DOE/PC/90176--T63
NOV 04 1991

FINAL TECHNICAL REPORT

September 1, 1990 through August 31, 1991

Project Title: New Reagents for Coal Desulfurization

DE-FG22-90PC90176

Project Coordinator: Dr. David H. Buchanan
Eastern Illinois University

Other Investigators: Dr. Stanislaw Kalembasa, EIU
Ms. Donna Olson, EIU
Mr. Shan Wang, EIU
Ms. Linda Warfel, EIU

DOE/PC/90176--T63

DE92 004199

Project Monitor: Dr. Daniel D. Banerjee, CRSC

ABSTRACT

Screening of new reagents and reactions for pre-combustion desulfurization of Illinois coal was the goal of this project. In this exploratory study we examined modifications of mild desulfurization reactions, found to work with model organosulfur compounds, to improve sulfur removal and reduce reagent cost. Reagent screening and development reactions utilized substituted thiophenes plus aryl and alkyl sulfides as the initial models for organic sulfur compounds in coal. Organosulfur compounds in solvent extracts of Illinois coals were used as second generation target compounds.

Transition metal salts reduced with $NaBH_4$ in aqueous ethanol converted dibenzothiophene to biphenyl in up to 31% yield in two hours at 50°C. The most active salt was nickel chloride which produced the reagent referred to as 'nickel boride' in the literature. Thiophene was completely desulfurized by this reagent. However benzothiophene, benzyl sulfide and octyl sulfide were converted to hydrocarbons in lower amounts than was DBT. Nickel aluminum alloy reduced by NaOH in ethanol also desulfurized these compounds but in lower conversions and thiols as well as hydrocarbons were found in the reaction mixtures. Both nickel based reagents desulfurized THF soluble fractions of IBC coals. In the best case, Ni/Al/NaOH in aqueous THF reduced the sulfur content of the THF extract from IBC-105 by 66%. Reactions of both nickel reagents with coal fractions were more effective in THF than in ethanol solvent. All data with both model compounds and coal fractions suggest that the active reagents were insoluble materials, probably hydrogen gas adsorbed on finely divided metallic nickel produced during the course of the reaction.

Minerals found in Illinois coals were reduced with $NaBH_4$ in aqueous ethanol to reagents with a small amount of desulfurization activity toward DBT. The most active system was a heavily oxidized sink fraction from a sink/float separation of Illinois No.6 coal. Up to 13% of 2-phenylthiophenol and biphenyl were found when this material was the reagent source for DBT desulfurization. Minerals in THF insoluble residues of IBC coals gave up to 2% desulfurization in a similar reaction.

$H\text{-}Fe(CO)_4$ produced from $Fe(CO)_5$ by reaction with NaOH or $NaBH_4$ in the presence of dibenzothiophene or benzothiophene produced small amounts of new compounds and left large amounts of unreacted starting material and gave no evidence of hydrocarbon products.

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

(This project is funded by the U. S. Department of Energy as part of its cost-shared program with Illinois Department of Energy and Natural Resources.)

EXECUTIVE SUMMARY

Pre-combustion desulfurization of Illinois coal will require removal of at least a portion of the organic sulfur present. However there is currently no practical process to do this. Because this sulfur is chemically bound into the organic matrix of the coal, removal requires selective chemical reactions. Processes such as simple solvent extraction have been shown unable to selectively concentrate and remove organosulfur compounds from coal. During the course of earlier research several possible desulfurization reactions were observed which were explored in the current project. Reactions at low temperatures and atmospheric pressure utilizing combinations of simple metal salts and reducing agents were investigated using both model compounds and soluble fractions of Illinois coals.

The known desulfurization of simple alkyl thiophenes using 'nickel boride' (sodium borohydride plus nickel chloride in aqueous ethanol) was modified to desulfurize benzothiophene (BT), dibenzothiophene (DBT), benzyl sulfide (BS) and octyl sulfide (OS). In previous studies we noted that desulfurization continued when perchloroethylene (PCE) was present as a co-solvent, conditions under which soluble chlorovinyl nickel complexes are known also to form. In this study we examined a variety of nickel based desulfurization reagents for desulfurization activity toward organosulfur compounds likely to be found in coal. In addition to nickel, other inexpensive metal salts and coal minerals were screened as potential desulfurization reagents under mild conditions.

The effects of time, temperature, and solvent on the nickel boride conversion of DBT to biphenyl (BP) were studied. Higher boiling alcohol solvents such as butanol or longer reaction times did not improve desulfurization. Thiophene was completely consumed by nickel boride. The best conversion of DBT to BP is about 30% at 50° within two hours. BT, BS and OS are also converted to hydrocarbons, but in lower yields. The reactions are specific for production of the hydrocarbon and material balances are nearly quantitative. Using the optimum conditions for nickel chloride, eleven other metal salts such as copper and iron chlorides and sulfates were screened for reactivity with DBT. All salts tested produced at least traces of biphenyl although none was as active as nickel chloride. Ferrous chloride was the next most active, however mineral pyrite showed only a trace of activity. Sodium molybdate, the source of active actalysts in other systems, was also less active than ferrous chloride in these systems.

The mineral rich sink fraction from a float/sink separation of an Illinois No. 6 coal available from a previous study also showed desulfurization activity toward DBT when reduced with $NaBH_4$. The sink fraction, which had been heavily oxidized during storage, converted about 13% of DBT to a mixture of biphenyl and 2-phenylthiophenol. This activity was almost completely destroyed when the sink fraction was washed with perchloroethylene (to remove elemental sulfur) and methanol/water (to remove traces of PCE) prior to testing with DBT and borohydride.

Because desulfurization activity was found in the coal sink fraction, THF insoluble residues from IBC coals were also tested as sources of desulfurization reactivity after reduction with $NaBH_4$. Removal of the THF soluble fraction (about 7-9% by weight of coal) was necessary in order to follow reactions of the DBT test compound by GC or HPLC. Residues from IBC-101, -104, -105, -106, and -108 at 50°C for two hours in aqueous ethanol all produced traces of biphenyl but none produced more than a 2% conversion.

Ni/Al alloy activated by aqueous NaOH, a cheaper reagent than nickel boride, also desulfurizes model sulfur compounds if an organic co-solvent is present to maintain solubility of the substrate. Reactivity of the test compounds is no better than with nickel boride and total desulfurization is lower since thiol products are also observed in the reactions of DBT and BT. Filtered solutions of the active reagents produced no desulfurization of the test compounds.

Alkali metals in THF solution are known to desulfurize condensed thiophenes such as DBT under single electron transfer conditions. Addition of an electron transfer agent such as naphthalene is necessary for some reactions. We have completely converted DBT to BP using K/THF without electron transfer agents. Similar reactions of THF extracts from IBC coals gave up to an 82% reduction in organic sulfur. A soluble chlorovinyl nickel complex added as electron transfer agent increased the desulfurization to 86%.

Attempts to produce active desulfurization reagents from iron pentacarbonyl with reducing agents in alcohol (conditions for the production of H-Fe$(CO)_4$) did not lead to useful desulfurization of DBT, BT or BS. As yet unidentified products were isolated from both the DBT and BS reactions and will be characterized in future studies although neither new compound was the major component of the reaction mixture.

We attempted to increase the quantity and variety of organosulfur compounds extracted from coal by simple solvents for our use in the screening of new desulfurization reagents. Several Argonne Premium coals plus IBC-105 were exhaustively extracted with pyridine and the solvent-free residues used as the starting material for additional extraction experiments. Extraction of the pyridine residue from IBC-105 with the carbon disulfide/N-methyl-2-pyrrolidinone (CS_2/MP) mixed solvent stimulated by ultrasonic irradiation produced an additional 3% extract beyond the 25% removed by pyridine. Coals from the Argonne Sample Program of lower and higher ranks gave up 9% additional extract. Pyridine-insoluble residues were also treated with 25% HCl at 100° followed by 49% HF at 70° to remove minerals which might be trapping potentially soluble material in blocked pores. After washing and drying to constant weight, the demineralized residues were again exhaustively extracted with pyridine. The amount of additional extract varies with coal rank and degree of oxidation (as is true for the raw coals). Low rank coals showed the largest increase in extract yield after demineralization although the total extract yield was still less than that for medium rank coals such as Illinois No. 6. For IBC-105 an additional 1% pyridine extract was isolated after acid demineralization.

In summary, significant desulfurization activity toward soluble organosulfur compounds was found for nickel based reagents at low temperature and short reaction time. Both model compounds and organo-sulfur compounds present in THF extracts of IBC coals were desulfurized. The reagents however are insoluble and depend on the solubility of the target compounds for effective activity makin the reagents unlikely candidates for pre-combustion desulfurization reactions at this time.

OBJECTIVES

The primary goal of this project was development and exploration of potential new desulfurization reagents for the removal of "organic sulfur" from Illinois coals by mild chemical methods under **Research Priority P.1.1**.

