DOE/PC/90176--T

DOE/PC/90176--T51

FINAL TECHNICAL REPORT

DE92 004187

September 1st 1990 through August 31st, 1991.

REC 30 1991

CHEMICAL COAL CLEANING USING SELECTIVE OXIDATION.

DE-FG 22-90PC 90176

Dr. Stephen R. Palmer and Dr. Edwin J Hippo

Mechanical Engineering and Energy Processes, Southern Illinois
University at Carbondale, Carbondale, IL 62901.

Project monitor: Daniel D. Banerjee, CRSC

Abstract

The combustion of high sulfur coals contributes substantially to the problems associated with acid rain. This project investigates the removal of sulfur from coal using selective oxidation. Desulfurization studies have been performed in which particle size, reaction time and reaction temperature parameters were varied. Results obtained support the following conclusions: (1) No improvement in the levels of desulfurization were achieved by grinding to very small particle sizes. This indicates that expensive grinding to very small particle sizes may not be necessary. (2) Cryogenically treating the coal prior to grinding did not significantly improve the selectivity of sulfur removal. (3) The sulfur contents of IBC 101 and 106 samples can be reduced by 40% and 50% respectively at room temperature, by 54% and 63% at 50°C and by 69% and 71% at 104°C. (4) Higher and more selective sulfur removals are possible at higher temperatures but the yield of solid coal is reduced. (5) Nearly 80% of the total sulfur can be removed from both the 101 and 106 coals if one is willing to sacrifice about 30% of the weight of the coal. Similarly if one sets a limit of 10% for the maximum allowable coal weight loss then about 60% of the sulfur in the IBC 106 coal and about 40% of the sulfur in the IBC 101 coal can be removed using the peroxyacetic acid procedure. (6) Although much of the sulfur removal can be attributed to pyrite dissolution, significant amounts of organic sulfur removal has also been observed. (7) In addition to removing sulfur peroxyacetic acid can be used to improve the ash contents of the coals. (8) Although Btu contents are lowered by selective oxidation the level of sulfur removal is much greater than the loss of heating value. (9) The peroxyacetic acid oxidation of coal may be an alternative method for the determination of organic sulfur contents. (10) Extracting the coal prior to reaction with peroxyacetic acid improved the selectivity of the desulfurization reaction. (11) The only quantitatively significant organic sulfur compound detected in the soluble oxidation products was methyl sulfonic acid. (12) Oxidation of pure pyrite gave sulfate as the primary product but it was anticipated that methylsulfonic acid was also formed via a rearrangement reaction between sulfate ion and the peroxyacetic acid or acetic acid. (13) