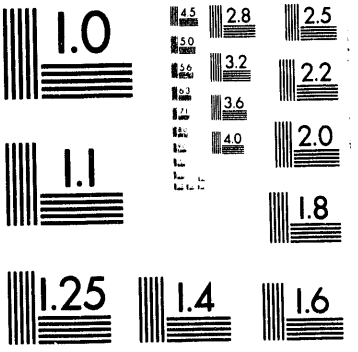
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2-41

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FINAL TECHNICAL REPORT
September 1, 1992 - August 31, 1993

Project Title: **SULFUR REMOVAL FROM HIGH-SULFUR ILLINOIS COAL BY LOW-TEMPERATURE PERCHLOROETHYLENE (PCE) EXTRACTION** DE-FC22-92PC92521

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Project Manager: K.K. Ho, Illinois Clean Coal Institute

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, the process is reported to be more effective for Ohio and Indiana coals than for Illinois 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) forms-of-sulfur analysis. The purposes of this research were to independently confirm and possibly to improve the organic sulfur removal from Illinois coals with the PCE desulfurization and to verify the ASTM forms-of-sulfur determination for evaluation of the process. An additional goal was to develop a dechlorination procedure to remove excess PCE from the PCE-treated coal.

A laboratory scale operation of the MWOPC PCE desulfurization process was demonstrated, and a dechlorination procedure to remove excess PCE from the PCE-treated coal was developed. We have determined that PCE desulfurization removes mainly elemental sulfur from coal. The higher the level of coal oxidization, the larger the amount of elemental sulfur that is removed by PCE extraction. The increased elemental sulfur during short-term preoxidation is found to be pH dependent and is attributed to coal pyrite oxidation under acidic (pH<2) conditions. The non-ASTM sulfur analyses confirmed the hypothesis that the elemental sulfur produced by oxidation of pyrite complicates the interpretation of analytical data for PCE process evaluation when only the ASTM forms-of-sulfur is used. When the ASTM method is used alone, the elemental sulfur removed during PCE desulfurization is counted as organic sulfur. A study using model compounds suggests that mild preoxidation treatment of coal described by MWOPC for removal of organic sulfur does not produce enough oxidized organic sulfur to account for the amounts of sulfur removal reported. Furthermore, when oxidation of coal-like organosulfur compounds does occur, the products are inconsistent with production of elemental sulfur, the product reported by MWOPC. Overall it is demonstrated that the PCE process is not suitable for organic sulfur removal and that the ASTM forms-of-sulfur is not a reliable method for forms-of-sulfur of weathered coals.

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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 reported to be effective in extracting organic sulfur and separating pyrite fines from coal by float-sink techniques; the process can be operated at low temperatures with minimal loss of solvent and is 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. The MWOPC process evaluation was based on the interpretation of ASTM data.

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 recently, no conclusive experimental evidence 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 MWOPC's higher reported organic sulfur removal.

One hypothesis underlying the ASTM analysis is that the 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 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 as a 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 the removal of sulfur by PCE extraction is organic in nature.

The goals of this research were: (1) to independently confirm and possibly to improve the organic sulfur removal from Illinois coals with the PCE desulfurization process developed by the MWOPC, (2) to verify the ASTM forms-of-sulfur analyses for evaluating the PCE desulfurization process, and (3) to develop a procedure to remove excess PCE from PCE-treated coals. This was 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 in the first year, and tasks 6 to 8 were carried out in the second year.

The preliminary PCE desulfurization was evaluated by measuring the level of total sulfur reduction in the PCE-treated coals using ASTM procedures and by measuring the amounts of elemental sulfur obtained in the PCE extracts. The removal of elemental sulfur from coal is reported by MWOPC to be enhanced by a preoxidation treatment. These results were confirmed in this study. The extractable elemental sulfur obtained in this study from a long-term ambient oxidized IBC-104 coal is 25 to 75 times greater than that from the unoxidized or short-term oxidized IBC-104 coal samples. Also, a dechlorination procedure to remove excess PCE from PCE-treated coals was developed.

Larger scale PCE desulfurizations on 50 grams of a short-term and a 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 results from the mass balance calculation indicate that 96% of all the sulfur and greater than 95% of all the iron were accounted for during our PCE desulfurization tests with both long-term ambient-oxidized IBC-104 coal and Ohio 5/6 coal.

The data from non-ASTM sulfur analyses including Sulfur K-edge X-ray Absorption Near Edge Structures Spectroscopy (XANES) analysis were examined and compared to that of the ASTM analysis. XANES analyses indicate that PCE desulfurization removes all the elemental sulfur from coals, but, organic sulfur (organic sulfide or thiophenic sulfur) in coal was not removed by PCE extraction. This observation was supported by a separate wet chemical method. The method uses a lithium aluminum hydride (LAH) reduction to eliminate the interference of elemental sulfur during a combustion technique for the determination of organic sulfur. During short-term oxidation tests, Ohio 5/6 coal appears to more readily produce elemental sulfur than Illinois coal. Oxidation of coals was found to facilitate subsequent PCE desulfurizations, and the higher elemental sulfur content in the Ohio coal results in higher apparent removal of organic sulfur by PCE extraction when monitored by the ASTM forms of sulfur method. Data from x-ray diffraction spectroscopy indicate that sulfate in long-term ambient oxidized IBC-104 coal exists mainly as gypsum

($CaSO_4 \cdot 2H_2O$), whereas, sulfate in oxidized Ohio 5/6 coal exists mainly as szomolnokite ($FeSO_4 \cdot H_2O$).

PCE desulfurization was examined under various short-term oxidation conditions. The results show that the increase in elemental sulfur is related to reaction temperature, moisture conditions, and the presence of oxidant. It was also shown that the acidity in the preoxidation liquid controlled the amount of elemental sulfur produced. Elemental sulfur production increased substantially in cases when the oxidation liquid was acidified to pH less than 2. There can be little doubt that the elemental sulfur extracted originates from pyrite oxidation. This study confirmed the hypothesis that elemental sulfur complicates ASTM analysis because ASTM forms-of-sulfur counts elemental sulfur, which is derived from pyrite oxidation, as organic sulfur. The hypothesis that PCE treatment inhibits the extraction of the coal-derived pyrite and iron sulfates during the ASTM procedures for forms-of-sulfur was not substantiated.

The oxidation reaction on the organosulfur compounds found in coal was examined under a set of conditions. These oxidation conditions were evaluated to set a lower limit for oxidation of the organosulfur compounds in coal to be removed by PCE desulfurization. The results indicated that the mild preoxidation treatment of coal described by MWOPC for removal of organic sulfur does not produce enough oxidized organic sulfur to support the level of sulfur removal reported. Furthermore, when air oxidation of coal-like organosulfur compounds does occur, the products are inconsistent with production of elemental sulfur, the product reported by MWOPC. Overall, the study demonstrated that the PCE process is not practical for organic sulfur removal. Also, it is recommended that all chemical desulfurization should utilize fresh feed coals, and if ASTM method is used for forms-of-sulfur analysis, the results should be verified with an alternate method, such as XANES.

OBJECTIVES

The goals of this research were: (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 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 were:

A. To conduct the PCE desulfurization of two coals under the proper process conditions. One coal, IBC-104, was from the Illinois Basin Coal Sample Program, and the other, Ohio 5/6 coal, from the Horizon Coal Company.

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 to 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 1 ton/day capacity by MWOPC at Plainville, IN. In addition, a mini-pilot plant of 5 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 was stressed by MWOPC. Efficiency of organic sulfur removal is reported to be affected by the initial moisture content of the coal (Fullerton et al., 1990). A pyrite derived "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, Feb. 1991). The MWOPC process has been reported to be effective for removal of 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 Eastern Illinois University (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 to 24 g) as compared to the other experiments in which 50 g 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).

