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

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ABSTRACT

The purposes of this project are to independently confirm and possibly to improve the organic sulfur removal from Illinois coals with the PCE process developed by the Midwest Ore Processing Co.(MWOPC), to verify the forms-of-sulfur determination using the ASTM method for evaluation of the PCE process, and to develop a dechlorination procedure to remove excess PCE from the PCE-treated coal. This is the second year of a two-year project.

Year-2 study includes two original (task 6 and 7), two extended (extended tasks 4 and 5), and one slightly modified tasks (task 8). The objectives for year-2 study are to verify the possible effect of PCE treatment on coal-derived FeS_2, $FeSO_4$, and $Fe_2(SO_4)_3$ on ASTM coal analysis (task 6), to investigate the behavior of sulfur during oxidation and PCE desulfurization using the isotopically signatured coal sample (task 7), to investigate the proprietary reagent on the oxidation of the organic sulfur model compounds with and without additives (extended task 4), to evaluate this new oxidation on the organic sulfur removal by PCE desulfurization (extended task 5), and to study other innovative pretreatment processes for the removal of organic sulfur from coal under mild conditions (task 8).

Task 6 & 7 are concluded in this quarter. Oxidation study on the organosulfur model compounds alone was completed in first quarter. The oxidation reactions were repeated on the organosulfur model compounds with the presence of hydrocarbon additives. These additives are known to easily produce hydroperoxides during air oxidation. Analysis of the reaction products is in progress.

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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 was reported to effectively remove organic sulfur from high-sulfur coals obtained from Ohio and Indiana (Leehe and Sehgal, 1988; Leehe, 1989; Lee et al., 1989). However, it has not yet proven to be as successful with Illinois coals (Lee et al., 1989; Buchanan et al., 1990).

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. The MWOPC process evaluation was based on the ASTM data interpretation. We have postulated that certain errors in interpreting ASTM data may result in higher organic sulfur removal reported by the MWOPC. One hypothesis 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 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 the removal of sulfur by PCE extraction is organic in nature.

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 developed by the MWOPC, (2) to verify the forms-of-sulfur determination using the ASTM method for forms of sulfur in evaluating the PCE desulfurization process, and (3) to develop a procedure to remove excess PCE from PCE-treated coals. This is a two-year project with a joint effort by the ISGS, EIU, the University of Illinois at Urbana/Champaign (UI-UC), and the University of Kentucky (UK). In year-1 study, the objectives in terms of demonstrating the operation of the MWOPC developed PCE desulfurization process, revealing the apparent reduction in ASTM organic sulfur to be elemental sulfur derived from pyrite ambient oxidation, and developing a dechlorination procedure to remove excess PCE from the PCE-treated coal have been met.

Year-2 study includes two original (task 6 and 7), two extended (extended tasks 4 and 5), and one slightly modified tasks (task 8). Task 6 will verify the possible effect of PCE treatment on coal-derived FeS_2, $FeSO_4$, and $Fe_2(SO_4)_3$ on ASTM coal analysis. Task 7 will investigate sulfur behavior during oxidation and PCE desulfurization using IBC-107 coal which contains isotopically signatured pyritic sulfur and organic sulfur. In the extended task 4 and 5, the oxidation study using model sulfur compounds will be performed. Any importance of the proprietary reagent oxidation on the PCE organic sulfur desulfurization will be evaluated. If the results indicate that the new oxidation procedure can be exploited as a desulfurization method, then optimization study will be performed (task 8). Other thermal and/or chemical pretreatment processes for the desulfurization activity under mild conditions will also be examined.

In Task 6, the mass balance data for both total iron and total sulfur were obtained for PCE treated and untreated oxidized IBC-105 samples. The dechlorination procedure was not applied to this PCE treated sample in order to examine the effect of its present to the ASTM analysis. Total iron content in samples before and after PCE extraction obtained through Lithium Tetraborate fusion and acid digestion are consistently lower than those obtained from cumulative measure by the ASTM analyses. The results indicate that the presence of PCE during ASTM analysis does contribute some of this difference. The effect, however, appears to be very small.

