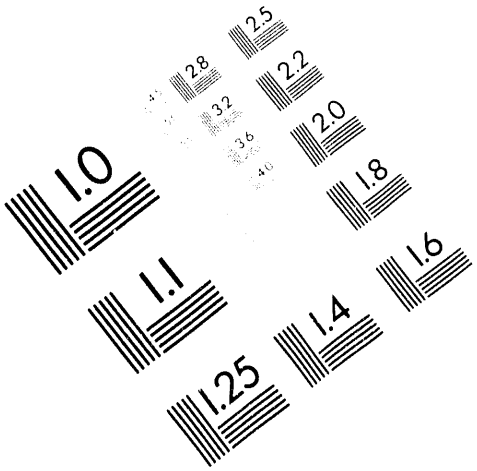

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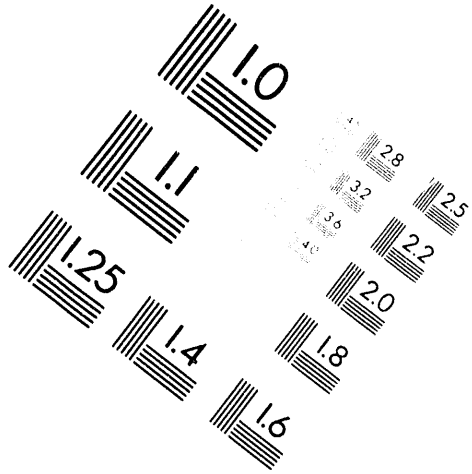

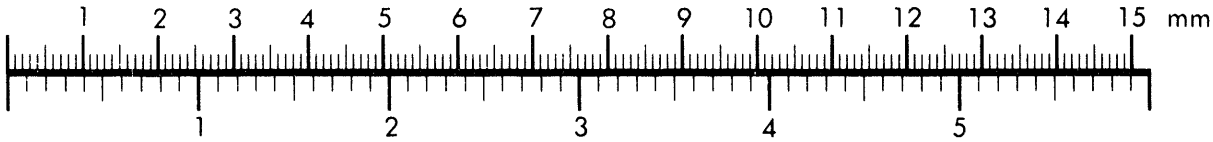

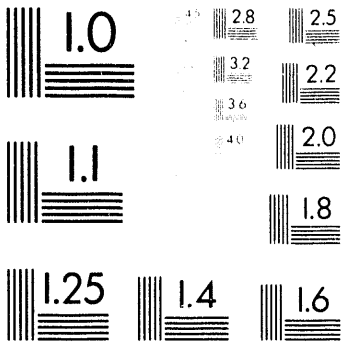

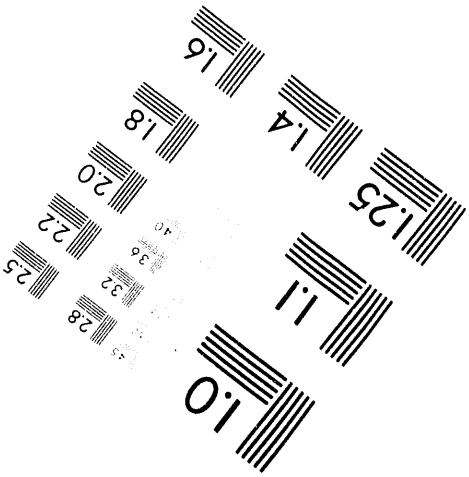

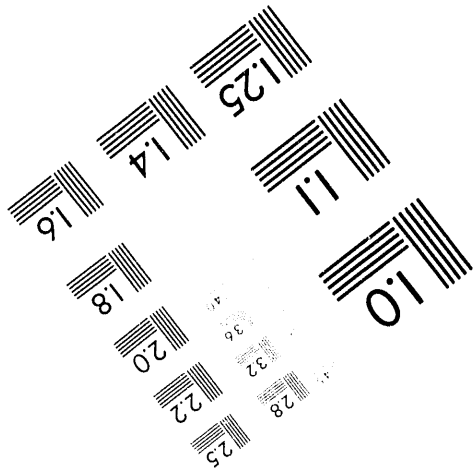

1 of 1

2.