Potential new desulfurization reagents were investigated using organic sulfur compounds of the types thought to be present in coals. Reagents included low-valent metal complexes based on nickel and on iron as well as possible Single Electron Transfer reagents. Soluble coal extracts served as second generation model compounds during this reagent development project.

Specific objectives of this project were to:

1) Define optimum desulfurization conditions for the $NiCl_2/NaBH_4$ reagent by study reactions with model compounds in several solvent systems, which include alcohols, THF and PCE. Model compounds will include substituted thiophenes, benzothiophenes and dibenzothiophenes, aryl sulfides and alkyl sulfides.

2) Study the desulfurization activity of nickel-aluminum alloy and reagents derived it on model compounds as in 1).

3) Test the best nickel based reagents with soluble coal extracts using the appropriate conditions selected from model compound studies.

4) Test iron salts, including iron sulfides, and other metal salts with reducing agents such as $NaBH_4$ and others for the formation of active desulfurization reagents for model compounds and soluble coal extracts.

5) Investigate single electron transfer (SET) reagents, including low-cost materials such as OH^- in alcohols, as replacements for $NaBH_4$ in the preparation of low-valent metal desulfurization reagents. Develop the reactions on model compounds and test the best on coal extracts.

6) Test the most promising reagents chosen from 1)-5) with fractions of coals IBC-101, -105, -106, -108 from the ISGS for desulfurization activity.

7) Compare the results of the most effective desulfurization system for demineralized coals with the corresponding whole coals.

INTRODUCTION AND BACKGROUND

During a previous CRSC project the desulfurization reaction of reduced nickel chloride with thiophene was observed and was the basis for further exploration of possible new desulfurization chemistry. This background was discussed more fully in previous Quarterly Reports. A study of both known and new reagents to desulfurize organosulfur compounds was undertaken. Thiophenes, benzo-thiophenes, dibenzothiophenes and alkyl substituted analogs were tested for conversion to hydrocarbons by new reagents. Desulfurization of dialkyl and alkyl aryl sulfides was also studied since these compounds are also possible components of coal. One portion of the project focused on developing

reaction systems in which reagents could be carried into the coal by penetrating solvents and the sulfur containing products could diffuse out. Chemical modification of minerals found in coal (such as iron salts) into reactive desulfurization reagents in situ was also examined. Although initial studies utilized hydride reducing agents such as $NaBH_4$, the goal was to exploit recent ideas in single electron transfer chemistry to accomplish the same reduction with cheaper reagents such as NaOH in non-aqueous solvents.(1)

Screening of possible reagents utilized several simple organosulfur compounds as models for the ASTM organic sulfur in coal: Dibenzothiophene, benzothiophene, benzyl sulfide and octyl sulfide. The abbreviations used in this report for these compounds and their possible reaction products are listed in Table 1. The THF soluble extracts of IBC coals were also used to test reagents for desulfurization activity since the soluble material contains about the same weight percent sulfur as the ASTM organic sulfur of the raw coal and is mineral free. Attempts to increase the amount of soluble material extracted from coal by adding $(nBu)_4NOH$ to pyridine for long extraction times or acid demineralization of insoluble residues followed by re-extraction gave only 1-3% increases in the amount of pyridine soluble material from Illinois coals.

EXPERIMENTAL PROCEDURES

Reagent grade compounds were purchased from Aldrich Chemical Co. and used without purification. Solvents were HPLC grade and used as received unless otherwise noted. Pyridine was distilled from BaO and THF was distilled from the sodium ketyl of benzophenone under nitrogen. NMR spectra were obtained on a GE QE-300 broadband FT-NMR spectrometer in $CDCl_3$ or acetone-d_6 solutions. Chemical shifts for ^1H and ^{13}C are reported relative to internal TMS, ^{31}P shifts are reported relative to external 85% H_3PO_4. FT-IR spectra were recorded on a Nicolet 20-DXB spectrometer.

Gas Chromatographic monitoring of model sulfur compound reactions used a Hewlett Packard 5890 capillary GC fitted with a 30m x 0.53mm Alltech SPB-5 column and a flame ionization detector. Temperature programmed elution was adjusted for each set of model compound and expected product(s) to give baseline peak separation while minimizing total analysis time. Calibration solutions of model compounds, expected products and an internal standard (IS) were analyzed and relative detector response of analyte to internal standard plotted as a function of concentration ratio. Linear response was found for each analyte/IS combination, although the FID detector is more sensitive to hydrocarbons than to sulfur containing species.

An HPLC method for monitoring reduction of DBT and related compounds to the hydrocarbons was also developed for eventual use in systems of high boiling compounds not suitable for GC methods. A 250 x 4.6mm Alltech 5U C_{18} reverse phase column protected by a 40 x 4.5mm guard column was connected to a Beckman Model 112 pump, Rheodyne 125 injector and a Schoeffel Spectroflow Monitor SF 770 variable wavelength UV detector set at 254 nm. For monitoring DBT reduction to biphenyl, a mobile phase of 77.5% methanol in water at 0.9 mL/min gave good peak separation. Calibration solutions were measured and used to convert peak areas into concentrations.

Coal samples were obtained from the Illinois Basin Coal Sample Program (C. Kruse, ISGS) and the Argonne Premium Coal Sample Program (K. Vorres).

Synthesis of 2-Phenylthiophenol The Klemm modification(2) of the Newman proce-

dure(3) was used to prepare 2-phenylthiophenol in low overall yield. 2-Phenylphenol was converted to the O-aryl dimethylthiocarbamate by treatment with N,N-dimethylthiocarbamyl chloride in aqueous potassium hydroxide solution at 12°C. Crude product was chromatographed on silica gel and recrystallized from methanol to give a 52% yield of product whose melting point, NMR and CMR spectra were in accord with the structure and literature values.(3) A portion of the O-aryl amide was pyrolyzed under nitrogen at 255°C for three hours and the resulting S-aryl amide hydrolyzed by aqueous potassium hydroxide without isolation to yield the thiol salt. Acidification with aqueous HCl followed by chloroform extraction, drying, and chromatography on Alumina gave a low yield of yellow, crystalline 2-phenylthiophenol. The thiol was shown to be pure by FT-NMR, FT-IR, GC, and HPLC and to co-elute with one of the products of DBT desulfurization using Ni/Al alloy.

Preparation of $NiCl_2[PPh_3]_2$: This dark green complex was prepared in 67-80% yield by reacting triphenyl phosphine (PPh_3) with nickel(II) chloride ($NiCl_2 \cdot 6H_2O$) in either acetic acid or absolute ethanol following the methods of Venanze(4) and Michael(5). The vacuum dried product decomposed at 248-250°C. (Lit. 249°C.)

Preparation of $NiCl(CCl{=}CCl_2)[PPh_3]_2$: The method of Carvajal(3) gave low (~10%) yields of recrystallized products. An improved synthesis of was developed using $NiCl_2[PPh_3]_2$ as the starting material. $NiCl_2[PPh_3]_2$ (1.54 mmole) and PCE (9.8 mmole) were dissolved in 20 mL ethanol in a round bottom flask fitted with a magnetic stirrer and nitrogen gas system. After nitrogen was bubbled through the mixture for 30 minutes, it was heated to about 50° and $NaBH_4$ (6.48 mmole) added in portions, keeping the temperature below 50°. After stirring for an additional 2 hours the mixture was cooled and filtered. The crude product was washed with cold ethanol and recrystallized from hot dichloromethane/ethanol. The brown-yellow product (0.47 g, 40%) decomposed at 187-188°. Elemental analysis: Found, C 61.22%; H 4.36%; Cl 18.96%. Calculated, C 60.93%; H 4.04%; Cl 18.93%. ^1H NMR ($CDCl_3$): Two multiplets 7.4 - 7.75 ppm; ^{31}P NMR: Singlet 22.0 ppm, (Lit. 22.0 ppm.) FT-IR as a KBr pellet, strong bands at: 1483, 1434, 703, 696, 523, 513 cm^{-1}.

Nickel Boride desulfurization: A 25 mL 3-neck round bottom flask was fitted with a magnetic stirrer, thermometer, condenser and rubber septum cap and the top of the condenser was closed with a rubber balloon. Ethanol (10 mL), model compound (for example, DBT, 0.80 mmole) and $NiCl_2 \cdot 6H_2O$ (1.60 mmole) were added, the flask closed with the septum and the contents heated to 50 - 60° with an electrically heated oil bath. To the stirred reaction mixture a total of 2.0 mL of 4.8M $NaBH_4$ in aqueous ethanol was added drop-wise via syringe over 45 minutes. The hydrogen gas produced inflated the balloon and was slowly consumed over an additional one hour of heating. The hot reaction mixture was filtered through a plug of glass wool and 7 mL cold water was added. The cooled mixture was extracted with 3x3 mL portions of dichloromethane. The combined extracts were dried over anhydrous sodium sulfate, filtered and diluted to 25 mL in a volumetric flask containing a known amount of internal standard for GC analysis. In several cases co-solvents such as PCE were added during the reaction. For reactions with THF soluble coal fractions, 300-500 mg samples of coal extract were used in place of the model compounds.