Differences in the level of preoxidation, the quantities of coal used and type of extraction equipment used have been advanced as reasons for the differences between the MWOPC claims and the EIU/ISGS efforts to substantiate them. For example, Soxhlet extraction rather than batch extraction is thought by some to decrease the activity of the catalyst that assists organic sulfur removal during PCE extraction. Use of a Soxhlet is thought by some to decrease the consistency of the temperature control. However, we have put more credence in the expectation that errors in the ASTM analyses of sulfur would eventually explain the discrepancies in the results. Specifically, we believed that elemental sulfur extracted by the PCE had a good probability of being 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 possibility considered is that during preoxidation, pyritic sulfur is converted into mineral form which gives PCE-extractable elemental sulfur and a pyrite-derived iron compound left in the coal sample. This hypothesis requires that the iron 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. One objective of this study was to develop data to confirm or reject these hypotheses.

EXPERIMENTAL PROCEDURES

Eight tasks were conducted to meet the objectives.

Task 1: Processing of Illinois coals and a mass balance study (ISGS/EIU).

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 project. Coal selection was based on the availability of the samples and on the reported desulfurization data 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. These tests were performed in a batch mode.

Task 1.1: Processing of coals.

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 (hot methanol, water and acetone) 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 size) were conducted on one short-term oxidized IBC-104 coal, one long-term oxidized IBC-104 coal, and one oxidized Ohio 5/6 coal. The feeds and products from these scale-up operations were split and distributed to co-investigators for non-ASTM analyses (Task 2) and a mass balance analysis (Task 1.2). In addition, a washing procedure, which sequentially washes the PCE-treated coal with boiling methanol, water, and acetone, for chlorine removal from the PCE-processed coals was successful.

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). Chlorine content in the feeds, and product coals was measured by a Leco chlorine

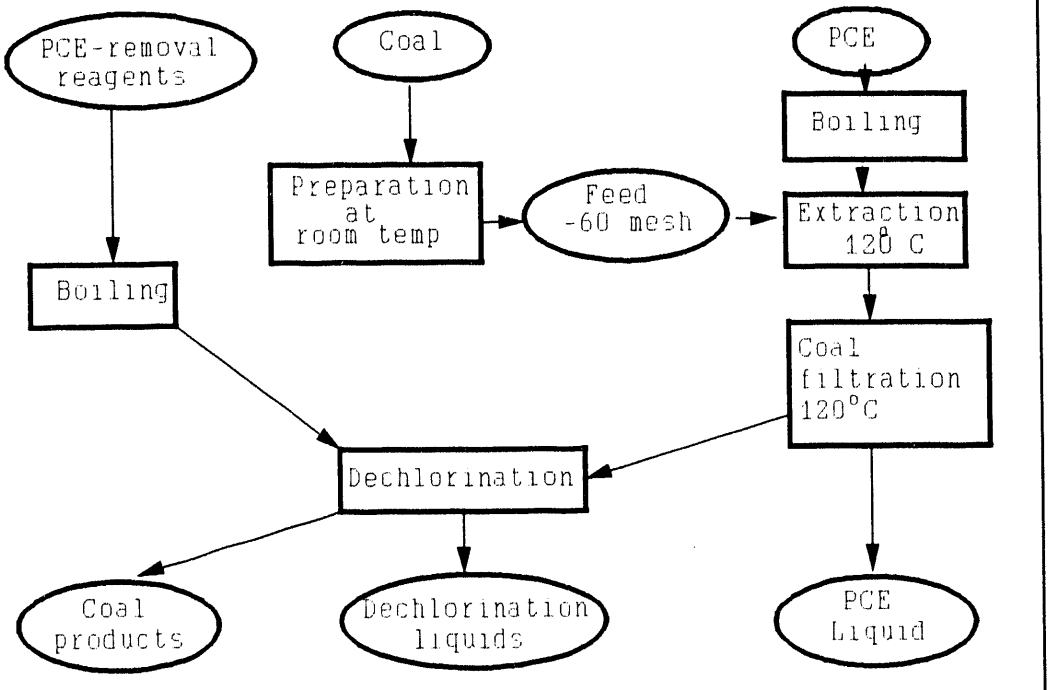


Figure 1. Flow Diagram for PCE Batch Extraction

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 ASTM D-2492 procedure, sample (-60 mesh) 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 was used to calculate pyritic sulfur. To obtain the total sulfur content, a separate split of coal was combusted in a Leco model SC32 total sulfur analyzer. 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.

A small scale (10 g) PCE extraction was also conducted in conjunction with various short-term oxidations of coals. This was accomplished by bubbling filtered air or air/oxidant through a coal/PCE slurry with or without water added. The reaction conditions varied from room temperature to 90°C and

for a length of time from 2 to 20 hours. After oxidation, the temperature was increased to 120°C and maintained at that temperature for 30 minutes. The extracts produced from PCE extraction were then isolated from the residues by hot filtration.

To measure the pH of the oxidation liquids, some oxidation experiments were repeated using a smaller sample size (1g) at 90°C for 2 hours. After oxidation the liquid phase was isolated by filtration, then separated into its PCE and aqueous fractions. The pH value was taken from the aqueous fraction. For PCE extraction, the same oxidation was repeated on another split of the sample. The water was boiled off at the end of the oxidation, and the PCE extraction was continued for another 30 minutes at 120°C.

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, and total sulfur in feeds and in the PCE-treated coals were used in the sulfur mass-balance calculation. Sulfatic sulfur concentration in the dechlorination liquids was obtained by inductively coupled plasma analysis (ICP). For the iron mass-balance calculation, the feeds and the solid products were ashed at 750°C for 20-24 hours or until no carbonaceous residue remained. The prepared ashes were fused with lithium tetraborate (a mixture of 1 part ash by weight and 9 parts of $Li_2B_4O_7$ $5H_2O$ 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 dechlorination liquids was determined by ICP.

<u>Task 2: Non-ASTM analysis for forms of sulfur determination (ISGS, UI-UC, & UK).</u>

The purpose of this study (Tasks 2.2 - 2.5) was to examine the transformation or removal of pyritic sulfur, aliphatic sulfur, and aromatic sulfur during PCE desulfurization. The results obtained from a wet chemical analysis and four non-destructive spectroscopic techniques were compared with those from the ASTM analysis.

A wet-chemical analysis (HCl/LAH) (Task 2.1, ISGS), 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 applied. The dried coal sample (-230 mesh) was extracted for sulfatic sulfur 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 extraction and precipitated as Ag_2S (Liu et al., 1987). To remove pyritic sulfur, the HCl-leached coal 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 which was combusted 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 sulfur analysis techniques used (Chou et al., 1992) are Sulfur K-edge X-ray Absorption Near Edge Structures Spectroscopy (XANES) (Task 2.2, University of Kentucky), X-Ray Diffraction (XRD) (Task 2.3, ISGS), Mössbauer spectroscopy (Task 2.4, UI-UC), and Scanning Electron Microscopy and Energy Dispersive X-ray Fluorescence Analysis (SEM-EDX) (Task 2.5, ISGS).

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, and UK).

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 removal by PCE extraction and that of ASTM forms-of-sulfur analysis.

Task 4: Conducting PCE desulfurization under various process conditions including expanded tests on model organosulfur compounds desulfurization (EIU/ISGS).

In addition to ambient oxidation, various short-term, air-oxidation effects (achieved by varying the amount of moisture, temperature, time, and oxidizing gas composition) on organic sulfur removal by PCE desulfurization were examined. Also, to determine the minimum conditions under which air oxidation of organosulfur model compounds would occur and to compare these conditions to the MWOPC conditions, extended tests on the desulfurization of organosulfur model compounds were

implemented.

