

DEPARTMENT OF ENERGY SUPPORT FOR  
USGS TOXIC SUBSTANCES FROM COAL COMBUSTION-  
FORMS OF OCCURRENCE ANALYSIS

Semiannual Report

Submitted to the U.S. Department of Energy

By

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Phase II

For the period ending  
September 30, 1999

## **Introduction**

Detailed information on trace-element modes of occurrence in coal is essential to understanding and predicting trace-element transformations taking place during coal combustion. The USGS has developed quantitative and semi-quantitative methods for determining the mode of occurrence of trace elements in coal. This information is needed to generate predictive models for trace-element behavior, the ultimate goal of DOE contract DE-AC22-95PC95101 "Toxic Substances From Coal Combustion- A Comprehensive Assessment" awarded to PSI, Inc. USGS activities in support of this contract have a direct bearing on the predictive equations being developed by PSI as the primary product of this program.

## **USGS Procedures**

The USGS procedure is intended to determine quantitatively or semi-quantitatively the mode of occurrence of trace elements in coal. This is accomplished by an iterative selective leaching protocol, used in combination with a range of complementary techniques. In the leaching protocol, the amount of each element removed by 4 different reagents is compared to the concentration of that element in the whole coal to obtain the fraction of an element residing in a given coal component. The sequence of leaching steps, and the intended results, are as follows: 1) exchangeable cations, and a fraction of the carbonate-hosted cations are removed by ammonium acetate; 2) cations primarily associated with carbonates and monosulfides such as galena, sphalerite and chalcopyrite are removed by hydrochloric acid; 3) silicate-associated cations are removed by hydrofluoric acid; and 4) elements associated with disulfides (pyrite and marcasite) are removed by nitric acid. Elements not leached by any of the four reagents may be present in the organic portions of the coal, or in insoluble phases such as zircon or titanium dioxides. Additionally, where mineral grains are completely encased by the organic matrix, these "shielded" grains may not be completely digested. As an internal check, leaching results are obtained for both the solid residues (by INAA) and leachates (by ICP-MS and ICP-AES). Element-specific methods are used for selenium (hydride generation) and mercury (see section on mercury). Quantitative results are obtained by interpreting the leaching data together with the results obtained by complementary techniques such as electron microprobe analysis. The microprobe is especially useful for pyrite grains, as many of the elements of interest are present at concentration levels above the detection limit of about 100 ppm. Other essential components of the USGS procedure include semi-quantitative determination of mineralogy by X-ray diffraction (XRD) analysis of low temperature ash (LTA), and confirmation of mineralogy for operator-selected grains using a scanning electron microscope (SEM) equipped with an energy-dispersive X-ray analyser (EDX).

The USGS approach complements results obtained by X-ray absorption fine structure (XAFS) by our colleagues at the University of Kentucky. The USGS technique also provides data for elements such as Se and Hg, whose concentrations are commonly too low to obtain XAFS spectra, and for elements with atomic numbers beyond the routine XAFS atomic number range of about 20 to 42 (Ca to Mo). For elements that are common to the two approaches, such as As and Cr, comparison of results obtained by the USGS and by XAFS provides an important confirmation of our results.

## Phase II Work Scheduled and Accomplishments

### *Analysis of Whole Coals*

Whole-coal elemental analysis is an important part of characterizing the project samples, in addition to providing the basis for determining fractions removed by selective leaching. The USGS uses a combined approach that includes the optimal results of ICP-MS, ICP-AES, and INAA multi-element methods, and element-specific methods for Se and Hg. A complete data set for each of the Phase II coals has been returned from our labs in Denver and these data are included in Table 1. These data are a composite of best values to date, and will change only if additional replicates are run. Discussion of the data by element, in the context of the leaching data, will be given in subsequent reports.

