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C.W. Kruse, C. Chaven, R.D. Harvey, and G.P. Huffman

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1994

Department of Energy and Natural Resources  
ILLINOIS STATE GEOLOGICAL SURVEY  
Morris W. Leighton, Chief

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## ABSTRACT

The Midwest Ore Processing Company (MWOPC) reported that a precombustion coal desulfurization process using perchloroethylene (PCE) at 120°C removes up to 70% of the organic sulfur. This process, however, was proven not to be as successful with Illinois coals as it was with Ohio and Indiana coals. Also, the high levels of organic sulfur removals reported by the MWOPC may be due to errors in interpreting data from the American Society For Testing and Materials (ASTM) method for forms-of-sulfur analysis. The purposes of this research were to confirm independently and possibly improve the organic sulfur removal from Illinois coals with the PCE desulfurization process, and verify the forms-of-sulfur determination using the ASTM method for evaluating the PCE process. A problem that limits commercial application of the PCE process is the high chlorine content in the PCE-treated coals. Another goal of this investigation was to develop a dechlorination procedure to remove excess PCE from the PCE-treated coal.

MWOPC's results were duplicated in the ISGS test on fresh IBC-104 coal. From mass balance calculations, 96% of the total sulfur and more than 95% of the total iron were accounted for during our PCE tests on both long-term oxidized IBC-104 coal and oxidized Ohio 5/6 coal. The amount of elemental sulfur generated during short-term oxidation of coal or pyrite in this study was controlled by reaction temperature, moisture conditions, and an oxidant we introduced. The elemental sulfur produced during ambient air oxidation appeared to originate mainly from pyrite oxidation. This elemental sulfur complicates the material balance during organic sulfur removal when the process evaluation depended solely on ASTM analysis. Elemental sulfur is more amenable than organic sulfur to removal by PCE. Ohio 5/6 coal appears to produce elemental sulfur more readily than Illinois coal during oxidation. Data from X-ray diffraction analyses indicate that sulfate in the oxidized Illinois IBC-104 coal occurs mainly as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), whereas, sulfate in a sample of oxidized Ohio 5/6 coal occurs mainly as szomolnokite ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ). These data suggest that the oxidation reaction for Ohio 5/6 coal might occur under conditions different from oxidation of IBC-104, which more readily converts pyrite to produce  $\text{FeSO}_4$  and elemental sulfur. The higher elemental sulfur content in the Ohio 5/6 coal results in higher apparent organic sulfur removal by PCE extraction. For this investigation, a procedure was developed to wash PCE from the PCE-treated coals. The procedure produced coals with chlorine contents as low as 0.03%.

## EXECUTIVE SUMMARY

The development of economical and practical processes to remove both organic and pyritic sulfur under mild reaction conditions would be highly beneficial to the Illinois coal industry. The Midwest Ore Processing Company (MWOPC) reported that a precombustion desulfurization process using perchloroethylene (PCE) at 120°C removes as much as 70% of the organic sulfur in the form of elemental sulfur. The MWOPC stressed the importance of oxidation and drying conditions, as well as temperature control. The desulfurization process is effective in extracting organic sulfur and separating pyrite fines from coal by float-sink. The process, which can be operated at low temperatures with minimal loss of solvent (Leehe and Sehgal 1988, Leehe 1989, Lee et al. 1989), was reported to effectively remove organic sulfur from Ohio and Indiana high-sulfur coals. The process, however, was proven not to be as successful with Illinois coals (Lee et al. 1989, Buchanan et al. 1990). The MWOPC evaluation of the PCE desulfurization process was based on interpretation of data obtained by using the ASTM method for determining forms of sulfur.

During the past few years, the Illinois State Geological Survey (ISGS) and Eastern Illinois University (EIU) jointly developed analytical methods to determine the presence of elemental sulfur in PCE extracts from high sulfur Illinois coals. Some elemental sulfur and limited amounts

of organic sulfur were removed from oxidized Illinois coals during these studies; however, the sulfur removals (<32%) were much lower than those reported by the MWOPC (>43%). Several hypotheses may explain these differences, but until now, no experiments had been conducted to support clearly these hypotheses. MWOPC assumed that organic sulfur removal was due mainly to the removal of aliphatic sulfur, and that the aliphatic sulfur component of organic sulfur in the Illinois coals may be less than that of the other coals tested. We have postulated that certain errors in interpreting ASTM data may result in the higher organic sulfur removals reported by the MWOPC.

One hypothesis, based on the assumptions underlying the ASTM analysis, is that elemental sulfur extracted by the PCE may be that derived from pyrite oxidation during coal preoxidation, rather than from organic sulfur removed by PCE. The ASTM forms-of-sulfur analysis does not distinguish between organic sulfur and elemental sulfur. Another similar hypothesis is that preoxidation of coal may convert pyrite into PCE-extractable sulfur and a form of pyritic iron that is not extractable by HCl but is extractable by  $\text{HNO}_3$ . If so, this iron would be considered as pyritic sulfur during the ASTM analysis. Since the ASTM "pyritic sulfur" appears to remain constant after PCE extraction and the ASTM organic sulfur is obtained by the difference between total sulfur and the sum of pyritic sulfur and sulfatic sulfur, this calculation would lead to an error in interpreting the ASTM results. The sulfur removed by PCE extraction would appear organic in nature, when it is not.

The goals of this research were to (1) confirm independently and possibly improve organic sulfur removal from Illinois coals with the PCE desulfurization process claimed by the MWOPC, (2) verify the forms-of-sulfur determination by the ASTM method in evaluating the PCE desulfurization process, and (3) develop a procedure to remove excess PCE from PCE-treated coals. This study is a joint effort by the ISGS, EIU, the University of Illinois at Urbana/Champaign (UI-UC), and the University of Kentucky (UK). Tasks 1 to 5 were completed, and tasks 6 to 8 will be conducted next year.

In the beginning of this investigation, the efficiency of the PCE desulfurization method was evaluated by measuring the level of total sulfur reduction in the PCE-treated coals and the amounts of elemental sulfur obtained in the PCE extracts. The removal of elemental sulfur from coal is enhanced by a preoxidation treatment. The elemental sulfur extracted from a long-term ambient-oxidized IBC-104 coal is 25 to 75 times greater than that extracted from the unoxidized or short-term oxidized IBC-104 coal samples.

Larger scale (50 g) PCE desulfurizations were conducted on a short- and long-term ambient-oxidized IBC-104 coal and on an ambient-oxidized Ohio 5/6 coal to obtain enough sample for ASTM analysis, non-ASTM sulfur analyses, and mass balance analysis. The data from non-ASTM sulfur analyses, including Sulfur K-Edge X-Ray Absorption Near Edge Structure Spectroscopy (XANES) analysis, were examined and compared to data from the ASTM analysis. XANES analyses indicated that long-term ambient oxidation may have oxidized some organic sulfur in coal, and that PCE desulfurization removed all the elemental sulfur from coals. The results also indicated the PCE process did not remove organic sulfide nor thiophenic forms of organic sulfur in coal. This finding was supported by the data from a wet chemical analysis, in which a lithium aluminum hydride reduction is used to delineate the interference of elemental sulfur during a combustion technique detect organic sulfur.

Mineralogical determination by X-ray diffraction indicates that sulfate in long-term ambient-oxidized IBC-104 coal exists mainly as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ), whereas sulfate in oxidized Ohio 5/6 coal exists mainly as szomolnokite ( $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ ). These data suggest that the ambient-oxidation reaction for Ohio 5/6 coal might occur under conditions different from the

oxidation conditions for the IBC-104 coal, which readily converts pyrite to  $\text{FeSO}_4$  and elemental sulfur. This interpretation also supports the observation that Ohio 5/6 coal appears to produce elemental sulfur more readily than Illinois coal during short-term oxidation. Oxidation of coals was found to facilitate subsequent PCE desulfurizations, and the higher elemental sulfur content in oxidized coal results in higher apparent removal of organic sulfur by PCE extraction when the process is monitored by the ASTM forms-of-sulfur method.

