

FINAL TECHNICAL REPORT  
September 1, 1986 through August 31, 1987

Project Title: Carbon Monoxide/Ethanol Desulfurization of Illinois High Sulfur Coal

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ABSTRACT

Recent experiments have been designed to refine estimates of material balance, revise forms-of-sulfur calculations, determine the reactions between reactor metals and reagents, and improve optimization of steps 1 and 2. High-volatile chars containing 0.05 to 0.2 percent organic sulfur have been produced. These sulfur percentages meet all federal emission regulations.

This contract year produced several significant results: 1) experiments with modern carbon-14-ethanol have shown that the worst-case loss of alcohol to coal at 400°C would be about \$10 per ton, and later tests with carbon-12/carbon-13 show no loss at 400°, 475°, and 550°C; 2) use of 95 percent ethanol may cut alcohol costs in half and increase efficiency of step 2; 3) new chemical analyses and a complete recalculation of sulfur mass balances have confirmed that earlier estimates were correct--average predicted troilite in products = 1.41 percent S and extracted troilite = 1.42 percent S; 4) additions of iron sulfate to the coal have proven that, when these minerals are formed by oxidation of coal, CO/ethanol converts them rapidly to troilite; 5) all experiments and a recent DOE patent suggest that high levels of recovery of carbonyl sulfide and acetaldehyde are feasible; 6) experiments show that last year's TGA-based mass balances were correct; 7) major effort was also required for the Interim Final Report and for updated sulfur mass-balance studies; 8) oldhamite (CaS) plays a significant role in the sulfur mass balance for certain samples; 9) several experiments are currently being run to determine ethanol losses to coal and reactor parts and to capture gaseous products, although leaky reactors are a major problem; 10) reagent/reactor interactions have been shown to cause 2-4 percent breakdown of ethanol to mainly acetaldehyde with minor methanol and acetone; 11) unfunded research at SIU-C and efforts funded by the Illinois Corn Marketing Board have shown further promise of ethanol/carbon monoxide mixtures, and magnetic removal of spent catalyts.

Proposed research is designed to optimize the process, test the feasibility of microwave-assist catalysis, control formation of CaS, examine "prep plant" and aggregate flotation coals, and investigate new catalytic approaches to sulfur removal. A two-year demonstration project will soon begin which will provide a continuous-flow reactor for future research and development.

Page 26 contains proprietary information.

## EXECUTIVE SUMMARY

As early as three years ago, we demonstrated that the amounts of sulfur measured as HCl-soluble pyrrhotite were the same as those predicted by conversion of pyritic sulfur in the feed coal to pyrrhotite in our products. X-ray diffraction (XRD) analysis also proved that all of the pyrite/marcasite in the feed coal was converted to pyrrhotite after Step 2 of our process and that no pyrrhotite, pyrite/marcasite, or iron sulfate remained after the HCl/CH<sub>3</sub>Cl wash. Recent Moessbauer analyses have further confirmed those results at extremely low detection levels. Confirmation of the fate of inorganic sulfur provides the best assurance that organic sulfur is accurately determined. Our determinations are also substantiated by a comparison with ASTM method D-2492 for sulfur determination in coals.

We have also reported for the last few years that some of our products may contain neoformed pyrrhotite and many do contain oldhamite (CaS) which dissolves in HCl but remains in bottom ash during combustion. Oldhamite therefore represents desulfurized product. Indeed, one of our goals for the latter part of this project is to investigate methods of increasing the formation of oldhamite and "new" pyrrhotite.

Another set of experiments confirmed our suspicion that sulfate in the feed coal is rapidly converted to troilite in steps 1 and 2 of the process. This finding may also make it possible to add iron scavengers and remove organic sulfur as Fe<sub>7</sub>S<sub>8</sub>.

The principal goals of this year's research were to: obtain more accurate material balances, particularly with respect to ethanol consumption; evaluate the trapping of reagents or volatile by-products in the coal-like product; and study the feasibility of capturing valuable by-products such as acetaldehyde and carbonyl sulfide. Two major advances have been made toward by-product capture. First, we have found a patent by researchers at the U.S. D.O.E. which recycles acetaldehyde during pyrolysis to remove H<sub>2</sub>S before it back-reacts with their coal-like product. Second, an innovative new approach using carbon-14-containing ethanol from corn was used to accurately measure the amount of trapping by the coal-like product of ethanol and its by-products. This method is based upon the fact that Illinois coal contains no carbon-14, and, therefore, any carbon-14 remaining in the solid product after a treatment step must represent trapped reagents or by-products. Carbon-12/carbon-13 ratios are also being used to this end. The carbon-12/carbon-13 analysis has an advantage over carbon-14 methods in that analyses require less time to perform and are less costly. Our results show a retention of ethanol carbon in the amount of 1.5 percent and 5 percent using the carbon-12/carbon-13 and carbon-14 determinations respectively. The accuracy of the carbon-12/carbon-13 analysis is less than the radiocarbon dating (carbon-14) procedure used, but the two methods have given comparable results.

Most of the research has focused on steps 1 and 2 for the removal of organic sulfur. Nine Illinois Basin coal samples have been tested with the process. The results are given in Table 1, which shows the sulfur remaining after step 2 and how much of it is organic sulfur. The

process is capable of lowering organic sulfur concentrations to below 10 percent of the original content, leaving all samples with a sulfur concentration of 0.2 percent or less. Recent experiments to determine the rate of desulfurization indicate steps 1 and 2 require about 15 minutes each. Both residence times are about as short as practicable for large-scale industrial processes.

Table 1. Desulfurization of Illinois Basin Coals

Local	Seam No. <sup>a</sup>	Wt % Pyr. S	Wt % Org. S	Wt % SO <sub>4</sub> S	Wt % Tot. S	Wt % CaO	Wt % Tot. S Before Cat. Removal		Wt % Org. S <sup>b</sup>
							Actual	Calcd.	
West Central	6	1.18	2.71	0.44	4.21	1.15	1.70	1.45	0.20
West Central	6	1.21	2.89	0.37	4.37	0.99	1.69	1.35	0.15
Southwestern	6	1.37	2.08	0.15	3.56	1.15	1.75	1.29	0.20
Southwestern	6	0.63	1.79	0.11	2.50	1.82	1.03	0.74	0.20
Southwestern	5	1.21	2.11	0.21	3.47	0.93	1.25	1.18	0.14
South Central	6	0.38	0.50	0.14	0.89	0.37	0.12	0.45	0.05
South Central	6	2.39	1.23	0.40	3.91	1.03	1.98	2.15	0.11
Southeastern	5	1.41	1.71	0.04	3.15	1.23	1.16	1.15	0.14
Southeastern	5	3.91	1.25	0.27	5.36	1.38	2.10	3.11	0.16

<sup>a</sup> No. 5 is the Springfield (No. 5) Coal Member, and No. 6 is the Herrin (No. 6) Coal Member. The samples were collected as fresh material at the mine and stored under an argon atmosphere.

<sup>b</sup> Assumes total catalyst removal.

Our recently funded project for 1987/1988 will make it possible to 1) derive an optimization equation for the entire process; 2) refine step 3 (magnetic separation of spent catalyst; 3) investigate new reductants and catalytic "stimulators"; 4) find the mechanism of formation of CaS and "new" trolite, and take advantage of the mechanisms to improve the process; 5) carry out feasibility tests on microwave-assist catalysis; and 6) transfer data and integrate the CRSC/ICDB research with the project to build and test a 2-20 lb/hr continuous reactor funded by DENR/PVF and Corn Marketing Board.

## OBJECTIVES

### Goals and Objectives: Current (September 1, 1986 - August 31, 1987).

The overall goal of this research is the development of a precombustion coal cleaning process in which chemical treatments are combined in a desulfurization process to remove both inorganic and organic sulfur from high-sulfur coals. This research addresses the main priorities of the Illinois Coal Development Board: first, production of a high-volatile coal-like product from coal which can be tested in small-scale or existing equipment. This research involves multiphase products: oil, gas, carbonyl sulfide, hydrogen sulfide, elemental sulfur and more importantly acetaldehyde, the by-product of ethanol dehydrogenation. Second, the goals of this research are directed toward the development of methods and reagents for chemical coal cleaning, emphasizing substantial removal of organic sulfur.