The procedures for the short-term oxidation/PCE extractions and a pH study were described in Task 1.1. For the extended tests on oxidation of organosulfur model compounds, model compounds such as di-n-octyl sulfide, dibenzyl sulfide, and dibenzothiophene (DBT) were used to represent organosulfur structures. An oxidation study without a promoter was carried out by dissolving the model compounds (1-4 g) in 50 - 100 ml PCE. The compounds were then oxidized in the same apparatus as was used for coal oxidations. Air with and without SO_2 was bubbled through the mixtures for two hours at 90°C. The cooled reaction mixtures were filtered and examined by GC and HPLC using conditions which separate the starting materials from possible products. Authentic samples were synthesized and used to show that hydrocarbon products (complete desulfurization) and related compounds such as phenols would have been detected under the conditions used. For products identification, crystalline sulfoxides and sulfones were isolated from the reaction mixtures and their identity verified by melting points and FTIR spectra.

To determine the minimum conditions under which air oxidation of organosulfur compounds could occur, oxidation of sulfur model compounds was carried out with a hydrocarbon additive in the absence of PCE. The model sulfur compound and an equal molar amount of the promoter, if present, were well mixed and placed in the bottoms of several identical tubes, which were flushed with either nitrogen gas (for controls) or air and sealed with a torch. The experiments were carried out in sealed glass tubes, 8 mm x 10 cm, in an electrically heated oil bath. For reactions in the absence of light, the tubes were wrapped with aluminum foil and loaded horizontally in a large oil bath at 125°C. For analyses of 24, 76, and 216 hours, tubes were withdrawn, cooled quickly in ice water and carefully cracked open. No extra gas pressure was observed, nor were low-molecular-weight sulfur compounds detected by their odors. The tube contents were dissolved in methylene chloride, filtered, diluted, and examined by GC or GC/MS. The reactions in the presence of light were conducted in a similar manner with the exception of the exposure of the unwrapped tubes to a 400 W photoflood light. Tubes were removed at pre-selected times and analyzed. In addition to the times listed above, dibenzylsulfide samples were also taken at 8, 52, and 120 hours. For several reactions of dibenzyl sulfide, a small amount of a reaction solution taken from a 76-hour reaction (either in light or darkness) was used as the oxidant-promoter-catalyst in place of air plus 9,10-dihydroanthracene (DHA) or diphenylmethane (DPM). These tubes were flushed with nitrogen gas before sealing, so all oxidation was due to intermediates formed in the previous reaction.

For the GC analyses, a 0.53 mm x 20 m DB-5 capillary column in an H-P 5890 Series I gas chromatograph equipped with an FID detector was used. Peak identification was made by co-injection with standard reference compounds (from Aldrich or prepared in-house as reported previously). DBT sulfone also was confirmed by HPLC analysis using a C-18 reverse-phase column. Further confirmation of several products was made using a 0.25 mm x 30 m DB-5 column in an H-P 5890 II GC equipped with a 5971 mass spectrometer (MS) detector. Identification was obtained by computer matching of the mass spectra with the Wiley MS Database. The mass spectra of sulfoxides and sulfones were not obtained because of their thermal instability. The decomposition probably occurred in the transfer line of the GC/MS rather than in the injector since these compounds were observed with the FID in the other GC analysis.

Task 5: Evaluating the parameters studied and their effect on process optimization (ISGS, EIU, UI-UC, and UK).

For the studies on 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.

In the extended tests, the conditions necessary for oxidation of the type of organic sulfur compounds found in coal were evaluated and compared with those of the MWOPC pre-oxidation..

Task 6: Verifying the possible effect of PCE treatment on coal-derived pyrite and iron sulfates on ASTM coal analysis.

An oxidized IBC-105 coal which contains coal-derived pyrite, sulfate, and elemental sulfur was used. The sample was riffled, split, and subjected to oven drying at 42°C for one week. A split of the dried sample was refluxed with 100 ml boiling PCE (120°C) for 1 hr. After hot filtration, the filtrate was made up to volume and analyzed for S° by HPLC. The residue was dried at 105°C for 24 hrs. and saved for further analysis.

Samples of oxidized IBC-105 before and after PCE extraction were subjected to ASTM forms of sulfur and ASTM total sulfur analyses. In addition to regular forms of sulfur, the residual coal from the pyritic sulfur determination was ashed for 24 hrs. at 800°C and re-extracted with aqua-regia to dissolve Fe. Both samples were also subjected to Lithium Tetraborate fusion, and the residues were dissolved in hot water and dilute HNO_3 in order to determine total iron. The ASTM-HCl and -HNO_3 extraction solutions were also analyzed for Fe

content. The mass balances for total iron and total sulfur were calculated.

Task 7: Monitoring sulfur behavior during oxidation and PCE desulfurization using coal with organic and inorganic sulfur that is isotopically distinguishable.

In the short-term oxidation experiments, additional elemental sulfur was produced. It is important to determine the source of this extra elemental sulfur. An IBC-107 coal which contains various forms of sulfur that carry unique stable sulfur isotope ratios (SSIR) was used to trace the origin of elemental sulfur produced in oxidation experiments (Hackley, et al, 1990). Since SO_2, if it was used as a co-oxidant, could conceivably contribute to the extra elemental sulfur, a study was also conducted to determine the SSIR of the SO_2. Oxidation of a split of the IBC-107 coal was conducted under the most successful known conditions for stimulating elemental sulfur extraction (Water/PCE/air/SO_2/90°/22 hrs.). The PCE extract was analyzed for elemental sulfur content, and the resulting sulfur was used for SSIR analysis.

Task 8: Studying the optimization conditions for the PCE desulfurization or other innovative pretreatment processes for the removal of organic sulfur from coal under mild conditions.

The results from the extended oxidation tests on the organosulfur compounds found in coal in the presence, as well as in the absence, of a promoter were examined. These oxidation conditions were evaluated to set a lower limit for oxidation of the organosulfur compounds in coal to be removed by PCE desulfurization. The conditions were also compared with that for the preoxidation treatment of coal described by MWOPC for removal of organic sulfur.

RESULTS AND DISCUSSION

Preliminary PCE desulfurization

Confirmation study based on ASTM analysis - Before performing a larger scale operation (50g), the PCE desulfurization was conducted in a smaller scale (10g) under conditions described by the MWOPC. The fresh IBC-104 coal used in this investigation is comparable to the Illinois coal sample processed by the developer (University of Akron). Thus, analysis of the products from before and after PCE extraction can be used to verify our PCE desulfurization tests.

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; I & II , two separate runs.

Oxidation and PCE desulfurization based on HPLC analysis - During PCE desulfurization, the amounts of elemental sulfur obtained in the PCE extracts were measured by HPLC analysis. The removal of elemental sulfur from coal by PCE extraction is enhanced by subjecting coal to a long-term ambient oxidation. These elemental sulfur analysis results confirm that preoxidation is important to PCE desulfurization. For example, the extractable elemental sulfur obtained 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 (Chou et al, 1992).

Dechlorination - If PCE is used for desulfurization, then dechlorination of the PCE-treated coal is also a concern for the success of this process. As indicated in Table 2, 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 very high chlorine content as much as 4.68%. When hot water washing was used in the dechlorination step, the resultant coal has 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). The chlorine contents for these resultant coals are too high for the coal 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 method can remove the excess PCE and yield a coal with a chlorine content as low as the original coal, 0.03% (Table 2).

Table 2. 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

PCE desulfurization

ASTM-analysis and HPLC analysis - For the larger scale PCE desulfurization, table 3 shows the results of the ASTM analyses of the feed and 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 two weeks oxidation (2W-IBC-104) 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 2-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%.

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.

Table 3. 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 basis				
	ASTM forms of sulfur				HPLC
Sample	Sulfatic	Pyritic	Organic	Total	S^0
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

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 by ASTM interpretation. From O-Ohio 5/6, 0.10% of the coal was extracted as elemental sulfur, and the sample shows a 21% organic sulfur reduction. From >5Y-IBC-104, 0.07% of elemental sulfur was extracted, and the sample shows a 10% organic sulfur reduction.

Mass balance analysis - Mass balance data (Chou et al., 1992) indicated 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 sulfatic sulfur and elemental sulfur content. No elemental sulfur was detected in the dechlorination liquids. Organic sulfur in PCE and in the dechlorination liquids were 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. 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.