DOE/PC/92521--T145

TECHNICAL REPORT
December 1, 1993 through February 28, 1994

Project Title: **REACTIVITY OF TARGET COMPOUNDS FOR CHEMICAL COAL DESULFURIZATION**

DOE Grant Number: DE-FC22-92PC92521 (Year 2)
ICCI Project Number: 93-1/5.3A-1P
Principal Investigator: Dr. David H. Buchanan, EIU
Other Investigators: Ms. Mandy Amin, EIU
Mr. Richard Cunningham, EIU
Ms. Janette Galyen, EIU
Project Manager: Dr. Ken K. Ho, ICCI

ABSTRACT

This project seeks to identify representative organosulfur compounds which are removed by coal desulfurization reactions. Demineralized coals from the Illinois Basin Coal Sample Program are solvent extracted and the extracts fractionated to separate and concentrate organosulfur compounds for analysis by Gas Chromatography / Mass Spectroscopy. After sulfur compounds are characterized, the parent extracts will be subjected to reactions previously shown to reduce the organic sulfur content of Illinois coals, fractionated and again analyzed for organosulfur content to determine which compounds reacted during the chemical treatment. The original coal will be subjected to chemical desulfurization, extraction, fractionation and analysis in order to correlate changes in organic sulfur content of the coal with reactions of specific sulfur compounds. These compcunds can thus be reliably considered as target molecules for the next generation of desulfurization processes.

During this quarter, work continued on developing efficient methods to isolate and analyze sulfur-rich coal extract fractions by GC/MS. Since only relatively non-polar compounds can analyzed, pyridine extracts must be fractionated. Direct extraction of several coals with toluene is quicker but did not give as much toluene soluble material as fractionation of pyridine extracts and is thus not suitable for preparation of representative analytical samples. We observe that most IBC sample program coals contain elemental sulfur due to oxidation of pyrite. There is less elemental sulfur in IBC-101 than in other Herrin coals. This coal was washed in a preparation plant to reduce pyrite concentration. Since elemental sulfur slowly reacts to produce organosulfur compounds in coal during storage or handling, this suggests that early removal of pyrite can reduce formation of these hard to remove compounds.

U.S. DOE Patent Clearence is NOT required prior to the publication of this document.

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EXECUTIVE SUMMARY

The goal of this project is improved chemical coal cleaning by determination of the reactivity of several desulfurization reagents with specific organosulfur compounds shown to be present in the feed coal. Reagent testing will be preceded by identification of a representative group of organosulfur compounds which can be extracted from coal with good solvents and then separated and concentrated by chromatography. Analytical methods such as Gas Chromatography/Mass Spectroscopy will be used to determine which sulfur compounds are converted to sulfur-free products during the course of the desulfurization reactions.

The reactivity of the sulfur compounds thus identified with several chemical desulfurization reactions be investigated in the second portion of the project. The reactions will be first applied to sub-fractions of coal extracts, rich in identified organosulfur compounds and the products will be analyzed by the same methods used to identify the original organosulfur compounds. Loss of or conversion of target molecules to hydrocarbons will be measured. These reactions will then be applied to unseparated coal extracts and the demineralized coals which will be fractionated and analyzed as before. In each case the amount of measured desulfurization which can be attributed to reactions of identified compounds will be determined and used to evaluate and characterize the desulfurization method. If patterns of desulfurization activity are observed, chemical modifications of the reagents to increase their reactivity toward the target compounds will be attempted.

Work during this quarter focused on improving the isolation and detection of target compounds from IBC-101 and -105 coals. Because pyridine extraction and fractionation of extracts is such a time-consuming procedure we investigated alternate methods to isolate the same material. Only about 30-50% of a typical pyridine extract can be analyzed by GC/MS methods. Less volatile material (polar and high molecular weight) in the extract must be removed prior to analysis. Direct toluene extraction yields less soluble material but what is isolated can be analyzed by GC/MS.

We extracted IBC-105 and Argonne premium coals 201, 301, and 401 with toluene before and after acid demineralization in an effort to maximize toluene solubles and compare them with pyridine extracts, and their toluene soluble portions, which we have previously studied. Direct toluene extraction of coal produces less soluble material than fractionating a pyridine extract into toluene soluble and insoluble material or column chromatography of the pyridine extract on alumina using hexane and toluene as eluting solvents.

We also observe that demineralization of Illinois No. 6 coals, after an initial toluene extraction, allows additional material to be removed by a second extraction with toluene. Although the total yields are still 2-3%, the relative yield in the second toluene extraction is 45% of the initial toluene extraction yield. This contrasts with a 12% relative yield for the second pyridine extraction following demineralization of the same coal. Results for Argonne 201 are second toluene - 129% relative yield; second pyridine 109% relative yield. A similar study of Argonne 401 is in progress. We attribute the high values for Argonne 201 to arise from acidification of insoluble acid salts known to be present in the raw coal. For both coals the relative yield in the second extraction is greater for toluene, which swells coal very poorly, than for pyridine, which swells coal very well. This is consistent with potentially soluble material being blocked by mineral matter in pores which cannot be removed by toluene. Such material can be removed by pyridine in the swollen coal via diffusion through the swollen organic network or through pathways opened around the minerals during swelling. This indicates that direct toluene extraction, although quicker and easier for isolation of GC/MS samples from coal may miss important material.