The main objective of this project was to work toward the completion of the basic research phase in the development of the desulfurization process and reaction kinetics, and to characterize the products formed during the process. More detailed work on mass balance and stream compositions have been carried out. The laboratory-scale experimentation is also designed to obtain data needed for engineering at the next level of development.

### Specific Goals and Objectives

1. To use the newly constructed gas-flow reactor to investigate the rate and efficiency of sulfur removal.
2. To collect and characterize the gaseous, liquid, and solid products by physical, spectral, and chemical methods.
3. To collect mass balance and stream composition data for the carbon monoxide and ethanol steps under various conditions.
4. To optimize the carbon monoxide and ethanol steps of the process.

## INTRODUCTION AND BACKGROUND

Iron sulfides derived from pyrite and marcasite have been used with some success as catalysts for the desulfurization of coal in a variety of experimental systems [1].

In 1975, staff members from SIU-C and the ISGS formed a research group to examine the nature of iron sulfides in coal and coal process residues [2-11]. The principal instrument used in that study was Fe<sup>57</sup> Moessbauer spectroscopy. These studies demonstrated that Moessbauer spectroscopy was a particularly valuable means of determining the iron sulfide transformations which accompany coal processing.

In 1980, the research group began to examine the use of Moessbauer spectroscopy to study catalysis by iron sulfides during coal processing. A selection of pyrrhotites containing various metallic impurities was prepared. Experiments employing these catalysts began in 1981. Significant gains have since been achieved in coal desulfurization as a result of the use of these iron sulfides as catalysts.

This project remains as a collaborative effort of researchers at ISGS and SIU-C. The primary activity of the SIU-C group is research on the catalytic properties of iron sulfides. The main effort at the ISGS is the study of iron-sulfide-catalyzed desulfurization. Both groups are dependent upon one another for information concerning the preparation, characterization, and catalytic properties of iron sulfides.

The desulfurization process arising from this research involves three steps as shown in Figure 1. In the first step, carbon monoxide (CO) is reacted with the whole coal at moderate temperatures and pressures. Pyrite in the coal is reduced to catalytically active troilite (FeS) with the concomitant production of carbonyl sulfide. In the second step, the troilite is used to catalyze ethanol reactions leading to the removal of organic sulfur from coal [11]. The third step of the process concerns the removal of the iron sulfide catalyst remaining in the desulfurized coal-like product after ethanol treatment.

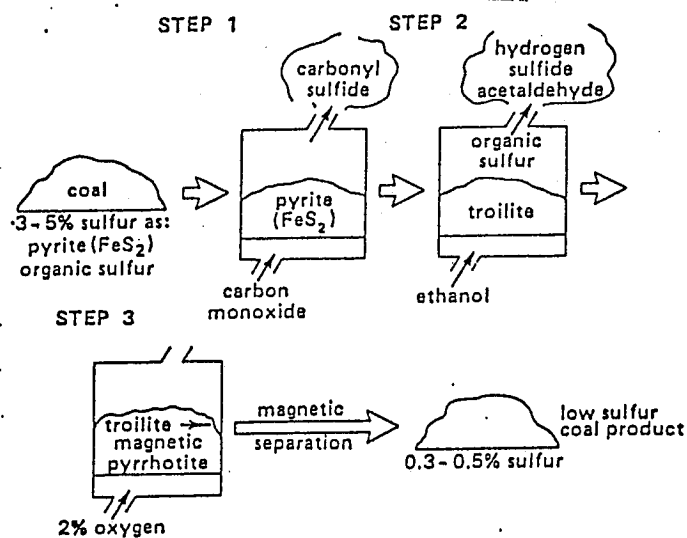


Figure 1. Carbon Monoxide-Ethanol coal desulfurization process.

Although our desulfurization process is considered a departure from past work, it does make use of the results of other desulfurization studies that used reactive gases to treat coal at elevated temperatures and pressures [12-23].

The relatively widespread work in this field is reflected in the general literature. A recent computer-assisted search of the National Technical Information Service (NTIS) files found 108 citations of coal desulfurization research. A search of Chemical Abstracts uncovered 479 related references since 1977. A coal desulfurization bibliography published in 1983 by the Technical Information Center of the U.S. D.O.E. contained 2,139 references. Any single source probably represents an incomplete collection of the available literature. Though many of these references touch coal desulfurization only tangentially, many report improvements of previously known methods, and others describe new approaches to the problem.

There are several new processes which have been reported. These include an elaboration of a nitric oxide treatment [24], the application of microwave technology [25], and an investigation of the chemistry of fused caustic desulfurization of coal [26].

In a search of the literature files described above, 235 citations to research were found which involve iron sulfide catalysis. The vast majority of these reports are related to studies of coal liquefaction. The catalytic role of iron sulfides in liquefaction has been recognized for several years [27, 28]. Iron sulfides derived from pyrite and marcasite have also been cited as possible aids in the desulfurization of coal [1]. Our desulfurization process uses iron sulfides (troilite) for in situ desulfurization of the organic sulfur in the coal [29,30].

The unique aspect of the process is the application of the chemical and mineralogical properties of iron sulfides to catalyze sulfur removal. At elevated temperatures, inorganic sulfur, organic sulfur, carbonyl sulfide and hydrogen sulfide form a complex equilibrium. This equilibrium is exploited in our process to remove half of the pyritic sulfur from coal in step 1 and most of the organic sulfur in step 2. When flowing-gas conditions are employed, the chemical equilibrium forces the composition of the iron sulfide from about  $Fe_{11}S_{12}$  toward FeS. With the use of pure iron sulfide systems, we have shown that FeS catalyzes the desulfurization of thiols, and that troilite is the only pyrrhotite that will desulfurize thiophene [11, 31], the most difficult to remove organic sulfur component in coal.

The success of the process is built around flowing-gas conditions which were found to be one of the most important design aspects. The process is designed to remove sulfur containing gases formed during each reaction. If not removed, hydrogen sulfide ( $H_2S$ ) and carbonyl sulfide (OCS) react rapidly with the solid product to form stable organic sulfur compounds. Carbonyl sulfide and hydrogen sulfide have been shown to react with pure carbon to produce residues containing 3 percent and 8 percent sulfur respectively. Similar findings have been obtained for coal and coal tars. These results are due to sulfide back-reactions [32-34].

## EXPERIMENTAL PROCEDURES

Coal samples were collected at mines in Illinois and immediately stored in a cannister under an argon atmosphere. Before use in desulfurization experiments, samples were ground in a glove box under an oxygen-free atmosphere to pass a U.S. 200-mesh standard sieve. The samples used are listed in Table 2.

The experimental conditions for the following desulfurization and analytical procedures are given in the December 15, 1982 to August 31, 1986 Final Technical Report. The procedures are as follows:

1. Static reactor conditions (ISGS).
2. Simulated gas-flow reaction conditions using 50 g samples (ISGS).
3. Simulated gas-flow reaction conditions using 10 g samples (ISGS).
4. Acid-leach catalyst removal procedures (ISGS).
5. Magnetic separation catalyst removal procedures (ISGS).
6. Coal oxidation techniques (ISGS).
7. Moessbauer spectroscopy (SIU-C).
8. X-ray diffraction (ISGS).
9. Thermogravimetric analytical procedures (SIU-C).
10. Gaseous product analysis (ISGS/SIU-C).
11. Plug flow catalytic reactor conditions (SIU-C).
12. Static flow catalytic reactor conditions (SIU-C).
13. Microbalance catalytic reactor conditions (SIU-C).

Table 2. Illinois coals used in the desulfurization process.

