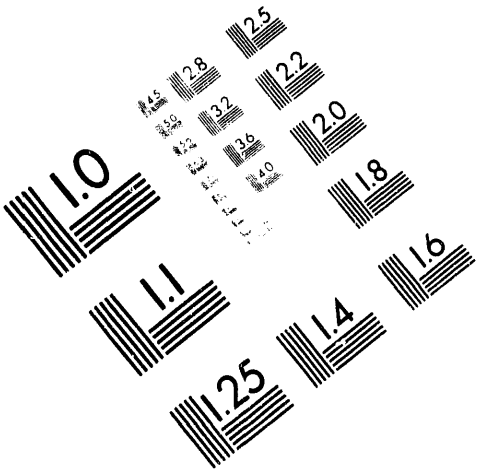

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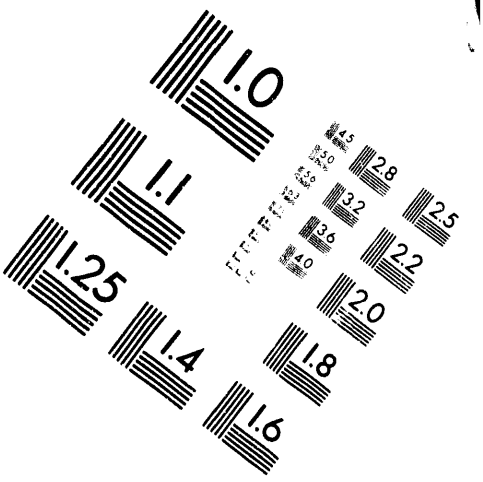

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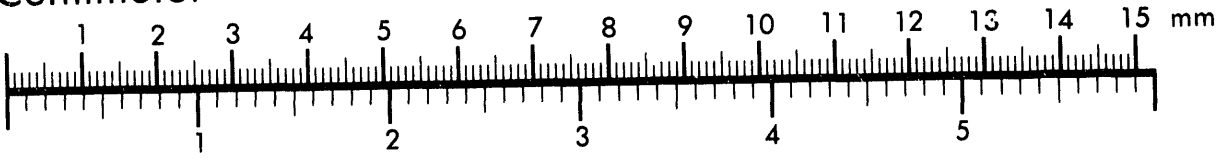

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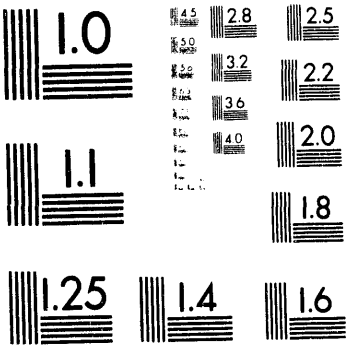

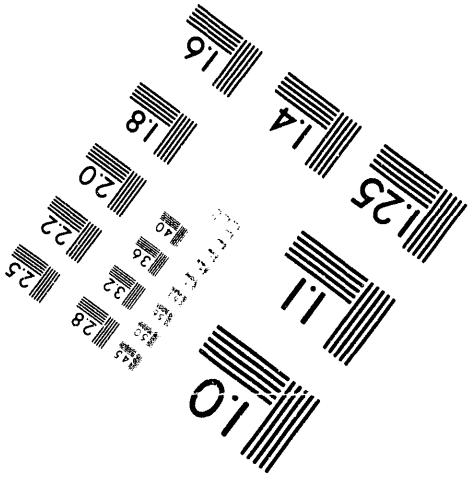

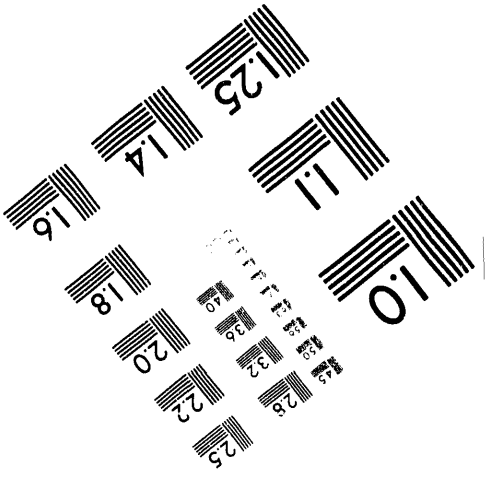

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ANNUAL REPORT

September 1, 1991 - August 31, 1992

DE-FC22-92PC92521

Project Titled: SULFUR REMOVAL FROM HIGH-SULFUR ILLINOIS COAL BY LOW-TEMPERATURE PERCHLOROETHYLENE (PCE) EXTRACTION

Principal Investigator: M.-I. M. Chou, Illinois State Geological Survey (ISGS)

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Project Manager: D.D. Banerjee (CRSC)

ABSTRACT

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

MWOPC's results have been repeated on our tests for the fresh IBC-104 coal. Oxidation of coals was found to affect subsequent PCE desulfurization. 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, whereas, sulfate in a sample of oxidized Ohio 5/6 coal occcurs mainly as szomolnokite ($FeSO_4 \cdot H_2O$). These data suggest that the oxidation reaction for Ohio 5/6 coal might occur under catalytic conditions which readily convert pyrite to produce $FeSO_4$ and elemental sulfur. The higher elemental sulfur content in the Ohio 5/6 coal results in higher ASTM apparent organic sulfur removal by PCE extraction. From mass balance calculations, 96% of the total sulfur and more than 95% of total iron were accounted for during our PCE tests with both long-term ambient-oxidized IBC-104 coal and ambient-oxidized Ohio 5/6 coal. The amount of elemental sulfur generated during short-term oxidation of coal or pyrite in this study is controlled by reaction temperature, moisture conditions, and an oxidant we introduced. 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 depending on ASTM analysis alone.

A procedure was developed to wash PCE from the PCE-treated coals. This procedure produced coals with chlorine contents as low as 0.03%.