In our extractions of IBC-105 coal, the non-polar extracts and non-polar fractions of pyridine extracts contains significant amounts of elemental sulfur (GC/MS identification). We have previously shown that the pristine version of IBC-105 - Argonne 301, does not contain this sulfur and that elemental sulfur arises from oxidation of pyrite during storage after mining. Thus, our samples of IBC-105 have undergone such oxidation during storage and handling in our laboratory. In contrast, the non-polar fractions of pyridine extracts of IBC-101 contain much less elemental sulfur. We believe this is significant in that both IBC-101 and -105 are Herrin Illinois No. 6 coals. IBC-101 was obtained from a commercial preparation plant in 1983 and has one of the lowest pyritic sulfur values for a conventionally-washed coal. Since elemental sulfur can be slowly incorporated into the coal as organic sulfur, removal of pyrite before storage appears to have the additional benefit of preventing conversion of easily removed mineral sulfur into difficult to remove organic sulfur.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

OBJECTIVES

The primary objective of this project is to identify as many as possible of those organosulfur compounds which may be extracted from coal by simple solvent treatment below 150°C and to determine their fate when the coal fractions in which they are found are treated with known coal desulfurization chemical reactions.

Specific goals of this project are to:

1. Maximize the organic material extracted from IBC-101 and -108 using pyridine/nBu_4NOH/ultrasound.

2. Demineralize Argonne Premium Coal Sample 301 (parent of IBC-105) and extract as in 1.

3. Fractionate pyridine extracts into sub-fractions using solubility in hexane and toluene for further analysis.

4. Separate and concentrate sub-fractions containing sulfur compounds using preparative chromatography and/or extrography.

5. Analyze sulfur-containing sub-fractions by GC/MS correlated with SEC, FT-IR and FT-NMR analyses to identify as many organosulfur compounds as possible.

6. Correlate analytical data with extraction and fractionation yields to develop mass balances for identified sulfur species.

7. Desulfurize characterized sub-fractions and total pyridine extracts by several methods such as: Dissolving metals, Nickel boride, Ni/Al alloy, and Lochmann's BASE.

8. Repeat goals number 3-6 on the desulfurized sub-fractions and extracts.

9. Use the best methods from goal 7 on demineralized coals and repeat goals 1-6 on the coal product.

10. Correlate and summarize the data to determine which organosulfur compounds react in the desulfurization methods and determine how much of the observed desulfurization can be accounted for in the reactions of identified compounds.

INTRODUCTION AND BACKGROUND

The need to understand sulfur chemistry in Illinois coals is central to our need to protect both the environment and the

job base in the Illinois coal fields. Even if all mineral sulfur were removed, most Illinois coals could not meet existing or scheduled sulfur emission standards. Organic sulfur must be removed and this will involve selective chemical reactions. Previous work at EIU has shown that simple processes such as solvent extraction do not selectively remove sulfur from coal - that is, during solvent extractions sulfur compounds were removed by both polar and non-polar solvents in approximately the same concentration as they were found in the original solid coal.[1] One impediment to the development of effective pre-combustion desulfurization technology is that the actual target compounds are not known. Although there have been many recent studies of organic sulfur in coal, including those sponsored by ICCI, few sulfur compounds have been identified as existing in whole coal. Non-destructive spectroscopic methods such as XANES and very high field ESR show great promise for determining the major classes of organosulfur functional groups present in coal or coal products. However, at the resolution available now or in the next few years, even these very expensive and sophisticated methods are not able to identify individual compounds.

It is unreasonable to expect advanced coal cleaning or utilization processes to develop if the actual target compounds in sulfur removal schemes are unknown. Knowing the <u>nature</u> of sulfur species present (*ie* relative amounts of aliphatic sulfides, aromatic sulfides, thiophenes, *etc.*) is important, but even more important is knowing the identity and amount present of the actual compounds. A simple example will illustrate the problem. Oxidation of sulfide to sulfoxide is the necessary first step in any oxidative desulfurization process. Dibutyl sulfide and dioctyl sulfide are very similar aliphatic sulfides, yet oxidation of sulfide sulfur to the sulfoxide by air in the presence of hydroaromatic promoter compounds is much faster for the butyl than for the octyl case and both react slower than dibenzylsulfide.[2] Because all three of these compounds involve $-S-CH_2-$ bonds, they would be measured as aliphatic S in the XANES analysis and the first two would not be observed by any current ESR technique. Design of desulfurization processes would be greatly improved by better information on the identity and reactivity of the target molecules in coal.

The benefits from identification of organic sulfur species in coal transcend improvement of an existing process. By identifying specific target molecules for desulfurization, more chemists will be encouraged to work on the necessary new chemistry since they will no longer be shooting at unknown targets. The new detailed structural information on coal and coal extracts available from this work will also be of use to groups seeking to isolate or prepare high-value products from coal. The advances in selective solubiliza-

tion and fractionation processes which will be further developed and refined during this project will also be of value as analytical tools for other workers in coal research.