Local		Seam No. <sup>a</sup>	Wt % Pyr. S	Wt % Org. S	Wt % SO <sub>4</sub> S	Wt % Tot. S	Wt % CaO
Northwestern	(NW)	2	1.33	0.96	0.42	2.71	0.27
West central <sup>b</sup>	(WC)	6	1.18	2.71	0.32	4.21	0.84
West central	(WC)	6	1.21	2.89	0.27	4.37	0.72
Southwestern	(SW)	6	1.37	2.08	0.11	3.56	0.84
Southwestern	(SW)	6	0.63	1.79	0.08	2.50	1.33
Southwestern	(SW)	5	1.21	2.11	0.15	3.47	0.68
South central	(SC)	6	0.38	0.50	0.10	0.89	0.27
South central	(SC)	6	2.39	1.23	0.29	3.91	0.75
Southeastern <sup>b</sup>	(SE)	5	1.41	1.71	0.03	3.15	0.90
Southeastern	(SE)	5	3.91	1.25	0.20	5.36	1.01

<sup>a</sup> No. 2 is the Colchester (No. 2) Coal Member, No. 5 is the Springfield (No. 5) Coal Member, and No. 6 is the Herrin (No. 6) coal member. The samples were collected as fresh material at the mine and stored under an argon atmosphere. They are not necessarily representative of the mine product.

<sup>b</sup> Preparation plant samples.

## RESULTS AND DISCUSSION

The identification of the inorganic or sulfur mineral phases in the ethanol product (Step 2) has received an increased amount of

attention. It was postulated that part of the organic phase of the coal product was being removed 1) during the acid leaching process which removes iron sulfides or 2) during the methylene chloride extraction prior to sulfur analysis, and not through the ethanol reduction step.

Other important questions have also arisen during the past year. Among these are: First, what is the fate of the ethanol during the second step of the process; second, to what degree does ethanol react with the coal and remain in the coal-like product; and finally, can a mass balance for the ethanol step and carbon monoxide step be developed?

Our discussion adheres to the following format: Mineralogy of the Ethanol Product During Acid Leaching, Origin of the Acid-Leach-Organic Sulfur Determination, Mass Balance After Acid Leaching and Methylene Chloride Extraction of a Southeastern Illinois Coal (Springfield No. 5), Nature of the Sulfur in the Acid-Leached Residue, Magnetic Separation of the Mineral Matter (Iron Sulfide Catalyst) from in the Ethanol Product, and Ethanol Material Balance.

### **Mineralogy of the Ethanol Product During Acid Leaching**

Although we have shown that troilite is the principal iron sulfide detected in XRD traces (Figure 2 - traces b and c), mass balance discrepancies persist between the actual (observed by analyses) and predicted sulfur concentrations (from the pyrite/marcasite content) before and after catalyst removal (Tables 1, 3, 4, 5, 6 and 7).

When the sulfur content of the sulfur-bearing minerals are added to the organic sulfur content in the ethanol product, the calculated sulfur concentrations are not always precisely compatible with the sulfur concentrations found by analysis (tables 1, 3, 4, 5, 6, 7, and Figures 3-9). Most of the actual sulfur percentages are slightly higher than predicted, but a few are lower. However, if all the actual and predicted sulfur contents are averaged, the mean varies by only 0.01% sulfur. There are several reasons for these differences:

1. Back reactions with coal minerals other than iron sulfides.
2. Process errors.
  - a. Side reactions with reactor materials.
  - b. Side reactions with reactor lubricants.
  - c. Sampling of heterogeneous coal samples.
  - d. Analytical errors.
3. Formation of CaS and "new" FeS.

The greatest source of inorganic sulfur in the ethanol product other than troilite is oldhamite (CaS). This calcium sulfide mineral is the product of hydrogen sulfide and/or carbonyl sulfide reaction with calcite in the coal. The possible oldhamite (CaS) contribution to the inorganic sulfur content is shown in Tables 4, 5, and 6. At present an analytical procedure capable of quantifying oldhamite concentrations is not available to us. X-ray diffraction can, however, be used in a qualitative way for this purpose.



Figure 10 illustrates an XRD trace of a southeastern Illinois Springfield (No. 5) ethanol product having a pronounced oldhamite peak (see Figures 2a and 9). This mineral survives coal combustion and remains in the bottom ash of furnaces and boilers. Its formation represents an effective alternative method of in situ desulfurization.

Another major source of sulfur residues in the ethanol product is the heavy metals associated with high temperature lubricants. For example: "Molylube" contains molybdenum di-sulfide. "Never Seez" lubricant contains copper and zinc which can be combined with sulfur to form copper and zinc sulfides. These two metals have been found in the ethanol products using XRD (Figure 11) and X-ray fluorescence (XRF).

In addition to the sulfide contamination associated with high-temperature lubricants, contamination associated with gas-frit and general reactor corrosion has also been noted. We have determined that 0.3 g of metal is lost from the gas-frit during each experiment.

Fortunately, during the analytical procedure used for organic sulfur determinations, the iron and other heavy metal sulfides are readily removed during the hydrochloric acid wash and therefore do not affect the results.

Process optimization and improved engineering practices will eliminate the majority of these problems.

#### **Origin of the Acid-Leach Organic Sulfur Determination**

The carbon monoxide/ethanol method of coal desulfurization has, from the beginning, been conceived as a method primarily for the removal of organic sulfur. Early in the project, it was recognized that no satisfactory method existed for the analysis of organic sulfur in thermally heated coal-like products ranging in volatile matter from zero percent (coke) through the low, medium, and high ranges, up to products containing virtually all of their volatile matter, but pyrrhotites instead of pyrite.

Acid leaching of FeS from the coal with hydrochloric acid started as the method of choice for a number of researchers. The theory for this choice was based on that used for coal analysis under the forms-of-sulfur procedure ASTM D-2492, which uses a hydrochloric (sulfatic) and nitric acid (pyritic) wash to determine the inorganic sulfur forms. The sample is then analyzed for total sulfur and the organic sulfur concentration is determined by difference.

It was quickly recognized that mass balance calculations were not working out properly. For example, when high temperature coal-like products were treated in the acid leaching process, the mole percentage of sulfur, based on hydrogen sulfide liberated, did not match the mole percentage of iron liberated from the product. The question as to why was answered in several experiments. We found that acid leaching (1:1 HCl) of pyrrhotite produced a sulfur-rich residue containing 17 percent of the total sulfur liberated during the acid leaching process (EPA Contract Report, August, 1981). In the presence of a demineralized coal-like product, 23 percent of the sulfur liberated remained in the residue, and

finally, a 40 percent increase in sulfur concentrations were found in the residues of demineralized coal-like products after being treated with an H<sub>2</sub>S infusion while boiling in hydrochloric acid. These sulfur precipitates were eliminated by using a methylene chloride extraction to remove the elemental sulfur formed in the coal-like products before sulfur analyses.

### Mass Balance After Acid Leaching and Methylene Chloride Extraction of a Southeastern Illinois (No. 5) Coal

A southeastern Illinois (No. 5) Coal was preoxidized for 1/2 hr at 190°C to reduce agglomeration during the thermal steps. The coal was then treated with carbon monoxide at 375°C for four hours. Flow rates were held at 300 cc/min while maintaining a back pressure of 300 psig.

Hydrochloric acid leaching to remove inorganic sulfur compounds produced a product containing 1.93 percent sulfur. After leaching, the sample was subjected to an acetone rinse to remove water and then extracted continuously for 24 hours with methylene chloride for elemental sulfur removal. The methylene chloride extracted sample contained 1.78 percent sulfur which should represent organic sulfur. The calculations are as follows:

$$\begin{array}{r r r r r} 1.93 \% & - & 1.78 \% & = & 0.15 \% \\ \text{acid} & & \text{methylene} & & \text{elemental} \\ \text{leached} & & \text{chloride extracted} & & \text{sulfur} \end{array}$$

These results are consistent with those obtained when pyrrhotite was acid leached in the presence of a demineralized coal-like product (see above). This coal-like product could have contained as much as 0.4 percent elemental sulfur after acid leaching, based on 40 percent elemental sulfur retention. Only 0.15 percent sulfur was removed during the methylene chloride extraction of the southeastern Illinois coal product.