A brief examination of the whole coal results shows that relative to the two low rank coals, the Ohio sample has higher concentrations of Fe (14,700 ppm), As (17.8 ppm), Se (1.78 ppm), and Hg (0.18 ppm), elements normally associated with pyrite. These results are consistent with the high pyrite content (2.7%, calculated from pyritic-S) of the Ohio coal relative to the other samples (North Dakota = 0.53%; Wyodak = 0.09%). The Hg content of the Ohio coal (0.18 ppm, determined by CVAA), is about average for over 7,000 U.S. coals in the USGS COALQUAL database [1]. Hg contents of the Wyodak (0.13 ppm) and North Dakota (0.08) samples are lower, but this distinction is lessened or reversed for low rank coals if they are considered on an equal-energy basis [2].

### *Leaching Studies*

Laboratory leaching procedures are conducted in duplicate in the coal chemistry lab at the USGS National Center in Reston. Leachates and solid residues are then sent to the Energy Program analytical labs in Denver for analysis. To date, the complete leaching procedure has been done (in duplicate) 3 times for the Ohio and North Dakota samples, and 2 times for the Wyodak sample. Repetition of the procedure was necessitated by problems with the nitric acid leaching step, resulting in incomplete digestion of pyrite, as outlined in figure 1. In the first repeat (Ohio and North Dakota only), this incomplete pyrite digestion was attributed to an error in the normality of the acid. After repeating the procedure with acid having the correct normality, we found that pyrite had still not been completely digested. As a result, a new procedure, modified from ASTM procedure D2492, section 7.3.1 for determination of pyritic sulfur, was developed. The main difference is in the shape of the digestion vessel- the old procedure used a disposable centrifuge tube, whereas in the new procedure, a standard laboratory flask is used (appendix 1). This "flask method" was used in the nitric acid step for a second repeat leaching of the Ohio and North Dakota samples, and a repeat leaching of the Wyodak coal. To further test the new method, solid residues from the incomplete HNO<sub>3</sub> leaching steps in the tube were re-leached using the flask method (fig. 1). Results for this re-leaching step confirm that 95-100% of the iron has been recovered for each of the 3 coals (see below). The first 3 steps of the procedure were unaffected by the problem with pyrite digestion in the last step. Therefore once all analyses are returned, we have 6 replicates for each of the first 3 steps of the procedure for the Ohio and North Dakota coals, and 4 replicates for the Wyodak coal for these steps of the procedure.

To date, analytical results have been returned for all but the last complete round of the 4-step leaching procedure. Preliminary results are shown in figure 2, consisting of complete analysis of leachates and

solid residues for Ohio 1,2,3,4, North Dakota 1,2,3,4 and Wyodak 1,2 for the first 3 leaching steps, and INAA analysis only for the solid residues of the HNO<sub>3</sub> re-leaching step (Fig 1). Note that these results lack leachate data for the re-leaching step, and all results from the final duplicate leachings, and therefore are subject to change in the final analysis.

For the Ohio 5/6/7 coal it is clear from the preliminary leaching data that iron and arsenic are strongly associated with pyrite, as in many bituminous coals, consistent with microprobe data for pyrite given in the last semi-annual report (Fig. 2). A much smaller pyrite association is indicated for Fe and As in the two low rank coals. These coals show a large HCl-leachable fraction we have previously interpreted as arsenate. For Cr, a significant HF-leachable fraction is shown for each of the coals, consistent with ion probe data for Cr in illite, reported in the section on microanalysis. However, each of the coals has significant (30-65%) unleached Cr, indicating an organic association for this fraction. For the other elements reported- potassium shows a strong silicate association- as it is a major component of illite/smectite. Sodium shows a significant ion-exchangeable component, especially in the low rank coals. Cobalt, uranium and scandium show mixed affinities that are dominated by organic, silicate, or HCl-leachable forms.