EXPERIMENTAL PROCEDURES

Coals studied this quarter include IBC-101, -105 and Argonne Premium Coal Samples 201 (Wyodak sub-bituminous), 301 (Illinois #6, the parent of IBC-105) and 401 (Pittsburgh #8). The Argonne coals were included in the study to maximize pyridine extraction yield since they offer a range of volatile and mineral matter contents. Solvent extraction and product purification and isolation follow our published procedures.[3] Coals, extracts and residues are dried at 100°C, 0.1 Torr for several hours before weights are recorded for mass balance calculations. Solvents are HPLC grade, often distilled from a drying agent before use. Elemental analyses of coal fractions were done by Galbraith Laboratories, Knoxville, TN. Acid demineralization uses a modification of standard methods reported last quarter.

Direct toluene extractions of coal on a 1-2 g scale were conducted using 10-20 mL of toluene or toluene/methanol in serum capped centrifuge tubes placed in an ultrasonic bath. The nitrogen degassed mixtures were sonicated for 1 hour and spun at 3,000 g prior to filtration through a 0.45 um Nylon membrane to separate the residue from the extract. Vacuum drying and 0.1 Torr and 100° removed the solvents prior to chromatography on silica gel. Hexane and toluene eluents from the column were analyzed by GC/MS as described in the first quarterly report.

The pyridine extract of IBC-101 was isolated using our published procedure[3] and fractionated by column chromatography on alumina to yield hexane and toluene eluents suitable for GC/MS analysis.

RESULTS AND DISCUSSION

Compounds extractable from Illinois coal which can be analyzed using the EIU system are those which will elute from the GC column below 320°C with mass less than 660 daltons (the upper limit of the HP 5971 quadrupole detector). These compounds occur primarily in non-polar fractions of the extracts and may be isolated either by extraction with toluene or by fractionating the pyridine extracts into toluene soluble and insoluble portions. During this quarter we compared direct toluene extraction of IBC-105 coal followed by silica gel chromatography to isolate a suitable fraction of extract for GC/MS analysis with chromatographic separation of a pyridine extract into hexane and toluene eluents. The latter produces more material and is thus

probably worth the extra effort. In addition it also isolates material which may be chemically different from that isolated in direct toluene extraction because of it's association with mineral matter.

Because mineral matter in coal is often found within the pores in the coal, it is possible that potentially soluble material is not being extracted due to blockage by the minerals. Our study of the effect of demineralization on solvent extraction using both toluene and pyridine is nearly complete. Table 1 summarizes the data collected to date. On several samples material balances have been routinely high and duplicate and triplicate determinations are in progress in order to determine the sources of the problems. From the data available however, it is clear that toluene yields after demineralization represent a significantly larger fraction of the initial extract yields than is the case for pyridine yields following demineralization. Previous work by the PI has shown that the toluene soluble fractions of pyridine extracts of Illinois No. 6 coal account for about only 50% of the material extracted by pyridine.[4] Taken together this suggests that the presence of mineral matter prevents toluene from removing material which is toluene-soluble. A working hypothesis is that minerals block pores such that toluene cannot reach potentially soluble material, which can be removed by pyridine which swells Illinois coals to more than two and one half times the original volume. Diffusion through the matrix or through pathways opened around mineral grains during swelling are possible routes for removal of this material. As a result of this study, we believe that fractionation of pyridine extracts rather than direct toluene extraction must be used for our future work.

Figure 1 shows the Total Ion Chromatogram (TIC) of the hexane fraction obtained from silica gel chromatography of the toluene extract of IBC-105 coal. The mass spectrum of the peak at 35.6 minutes shows it to be S_8. A GC/MS of the hexane chromatographic fraction of the pyridine extract of IBC-101 had only a minor peak near 35.6 min. Previously we have shown that air oxidation of a variety of coals produces elemental sulfur from the pyrite present.[5 6] We believe that the low level of elemental sulfur in IBC-101 is due to the removal of surface-active pyrite during the cleaning process when the coal sample was collected in 1983. We previously showed that elemental sulfur can slowly react with the organic material in coal forming difficult to remove organosulfur compounds. If the lack of elemental sulfur can be verified in other samples of cleaned coals, we believe this provides a good argument in favor of physical cleaning of coal immediately upon mining, even if it is to undergo additional processing later.

During this quarter, the GC/MS instrument was out of service

part of the time for maintenance connected with both hardware and software problems. The portion of the project dependent upon the GC/MS has thus not progressed as fast as projected. Standard test samples of polycyclic aromatic hydrocarbons which we use to calibrate the instrument and the method run on March 2, 1994 show as good or better resolution and sensitivity as those run on November 11, 1993, so the instrument appears to back to normal.

