Biochemical Removal of HAP Precursors From Coal

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BIOCHEMICAL REMOVAL OF HAP PRECURSORS FROM COAL

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Abstract

Column biooxidation tests with Kentucky coal confirmed results of earlier shake flask tests showing significant removal from the coal of arsenic, selenium, cobalt, manganese, nickel and cadmium. Rates of pyrite biooxidation in Kentucky coal were only slightly more than half the rates found previously for Indiana and Pittsburgh coals. Removal of pyrite from Pittsburgh coal by ferric ion oxidation slows markedly as ferrous ions accumulate in solution, requiring maintenance of high redox potentials in processes designed for removal of pyrite and hazardous air pollutant (HAP) precursors by circulation of ferric solutions through coal. The pyrite oxidation rates obtained in these tests were used by Unifield Engineering to support the conceptual designs for alternative pyrite and HAP precursor bioleaching processes for the phase 2 pilot plant. Thermophilic microorganisms were tested to determine if mercury could be mobilized from coal under elevated growth temperatures. There was no evidence for mercury removal from coal under these conditions. However, the activity of the organisms may have liberated mercury physically. It is also possible that the organisms dissolved mercury and it readsorbed to the clay preferentially. Both of these possibilities are undergoing further testing. The Idaho National Engineering and Environmental Laboratory's (INEEL) slurry column reactor was operated and several batches of feed coal, product coal, waste solids and leach solutions were submitted to LBL for HAP precursor analysis. Results to date indicate significant removal of mercury, arsenic and other HAP precursors in the combined physical-biological process.

Executive Summary

This sixth quarterly report covers the period of January 1997 through March, 1997. A column test was conducted during this quarter, which showed that Kentucky coal was more slowly depyritized than in previous tests with Indiana and Pittsburgh coals. The HAP precursors As, Cd, Co, Mn and Ni were removed significantly from coal in column tests, in agreement with past shake flask leaching tests. Analyses were not yet complete at the end of the quarter.

Experiments were done to determine the kinetics of pyrite biooxidation with ferric ions. Pyrite biooxidation rates declined markedly with declining solution redox potential. A relatively small ratio of ferrous iron to ferric iron depressed the redox potential. Consequently, significant concentrations of ferric iron alone are not sufficient for the fastest rates of dissolution of pyrite and associated HAP precursors. These data were used for designs by Unifield Engineering of potential phase 2 pilot plant processes. Conceptual designs for two competing processes were completed. Oxidation of pyrite may need to be based on application of a biogenic ferric ion stream as opposed to heaps due to the potentially large amount of heat generated in heaps by microbial oxidation of pyrites.

Mercury has emerged recently as perhaps the key HAP precursor to be removed from coal. Thermophilic microorganisms may possess greater potential than mesophilic bacteria for breaking Hg-S bonds in coal. Experiments were done to determine if moderate and extreme thermophiles could remove mercury from Pittsburgh coal at 50°C and 65°C, respectively. The moderate thermophiles may have mobilized mercury

either through a physical or chemical process. Additional tests are in progress to determine which process likely occurs.

The INEEL slurry column reactor was operated on several batches of Pittsburgh coal. This reactor is a combined physical-microbial process for coal depyritization. The preliminary analytical data comparing feed coal and product coal indicate product coal contains significantly lowered concentrations of mercury and arsenic along with other HAP precursors. Additional analyses and mass balance determinations are in progress.

Introduction

This project is investigating microbiological removal of 13 HAP precursors and pyrite from four U.S. coals. Shake flask and column tests are being conducted to determine the rate and extent of the process. Each test determines the rate of microbial pyrite oxidation, the extent of HAP precursor removal, and the mass balance of HAP precursor elements. Slurry column tests are being conducted at INEEL to determine the extent of HAP precursor removal with this advanced concept for physical-microbial coal depyritization.

Results and Discussion

1. Shake Flask Tests--Results of Kentucky Coal (Task 2)

The previous quarterly report (quarter 5, ending December 31, 1996) described and discussed most of the analytical results for this final shake flask test. Table 1 shows the nearly completed analytical results for this test. The additional data include short proximate and forms of sulfur analyses of the raw coal and the Cl and F data for biotreated and control residues. The ultimate analysis of the raw coal is not yet completed. The forms of sulfur analyses confirmed the solution iron and sulfate data showing removal of nearly all pyritic sulfur from biotreated coal. The removal of Cl and F was not indicated by solution analyses and these results were confirmed by the residue analysis in Table 1. The completed summary of HAP precursor mass balances for the Kentucky coal shake flask test, including Cl and F, appears as Table 2.