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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 Co. (MWOPC) has reported a precombustion desulfurization process operating at 120 °C using perchloroethylene (PCE) to remove up to 70% of the organic sulfur as elemental sulfur. The MWOPC stresses the importance of oxidation and drying conditions as well as temperature control. The process is effective in extracting organic sulfur and separating pyrite fines from coal by float-sink; the process can be operated at low temperatures with minimal loss of solvent (Leehe and Sehgal, 1988; Leehe, 1989; Lee et al., 1989) and was reported to effectively remove organic sulfur from high-sulfur coals obtained from Ohio and Indiana. However, it has not yet proven to be as successful with Illinois coals (Lee et al., 1989; Buchanan et al., 1990). The MWOPC process evaluation was based on interpretation of data obtained by the ASTM method for forms-of-sulfur determinations.

Over the past few years, the Illinois State Geological Survey (ISGS) and Eastern Illinois University (EIU) have jointly developed analytical methods to measure forms-of-sulfur in the PCE extracts from PCE extraction of high-sulfur Illinois coals. Some elemental sulfur and limited amounts of organic sulfur have been removed from oxidized Illinois coals during these studies; however, these sulfur removals (<32%) were much lower than those reported by the MWOPC (>43%). Several hypotheses may explain these differences, but until now, no experimental support has been reported. 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, which is 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, not organic sulfur removed by the 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 pyrite-derived form of iron not extractable by HCl but extractable by HNO_3. If so, this iron would be counted 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, making it appear that sulfur removed by PCE extraction is organic in nature, when it is not.

The goals of this research are: 1) to independently confirm and possibly to improve the organic sulfur removal from Illinois coals with the PCE desulfurization process clamed by the MWOPC, 2) to verify the forms-of-sulfur determination by the ASTM method in evaluating the PCE desulfurization process, and 3) to develop a procedure to remove excess

PCE from PCE-treated coals. This is a joint effort by the ISGS, EIU, the University of Illinois at Urbana/Champaign (UI-UC), and the University of Kentucky (UK). Tasks 1-5 were completed, and tasks 6-8 will be carried out next year.

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

Larger scale (50g) PCE desulfurizations on a short- and long-term ambient oxidized IBC-104 coal, and on an ambient oxidized Ohio 5/6 coal were conducted to obtain enough sample for ASTM analysis, non-ASTM sulfur analyses and a mass balance analysis. The data from non-ASTM sulfur analyses including XANES analysis were examined and compared to that of the ASTM analysis. XANES analyses indicate that long-term ambient oxidation may have oxidized some organic sulfur in coal, and that PCE desulfurization removes all the elemental sulfur from coals. The results also suggest that no organic sulfide nor thiophenic forms of organic sulfur in coal were removed by PCE. This is supported by the data from a wet chemical analysis which uses a lithium aluminum hydride reduction to delineate the interference of elemental sulfur during a combustion technique for the determination of organic sulfur.

Mineralogical determination by x-ray diffraction indicate that sulfate in long-term ambient oxidized IBC-104 coal exists mainly as gypsum, whereas, sulfate in oxidized Ohio 5/6 coal exists mainly as szomolnokite ($FeSO_4$, H_2O). These data suggest that the ambient oxidation reaction for Ohio 5/6 coal might occur under catalytic conditions which readily convert pyrite to produce $FeSO_4$ and elemental sulfur. This interpretation also supports the observation that Ohio 5/6 coal appears to more readily produce elemental sulfur than Illinois coal during short-term oxidation. Oxidation of coals was found to facilitate subsequent PCE desulfurizations, and the higher elemental sulfur content in that coal results in higher apparent removal of organic sulfur by PCE extraction when 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 both long-term ambient-oxidized 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. These are three key operating variables reported or claimed by Lee, et al., at the University of Akron, and Leehe, et al., 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 depending on the ASTM method of analysis alone. The source of the increased elemental sulfur and the nature of the pyritic and organic sulfur in the sample treated by the technique using an oxidant we introduced are currently under investigation.

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

DISCLAIMER

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OBJECTIVES

The goals of this research are: 1) to independently confirm and possibly improve the removal of organic sulfur from Illinois coals with the perchloroethylene (PCE) process developed by the MWOPC, 2) to verify the ASTM method for forms-of-sulfur determination, and 3) to 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 are:

A. To conduct the PCE desulfurization of two coals [IBC-104 (Illinois Basin Coal Sample Program); Ohio 5/6 coal(Horizon Coal Company)] under the proper process conditions.

B. To carry out an extensive material balance study on the feed materials and products from the two coals tested in the PCE desulfurization process.

C. To conduct non-ASTM analyses and compare the results with those from the ASTM method for forms-of-sulfur.

D. To investigate coal oxidation chemistry and its effect on the mechanisms of sulfur removal by the PCE desulfurization process.

E. To examine the role that pyrite in coal plays during the PCE desulfurization process and its influence, if any, on process optimization.

F. To evaluate and possibly improve the effectiveness of the PCE desulfurization process for Illinois coals.

BACKGROUND

MWOPC has 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). Process studies, partially supported by the Electric Power Research Institute (EPRI), have been made in a pilot plant of one ton/day capacity by MWOPC at Plainville, IN. In addition, a mini-pilot plant of five-lb/hr capacity is being operated at The University of Akron (UA, Lee, et al., 1989). Results from the mini-pilot plant indicated that the PCE process effectively extracts organic sulfur, and is equally effective in separating pyrite fines from coal. The process is reported to operate 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. Efficiency of organic sulfur removal is affected by the initial moisture content of the coal (Fullerton, et al., 1990). A "catalyst" involved in the process, which

renders organic sulfur more accessible to the PCE extraction, has been suggested (personal communication to PI, G.A. Atwood, MWOPC, 1991). This process has been found to effectively remove organic sulfur from high-sulfur coals obtained from Ohio and Indiana. However, it has not proven to be as successful with Illinois coals (Lee, et al., 1989).