CONCLUSIONS AND RECOMMENDATIONS

Fractionation of pyridine extracts to isolate suitable samples for GC/MS analysis of coal extracts, although more time-consuming, appears to be better than direct toluene extraction in terms of providing a complete set of toluene soluble compounds. IBC-101 and -105 have been extracted, IBC-108 will be studied next quarter.

IBC-101 coal has less elemental sulfur in the non-polar extract fraction than IBC-105 and other IBC coals studied on previous projects. Both IBC-101 and -105 are Illinois No. 6 coals from the Herrin seam. Apparently early removal of at least half of the pyrite by conventional coal cleaning of IBC-101 has decreased elemental sulfur production by the previously documented pyrite oxidation route. This suggest that early pyrite removal is better than later, even if additional cleaning steps will be used.

During the third quarter, desulfurization reactions of pyridine extracts of IBC-101 and -105 coals will be started. Fractionation and GC/MS analysis of solvent extracts will continue in order to determine organosulfur compounds removed by the desulfurization reactions.

PI, Buchanan, is one of 24 chemists speaking at a symposium on the current status of research using the Argonne Premium Coal Samples. He will review recent work in the solvent extraction of coal from his and other laboratories.

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(1) Buchanan, D.H. in Proceedings: 1987 Workshop on Coal Structure, EPRI Report **1988**, ER-6099-SR, 9-1.

(2) a) Mill, T.; Tse, D.S.; Loo, B.; Yao, C.C.D.; Canavesi, E. *Prepr. Pap.-Am. Chem. Soc., Div. Fuel Chem.* **1992**, *37(3)*, 1367-1375. b) Recent results by L. Warfel at EIU and personnel communication with T. Mill at SRI.

(3) Buchanan, D.H.; Osborne, K.R.; Warfel, L.C.; Mai, W.; Lucas, D. *Energy Fuels* **1988**, *2*, 163.

(4) Mayo, F.R.; Buchanan, D.H.; Pavelka, L.A.; Hirschon, A.S. *Fuel*, **1988**, *67*, 600-606.

(5) Buchanan, D.H.; "Organic Sulfur Removal for Illinois Coal" Final Technical Report, CRSC Project 89/1.2/A-2, 8/31/90.

(6) Chou, M.-I.M.; Lytle, J.M.; Ruch, R.R.; Kruse, C.W.; Chaven, C.; Buchanan, D.H. *Prep. Pap. Am. Chem. Soc., Div. Fuel Chem.*, **1992**, *37*(4), 2002-2009 and references therein.

TABLE 1 EFFECT OF DEMINERALIZATION OF SOLVENT EXTRACTION

COAL SAMPLE BANK	ARGONNE #201	ARGONNE #301	ARGONNE #401	IBC #105	IBC #101
MAF % C	75.0	77.7	83.2	78.0	77.2
DRY ASH %	8.8	15.5	9.2	18.6	10.5
PYRIDINE EXTRACTION					
INITIAL					
EXTRACT %	8.4	25.8	30.7	22.4	26.0
RESIDUE %	90.2	75.9	63.3	75.5	87.0
AFTER DEMINERAL					
EXTRACT %	9.2	3.1	3.8		
RESIDUE %	92.5	95.8	94.0		
TOTAL EXTRACT %	17.5	28.9	34.6		
% INCREASE DUE TO DEMINERALIZATION	109.3	12.2	12.5		
TOLUENE EXTRACTION					
INITIAL					
EXTRACT %	0.92	1.38	0.51	0.69	
RESIDUE %	98.0	100.0	100.5	101.0	
AFTER DEMINERAL					
EXTRACT %	1.19	0.62		0.55	
RESIDUE %	101.2	101.4		102.0	
TOTAL EXTRACT %	2.1	2.0		1.2	
% INCREASE DUE TO DEMINERALIZATION	129.3	44.9		79.7	