Results from the mass balance calculations indicate that 96% of the total sulfur and more than 95% of total iron were accounted for in both long-term IBC-104 coal and Ohio 5/6 coal during PCE desulfurization tests.

PCE desulfurization under various short-term oxidation conditions was examined. The results of this oxidation study show that the increase in elemental sulfur is related to reaction temperature, moisture conditions, and the presence of an oxidant we introduced. The significance of these three key operating variables were noted by Lee, et al. (1989) at the University of Akron and Leehe, et al. (1988) at MWOPC. Oxidation of coal produces more elemental sulfur to be removed by PCE extraction. The elemental sulfur produced during ambient air oxidation appears to originate mainly from pyrite oxidation. This elemental sulfur complicates the material balance concerning organic sulfur removal when only the ASTM method of analysis is used. The origin of the elemental sulfur during oxidation and the nature of the pyritic and organic sulfur in the sample treated with an oxidant we introduced are currently under investigation.

Finally, a washing procedure that produced coals with chlorine contents as low as 0.03% was developed to remove PCE from PCE-treated coals.

## **OBJECTIVES**

The goals of this research were to (1) confirm independently and possibly improve the removal of organic sulfur from Illinois coals using the perchloroethylene (PCE) process developed by the MWOPC, (2) verify the ASTM method for forms-of-sulfur determination, and (3) develop a procedure to remove excess PCE from PCE-treated coals. Successful removal of organic sulfur by PCE extraction or by other methods developed to improve PCE extraction of Illinois coals can greatly improve the marketability of high-sulfur Illinois coal.

Specific objectives were to:

- Conduct the PCE desulfurization of two coals (IBC-104 from Illinois Basin Coal Sample Program and Ohio 5/6 coal from Horizon Coal Company) under the proper process conditions.
- Conduct an extensive material balance study on the feed materials and products from the two coals tested in the PCE desulfurization process.
- Conduct non-ASTM analyses and compare the results with those from the ASTM method for forms of sulfur.
- Investigate coal oxidation chemistry and its effect on the mechanisms of sulfur removal by the PCE desulfurization process.
- Examine the role of pyrite during the PCE desulfurization process and its influence, if any, on process optimization.
- Evaluate and possibly improve the effectiveness of the PCE desulfurization process for Illinois coals.

## BACKGROUND

MWOPC reported a method of removing organic sulfur from high-sulfur coal using PCE extraction at 120°C (Starbuck 1980, Leehe and Sehgal 1988, Leehe 1989). The MWOPC conducted PCE process studies, partially supported by the Electric Power Research Institute (EPRI), at a pilot plant in Plainville, Indiana. The plant has the capacity to process 1 ton of coal per day. In addition, the University of Akron operates a mini-pilot plant that has the capacity to process 1 pound of coal per hour (Lee, et al. 1989). The studies demonstrated that the PCE process effectively extracts organic sulfur and separates pyrite fines from coal. The process is conducted at low temperatures with a minimum loss of solvent (Lee, et al. 1989). The importance of oxidation and drying conditions, as well as temperature control, is stressed by MWOPC. The efficiency of organic sulfur removal is affected by the initial moisture content of the coal (Fullerton, et al. 1990). A. G. Atwood (MWOPC, personal communication 1991) suggested adding pyrite as a "catalyst" to the process to render organic sulfur more accessible to the PCE extraction. This process was found to remove effectively organic sulfur from Ohio and Indiana high-sulfur coals; however, it was proven not to be as successful with Illinois coals (Lee, et al. 1989).

In 1988, the EIU and the ISGS initiated a cooperative study (Buchanan, et al. 1990) on PCE desulfurization of Illinois coals. The procedure they developed was different from that of MWOPC in that (-60 mesh) coals were not preoxidized before PCE extraction. Also, these experiments were mainly conducted in a Soxhlet extraction apparatus using a small sample size (1–24 g); 50 grams or more were used in experiments by the University of Arizona (Lee, et al. 1989). Buchanan et al. (1990) concluded that pyrite was the source of the elemental sulfur extracted from coal by PCE under these conditions and that little organic sulfur was removed. These results differ from those of the MWOPC study, which reported that as much as 43% of organic sulfur was removed from an Illinois coal (Buchanan, et al., 1990) by ASTM interpretation.

Differences between the results of the MWOPC and EIU/ISGS may be due to the use of different process conditions with respect to preoxidation, extraction apparatus, and sample size. For example, Soxhlet extraction rather than batch extraction could decrease the activity of the catalyst that assists organic sulfur removal during PCE extraction. Soxhlet extraction could also decrease the consistency of the temperature control. We have postulated, however, that possible errors in the ASTM analyses of sulfur may explain the discrepancies in the results. For example, during preoxidation, pyritic sulfur might be converted into PCE-extractable elemental sulfur and the iron derived from pyrite might be left behind. This iron might remain insoluble in HCl but soluble in HNO<sub>3</sub> during ASTM analysis. In this case, a portion of the iron no longer associated with sulfur would be calculated as pyrite. Since the elemental sulfur would be removed by PCE, the total sulfur content would decrease and the calculated amount of organic sulfur would decrease. This calculation would lead to an error in interpreting the results from the ASTM method, making the PCE extraction appear to have removed the organic sulfur (Buchanan, 1990). These hypotheses need verification.

## EXPERIMENTAL PROCEDURES

Eight tasks will be conducted to meet our objectives. Tasks 1-5 were completed during 1991-1992.

### Task 1: Processing of Illinois Coals and a Mass Balance Study

PCE desulfurization was performed on the selected Illinois coal under conditions described by the MWOPC procedures. Thus, the products from before and after PCE extraction can be used

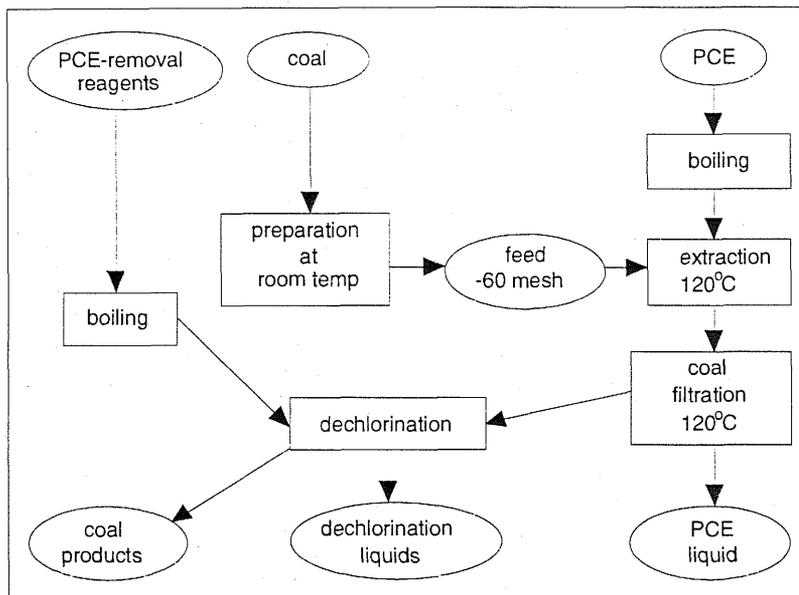


Figure 1 Flow diagram of perchloroethylene (PCE) batch extraction.

to evaluate the fate of sulfur during the PCE extraction process and also to verify the results from the ASTM method of analysis.