Screening of Metal Salts for Catalytic Desulfurization Activity A slight variation on the best reverse addition conditions for the nickel boride reaction were used to screen a variety of metal salts and coal derived materials for their ability to desulfurize DBT. "Reverse Addition" always refers to addition of the catalyst source (usually a metal salt) to a mixture of reducing agent and substrate in solvent. For each reaction, 0.8 mmole of

DBT, 4.8 mmole $NaBH_4$ and 10 mL 95% ethanol were placed in a 3 neck round bottom flask fitted with a thermometer, rubber septum, and water cooled condenser fitted with a balloon to retain any hydrogen gas formed in the reaction. This mixture was heated with an oil bath to the desired temperature and held for 1 hour at which time 2 mL of a water solution of the test salt (1.6 mmole) was added *via* syringe in 0.5 mL portions every 15 minutes over an hour. Water insoluble catalysts were either added dry, from a solid addition tube, or normal addition conditions ($NaBH_4$ added to mixture of DBT plus salt) were used. The reaction mixture was transferred to a separatory funnel through a glass wool filter to remove any solids present and diluted with 10 mL water. The water layer was acidified with HCl to pH 4 and extracted with 3 x 5 mL of methylene chloride. The combined extracts were dried with anhydrous sodium sulfate, filtered and analyzed by GC as described previously. DBT, BP and PTP were the only compounds observed. In several cases an internal standard (naphthalene) was added for quantitative analyses.

Desulfurization Reactions Using Ni/Al Alloy The procedure of Papa, *et al*(6) was modified by addition of an organic co-solvent, since all previous compounds investigated were water soluble under the basic reaction conditions. In a typical reaction with dibenzothiophene, 1 mmole of DBT was added to 5 mL of a 10% by weight NaOH solution in 50% THF in a 3-neck round bottom flask and warmed to 60°. To the stirred mixture, 9-10 mmoles of Ni/Al alloy was added (amount based on Ni content). The temperature of the mixture rose to 65° and vigorous bubbling took place. After two hours, the mixture was cooled, diluted with 10 mL water and the insoluble gray solid separated. The solution was acidified with HCl and extracted with three volumes of methylene chloride. The organic phase was washed with water, dried with sodium sulfate and analyzed by both HPLC and GC. Extraction of the basic aqueous phase, prior to acidification, served to separate any thiol products from the hydrocarbon product and un-reacted starting material. For reactions with THF soluble coal fractions, 300-500 mg samples of coal extracts were used in place of the model compounds.

Alkali Metal Reduction of Organosulfur Compounds The method of Stock(7) was used as follows: Distilled THF (100 mL) was added to a dry 3-neck round bottom flask fitted with a magnetic stirrer, thermometer, condenser, nitrogen gas system and solid addition tube containing 20.56 mmole dibenzothiophene. Naphthalene (1.94 mmole) and hexane-washed potassium metal (63.9 mmole) were added while flushing the solvent with nitrogen. The dark green-black reaction mixture was heated at reflux for 30 minutes and the DBT was added in one portion from the solid addition tube. The dark red-black mixture was heated for an additional 24 hours and cooled to ice bath temperature. A mixture of 4.5 g ammonium chloride and 10 mL water was added to quench the reaction (pH 7 at this point). The mixture was flash evaporated to near dryness and a mixture of water and dichloromethane added. The aqueous phase was extracted several times with fresh dichloromethane. The combined extracts were dried with anhydrous sodium sulfate and filtered through a 0.45 μm membrane filter for HPLC analysis. Both biphenyl and DBT plus a new compound eluting just before biphenyl were detected.

Alkali Metal Reduction of THF Soluble Coal Fractions The method of Stock was modified as follows for use with coal extracts. Dry THF (50 mL) and potassium metal (1g, 25 mmol) were placed in a flask together with the catalyst, $NiCl(CCl{=}CCl_2)(PPh_3)_2$ (0.3744g, 0.4997 mmol). After about 30 min of stirring, 0.408g of the THF soluble fraction of IBC-105 coal was added and the reaction mixture was heated at reflux under nitrogen for 24 hours at which time fresh potassium metal (0.5g) was added and the reaction run for another 24 hours. After a total of 48 hours, the reaction mixture was cooled in an ice bath and acidified with dilute NH_4Cl/HCl to pH 5, and THF was removed on a rotary evaporator. The soluble products were extracted into methylene chloride which

was washed with water and dried over anhydrous magnesium sulfate. The solvent was completely evaporated and the product vacuum dried over night to yield the soluble product fraction. The insoluble fraction was washed with methylene chloride followed by water, separated and vacuum dried as above to yield the insoluble fraction. Reactions with catalysts were compared to the reaction of the THF fraction with potassium alone. FT-IR spectra were obtained on each fraction and portions sent for elemental analyses.

Reactions with $Fe(CO)_5$ and reducing agents. In a three-neck round bottom flask fitted with a condenser, nitrogen system and magnetic stirrer, 70 mL of solvent (ethanol or n-butanol) containing 3 mmole of test compound (DBT, BT or BS) and 7-8 mmole of reducing agent ($NaBH_4$ or NaOH) was degassed with a stream of nitrogen gas for 30 minutes at which time 7.6 mmole of filtered $Fe(CO)_5$ was added via syringe. Gas was evolved and the mixture became orange and finally violet red. The mixture was heated at room temperature for 2 hours and stirred for an additional 24 hours. Solvent was evaporated at reduced pressure and mixture acidified to pH 2 with dilute HCl and extracted several times with dichloromethane. The combined organic phases were dried with sodium sulfate, filtered and concentrated at reduced pressure. GC, HPLC and thin layer chromatographic analyses of the extracts were used to monitor reactions of the model sulfur compounds. In the case where unknown compounds were produced, FT-IR and FT-NMR spectra were obtained.

Coal extraction methods used in this project were reported earlier for sequential solvent extractions of coal.(8) For both Soxhlet and batch extractions, the insoluble residues (coal products) were collected on a 0.45 µm PTFE membrane filter, washed with hot 80% methanol/water, and dried to constant weight at 0.05 Torr., 100°C. Solvents were removed from extracts under vacuum and products dried to constant weight as above. A sample of the Argonne Premium Illinois coal was extracted with $(nBu)_4NOH$/pyridine as described by Liotta et al(9) but without ultrasound enhancement. After extraction for 24 hours, residue was separated from extract by centrifugation for 30 min. at 2500 rpm and extracted for an additional 48 hours with fresh solvent mixture. Washing of the residue and the combined extracts with 80% methanol/water greatly reduced the volume of wash solvent needed to completely remove chloride ions compared with the Liotta procedure. Washed extracts and residue were dried to constant weight at 100°, 0.1 Torr. to give 27% by weight of extract. The extraction was repeated on a separate coal sample for 57 days under a nitrogen atmosphere to produce a 30% yield of purified extract.

Ultrasonically Enhanced Extraction of Coal The method of Iino(10) was modified as follows: A 2 gram sample of vacuum dried coal was placed in a 100 mL glass centrifuge tube, 50 mL of mixed solvent (CS_2/MP 1:1 vol.) was added and the coal soaked for 15 minutes. The mixture was irradiated for 30 minutes at room temperature with 19.9 kHz ultrasound at 35% power on a 19 mm probe in the Biosonik III, Bronwill generator. Residue was washed from the probe into the tube with a small portion of mixed solvent, the mixture spun at 2500 rpm in a Centra 7 centrifuge for 45 minutes and the supernatant collected. Fresh mixed solvent was added and the mixture irradiated for 15 minutes and fractionated as above. This procedure was repeated (up to 15 times) until the supernatant was nearly colorless. The combined supernatants were filtered through a 0.45 µm membrane filter and reduced in volume on the rotary evaporator and vacuum pump. In order to remove traces of MP, the residue was irradiated three times for ten minutes with 50 mL of 80% methanol/water, centrifuged, collected on a membrane filter and dried to constant weight in the Abderhalden apparatus at 100°, 0.1 Torr.

Coal Demineralization for Extraction The method of Kuhn(11) was modified locally. The

solvent-free residue from a pyridine extraction of coal was vacuum dried and a 10-14 gram portion placed in a 250 mL round bottom flask containing 50 mL of 25% HCl and fitted with an ice-filled cold finger condenser. The mixture was heated at 100° for 2 hours with an electrically heated oil bath. After cooling, the coal was collected on a Whatman No. 1 filter and washed with deionized water until the pH was 5.5. The residue was dried overnight at room temperature and transferred to a 500 mL polyethylene centrifuge bottle (Nalgene Centrifuge Ware PP). A 50 mL portion of 49% HF was carefully added, the bottle loosely capped, and the contents heated at 70° for 2 hours with an oil bath. After cooling, the residue was diluted with deionized water, washed onto a Whatman No. 1 filter in a polyethylene funnel, washed with deionized water to pH 5.5 and vacuum dried to constant weight at 100° in the Abderhalden apparatus. The dried residue was then re-extracted with pyridine in the normal manner.