limited

Figure 1

File : C:\HPCHEM\1\DATA\RICK\RCAH1.D
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Instrument : 5971 - In
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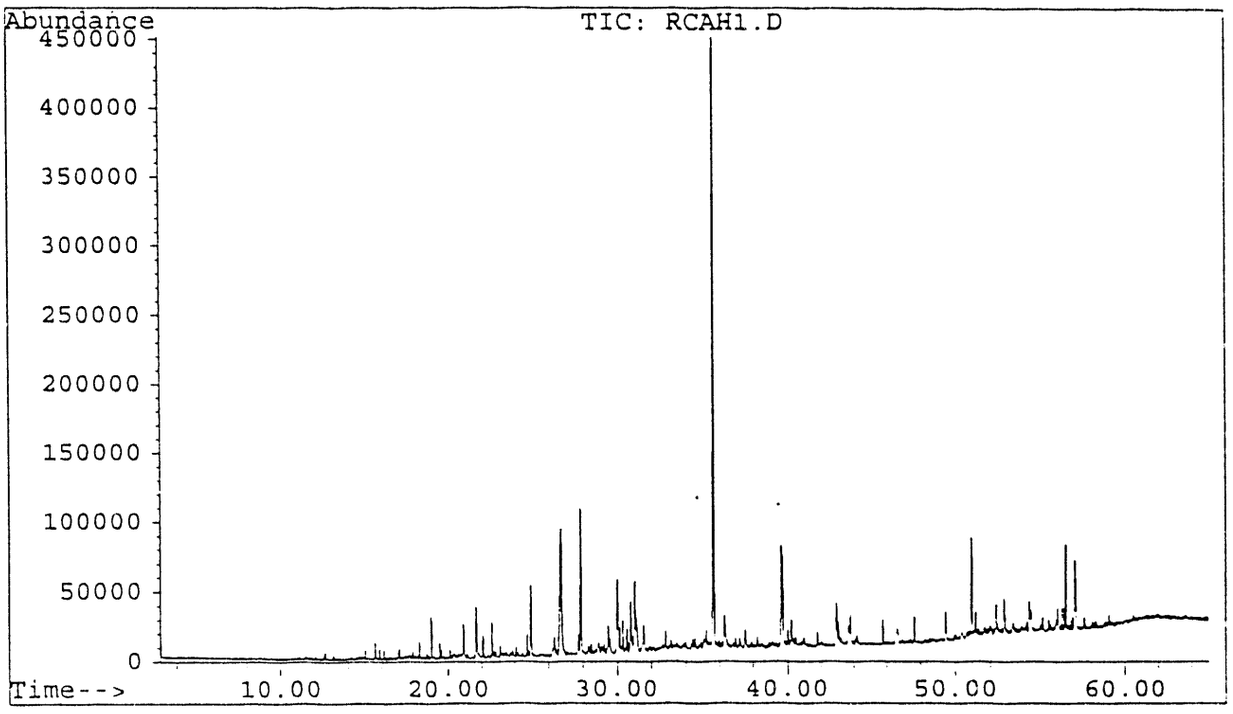
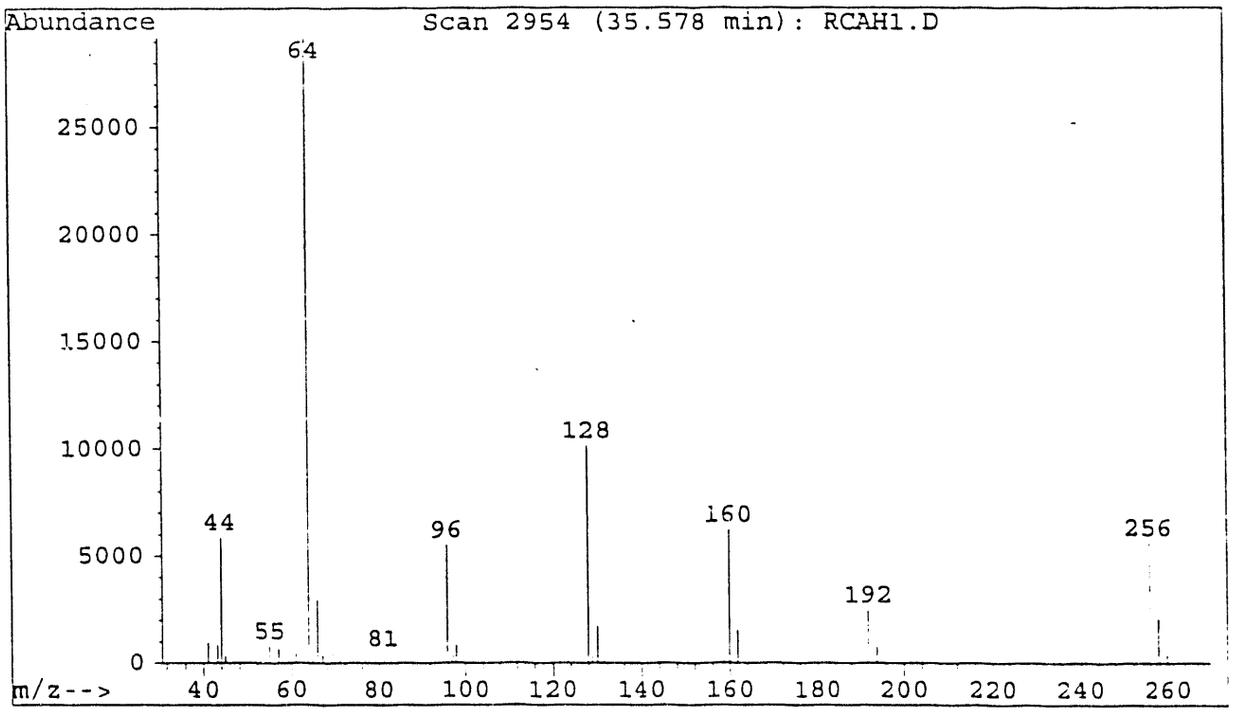
Vial Number: 1