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

	Raw coal	Biotreated	Control	%loss-microbial	% loss-control
% carbon		70.99 70.89	68.85 68.20		
% hydrogen		4.52 4.51	4.33 4.57		
% nitrogen		1.44 1.45	1.39 1.38		
% sulfur	4.27	3.25 3.22	4.77 4.59	24 25	0 0
% ash	13.65	12.15 11.92	13.82 14.03	11 13	0 0
% oxygen (difference)		7.65 8.01	6.84 7.23		
Btu/lb	12007	12422 12471	12243 12245		
% pyritic S	1.32	0.13 0.17	1.68 1.95	90 87	0 0
% sulfate S	0.62	1.08 1.06	1.01 0.96		
% organic S (difference)	2.33	2.04 1.99	2.08 1.68		
HAPs, ug/g coal					
mercury	0.06	0.08 0.09	0.08 0.07	0 0	0 0
arsenic	8.6	4.6 4.6	9.0 8.4	47 47	0 2
cadmium	0.3	<0.1 <0.1	0.1	>67 >67	67
chromium	9.7	9.4 9.9	9.9 9.7	3 0	0 0
selenium	1.1	0.9 0.9	1.1 1.0	31 31	15 23
antimony	<0.9	<0.9 <0.9	<0.9 <0.9	0 0	0 0
beryllium	0.4	0.4 0.4	0.4 0.4	0 0	0 0
cobalt	2.7	1.4 1.9	1.8 2.2	48 30	33 19
lead	11	9.8 8.9	9.5 9.4	11 19	14 15
manganese	74	16 15	19 18	78 80	74 76
nickel	7.8	4.0 4.1	5.9 6.5	49 47	24 17
chlorine	830	840 810	780 820	0 2	6 1
fluorine	73	50 50	50 50	32 32	32 32

Table 2. Mass Balances for Kentucky Coal Shake Flask Test*

	starting coal mg	solution mg	final coal mg	% recovery
Hg	0.0021	cells	0.0027	129
		cells	0.0031	148
		control	0.0030	143
		control	0.0025	119
arsenic	0.301	0.129	0.161	96
		0.129	0.161	96
		0.008	0.315	107
		0.007	0.294	100
cadmium	0.011	0.014	<0.002	127
		0.013	<0.002	118
		0.004	0.004	73
		0.004	0.011	136
chromium	0.340	0.001	0.329	97
		0.001	0.347	102
		0.001	0.347	102
		0.001	0.340	100
selenium	0.039	0.005	0.033	97
		0.005	0.032	95
		<0.001	0.039	100
		<0.001	0.036	93
antimony	<0.018	<0.001 (all)	<0.018 (all)	--
beryllium	0.014	<0.001	0.015	107
		<0.001	0.015	107
		<0.001	0.014	100
		<0.001	0.014	100
cobalt	0.095	0.053	0.049	107
		0.046	0.068	120
		0.033	0.062	100
		0.037	0.076	119
lead	0.368	0.062	0.342	109
		0.045	0.311	97
		0.031	0.331	98
		0.007	0.329	91
manganese	2.583	1.958	0.550	97
		1.901	0.525	94
		1.922	0.648	100
		1.908	0.613	98
nickel	0.273	0.140	0.140	100
		0.144	0.144	100
		0.207	0.207	98
		0.228	0.228	107
chlorine	29.05	<0.280	29.40	101
		<0.280	28.35	98
		<0.280	27.30	94
		<0.280	28.70	99
fluorine	2.555	<0.007	1.750	68
		<0.007	1.750	68
		<0.007	1.750	68
		<0.007	1.750	68

*Four values appear 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. Mass balances were determined by adding the Total mg in solution (mg/l x liters) to the mg recovered in coal residues (mg/kg x kg) divided by the mg in raw coal (mg/kg x kg).