RESULTS AND DISCUSSION

Reactions Using Nickel Boride "Nickel Boride" is the name given the active material formed by sodium borohydride reduction of aqueous nickel chloride in ethanol. The reactions described in Quarterly Reports 1-3 have been varied in an effort to improve desulfurization. Results are reported in Tables 2 and 3 for ethanol, butanol and mixtures of ethanol/PCE as solvent and show that reaction in aqueous ethanol at 50° gives the best results. Two reaction methods were compared: 1) Normal addition in which a solution of sodium borohydride is slowly added to a mixture of nickel chloride and sulfur compound in ethanol; and 2) Reverse addition in which an aqueous solution of the nickel salt is added to the mixture of borohydride and sulfur compound. Transient brown colored compounds were present in the extracted reaction mixture during work-up of the reverse addition reaction but not the normal reaction.

From the data in Table 3, it can be seen that higher temperature (butanol) does not improve desulfurization. The best conditions appear to be 50-60° in ethanol leading to desulfurization of DBT of about 30%. Although the reaction is disappointing because of the modest conversion, the reaction is clean and material balances are good. No partially reduced thiol is formed, only the biphenyl product and un-reacted DBT are observed by GC or HPLC.

Reactions Using Ni/Al Alloy In order to explore systems based on less expensive reagents than nickel boride, the known desulfurization reagent Ni/Al alloy/NaOH was studied. In contrast to the nickel boride reactions, most Ni/Al alloy reactions produced thiols in addition to the expected hydrocarbon products. Results are summarized in Table 4. The reaction differs from that with nickel boride in that benzothiophene is more reactive than dibenzothiophene. An organic co-solvent is necessary to keep the substrate soluble in the aqueous base reaction mixture. THF appears to be better for this purpose than either ethanol or butanol, perhaps because the active reagent is less solvated by the THF than by the alcohol. Partially reduced compounds (thiols) are always observed in addition to the fully reduced hydrocarbon products in these reactions. As observed for the nickel boride reductions, the best conversions are modest (34% reaction to a mixture of thiol and hydrocarbon.) Since even this conversion requires an expensive co-solvent, at this point, there does not seem to be any advantage for Ni/Al over nickel boride. The last two entries in Table 4 are notable. $NaBH_4$ cannot be substituted for NaOH to generate the reducing agent in this system. Furthermore the reducing agent is not soluble in the mixed solvent. This is consistent with the view that the active agent is molecular hydrogen adsorbed on nickel metal produced by the reaction of strong base with aluminum

metal and that the soluble aluminum ions or complexes formed are not themselves active reducing agents. Testing of this last point was one of the ideas to be evaluated in this project and results point to heterogeneous rather than homogeneous reagents or catalysts as the active species in these reactions.

Reactions using Metal Salts and Sodium Borohydride The reaction to produce 'nickel boride' was modified to test a variety of other transition metal salts as possible desulfurization catalysts. The most favorable reaction conditions for the nickel salt were used to screen for desulfurization of DBT by the ten relatively inexpensive salts listed in Table 5 in one hour reactions. After the normal workup, gas chromatograms were examined for the appearance of biphenyl or 2-phenylthiophenol. Ferrous chloride and sulfate and cupric chloride showed some activity, but no salt was as effective as nickel chloride in this test reaction. Salts of molybdenum are known desulfurization catalysts or reagents. Their chemistry has been reported by other groups, for example the Malin Corporation.(12) In our system sodium molybdate and sodium borohydride gave a 1% yield of biphenyl. Although the reactions in Table 5 have not been individually optimized, experience with the nickel salt suggests that even with adjustments in time, temperature and solvent the amount of desulfurization is unlikely to reach 50%. The activity of the ferrous salts is of interest because of the presence of iron (as pyrite) in all Illinois coals. However, mineral pyrite was not effective as the source of a catalyst in this system.

Table 6 summarizes several desulfurization reactions of model compounds comparing our results with those from the literature. The single electron transfer reaction of potassium in THF, with or without an added electron transfer agent is most effective but uses reagents unsuitable for scale up to coal desulfurization. Our results, while modest in total desulfurization, utilize low temperatures, short times and relatively inexpensive reagents and encouraged us to test the method on coal derived organosulfur compounds.

Desulfurization Reactions of THF Soluble Coal Fractions Table 7 summarizes the desulfurization of THF extracts from IBC-105, -106, and -108 coals. The results are also presented in Figure 1. As expected, K/THF showed the greatest amount of sulfur removal, see below. Of the nickel based reagents (NiBoride or Ni/Al alloy), the nature of the solvent is as important as the nature of the reagent. Reactions in aqueous ethanol show less sulfur removal than those in aqueous THF. Since the coal fraction was totally soluble in THF but not in ethanol, this is consistent with our other data indicating an insoluble desulfurization reagent - the sulfur compounds must be brought to the active surface for the reaction to occur. While the amounts of desulfurization are actually quite good for the simple reagents employed, the insoluble nature of the reagents precludes their use with solid coals. For this reason, these reagents were not tested with whole samples as had been planned at the beginning of the project.

Reactions Using K/Naphthalene/THF (SET Conditions) Our initial problems in reproducing literature results with this system were traced to incomplete drying of solvent or reagent and corrected. Potassium metal in dry THF at 67° for 24 hrs. followed by quenching with aqueous ammonium chloride completely converted DBT to biphenyl as judged by both GC and HPLC. In our hands, the addition of naphthalene as an electron transfer agent was not necessary for DBT reduction, apparently DBT or BP is acting as the electron acceptor from the metal. Traces of water in the system produced (after workup) significant amounts of the corresponding thiol product (PTP). The potassium in THF reaction was applied to THF soluble extracts of IBC coals, first without added electron transfer agents and then using $NiCl(CCl{=}CCl_2)PPh_3$ as a possible catalyst precursor or

electron transfer agent, Table 7. Stock has already shown that naphthalene is an effective transfer agent in this system,(13) our interest is in nickel complexes which may be related to the reaction of nickel boride chemistry. The THF extract was 9% of the feed coal by weight and contained 3.76% S and less than 1% ash so it is a good source of ogranosulfur compounds. Addition of the chlorovinyl nickel complex (NiLX in Table 7) increased the desulfurization from 82 to 86%. This indicates that the coal compounds themselves are serving in this role, reasonable behavior for material with significant aromatic content.

Reactions Using Minerals in Coal as a Catalyst Source The sink fraction from a float/sink separation of Illinois No.6 coal was available from a previous project and was tested as a catalyst source as summarized in Tables 8 and 9. Aqueous $NaBH_4$ was used to reduce the minerals in the sink fraction to form a reagent which caused a small amount of desulfurization of DBT added to the mixture. Aqueous ethanol was the solvent. An analysis of the sink fraction is shown in Scheme 1. The small amount of desulfurization activity present in the coal sink fraction is mostly lost when the sink is extracted with hot PCE to remove elemental sulfur (°S) followed by washing with methanol/water and vacuum drying. The presence of both °S and sulfate plus the low pH of an aqueous slrry of the fraction indicates that the sink fraction has been heavily oxidized.

Although the amount of desulfurization was modest, the fact that the catalyst source is coal derived encouraged us to continue screening reactions with other coal derived minerals. For this study, the insoluble residues from THF extractions of IBC coals were treated with $NaBH_4$ in the presence of DBT in either ethanol/water or THF/water. The reaction mixtures were extracted with dichloromethane and analyzed for the production of biphenyl or 2-phenylthiophenol and the loss of DBT. These results are also summarized in Tables 8 and 9. Control experiments showed that no BP was produced in the absence of either $NaBH_4$ or the coal mineral fraction.

Reactions of $Fe(CO)_5$ with Model Compounds Keiter has shown that both BH_4^- or ^-OH in alcohol solvents reduces $Fe(CO)_5$ to the active $H\text{-}Fe(CO)_4$ species.(14) The fact that hydroxide ion could serve as the reducing agent to produce an iron based reagent was attractive as a possible entry into coal derived reagents. We screened DBT, BT and BS for desulfurization by this system in ethanol and butanol using both $NaBH_4$ and NaOH to generate the reagent. The results are summarized in Scheme 2. In no case tested was there significant conversion of model organosulfur compound to the hydrocarbon. Starting material was the major component of each reaction mixture. Unknown compounds were reproducibly obtained from both DBT and BS. Neither has yet been completely characterized. This new chemistry will be pursued as part of the MS thesis of S. Wang. Becuase of the uncertain nature of the reactions observed this reagent system has not yet been applied to coal fractions.