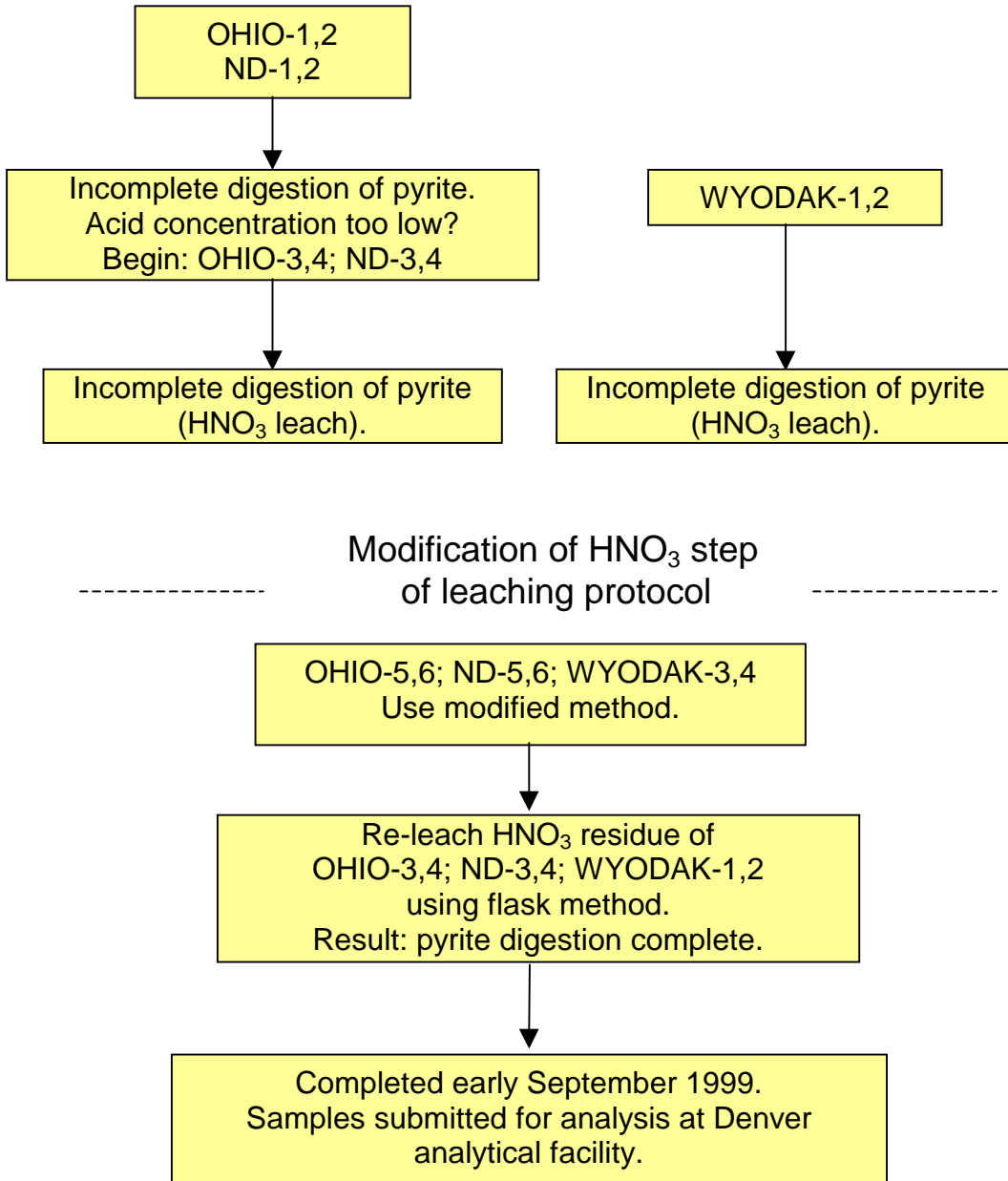
### *Mercury analysis*

In the last semiannual report, we reported on development work for an alternate method of Hg analysis vs. the Cold Vapor Atomic Absorption (CVAA) method used in Phase 1 of this program. Tests of the new method, cold vapor atomic fluorescence (CVAF) indicated that the minimum detection limit by this method was limited by a total analytical blank level in the 0.01 to 0.02 ppm (10-20 ppb) range, similar to the detection limit for CVAA. Although the CVAF blank-level problem is potentially resolvable, our analysts in Denver have halted development of this procedure in favor of a new direct analyzer for Hg that the USGS is in the process of acquiring. The new analyzer is compliant with EPA method 7473 and offers the following advantages: 1) sample digestion is unnecessary, thereby eliminating reagent blank-level problems; 2) sensitivity is similar to or better than levels we were hoping to achieve with CVAF; and 3) the new analyzer has a standard auto-sampler, allowing analysis of multiple samples in an automated mode. The new method will not be available until January, 2000 or some time thereafter. The old method (CVAA) will be used in the interim, or in cases where its detection limit is sufficient.

