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Technical Report

# Progress report Trace elements in coal--Modes of Occurrence Analysis DE-AI22-95PC95156

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The following report is preliminary and represents data collected until March 31, 1996. This report will include a description of the methods used as well as suggested modifications to improve the methods. In addition, some preliminary data will also be presented.

## Introduction

Originally, coal cleaning technologies were used only to remove ash-forming mineral matter. After passage of the 1970 Clean Air Act, coal cleaning processes were applied to a second purpose--sulfur reduction--accomplished primarily by removing the sulfur-bearing mineral pyrite. A great deal of geochemical information concerning the modes of occurrence of pyrite in coal was gathered and used to develop new methods of sulfur removal and to enhance existing methods. Today, coal cleaning plays a larger role in controlling $SO_2$ emissions than all post combustion-control systems combined.

The 1990 Amendments to the Clean Air Act name 189 substances as hazardous air pollutants (HAP's) including 14 elements or their compounds found in coal in trace concentrations. All of these elements can be reduced by physical, chemical, or possibly biological coal cleaning methods. The approach of combining mineral processing and geochemical expertise to control emissions of these elements is even more important now than in 1970 because control of a large number of elements, rather than just sulfur, is required.

CQ Inc. proposed to quantify the relationship between the modes of occurrence of twelve trace HAP's elements in coal and the degree that each element can be removed by existing and advanced physical and chemical coal cleaning processes. They also proposed to investigate new chemical and biological trace element removal processes, and estimate the concentration and stability of trace elements in coal preparation plant tailings. The ultimate goal of this effort is to produce a software tool that will predict the most amenable integration of processes for select trace element emissions control.

In support of this effort, the USGS is performing trace element modes of occurrence analyses on coal samples provided by CQ, Inc. The objective of this work to determine the modes of occurrence of as many as twelve trace HAP's elements in coal. The HAP's elements can occur in coal in numerous forms. For example, antimony is generally thought to be present in pyrite, accessory sulfides such as stibnite, and possible organically bound; arsenic is primarily associated with late-stage (epigenetic) pyrite; cadmium with sphalerite; chromium may be organically bound, associated with clays, or contained in chromium-bearing mineral; mercury is thought to occur predominately in epigenetic pyrite; and selenium may be organically bound or associated with pyrite or accessory minerals such as clausthalite and galena.

## Phase I

Four coals (Northern Appalachian, Southern Appalachian, Eastern Interior, and Powder River) are being analyzed for trace element modes of occurrence. The analytical procedure, as described below, will be performed for each raw coal sample and natural fines (-100 mesh) sample. Additional samples representing anomalies or investigation of maceral separations shall be analyzed as required.

All of the samples are being treated by a selective leaching procedure, a powerful methodology for approximating modes of occurrence using different combinations of solvents at different temperatures and concentrations. Splits of the coal will be leached with mineral solvents (ammonium acetate, hydrochloric acid, hydrofluoric acid, nitric acid) according to the methods developed at the USGS. Results from these leaching tests will provide essential information on chemical bonding of the elements.

Experiments also will be conducted to determine volatility of the elements by heating the coal samples to temperatures ranging form less than 200°C to more than 1,000°C. A split of each coal sample will be ashed using a low temperature ashing device. In this procedure the coal is oxidized at temperature of less than 200°C, resulting in a residue of unaltered minerals. This low temperature ash residue will then be chemically analyzed to determine the volatility of the elements at low temperature. This information, in conjunction with other tests, provides insight into the elements chemical bonding. The low temperature ash will then be used for semiquantitative mineralogical determination by X-ray diffraction.

These procedures provide indirect evidence, or approximations of the modes occurrence of the trace elements in coal. They will be complimented by direct procedures such as scanning electron microscopy (SEM)-energy dispesive analysis (EDX) of polished blocks of coal. This procedure provides information on the chemistry of organic matrix and minerals as small as 1µm and textural relationships of the various phases, Interpretation of the textural relations is crucial for this project because it is the textural relation of the mineral that dictates its behavior during coal cleaning. The mineralogical, geological, and geochemical expertise of the USGS will provide unique and critical insights.