Solvent Extractions of Coal Samples In order to test desulfurization reagents on coal derived sulfur compounds, solvent extracts were selected since they are easier to work with. Pyridine is the best single solvent for removing the greatest amount of soluble material from coal. For example, it will extract about 25% by weight of an Illinois No. 6 coal. However this still leaves nearly 70% of the organic sulfur in the insoluble residue. In order to increase the amount of extract from coals for use in this and future projects, the pyridine insoluble residues of several coals were demineralized by hot HCl and hot HF in an effort to remove additional soluble material which may have been blocked by minerals in pores. The results are summarized in Table 10 and Figure 2. The increase in extract after demineralization was greater for lignite and sub-bituminous coals than for the Illinois or Pittsburgh coals although the total extract yields from the latter two are still much greater. The mixed solvent (CS_2/MP) was also used to extract pyridine insoluble

residues to increase extraction yields. Increases were modest as shown in Table 10 and the MP solvent is very difficult to remove from both the extract and residue as judged by FT-IR analyses. Because not all of the pyridine extracts were soluble in the solvents used for desulfurization in this study, these extracts were not tested with the desulfurization reagents. Future studies of desulfurization should also examine these extracts.

CONCLUSIONS AND RECOMMENDATIONS

Transition metal salts reduced with $NaBH_4$ in aqueous ethanol convert dibenzothiophene to biphenyl in up to 31% yield at 50° in two hours. The most active salt is nickel chloride which produces the reagent referred to as 'nickel boride' in the literature. Thiophene is completely desulfurized by this reagent. Benzothiophene, Benzyl sulfide and Octyl sulfide are converted to hydrocarbons in lower amounts than DBT. Nickel aluminium alloy reduced by NaOH in ethanol also desulfurizes these compounds but in lower conversions and thiols as well as the hydrocarbons are found in the reaction mixtures. Both nickel based reagents desulfurize THF soluble fractions of IBC coals. In the best case, Ni/Al/NaOH in aqueous THF reduced the sulfur content of the THF extract from IBC-105 by 66%. Reactions of both nickel reagents with coal fractions were more effective in THF than in ethanol solvent. All data with both model compounds and coal fractions suggest that the active reagents are insoluble materials, probably hydrogen gas adsorbed on finely divided metallic nickel, both produced during the course of the reaction.

Minerals found in Illinois coals reduced with $NaBH_4$ in aqueous ethanol also have a small amount of desulfurization activity toward DBT. The most active system was a heavily oxidized sink fraction from a sink/float separation of Illinois No.6 coal. Both 2-phenylthiophenol and biphenyl were found in up to 13% conversion when this material was the reagent source for DBT desulfurization.

$H\text{-}Fe(CO)_4$ produced from $Fe(CO)_5$ by reaction with NaOH or $NaBH_4$ in the presence of DBT or BT produced small amounts of new compounds and large amounts of unreacted starting material.

Attempts to increase the amount of coal extracted by pyridine by demineralization of the insoluble residue followed by re-extraction gave significant increases for low-rank, but not for Illinois coals. CS_2/MP mixed solvent also removes new material from insoluble residues but is itself difficult to remove from both the extract and the final residue.

The best desulfurization reagents developed in this project are the heterogeneous materials 'nickel boride' and the activated Ni/Al alloy. While they are usable with solutions of model compounds or even with coal extracts they do not appear to be suitable for pre-combustion desulfurization of whole coal and do not satisfy our quest for soluble reagents or catalysts. Further development of reagents based on these compounds will depend upon discovery of soluble analogs.

Table 1. Compound Abbreviations Used in Tables

Starting Material		Possible Products			
DBT	Dibenzothiophene	BP	Biphenyl	PTP	2-Phenylthiophenol
BT	Benzothiophene	EB	Ethylbenzene	ETP	2-Ethylthiophenol
BS	Benzylsulfide	Tol	Toluene	MTP	2-Methylthiophenol
OS	Octylsulfide	Oct	n-Octane	OSH	1-Octanethiol

Table 2. Desulfurization Using Nickel Boride Reagent in EtOH

			Recover				
Start Mat.	mMole SM	Temp. 'C	mMoles SM	Product Identity	mMoles	Mat Bal Wt %	Desulfurization %
DBT	.80	0	.37	BP	.12	61.2	14.4
DBT	.80	22	.42	BP	.16	72.5	19.5
DBT	.80	50	.49	BP	.17	82.5	21.1
DBT	.80	50[a]	.52	BP	.25	96.2	31.0
DBT	.80	60[b]	.33	BP	.086	52.5	10.8
DBT	.80	78	.52	BP	.21	91.2	26.4
BT	.80	78	.62	EB	.13	93.8	15.8
BS	.37	50	.28	Tol	.20	102.7	26.1
OS	.40	50	.28	Oct	.05	77.5	6.6

a Reverse addition, $NiCl_2$ added to $DBT/NaBH_4$
b Perchloroethylene (PCE) added as co-solvent

Table 3. Desulfurization of DBT with Nickel Boride

All reactions started with 0.8 mmol DBT, time 2 hrs

Conditions		Temp °C	Recov DBT mmol	Yield BP mmol	DBT Recov %	BP Yield %	Mat'l Bal %
RevAddn	BuOH	65	.77	.036	96.1	4.6	100.6
RevAddn	BuOH	115	.74	.024	92.4	3.0	95.4
RevAddn	BuOH/.5 hr	115	.80	.025	99.6	3.1	102.7
RevAddn	BuOH/ 3 hr	115	.73	.038	91.3	4.7	96.0
RevAddn	EtOH/PCE	50	.71	.046	88.5	5.8	94.3
RevAddn	EtOH	50	.52	.250	65.0	31.2	96.2*
StandAddn	BuOH	115	.80	.074	100.4	9.2	109.6
StandAddn	EtOH/PCE	60	.33	.085	41.2	10.6	51.2
StandAddn	EtOH/PCE	50	.70	.080	87.0	10.0	97.0
StandAddn	EtOH	78	.52	.210	65.0	26.2	91.2*

* Best conditions, (Quarterly Report #2.)

Table 4. Desulfurization Using Nickel/Aluminum Alloy
All reactions used 10% NaOH in water to produce the reagent.

Compound	Co-Solvent	Cmpd mmol	Ni mmol	Temp °C	Time Hr	Rel Amnt Recovr St Mat	Rel Amnt Yield RH	Rel Amnt Yield Thiol
DBT	50% THF	1.34	10.33	65	2	83	3	14
BS	50% THF	2.27	12.66	65	2	87	13	0
OS	50% THF	1.16	9.45	65	2	81	1	18
Thianthrene	50% THF	1.92	14.11	65	2	100	NR	NR
BT	50% THF	1.63	9.53	65	2	66	17	17
BT	50% THF	1.18	4.82	65	2	85	14	1
BT	50% THF	1.34	10.33	65	0.5	87	6	17
BT	50% THF	4.89	9.23	65	21	98	2	0
BT	50% THF	6.86	24.18	25	2	99	1	0
BT	None	4.07	7.94	65	2	96	3	1
BT	50% EtOH	1.55	10.33	65	2	93	6	1
BT	n BuOH	3.74	13.05	116	2	100	NR	NR
BT	80% BuOH	3.93	11.93	103	2	100	NR	NR
BT[a]	60% EtOH	3.96	26.81	65	2	99	0	1
BT[b]	50% THF	5.43	31.64	65	2	100	NR	NR

NR = No Reaction
[a] $NaBH_4$ used in place of 10% NaOH to activate alloy.
[b] Supernatant from Ni/Al/10% NaOH reaction used as reagent.

Table 5. Comparison of Desulfurization of DBT with Salts.
Reverse Addition - Metal salt added to substrate plus $NaBH_4$
Solvent: Ethanol/Water, 50-55°, 1 hour.

Salt Used	Relative Amounts of BP	PTP	DBT	Quantitative % BP	% DBT
$NiCl_2 \cdot 6H_2O$[a]	-	0	--	31%	65%
$NaMoO_4 \cdot H_2O$	-	0	--	1.2	65
$MnCl_2 \cdot 4H_2O$	3	5	92		
$CuCl_2 \cdot 4H_2O$	2	11	87		
$ZnCl_2$	0.5	6	94		
$SnCl_2$	Trace	0	100		
$FeCl_2 \cdot 4H_2O$	7	14	79		
$FeSO_4 \cdot 7H_2O$	5	0	95		
$FeCl_3 \cdot 6H_2O$	2	0	98		
$K_4Fe(CN)_6 \cdot 3H_2O$	0	0	100		
FeS_2 (Aldrich)[b]	1	0	99		
FeS_2 (Aldrich)[c]	Trace	0	100		

[a] Best conditions for Nickel Boride.
[b] Normal Addition, $NaBH_4$ added to salt plus substrate.
[c] Salt added *via* dry addition tube.

Table 6.

Comparison of Desulfurization Model Compounds

	Catalyst/Reagent	Temp C	Time hrs	% Biphenyl	Ref.
DBT					
	Co/Mo/Alumina/H_2	550°	Flow	82	1.
	Ni[2,2'bipy]COD	55°	48	45	2.
	K/THF	RmT	168	52	3.
		68°	24	~100	4.
	NiBoride	50°	2	31	5.
	Ni/Al alloy/NaOH	65°	2	2	5.
BT					
	NiBoride	78°	2	16	5.
	Ni/Al alloy/NaOH	65°	2	13 + 13	5.
Octyl Sulfide					
	NiBoride	50°	2	7	5.
	Ni/Al alloy/NaOH	65°	2	16	5.