In Task 7, 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 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 elemental sulfur isolated after stimulated oxidation using air/SO_2 has an SSIR value of 5.7 compared with 20.1 or 20.6 for elemental sulfur isolated after air oxidation. It appears that this elemental sulfur has been derived, in part, from the sulfur in the sulfur dioxide added to the reaction mixture. The results also suggest that the increase in elemental sulfur upon stimulated oxidation is a function of the amount of pyritic sulfur present. The absolute amount of elemental sulfur found is also, of course, related to pyritic sulfur content.

In the extended Task 5, the fist subtask for the oxidation study on the organosulfur model compounds without additives was completed in first quarter. The oxidation reactions were repeated on the organosulfur model compounds with the presence of hydrocarbon additives which are known to easily form hydroperoxides during air oxidation. Oxidation experiments and analysis of these reaction products are in progress.

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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 forms-of-sulfur determination, and (3) to develop a procedure to remove excess PCE from PCE-treated coals. This is the second year of the two-year project. In year-1 study, the objectives in terms of demonstrating the operation of the claimed PCE desulfurization process, revealing the apparent reduction in ASTM organic sulfur to be elemental sulfur derived from pyrite ambient oxidation, and developing a dechlorination procedure to remove excess PCE from the PCE-treated coal have been met.

The objectives for year-2 study are

1) to verify the possible effect of PCE treatment on coal-derived FeS_2, $FeSO_4$, and $Fe_2(SO_4)_3$ on ASTM coal analysis,
2) to investigate the behavior of sulfur during air/SO_2 oxidation and PCE desulfurization procedure using the isotopically signatured coal sample,
3) to regulate the air/SO_2 on the oxidation of the organic sulfur model compounds with and without additives,
4) to evaluate the effect of air/SO_2 oxidation on the organic sulfur removal by PCE desulfurization, and
5) to study other thermal and/or chemical pretreatment processes for the removal of organic sulfur from coal under mild conditions.

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 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, Feb. 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 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).

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 postulates need verification.

In several presentations and personnel communications, Atwood and Leehe of Mid West Ore stated that pre-oxidation of coal was the key to their PCE-based process for removing organic sulfur from coal and that aliphatic sulfur was being removed. They speculated that the brief oxidation they gave the coal did something to aliphatic sulfur to make it susceptible to removal. In our proposal we referred to earlier work by Bronikowski, et al. (1989) in which they used small amounts of SO_2 in air as an oxidizing sulfur removal agent for coal. In their papers they also claimed that air/SO_2 oxidized (and maybe desulfurized) Dibenzithiophene (DBT).

It has been demonstrated in the year-1 study that oxidation of coal in water/PCE prior to extraction with hot PCE increases the amount of elemental sulfur recovered in the PCE extract. In view of the increase in elemental sulfur extracted when air containing a small

amount of sulfur dioxide is used as the oxidizing agent, it is important to determine the source to the extracted elemental sulfur. In particular, is any of that elemental sulfur derived from the organic sulfur or the pyritic sulfur of the coal? Answer to this question is important since the proponents of the PCE desulfurization process at Mid-West Oil Processing Company and University of Akron emphasize that pre-oxidation and pyrite content in coal are crucial to the PCE process.

EXPERIMENTAL PROCEDURES

Year-2 study includes two original (task 6 and 7), two extended (extended tasks 4 and 5), and one slightly modified tasks (task 8).

Task 6: To verify the possible effect of PCE treatment on coal-derived FeS_2, $FeSO_4$, and $Fe_2(SO_4)_3$ on ASTM coal analysis.

An ambient oxidized sink fraction of IBC-104 (1040X/SF) which contains coal derived pyrite (FeS_2) were subjected to PCE extraction, and the PCE extracts were analyzed for elemental sulfur. In addition, an oxidized IBC-105 (C-32806) which contains coal-derived pyrite, sulfate, and elemental sulfur was used after it was dried in a drying oven at 108°F for one week. Both the oxidized sink fraction of IBC-104 (1040X/SF) and the oxidized IBC-105 were riffled, split, and subjected to PCE extraction.

A split of sample was treated with 100 ml boiling PCE (120°C) and refluxed for 1 hr., hot filtrated and the PCE filtrate was made up to volume and analyzed for S°. The residue remaining on the filter was dried at 105°C for 24 hrs. and saved for further analysis. The extracts were analyzed for elemental sulfur using HPLC method as before.