A cooperative study (Buchanan, et al., 1990) between EIU (Buchanan) and ISGS (Chaven and Hackley) was initiated in 1988. The procedure developed was different from that of MWOPC in that (-60 mesh) coals were used without preoxidation prior to PCE extraction. Also, these experiments were mainly conducted in a Soxhlet extraction apparatus using a small sample size (1-24g) as compared to the other experiments in which 50g or more was used. The authors concluded that the source of the elemental sulfur extracted from coal by PCE under these conditions was pyrite and that little organic-sulfur was removed (Buchanan, et al., 1990). These results differ from those of MWOPC's study in which as much as 43% removal of organic sulfur from an Illinois coal was reported (Buchanan, et al., 1990).

The differences between the results of the MWOPC and EIU/ISGS may have been due to the use of different process conditions such as 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. It could also decrease the consistency of the temperature control. However, we have postulated that some 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 pyrite-derived iron might be left behind. This iron might remain insoluble in HCl but soluble in HNO_3 during ASTM analysis. In this case, a portion of the iron no longer associated with sulfur would be calculated as pyrite. Because the elemental sulfur would have been 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 interpretation of the results from the ASTM method, making it appear that the PCE extraction removed organic sulfur (Buchanan, 1990). These hypotheses need verification.

EXPERIMENTAL PROCEDURES

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

Task 1: Processing of Illinois Coals and a Mass Balance Study (ISGS/EIU) - The purpose of this task was to perform PCE desulfurization on the selected Illinois coal under conditions described by the MWOPC procedures. Thus, the products from before and after PCE extraction can be used 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, one from the Illinois Basin Coal Sample Program (IBC-104) and the other from the Horizon Coal Company (Ohio 5/6 coal) were selected for this task. Coal selection was based on the availability of the samples and on the desulfurization data reported by the MWOPC and the UA. This 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. A flow diagram for the PCE batch extraction is shown in Figure 1. Coal samples were ground at room temperature to 60 mesh. The coal sample was fed into the 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 (50g) on one short-term oxidized IBC-104 coal, one long-term oxidized IBC-104 coal, and one oxidized Ohio 5/6 coal were completed during the second quarter. The feeds and products from these scale-up operations were split and distributed to co-investigators for independent analyses (Task 2) and a mass balance analysis (Task 1.2). In addition, a procedure for removing chlorine from the PCE-processed coals was developed.

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_2 (Pasiuk-Bronikowsa, et. al., 1989) through a coal/PCE slurry with or without water added. The reaction was conducted at various temperatures from room temperature to 90 °C and for durations ranging from 2-20 hours. After oxidation, the temperature was increased to 120 °C and maintained at this temperature for 30 minutes. The extracts produced from PCE extraction were then isolated from the residues by hot filtration.

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

Chlorine content of the feeds, and product coals was measured with 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 using the ASTM D-2492 procedure (1991).

In the forms-of-sulfur examination by the ASTM method D2492 the (-60 mesh) sample was first digested with a dilute HCl solution. The acidic solution was filtered and sulfatic sulfur was precipitated and quantified as $BaSO_4$. After washing with distilled water, the HCl-free residue was digested with dilute HNO_3. The suspension was filtered and the filtrate was adjusted to volume for atomic absorption (AA) determination of iron. The iron content

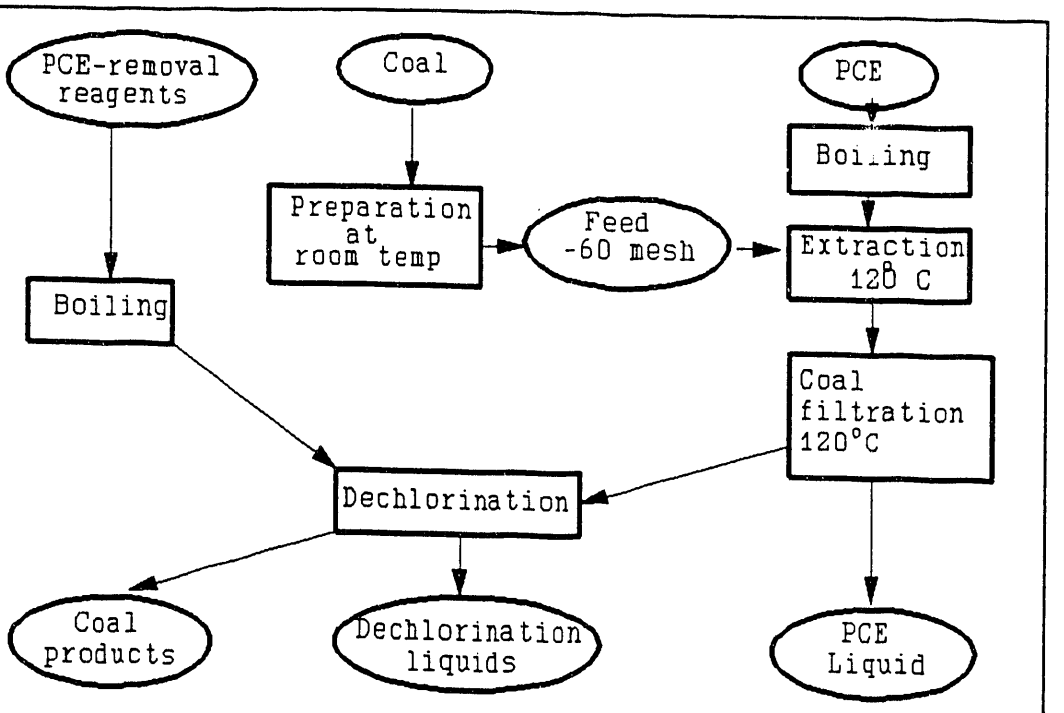

Figure 1. Flow Diagram for PCE Batch Extraction

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 which was used to monitor 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 is counted as organic sulfur, since it was not reported as pyritic or sulfatic sulfur.