### *Microanalysis*

Since early June, emphasis has been placed on microanalysis of clay minerals in project coals in preparation for use of the Stanford/USGS SHRIMP RG Ion Microprobe during August, 1999. During the week of August 23, Allan Kolker traveled to Stanford University to conduct these analyses. The 2.6M instrument is the only SHRIMP facility in the U.S. with reversed geometry (RG). This instrument has the advantages of high sensitivity, and very high mass resolution, compared to smaller ion probes and the forward geometry (FG) SHRIMP. The purpose of Allan's visit was to evaluate the usefulness of the SHRIMP for project purposes, specifically to generate data on the contents of Cr and other metals of interest (Co, Ni, Mn, Cu, Zn, Ti, V, etc.) in clays (illite/smectites) in project coals. Preliminary results for Cr in the three Phase II coals and the Illinois #6 coal from Phase I are given in Figure 3. The SHRIMP-RG data confirm that Cr is present at concentrations of about 20 to 120 ppm, just below the electron

Figure 1: Leaching Study Timeline



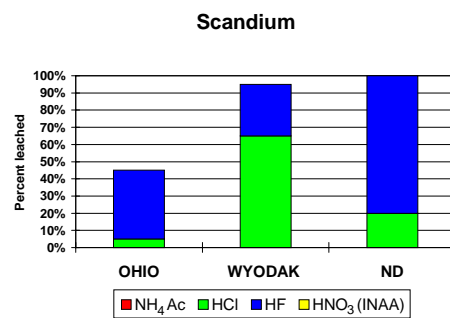
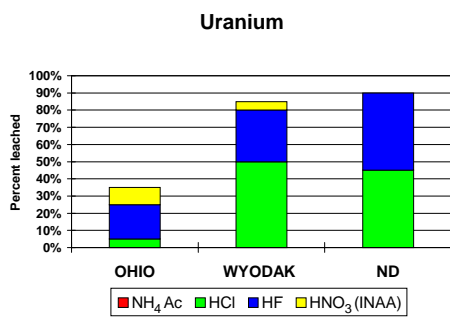
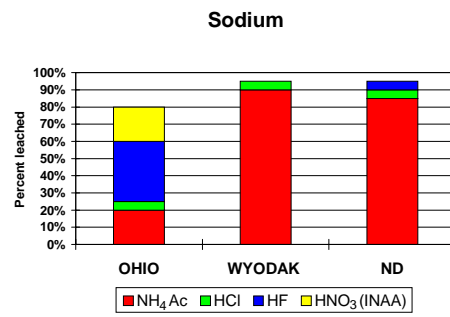
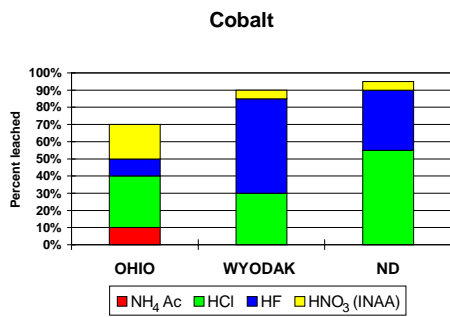
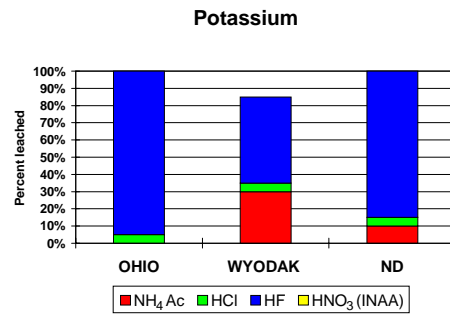
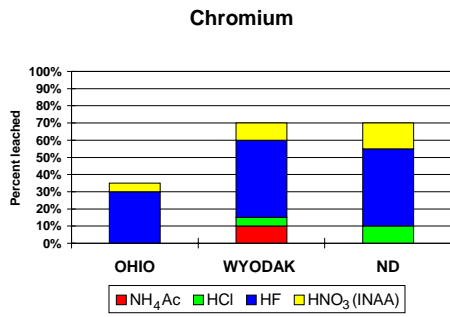
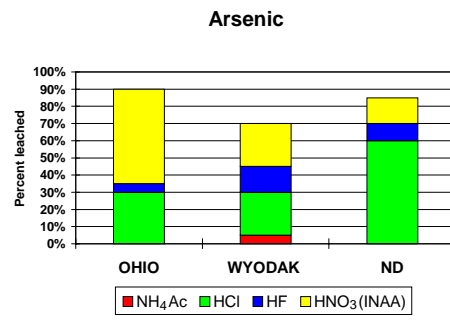
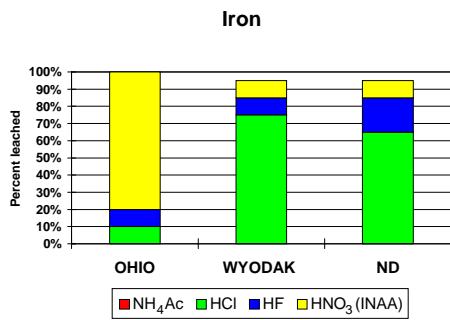
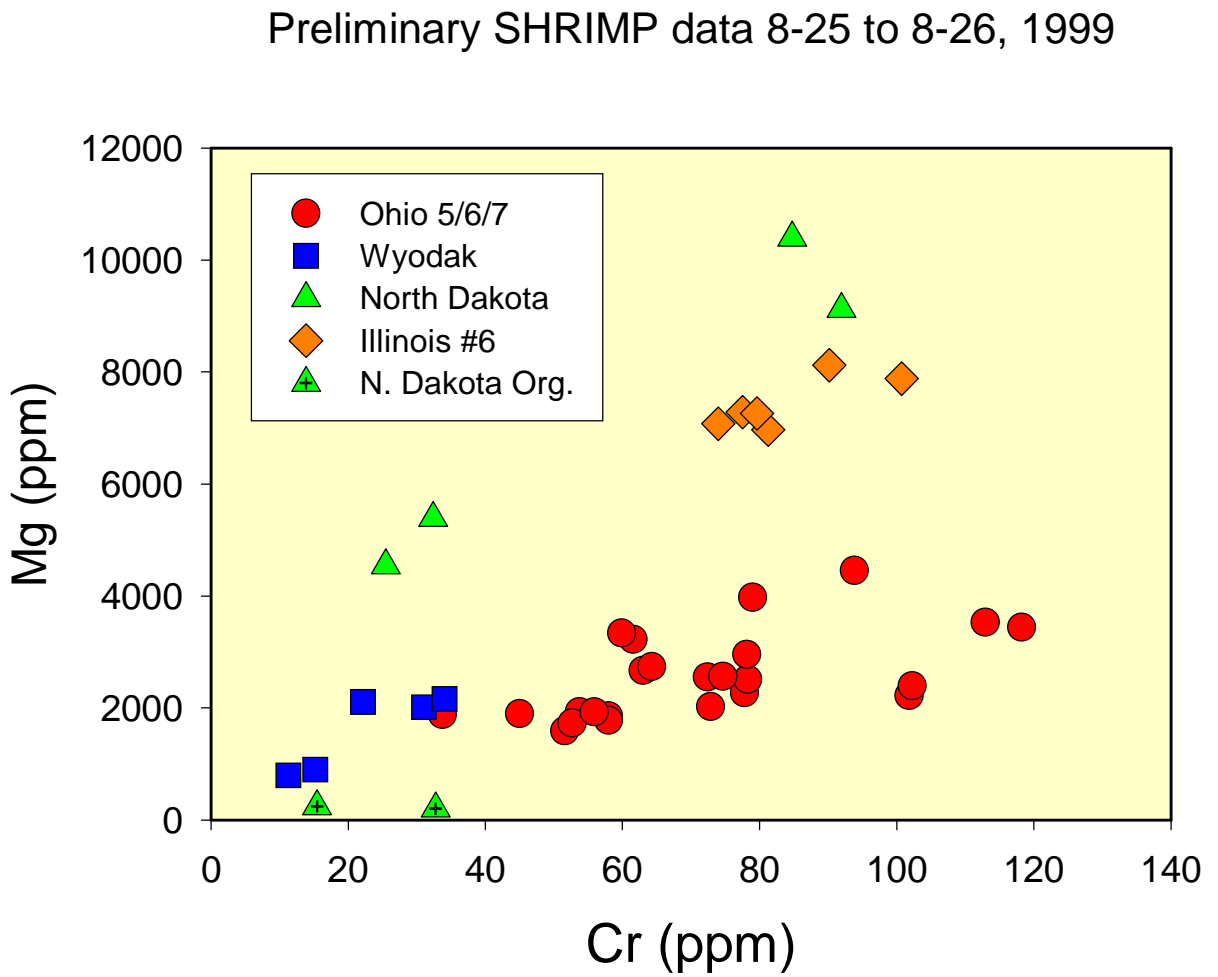