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). In addition to regular forms of sulfur, the residue coal from pyritic sulfur determination was ashed for 24 hrs. at 800°C and re-extracted with aqua-regia to dissolve Fe. Total iron in both samples were also subjected to Lithium Tetraborate fusion and the residue dissolve in hot water and diluted HNO_3. The ASTM HCl and HNO_3 extraction solutions were also analyzed for Fe content. The mass balance for total iron and total sulfur were calculated.

Task 7: To monitor sulfur behavior during oxidation and PCE desulfurization using coal with isotopically signified organic and inorganic sulfur.

In this task, an Illinois No.6 coal (IBC-107) in which the various forms of sulfur carry unique stable sulfur isotope ratios (SSIR),

was used to trace the origin of elemental sulfur produced in oxidation experiments. In the previous oxidation experiments, additional elemental sulfur was produced. It is important to determine the source of this extra elemental sulfur: from pyrite, from organic sulfur, or from the used SO_2 as a co-oxidant. Since SO_2 co-oxidant could conceivably contribute to the extra elemental sulfur, a pre-study was conducted in the first quarter to determine the SSIR of the SO_2. In this quarter, a split of IBC-107 coal was oxidized under the most successful conditions (Water/PCE/air/SO_2/90°/22 hrs.) for stimulating elemental sulfur extraction. The PCE extraction solution was analyzed for elemental sulfur content, and than the sulfur was used for SSIR analysis.

Extended task 4 and 5: To further investigate and to evaluate the air/SO_2 oxidation reaction using model sulfur compounds.

In the first quarter, oxidation of sulfur model compounds without hydrocarbon additives was completed. In this quarter, the same model compounds reactions were conducted to examine various hydroaromatic hydrocarbons additives as possible catalysts for organic sulfur oxidation. The oxidation of di-n-octyl sulfide, dibenzyl sulfide and dibenzothiophene were carried out in wet PCE in the presence of easily oxidized hydrocarbons such as 9,10-dihydroanthracene which might act as intermediate oxidants of the organic sulfur in coal. The conditions used were those reported last quarter for stimulating sulfur removal from coal. The course of the reaction was followed by GC.

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

If the air/SO_2 oxidation studies turn up results which can be exploited further as a desulfurization method, the optimization condition for PCE desulfurization using the air/SO_2 oxidation technique as a pretreatment process will be determined.

If the results of the new oxidation studies confirm the conclusions of year-1 study that the apparent reduction in ASTM organic sulfur is just elemental sulfur derived from pyrite oxidation, other thermal and/or chemical pretreatment processes for organic sulfur desulfurization activities under mild conditions will be examined.

RESULTS AND DISCUSSION

The Effect of PCE Extraction on the ASTM Forms of Sulfur Analysis:

The purpose of this task is to ascertain if the extraction of coal by PCE effected the ASTM D2492 procedure for "forms of sulfur". IF PCE coated the coal surface such that HCl was not able to penetrate and dissolve the sulfate fraction then the sulfitic sulfur would report as pyrite. This would lead to a false interpretation that any sulfur lost via PCE extraction was organic in nature.
This possibility was 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 residue coal from pyritic sulfur determination was also subjected to ashing for remaining Fe content determination. These data give a cumulative measure of the total iron content. The mass balance data for total iron and total sulfur were calculated and shown in Table 1 and Table 2 respectively. Total iron content in both samples before and after PCE extraction obtained through Lithium Tetraborate fusion and acid digestion are consistently lower than those obtained from cumulative measure by the ASTM analyses. This is partially due to some losses in the fusion process as well as the following 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 PCE treated sample (0.89) than that (0.98) for the feed. This implies that this difference may, in part, be contributed from the presence of PCE during the analysis. Comparison between the ratio of 0.98 with the ratio of 0.89, the effect, however, seems to be very limited.

Those conclusions are found upon an extensive mass balance approach of both Fe and S in the various fractions as described below. At this time no further testing of $FeSo_4$ or other material is deemed necessary.

Table 1. Iron Material Balance.

	C-32806 Feed coal basis	C-32807 Extracted (%)	PCE free (%)
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 (After 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 2. Sulfur Material Balance.

	C-32086 Feed coal	C-32807 Extreated	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

** PCE in the residue is 3.74%.

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 of 7301 and the air/SO_2 oxidized product of 7302 are shown in Table 3.