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

Total iron contents in feeds and in solid products were obtained after fusion of the ashed sample in lithium metaborate. The sample was ashed at 750 °C for 20-24 hours or until no carbonaceous residue remains. The prepared ashes were fused with lithium tetraborate (a mixture of one part ash by weight and nine parts of $Li_2B_4O_7 \cdot 5H_2O$ by weight) in platinum crucibles at 1000 °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 (ISGS/UI-UC/UK) - The purpose of Tasks 2.1-2.5 was to examine the transformation or removal of pyritic sulfur, aliphatic sulfur, and aromatic sulfur during PCE desulfurization. The data collected from these tasks allowed us to explore the identity of organic sulfur removed by PCE extraction and that of ASTM forms-of-sulfur analysis.

Task 2.1: A Wet-Chemical Analysis (HCl/LAH) (ISGS) - This method, which combines a lithium aluminum hydride (LAH) reduction technique for the direct determination of pyritic sulfur and a combustion technique for the determination of organic sulfur (Westgate and Anderson, 1982; Liu,et al., 1987), 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 first dried and then sulfatic sulfur was extracted using a dilute HCl solution. The acidic solution was filtered and sulfatic sulfur precipitated as $BaSO_4$. If any mono-sulfide sulfur was present, it was released as H_2S during the HCl leaching step and precipitated as Ag_2S (Liu, et al., 1987). To remove pyritic sulfur, the HCl-leached coal residue was treated with LAH. The pyritic sulfur was released as H_2S, trapped, and precipitated as Ag_2S. Any elemental sulfur present in the residue was reported as pyritic sulfur. The sulfur remaining in the HCl/LAH-leached coal residue is assumed to be organic sulfur. To obtain the organic sulfur, the LAH-leached residue was combusted in a high temperature furnace. Organic sulfur was oxidized to SO_2, trapped and precipitated as $BaSO_4$. The amount of each form of sulfur was then calculated based on the quantities of $BaSO_4$ and Ag_2S obtained from each extraction. An analysis of total sulfur, independent of the cumulative total from the HCl, LAH, and oxidation procedure, was also determined by high-temperature combustion (HTC). The forms of sulfur were reported on a dried basis as wt% sulfur.

Four non-destructive spectroscopic techniques (Tasks 2.2-2.5) were used for determining 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 (XANES) (UK) - This method was developed (Huffman, et al., in press) for the quantitative determination of all major sulfur forms in coal, both organic and inorganic. The method is based on the least-squares analysis and deconvolution of the x-ray absorption near-edge structure, or XANES, into a series of peaks that represent 1s → np photoelectron transitions. The major sulfur forms occurring in coal (pyrite, organic sulfide, thiophene, sulfoxide, sulfone, and sulfate) have characteristic s → 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. Because the XANES signal is derived from the bulk of the sample, detailed information concerning various groups of organic sulfur removed during PCE desulfurization were obtained.

Task 2.3: X-Ray Diffraction (XRD) - The XRD method has been widely used as a reliable technique for the identification of mineral matter in coals. The coal samples received for 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 removing the organic fraction by low temperature ashing. Determination of pyrite, various iron sulfides and sulfates, clay minerals, and other common non-clay minerals were performed (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 (UI-UC) - Mössbauer spectroscopy was used to differentiate the Fe sulfide/sulfate species present in feed, oxidized, and PCE-treated coal samples. By comparing isomer shifts, quadrupole splitting, and magnetic hyperfine fields of the spectral components obtained, the minerals pyrite (FeS_2), troilite (FeS), and pyrrhotite (Fe_xS_y, where x:y varies between approximately 0.8 and 0.95), which display very different Mössbauer spectroscopic features, are discernible in mixed samples. Pyrite in feed, intermediate, and final products was determined at room temperature. The instrument used is also capable of variable temperature and 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 with a 50 mCi ^{57}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), which assumed Lorenzian line shapes.

Task 2.5: Scanning Electron Microscopy and Energy Dispersive X-Ray Fluorescence Analysis (SEM-EDX) - SEM-EDX was used to determine non-pyritic 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 with a scanning electron microscope equipped with an energy dispersive x-ray analyzer (SEM-EDX).

Sulfur determinations were made at representative spot locations within each selected maceral. The spots were approximately 1-4μm across and possibly 3-5μm 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 and the resultant value includes any elemental sulfur that is present in the tested sample. The determined value is on the dry mineral-matter-free basis and was converted to the whole coal basis by the commonly used Parr equation. This equation uses the ash and total sulfur values from routine ASTM analyses.

<u>Task 3: Evaluating the Effectiveness of Using the PCE Desulfurization Process on the Selected Illinois Coal, and Verifying the ASTM Forms of Sulfur Analyses (ISGS/EIU/UI-UC/UK)</u> - The data obtained from Tasks 1 and 2 on sulfur removal for the two coals processed 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 2.2-2.5) 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 (EIU/ISGS) - The purpose of this task was to determine the effects that various process conditions have on PCE desulfurization. The study on the effects of ambient oxidation on the 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 were described in Task 1.1.

Conducting PCE desulfurization under proprietary preoxidation conditions will be extended into the second year for more detailed fundamental and application studies.

Task 5: Evaluating the Parameters Studied and Their Effect on Process Optimization (ISGS/EIU/UI-UC/UK) - This task was completed in the first year for the fresh and ambient oxidized samples. The results of the ASTM forms-of-sulfur analyses in oxidized coals were compared with those in the non-oxidized coal. The effects that preoxidation conditions have on sulfur removal during PCE extraction were assessed.

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

RESULTS AND DISCUSSION

Confirmation Study

Preliminary PCE Desulfurization Based on ASTM Analysis - Shown in Table 1 are the ASTM analysis results of an Illinois No. 6 coal before and after PCE extraction. The Illinois coal sample, which was processed by the developer, University of Akron (shown on the top: UA), is comparable to the fresh IBC-104 coal used by this investigation (shown on the bottom: ISGS/EIU). The data of the University of Akron show a removal of 5% for total sulfur content and a decrease of 12% in the ASTM organic sulfur content. From this investigation, the ASTM data on fresh IBC-104 coal show a total sulfur removal of 4-9% and an organic sulfur removal of 9-14%. These data confirm that we have repeated the developer's results on our tests for fresh IBC-104 coal based on the ASTM analysis.