References

1. Klemm, *J. Heterocyclic Chem.* 1977 15, 281.
2. Eisch, *J. Org. Chem.* 1983 48, 2963.
3. Ignasiak, *J. Org. Chem.* 1977 42, 312.
4. Stock, *Energy & Fuels* 4, 402.
5. THIS WORK

Table 7. DESULFURIZATION OF THF SOLUBLE COAL FRACTIONS

REAGENT	Solvent	IBC Coal	%C DAF	%H DAF	%S DAF	Relative S Reduction	S/100C
None		105	78.79	6.47	3.76	---	1.79
Ni/Al/NaOH	THF	105	79.99	8.13	1.26	-66.5	0.59
NiBoride	EtOH	105	77.51	6.61	2.89	-23.1	1.40
K/THF	THF	105	79.26	9.28	0.67	-82.5	0.32
K/THF/NiLX	THF	105	69.02	8.53	0.54	-85.6	0.29
None		106	79.89	6.55	2.01	---	0.94
Ni/Al/NaOH	THF	106	76.48	6.78	0.84	-58.2	0.41
NiBoride	EtOH	106	78.63	6.14	1.50	-25.4	0.71
K/THF/NiLX	THF	106	70.15	7.59	0.34	-83.3	0.18
None		108	79.97	6.57	2.17	---	1.02
Ni/Al/NaOH	THF	108	81.22	7.77	1.52	-30.0	0.70
Ni/Al/NaOH	EtOH	108	70.98	6.09	1.44	-33.5	0.76
NiBoride	THF	108	82.17	6.63	1.27	-41.5	0.58
NiBoride	EtOH	108	77.52	6.68	2.14	-1.4	1.04

Table 8. Desulfurization of DBT with Coal Fractions and $NaBH_4$. Ethanol/water solvent, 50°.

Used	Amnt Used	mmol DBT	mmol $NaBH_4$	Temp °C	Time Hr	BP %	PTP %
ILL # 6 Sink	0.2088g	1.04	5.9	50	1	2	11
PCE Washed Sink	0.2340	0.81	5.6	50	1	1	0
THF Residue 101	3.1480	0.87	6.6	50	2	.89	-
THF Residue 104	3.1969	0.84	5.5	50	2	.88	-
THF Residue 105	3.0085	0.79	5.7	50	24	2	0
THF Residue 106	3.0609	1.04	6.8	50	2	.74	-
THF Residue 108	3.2122	0.90	5.6	50	2	.74	-
THF Residue 5/6	3.0746	0.84	6.2	50	2	.80	-

Table 9. Desulfurization of DBT with Coal Fractions and $NaBH_4$. Solvent: Ethanol/Water, 50°.

Salt Used	Relative Amounts of BP	PTP	DBT	Quantitative % DBT	% BP
Ill # 6 Sink	2	11	87		
Coal Sink - PCE washed	1	0	99	59.2%	1.2%
THF Residue IBC-101				50.8	0.9
THF Residue IBC-104				53.1	0.9
THF Residue IBC-105	1	0	99	91.6	1.6
THF Residue IBC-106				39.9	0.7
THF Residue IBC-108				28.0	0.7
THF Residue Ohio5/6				39.3	0.8

Table 10. Multiple Extraction of Argonne Pristine Coals

Coal #:	2	3*	4	8
Extraction #1: Dry Coal Extracted with Pyridine				
Initial Wt g	16.1470	20.8410	19.7607	14.0022
Extract Wt g	1.6053	5.2901	6.3446	0.4078
Wt% Extract #1	9.94	25.3	32.1	2.91
Residue Wt g	14.3735	15.3509	13.0665	13.4065
Wt% Residue #1	89.0	73.6	66.1	93.7
Pyridine Residue #1 Extracted with CS_2/MP Mixed Solvent				
Initial Wt g	2.0048	2.0757	2.0163	2.0535
Extract Wt g	0.1181	0.0835	0.1825	0.1940
Wt% Extract #2 (Based on Residue #1)	5.89	3.02	9.05	9.44
Residue Wt g	1.6238	1.7830	1.7928	1.7434
Wt% Residue #2	81.0	85.9	88.9	84.9
Pyridine Residue #1 HCl/HF Demineralized and Extracted with Pyridine				
Initial Wt g	10.8610	11.2843	10.6238	11.1732
Wt after Demineralize	9.7001	9.4490	8.5236	9.3480
Extract Wt g	0.5421	0.0891	.0852	0.3894
Wt% Extract #3 (Based on Residue #1)	5.59	0.94	1.00	4.16
Residue Wt g	9.6816	9.2299	8.4742	8.4376
Wt% Residue #3	99.8	97.7	99.4	90.3
Total Wt% Extract (1+3)	14.93	26.17	32.91	6.40

* Argonne #3 is the parent of IBC-105 coal.

Scheme 1. Analysis of Illinois No.6 Coal Sink Fraction

```
                    Coal Sink Fraction (d > 1.5 g/cc)
                              |
                              | Moisture = 16.65 %
                              | Ash = 40.32±0.06 %      |
                              | 0.255% S˙ by Wt.        | Dry Basis
                              | Elemental Analysis      |
                              |     3.75% Carbon
                              |     1.53% Hydrogen
                              |    30.24% Sulfur
                              |    16.80% Iron
                              |
                              | 0.5173 g of sink fraction in
                              | 20 mL water gave pH = 1
                              |
                          Filtered
                              |
        ____________________________|____________________
        |                                                |
  Soluble (pale yellow)                              Insoluble
        | (pH = 1)                                 0.2797g  54.07% by Wt.
        |                                             Ash = 46.42%
        |
  ______|____________________________________________________________
  |         |         |         |         |                  |
  |         |         |         |         |                  |
AgNO3      NaOH      HCl       BaCl2     K2Fe(CN)6˙H2O,     -dipyridyl
  |         |         |         |         |                  |
NR   Brown Solid  Brt.Yellow  White Solid  Prussian Blue     Red
                              (SO4=)        (Fe+3)          (Fe+2)
```

```
                    Coal Sink Fraction
                        (1.2336g)
                              |
                  PCE, 55 mL, 45 min, 120˙
                              |
                              |
                    ___________|___________
                    |                     |
                 Soluble              Insoluble
              0.0074g 0.60%        1.0066g 81.60%
                0.26% ˙S         (Used for Tables 8/9)
```

Scheme 2.

Reactions of $Fe(CO)_5$ Reactions with Model Compounds

CMPD + $Fe(CO)_5$ + $NaBH_4$ or NaOH + EtOH or n-BuOH reflux 2-24 hr

DBT

Traces of Biphenyl plus Unknown Compound

Unknown is probably Q-$Fe(CO)_4$

HPLC, FT-IR, ^{13}C NMR

Benzyl Sulfide

Unknown Compound Only Product, Recover BS

Unknown not an iron carbonyl

May be product of solvent with benzyl group

Benzothiophene

No Reaction

Figure 1.