2. Kentucky Coal Column Test (Task 3)

A column test was conducted to test bioremoval of pyrite and HAP precursors from Kentucky No. 9 coal. Two columns each contained 100 g of 28 x 100 mesh coal and were leached with 200 ml of MKM salts solution (pH 2.0) containing a mixed population of pyrite oxidizing bacteria pregrown on Kentucky coal. The columns drained into a common reservoir (400 ml total). The reservoir was aerated to encourage the biooxidation of iron. Two additional columns served as abiotic controls, these were uninoculated and received thymol as a biocide. Columns were operated for a total of 60 days. Samples were removed periodically for analysis of pH, redox potential, sulfate and iron to determine the progress of coal pyrite oxidation. HAP precursors leached into solutions at intermediate time points and in the final leach solution were determined. Figure 1 shows the time course biodepyritization of the coal.

Fig. 1. Biodepyritization of Kentucky Coal in Columns

A lag phase of nearly 3 weeks occurred before microbial activity in the columns became significant, as indicated by significant increases in the redox potential and ferric iron to ferrous iron ratio in leach solutions. The rate of pyrite biooxidation was calculated over the period from day 21 to day 60 and is shown in Table 3.

Table 3. Rate of Pyrite Oxidation (% per day) in Kentucky Coal in Columns¹

column	based on solution Fe	based on solution sulfate
cells	0.70	0.64
control	0.11	0.13

¹duplicate columns

The rate of pyrite oxidation in controls is considered an overestimate since the redox potential began to rise late in the time course due to growth of pyrite oxidizing bacteria that entered the system. A second dose of thymol slowed, but did not stop, the growth of these organisms. The rate of pyrite biooxidation was only slightly more than half of that observed with Pittsburgh and Indiana coals (see fourth quarterly report) which were depyritized at about 1.2 to 1.3% per day.

Analyses coal residues are shown in Table 4, the percentage of HAP precursors leached into solution appear in Table 5, and the mass balances for HAP precursors appear in Table 6. Some analyses are not yet complete--the empty boxes in the tables reflect the incomplete results.

Results of residues analyzed to date (Table 4) indicate significant leaching of arsenic, selenium, cobalt, manganese, nickel and cadmium into solution due to microbial activity. Significant manganese, cadmium and cobalt were also leached abiotically. The solution analyses to date (Table 5), confirm the significant removal of cadmium, cobalt, nickel and manganese into solution in both inoculated and uninoculated columns. These results are in agreement with the shake flask tests with Kentucky coal described in the previous quarterly report showing manganese was removed as extensively from controls as from biotreated coal, with cadmium, nickel, and cobalt removed somewhat more effectively biologically as compared to control samples. Part of the removal of HAP precursors in control coal may be due to some growth of contaminant pyrite oxidizing bacteria as discussed above.

Table 4. Analysis of Kentucky No. 9 Coal, Column Test (28 x 100 mesh, dry basis).

	Raw coal	Biotreated	Control	%loss-microbial	% loss-control
% carbon	70.07				
% hydrogen	4.73				
% nitrogen	1.45				
% sulfur	3.84				
% ash	11.20				
% oxygen (difference)	8.71				
Btu/lb	12495				
% pyritic S	1.51				
% sulfate S	0.36				
% organic S (difference)	1.97				
HAPs, ug/g coal					
mercury	0.04	0.05	0.05	0	0
arsenic	6.5	5.4	5.9	17	9
cadmium	0.3	<0.10	<0.10	>67	>67
chromium	8.3	8.9	8.5	0	0
selenium	0.7	0.4	0.7	43	0
antimony	<1.0	<1.0	<1.0	--	--
beryllium	0.4	0.4	0.4	0	0
cobalt	2.6	1.6	1.0	38	62
lead	6.5	10.6	8.3	0	0
manganese	39	6.7	11	83	72
nickel	5.6	3.6	4.7	36	16
chlorine	900				
fluorine	56				

Table 5. % of Coal HAP Precursors in Leach Solutions¹ in Kentucky No. 9 Columns

	Day 21	Day 33	Final - Day 60
% pyrite biooxidation ²	14 (cells) 10 (control)	22 9	39 15
Arsenic			
Cadmium	19 19	41 24	53 32
Selenium			
Beryllium	2 <2	2 2	2 2
Cobalt	30 24	31 24	31 26
Lead	<2 <2	<2 <2	8 4
Manganese	57 60	58 62	55 68
Nickel	29 24	33 25	37 32

¹ less than 1% of Sb, Hg, Cl, Cr and F was solubilized.