It is true that in one or two early experiments carried out at low temperatures (375°C ethanol treatment), the calculated contents of leachable pyrrhotite in the ethanol product did not match well with the actual values (Figures 3-9, Tables 1, 3, 4, 5, 6, and 7). However, the majority of the calculations were very close to actual results. At higher temperatures, only one coal is really out of line. The calculated value for the ethanol product from the southeastern Illinois (No. 5) raw coal containing 5.36 percent total sulfur was too high compared to the actual sulfur content (Table 7). This result shows that there are also significant random errors in sulfur determination. This difference disappeared when the same coal was run as a preparation-plant coal (1.16 actual/1.15 calculated).

### Nature of the Sulfur in the Acid Leached Residue

The sulfur in pyrolytic coal products after acid leaching has, in the past, been considered as "organic" in nature. However, this has never been proven. In reality, these sulfur residues which are below 0.2% for all of the coals tested, could very well represent inorganic sulfur.

XRD traces do not, however, indicate the presence of pyrite, pyrrhotite, or sulfates as crystalline materials. Moessbauer, on the other hand, has indicated the presence of small amounts of finely dispersed iron. It could be postulated that this residue is due to an ion exchange reaction. That is, iron and sulfur as sulfide or sulfate may be located on the active sites of the organic matrix. The question as to whether this sulfur is organic or inorganic remains unsolved at this time and will be investigated in the near future.

**Magnetic Separation of the Mineral Matter (Iron Sulfide Catalyst) from the Ethanol Product (carried out under separate contract).**

A coal-like product sample was made up from three west-central Illinois samples which had been treated with CO and ethanol (Steps 1 and 2). The samples had higher organic sulfur contents than usual, but too little low-organic sulfur products were available to make up a sufficiently large sample for oxidation experiments. However, this difference presents no problem, because organic sulfur has no effect on the oxidation and magnetic separation of pyrrhotite. The homogenized sample was analyzed by size fractions for forms of sulfur (Table 8). This sample was then subjected to oxidation with 2 percent oxygen (in argon) under various conditions.

The sample oxidized for 1.0 hour at 325°C and 75 psig was chosen for magnetic separation study. X-ray diffraction analysis indicated that this sample contained monoclinic pyrrhotite. This sample was divided into four size fractions. Initially, only the -200 mesh fraction was subjected to magnetic separation. Highly magnetic material was removed with a simple pencil-sized hand magnet until >10 percent of the material (by weight) was removed. The recovered material was then analyzed for total sulfur. The percent pyrrhotite removed could then be easily calculated.

The sulfur analyses of the starting product size fractions are given in Table 8. Organic sulfur is essentially constant, but sulfatic and especially sulfidic sulfur are most highly concentrated in the -200 mesh fraction. This enrichment is also evident from the intensities of pyrrhotite XRD peaks (table 8).

The oxidized sample was found to contain pyrrhotite of composition  $Fe_7S_8$  (main pyrrhotite peak at  $44^\circ 2\theta$ ). This sample was divided into size fractions as shown in Table 9. The highly magnetic material was removed from the -200 mesh fraction with the hand magnet until 11.0 percent of the sample (by weight) had been removed. The remaining (89.0 percent) was then analyzed and found to contain 1.74 weight percent sulfur. A mass balance was calculated to determine the amount of pyrrhotitic sulfur in the rejected and recovered fractions. It was assumed that organic and sulfatic sulfur concentrations remained the same in both. The balance, by mass and weight percent, of sulfur forms is given in Table 10. The results show that 83.9 percent of the pyrrhotite was removed during magnetic separation. Accounting for the sample weight removed, this translates to a reduction in sulfidic sulfur of 81.5 percent.

Analyses of the size fractions of the starting coal-like product sample show that the pyrrhotite is most concentrated in the -200 mesh fraction. This is supported by the decrease in pyrrhotite over the 65 x 200 mesh range with decreasing size. In successively finer fractions, more of the pyrrhotite would be freed from the coal and give lower pyrrhotite concentrations, until the -200 mesh fraction where the freed pyrrhotite is concentrated. This points to the importance of maintaining a -200 mesh sample size during Step 3 of the desulfurization process.

The magnetic separation of the -200 mesh fraction is very encouraging, showing that over 80 percent reduction of sulfidic sulfur with nearly 90 percent weight recovery of clean product can be achieved with a simple hand magnet. The assumptions involved in the balance calculation--that the concentration of organic and sulfatic sulfur are the same in the rejected and recovered fractions--seem to be reasonable. If anything, the assumption about the sulfatic sulfur may not be correct, if the sulfate is intimately associated with the pyrrhotite. In the extreme case where the association is so intimate that sulfate is removed in the same proportion as pyrrhotite, the percentage of pyrrhotite removed would be 67.0 percent. The amount of inorganic sulfur removed would be the same, but in this case some of it would be sulfatic. The results are encouraging. When the possible range of pyrrhotite removal found here (67.0-83.9 percent) is applied to the average low-organic sulfur coal-like product, along with a simple sulfate water wash, the final sulfur concentrations are low (Table 11). The final product was well below the 1.2 lbs-of-sulfur-dioxide per-million-Btu requirement of the Clean Air Act's New Source Performance Standard. In the better case, the 90 percent reduction of the stricter Revised New Source Performance Standard is met.

It seems reasonable to assume that a compliance product can be produced with this process. This is especially true considering that commercial magnetic separators would be much more efficient than a hand magnet. In fact, a compliance product can be produced with even less efficient organic sulfur and/or pyrrhotite removal. This would allow greater product recovery and lead to even better process economics (refer to Figure 12 for further information).

### **Ethanol Material Balance**

The need for an improved material balance has been a principal task of this year's research. This effort included a new chemical analysis of all feed coals, a detailed study of the resulting forms of sulfur in products, a reaffirmation of the effectiveness of the chemical method of removing catalyst (Step 3), use of hydrous and anhydrous corn alcohol which contains carbon-14 and a different carbon-12/carbon-13 (coal contains no carbon-14) to determine whether any ethanol is lost to the solid product, and determination of the amount of ethanol required to achieve 90 percent sulfur removal.

**Ethanol Recovery:** A series of experiments were designed to determine the systematic losses of ethanol caused by ethanol decomposition on metal surfaces, autoclave leaks, and leaks in trapping systems used for the high volume of gases being emitted from the reactor. The current experiments are given in the following outline:

1. Determination of an analytical procedure for ethanol and water mixtures.
2. Determination of systematic (reactor) losses.
3. Determination of the alcohol losses in the presence of coal.

In the development of an analytical procedure for measuring ethanol captured, a water collection system followed by distillation was used. In this system, dilute solutions of alcohol were distilled, collected, and weighed. Virtually 100 percent of the alcohol used as a null test was accounted for by gas chromatography (GC). It was also recognized that volatile fractions present in the collected ethanol/water mixture might be lost during distillation. The collection system was modified to use approximately 50 ml of water and to inject the mixture directly into the GC without distillation. Results from experiments performed in the autoclave without coal showed that in addition to the water and ethanol, acetaldehyde was formed at temperatures above 200°C, methanol above 300°C, and acetone above 400°C. The unexpected catalytic behavior of the autoclave refocused work on identifying the various chemical by-products. In experiments utilizing product from the CO step (1), methane, carbon dioxide, ethane/ethylene, hydrogen sulfide, water, methanol, acetaldehyde, ethanol, acetone, and possibly ethylene glycol have been identified. With the majority (>95 percent) of the products identified, work is progressing on quantitative analysis utilizing the integrated peak areas and a thermal conductivity detector. A quantitative standard is not being used in this determination at the present time.

The determination of the systematic (reactor) loss of ethanol was evaluated using 10 to 72 grams of absolute ethanol. Recoveries in water tended to range between 40 and 85 percent. The drastic range in recoveries led to an investigation of the autoclave seal. In many cases, evidence of head gasket leakage was observed. Equipment design is a major contribution to this problem. The equipment was designed for high pressure reactions up to 5000 psig. It was discovered that the "Never-Seez" compound used to seat the diamond-shaped metal gasket was partially dissolved by the ethanol allowing the loss of material. Additionally, the gasket, because it seals by deforming with each use, under our operating conditions has an apparent life of between 5 and 20 cycles. Even with great caution, it cannot be predicted when a gasket failure will occur. Greater care is now taken in the assembly/disassembly and the cleaning of all the autoclave parts. Investigations are continuing in an effort to find a more reliable sealing gasket, preferably one which can be disposed of after each experiment.