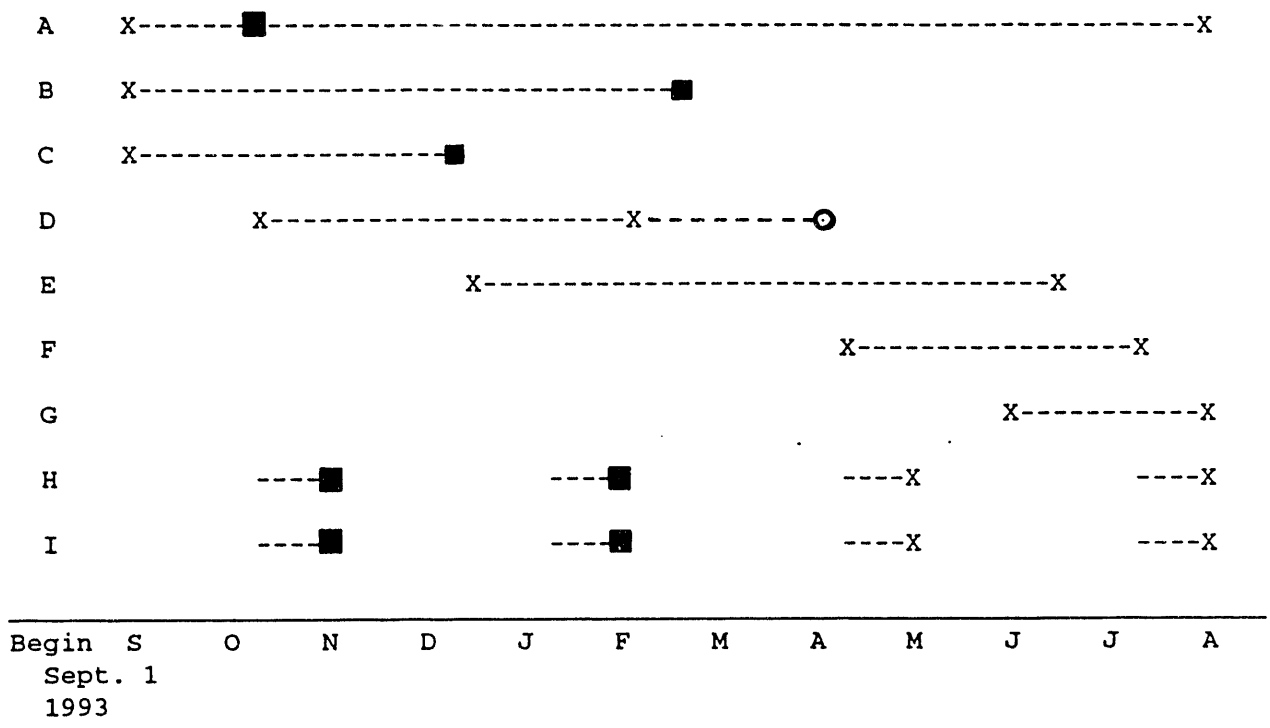
PROJECT MANAGEMENT REPORT
December 1, 1993 through February 28, 1994

Project Title: **REACTIVITY OF TARGET COMPOUNDS FOR CHEMICAL COAL DESULFURIZATION**

DOE Grant Number:	DE-FC22-92PC92521 (Year 2)
ICCI Project Number:	93-1/5.3A-1P
Principal Investigator:	Dr. David H. Buchanan, EIU
Other Investigators:	Ms. Mandy Amin, EIU
	Mr. Richard Cunningham, EIU
	Ms. Janette Galyen, EIU
Project Manager:	Dr. Ken K. Ho, ICCI

COMMENTS

SCHEDULE OF PROJECT MILESTONES



Milestones:

A. Personnel employed
B. Sample acquisition and preparation
C. Extraction of coal to maximize yield
D. Fractionation of extract to concentrate sulfur compounds
E. Analyses of fractions for sulfur compounds
F. Desulfurization reactions of extract and analysis of products
G. Desulfurization of coal, extraction and analysis of fractions
H. Technical Reports Prepared and Submitted
I. Project Management Reports prepared and submitted

Comment: D. Hardware and software probelms with GC/MS has delayed completion of analysis of extracts used to develop the fractionation method.