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 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 those obtained from the ASTM analysis.

Data from both Mössbauer spectroscopy and x-ray diffraction spectroscopy indicate a loss of $Fe(II)SO_4$ in the product coals. Data from x-ray diffraction spectroscopy (Table 4) 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 the O-Ohio 5/6 sample is mainly in the form of szomolnokite ($FeSO_4 \cdot H_2O$). These data suggest that the oxidation reaction for Ohio 5/6 coal might occur under Fe(III) catalytic conditions which readily convert pyrite to $FeSO_4$ 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 4. Mineral matter composition by x-ray diffraction analysis

	Weight (%)					
Sample	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	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

K-edge x-ray absorption near edge structures (XANES) spectroscopy was used to resolve the sulfur forms other than pyrite and sulfate into elemental sulfur (S°), organic sulfide (O-sulfide), thiophenic sulfur (Thioph.), and oxidized organic sulfur (Oxid.), such as sulfone and sulfoxide. Pyrite content obtained from Mössbauer spectroscopic analysis tends to have a larger determination error than the ASTM analysis. Thus, the most precise data on sulfur forms were the data from XANES analysis combined with wt% pyritic sulfur in coal from the ASTM analysis. The results are listed in Table 5. The data show that a 2-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 organic sulfur (organic sulfide and thiophenic sulfur).

The 5-year oxidized sample differs significantly from the 2-week oxidized sample in that 35% of the pyritic sulfur has been oxidized to sulfate plus elemental sulfur. In addition, the sum of organic sulfide and thiophenic sulfur appears to be 10% lower in the 5-year oxidized sample than in the 2-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 removes soluble sulfates.

Table 5. 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^0	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 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% to 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 data, as well as the data from ASTM, SEM-EDX, and HCl/LAH (Chou et al, 1992), has been analyzed and compared in Figure 2. Here, sulfur other than pyrite and sulfate was graphed as organic sulfur versus the method of analysis. 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 forms other than pyrite and sulfate into elemental sulfur (S°), 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 uses only the data from unxidized organic sulfur (the sum of organic sulfide and thiophenic sulfur). On the other hand, the organic sulfur shown for XANES (B) in Figure 2 uses the data of unoxidized organic sulfur plus elemental sulfur and oxidized forms of organic sulfur. From the XANES (A) graph, essentially no reduction of the 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) is similar to that observed by the ASTM analysis. This suggests that the higher elemental sulfur content of the Ohio coal produces more elemental sulfur to be extracted by the PCE, and results in a higher apparent level of organic sulfur removal by the ASTM analysis. The Ohio 5/6 coal contains 0.26% elemental sulfur and >5Y-IBC-104 contains 0.17% elemental sulfur. Twenty one percent of the "organic sulfur" was removed from the 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 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 organic sulfide nor thiophenic sulfur, but they do show that there was total removal of the elemental sulfur.

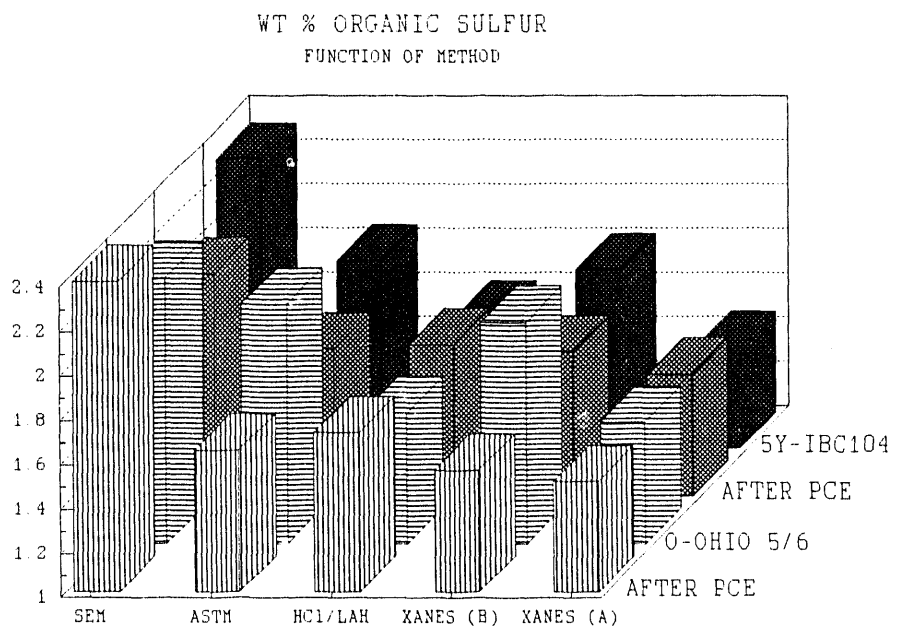


Figure 2. Organic sulfur in coals before and after PCE extraction as a function of analytical method.

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 organic sulfide and thiophenic 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 between 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 of Coal Samples

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 on a fresh IBC-104 coal, an oxidized Ohio coal, an oxidized Illinois coal, and a mineral pyrite. The amounts of elemental sulfur produced during oxidation were used as a measure to evaluate the effect of pre-oxidation conditions on PCE extraction.

All the short-term pre-oxidation experiments were conducted by oxidizing the samples in the presence of PCE. Shown in Table 6 are short-term oxidation conditions and the HPLC results on the amounts of elemental sulfur removed from each PCE extraction.

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 oxidation reagent at room temperature. However, when the experiment was conducted at 90°C, with water present, by bubbling air for 2 hours, the elemental sulfur production was doubled. By addition of a small amount of SO_2, the elemental sulfur production was further increased by 4-fold. Furthermore, when the duration was extended from 2 hrs to 20 hrs, the elemental sulfur production was increased by 18 times.

The ambient-oxidized IBC-104 coal (>5Y-IBC-104) had 0.07% elemental sulfur in the PCE extract before further oxidation (Table 6). By bubbling air under moist conditions for 2 hours at 90°C, the elemental sulfur production was slightly increased from 0.07% to 0.10%. Under the same conditions, by

adding a small amount of oxidant, a further increase in elemental sulfur production from 0.10% to 0.13% was indicated. Overall, the amount of elemental sulfur production is increased about 2-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 6). Oxidation under conditions similar to those used for the O-Ohio 5/6 coal sample with the oxidant, the S° production was increased from 0.13% to 0.35%. Overall, the amount of elemental sulfur production in the O-Ohio 5/6 coal sample was increased almost 3-fold. These results indicate that Ohio 5/6 coal more easily produces elemental sulfur than the Illinois coal during oxidation.

Table 6. 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-year	Room Temp.	0.07
F-IBC-104	100/0	Air	2 hours	24	0.01
F-IBC-104	100/0	Air/SO_2	2 hours	24	0.01
F-IBC-104	100/20	Air	2 hours	90	0.02
F-IBC-104	100/20	Air/SO_2	2 hours	90	0.04
F-IBC-104	100/20	Air/SO_2	20 hours	90	0.18
5Y-IBC-104	100/0	None	-	-	0.07
5Y-IBC-104	100/20	Air	2 hours	90	0.10
5Y-IBC-104	100/20	Air/SO_2	2 hours	90	0.13
O-Ohio 5/6	100/0	None	-	-	0.13
O-Ohio 5/6	100/20	Air	2 hours	90	0.10
O-Ohio 5/6	100/20	Air/SO_2	2 hours	90	0.35
Oxidized Pyrite	100/0	None	-	-	0.02
Oxidized Pyrite	100/20	Air	2 hours	90	0.02
Oxidized Pyrite	100/20	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.