**Task 1.1: Processing of coals** Two coals—IBC-104 from the Illinois Basin Coal Sample Program and Ohio 5/6 from the Horizon Coal Company—were selected for this task. Coal selection was based on the availability of samples and desulfurization data reported by the MWOPC and the UA. The data gave a baseline of comparison between the data generated in this investigation and those reported (Lee, et al., 1989). The two coals selected were tested as received and in their oxidized form in the first quarter. These tests were performed in a batch mode. Figure 1 is a flow diagram for the PCE batch extraction. Coal samples were ground at room temperature to -60 mesh. The coal sample was fed into a PCE extractor maintained at 120°C, the boiling point of the PCE. The extraction continued for 30 minutes, then the treated coal was filtered through a glass fiber filter. The filter was maintained at the same temperature as the extractor. After filtration, dechlorination reagents were introduced to the filter to wash the treated coal sample. The resulting coal product was dried under vacuum.

Larger scale PCE extractions (50 g) on a short-term oxidized IBC-104 coal, a long-term oxidized IBC-104 coal, and an oxidized Ohio 5/6 coal were completed during the second quarter. The feeds and products from these scaled-up operations were split and distributed to coinvestigators for independent analyses (task 2) and a mass balance analysis (task 1.2). A washing procedure for removing chlorine from the PCE-processed coals was also examined. During the third quarter, PCE extraction was conducted in conjunction with short-term oxidations of coals. The coal was oxidized by bubbling filtered air or air/SO<sub>2</sub> (Pasiuk-Bronikowska, et. al. 1989) through a coal/PCE slurry with or without water added. The reaction was observed at various temperatures from room temperature to 90°C and for durations ranging from 2 to 20 hours. After oxidation, the temperature was increased to 120°C for 30 minutes. The extracts produced from PCE extraction were then isolated from the residues by hot filtration.

The PCE filtrate was purified first by passing the solution through a Florisil Column. Then the elemental sulfur contents were determined with a Perkin-Elmer Model LC65 high performance liquid chromatograph (HPLC) equipped with an ultraviolet-visible light (UV-VIS) detector.

Chlorine content of the feeds and product coals was measured using a Leco chlorine analyzer. Moisture, volatile matter, ash, and fixed carbon contents were determined by the ASTM proximate analysis. Sulfatic, pyritic, and total sulfur contents in the feeds and final products were obtained by using the ASTM D2492 procedure (ASTM 1991).

In the forms-of-sulfur examination by the ASTM D2492 method, the sample (-60 mesh) was first digested with a dilute HCl solution. The acidic solution was filtered and sulfatic sulfur was precipitated and quantified as  $\text{BaSO}_4$ . After washing with distilled water, the residue free of HCl was digested with diluted  $\text{HNO}_3$ . The suspension was filtered and the filtrate was adjusted to volume for iron analysis by atomic absorption (AA). The iron content was used to calculate pyritic sulfur. To obtain the total concentration of sulfur, a separate split of coal was combusted in a Leco model SC32 total sulfur analyzer equipped with an on-line IR detector to monitor  $\text{SO}_2$  production. The organic sulfur content was obtained by calculating the difference between total sulfur content and the sum of pyritic and sulfatic sulfur contents. Any elemental sulfur present was counted as organic sulfur, since it was not reported as pyritic or sulfatic sulfur.

**Task 1.2: Mass balance study** A complete material balance study was conducted on the two coals during the PCE extraction process. Elemental sulfur in the PCE extract was determined by using a high pressure liquid chromatograph (HPLC) equipped with an UV-VIS detector. Total sulfur in feeds and PCE-treated coals was used to calculate the sulfur mass balance. Sulfate sulfur concentration in the dechlorination liquids was obtained by inductively coupled plasma analysis (ICP).

Total iron contents in feeds and solid products were obtained after fusion of the ashed sample in lithium metaborate. The sample was ashed at  $750^\circ\text{C}$  for 20 to 24 hours or until no carbonaceous residue remained. The prepared ashes were fused with lithium tetraborate (a mixture of one part ash by weight and nine parts  $\text{Li}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$  by weight) in platinum crucibles at  $1000^\circ\text{C}$ . The fused mixture was dissolved in water and diluted to a volume for iron analysis by AA. Iron content in the samples of dechlorination liquids was determined by ICP.

## **Task 2: Non-ASTM Analysis for Forms-of-Sulfur Determination**

The transformation or removal of pyritic sulfur, aliphatic sulfur, and aromatic sulfur during PCE desulfurization was examined in tasks 2.1 to 2.5. The data collected from these tasks allowed us to explore the identity of organic sulfur removed by PCE extraction and the accuracy of ASTM forms-of-sulfur analysis.

**Task 2.1: A wet-chemical analysis** In this method, a lithium aluminum hydride (LAH) reduction technique used to determine pyritic sulfur is combined with a combustion technique used to determine of organic sulfur (Westgate and Anderson 1982; Liu, et al. 1987). This method was conducted and compared with the ASTM results in task 1.2.

A representative split of the coal sample was pulverized to -230 mesh. The powdered coal sample was dried first and then sulfatic sulfur was extracted using a diluted HCl solution. The acidic solution was filtered and sulfatic sulfur precipitated as  $\text{BaSO}_4$ . If any monosulfide sulfur was present, it was released as  $\text{H}_2\text{S}$  during the leaching of HCl and precipitated as  $\text{Ag}_2\text{S}$  (Liu, et al. 1987). To remove pyritic sulfur, residue from HCl-leached coal was treated with LAH. The pyritic sulfur was released as  $\text{H}_2\text{S}$ , which was trapped and precipitated as  $\text{Ag}_2\text{S}$ . Any elemental

sulfur present in the residue was reported as pyritic sulfur. The sulfur remaining in residue from the HCl/LAH-leached coal was assumed to be organic sulfur. To obtain the organic sulfur, residue from LAH-leached coal was combusted in a high temperature furnace. Organic sulfur was oxidized to  $\text{SO}_2$ , then trapped, and precipitated as  $\text{BaSO}_4$ . The amount of each form of sulfur was then calculated from the quantities of  $\text{BaSO}_4$  and  $\text{Ag}_2\text{S}$  obtained from each extraction. An analysis of total sulfur, independent of the cumulative total from the HCl, LAH, and oxidation procedure, was also conducted by high-temperature combustion (HTC). The forms of sulfur were reported as weight percentages of dried coal.

Four nondestructive spectroscopic techniques (tasks 2.2 to 2.5) were used to determine the fate of organic sulfur, pyritic sulfur, and sulfur-containing iron salts in each step of the PCE desulfurization process.

**Task 2.2: Sulfur K-edge X-ray absorption near edge structures spectroscopy** Huffman, et al. (1991) developed this method to determine the quantity of all major sulfur forms, both organic and inorganic, in coal. The method is based on the least-squares analysis and deconvolution of the X-ray absorption near-edge structure (XANES) into a series of peaks that represent  $1s \rightarrow np$  photoelectron transitions. The major sulfur forms (pyrite, organic sulfide, thiophene, sulfoxide, sulfone, and sulfate) that occur in coal have characteristic  $s \rightarrow p$  transition energies. The relative peak area contributed to the XANES by each sulfur form can be determined. These peak areas are converted to weight percentages of sulfur using calibration constants derived from XANES data from standard compound mixtures. Since the XANES signal is derived from the bulk of the sample, detailed information was obtained on various groups of organic sulfur removed during PCE desulfurization.