Table 1. Wt% sulfur on moisture-free whole coal basis

	ASTM			
Sample	Sulfatic	Pyritic	Organic	Total
UA				
Illinois #6(F-IBC-104)	0.01	2.54	1.55	4.10
After PCE	0.01	2.52	$1.36^{-12\%}$	$3.89^{-5\%}$
ISGS/EIU				
F-IBC-104	0.07	2.22	1.94	4.23
After PCE,I	0.04	2.24	$1.77^{-9\%}$	$4.05^{-4\%}$
After PCE,II	0.04	2.15	$1.66^{-14\%}$	$3.85^{-9\%}$

F-IBC-104, fresh IBC-104 coal sample

Oxidation and PCE Desulfurization Based on HPLC Analysis - PCE desulfurization was also evaluated based on 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 extractable elemental sulfur obtained from a long-term ambient oxidized IBC-104 coal is 25-75 times greater than that from the unoxidized or short-term oxidized coal samples. These results confirm that preoxidation is important to PCE desulfurization.

Scale-Up PCE Desulfurization - A larger scale (50g) PCE desulfurization was conducted on three oxidized coal samples (Task 1.1). The purpose of this scale-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 are 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 the results of the ASTM analyses of the feed coals and the treated coals and the HPLC analyses of the PCE extracts. The data indicate that the extractable elemental sulfur obtained from the two highly oxidized coal samples is greater than that from the mildly oxidized sample. The sample from 2W-IBC-104 oxidation shows no detectable amount of elemental sulfur in the PCE extract. However, the two samples from a long-term ambient oxidation (>5Y-IBC-104 and O-Ohio 5/6) show a noticeable amount of elemental sulfur in the PCE extracts. The elemental sulfur of 0.07% was extracted from >5Y-IBC-104 and the elemental sulfur of 0.10% was extracted from O-Ohio 5/6 sample.

The ASTM data also show a greater reduction in organic sulfur after PCE extraction for the highly oxidized coal samples. These results are consistent with those obtained from the smaller scale extractions. The sample from two weeks oxidation shows no total sulfur removal. A slight increase in organic sulfur content of this sample shown by ASTM analysis is attributed to an error of the ASTM analysis. 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 from the two-week oxidized samples by PCE extraction may be too small to offset this cumulative error. However, 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 total sulfur reduction of 20% and a noticeable organic sulfur reduction of 21%.

Table 2. Elemental Sulfur from PCE Extraction and ASTM Forms-of-Sulfur in Three Ambient Oxidized Coal Samples Before and After PCE Extraction

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

$^{-20\%}$, percent of reduction in total sulfur or organic sulfur

Based on ASTM analysis, the organic sulfur removed from the Ohio 5/6 coal is about twice as much as that removed from the Illinois coal. 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. From 0-Ohio 5/6 coal, 0.10% of elemental sulfur was extracted, and the sample shows a 21% of organic sulfur removal. From >5Y-IBC-104, 0.07% of elemental sulfur was extracted, and the data show that 10% of the organic sulfur was removed.

Mass Balance Analysis - Table 3 shows the sulfur mass balance data for the long-term oxidized IBC-104 coal and the oxidized Ohio 5/6 coal samples. 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 content. No elemental sulfur was detected in the dechlorination liquids. Organic sulfur in PCE and in the dechlorination liquids was not measured due to the absence of a reliable method. However, the data obtained (96% recovery) indicate a good sulfur mass balance for both long-term oxidized IBC-104 and oxidized Ohio 5/6 coals.

Table 3. Total Sulfur Mass Balance for the Long-Term Oxidized IBC-104 and Oxidized Ohio 5/6 Coal Samples

Long-term oxidized IBC-104 coal (100g)		Oxidized Ohio 5/6 (100g)	
Total sulfur before extraction, 4.11g		Total sulfur before extraction 3.5g	
PCE extract (S°)	0.07g	PCE extract (S°)	0.10g
Dechlorination reagent A	Not available	Dechlorination reagent A	Not available
Dechlorination reagent B	0.56g	Dechlorination reagent B	0.46g
Dechlorination reagent C	Not available	Dechlorination reagent C	Not available
Treated coal	3.31g	Treated coal	2.79g
Total Sulfur after extraction, 3.94g		Total Sulfur after extraction, 3.35g	
Percent of recovery 96%		Percent of recovery 96%	

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 4. Total Iron Mass Balance for the Long-Term Oxidized IBC-104 and Oxidized Ohio 5/6 Coal Samples

Long-term oxidized IBC-104 (100g)		Oxidized Ohio 5/6 (100g)	
Total Iron before extraction 2.76g		Total iron before extraction 1.57g	
PCE extract	Not available	PCE extract	Not available
Dechlorination reagent A	0.00g	Dechlorination reagent A	0.04
Dechlorination reagent B	0.08g	Dechlorination reagent B	0.47g
Dechlorination reagent C	Not available	Dechlorination reagent C	not available
Treated coal	2.60g	Treated coal	1.00g
Total iron after extraction 2.68g		Total iron after extraction 1.51g	
Percent of recovery 97%		Percent of recovery 96%	

Non-ASTM sulfur analyses - Several non-ASTM methods were used to analyze the two oxidized coal samples (>5Y-IBC-104 and 0-Ohio 5/6) before and after PCE extraction. Mössbauer spectroscopy and x-ray diffraction spectroscopy were applied for mineral matter analysis. SEM-EDX, HCl/LAH, and XANES analyses were applied mainly for organic sulfur determination. The results of these organic sulfur analyses were compared with that obtained from the ASTM analysis.

Data from both Mössbauer spectroscopy (Table 5) and x-ray diffraction spectroscopy (Table 6) indicate a loss of $Fe(II)SO_4$ in the product coals. This is because ferrous sulfate was removed 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 ($CaSO_4 \cdot 2H_2O$), whereas sulfate in 0-Ohio 5/6 sample is mainly in form of szomolnokite ($FeSO_4$, H_2O). These data suggest that the oxidation reaction for Ohio 5/6 coal might occur under Fe(III) catalytic conditions which readily convert pyrite to produce $FeSO_4$ and elemental sulfur. This interpretation seems to support the observation obtained during the short-term oxidation study that Ohio 5/6 coal is more likely to produce elemental sulfur than Illinois coal.