To determine if pyrite is a possible source of S° produced during coal oxidation, short-term oxidation conditions were applied to a sample of slightly oxidized mineral pyrite. The sample before short-term oxidation had 0.02% S° in the PCE extract (Table 6). After bubbling air for 2 hours at 90° C with and without water present, no improvement in S° production was indicated. With oxidation reagent present and no water, the elemental sulfur production was increased slightly from 0.02% to 0.03%. However, with both oxidant and water present, the elemental sulfur production was increased from 0.03% to 0.05%. Also, XANES data on coals before and after Air/SO_2 stimulated oxidation/PCE extraction were examined. The results indicate that, similar to ambient air oxidation, organic sulfur in coal is not the major source of elemental sulfur produced during stimulated oxidation (Table 7).

Table 7. XANES analysis of sulfur forms in coals before and after Air/SO_2 stimulated oxidation/PCE extraction.

Coal	Total Wt% Sulfur*	Wt% sulfur in different forms (XANES) Pyritic	O-Sulfide	Thioph.	Oxid.	Sulfatic
F-IBC-104	4.23	2.22	0.72	1.12	0.00	0.11
After Air/SO_2, PCE/H_2O	4.06	2.00	0.72	1.02	0.02	0.12

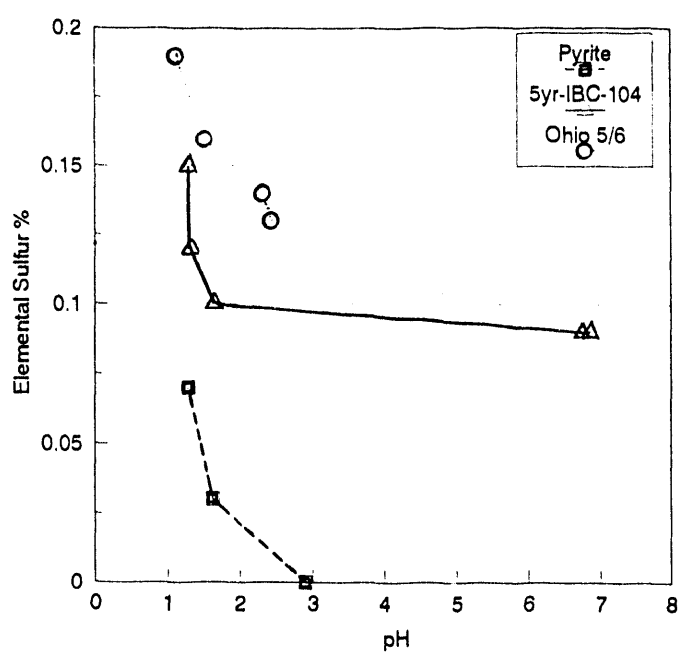


Figure 3: The relationship between the pH of the oxidation solution and the amount of elemental sulfur extracted.

Both oxidized IBC-104 and Ohio 5/6 coals as well as mineral pyrite were examined under various oxidation conditions tested before. This time, the pH of the oxidation solution was measured. The results indicated that the pH of the oxidation solution appears to be a key factor in elemental sulfur generation for PCE removal. As shown in figure 3, no matter what condition is used, the amounts of elemental sulfur produced by preoxidation and removed by PCE extraction increases as the oxidation solution increases in acidity, especially with pH<2. Overall, it is demonstrated that oxidation produces more elemental sulfur in coal that can be extracted by PCE. The increase in elemental sulfur in coal during oxidation is related to reaction conditions (temperature, moisture, and oxidant) preferably in an acidic environment. Pyrite oxidation contributes to the elemental sulfur in coal to be extracted by PCE. Also, the Ohio 5/6 coal appears to more readily produce elemental sulfur than Illinois coal during oxidation.

The Effect of PCE Treatment on the ASTM Forms-of-Sulfur Analysis

As originally proposed, if PCE coats the coal surface such that HCl is not able to penetrate and dissolve the sulfate fraction then the sulfatic sulfur will be reported as pyrite. This leads to a false interpretation that any sulfur lost via PCE extraction is "organic" in nature. This possibility is critically tested by extracting a highly oxidized coal with PCE and analyzing for the forms of sulfur. The oxidized coal, without PCE extraction, was analyzed by the ASTM D2492 method as a background. Samples of oxidized IBC-105 before(C-32806) and after (C-32807) PCE extraction were subjected to serial acid extraction (ASTM D2492) and total sulfur analysis (ASTM D 4239). The residual coal from the pyritic sulfur determination was also subjected to ashing to determine the remaining Fe content. These data give a cumulative measure of the total iron. The mass balance data for total iron and total sulfur are calculated and shown in Table 8 and Table 9 respectively. Total iron content in both samples before and

Table 8. Iron Material Balance.

	Feed Coal (%)	Extracted Coal (%)	PCE Free Basis (%)
Total Fe by fusion	2.65*	2.30*	2.38
Fe in HCl fraction	1.89	1.76	1.95
Fe in HNO_3 fraction	0.76	0.72	0.73
Fe in residue from HNO_3	0.07	0.09	0.09
Total Fe recovered	2.72	2.57	2.65
Total Fe by fusion/ Total Fe recovered	0.97	0.89	0.90

* Expected some losses in LiB_4O_7 fusion, incomplete dissolution in H_2O-HNO_3.

Table 9. Sulfur Material Balance.

	Feed Coal (%)	Extracted Coal (%)	PCE Free Basis(%)*
Total S	4.35	3.93	4.08
Sulfate	1.35	1.24	1.29
pyrite	0.99	0.93	0.94
Elemental	0.11	0	0
Organic (no S°)	1.90	1.76	1.82

* The PCE content in the residue (3.74%) was calculated from the chlorine content of the residue.

after PCE extraction, obtained through Lithium Tetraborate fusion and acid digestion, are consistently lower than those obtained from the cumulative measure of the ASTM analyses. This is partially due to some losses in the fusion process as well as in the succeeding incomplete acid dissolution.

The results also indicate that the ratio of the iron content obtained from fusion relative to that obtained from recovery is less for the PCE-treated sample (0.89) than that (0.97) for the feed. This implies that the difference may, in part, be attributed to the presence of PCE during the analysis. Comparing the percentage of 0.97 for the feed coal with the 0.89 for the extracted coal, the effect of PCE, however, seems to be very limited. From the extensive mass balance calculation for both Fe and S in the various fractions, as described, it is concluded that the effect of PCE on the ASTM determination of sulfur forms, mainly pyrite and sulfates, is very minor, and no further testing of other materials was deemed necessary.

Stable Sulfur Isotope Ratio Study of Coal Oxidation in Hot PCE

IBC-107 coal was oxidized under the conditions previously shown to stimulate production of elemental sulfur from other IBC coals, with and without added SO_2. The conditions used to produce the air oxidized product (sample 7301) and the air/SO_2 oxidized product (sample 7302) are shown in Table 10.

Table 10. Oxidation and PCE Extraction of IBC-107 Coal

Sample ID	Wt used (g)	Vol PCE (mL)	Vol H_2O (mL)	Temp (°C)	Time (hr)	Oxidant	S° (wt%)
7301	21.9369	200	40	90	22	Air, 20mL/s	0.047%
7302	10.7384	100	20	90	22	Air/SO_2	0.090%

The elemental sulfur in the PCE extracts from both air oxidized and air/SO_2 oxidized samples were collected and analyzed for their SSIR values. The data are shown in Table 11. It is significant to note that the SSIR value for the elemental sulfur isolated from air oxidized sample (7302) confirms the results obtained several years ago on another sample of air-oxidized IBC-107 (20.1 vs 20.6) (Hackley, et al,

1990). This not only shows that the elemental sulfur is derived from pyrite, but also indicates that the analytical methods are reliable. The elemental sulfur isolated after stimulated oxidation using air/SO_2 has an SSIR value of 5.7 (sample 7301) compared with 20.1 for elemental sulfur isolated after air oxidation (sample 7302). While the increase in the amount of elemental sulfur stimulated by SO_2 has a lower SSIR value (5.7) than that found in the sir-oxidized sample (20.1), these results show that the elemental sulfur isolated has been diluted with the lighter isotope, most likely from the SO_2 gas for which the SSIR value is 0.2.