**Task 2.3: X-ray diffraction** The XRD method is a widely used, reliable technique for identifying mineral matter in coals. Coal samples in this study were ground and X-rayed as "whole coals." McCrone grinders were used for specimen preparation to assure reliable XRD measurement. The samples were also X-rayed after the organic fraction was removed by low temperature ashing. Procedures were performed to determine pyrite, various iron sulfides and sulfates, clay minerals, and other common nonclay minerals (Hughes and Warren 1989). Results were reported on a 100% mineral-matter-free basis and as a percentage of whole coal.

**Task 2.4: Mössbauer spectroscopy** Mössbauer spectroscopy was used to differentiate the Fe sulfide/sulfate species present in feed, oxidized, and PCE-treated coal samples. The minerals pyrite ( $\text{FeS}_2$ ), troilite ( $\text{FeS}$ ), and pyrrhotite ( $\text{Fe}_x\text{S}_y$ , where  $x:y$  varies between approximately 0.8 and 0.95) display very different Mössbauer spectroscopic features. These species are discernible in mixed samples by comparing isomer shifts, quadruple splitting, and magnetic hyperfine fields of the spectral components. Pyrite in feed and intermediate and final products was determined at room temperature. The instrument used is also capable of operating at variable temperature and performing magnetic Mössbauer measurements for monitoring iron-containing sulfates in oxidized coal samples. Spectra were acquired in the triangular waveform mode using a Ranger Scientific MS-900 spectrometer equipped with a 50 mCi  $^{57}\text{Co}$  source (in 10% Rh matrix). Results were analyzed on a VAX computer using a least-squares, curve-fitting program similar to that described by Chrisman and Tumolillo (1971). The computer program assumed Lorentzian line shapes.

**Task 2.5: Scanning electron microscopy and energy dispersive X-ray fluorescence analysis** A scanning electron microscope equipped with an energy dispersive X-ray analyzer (SEM-EDX) was used to determine nonpyritic sulfur content within a statistically representative number of maceral components in samples of feed and PCE-extracted coal (Harvey and Demir 1990).

Representative macerals were first selected for analysis and identified optically, then analyzed at high magnifications using SEM-EDX.

Sulfur determinations were made at representative spots within each selected maceral. The spots were approximately 1 to 4  $\mu\text{m}$  across and possibly 3 to 5  $\mu\text{m}$  deep within the maceral. Spots without X-ray signal from iron or calcium were accepted and recorded as organic sulfur. Elemental sulfur can not be distinguished by this method; therefore, the resultant value of organic sulfur includes any elemental sulfur that is present in the tested sample. The value of organic sulfur was determined on the dry-mineral-free matter basis and converted to the whole coal basis by the Parr equation. This equation uses the ash and total sulfur values from routine ASTM analyses.

### **Task 3: Evaluating the Effectiveness of the PCE Desulfurization Process on the Selected Illinois Coal, and Verifying the ASTM Forms-of-Sulfur Analyses**

Data obtained from tasks 1 and 2 on sulfur removal for the two coals were examined, evaluated, and interpreted. Data from ASTM analysis (task 1.2), LAH analysis (task 2.1), and XANES analysis (task 2.2) for sulfur removal using the PCE desulfurization process were compared. Data from spectroscopic analyses (tasks 2.2 to 2.5) were examined with respect to the transformation or removal of pyritic sulfur, organic sulfide, and thiophenic sulfur during PCE desulfurization. These data allowed us to explore the identity of sulfur removed by PCE extraction and that of ASTM forms-of-sulfur analysis.

### **Task 4: Conducting PCE Desulfurization under Various Process Conditions**

The effects of various process conditions on PCE desulfurization were determined. The study on the effects of ambient oxidation on sulfur removal by PCE extraction were concluded. In addition to ambient oxidation, various short-term, air-oxidation effects (achieved by varying the amount of water, temperature, time, and oxidizing gas composition) were examined. The procedures for these short-term oxidation/PCE extractions are described in task 1.1.

Conducting PCE desulfurization under preoxidation conditions using air/SO<sub>2</sub> (Pasiuk-Bronikowska, et al. 1989) will be extended into the second year to gather more detailed fundamental and application information.

### **Task 5: Evaluating the Parameters Studied and Their Effects on Process Optimization**

This task was completed in the first year for fresh and ambient-oxidized samples. The results of the ASTM forms-of-sulfur analyses in oxidized coals were compared with those in the nonoxidized coal. The effects that preoxidation conditions have on sulfur removal during PCE extraction were assessed.

Tasks 6 to 8 will be completed during the second year of the project.

## **RESULTS AND DISCUSSION**

### **Confirmation Study**

**Preliminary PCE desulfurization based on ASTM analysis** Table 1 shows the results of ASTM analysis on an Illinois No. 6 coal before and after PCE extraction. The Illinois coal sample, which was processed by the developer (UA), is comparable to the fresh IBC-104 coal used in this investigation. Data of the University of Akron show 5% removal for total sulfur content and a 12% decrease for the ASTM organic sulfur content. From this investigation, the ASTM data on fresh IBC-104 coal show a total sulfur removal of 4% to 9% and an organic sulfur removal

**Table 1** Weight percentage of sulfur on moisture-free whole coal basis.

| Sample   | ASTM forms of sulfur |         |                      | Total               |
|--|----------------------|---------|----------------------|---------------------|
|  | Sulfatic             | Pyritic | Organic              |                     |
| University of Akron  |                      |         |                      |                     |
| Illinois No.6 (F-IBC-104)                                    | 0.01                 | 2.54    | 1.55                 | 4.10                |
| After PCE  | 0.01                 | 2.52    | 1.36 <sup>-12%</sup> | 3.89 <sup>-5%</sup> |
| Illinois State Geological Survey/Eastern Illinois University |                      |         |                      |                     |
| F-IBC-104  | 0.07                 | 2.22    | 1.94                 | 4.23                |
| After PCE,I  | 0.04                 | 2.24    | 1.77 <sup>-9%</sup>  | 4.05 <sup>-4%</sup> |
| After PCE,II   | 0.04                 | 2.15    | 1.66 <sup>-14%</sup> | 3.85 <sup>-9%</sup> |

<sup>-5%</sup> = percentage of reduction in total sulfur or organic sulfur

F-IBC-104 = fresh IBC-104 coal sample, ASTM = American Society for Testing and Materials

of 9% to 14%. These data confirm that we repeated the developer's results in our tests of fresh IBC-104 coal based on the ASTM analysis

**Oxidation and PCE desulfurization based on HPLC analysis** PCE desulfurization was also evaluated on the basis of the amounts of elemental sulfur obtained in the PCE extracts. The removal of elemental sulfur from coal by PCE extraction is enhanced by subjecting coal to a long-term ambient oxidation. The amount of extractable elemental sulfur from a long-term ambient-oxidized IBC-104 coal is 25 to 75 times greater than that from the unoxidized or short-term oxidized coal samples. These results confirm that preoxidation is important to PCE desulfurization.

**Scaled-up PCE desulfurization** A larger scale (50 g) PCE desulfurization was conducted on three oxidized coal samples (task 1.1). The purpose of this scaled-up operation was to produce enough sample for analysis. These samples were subjected to ASTM analysis, non-ASTM sulfur analyses, and a mass balance analysis. The three oxidized coal samples were a short-term (2 weeks) oxidized IBC-104, a long-term (>5 years) oxidized IBC-104, and an oxidized Ohio 5/6 coal. Both total iron and total sulfur mass balance were examined for the two highly oxidized coal samples.

**ASTM analysis and HPLC analysis** Table 2 shows results of the ASTM analyses of the feed coals and treated coals and HPLC analyses of the PCE extracts. The data indicate that the amount of the extractable elemental sulfur from the two highly oxidized coal samples is greater than the amount extracted from the mildly oxidized sample. The sample from the two-week oxidation (2W-IBC-104) shows no detectable amount of elemental sulfur in the PCE extract. The two samples from a long-term ambient oxidation (>5Y-IBC-104 and O-Ohio 5/6), however, show a noticeable amount of elemental sulfur in the PCE extracts. The amount of elemental sulfur extracted from >5Y-IBC-104 was 0.07%; the amount extracted from the O-Ohio 5/6 sample was 0.10%.