Table 3. 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 4. It is gratifying 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). This not only shows that the elemental sulfur is derived from pyrite, but also indicates that the analytical methods are reliable and have not changed over time. The elemental sulfur isolated after stimulated oxidation using air/SO_2 has an SSIR value of 5.7 (from 7301) compared with 20.1 or 20.6 for elemental sulfur isolated after air oxidation (from 7302). It appears that this elemental sulfur has been derived, in part, from the sulfur in the sulfur dioxide added to the reaction mixture. While the increase in the amount of elemental sulfur stimulated by SO_2 is less than that found in other Illinois coals, these results show that the S isolated has been diluted with the lighter isotope, most likely from the SO_2 gas for which the SSIR value is 0.2.

It is interesting to note that coals IBC-105 and Ohio 5/6, both of which showed a greater increase in elemental sulfur content upon SO_2 stimulated oxidation, both contain much more pyritic sulfur than IBC-107. It may be that the increase in elemental sulfur upon stimulated oxidation is a function of the amount of pyritic sulfur present. The absolute amount of elemental sulfur found is also, of course, related to pyritic sulfur content.

Table 4. 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	1.5

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

As indicated in Table 4, the SSIR of the organic sulfur in the coal residue has not changed upon air oxidation (compare 7300 with 7302), but it increased slightly in the presence of sulfur dioxide (compare with 7301). The results from forms of sulfur analyses by

wet chemical method showed that the amount of organic sulfur remaining after the stimulated oxidation was the same as in the feed coal, which agrees with the previous studies of PCE extraction.

Table 5. Forms of Sulfur by LAH method for PCE treated and untreated IBC-107 coal (averages of two or more duplicates)

Sample ID	Acid-leac SO4 S.%	PCE ele.S%	LAH Pyr S%	Combust. Org S%	Calcl. Org S%^	Calcl. Cumul S%	Total Cumb. 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.)

As indicated in Table 5, the amounts of sulfate is increased with SO_2 treatment.The calculated values indicate that about 63% of the sulfate in 7301 is derived from the added SO_2. It is noted that (Table 4) the SSIR of the sulfatic sulfur decreased and the amount of sulfatic sulfur increased with SO_2 treatment. The small drop (from 27 to 23.4) in SSIR of the pyritic sulfur after SO_2 oxidation is very interesting in terms of the mechanism of pyrite oxidation with air and with air/sulfur dioxide. As the light isotopes of pyritic sulfur were lost to the elemental sulfur, the SSIR of the pyritic sulfur remaining in the coal residue should increase. This is apparent by comparing 7300 and 7302. That the SSIR of 7301 is less than that of the starting pyrite (23.4) must mean that sulfur from the added sulfur dioxide has also been incorporated into the remaining pyrite. (Remember, this is at 120°C with only a few percent of SO_2 in the gas stream at atmospheric pressure.) This could be a very useful tool for future studies of the chemistry of coal pyrite.

Air Oxidation of Organosulfur Compounds:

The air oxidation of model organosulfur compounds was examined under several sets of conditions in a search for conditions/reagents which might promote the sulfur oxidation which Mid-West Ore claims is necessary for successful coal desulfurization in their "PCE process."

In the first quarter, none of the organosulfur compounds tests (Table 6) showed significant oxidation when air was bubbled through hot PCE solutions of the compounds - the conditions used for coal oxidations. In this quarter, oxidation study on the organosulfur model compounds was conducted with a hydrocarbon additive, 9,10-dihydroanthracene (DHA). This hydrocarbon compound (DHA), according to Mill, 1992, was the most successful compound in

promoting the air oxidation of dimethyl sulfide and di-n-butylsulfide to the sulfoxides.

This study is in progress. The preliminary results on interactions of the model compounds with air or oxygen at several temperatures in the presence and absence of DHA are shown in Table 6. At present, only qualitative data is available to indicate reaction has occurred. Product identification is only by Gas Chromatography retention time. These data will be verified by GC/MS in the next quarter. When a product such as anthracene or the sulfoxide is indicated in Table 6, it means that oxidation reaction take place with enough products to be measured by GC.