**Carbon-14 Experiments:** A series of experiments designed to determine if ethanol is reacting with the coal have been designed using fuel-grade corn ethanol (containing 5 percent water) and anhydrous ethanol (distilled with benzene at the ISGS). These experiments take advantage of the fact that coal contains "dead" carbon (no carbon-14 present). Corn alcohol on the other hand contains normal amounts of carbon-14. Any increase in the carbon-14 level in the ethanol product (Step 2) can then be attributed to the incorporation of the ethanolic carbon in the coal.

A southeastern Illinois (No. 5) coal was reacted with carbon monoxide at 300°C for 1 hour and then at 375°C for 4 hours. This product was then used as a feed stock for the carbon-14 experiments.

Reactions were performed at 400°C using both the anhydrous and fuel-grade corn ethanol. The results indicated that 5 and 7 percent of the alcohol was absorbed by the coal for the fuel grade and the anhydrous forms respectively. This would translate into a \$10/ton increase in processing cost. Since it was impossible to determine if the alcohol was decomposing on the reactor surface and falling back into the product or whether the alcohol actually reacted with the coal, the experiments were designed for a quartz tube-furnace instead of the autoclave using other isotopic tracers.

**Carbon-12/Carbon-13 Experiments:** The carbon-14 experiments were temporarily discontinued in favor of carbon-12/carbon-13 isotopic tracer experiments. The carbon-14 experiment was modified to use carbon-12/carbon-13 ratios for the following reasons: the decreased cost of the latter method (about 1/5 the cost) and a faster analysis time.

The same coal and ethanol were used as in the carbon-14 experiments. Experiments were carried out under argon flow at 400°C, 475°C, and 550°C. The ethanol was carried into the reactor by argon continuously for 30 minutes while the sample was at the desired temperature (similar to the carbon-14 experiment).

All of the results showed that compared to blanks (coals treated thermally but not exposed to ethanol) the ethanolic carbon content was <1.5 percent. This value is at the limit of the accuracy of the method used so precise conclusions cannot be made. The difference from the carbon-14 values may be due to the absence of the decomposed carbon falling back into the product, the difference in the accuracy of the carbon-12/carbon-13 versus carbon-14 methods, or some combination of the two.

The overall results between the two methods appear to be congruent and further studies will utilize both methods to refine the ethanol retention of the step 2 product.

Table 3. Desulfurization of Illinois coals (50 g sample): Static and Simulated Flow Methods.

Local and Seam <sup>a</sup>	Wt % Pyr. S	Wt % Org. S	Wt % SO <sub>2</sub> S	Wt % Tot. S	Static Method		Simulated Flow Method	
					Wt % Tot. S		Wt % Tot. S	
					Before Cat. Removal	Org. Actual/Calcd.	Before Cat. Removal	Org. Actual/Calcd.
NW 2	1.33	0.96	0.42	2.71	2.03/1.74	0.39	--/--	--
WC 6	1.18	2.71	0.32	4.21	2.43/2.36	1.22	1.55/1.85	0.60
WC <sup>b</sup> 6	1.21	2.89	0.27	4.37	--/--	--	1.69/1.62	0.42
SW 6	1.37	2.08	0.11	3.56	2.30/1.86	0.86	1.69/1.54	0.45
SW 6	0.63	1.79	0.08	2.50	--/--	--	1.08/1.01	0.47
SW 5	1.22	2.11	0.15	3.47	--/--	--	1.57/1.56	0.52
SC 6	0.38	0.50	0.10	0.89	0.74/0.74	0.37	--/--	--
SE <sup>b</sup> 5	1.41	1.71	0.03	3.15	2.07/2.02	1.10	1.53/1.67	0.66

<sup>a</sup> No. 2 is the Colchester (No. 2) Coal Member, No. 5 is the Springfield (No. 5) Coal Member, and No. 6 is the Herrin (No. 6) Coal Member. The samples were collected as fresh material at the mine and stored under an argon atmosphere, but are not necessarily representative of the mine product.

<sup>b</sup> Preparation plant samples.

Table 4. Desulfurization of Illinois coals (50 g samples) Static Method. (Calculations)

Coal	% Pyr. S	% Org. S	% SO <sub>2</sub> S	% Tot. S	% CaO	Ethanol Product						
						Wt % Tot. S Before Cat. Removal		% Org. S	% CaO	% CaS/S	% FeS S	% SO <sub>2</sub> S
						Actual	Calcd.					
Northwestern 2	1.33	0.96	.42	0.271	0.27	2.03	1.74	0.39	0.33	0.43/.19	.83	.52
West Central 6	1.18	2.71	.32	4.21	0.84	2.43	2.36	1.22	1.05	1.35/.60	.74	.44
West Central 6	1.21	2.89	.27	4.37	0.72	--	--	--	--	--	--	--
Southwestern 6	1.37	2.08	.11	3.56	0.84	2.30	1.86	0.86	1.05	1.35/.60	.86	.14
Southwestern 6	0.63	1.79	.08	2.50	1.33	--	--	--	--	--	--	--
Southwestern 5	1.21	2.11	.15	3.47	0.68	--	--	--	--	--	--	--
South Central 6	0.38	0.50	.10	0.89	0.27	0.74	0.74	0.37	0.33	0.43	.24	.13
South Central 6	2.39	1.23	.29	3.91	0.75	--	--	--	--	--	--	--
Southeastern 5	1.41	1.71	.03	3.15	0.90	2.07	2.02	1.10	1.12	1.44	.88	.04
Southeastern 5	3.91	1.25	.20	5.36	1.01	--	--	--	--	--	--	--

Table 5. Desulfurization of Illinois coals (50 g samples) Simulated Flow Method. (Calculations)

Coal	% Pyr. S	% Org. S	% SO <sub>2</sub> S	% Tot. S	% CaO	Ethanol Product						
						Wt % Tot. S Before Cat. Removal		% Org. S	% CaO	% CaS/S	% FeS S	% SO <sub>2</sub> S
						Actual	Calcd.					
Northwestern 2	1.33	0.96	.42	2.71	0.27	--	--	--	--	--	--	--
West Central 6	1.18	2.71	.32	4.21	0.84	1.55	1.85	.60	1.15	1.48/.66	0.18	.44
West Central 6	1.21	2.89	.27	4.37	0.72	1.69	1.62	.42	0.99	1.28/.57	0.83	.37
Southwestern 6	1.37	2.08	.11	3.56	0.84	1.69	1.54	.45	1.15	1.48/.66	0.94	.15
Southwestern 6	0.63	1.79	.08	2.50	1.33	1.08	1.01	.47	0.82	2.35	0.43	.11
Southwestern 5	1.21	2.11	.15	3.47	0.68	1.57	1.56	.52	0.93	1.20	0.83	.21
South Central 6	0.38	0.50	.10	0.89	0.27	--	--	--	--	--	--	--
South Central 6	2.39	1.23	.29	3.91	0.75	--	--	--	--	--	--	--
Southeastern 5	1.41	1.71	.03	3.15	0.90	1.53	1.67	.66	1.23	1.59	0.97	.04
Southeastern 5	3.91	1.25	.20	5.36	1.01	3.26	3.73	.78	1.38	1.78	2.68	.27

Table 6. Desulfurization of Illinois coals simulated flow reactor 10 g. Samples (Calculations).