For a more sensitive and quantitative analysis an electron microprobe analyzer is being used. Other, non-routine methods, such as analytical transmission electron microscopy and infrared spectroscopy, will be used as necessary.

Raw coal trace element contents will be obtained by region from USGS COALQUAL database. Clean coal trace element contents will be calculated from a modified version of this database.

### Phase II (if approved)

Phase II will provide more detailed data on heating experiments as well as using size and density procedures to provide a more detailed description of the mode of occurrence of the twelve trace HAP's elements. Leaching procedures will be scaled up to provide a larger sample which will allow for more detailed chemical analysis. Details of the phase two work will be determined using the results from Phase I

## Experimental

This report will only describe experimental procedures for which work have been started prior to March 31, 1996. Other procedures will be described in future reports.

### Selective leaching

The sequential selective leaching procedure used in this study is similar to one described by Palmer et al. (1993) which was modified from Finkelman et al. (1990). Duplicate 5g samples were sequentially leached with 35 ml each of 1N ammonium acetate ($CH_3COONH_3$), 3N hydrochloric acid (HCl), concentrated hydrofluoric acid (HF; 48%) and 2N (1:7) nitric acid ($HNO_3$) in 50 ml polypropylene tubes. Each tube was shaken for 18 hrs on a Burrell[1] wrist action shaker. Because of the formation of gas during some of the leaching procedures it was necessary to enclose each tube in two polyethylene bags each closed with plastic coated wire straps to allow gas to escape but not to allow for the release of liquid. Approximately 0.5 g of residual solid was removed from each tube for instrumental neutron activation analysis ( INAA). The solutions were saved for inductively coupled argon plasma (ICP) analysis.

### SEM and Microprobe

1 - Coal pellet casting and polishing

The pellet formation procedure follows the ASTM D2797-85 technique for anthracite and bituminous coal as modified by Pontolillo and Stanton (1994). The casting procedure impregnants, under pressure, approximately 7-8 grams of crushed sample with Armstrong C4 epoxy. The resultant mold is cured overnight at 60° C. A label is incorporated with the sample.

The pellet block is ground and polished using ASTM D2797-85 standards as modified by Pontolillo and Stanton (1994). The epoxy-coal pellet is ground with a 15 $\mu$m diamond platen and 600 SiC grit paper until flat and smooth. Rough polishing is done with 1 $\mu$m alumina and final polishing is completed with 0.06 $\mu$m colloidal silica. Ultrasonic cleaning between and after the various steps insures a final product relatively free of extraneous abrasive material.

Two pellets were prepared from each sample. One pellet from each sample was sectioned with a thin, slow-speed diamond saw and carbon coated for SEM and microprobe analysis.

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[1] Use of trade names and trademarks in this publication is for descriptive purposes only and does not constitute endorsement by the U. S. Geological Survey.

2 - Scanning electron microscope analysis.

A JEOL-840 scanning electron microscope equipped with a Princeton Gamma-Tech. energy-dispersive X-ray analytical system was used for petrographic examination. The data from X-ray system allows tentative identification of inorganic phases.

3 - Electron microprobe analysis.

A JEOL-8900 fully-automated, 5 spectrometer instrument was used to quantitatively determine element concentrations in sulfides by the wavelength-dispersive technique. Natural and synthetic standards were used. The samples were analyzed at 20 keV with a 30 nanoamp beam current. Counting times were 30 seconds for Fe and S and 60 seconds for the remaining elements.

## Results

### Selective leaching

Since receiving the first samples in March we have completed the preliminary leaching study on the four raw coal samples and a U.S. Geological Survey standard coal ( CLB-1). This entire experiment will be repeated and results reported in the next semiannual report. It is expected that the data will not be identical to the data included in this report because of changes in the leaching procedure instituted in response to difficulties encountered in the initial leaching experiment. Samples have been submitted for chemical analysis but as of April 1, 1996 the analyses have not been completed. The only data collected so far is the mass balance for each of the leaches (Table 1).

