxidation (based on solution sulfate concentration)	72 (cells) 61 (cells) 9 (control) 9 (control)	79 69 10 9	83 76 13 12
Arsenic	34% 29 1 1	37% 37 1 1	44% 41 1 1
Cadmium	28 28 19 16	26 26 18 18	31 34 22 23
Cobalt	41 41 32 30	42 39 31 30	46 45 33 32
Manganese	55 54 42 45	97 53 43 44	62 60 42 69
Nickel	32 31 16 15	33 31 16 15	39 38 17 17

Values in above boxes are for duplicate inoculated (first two values) and control (second two values) flasks. Values are % of HAP precursor in coal that has been solubilized

Table 8. Mass Balances--Indiana 5 Shake Flask Test

	starting coal mg	solution mg	final coal mg	% recovery	% loss (by solution)
mercury	0.0048	<0.0002	0.0047	98	<4
	0.0048	<0.0002	0.0041	85	<4
	0.0048	<0.0002	0.0049	102	<4
	0.0048	<0.0002	0.0054	113	<4
arsenic	0.224				
cadmium	0.048	0.015	0.015	63	31
	0.048	0.016	0.025	85	33
	0.048	0.011	0.018	60	23
	0.048	0.011	0.030	85	23
chromium	0.476	0.021	0.499	109	4
	0.476	0.020	0.487	107	4
	0.476	0.012	0.472	102	3
	0.476	0.018	0.464	101	4
selenium					
antimony	0.028				
beryllium	0.033	0.003	0.028	94	9
	0.033	0.004	0.027	94	12
	0.033	0.003	0.033	109	9
	0.033	0.003	0.025	85	9
cobalt	0.190	0.087	0.093	95	46
	0.190	0.085	0.125	111	45
	0.190	0.063	0.123	98	33
	0.190	0.060	0.093	81	32
lead	0.384	0.038	0.330	96	10
	0.384	0.038	0.345	100	10
	0.384	<0.005	0.400	104	<1
	0.384	<0.005	0.347	90	<1
manganese	1.645	1.021	0.536	95	62
	1.645	0.981	0.786	107	60
	1.645	0.688	0.648	81	42
	1.645	1.138	0.689	111	69
nickel	0.633	0.246	0.393	101	39
	0.633	0.241	0.550	125	38
	0.633	0.110	0.583	109	17
	0.632	0.108	0.395	80	17
chlorine	4				
fluorine	2.80				

3. Analytical Developments

Although analysis of HAP precursors in leach solutions is straightforward, digestions are required to prepare solid samples (raw coal and recovered coal residues) for analysis of most of the HAP precursors. As discussed in the first quarter report, a digestion based on a modification of ASTM D3683 works well for most of the HAP precursors. However, that report indicated some issues were not resolved in the

analyses of 3 of the HAP precursors: Hg, Se and Sb. As described below, these issues are largely resolved: EPA method 7471 is now being used for mercury analysis and Eschka oxidation for As and Sb analysis. Se remains problematic.

Mercury. Initially we used a refluxing sulfuric acid nitric acid method (U.S. Bureau of Mines RI 7609) to digest coal prior to analysis of mercury by cold vapor atomic absorption spectrophotometry (CVAAS). We have since adopted a more rapid digestion method, EPA 7471, which involves heating in aqua regia followed by permanganate treatment.

According to results of an interlaboratory study of the analysis of mercury in coal conducted by CONSOL, comparable results were obtained by method 7471, oxygen bomb combustion (ASTM D3684), neutron activation analysis and atomic fluorescence analysis (reported in *Energeia*, vol 6, No. 5, 1995).