The ASTM data also show a greater reduction in organic sulfur for the highly oxidized coal samples after PCE extraction. The results are consistent with those obtained from the smaller scale extractions. The sample from the two-week oxidation shows no total sulfur removal. The slight increase in organic sulfur content in this sample shown by ASTM analysis is attributed to

**Table 2** Elemental sulfur from PCE extraction and ASTM forms of sulfur in three ambient-oxidized coal samples before and after PCE extraction.

| Sample      | Weight (%), moisture-free, whole-coal basis |                      |                      |                       |                |
|-------------|---|----------------------|----------------------|-----------------------|----------------|
|             | Sulfatic                                    | ASTM forms of sulfur |                      |                       | HPLC           |
|             |   | Pyritic              | Organic              | Total                 | S <sup>o</sup> |
| 2W-IBC-104  | 0.12  | 2.17                 | 1.68                 | 3.97                  |                |
| After PCE   | 0.05  | 2.18                 | 1.75 <sup>+4%</sup>  | 3.98 <sup>+0.3%</sup> | 0.00           |
| >5Y-IBC-104 | 0.87  | 1.40                 | 1.84                 | 4.11                  |                |
| After PCE   | 0.25  | 1.40                 | 1.66 <sup>-10%</sup> | 3.31 <sup>-20%</sup>  | 0.07           |
| O-Ohio 5/6  | 0.63  | 0.79                 | 2.08                 | 3.50                  |                |
| After PCE   | 0.28  | 0.87                 | 1.64 <sup>-21%</sup> | 2.79 <sup>-20%</sup>  | 0.10           |

<sup>-20%</sup> = percent of reduction in total sulfur or organic sulfur, HPLC = high performance liquid chromatography, S<sup>o</sup> = elemental sulfur, 2W-IBC-104 = two-week oxidized IBC-104 coal sample, >5Y-IBC-104 = long-term oxidized IBC-104 coal sample, O-Ohio 5/6 = oxidized Ohio 5/6 coal sample

an error. In the ASTM forms-of-sulfur determination (ASTM D-2492, 1991), the error in organic sulfur content is a cumulative error from sulfate, pyrite, and total sulfur determinations. The reduction in sulfur content by PCE extraction for samples oxidized two weeks may be too small to offset this cumulative error. The highly oxidized Illinois sample, >5Y-IBC-104, shows a noticeable reduction in both total sulfur (20%) and organic sulfur (10%). Similarly, the highly oxidized Ohio sample, O-Ohio 5/6, shows a noticeable reduction in both total sulfur (20%) and organic sulfur (21%).

The organic sulfur removed from the Ohio 5/6 coal is about twice as much as that removed from the Illinois coal, as determined from ASTM analysis. These data confirm the developer's observation that the PCE process is more effective for the Ohio coal than for the Illinois coal, and that oxidation is an important factor in PCE desulfurization.

A relationship is indicated between the amounts of elemental sulfur in the PCE extracts analyzed by HPLC and the amount of organic sulfur removal determined by ASTM analysis. A higher level of elemental sulfur in the PCE extract indicates a higher level of organic sulfur removal according to ASTM interpretation. The amount of elemental sulfur extracted from O-Ohio 5/6 coal was 0.10%; organic sulfur removal was 21%. From >5Y-IBC-104, 0.07% elemental sulfur was extracted and 10% organic sulfur was removed.

**Mass balance analysis** Table 3 shows the sulfur mass balance data for the samples of long-term oxidized IBC-104 coal and oxidized Ohio 5/6 coal. The data indicate that elemental sulfur in the PCE extract from oxidized Ohio 5/6 coal was greater than that from long-term oxidized IBC-104 coal. Dechlorination liquids were analyzed for sulfate sulfur and elemental sulfur. Elemental sulfur was not detected in the dechlorination liquids. Organic sulfur in PCE and dechlorination liquids was not measured because a reliable method was not available. The data obtained (96% sulfur recovery), however, indicate a good sulfur mass balance for both long-term oxidized IBC-104 and oxidized Ohio 5/6 coals.

Total iron mass balance data show an accountability of greater than 95% for both the long-term oxidized IBC-104 coal sample and the oxidized Ohio 5/6 coal sample (table 4).

**Table 3** Total sulfur mass balance for long-term (>5 years) oxidized IBC-104 and oxidized Ohio 5/6 coal samples.

|                                  | >5Y-IBC-104 (100 g) | O-Ohio 5/6 (100 g) |
|----------------------------------|---------------------|--------------------|
| Total sulfur before extraction   | 4.11 g              | 3.5 g              |
| PCE extract (S <sup>0</sup> )    | 0.07 g              | 0.10 g             |
| Dechlorination liquid – methanol | Not available       | Not available      |
| Dechlorination liquid – water    | 0.56 g              | 0.46 g             |
| Dechlorination liquid – acetone  | Not available       | Not available      |
| Treated coal                     | 3.31 g              | 2.79 g             |
| Total Sulfur after extraction    | 3.94 g              | 3.35 g             |
| Percent of recovery              | 96%                 | 96%                |

**Table 4** Total iron mass balance for the long-term (>5 years) oxidized IBC-104 and oxidized Ohio 5/6 coal samples.

|                                  | >5Y-IBC-104 (100 g) | O-Ohio 5/6 (100 g) |
|----------------------------------|---------------------|--------------------|
| Total iron before extraction     | 2.76 g              | 1.57 g             |
| PCE extract                      | Not available       | Not available      |
| Dechlorination liquid – methanol | 0.00 g              | 0.04 g             |
| Dechlorination liquid – water    | 0.08 g              | 0.47 g             |
| Dechlorination liquid – acetone  | Not available       | Not available      |
| Treated coal                     | 2.60 g              | 1.00 g             |
| Total iron after extraction      | 2.68 g              | 1.51 g             |
| Percent of recovery              | 97%                 | 96%                |

**Non-ASTM sulfur analyses** Several non-ASTM methods were used to analyze the two oxidized coal samples (>5Y-IBC-104 and O-Ohio 5/6) before and after PCE extraction. Mössbauer spectroscopy and X-ray diffraction spectroscopy were used for mineral matter analysis. SEM-EDX, HCl/LAH, and XANES analyses were used mainly for organic sulfur determination. The results of these organic sulfur analyses were compared with those obtained from the ASTM analysis.

Data from both Mössbauer spectroscopy (table 5) and X-ray diffraction spectroscopy (table 6) indicate a loss of Fe(II)SO<sub>4</sub> in the product coals. This loss is due to the removal of ferrous sulfate during the dechlorination step after PCE-extraction.