From this preliminary data, it is indicated that the presence of DHA does promote oxidation of sulfide to the sulfoxide and possibly the sulfone. The dihydroanthracene is converted to anthracene and in some cases small amounts of the anthrone. There is no evidence, however, for C-S bond cleavage, which is necessary for sulfur removal. Also, it is indicated that such oxidation occurred under more constrain conditions, not under the conditions used by Mid-West Ore in their PCE coal treatments. This is an additional evidence against their claim that mild air oxidation of organic sulfur in the presence of hot PCE leads to coal desulfurization.

Table 6. Air Oxidation of Organosulfur Compounds

Compound	Temp.	Solvent	Oxidant	Time	DHA	Evidence Rxn*
Dibenzylsulfide	120	PCE	O_2 flo	20 h	No	GC: None
Dibenzylsulfide	120	PCE	O_2 flo	20 h	Yes	GC: None
Dibenzylsulfide	190	None	O_2 flo	3 h	Yes	GC: SO, AN
Dibenzylsulfide	125	None	air[a]	52 h	Yes	GC: SO, AN, ANO
Di-n-octylsulfide	120	PCE	O_2 flo	20 h	Yes	GC: None
Di-n-octylsulfide	125	None	air[a]	52 h	Yes	GC: SO, AN
Dibenzothiophene	120	PCE	O_2 flo	20 h	Yes	GC: None
Dibenzothiophene	125	None	air[a]	52 h	Yes	GC: SOO, AN, ANO

* SO = Sulfoxide, SOO = Sulfone, AN = Anthracene, ANO = Anthrone
[a] Reaction in air-filled, scaled glass tubes, DHA = 9,10-dihydroanthracene

In the next quarter, GC/MS will be used to verify and quantify the tentative product identifications by GC. Also, the last phase of this study will be conducted which is to substitute coal for DHA in the above reactions. The experiment will be conducted by mixing the model compounds with coal, heating the mixture in air, extract it with a non-polar solvent, and using GC/MS to search for oxidation products of the added sulfides in the extracts. Various, obvious control reactions will enable us to show whether or not any such products came from the added sulfide.

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PROJECT MANAGEMENT REPORT

September 1, 1992 through November 30, 1992

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

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

Funded Co-investigator: D.H. Buchanan
Eastern Illinois University (EIU)

ISGS Co-investigators: J.M. Lytle, R.R. Ruch, C.W. Kruse, C. Chaven, K.C. Hackley, R.E. Hughes, R.D. Harvey

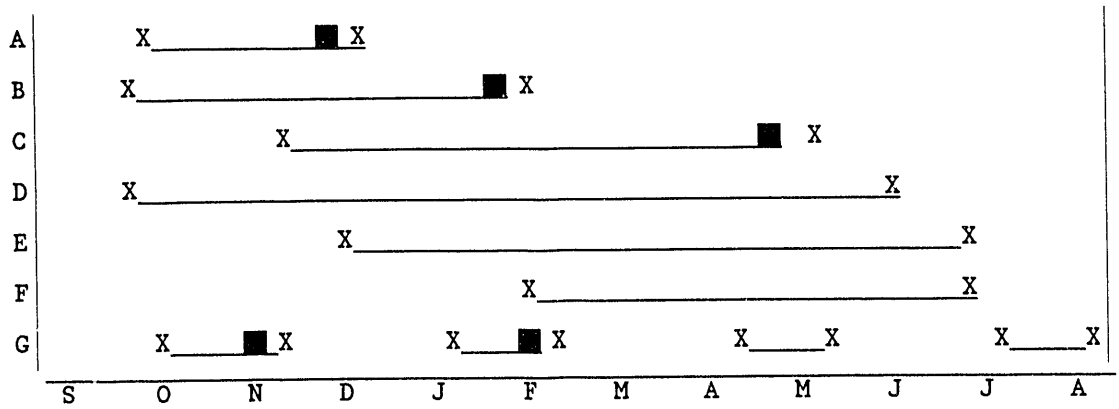
Other Co-investigators: J.W. Stucki, University of Illinois, G.P. Huffman and F.E. Huggins, University of Kentucky

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

COMMENTS

Contract for EIU, and analyses services from coal analysis laboratory have not yet been paid. These works are in progress but payments are made on a cost reimbursement basis after the works are completed. Thus, expenditures were less than expected for this quarter.