Table 1. Percent Material Leached. (Negative numbers indicate a net gain of material)

| Sample ID | $CH_3COONH_3$ | HCl | HF | $HNO_3$ |
|---|---|---|---|---|
| APP1 | 1 | 2 | 53 | -6 |
| APP2 | 0 | 2 | 54 | -7 |
| PR1 | 31 | 1 | 10 | 2 |
| PR2 | 19 | 0 | 9 | 0 |
| EI1 | 8 | 1 | 29 | -2 |
| EI2 | 7 | 1 | 28 | -2 |
| PG1 | 1 | 0 | 18 | -8 |
| PG2 | 2 | -1 | 22 | -7 |

APP= Southern Appalachian sample
PR= Powder River Basin sample
EI= Eastern Interior sample
PG=Pittsburgh (Northern Appalachian sample).

There was generally good reproducibility among duplicates with the exception of the $CH_3COONH_4$ leach of the Powder River Basin sample. The gain of material in $HNO_3$ leaches may be due to oxidation of the organics. We are testing this hypothesis. It may be necessary to determine percent leached in other ways such as ash determination.

SEM and Microprobe

Three samples have been examined by SEM. The data from the SEM are summarized in Table 2. Minerals listed are based on major element chemistry. The major minerals quartz, clays, and pyrite were found in all samples. The forms of pyrite are also given as different forms may have different trace element concentrations. Calcite which is also common in coals was found in 2 of 3 of the samples.

Data from microprobe analysis of several forms of pyrite in the Northern Appalachian coal is given in Table 3. The table is divided into two parts. The data is shown as weight percent which is the common way to report trace elements and atomic percent which is helpful in determining the

Table 2. Minerals observed by SEM

Inorganic phases observed; Minerals listed are based on major element chemistry:

Sample 95110901 Northern Appalachian
zircon
barite
monazite
quartz
clay
pyrite was observed as irregular-shaped masses, framboids, as vein fillings in silica, and blades

Sample 95120401 Southern Appalachian
iron oxide
aluminum phosphate
chalcopyrite
Th-bearing monazite
monazite
barite
zirconium oxide
zircon
sphalerite
xenotime
apatite
calcite
quartz
clay
iron disulfide (pyrite) was observed as irregular-shaped masses, framboids, and as vein fillings in silica

Sample 95110701 Powder River Basin
apatite
barite
titanium dioxide
cassiterite
Th-bearing monazite
iron oxide
quartz
calcite
clay
calcium sulfate
pyrite was observed as vein fillings in coal, and as irregular-shaped masses