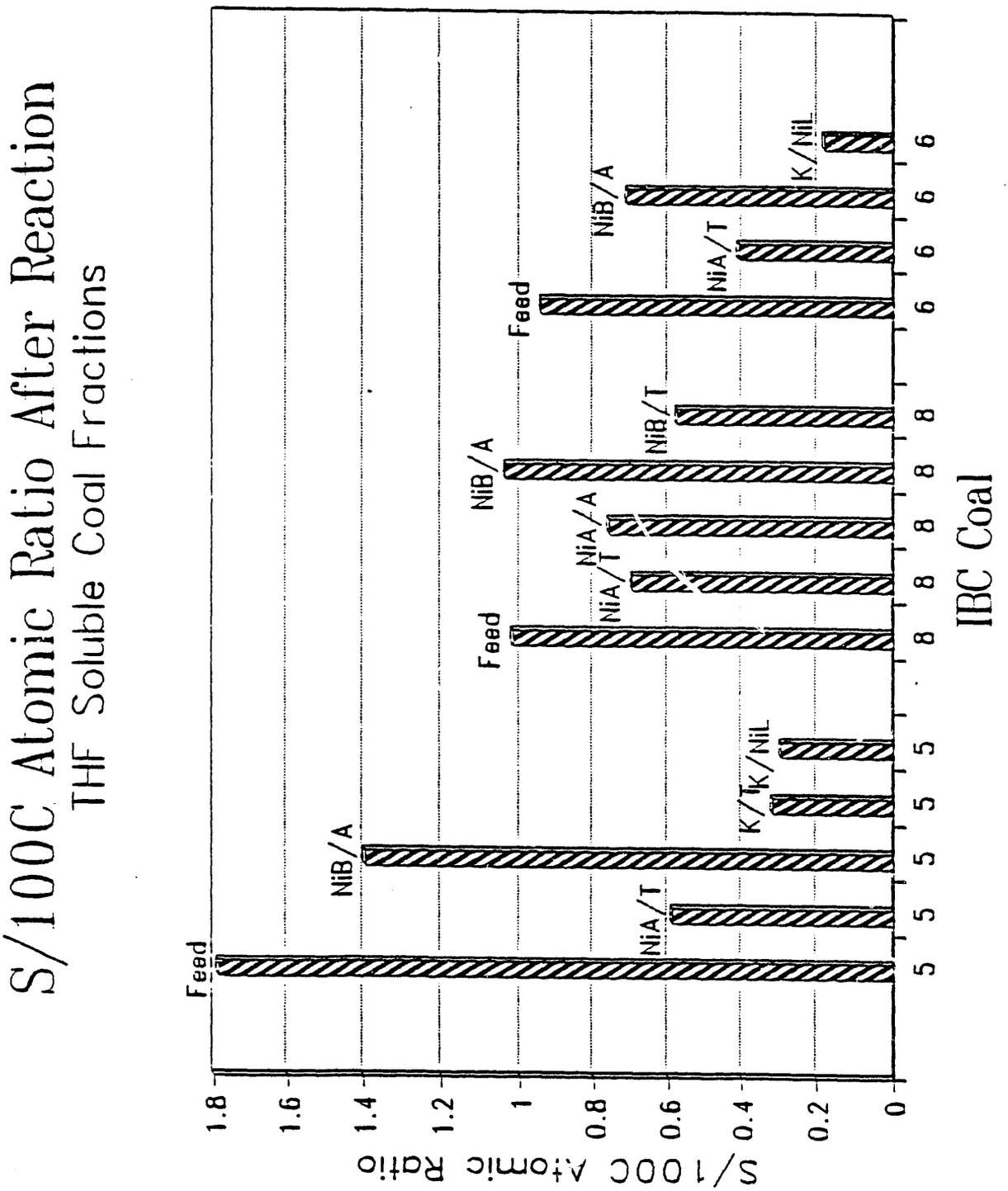
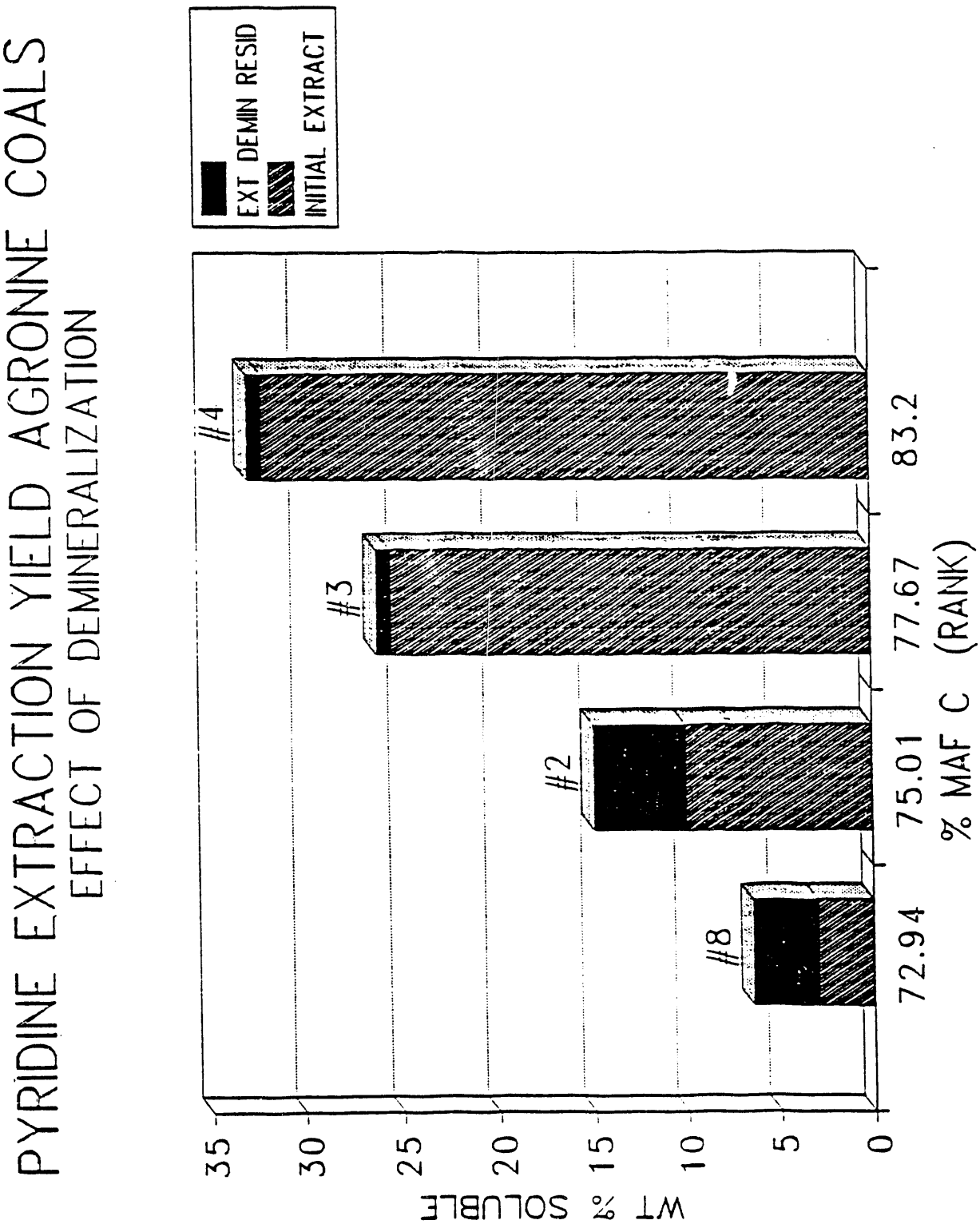

S/100C Atomic Ratio After Reaction
THF Soluble Coal Fractions
S/100C Atomic Ratio
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
Feed
NiB/A
NiA/T
K/T
K/NiL
NiA/A
NiB/T
IBC Coal
5
5
5
5
5
8
8
8
8
8
6
6
6
6
6

Figure 2.


PYRIDINE EXTRACTION YIELD AGRONNE COALS
EFFECT OF DEMINERALIZATION
EXT DEMIN RESID
INITIAL EXTRACT
WT % SOLUBLE
35
30
25
20
15
10
5
0
#8
#2
#3
#4
72.94
75.01
77.67
83.2
% MAF C (RANK)

REFERENCES

(1) Sawyer, D.T.; Roberts, J.L., Jr. Acc. Chem. Res. **1988**, 21, 469.

(2) Klemm, L.H.; Karchesy, J.J. J Heterocyclic Chem **1978** 15, 281.

(3) Newman, M.S.; Hetzel, F.W. "Org. Syn., Coll. Vol. 6" **1988** 824.

(4) Venanze, L. J. Chem. Soc. **1959**, 719.

(5) Michael, C.H.; Sortiris, J.; Edward, H.S. J. Org. Chem. **1989**, 54, 3015.

(6) Papa, D.; Schwenk, E.; Ginsberg, H.F. J. Org. Chem **1949** 14, 723.

(7) Chatterjee, K; Wolny, R.; Stock, L.M. Energy & Fuels **1990**, 4, 402.

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

(9) Matturro, M.G.; Liotta, R.; Reynolds, R.P. Energy & Fuels **1990**, 4, 346.

(10) Takanohashi, T.; Iino, M. Energy & Fuels **1990**, 4, 452.

(11) Kuhn, J.K.; Fiene, F.L.; Cahill, R.A.; Gluskoter, H.J.; Shimp, N.F. Environmental Geological Notes No. 88., Illinois State Geological Survey, **1980**.

(12) Malin Research Corporation, Marion IL 62959, Process for Desulfurization of Coal, Technical Reference Manual, Technical Conference, **1988**, available SIU: Library, Q662.623p9632.

(13) Stock, L.M.; Chatterjee, K.; Wolny, R. Energy & Fuels **1990** 4, 402.

(14) Keiter, R.L.; Keiter, E.A.; Hecker, K.H.; Boecker, C.A. Organometallics, **1988**, 7, 2466.

(15) Eisch, J.J. J. Org. Chem. **1983**, 48, 2963.

(16) Ignasiak, L. J. Org. Chem. **1977**, 42, 312.

PROJECT MANAGEMENT REPORT

June 1, 1991 through August 31, 1991

Project Title: New Reagents for Coal Desulfurization

Project Coordinator: Dr. David H. Buchanan, EIU

Other Investigators: Dr. Stanislaw Kalembasa
Ms. Donna Olson
Mr. Shan Wang
Ms. Linda Warfel

Project Monitor: Dr. Daniel D. Banerjee, CRSC

(This project is funded by the U. S. Department of Energy as part of its cost-shared program with Illinois Department of Energy and Natural Resources.)