EXPENDITURES - EXHIBIT B

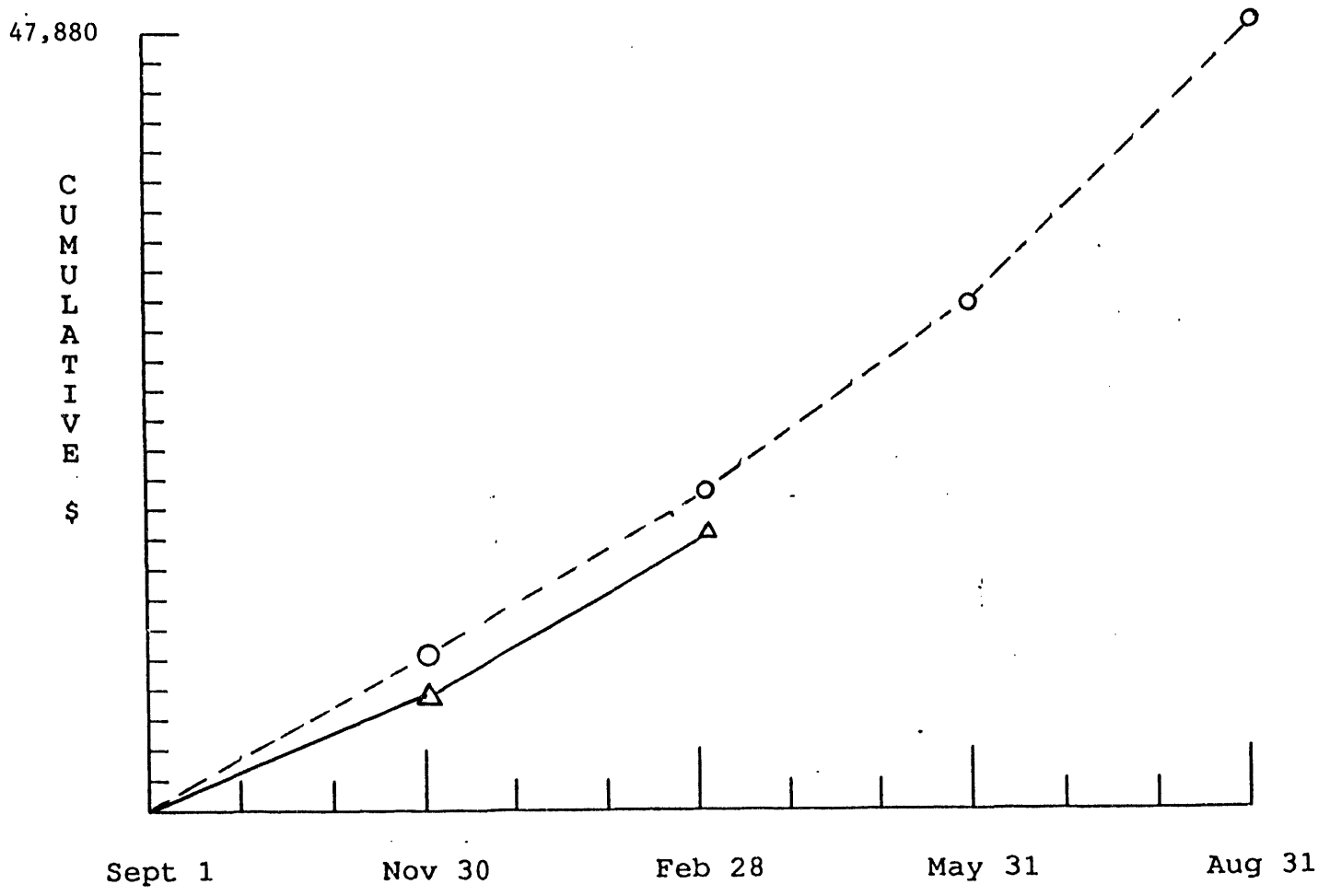
CUMULATIVE PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials & Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1993 to Nov. 30, 1993	Projected	6,860	635	600	25	-0-	700	882	9,702
	Estimated	4,514	268	448	-0-	-0-	20	525	5,775
Sept. 1, 1993 to Feb. 28, 1994	Projected	13,720	1,270	1,200	50	400	1,300	1,794	19,734
	Estimated	10,715	1,639	1,321	-0-	112	366	1,415	15,568
Sept. 1, 1993 to May 31, 1994	Projected	20,580	1,905	1,800	50	850	1,900	2,708	29,793
	Estimated								
Sept. 1, 1993 to Aug. 31, 1994	Projected	34,591	3,247	2,400	139	850	2,300	4,353	47,880
	Estimated								

***Cumulative by Quarter**

CUMULATIVE COSTS BY QUARTER -- EXHIBIT C

Reactivity of Target Compounds for Chemical Coal Desulfurization



Months and Quarters

O = Projected Expenditures ----------

Δ = Actual Expenditures ————————

Total ICCI Award $ 47,880

DATE
FILMED
6/29/94

END