Table 5. Iron Analysis by Mössbauer Spectroscopy

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

IS, Isomer shift; D, Quadropole splitting; χ^2, Statistical parameter.

Table 6: Mineral Matter Composition by X-Ray Diffraction Analysis

Sample	Quartz	Calcite	Pyrite	Gypsum	Szomolnokite	Nonclays
			(Weight %)			
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	0.2	2.5	1.1	0.0	16.8
O-Ohio 5/6	1.8	0.0	1.4	-	3.4	6.6
After PCE	1.3	0.0	1.5	-	1.5	4.3

F-IBC-104: Fresh IBC-104 coal sample

Least-squares sulfur K-edge x-ray absorption near edge structures (XANES) spectroscopy analysis was used to resolve the sulfur other than pyritic and sulfate sulfur into elemental sulfur (S°), 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, the data from XANES analysis were

combined with wt% 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. However, the data for the 2-week oxidized sample, similar to the data from ASTM analyses, do not exhibit any decrease in initial forms of organic sulfur (organic sulfide and thiophenic sulfur).

Table 7: Analysis of Sulfur Forms by XANES in Three Oxidized Coals Before and After PCE Desulfurization

Coal	Total Wt% Sulfur*	Wt% sulfur in different forms (XANES)					
		Pyritic*	S°	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	0.40
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	0.30

*Total sulfur and pyritic sulfur determinations from ASTM.

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 (organic sulfide and thiophenic sulfur) of organic 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 is again attributed to the dechlorination step after PCE extraction.

XANES results as well as the results from ASTM, SEM-EDX, and HCl/LAH analyses are listed in Table 8. 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 the sulfur other than pyritic and sulfate sulfur into elemental sulfur (S^{o}), 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. On the other hand, 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. From the XANES (A) graph, no reduction of the initial forms of organic sulfur by PCE extraction for either Illinois coal or Ohio coal is indicated.

However, as shown for XANES (B) graph (Figure 2), some level of organic sulfur removal by PCE extraction is indicated. And, the amount of organic sulfur removed from 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 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: The Overall Data Obtained from ASTM, SEM-EDX, HCl/LAH, and XANES Analyses

		Wt% on moisture-free whole coal basis		
Sample	Method	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[e]	1.40[a]
	XANES (B)			1.70[b]
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[e]	1.44[a]
	XANES (B)			1.51[b]
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[e]	1.50[a]
	XANES (B)			1.90[b]
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[e]	1.58[a]
	XANES (B)			1.62[b]

[e] Pyritic sulfur from ASTM analysis
[a] Organic sulfide and thiophenic sulfur
[b] Organic sulfide, thiophenic, elemental, and oxidized organic sulfur

Some 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 do show that there was total removal of the elemental sulfur.

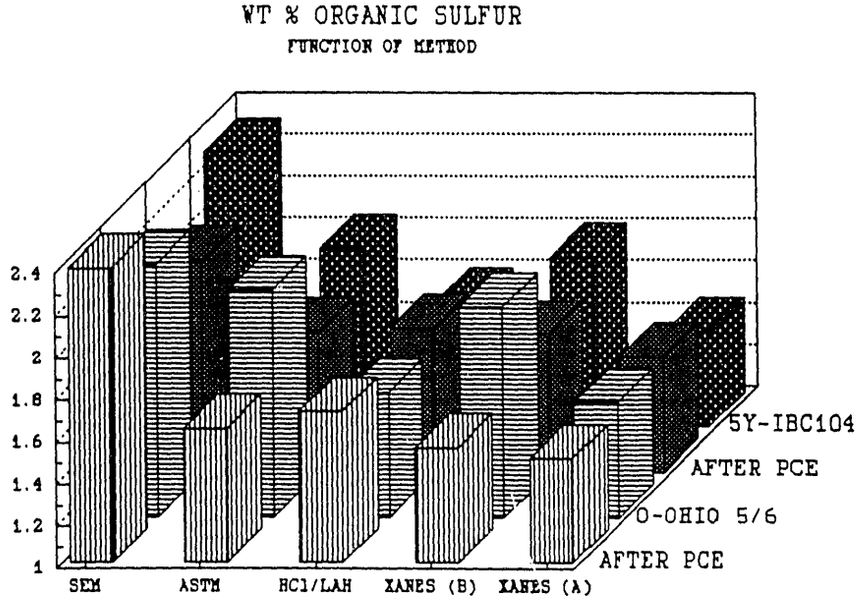

Figure 2. Organic sulfur in coals before and after PCE extraction as a function of analytical method.

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. This is because during HCl/LAH analysis, elemental sulfur in the coal was 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; but, for the Ohio coal, a slight increase was observed. The reason for this difference for the two samples 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

As mentioned earlier, XANES data indicate that no initial forms of organic sulfur removal occurs during PCE extraction. It simply dissolves elemental sulfur from the coal sample. Thus, the amount of S° in coal determined by XANES analysis may be estimated by the amount of S° extracted by the PCE. From the analytical standpoint, the HPLC analysis is more convenient than the XANES analysis, thus, HPLC analysis was used as a method to evaluate the effect of pre-oxidation conditions on PCE extraction.

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.

All the short-term pre-oxidation/PCE extraction experiments were conducted by oxidizing in the presence of PCE. Shown in Table 9 are 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 S° content in the PCE extract after bubbling air into a PCE coal slurry for two hours with or without trace amounts of SO_2 at room temperature. However, when the experiment was conducted at 90 °C, with water present, by bubbling air for two hours, the S° production was doubled. By addition of a small amount of SO_2 as an oxidant, the S° production was further increased by four-fold. Furthermore, when the duration was extended from 2 hrs to 20 hrs, the S° production was increased by 18 times.

For the purpose of comparing the oxidation sensitivities of Illinois IBC-104 coal and Ohio 5/6 coal, the two ambient-oxidized coal samples were used for the short-term oxidation.