Figure 2: Preliminary Leaching Data

Figure 3. Preliminary SHRIMP-RG results for Cr in illite/smectite and organics (North Dakota only).



### *Microanalysis- continued*

microprobe detection limits (100-200 ppm), as suspected from Phase I microprobe work and previous studies of clay mineral separates [3]. Final SHRIMP-RG numbers for the illites will be given in a subsequent report, as we are still in the process of refining the data. Reconnaissance analysis of organic parts of the North Dakota sample show measurable Cr, as also indicated by preliminary XAFS work [4].

In preparation for use of the SHRIMP-RG suitable coarse (> 60 mesh) material was separated from project coals, and duplicate splits were made for preparation of polished grain mounts. One set of samples was sent to Stanford for preliminary tests of ionization of Cr in the illites. The other set of grains was retained for analysis and chemical mapping using the electron microprobe. These analyses were conducted in Reston prior to use of the SHRIMP-RG. Electron microprobe elemental maps and major element data were used as a guide for locating illite/smectite grains to analyze with the SHRIMP-RG. Additionally, because the SHRIMP-RG gives major, minor, and trace-element results simultaneously, these results were used together with corresponding electron microprobe data to minimize grain-overlap problems with adjacent minerals, typically quartz, pyrite, kaolinite, and calcite.

Analysis of the illite/smectites made use of the  $O^-$  ion source currently available at the SHRIMP-RG. Subsequent work on trace-metals in sulfides, and arsenic in fly ash, will likely utilize a new  $Cs^+$  ion source, currently being tested. The  $Cs^+$  ions are more energetic and are needed to ionize heavier elements such as Hg. Preliminary analysis of arsenic in doped-glass standards using the  $O^-$  ion source suggests that the  $^{75}As$  peak is resolvable from organic interferences at the same mass, something we have been unable to do in reconnaissance studies using smaller ion probes. The  $Cs^+$  ion source will be needed to obtain a sufficient count rate for As and Hg analysis.

### *SEM/LTA/XRD and other supporting procedures*

Low temperature ashing of the 3 project coal samples is complete, followed re-ashing of the North Dakota sample after leaching with ammonium acetate to remove the carboxyl-bound cations that may neutralize the oxygen plasma, and to prevent fixation of the organic sulfur as sulfate. These problems were outlined in the last semiannual report, and have now been overcome. X-ray diffraction studies of the 3 project coals are underway. These results will provide semi-quantitative estimates of the modal proportions of minerals present in the coal, to be used in conjunction with the SEM data.

A large number of pellets have been prepared for routine SEM examination of residues after leaching, to insure that mineral matter, especially pyrite, is completely digested. Polished mounts of these residues are currently being examined.