² based on solution SO₄ concentration

Table 6. Mass Balances for Kentucky No. 9 Coal Column Test*

	starting coal mg	solution mg	final coal mg	% recovery
Hg cells	0.008	<0.005 <0.005	0.010 0.010	119
				119
control				
arsenic	1.30			
cadmium	0.052	0.032 0.019	<0.020 <0.020	
chromium	1.66	0.014 0.029	1.79 1.70	109 104
selenium	0.140			
antimony	<0.020			
beryllium	0.088	0.002 0.001	0.088 0.086	102 99
cobalt	0.514	0.159 0.136	0.326 0.191	94 64
lead	1.32	0.11 0.06	2.12 1.65	148 130
manganese	7.80	4.32 5.32	1.34 2.16	73 96
nickel	1.12	0.412 0.362	0.714 0.930	105 115
chlorine				
fluorine				

*Three values are shown for each HAP precursor. As shown for Hg above, the first two rows in each box are for the two inoculated columns, the last row is for the control columns. Complete results for As, Se, Sb, Cl and F are not yet available

3. Pyrite Removal from Coal with High Concentration Ferric Solutions

Experiments were done to determine the short-term rate of pyrite oxidation in Pittsburgh coal by a biogenic, high strength ferric solution. The data was used for process engineering calculations by subcontractor Unifield Engineering of the rate of pyrite oxidation and HAP precursor removal from coal. This is the same coal used in the slurry column reactor tests at INEEL.

Ten gram quantities of coal (-28/+100 mesh) were mixed with 30 ml of either high ferric solution or control (MKM salts pH 2) solution in a shake flask for 24 hours at 25°C. After each sampling sulfuric acid was added, if necessary, to bring the pH back to 2.0.

Chemical parameters of the high ferric solution: pH 1.91, ORP 849 mV, Fe²⁺ 31 mg/l (0.55 mM), total Fe 16608 mg/l (297 mM).

The starting ferrous iron in the solution (0.6 mM) and the control ferrous iron values (representing dissolution of pyrite by acid and oxygen) were subtracted from the high ferric solution ferrous iron values to give the ferrous iron produced from oxidation of pyrite. Complete oxidation of pyritic sulfur to sulfate by the ferric ions was assumed according to the following reaction:

Based on this stoichiometry, 15 ferrous ions are produced for every pyrite oxidized. Measurement of ferrous iron production for short term tests of rates of pyrite oxidation by ferric ions has been described in the literature.

The chemical parameters of the solutions at each sampling time are shown in Table 7.

Table 7. Time Course Oxidation of Pyrite in Pittsburgh Coal

time, hr	sample	pH	Eh (mV she)	Fe ²⁺ , mg/l	Fe ²⁺ , mM
0.33	control	3.27	584	125	2.2
	hi ferric	1.98	744	275	4.9
1.0	control	3.52	629	144	2.6
	hi ferric	2.01	728	432	7.7
3.5	control	2.97	622	157	2.8
	hi ferric	2.07	712	714	12.8
8.8	control	2.40	630	194	3.5
	hi ferric	2.12	700	1158	20.7
24.0	control	2.09	634	376	6.7
	hi ferric	2.01	682	2141	38.3

The rate of pyrite oxidation was calculated from the ferrous iron production data and is shown in Table 8.

Table 8. Rate of Pyrite Oxidation in Pittsburgh Coal by Ferric Ions

hours	net mmoles Fe ²⁺ produced	mmoles pyrite oxidized	mg pyritic S oxidized	% pyritic S oxidized	% per day
0.33	0.063	0.0042	0.27	0.18	13
1.0	0.135	0.0090	0.58	0.39	9.4
3.5	0.282	0.0188	1.20	0.80	5.5
8.8	0.498	0.0332	2.12	1.4	3.8
24	0.930	0.062	3.97	2.7	2.7

The rate of pyrite oxidation declined with reaction time (last column in table above). Despite the presence of over 10 g/l of ferric iron in solution, the redox potential of the leach solution after 24 hours had fallen to 682 mV. A fairly small ratio of ferrous iron to

total iron (0.1 to 0.2) was sufficient to significantly depress the redox potential and slow the rate of pyrite oxidation considerably.