We found comparable Hg results in our analysis of starting Indiana 5 coal using either EPA method 7471 or the more vigorous Bureau of Mines digestion procedure. However, our mercury results were less than one tenth of the expected value for Indiana 5 coal. According to information supplied with the Indiana 5 coal by the Illinois Basin Coal Sample Program, the Indiana 5 coal sample (IBC-110) contains nearly 2 ug/g of Hg. Given this result and the lack of a coal standard certified for mercury content, we sent some coal samples to Huffman Laboratories for comparative analyses. Ron Kyle, Inorganic Lab Director at Huffman, indicates they use a nitric acid-refluxing perchloric acid digestion followed by CVAAS. As shown in Table 9 below, our results are close to those determined by Huffman. To date we have analyzed Pittsburgh No. 8 coal for its mercury content using only the Bureau of Mines digestion followed by CVAAS.

Table 9. Mercury (ug/g) in Duplicate Coal Samples Analyzed at Huffman Labs and at Little Bear Laboratories

coal sample	Huffman	LBL[1]	(s.d.)[2]
Pitt 8 starting coal	0.16	0.18	(0.02)
Ind 5 starting coal	0.12	0.11	(0.00)
Ind 5 biooxidized residue	0.13	0.13	(0.01)
Ind 5 dup biooxidized residue	0.11	0.11	(0.01)
Ind 5 control residue	0.13	0.11	(0.01)
Ind 5 dup control residue	0.15	0.13	(0.01)

[1]LBL method is EPA 7471 (Ind 5) or Bureau of Mines RI 7609 (Pitt 8)
[2]standard deviation for triplicate digestions

Antimony. This element is present in NIST SRM 1632b at our detection limit (0.2 ug/g). Consequently, we relied on spike recovery of antimony to assess the analytical method. As reported in the first quarter report, post digestion spikes of antimony into the matrix

resulting from D3683 digestion were poorly recovered. Modification of hydridization conditions failed to improve Sb recovery, so we turned our attention to an Eschka procedure. Despite initial poor spike recoveries, the matrix resulting from Eschka ignition gave good Sb recovery. Finally, we modified the Eschka oxidation procedure, placing crucibles into a hot muffle furnace. This resulted in >80% spike recoveries of antimony. Furthermore, arsenic determined under these conditions in NIST SRM 1632b was close to 100%. Consequently, the hot muffle furnace Eschka oxidation will be used for the analysis of As and Sb in coal.

Selenium. The modified Eschka analysis above made only slight improvements in selenium spike recovery. Though post Eschka spikes of Se into the analysis solution are recovered at near 100%, pre Eschka spikes of Se are recovered at only 10 to 20%. Se is apparently volatilized during Eschka treatment. It may be possible to quantify Se in acid digests of coal. Se determinations in aqua regia digests of NIST coal will be tested next.

4. Assembly of Bench Scale Leach Column-Rotating Biological Contactor (RBC)

By the end of the quarter a system had been assembled to conduct bench scale column leaching tests. A test with 28 x 100 mesh Pittsburgh coal was begun at the end of the quarter. The details of the experiment will be described in the next report.

The column-RBC system consists of pairs of plastic columns of 300 ml capacity, 4 x 30 cm in size. The columns are positioned above plastic reservoirs. Leach solution is percolated through the columns through the use of a multichannel peristaltic pump. A gear motor turns a series of 7 cm diameter plastic disks at 36 rpm. The disks are partially submerged in the reservoirs. Biofilms of iron oxidizing bacteria should develop on the disks, and the RBC should maintain sufficient aeration of the system to permit efficient iron biooxidation. The ferric-rich solution will then be pumped to the top of the columns.

5. Effects of Results on Future Work

The project is proceeding on schedule. HAP precursor quantitation in coal is, for the most part, proceeding well with good mass balances. Only selenium continues to present analytical difficulties. Additional work will be devoted to this problem in April. Samples were taken too late in the Indiana No. 5 and Pittsburgh No. 8 shake flask tests to determine the extent of HAP precursor leaching in the early stages of biodepyritization. Better timing of sampling of solutions for HAP precursor analysis will be required in future shake flask and leach column tests.

A determination of binding of HAP precursors in solution to coal will be made. This finding will be important in determining the effectiveness of bioleaching of these elements from coal and for process design and operation.