To help integrate the leaching and XAFS portions of this project, XAFS splits have been taken for analysis from each of the leaching steps conducted, including rounds that were repeated due to problems outlined in the section on leaching results. During the recent Program review meeting, we met with Dr.'s Huggins and Huffman to discuss their plans for upcoming analyses, and to prioritize the samples. We expect to provide the highest priority samples for their upcoming XAFS work at the end of October, 1999.



## Summary

Leaching procedures have been completed for the three Phase 2 coals. Chemical analyses have been returned for the whole coals, allowing leaching results to be determined as data on the leachates and solid residues become available. Problems with the nitric acid leaching step twice necessitated repeating the entire procedure for the Ohio and North Dakota samples. Similarly, leaching of the Wyodak sample was repeated once. Analytical results have been returned for all but the last complete round of leaching, which was conducted after modification of the procedure for the nitric acid step. Re-leaching of solid residues prepared under the old procedure confirms that pyrite recovery using the new method is complete. Development of an improved analytical method for Hg continues, but emphasis has shifted from the atomic fluorescence method to an automated direct analysis method that offers similar or better sensitivity. The cold vapor atomic absorption (CVAA) method has been used in the interim for whole coals.

During the reporting period Dr. Kolker traveled to Stanford University to evaluate the Stanford/USGS SHRIMP-RG ion microprobe for project purposes and generate trace-element results for illite/smectite in project coals. Initial SHRIMP results for Cr in these samples confirm the Phase 1 conclusion that its concentration in clays is just below the detection limit (~100-200 ppm) for electron microprobe analysis. The SHRIMP-RG offers promise for other project priorities, including determination of Hg in sulfides and of As in fly-ash. Use of the SEM and electron microprobe continued during the last half-year, and has been especially useful in support of the ion probe effort.

Among other procedures conducted, low temperature ashing has been completed and XRD determinations are underway. Splits of leached residues have been taken for XAFS analysis. We expect the first of these to be determined shortly by our Univ. of Kentucky colleagues. These results will be very useful in integrating the leaching and XAFS results and in resolving possible discrepancies.

## References

- [1] Bragg, L. J., Oman, J. K., Tewalt, S. J., Oman, C. L., Rega, N. H., Washington, P. M., and Finkelman, R. B., 1998, U.S. Geological Survey Coal Quality (COALQUAL) Database, V. 2.0, U.S. Geological Survey Open File Report 97-134, CD-ROM.
- [2] Toole-O'Neil, B., Tewalt, S. J., Finkelman, R. B., and Akers, D. J., 1999, Mercury concentration in coal-unraveling the puzzle: *Fuel*, v. 78, p. 47-54.
- [3] Palmer, C. A., and Lyons, P. C., 1996, Selected elements in major minerals from bituminous coal as determined by INAA: Implications for removing environmentally sensitive elements from coal: *International Journal of Coal Geology*, v. 32, p. 151-166.
- [4] Frank Huggins, personal communication, DOE Contract DE-AC22-95PC95101, Phase II, Program Review Meeting, Pittsburgh, 9-30-99

Table 1: PSI PRDA PHASE II - Elemental Concentrations for Whole Coals.  
 Values are in ppm on a dry basis.