Data from X-ray diffraction spectroscopy further indicate that sulfate in the >5Y-IBC-104 sample is mainly in the form of gypsum (CaSO<sub>4</sub> · 2H<sub>2</sub>O), whereas sulfate in the O-Ohio 5/6 sample is mainly in form of szomolnokite (FeSO<sub>4</sub> · H<sub>2</sub>O). These data suggest that the oxidation reaction for Ohio 5/6 coal might occur under Fe(III) catalytic conditions that readily convert pyrite to produce FeSO<sub>4</sub> and elemental sulfur. This interpretation seems to support the observation

**Table 5** Iron analysis by Mössbauer spectroscopy.

| Sample      | $\chi^2$ | Peaks | Fe state | IS (mm/s) | D (mm/s) | Relative area (%) | Line width (mm/s) |
|-------------|----------|-------|----------|-----------|----------|-------------------|-------------------|
| >5y-IBC-104 | 0.86     | 1,4   | Fe(II)   | 1.127     | -2.748   | 4.6               | 0.139             |
|             |          | 2,3   | Fe(III)  | 0.276     | -0.617   | 95.4              | 0.315             |
| After PCE   | 1.20     | 1,2   | Fe(III)  | 0.261     | -0.637   | 100               | 0.329             |
| O-Ohio 5/6  | 1.52     | 1,4   | Fe(II)   | 1.222     | -2.550   | 30.6              | 0.332             |
|             |          | 2,3   | Fe(III)  | 0.264     | -0.608   | 69.4              | 0.317             |
| After PCE   | 1.39     | 1,2   | Fe(III)  | 0.242     | -0.558   | 100               | 0.251             |

IS = Isomer shift, D = Quadrupole splitting,  $\chi^2$  = Statistical parameter

>5Y-IBC-104 = long-term oxidized IBC-104 coal sample, O-Ohio 5/6 = oxidized Ohio 5/6 coal sample

**Table 6** Mineral matter composition by X-ray diffraction analysis.

| Sample      | Weight %  |         |        |        |              |          |
|-------------|-----------|---------|--------|--------|--------------|----------|
|             | Quartz    | Calcite | Pyrite | Gypsum | Szomolnokite | Nonclays |
| F-IBC-104   | 18.8      | 3.1     | 3.9    | 0.3    | —            | 26.1     |
| >5y-IBC-104 | 12.8      | 1.4     | 2.5    | 3.3    | 0.5          | 20.4     |
|             | After PCE | 12.9    | 1.4    | 2.5    | 1.1          | 0.0      |
| O-Ohio 5/6  | 1.8       | 0.0     | 1.4    | —      | 3.4          | 6.6      |
|             | After PCE | 1.3     | 0.0    | 1.5    | —            | 1.5      |

F-IBC-104 = fresh IBC-104 coal sample, >5Y-IBC-104 = long-term oxidized IBC-104 coal sample, O-Ohio 5/6 = oxidized Ohio 5/6 coal sample, — = not detected

**Table 7** Analysis of sulfur forms by XANES in three oxidized coals before and after PCE desulfurization.

| Coal        | Weight % in different forms (XANES) |          |                |           |         |       |          |
|-------------|-------------------------------------|----------|----------------|-----------|---------|-------|----------|
|             | Total sulfur weight%                | Pyritic* | S <sup>0</sup> | O-Sulfide | Thioph. | Oxid. | Sulfatic |
| 2W-IBC-104  | 3.97                                | 2.17     | 0.00           | 0.61      | 1.07    | 0.00  | 0.12     |
| After PCE   | 3.98                                | 2.18     | 0.00           | 0.61      | 1.12    | 0.00  | 0.07     |
| >5Y-IBC-104 | 4.11                                | 1.40     | 0.17           | 0.54      | 0.86    | 0.13  | 1.01     |
|             | After PCE                           | 3.31     | 1.40           | 0.00      | 0.56    | 0.88  | 0.07     |
| O-Ohio 5/6  | 3.50                                | 0.79     | 0.26           | 0.50      | 1.00    | 0.14  | 0.81     |
|             | After PCE                           | 2.79     | 0.87           | 0.00      | 0.54    | 1.04  | 0.04     |

\*Total sulfur and pyritic sulfur determinations from ASTM

S<sup>0</sup> = elemental sulfur, O-Sulfide = organic sulfide, Thioph. = thiophenic sulfur, Oxid. = oxidized organic sulfur, 2W-IBC-104 = two-week oxidized IBC-104 coal sample, >5Y-IBC-104 = long-term oxidized IBC-104 coal sample, O-Ohio 5/6 = oxidized Ohio 5/6 coal sample

during the short-term oxidation study that Ohio 5/6 coal is more likely to produce elemental sulfur than Illinois coal.

Least-squares sulfur K-edge X-ray absorption near edge structures (XANES) spectroscopy analysis was used to define the sulfur other than pyritic and sulfate sulfur into elemental sulfur ( $S^0$ ), organic sulfide (O-sulfide), thiophenic sulfur (Thioph.), and oxidized organic sulfur (Oxid.), such as sulfone and sulfoxide. Mössbauer spectroscopic analysis tends to have a larger determination error than the ASTM analysis. Thus, considering the most precise data on sulfur forms, we combined the data from XANES analysis with weight percentage of pyritic sulfur in coal from the ASTM analysis. The results are listed in Table 7. The data show that a two-week oxidation has little effect on elemental sulfur extraction, consistent with the HPLC analysis result. Data for the two-week oxidized sample, similar to the data from ASTM analyses, do not, however, exhibit any decrease in initial forms of organic sulfur (organic sulfide and thiophenic sulfur).

The five-year oxidized sample differs significantly from the two-week oxidized sample in that 35% of the pyritic sulfur has been oxidized to sulfate plus elemental sulfur. In addition, the initial forms of organic sulfur (organic sulfide and thiophenic sulfur) appear to be 10% lower in the five-year oxidized sample than in the two-week oxidized sample, suggesting that some organic sulfur may have been oxidized. The XANES data also indicate that PCE treatment removes all the elemental sulfur and about half of the oxidized organic sulfur. The apparent difference in sulfate content before and after PCE extraction is attributed to the dechlorination step after the PCE treatment, which also removes soluble sulfates.

The oxidized Ohio 5/6 sample behaves similarly to the >5Y-IBC-104 coal in that the PCE treatment removes all the elemental sulfur and some oxidized organic sulfur (from 0.14–0.04%). The PCE treatment has little or no effect on other forms of sulfur. Similar to the oxidized >5Y-IBC-104 coal sample, the large decline in sulfate content in oxidized Ohio 5/6 is again attributed to the dechlorination process conducted after PCE extraction.

Table 8 lists XANES results, as well as results from ASTM, SEM-EDX, and HCl/LAH analyses. Sulfur other than pyritic and sulfatic sulfur was graphed as organic sulfur versus the method of analysis shown in figure 2. The amount of organic sulfur in coal samples before and after PCE extraction was examined and compared with that from ASTM analysis.

As mentioned earlier, XANES analysis can differentiate sulfur, other than pyritic and sulfate sulfur, into elemental sulfur ( $S^0$ ), organic sulfide (O-sulfide), thiophenic sulfur (Thioph.), and oxidized organic sulfur (Oxid.), such as sulfone and sulfoxide. The organic sulfur shown for XANES (A) in figure 2 contains only the initial forms of organic sulfur. The organic sulfur shown for XANES (B) in figure 2 contains the initial forms of organic sulfur plus elemental sulfur and oxidized form of organic sulfur. The XANES (A) graph does not indicate a reduction of the initial forms of organic sulfur by PCE extraction for either Illinois or Ohio coal.

XANES (B) graph (fig. 2), however, shows some level of organic sulfur removal by PCE extraction. The amount of organic sulfur removed from the Ohio coal sample is greater than that removed from the Illinois coal sample. These trends in organic sulfur variation shown for XANES (B) are similar to those observed by the ASTM analysis. This similarity suggests that the higher elemental sulfur content of the Ohio coal provides more sulfur that can be extracted by the PCE, and results in a higher apparent level of organic sulfur removal by the ASTM analysis. The O-Ohio 5/6 coal contains 0.26% elemental sulfur and >5Y-IBC-104 contains 0.17% elemental sulfur.