Coal	% Pyr. S	% Org. S	% SO <sub>2</sub> S	% Tot. S	% CaO	Ethanol Product						
						Wt % Tot. S Before Cat. Removal		% Org. S	% CaO	% CaS/S	% FeS S	% SO <sub>2</sub> S
						Actual	Calcd.					
Northwestern 2	1.33	0.96	.42	2.71	0.27	2.03	1.88	.30	0.37	0.48/.21	0.91	.58
West Central 6	1.18	2.71	.32	4.21	0.84	1.70	1.45	.20	1.15	1.48/.66	0.81	.44
West Central 6	1.21	2.89	.27	4.37	0.72	1.69	1.35	.15	0.99	1.28/.58	0.83	.37
Southwestern 6	1.37	2.08	.11	3.56	0.84	1.75	1.29	.20	1.15	1.48/.66	0.94	.15
Southwestern 6	0.63	1.79	.08	2.50	1.33	1.03	0.74	.20	1.82	2.35/1.04	0.43	.11
Southwestern 5	1.21	2.11	.15	3.47	0.68	1.25	1.18	.14	0.93	1.20/.53	0.83	.21
South Central 6	0.38	0.50	.10	0.89	0.27	0.12	0.45	.05	0.37	0.48/.21	0.26	.14
South Central 6	2.39	1.23	.29	3.91	0.75	1.98	2.15	.11	1.03	1.33/.59	1.64	.40
Southeastern 5	1.41	1.71	.03	3.15	0.90	1.16	1.15	.14	1.23	1.59/.71	0.97	.04
Southeastern 5	3.91	1.25	.20	5.36	1.01	2.10	3.11	.16	1.38	1.78/.79	2.68	.27

Table 7. Comparison of the desulfurization of Illinois coals using ten grams and fifty gram samples.

Local and Seam <sup>a</sup>	Wt % Pyr. S	Wt % Org. S	Wt % SO <sub>2</sub> S	Wt % Tot. S	50 g Sample		10 g Sample	
					Wt % Tot. S		Wt % Tot. S	
					Before Cat.		Before Cat.	
					Removal		Removal	
				Actual/Calcd.	Org. S	Actual/Calcd.	Org. S	
NW 2	1.33	0.96	0.42	2.71	2.03/--	0.39	--/--	--
WC 6	1.18	2.71	0.32	4.21	1.55/1.85	0.60	1.70/1.45	0.20
WC <sup>b</sup> 6	1.21	2.89	0.27	4.37	1.69/1.62	0.42	1.69/1.35	0.15
SW 6	1.37	2.08	0.11	3.56	1.69/1.54	0.45	1.75/1.29	0.20
SW 6	0.63	1.79	0.08	2.50	1.08/1.01	0.47	1.03/0.74	0.20
SW 5	1.22	2.11	0.15	3.47	1.57/1.56	0.52	1.25/1.18	0.14
SC 6	0.38	0.50	0.10	0.89	0.74/--	0.37	0.12/0.45	0.05
SC 6	2.39	1.23	0.29	3.91	--/--	--	1.98/2.15	0.11
SE 5	1.41	1.71	0.03	3.15	1.53/1.67	0.66	1.16/1.15	0.14
SE 5	3.91	1.25	0.20	5.36	3.26/3.73	0.78	2.10/3.11	0.16

<sup>a</sup> No. 2 is the Colchester (No. 2) Coal Member, No. 5 is the Springfield (No. 5) Coal Member, and No. 6 is the Herrin (No. 6) Coal Member. The samples were collected as fresh material at the mine and stored under an argon atmosphere, but are not necessarily representative of the mine product.

<sup>b</sup> Preparation plant samples.

Table 8. Analyses of starting coal-like product sample by size fraction.

Size (US Mesh)	Forms of Sulfur (weight %)			Pyrrhollite Peak Intensity (chart units)
	Sulfide	Organic	Sulfate	
65 X 100	0.88	1.24	0.16	300
100 X 140	0.79	1.20	0.14	325
140 X 200	0.71	1.19	0.19	325
- 200	1.08	1.22	0.32	575

Table 9. Size fraction distribution of sample 1003-104.

Size (US Mesh)	Weight (g)	Percent
65 X 100	0.35409	15.22
100 X 140	0.26629	11.45
140 X 200	0.55934	24.04
-200	1.14683	49.29

Table 10. Mass balance of magnetic separation of -200 mesh fraction of sample 1003-104.

	Starting -200 Mesh		Magnetic Fraction		Recovered Fraction	
	Weight (g)	Weight %	Weight (g)	Weight %	Weight (g)	Weight %
Sulfide Sulfur	0.0124	1.08	0.0104	8.22	0.0020	0.20
Organic Sulfur	0.0140	1.22	0.0015	1.22	0.0125	1.22
Sulfate Sulfur	0.0037	0.32	0.0004	0.32	0.0033	0.32
Total Sulfur	0.0301	2.62	0.0123	9.76	0.0178	1.74
Total Weight	1.14683 g		0.12654 g		1.02029 g	



Table 11. Estimates of sulfur remaining after oxidation and magnetic separation of average low-organic sulfur coal-like product sample (weight %).

	Average Char Sample After Steps 1 and 2	After Removal of: 67% Pyrrhotite 100% Sulfate	After Removal of: 83.9% Pyrrhotite 100% Sulfate
Sulfide Sulfur	0.99	0.37	0.18
Organic Sulfur	0.15	0.15	0.15
Sulfate Sulfur	0.28	0	0
Total Sulfur	1.42	0.52	0.34
Pounds of SO <sub>2</sub> /million Btu**		0.77	0.51
Percent S Reduction***		85.1	90.3

\* Based on 89.0 percent weight recovery.

\*\* Based on 13,440 Btu/lb.

\*\*\* Based on starting total sulfur of average coal sample (3.5% total sulfur).

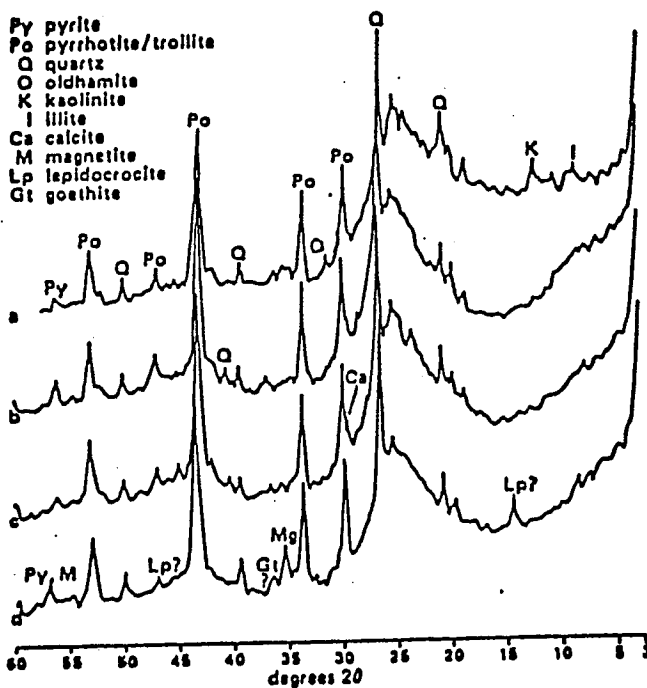


Figure 2. XRD trace of product after treatment with (a) CO at 375°C; (b) ethanol at 550°C. The product was exposed to air and ground in a mortar between treatments; (c) ethanol at 550°C in a closed autoclave; (d) same oxidation at 500°C of product c.