The time course experiment was repeated with similar results. The partially biooxidized coal was recovered, washed, and reexposed to ferric ions. Again, the rate of pyrite oxidation was similar, indicating that leaching of any iron oxidation products that may have been present in the coal was not contributing significantly to the release of iron into solution.

The results show that the redox potential must be kept high in a process relying on circulation of ferric ion solutions to remove pyritic sulfur from coal. Normally, microbial activity in a well-aerated heap of coal would keep the redox potential high due to efficient conversion of ferrous to ferric iron by bacteria attached to coal and pyrite surfaces. However, significant heating of leach solutions will occur under these conditions, due to the exothermic reaction of pyrite oxidation. The heating phenomenon has been observed during studies of heap depyritization of Pittsburgh coal and commercial heap biooxidation of gold ores. Both coal and ore in these tests contained approximately 1.5 to 2% pyritic sulfur.

Thus, efficient heap biooxidation of coal may not be possible due to the risk of heating and combustion. The fastest rates of microbial coal depyritization and associated HAP precursor removal may only be achievable by cycling ferric ion rich solutions through the coal at a rate sufficient to maintain a high redox potential. The trade off in processing costs versus reaction rate will be how high to keep the redox potential. This will affect the residence time, coal to solution ratio, reactor sizes, and other factors.

4. Mercury Removal from Coal with Thermophilic Microorganisms

As this project has progressed, mercury has emerged as the HAP precursor element of most concern to DOE. Project results to date indicate that while pyrite oxidizing bacteria can expose or render mercury more available for extraction with HCl, they apparently do not solubilize the mercury.

Microorganisms that oxidize pyrite at higher temperatures were tested for their ability to dissolve mercury from Pittsburgh seam coal. These so called moderate (growth at 50°C) and extreme (growth at 65°C) iron and sulfur oxidizing thermophiles may stand a better chance of breaking mercury-sulfur bonds under the more vigorous conditions that these organisms grow.

Flasks containing 28 x 100 mesh Pittsburgh coal and MKM salts at pH 2.0 were inoculated with moderate or extreme thermophiles and were incubated on orbital shakers at 50°C and 130 r.p.m. or at 65°C and 115 r.p.m. The pH, redox potential, ferrous and total iron concentrations and sulfate concentrations were monitored 1-2 times weekly to follow the progress of pyrite biooxidation.

The organisms readily oxidized pyrite in the coal, causing redox potentials to increase to over 800 mV in the inoculated flasks. Redox potentials remained under 600 mV in the uninoculated flasks. The flasks were left to incubate for 39 days, well past the time where near complete pyrite dissolution was indicated by solution sulfate analysis.

Mercury was not detected in leach solutions from any of the flasks (<0.0002 mg/l). Analysis of the coal residues following biooxidation indicated little mercury removal from the coal (Table 9). However, it was noted that a clay-like layer remained above a darker coal layer when the contents of flasks that contained moderately thermophilic microorganisms were allowed to settle. This clay layer contained three times the mercury concentration of the coal. The clay layer formed in the control flask was less distinct and contained no more mercury than the coal. The flasks incubated at 65°C showed no evidence of a distinct clay layer upon settling.

Table 9. Mercury in Coal and Clay Layers Following Treatment with Thermophilic Microorganisms

flask	residue	Hg, ug/g	total ug	mass balance, %
raw coal		0.106	5.30	--
65°C-cells	coal	0.103	5.11	96
65°C-control	coal	0.094	5.06	95
50°C-cells	clay layer	0.287	0.89	91
	coal layer	0.087	3.91	
50°C-control	clay layer	0.103	0.28	85
	coal layer	0.094	4.24	

The moderately thermophilic microorganisms may have achieved some mineral matter liberation resulting in mercury concentration in the ash. It is also possible that these organisms liberated mercury from coal that was readsorbed preferentially to the ash.

Tests were begun to examine leaching of mercury from coal by ferric ions at elevated temperature, the adsorption of mercuric ions to coal and clay material, and the ability of thermophilic microorganisms to mobilize mercury from HgS in the absence of coal and clay. Results will be reported in the next quarterly report.