EXPENDITURES - EXHIBIT B

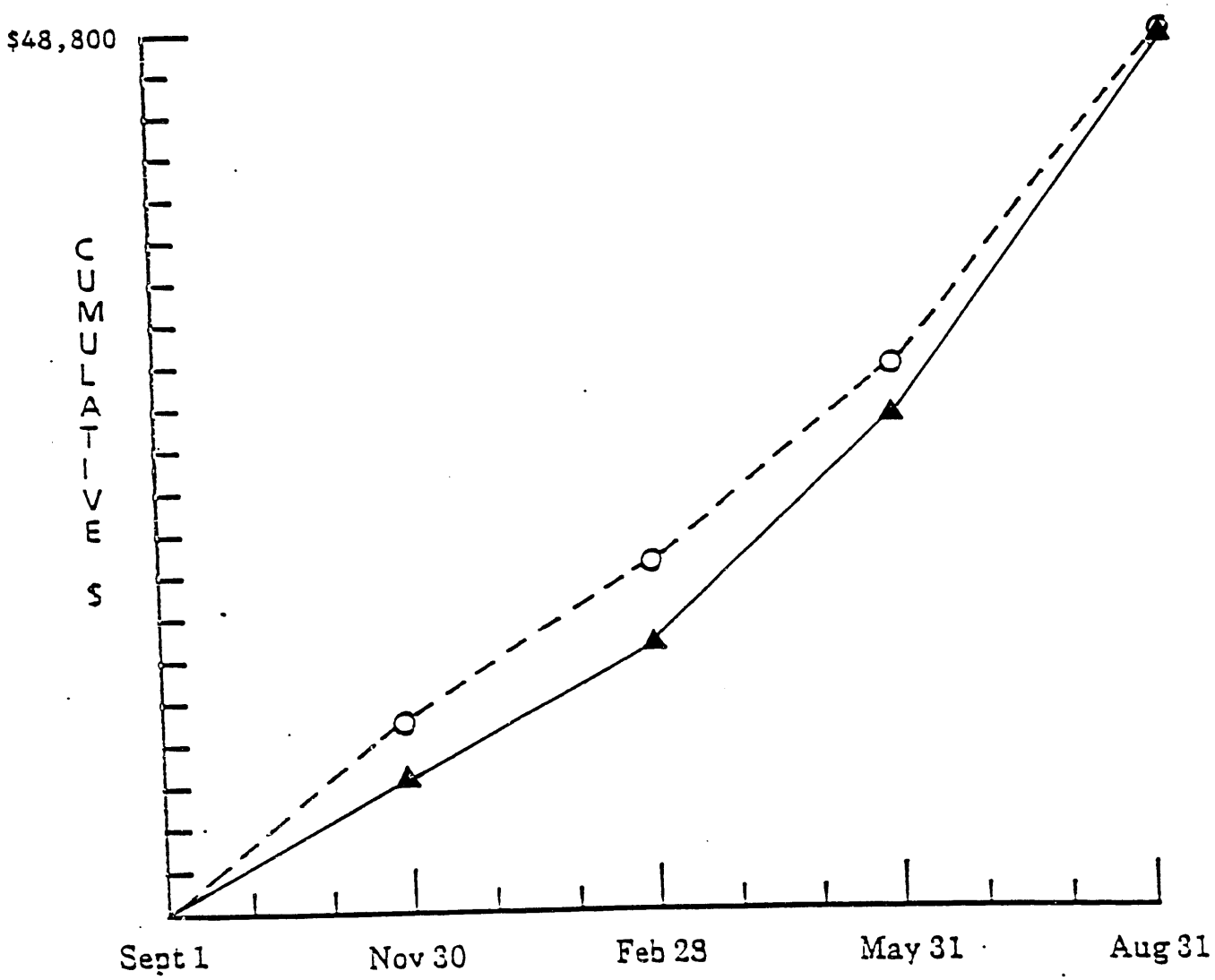
Projected and Estimated Actual Expenditures by Quarter

Quarter*	Types of Cost	Direct Labor	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Costs	Total
Sept. 1, 1990 to Nov. 30, 1990	Projected	6,800	600	----	400	500	830	9,130
	Estimated Actual	4,738	362	340	0	620	606	6,666
Sept. 1, 1990 to Feb. 28, 1991	Projected	13,600	1,200	100	800	1,200	1,690	18,590
	Estimated Actual	10,280	1,191	367	0	780	1,262	13,880
Sept. 1, 1990 to May 31, 1991	Projected	20,400	1,800	1,000	1,200	1,900	2,630	28,930
	Estimated Actual	18,274	2,331	884	200	1,816	2,350	25,855
Sept. 1, 1990 to Aug. 31, 1991	Projected	36,564	2,400	1,400	1,200	2,800	4,436	48,800
	Estimated Actual	36,564	2,400	1,400	1,200	2,800	4,436	48,800

*Cumulative by quarter

COSTS BY QUARTER - EXHIBIT C

New Reagents for Coal Desulfurization



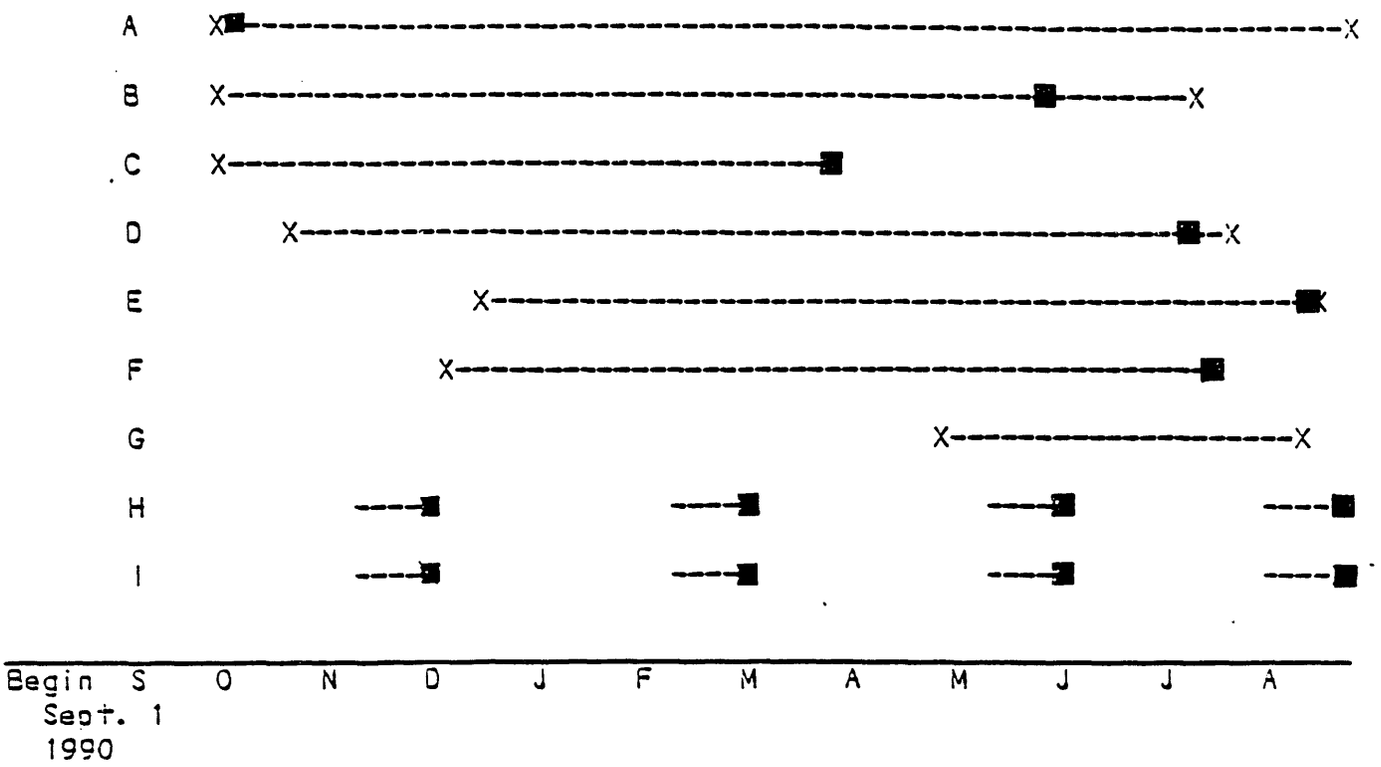
Months and Quarters

0 = Projected Expenditures ----------

▲ = Actual Expenditures ————————

Total CRSC Award $ 48,800

SCHEDULE OF PROJECT MILESTONES



Milestones:

A. Personnel employed
B. Sample acquisition and preparation
C. Model compounds acquired/prepared
D. Nickel reagents tested with model compounds
E. Iron reagents tested with model compounds
F. Coal extract reactions with favorable reagents
G. Coal reactions with favorable reagents
H. Technical Reports Prepared and Submitted
I. Project Management Reports prepared and submitted

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.

END

DATE
FILMED
2/10/92

I