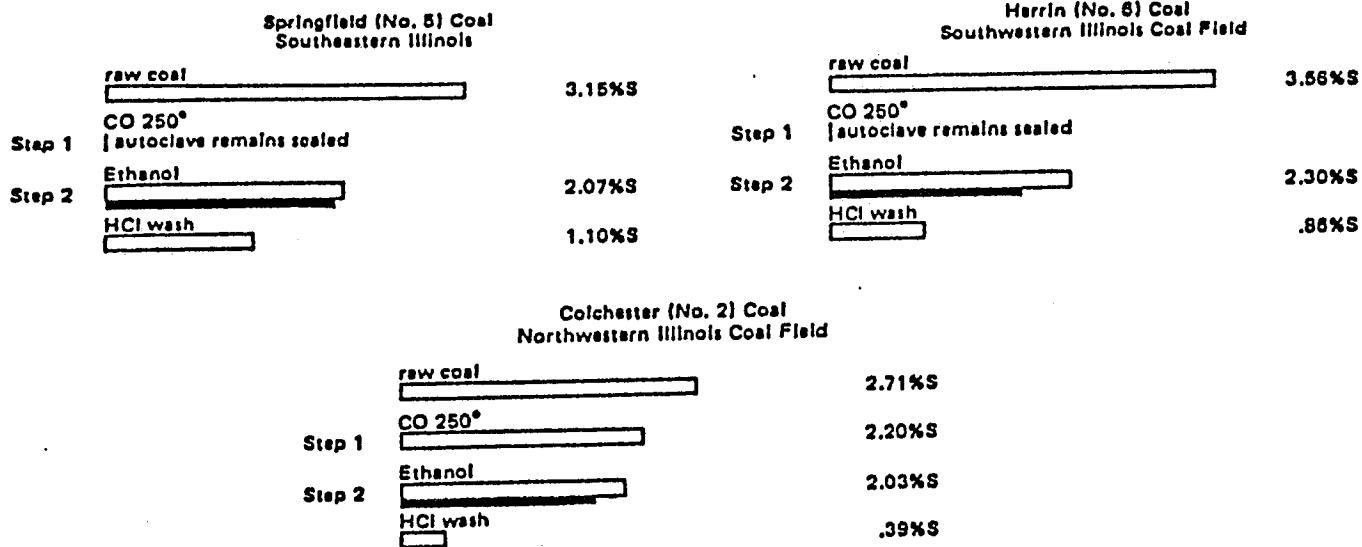


Figure 3. Sulfur content for steps 1 and 2 using the Static Reaction System: actual values, calculated values.

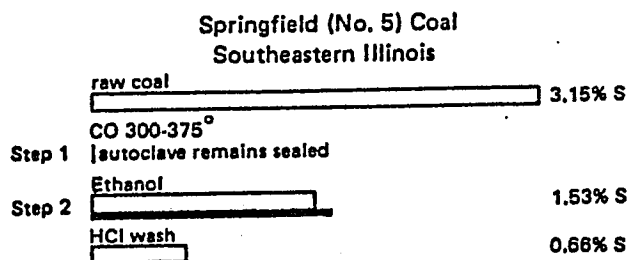


Figure 4. Sulfur content for steps 1 and 2 using the modified system: actual values, calculated values.

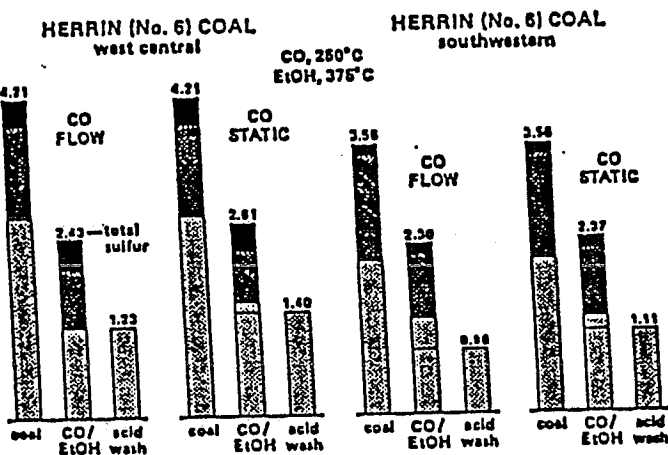
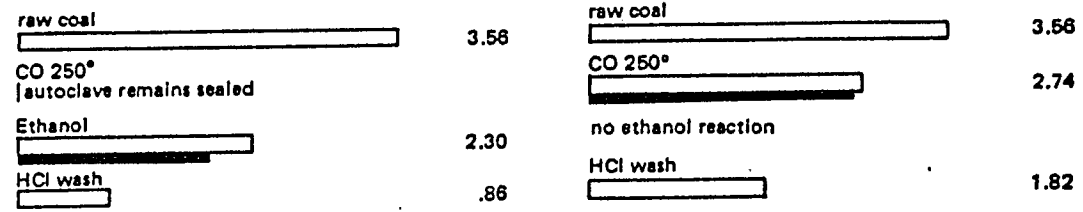


Figure 5. Histograms of two Illinois Herrin (No. 6) coals showing the importance of flowing gas conditions in terms of sulfur types. Sulfur types from top to bottom are: sulfate, pyritic (or sulfide), and organic.

Herrin (No. 6) Coal  
Southwestern Illinois Coal Field



Herrin (No.6) Coal  
West Central Illinois Coal Field

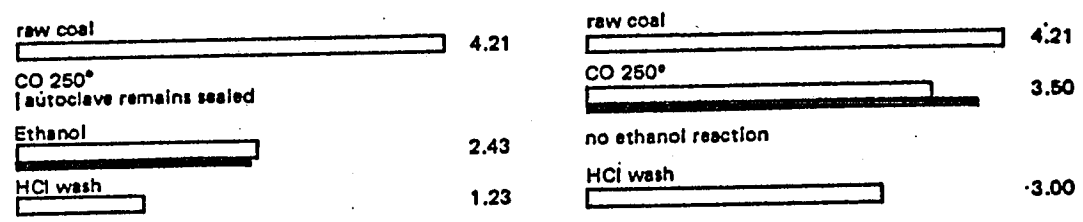
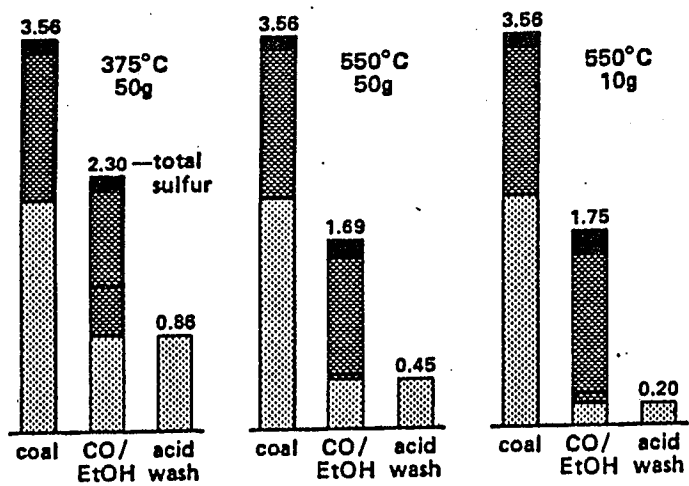
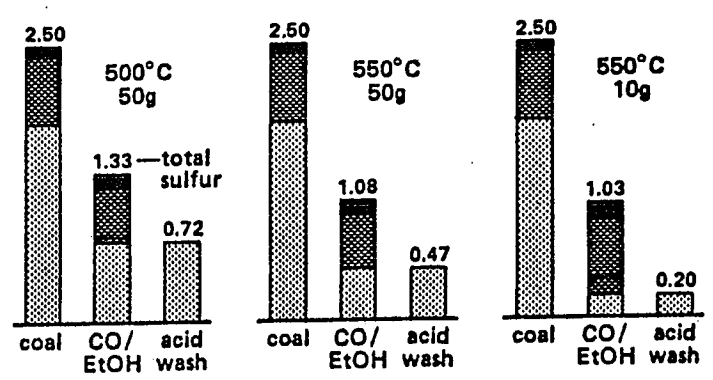


Figure 6. A comparison of sulfur removal with and without the ethanol treatment. actual values, calculated values.

HERRIN (No. 6) COAL  
southwestern



HERRIN (No. 6) COAL  
southwestern



Figures 7 and 8. Histograms showing progress of the desulfurization reactions in terms of the distribution of sulfur types for two Herrin (No. 6) Coals from southwestern Illinois. Sulfur types from top to bottom are: sulfate, pyritic (or sulfide) and organic.