5. INEEL Slurry Column Test Work (Task 4)

Removal of HAP precursors from Pittsburgh No. 8 coal is being tested in the INEEL slurry column reactor. This reactor employs both physical and microbial removal of pyritic sulfur from coal. Eighteen batches have been completed to date. All batches were conducted at a 35% w/w slurry. The first run allowed pyrite oxidizing bacteria to adapt to the coal, while the next five runs were done to check operating and sampling procedures. Beginning with run 7, solid and liquid samples were removed to determine the effectiveness of the slurry column reactor in removing HAP precursors from the coal. The distribution of HAP precursors among process solids and solutions is being determined at Little Bear Labs. Solid samples taken from each batch were feed coal, waste coal, product coal and wastewater solids after neutralization with lime. Liquid samples were wastewater liquid after neutralization with lime and fresh dechlorinated tap water. Other samples were analyzed for HAP precursors were lime for neutralizing wastewater, sulfuric acid for adjusting the pH in the reactors, and nitric acid for adjusting the pH of the wash water. In this manner, mass balances for operation of the slurry column reactor can be calculated. In addition to HAP precursors, solid samples are being analyzed for forms of sulfur and a short proximate analysis is being done also.

Three main process variables are being investigated: slurry concentration, coal retention time, and amount of wash water. Slurry concentration and coal retention time go hand in hand; the larger the slurry concentration and the lower the retention time, the smaller the reactor. The initial conditions of 35% w/w slurry and 5 day retention time were chosen based on past experience. At these conditions, 90% pyritic sulfur reduction with 90% BTU recovery was obtained in a slurry trough reactor. The volume of wastewater controls the hydraulic residence time. If the volume is small compared to the water needed to make 34 liters of 35% w/w slurry, then the hydraulic residence time is long compared to the coal residence time. Also, wash water consumption and wastewater volumes are small, few bacteria are lost from the process in the wastewater, but metals leaching from the coal may accumulate to inhibitory levels in the liquid. Retention time will be decreased in subsequent runs while varying the amount of wastewater.

Good physical separation of ash forming minerals from coal has occurred (Table 10). When fresh coal is added to the clean coal reactor (CCR), the Eh is approximately 475 to 500 mV and then increases to 550 to 600 mV at the end of the 5 day retention time. When the high pyritic coal drainings from the CCR are placed in the rougher/propagator (R/P), Eh has the same trend except that the Eh starts at 575 to 600 mV and increases to 610 to 650 mV. The increase in Eh is an indicator of the rate and extent of the pyrite being oxidized to ferric iron and sulfates. Total iron and sulfates have the same trend as Eh, a lower value when feed coal is added and increases over the retention time.

Analyses of HAP precursors were only partially complete at the end of the quarter. Results showed significantly lower Hg, As, Co, Se Mn, Pb and Ni in the product coal compared to the feed coal. Among the HAP precursors of most concern, over half the mercury and arsenic and about one third of the selenium was removed from the feed coal. Complete results will be presented in the next quarter report.

Table 10. Coal-Ash Separations in Runs of Slurry Column Reactor at INEEL

Run #	Days	% Solids	Waste water (liters)	% Ash in product coal	% Ash in waste coal
1	41	35	10	12.2	43.8
2	19	35	10	11.6	46.1
3	10	35	10	12.9	25.4
4	17	35	10	15.7	53.0
5	11	35	10	9.9	35.7
6	8	35	10	9.9	34.0
7	5	35	10	11.4	35.5
8	5	35	10	10.0	40.2
9	5	35	10	11.8	46.9
10	5	35	10	10.3	45.4
11	5	35	10	11.1	47.5
12	5	35	10	10.9	43.7
13	5	35	10	11.6	38.5
14	5	35	10	10.6	48.2
15	4	35	6	10.6	41.3
16	5	35	5		
17	5	35	5		
18	5	35	5		

6. Process Design (Unifield Engineering)

A process design for the phase 2 pilot plant has been completed through the conceptual stage. The pilot plant will be operated to analyze the removal of 13 HAP precursors and sulfur from coal. The pilot process will provide the contact of the coal with a high ferric concentration leach solution, oxidizing the pyrite in the coal and solubilizing the HAP precursors. Regeneration of the leach solution will be accomplished by biologically oxidizing ferrous iron to ferric iron. The pilot process will be located in an enclosed building.