As indicated in Table 11, the SSIR of the organic sulfur in the coal residue is not changed upon air oxidation (compare 7300 with 7302), but it increases slightly in the presence of sulfur dioxide (compare those with 7301).

Table 11. Stable Sulfur Isotope Ratios (SSIR) for Sulfate, Elemental Sulfur, Pyrite, and Organic Sulfur

(Delta ^{34}S of SO_2 used in oxidation = 0.18°/∘∘)

	Delta ^{34}S (°/∘∘)			
Sample ID	S°/∘∘ SO_4	S°/∘∘ Elem. S	S°/∘∘ Pyr.	S°/∘∘ Org. S
7300 (feed coal)	13.4	(20.6*)	26.2	1.5
7301 (PCE + air/SO_2)	5.5	5.7	23.4	1.9
7302 (PCE + air)	14.4	20.1	27.6	1.[illegible]

* Single value from a previous project on PCE extraction of air-oxidized IBC-107 coal

Table 12. Forms of Sulfur by LAH method for PCE treated and untreated IBC-107 coal (averages of two or more duplicates)

Sample ID	Acid-leach SO_4 S %	PCE S%	LAH Pyr S%	Combust Org S%	Calcl. Org S%^	Calcl. Cumul S%	Total Comb. Total S%
7300 (feed coal)	0.27		0.52	2.80	2.72	3.58	3.50
7301 (PCE+ air/SO_2)	0.32	0.09	0.45	2.85	2.85	3.70	3.70
7302 (PCE+ air)	0.02	0.047	0.41	2.66	2.73	3.22	3.30

^ Calculated Org. S. = % Tot. S - (%SO_4 + %Py. S + %Elem. S)

The results of forms of sulfur analyses by wet chemical method (Table 12) show that the amount of organic sulfur remaining after the stimulated oxidation is the same as in the feed coal. These results agree with the previous results on scale-up PCE extraction. Overall, this study and the previous XANES data indicate that the increase in the amount of elemental sulfur is derived, in part, from pyrite in coal and, in part, from the sulfur in the sulfur dioxide added to the reaction mixture. The sulfur from unoxidized forms of organic sulfur

(organic sulfide and thiophenes) do not contribute to the source of this elemental sulfur.

Extended Oxidation Study Using Organosulfur Model Compounds

The air oxidation of model organosulfur compounds was examined under several sets of conditions (extended Task 4) which might promote the organic sulfur oxidation because MWOPC claims it is necessary for successful coal desulfurization in their PCE desulfurization process.

Oxidation of organosulfur model compounds without a promoter - The experiments were conducted under the conditions used for coal oxidations. The conditions and the results are shown in Table 13. The data indicate that none of the organosulfur compounds tested have been significantly oxidized under these conditions. In the air and air/SO_2 reactions, nearly quantitative recoveries of starting materials were observed. Traces of octyl thiol were detected from dioctyl sulfide. The other compounds did not yield thiols. The results from this study are consistent with that of a study by Mill et al. (1992) in which the air oxidation of organic sulfides in asphalts and as model compounds was examined. It was found that there was no direct air oxidation of organic sulfides alone, but that oxidation could happen by the addition of hydrocarbons known to easily form hydroperoxides during air oxidation. For products confirmation both sulfoxides and sulfones were prepared by 40% peracetic oxidation in dichloromethane. Short reaction times at 0°C gave good yields of sulfoxides while long reaction times or higher temperatures gave near quantitative yields of sulfones.

Table 13. Organosulfur model compounds oxidation

Compound	Oxidant	Solvent	Temp.	Product	Verify by:
Dioctyl sulfide	Air	PCE	90	Trace octylthiol	GC
Dioctyl sulfide	Air/SO_2	PCE	90	Trace octythiol	GC
Dibenzyl sulfide	Air	PCE	90	No reaction	GC, HPLC
Dibenzyl sulfide	Air/SO_2	PCE	90	No reaction	GC, HPLC
Dibenzothiophene	Air	PCE	90	No Reaction	GC, HPLC
Dibenzothiophene	Air/SO_2	PCE	90	No Reaction	GC, HPLC

The Organosulfur compounds were also oxidized using H_2O_2 in acetone and CH_3CO_3H in CH_2Cl_2 yielding sulfones or sulfoxides for product confirmation.

Oxidation of organosulfur model compounds in the presence of a promoter - The oxidation of the organosulfur model compounds was repeated in the presence of a hydrocarbon additive, which is known to easily produce hydroperoxides (Mill et al., 1992) during air oxidation. The presence of a hydrocarbon additive, either 9,10-dihydroanthracene (DHA) or diphenylmethane (DPM), does induce sulfide to produce sulfoxide and sulfone. The qualitative results from a large number of tests indicate that in the presence of hydrocarbon promoters, dibenzyl sulfide was the most reactive model compound during air oxidation. It is followed in degree of reactivity by di-n-octyl sulfide and dibenzothiophene. The oxidized products observed were benzylsulfoxide and benzylsulfone, octylsulfoxide, and dibenzothiophene sulfone (DBT-1,1-dioxide). The DBT sulfoxide was not observed, because this compound is unstable and is likely to convert to sulfone.

The oxidation reactions are complex and in each case are accompanied by the production of trace amounts of unidentified compounds which increase with time. The oxidation solution of dibenzyl sulfide in the presence of DHA or DPM contained an active oxidizing agent. This was indicated by the conversion of a fresh sample of dibenzyl sulfide to sulfoxide or sulfone using the oxidation solution alone. The highest yield of about 4% was obtained for benzylsulfoxide under this reaction condition. In any case, elemental sulfur was not detected as a result of these oxidation reactions.

These studies should set a lower limit on the conditions necessary for air oxidation of the type of organosulfur compounds found in coal. MWOPC states that coal desulfurization takes place when coal as a suspension in PCE is preoxidized in air at about 70°C for one-half hour prior to their PCE desulfurization process. The mild preoxidation condition described by MWOPC does not produce enough oxidized organic sulfur to support the level of sulfur removal reported. Overall, the PCE desulfurization process was found not to be practical for organic sulfur removal. Furthermore, when air oxidation of coal-like organosulfur compounds does occur, the products are inconsistent with production of elemental sulfur, the product reported by MWOPC.

SUMMARY AND MAJOR CONCLUSIONS

* A laboratory scale operation of the MWOPC process developed for coal desulfurization with PCE extraction was demonstrated, and a dechlorination procedure to remove excess PCE from the PCE-treated coal was developed.

* PCE desulfurization removes mainly elemental sulfur from coal. A higher level of coal oxidization results in a

larger amount of elemental sulfur to be removed by PCE extraction.

* The amount of elemental sulfur produced during preoxidation is controlled by the reaction time, temperature, moisture, and reactant. The increase in elemental sulfur during preoxidation is found to be pH dependent and is attributed to coal pyrite oxidation under acidic (pH<2) conditions.

* The elemental sulfur produced complicates the PCE process evaluation in that the ASTM forms-of-sulfur analysis interprets elemental sulfur removed during PCE desulfurization as a decrease in organic sulfur.

* The hypothesis concerning the effect of PCE treatment on inhibiting the extraction of the coal-derived pyrite and iron sulfates during the ASTM procedures for forms-of-sulfur was not confirmed.

* The mild preoxidation treatment of coal described by MWOPC for removal of organic sulfur does not produce enough oxidized organic sulfur to support the sulfur removal results. When oxidation of coal-like organosulfur compounds does occur, the products are inconsistent with production of elemental sulfur, the product reported by MWOPC.

* The PCE process is not practical for organic sulfur removal. Also, it is recommended that all chemical desulfurizations should utilize fresh feed coals, and if the ASTM method is used for forms-of-sulfur, the results should be verified by an alternate method, such as XANES.