**SPRINGFIELD (No. 5) COAL**  
southeastern

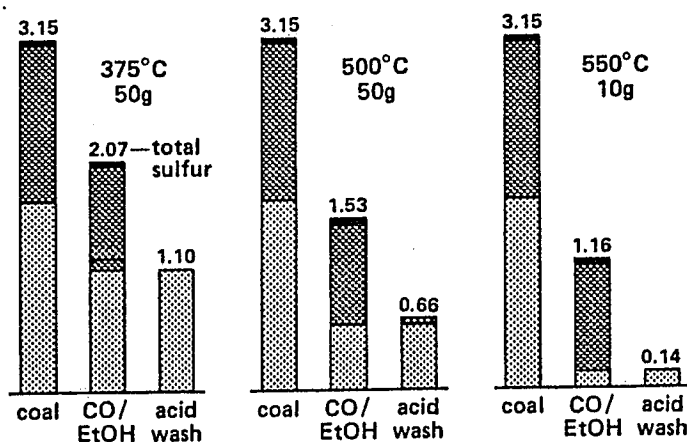


Figure 9. Histograms showing progress of the desulfurization reactions in terms of the distribution of sulfur types for a Springfield (No. 5) coal from southeastern Illinois. Sulfur types from top to bottom are: sulfate, pyritic (or sulfide), an organic.

**HERRIN (No. 6) COAL**  
west central

**HERRIN (No. 6) COAL**  
southwestern

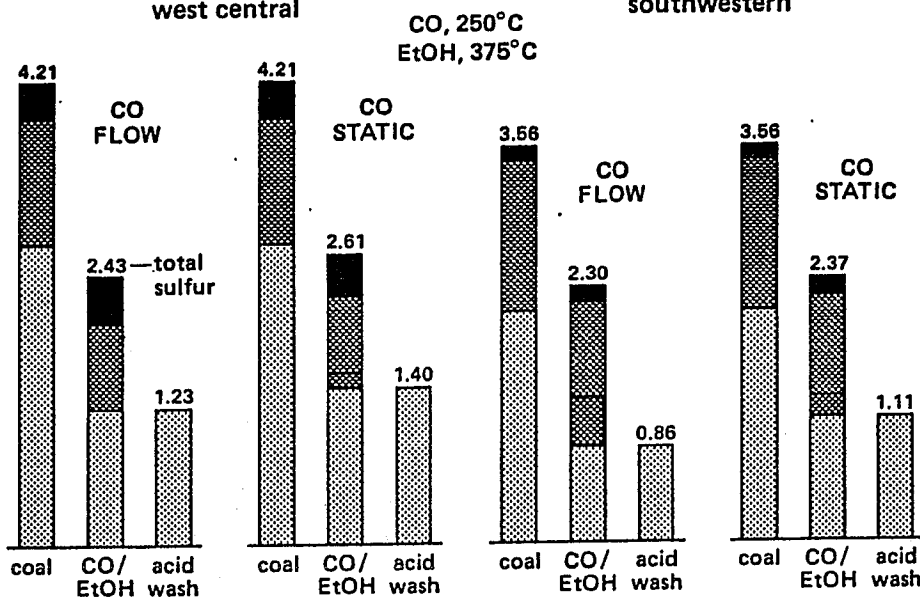


Figure 10. XRD trace after treatment as in figure 5 illustrating the formation of oldhamite. Quartz (Q), pyrrhotite/troilite (Po), and oldhamite (O) are present in this sample.

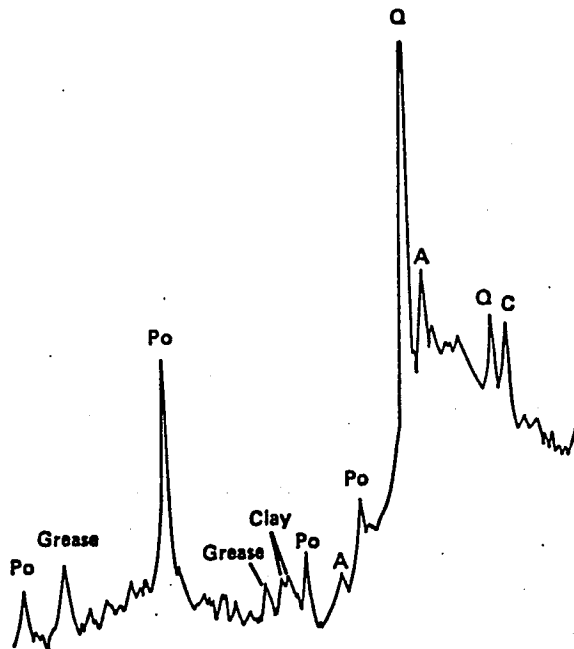


Figure 11. X-ray diffraction trace of a southeastern Illinois (No. 5) coal containing the high temperature lubricant (grease) "No Sieze". The sample has been contaminated with copper and zinc.

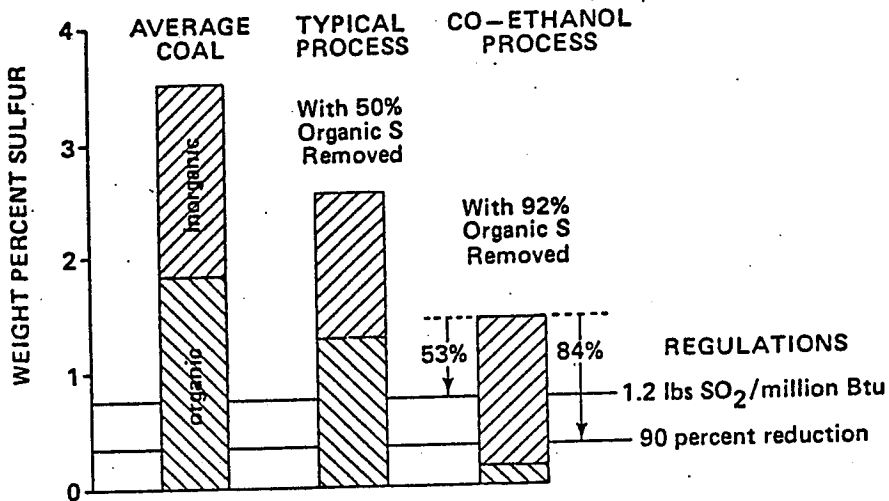


Figure 12. Comparison of a typical thermal desulfurization process and the carbon monoxide-ethanol process.

## CONCLUSIONS AND RECOMMENDATIONS

### Conclusions

1. We continue to demonstrate 92-98 percent desulfurization.
2. It has been shown that reported organic sulfur values in our products are accurate to within a few hundredths of a percent, and that the acid leach method removes only troilite and CaS--not organic sulfur.
3. The recently designed experiments with carbon-13- and carbon-14-containing reagents meet all goals for this year's research effort.
4. We demonstrated that iron sulfates in the feed coal are rapidly reduced to troilite in Steps 1 and 2 of the process.
5. Revised mass balance calculations show that there are several sources of errors in these calculations, but most of the analyses are close to expected levels and the average of actual and predicted troilite contents vary by only .01 percent.
6. Preliminary studies funded by a separate contract have shown promise for the partial oxidation and magnetic separation step.
7. The U.S. DOE patent on recycling acetaldehyde suggest that our plan to capture that valuable by-product is feasible.

### Recommendations

Several short-term goals are critical to the continued development of this process. First, a one-, two-, or three-stage reactor with provisions for continuous flow of coal and gas will provide the first valid data for mass balance and economic analysis. Second, proposed funding of research on microwave-assisted catalysis promises to improve efficiency and reduce reaction temperatures to such a degree that it could represent an immediately competitive process.

The other research tasks funded for the 1987/1988 CRSC research year seem reasonable and very promising goals for future research in this area. Primarily, we will attempt to produce a whole-process optimization equation and investigate Step 3 in greater detail. Studies of alternate reductants, catalysts, and controlling CaS and "new" FeS should yield a much better understanding of the process.

In addition to conditions necessary to generate a compliance product under Revised New Source Performance Standards (RNSPS), work to "de-tune" the CO/Ethanol process will be performed. Since the 90 percent sulfur reduction called for by the RNSPS is not required at this time, lowering reaction conditions in the process may produce a product with more desirable properties to utilities (specifically, a greater retention of volatile matter).

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