Table 3. Representative analysis of pyrite from the Northern Appalachian sample

| No. of points | 1 | 1 | 1 | 1 | 2 | 2 |
|---|---|---|---|---|---|---|
| S (wt.%) | 52.67 | 53.64 | 54.09 | 53.74 | 52.86 | 53.37 |
| As | 0.09 | 0.22 | 0.04 | 0.00 | 0.08 | 0.08 |
| Se | 0.00 | 0.04 | 0.00 | 0.00 | 0.01 | 0.00 |
| Cu | 0.02 | 0.53 | 0.00 | 0.00 | 0.01 | 0.01 |
| Ni | 0.11 | 0.28 | 0.00 | 0.02 | 0.01 | 0.00 |
| Zn | 0.02 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 |
| Co | 0.08 | 0.12 | 0.07 | 0.07 | 0.09 | 0.09 |
| Fe | 46.08 | 45.15 | 46.46 | 45.96 | 46.53 | 46.41 |
| Mn | 0.28 | 0.00 | 0.00 | 0.00 | 0.01 | 0.01 |
| Pb | 0.00 | 0.33 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cd | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Sb | 0.01 | 0.01 | 0.00 | 0.02 | 0.01 | 0.01 |
| Sum | 99.36 | 100.32 | 100.68 | 99.82 | 99.61 | 100.00 |
| Comment | 95110901.10<br>10 um framboid | 95110901.11<br>10x30 um blade | 95110901.11<br>20x60 um blade | 95110901.12<br>20x30 um framboid | 95110901.121,122<br>20x50 um rectangular grain | 95110901.123,124<br>100x100 um framboid mass |
| | | | | | | |
| S (atomic %) | 66.29 | 66.87 | 66.92 | 67.02 | 66.34 | 66.62 |
| As | 0.05 | 0.12 | 0.02 | 0.00 | 0.04 | 0.04 |
| Se | 0.00 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cu | 0.01 | 0.33 | 0.00 | 0.00 | 0.00 | 0.00 |
| Ni | 0.07 | 0.19 | 0.00 | 0.01 | 0.01 | 0.00 |
| Zn | 0.01 | 0.00 | 0.01 | 0.00 | 0.00 | 0.00 |
| Co | 0.06 | 0.08 | 0.05 | 0.05 | 0.06 | 0.06 |
| Fe | 33.30 | 32.32 | 33.00 | 32.91 | 33.53 | 33.26 |
| Mn | 0.20 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 |
| Pb | 0.00 | 0.06 | 0.00 | 0.00 | 0.00 | 0.00 |
| Cd | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| Sb | 0.00 | 0.00 | 0.00 | 0.01 | 0.00 | 0.00 |
| Sum | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 | 100.00 |

purity of major minerals. For example pyrite ($FeS_2$) is theoretically 33.3 atomic percent Fe and 66.7 atomic percent S. All samples analyzed were "pure" within the error of the technique. One pyrite blade sample (95110901.11) had significantly more As, Se, Cu, Ni, Co and Pb than the other samples analyzed.

Table 4 shows representative analysis of chalcopyrite and pyrite from the Southern Appalachian sample.

Table 4. Representative analysis of chalcopyrite and pyrite from the Southern Appalachian sample

| | chalcopyrite | pyrite | pyrite |
|---|---|---|---|
| No of points | 2 | 2 | 1 |
| S (wt.%) | 34.57 | 51.47 | 51.51 |
| As | 0.09 | 0.21 | 0.11 |
| Se | 0.00 | 0.02 | 0.00 |
| Cu | 34.41 | 0.00 | 0.01 |
| Ni | 0.00 | 0.00 | 0.01 |
| Zn | 0.06 | 0.03 | 0.04 |
| Co | 0.06 | 0.09 | 0.09 |
| Fe | 30.07 | 46.81 | 46.31 |
| Mn | 0.00 | 0.01 | 0.00 |
| Pb | 0.00 | 0.08 | 0.06 |
| Cd | 0.00 | 0.00 | 0.00 |
| Sb | 0.01 | 0.01 | 0.00 |
| Sum | 99.27 | 98.72 | 98.13 |
| Comment | 95120401.8,9 | 95120401. 10,11 | 95120401.15 |
| | 7 um irregular shape | 20 um irregular shape | 15 um framboid |
| | | | |
| S (atomic %) | 49.88 | 65.55 | 65.84 |
| As | 0.06 | 0.11 | 0.06 |
| Se | 0.00 | 0.01 | 0.00 |
| Cu | 25.05 | 0.00 | 0.01 |
| Ni | 0.00 | 0.00 | 0.01 |
| Zn | 0.04 | 0.02 | 0.02 |
| Co | 0.05 | 0.06 | 0.06 |
| Fe | 24.91 | 34.23 | 33.99 |
| Mn | 0.00 | 0.00 | 0.00 |
| Pb | 0.00 | 0.02 | 0.01 |
| Cd | 0.00 | 0.00 | 0.00 |
| Sb | 0.00 | 0.00 | 0.00 |
| Sum | 100.00 | 100.00 | 100.00 |

## Summary

Phase I Characterization of four coals is progressing satisfactorily. One round of selective leaching has been completed, the second is underway. Four samples have been submitted for bulk chemical analysis. SEM and microprobe analysis have been started. Preliminary data are presented in this report.

## References Cited

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