The ambient-oxidized IBC-104 coal (>5Y-IBC-104) had 0.07% S° in the PCE extract before further oxidation (Table 9). By bubbling air under moist conditions for two hours at 90 °C, the S° content was slightly increased from 0.07% to 0.10%. Under the same conditions, by adding a small amount of SO_2 oxidant, a further increase in S° content from 0.10% to 0.13% was produced. Overall, the amount of elemental sulfur in the sample was increased about two-fold.

Table 9. The Effects of Oxidation Condition on the Amounts of Elemental Sulfur Removed by PCE Extraction

Starting coal	PCE/H_2O (mL/mL)	Oxidation Method	Time	Temp. (°C)	S° %
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_2	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_2	2 hours	90	0.04
F-IBC-104	100/20	bubbling air/SO_2	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_2	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_2	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_2	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_2	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, 20ml/sec	2 hours	90	0.02
Mineral Pyrite	100/0	bubbling air/SO_2	2 hours	90	0.03
Minearl Pyrite	100/20	bubbling air/SO_2	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 wt%, moisture-free, whole-coal basis.

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_2 present increased the S° 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 Ohio 5/6 coal appeared to more readily produce elemental sulfur than the Illinois coal during oxidation.

To determine the possible source of S° 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% S° in the PCE extract (Table 9). After treatment with bubbling air for two hours at 90 °C with and without water present, no increase in S° production was indicated. With a small amount of SO_2 present and no water, the concentration of elemental sulfur increased slightly from 0.02% to 0.03%. However, with both SO_2 and water present, the elemental sulfur concentration increased from 0.03% to 0.05%.

Overall, these experiments demonstrated that oxidation increased the amount of S° 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 MWOPC); and G. Atwood, 1990 (personal communication to J. Lytle and M. Chou). The Ohio 5/6 coal appeared to more readily produce elemental sulfur than Illinois coal during oxidation. Also, pyrite oxidation probably contributed to some of the S° in the coals that was extracted by PCE treatment.

The source of the increased elemental sulfur and the identity of the pyritic and organic sulfur in the sample treated with the SO_2 oxidant that we introduced are currently under investigation.

Dechlorination

If PCE is used for desulfurization, then dechlorination of the PCE-treated coal is also a concern for the success of this implicit process. 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 applying 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%. Steam dechlorination was used by the University of Akron for dechlorination of 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), which washes PCE-treated coal 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-IBC104-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 CONCLUSION

MWOPC's results have been repeated on our tests for fresh IBC-104 coal. Oxidation of coals was found to affect subsequent PCE desulfurization. Elemental sulfur are more amenable to removal than initial forms of organic sulfur by PCE desulfurization. Ohio 5/6 coal appears to more readily produce elemental sulfur 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.

The 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 are key operating variables reported or implied by Lee, et al. (at Akron), and Leehe, et al.(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. However, 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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PROJECT MANAGEMENT REPORT

September 1, 1991 through August 31, 1992

Project Titled: SULFUR REMOVAL FROM HIGH-SULFUR ILLINOIS COAL BY LOW-TEMPERATURE PERCHLOROETHYLENE (PCE) EXTRACTION

Principal Investigator: M.-I. M. Chou, Illinois State Geological Survey (ISGS)
Other Investigators: J.M. Lytle, R.R. Ruch, C.W. Kruse, C. Chaven, K.C. Hackley, R.E. Hughes, R.D. Harvey, J.K. Frost (ISGS); D.H. Buchanan (EIU); J.W. Stucki (UI-UC); G.P. Huffman, F.E. Huggins (UK)
Project Manager: D.D. Banerjee (CRSC)

COMMENTS

A trip was made to the 203rd ACS National Meeting in San Francisco held on April 4-9, 1992. A paper entitled "Oxidized Coal Char As a Catalyst: 1. Characterization," was presented by M.-I. M. Chou. This trip was partially supported by this contract.

Year-1

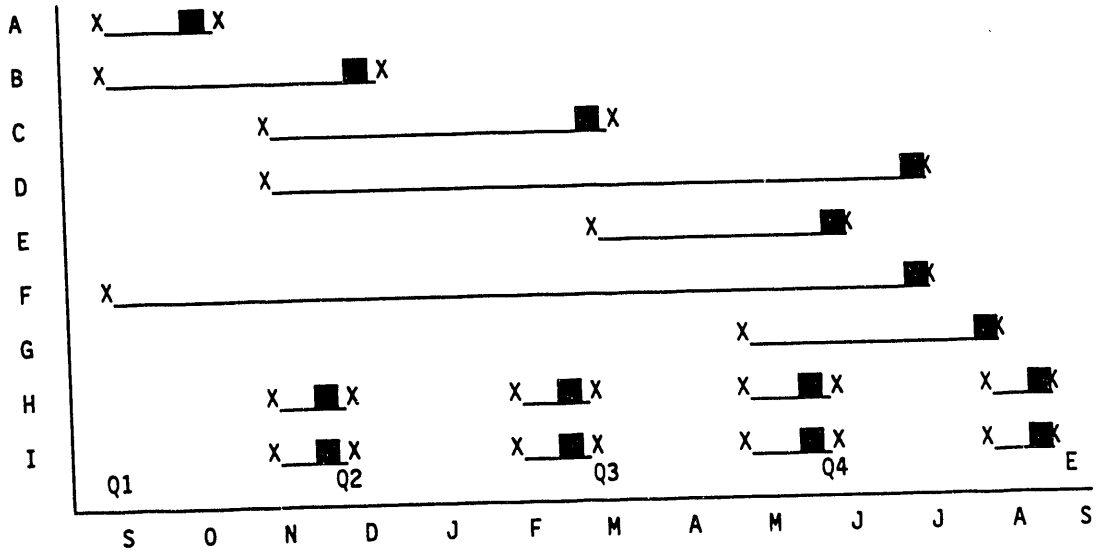
EXPENDITURES - EXHIBIT B

Projected and Estimated Actual Expenditures by Quarter

Quarter (cumulative by quarter)	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1991 to Nov. 30, 1991	Projected	6,442	1,250	100	0	10,000	1,797	19,589
	Est. Actual	6,000	188	531	0	0	672	7,390
Sept. 1, 1991 to Feb. 28, 1992	Projected	12,883	2,250	900	0	20,000	3,594	39,627
	Est. Actual	11,575	306	531	0	476	1,315	14,203
Sept. 1, 1991 to May 31, 1992	Projected	19,324	2,750	1,150	0	31,368	5,391	59,983
	Est. Actual	17,392	1,270	1,684	0	15,927	5,161	41,434
Sept. 1, 1991 to Aug. 31, 1992	Projected	25,766	3,000	1,750	0	41,368	7,188	79,072
	Est. Actual	22,405	3,000	1,900	0	44,579	7,188	79,072