Element	OHIO	WYODAK	ND
Li	11	3.7	5.1
Be	2.6	0.3	0.8
B	86	42	130
Na	280	860	3800
Mg	340	1900	4000
Al	9100	7400	9000
Si	19000	13000	25000
P	270	570	170
K	1600	190	1700
Ca	1100	11000	15000
Sc	3.8	1.9	1.9
Ti	580	670	410
V	25	18	15
Cr	15.3	7.9	11.5
Mn	20	8.2	59
Fe	14700	3030	7870
Co	4.91	5.66	9.1
Ni	18	4.8	4.3
Cu	9.6	14	5.5
Zn	21	8.2	12
Ga	6.0	2.5	2.3
Ge	9.8	0.37	1.3
As	17.8	1.74	10
Se	1.78	1.31	0.97
Br	18.7	1.1	2.58
Rb	11.3	2.1	7.2
Sr	100	260	420
Y	9.7	3.5	4.8
Zr	14	18	26
Nb	3.0	2.8	3.1
Mo	4.9	1.1	2.3
Ag	<0.2	<0.2	<0.3
Cd	0.1	0.1	<0.1
Sn	1.0	<0.9	<1.5
Sb	1.94	0.23	0.70
Te	<0.2	<0.2	<0.3
Cs	0.75	0.136	0.58
Ba	66	450	590
La	9.82	5.60	4.96
Ce	18.4	9.3	7.8
Sm	2.17	0.96	0.75
Eu	0.427	0.193	0.149
Tb	0.319	0.11	0.111
Yb	0.98	0.42	0.49
Lu	0.137	0.049	0.070
Hf	0.61	0.59	0.61
Ta	0.20	0.159	0.137
W	1.1	0.48	2.99
Au	<1.0	<0.9	<1.5
Hg	0.18	0.13	0.08
Tl	1.3	<0.2	<0.3
Pb	9.1	1.9	1.5
Bi	<0.2	<0.2	<0.3
Th	2.14	1.85	1.67
U	1.25	0.73	1.12

## Appendix 1: Text of MEMO from Stan Mroczkowski on modifications to leaching protocol

### Memorandum

To: Mode of occurrence leaching-protocol interest group  
From: Stan Mroczkowski  
Subject: Modification of HNO<sub>3</sub> leaching step  
Date: June 1, 1999

In the past we have had difficulty removing all of the pyrite from some of the samples we have studied. Samples we had difficulty with included the Elkhorn/Hazard coal from the PSI PRDA Phase I, and two Pittsburgh cleaned coals from the CQ CRADA. More recently, this problem has re-occurred during leaching of the North Dakota lignite and Ohio coal samples from the PSI PRDA Phase II and the Canadian coal from the IEA Round Robin. These last three samples were leached in quadruplicate. The extent of pyrite dissolution varied widely within each sample set regardless of rank or pyrite content.

Recently conducted experiments have revealed the cause of the problem. Samples are normally placed in 50ml centrifuge tubes on a wrist shaker for 18 hours. Experiments were performed on duplicate raw splits of the above six coals in which the samples were placed in 125ml Erlenmeyer flasks with 40ml of 2N HNO<sub>3</sub>. Samples were stirred briefly with Teflon stir-bars to ensure complete wetting and then allowed to sit overnight. This procedure is based on the method for pyritic sulfur determination from ASTM D2492. (The goal in D2492 is to dissolve all of the pyrite, analyze the leachate for Fe, and then calculate the amount of pyritic sulfur based on a stoichiometric ratio with Fe.) Based on Fe determination by flame-AAS, it appears that this procedure successfully removed all of the pyrite from each sample.

The reaction of pyrite with 2N HNO<sub>3</sub> is relatively slow. In addition, when we arrive at the HNO<sub>3</sub> step of the leaching protocol, the sample basically contains only organic-matter and pyrite. This extreme density gradient combined with slow reaction kinetics probably allows the pyrite to settle to the bottom of the centrifuge tubes while it is on the wrist shaker. The problem is compounded by the fact that the centrifuge tubes are pointed at the bottom. Thus, even though the sample is being agitated, the pyrite grains are so dense they probably remain on the bottom of the tube, and therefore may not be sufficiently exposed to the solvent, especially if some of the coal particles cover the pyrite at the bottom of the tube. The flasks, on the other hand, have a very large surface area for the pyrite grains to spread out on, making it much easier for them to contact the solvent.

As an interesting side note, to test this "surface area" theory a separate set of experiments were run. Duplicate raw splits of the same six samples were placed into centrifuge tubes with HNO<sub>3</sub> just as before, but instead of placing them on the wrist shaker, they were briefly shaken by hand, and then laid flat on the bench top and allowed to sit overnight. (This effectively distributed the sample along the side of the tube.) All of the pyrite was removed from these samples as well.

Therefore, in light of these data, all future leaching experiments will follow the procedure modified from ASTM D2492, utilizing the Erlenmeyer flasks for the HNO<sub>3</sub> step. The rest of the procedure will remain the same.