The scope of the phase 2 pilot has been expanded without impacting the overall cost of the pilot system. During the design process, the choice of whether to propose a continuous vat reactor-based process or a heap-column reactor based process must be established on the most attractive full scale process economics. The assumptions

used for the kinetics of each pilot reactor design were derived from limited laboratory data. The basic economic data required to determine the most successful type of full scale process is questionable without pilot data. Therefore, the design of the phase 2 pilot plant now incorporates both types of columns. This is accomplished by providing two distinct types of columns in the pilot for testing, with common ancillary equipment for the balance of the process. The two types of columns that will be incorporated in the phase 2 proposal are as follows:

1. Heap/leach columns - for simulation of heap leaching
2. Flood/drain columns - for simulation of continuous vat leaching

The following provides the status of key work items leading to the phase 2 proposal:

Pilot conceptual design basis	complete
Pilot conceptual design - flow sheets and mass balance	complete
Pilot process narrative	complete
Pilot cost estimate	in progress
Equipment specifications for major items	complete
Vendor bids for equipment fabrication	in progress
Pilot general arrangement drawing	in progress
Economic analysis of process	in progress
EHSS proposal preparation	in progress
Pilot design scale-up methodology	not started
Phase 2 technical proposal preparation	not started

Phase 2 Pilot Conceptual Design

A. Rotating Biological Contactor Design

Letter specifications were submitted to vendors for fabrication of the pilot scale rotating biological contactor (RBC) used to biologically generate the high ferric solution required by the leach reactor. The vendors of RBC equipment have declined to bid on a pilot scale unit due to the low pH of the working fluid. Manufacturers of screw conveyors were then contacted to respond to design and build a four compartment unit with 26 each 1 meter diameter disks, based on our design concept. The vendors are in the process of evaluating cost and schedule for the pilot unit.

B. Competing Designs for the Leach Reactor

Two competing design reactor flow sheets were completed. The InnoVat™, which is a continuous vat reactor, may be ideal for HAP precursor removal as it provides a continuous process and will allow superior contact of lixiviant with a 1/2" top size coal. A column reactor, simulating a heap leach process, is the low cost candidate for HAP precursor removal, but rates may be too slow to be economically viable. Both the continuous vat reactor and column reactor designs were based upon leaching a 1000

kg batch of 3% sulfur Pittsburgh seam coal using a biooxidatively generated ferric solution to remove 50% of the 1.5% pyritic sulfur from the coal. Both designs utilize a high concentration ferric solution (redox potential of 850 mV) at the input of the leach column, while maintaining a high concentration ferric solution (redox potential > 710 mV) at the exit of the column. During the design process it was determined that piloting of both systems could be accomplished with essentially the same equipment.

Phase 2 pilot tests would be batch wise, and would test the following parameters to address the comparison between the two types of leach processes. The ultimate use of the data is to provide scale-up economics for the next step in process maturity:

1. Mass transfer of lixiviant to solids
2. The importance of the high ferric leach solution compared with oxygenated heaps
3. The effect of particle size on processing rate and dustiness of product
4. The effect of column height on processing rate
5. The effect of leachate redox potential on processing rate
6. The effect of ferric ion concentration on processing rate

7. Reporting (Task 5)

INEEL hosted a meeting with Howard Feibus of DOE Headquarters to review biotechnology-related projects. Representatives of Little Bear Labs and Unifield Engineering along with Karl Noah of INEEL presented a review of this project on biochemical removal of HAP precursors from coal.

Conclusions

Significant arsenic, cadmium, cobalt, manganese, selenium and nickel can be removed from Kentucky coal. Pyrite removal from Kentucky coal in columns is slower than with Pittsburgh and Indiana coals.

Maintenance of high redox potentials is key in solution ferric ion based removal of pyrite and HAP precursors from coal. Two processes could be designed for such applications. Efficient heap biooxidation of pyrite in coal may be difficult due to heat generation.

Thermophilic microorganisms do not appear to remove mercury from coal. However, these organisms may be able to mobilize some mercury through a physical or chemical process.

Preliminary data shows that the INEEL slurry column reactor removes significant mercury, arsenic, and other HAP precursors from coal.