REFERENCES

American Society for Testing and Materials, 1991, *Annual Book of ASTM Standards*, D-2492, Forms of Sulfur in Coal, p. 289-294.

Atwood, G., H. Leehe, and G.J. Shell, 1990, "Desulfurization and Benefication of Coal Using Perchloroethylene," *in Proceedings: Fifteenth Annual Conference on Fuel Science*. EPRI. Alto, CA, June 19-21.

Atwood, G. and H. Leehe, 1991, "Perchloroethylene Coal Cleaning," J. Coal Preparation. Vol. 11, p. 77-86.

Buchanan, D., K. Coombs, C. Chaven, C. Kruse, K. and Hackley, 1990, "Sulfur Removal from Illinois Coals by Extraction with Perchloroethylene," *Processing and Utilization of High Sulfur Coals III*, eds. R. Markszewski, T. Wheelock, Elsevier, 79.

Chrisman, B.L. and T.A. Tumolillo, 1971, "Computer Analysis of Mössbuaer Spectra," *Comp. Phys. Comm.* 2:322-330. *in* Illinois coals and their washed products, ISGS Contract/Grant 1985-2, 49p.

Chou, M.-I., D. Buchanan, J. Lytle, R. Ruch, C. Kruse, C. Chaven, K. Hackley, R. Hughes, R. Harvey, J. Stucki, G. Huffman, and F. Huggins. 1992. Sulfur Removal From High-Sulfur Illinois Coal by Low-Temperature Perchloroethylene (PCE) Extraction. Annual Report to the Illinois Coal Development Board, Illinois Clean Coal Institute; *ISGS Open File Series*, in press.

Fullerton, K.L., V.R. Parmaeswaran, and H. Leehe, 1990, " A Novel Coal Refining Process Using Perchloroethylene." AIChE National Meeting, Chicago, IL. November.

Hackley K., D. Buchanan, K. Coombs, C. Chaven, and C. Kruse, 1990, "Solvent Extraction of Elemental Sulfur from Coal and a Determination Oof Its Source Using Stable Sulfur Isotopes," *Fuel Proc. Tech.*, 24, 431.

Harvey, R.D. and I. Demir, 1990, "Characterization of Organic Sulfur in Macerals and Chars," Final Report, Ill. Coal Dev. Board, *ISGS Open File Series* 1991-3, 24p.

Huffman, G.P., S. Mitra, F.E. Huggins, N. Shah, S. Vaidya, and Fulong Lu, 1991, "Quantitative Analysis of All Major Forms of Sulfur in Coal by XAFS Spectroscopy" *Energy and Fuel*. Vol.5, p. 574-581.

Hughes, R.E. and R.L. Warren, 1989, "Evaluation of the

Economic Usefulness of Earth Materials by X-ray Diffraction," *in Proceedings, 23rd Forum on the Geology of Industrial Minerals*, R.E. Hughes, and J.C. Bradbury (eds.), *ISGS, Industrial Minerals Notes*, 102, pp. 47-57.

Lee, S., K.L. Fullerton, S.K. Kesavan, V.R. Parameswaran, B.G. Lee, and S. Nitirahardja, 1989, "The Percholoethylene Refining Process of High Sulfur Coals," *in Proceedings: Fourteenth Annual Conference on Fuel Science and Conversion*, EPRI, Alto, CA, May 18-19.

Lee, S., S.K Kesavan, B.G. Lee, A. Ghosh, and C.J. Kulik, 1989, "Selective Removal of Organic Sulfur from Coal by Perchloroethylene Extraction," *Fuel Science and Technology International*, Vol. 1, No. 4, pp. 443-468.

Leehe, H.H., 1989, "Midwest Ore Processing Company's Coal Benefication Technology; Recent Prep Plant Scale and Laboratory Activities," *in Proceedings: Fourteenth Annual Conference on Fuel Science and Conversion*, EPRI, Palo Alto, CA, May 18-19.

Leehe, H.H. and R.S. Sehgal, 1988, "Pyritic and Organic Sulfur Removal From Coal With Perchloroethylene," *Proceedings: 1987 Work Shop on Coal Structure*, Electric Power Research Institute, EPRI ER-6099-SR, pp. 8-1 to 8-18, Nov.

Liu, C.L., K.C. Hackley, and D.D. Coleman, 1987, "Use of Stable Sulfur Isotopes to Monitor Directly the Behaviour of Sulfur in Coal During Thermal Desulfurization," *Fuel*, 66, pp. 683-687.

Mill, T., D.S. Tse, B. Loo, C.C. D. Yao, and E. Canavesi, 1992, "Oxidation pathways for Asphalt" *Prepr. Pap. Amer. Chem. Soc.*, Div. fuel Chem. 37(3), 1992, 1367-1375.

Starbuck, A.E., 1980, "Process for De-Sulfurization of Coal and Ore," *U.S. Patent 4,213,793*, July; and Reissue Re. 32,454, July (1987).

Westgate, L.M. and T.F. Anderson, 1982, " Extraction of Various Forms of Sulfur from Coal and Shale for Stable Sulfur Isotope Analysis," *Anal. Chem.*, Vol.54, pp.2136-2139.

PROJECT MANAGEMENT REPORT
June 1, 1993 through August 31, 1993

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, 615 E. Peabody Drive, Champaign, IL 61820
Funded Co-investigator: D.H. Buchanan, Eastern Illinois University (EIU)
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 and F.E. Huggins (UK)
Project Manager: K.K. Ho, Illinois Clean Coal Institute

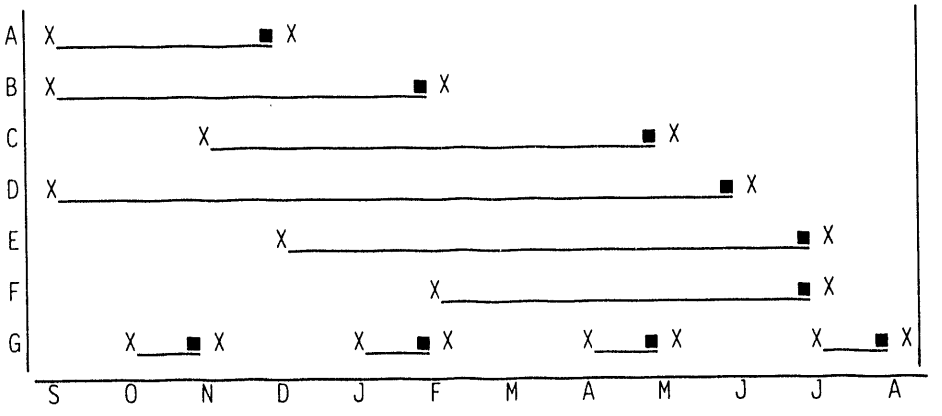
COMMENTS

Projected and Estimated Actual Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Cost	Total
Sept. 1, 1992 to Nov. 30, 1992	Projected	7,350	960	1,000	0	0	7,962	1,727	18,999
	Estimated	6,000	600	800	0	0	800	820	9,020
Sept. 1, 1992 to Feb. 28, 1993	Projected	14,700	1,919	1,420	0	0	15,923	3,396	37,358
	Estimated	14,000	1,400	900	0	0	2,500	1,358	20,158
Sept. 1, 1992 to May 31, 1993	Projected	22,049	2,879	1,840	500	0	23,885	5,080	55,883
	Estimated	18,500	2,200	1,200	520	0	2,500	2,930	27,330
Sept. 1, 1992 to Aug. 31, 1993	Projected	28,334	3,699	2,350	800	0	32,444	5,693	73,320
	Estimated	25,885	2,598	2,350	813	0	35,979	5,693	73,320