**Table 8** Overall data obtained from ASTM, SEM-EDX, HCl/LAH, and XANES analyses.

| Sample      | Method    | Weight % on moisture-free whole coal basis |                   |                   |
|-------------|-----------|--|-------------------|-------------------|
|             |           | Sulfatic                                   | Pyritic           | Organic           |
| >5Y-IBC-104 | SEM       |  |                   | 2.30              |
|             | ASTM      | 0.87                                       | 1.40              | 1.84              |
|             | HCl/LAH   | 0.90                                       | 1.48              | 1.59              |
|             | XANES (A) | 1.01                                       | 1.40 <sup>®</sup> | 1.40 <sup>a</sup> |
|             | XANES (B) |  |                   | 1.70 <sup>b</sup> |
| After PCE   | SEM       |  |                   | 2.00              |
|             | ASTM      | 0.25                                       | 1.40              | 1.66              |
|             | HCl/LAH   | 0.27                                       | 1.43              | 1.68              |
|             | XANES (A) | 0.40                                       | 1.40 <sup>®</sup> | 1.44 <sup>a</sup> |
|             | XANES (B) |  |                   | 1.51 <sup>b</sup> |
| O-Ohio 5/6  | SEM       |  |                   | 2.20              |
|             | ASTM      | 0.63                                       | 0.79              | 2.08              |
|             | HCl/LAH   | 0.66                                       | 0.96              | 1.59              |
|             | XANES (A) | 0.81                                       | 0.79 <sup>®</sup> | 1.50 <sup>a</sup> |
|             | XANES (B) |  |                   | 1.90 <sup>b</sup> |
| After PCE   | SEM       |  |                   | 2.40              |
|             | ASTM      | 0.28                                       | 0.87              | 1.64              |
|             | HCl/LAH   | 0.13                                       | 0.86              | 1.72              |
|             | XANES (A) | 0.30                                       | 0.87 <sup>®</sup> | 1.58 <sup>a</sup> |
|             | XANES (B) |  |                   | 1.62 <sup>b</sup> |

<sup>®</sup> Pyritic sulfur from ASTM analysis

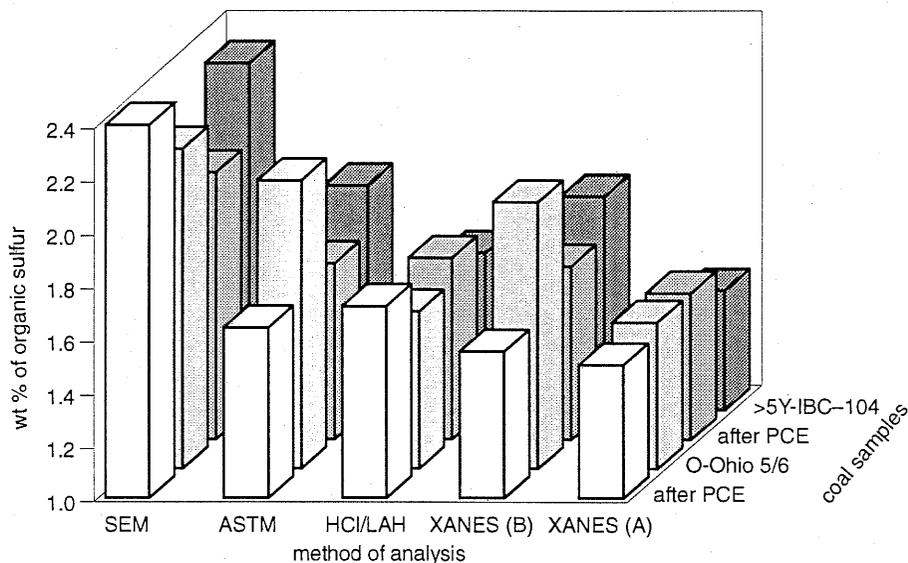
<sup>a</sup> Organic sulfide and thiophenic sulfur

<sup>b</sup> Organic sulfide, thiophenic, elemental, and oxidized organic sulfur

About 21% of the organic sulfur was removed from the O-Ohio 5/6 coal and 10% of the organic sulfur was removed from the Illinois coal during the ASTM analysis. If all or part of this elemental sulfur in the coal originated from sources other than organic sulfur, then any elemental sulfur in a coal will complicate the evaluation of the PCE process by the ASTM analysis.

The XANES data show no removal of either organic sulfide or thiophenic sulfur, but they show a total removal of the elemental sulfur.

The organic sulfur variation obtained from HCl/LAH analysis is fairly similar to that indicated by the XANES (A). The data show no organic sulfur reduction with respect to the PCE extraction. A reduction does not occur because during HCl/LAH analysis, elemental sulfur in the coal was



**Figure 2** Organic sulfur in coals before and after PCE extraction as a function of analytical method.

first removed by LAH digestion during the pyrite determination. Thus, the organic sulfur obtained from HCl/LAH analysis consists mainly of initial forms of organic sulfur. Similarly, organic sulfur in XANES (A) represents only initial forms of organic sulfur. The data obtained from the HCl/LAH analysis confirm those obtained from the XANES (A) analysis.

The results of the SEM-EDX analyses show a slight loss of organic (plus elemental) sulfur in the Illinois coal after PCE extraction; however, for the Ohio coal, a slight increase was observed. This difference is thought to be due to the enhanced amount of elemental sulfur that formed in the more readily oxidized Ohio sample. While this method of analysis is not well suited to evaluate the PCE extraction process, the data do not support a significant loss of organic sulfur in the extracted residue.

### Preoxidation

In addition to ambient oxidation, PCE desulfurization under various short-term oxidation conditions, including those recommended by the MWOPC (Atwood, et al. 1990, task 4) were examined. As mentioned earlier, XANES data indicate that no initial forms of organic sulfur removal occur during PCE extraction. PCE extraction simply dissolves elemental sulfur from the coal sample. Thus, HPLC analysis of elemental sulfur was used as a method to evaluate the effect of preoxidation conditions on PCE extraction.

All the short-term preoxidation-PCE extraction experiments were conducted by oxidizing in the presence of PCE. Table 9 shows short-term oxidation conditions and oxidation results for a fresh IBC-104 coal, an oxidized Ohio coal, two oxidized Illinois coals, and a mineral pyrite. The fresh IBC-104 had 0.01% of elemental sulfur in the PCE extract before short-term oxidation. This sample shows no increase in elemental sulfur content in the PCE extract after bubbling air into a PCE coal slurry for 2 hours with or without trace amounts of SO<sub>2</sub> at room temperature. When the experiment was conducted at 90°C, with water present, the production of elemental sulfur doubled. The production of elemental sulfur was further increased four-fold by