SCHEDULE OF PROJECT MILESTONES

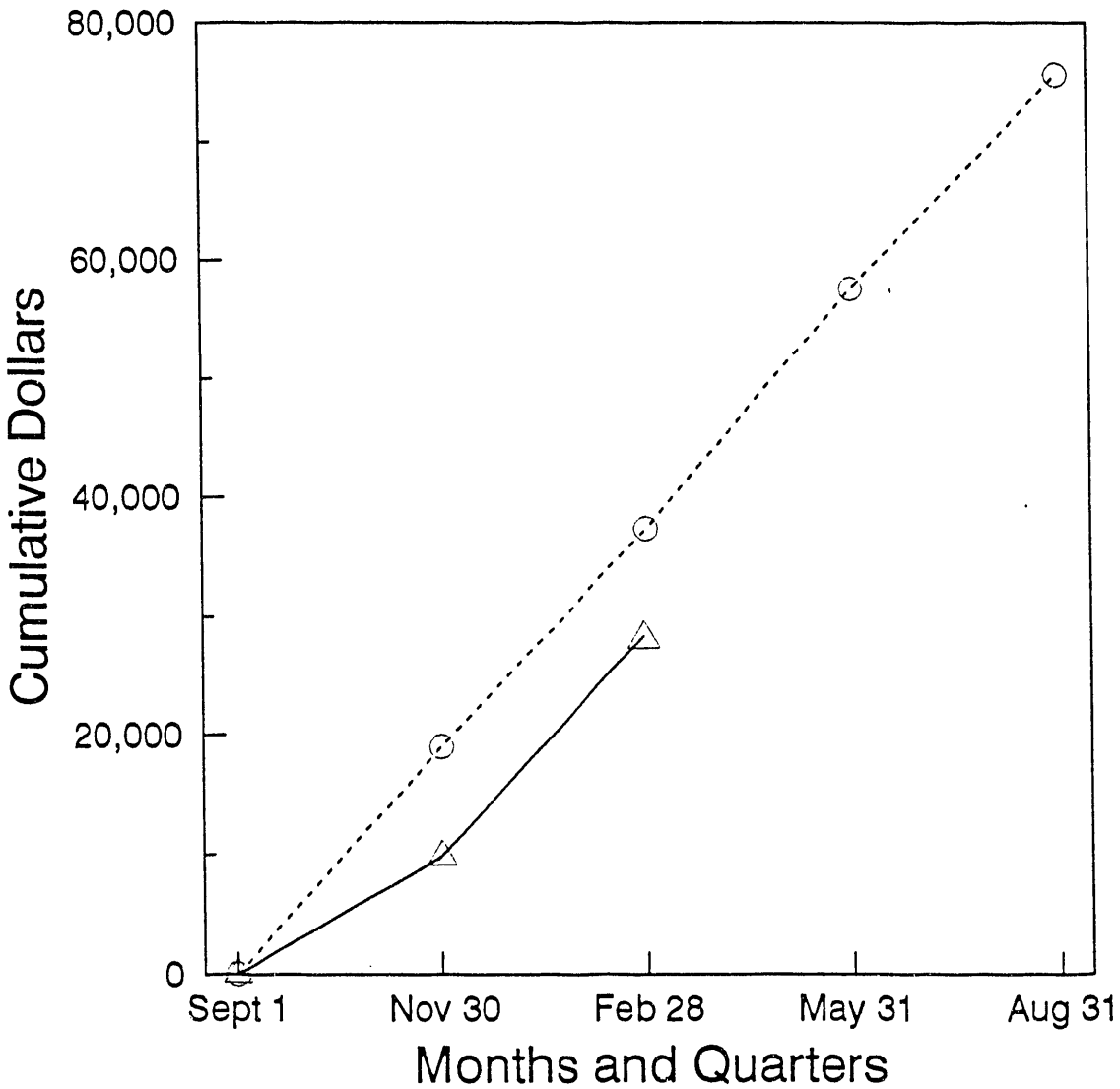


Milestones:

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

COSTS BY QUARTER - EXHIBIT C

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



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

△ Actual Expenditures ————————

Total CRSC Award $ 72,820

budget removed, ds

END

DATE
FILMED
6/11/93