*Cumulative by Quarter

SCHEDULE OF PROJECT MILESTONES

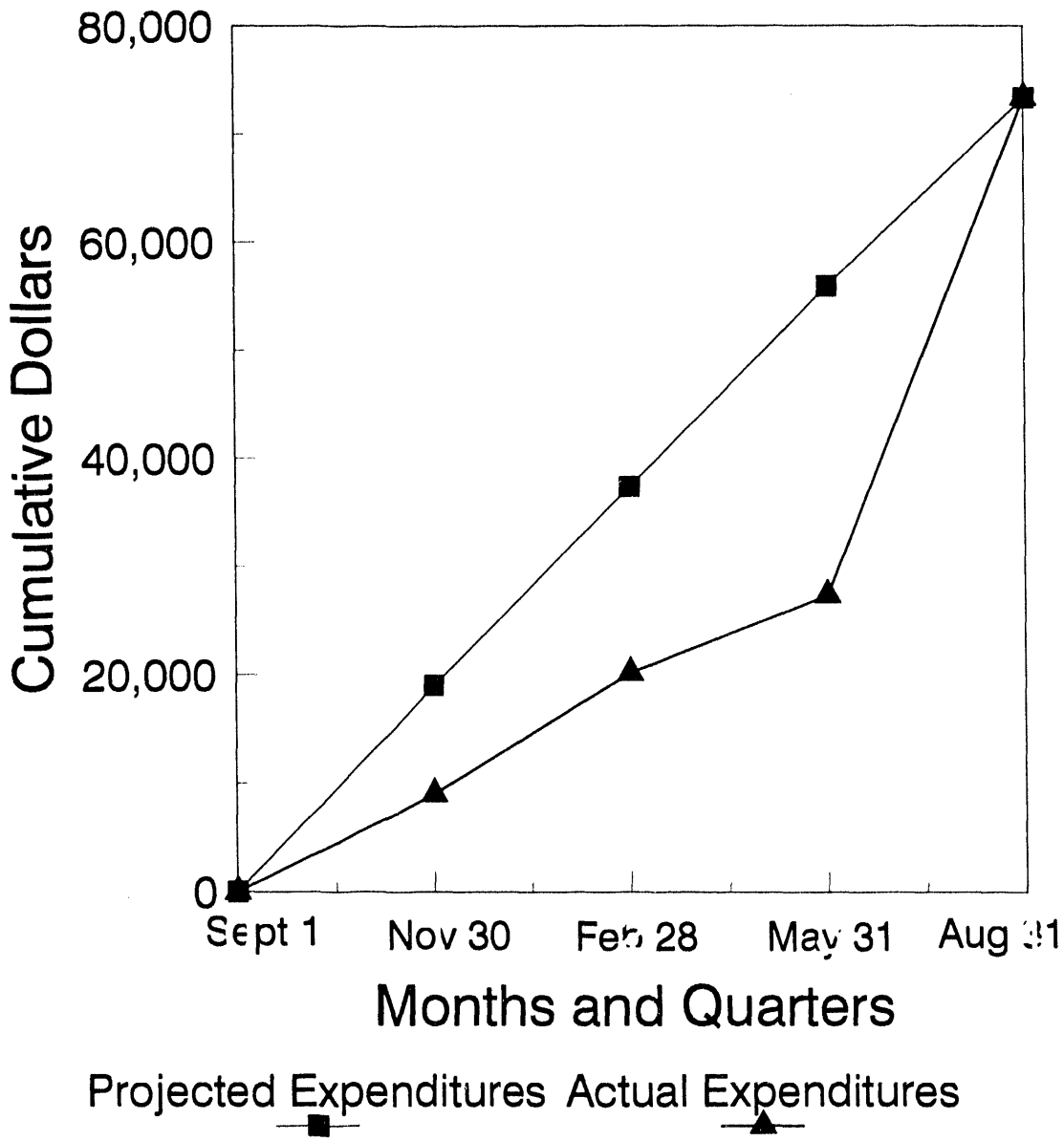


Milestones:

A. Sample requisition and student helper hired
B. Base line study (Task 6)
C. Radioactive trace study (Task 7)
D. Oxidation study (Extended Task 4)
E. Data evaluation (Extended Task 5)
F. Process application and/or optimization (Task 8)
G. Technical project management reports prepared and submitted

COST BY QUARTER - EXHIBIT C

SULFUR REMOVAL FROM HIGH-SULFUR ILLINIOS COAL BY LOW TEMPERATUR PERCHLOROETHYLENE (PCE) EXTRACTION



LIST OF PUBLICATIONS AND PRESENTATIONS
September 1, 1992 through August 31, 1993

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, 615 E. Peabody Drive, Champaign, IL 61820

A poster was presented at the ICCI Contractors' Meeting in Champaign, held on August 3-5, 1993. A paper was also presented at the 205th ACS National Meeting in Denver Colorado, held on March 28 - April 2, 1993.

Publications:

M.-I. M. Chou, J. M. Lytle, R. R. Ruch, C. W. Kruse, C. Chaven, and D. H. Buchanan, "Pre-oxidation and Perchloroethylene (PCE) Desulfurization of Illinois Coals." Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem., 1992, vol. 37, No. 4, pp. 2002-2009.

M.-I. M. Chou, J. M. Lytle, C. W. Kruse, and K. K. Ho, "Organic Volatile Matter and Its Sulfur-Containing Compounds Produced by Coal Pyrolysis." Prepr. Pap. Am. Chem. Soc. Div. Fuel Chem., 1993, vol. 38, No. 2, pp. 655-661.

M.-I. M. Chou, J. M. Lytle, R. R. Ruch, C. W. Kruse, C. Chaven, K. C. Hackley, R.E. Hughes, R.D. Harvey, J.K. Frost, D.H. Buchanan, J.W. Stucki, G.P. Huffman and F.E. Huggins, "Sulfur Removal From High Sulfur Illinois Coals by Low Temperature Perchloroethylene (PCE) Extraction." Illinois State Geological Survey, Open File Series, in press.

Gerald P. Huffman, Naresh Shah, Frank E. Huggins, Leon M. Stock, Kuntal Chatterjee, John J. Kilbane II, Mei-In M. Chou, and David H. Buchanan, "Sulfur Speciation of Desulfurized Coals by XANES Spectroscopy." Fuel, in preparation.

Buchanan, D., K. Coombs, P. Murphy, C. Chaven, 1993, "A Convenient Method for the quantitative Determination of Elemental Sulfur in Coal by HPLC analysis of Perchloroethylene Extracts," Energy & Fuels, 7, 219-221.

HAZARDOUS WASTE REPORT

Solicitation No.	ICCI/RFP92-1
Program Area	Coal Cleaning
Proposer	Illinois Clean Coal Institute
Principal Investigator	Mei-In M. Chou
Project Title	Sulfur Removal from High Sulfur Illinois Coal by Low Temperature Perchloroethylene Extraction
Project Duration	September 1, 1992 - August 31, 1993
Total Estimated Cost	$73,320

No solid waste was produced by this project.

Substance/chemical	EPA Hazardous Waste No.	EPA Hazard Code.
Perchloroethylene	F001	(T)
Other solvents used:		
Phenol	U188	108-95-2(Chem. Abs. #)
Methanol	F003	(I)
Acetone	F003	(I)

Quantity purchased, utilized, or generated:

Perchloroethylene	6 gallons
Phenol	0.5 gallon
Methanol	2 gallons
Acetone	5 gallons

Hazardous Waste Transporter:
The Office of Environmental Safety & Health, University of Illinois, would make necessary determination and dispose of the waste in the manner approved by the IL EPA.

Office of Health & Safety, University of Illinois: 101 S. Gregory, Urbana, Illinois 61801 (Van Anderson) (217)244-9278

Hazardous Waste Disposal Facility, Contractor, and Location:
All collection, treatment and disposal was in accordance with all RCRA and TSCA rules/regulations. Incineration or treatment was at certified facilities. The current University of Illinois contract (annually bid) is with Rollins, Inc., Which has facilities in Baton Rouge, LA and Deer Park, TX.

Hazardous Waste Treatment Method: Incineration or treatment.

DATE FILMED

4 / 12 / 94

END