SCHEDULE OF PROJECT MILESTONES

Year 1



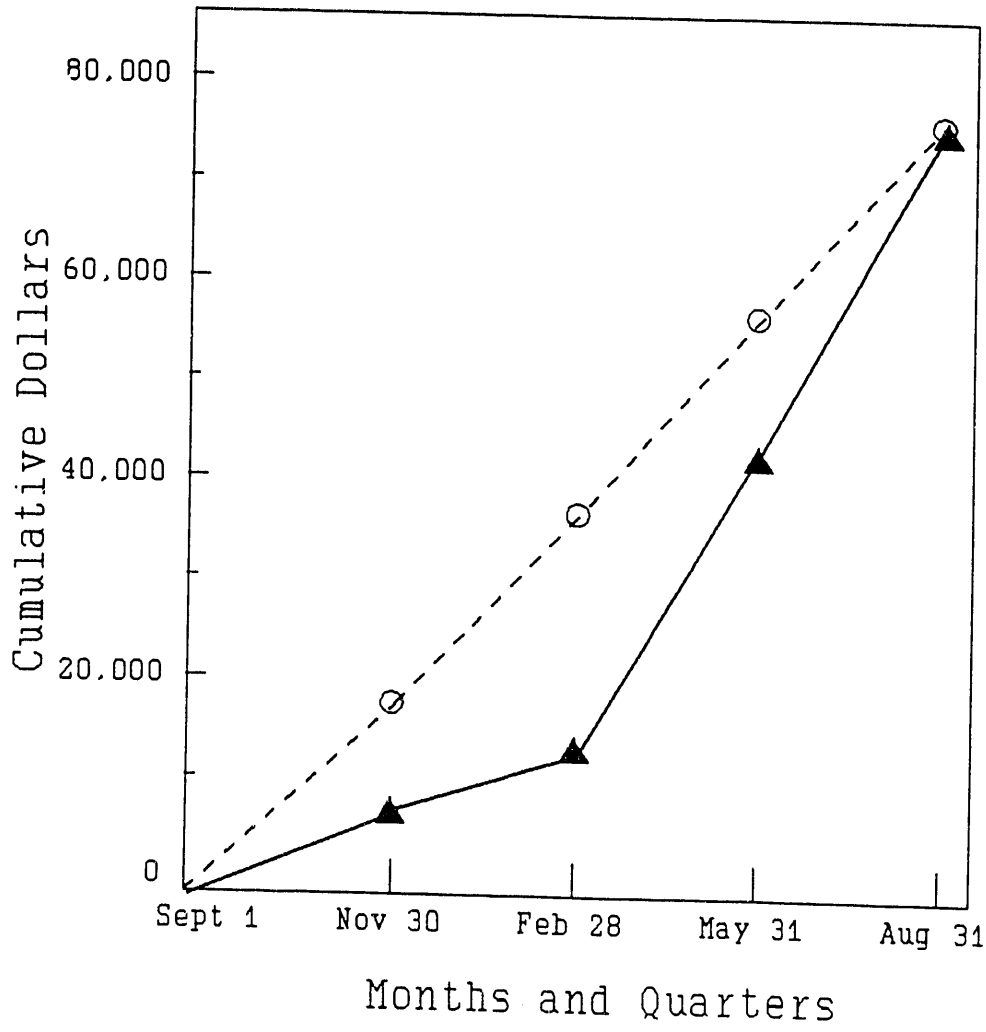
September 1, 1991 through August 31, 1992

Milestones:

A. Coal sample preparation
B. PCE desulfurization (Task 1.1)
C. Material balance study (Task 1.2)
D. Multiple independent analysis (Task 1.2)
E. Desulfurization data evaluation (Task 3)
F. Study various parameters for PCE desulfurization (Task 4)
G. Data evaluation (Task 5)
H. Technical reports
I. Financial reports

COSTS BY QUARTER - EXHIBIT C (Year 1)

SULFUR REMOVAL FROM HIGH-SULFUR ILLINOIS COAL BY LOW-TEMPERATURE PERCHLOROETHYLENE (PCE) EXTRACTION



○ Projected Expenditures - - - - - - - - - - - -

▲ Actual Expenditures ————————

Total CRSC (ICCI) Award $ 79,072

LIST OF PUBLICATION AND PRESENTATIONS

September 1, 1991 through August 31, 1992

Project Title: SULFUR REMOVAL FROM HIGH-SULFUR ILLINOIS COAL BY LOW-TEMPERATURE PERCHLOROETHYLENE (PCE) EXTRACTION

Principal Investigator: M.-I. M. Chou, Illinois State Geological Survey (ISGS)

A paper was presented at the ICCI Contractors' Meeting in Urbana, held on August 4-6, 1992. A paper was also presented at the 204th ACS National Meeting in Washington DC, held on August 23-28, 1992. Attached is a copy of the ACS preprint paper.

M.-I. M. Chou, J.M. Lytle, R.R. Ruch, C.W. Kruse, C. Chaven, and D.H. Buchanan. 1992. "Pre-Oxidation and Perchloroethylene (PCE) Desulfurization of Illinois Coals." Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem., 1992. 37(4):2002-2009.

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