**Table 9** Effects of oxidation condition on amounts of elemental sulfur removed by PCE extraction.

| Starting coal  | PCE/H <sub>2</sub> O<br>(mL/mL) | Oxidation method                | Time      | Temp.(°C)  | S°<br>% |
|----------------|---------------------------------|---------------------------------|-----------|------------|---------|
| F-IBC-104      | 100/0                           | None                            | —         | —          | 0.01    |
| F-IBC-104      |                                 | Long-term ambient air oxidation | > 5 years | Room temp. | 0.07    |
| F-IBC-104      | 100/0                           | Bubbling air, 20 ml/sec         | 2 hours   | 24         | 0.01    |
| F-IBC-104      | 100/0                           | Bubbling air/SO <sub>2</sub>    | 2 hours   | 24         | 0.01    |
| F-IBC-104      | 100/20                          | Bubbling air, 20 ml/sec         | 2 hours   | 90         | 0.02    |
| F-IBC-104      | 100/20                          | Bubbling air/SO <sub>2</sub>    | 2 hours   | 90         | 0.04    |
| F-IBC-104      | 100/20                          | Bubbling air/SO <sub>2</sub>    | 20 hours  | 90         | 0.18    |
| >5Y-IBC-104    | 100/0                           | None                            | —         | —          | 0.07    |
| >5Y-IBC-104    | 100/20                          | Bubbling air, 20 ml/sec         | 2 hours   | 90         | 0.10    |
| >5Y-IBC-104    | 100/20                          | Bubbling air/SO <sub>2</sub>    | 2 hours   | 90         | 0.13    |
| O-Ohio 5/6     | 100/0                           | None                            | —         | —          | 0.13    |
| O-Ohio 5/6     | 100/20                          | Bubbling air, 20 ml/sec         | 2 hours   | 90         | 0.10    |
| O-Ohio 5/6     | 100/20                          | Bubbling air/SO <sub>2</sub>    | 2 hours   | 90         | 0.35    |
| O-IBC-101      | 100/0                           | None                            | —         | —          | 0.06    |
| O-IBC-101      | 100/0                           | Bubbling air, 20 ml/sec         | 2 hours   | 90         | 0.06    |
| O-IBC-101      | 100/0                           | Bubbling air/SO <sub>2</sub>    | 2 hours   | 90         | 0.10    |
| O-IBC-101      | 100/20                          | Bubbling air, 20 ml/sec         | 2 hours   | 90         | 0.10    |
| O-IBC-101      | 100/20                          | Bubbling air/SO <sub>2</sub>    | 2 hours   | 90         | 0.11    |
| Mineral pyrite | 100/0                           | None                            | —         | —          | 0.02    |
| Mineral pyrite | 100/0                           | Bubbling air, 20 ml/sec         | 2 hours   | 90         | 0.02    |
| Mineral pyrite | 100/20                          | Bubbling air, 20 ml/sec         | 2 hours   | 90         | 0.02    |
| Mineral pyrite | 100/0                           | Bubbling air/SO <sub>2</sub>    | 2 hours   | 90         | 0.03    |
| Mineral pyrite | 100/20                          | Bubbling air/SO <sub>2</sub>    | 2 hours   | 90         | 0.05    |

F-IBC-104 = fresh IBC-104 coal, O-IBC-101 = slightly ambient-oxidized IBC-101 coal

S° % = elemental sulfur by HPLC analysis of PCE extracts, in weight %, moisture-free, whole-coal basis

the addition of a small amount of SO<sub>2</sub> as an oxidant. Furthermore, when the duration was extended from 2 to 20 hours, the amount of elemental sulfur produced increased 18 times.

The oxidation sensitivities of Illinois IBC-104 coal and Ohio 5/6 coal were compared by using the two ambient-oxidized coal samples for the short-term oxidation. The ambient-oxidized IBC-104 coal (>5Y-IBC-104) had 0.07% elemental sulfur in the PCE extract before further oxidation (table 9). The experimental sulfur content was slightly increased from 0.07% to 0.10% by bubbling air under moist conditions for 2 hours at 90°C. Under the same conditions, the amount of elemental sulfur produced was further increased from 0.10% to 0.13% by adding a

small amount of SO<sub>2</sub> oxidant. Overall, the amount of elemental sulfur in the sample was increased about two-fold.

The ambient-oxidized Ohio 5/6 coal (O-Ohio 5/6) had 0.13% elemental sulfur in the PCE extract before further oxidation (table 9). Oxidation under conditions similar to those used for the O-Ohio 5/6 coal sample with a small amount of SO<sub>2</sub> present increased the elemental sulfur content in the sample from 0.13% to 0.35%. Overall, the amount of elemental sulfur production in the O-Ohio 5/6 coal sample was increased almost three-fold. These results indicate that the Ohio 5/6 coal appeared to produce elemental sulfur more readily than the Illinois coal during oxidation.

To determine the possible source of elemental sulfur generated during coal oxidation, a sample of pure mineral pyrite was subjected to short-term oxidation. The sample before short-term oxidation had 0.02% elemental sulfur in the PCE extract (table 9). After treatment with bubbling air for 2 hours at 90°C with and without water present, the sample had no increase in elemental sulfur production. With a small amount of SO<sub>2</sub> present and no water, the concentration of elemental sulfur increased slightly from 0.02% to 0.03%. With both SO<sub>2</sub> and water present, however, the elemental sulfur concentration increased from 0.03% to 0.05%.

Overall, these experiments demonstrated that oxidation increased the amount of elemental sulfur in coal that could then be extracted by PCE. The amount of elemental sulfur produced in coal during oxidation is related to reaction temperature, moisture conditions, and the presence of oxidant. These are three key operation variables reported or implied by Lee, et al. (1990) at Akron; Leehe, et al. (1990) at the MWOPC; and G. Atwood (personal communication 1990). The Ohio 5/6 coal appeared to produce elemental sulfur more readily than Illinois coal during oxidation. Also, pyrite oxidation probably contributed to some of the elemental sulfur, extracted by PCE treatment, in the coals.

The source of the increased elemental sulfur and the identity of the pyritic and organic sulfur in the sample treated with the SO<sub>2</sub> oxidant that we introduced are currently under investigation.

### **Dechlorination**

If PCE is used for desulfurization, dechlorination of the PCE-treated coal is also required for the process to succeed. As indicated in table 10, the raw fresh coal, (F-IBC-104) has a chlorine content of 0.03%. The PCE-treated coal (F-IBC-104-PCE), without application of any dechlorination procedure, can have a chlorine content as high as 4.68%. When hot water washing was used in the dechlorination step, the resultant coal had a chlorine content of 2.96%. The University of Akron used steam dechlorination on an Illinois coal, and the reported chlorine content for that coal was 0.9% (Atwood and Leehe 1991). These chlorine contents are too high for the coals to be used in an industrial utility boiler. We have developed a procedure (ISGS method) in which PCE-treated coal is washed sequentially with hot methanol, water, and acetone. The procedure can remove the excess PCE and yield a coal with a chlorine content as low as the original coal, 0.03% (table 10).

**Table 10** Dechlorination of PCE-treated coals.

| Sample          | Method of washing | Total chlorine (%) |
|-----------------|-------------------|--------------------|
| F-IBC-104       |                   | 0.03               |
| F-IBC-104-PCE   | none              | 4.68               |
| F-IBC-104-PCE   | Hot water         | 2.96               |
| F-IBC-104-PCE   | Hot methanol      | 0.17               |
| F-IBC-104-PCE   | ISGS method       | 0.03               |
| >5Y-IBC-104-PCE | ISGS method       | 0.03               |

## SUMMARY AND CONCLUSIONS

Results of the MWOPC study were duplicated in our tests for fresh IBC-104 coal. Oxidation of coals was found to affect PCE desulfurization. Elemental sulfur is more amenable to removal by PCE desulfurization than initial forms of organic sulfur. Ohio 5/6 coal appears to produce elemental sulfur more readily than Illinois coal during oxidation. The higher elemental sulfur content in the coal results in higher organic sulfur removal by PCE extraction as measured by the ASTM forms-of-sulfur method. Results of mass balance calculations indicate that 96% of the total sulfur and more than 95% of the total iron can be accounted for in both the long-term ambient-oxidized IBC-104 coal and the ambient-oxidized Ohio 5/6 coal during PCE desulfurization.

Results of the oxidation studies show that the increase in elemental sulfur is related to reaction temperature, moisture conditions, and the presence of oxidant. These key operating variables were reported or implied by Lee, et al. (1990) at Akron, and Leehe, et al. (1990) at MWOPC. The elemental sulfur produced during air oxidation appears to originate from pyrite oxidation. This elemental sulfur complicates the process evaluation concerning organic sulfur removal by ASTM analysis. The source of the increased elemental sulfur and the identity of the pyritic and organic sulfur in the sample treated with an oxidant that we introduced are currently under investigation.

PCE-treated coals contain high residual chlorine content. An effective dechlorination procedure was discovered for PCE removal, which yields a coal with chlorine content as low as 0.03%.

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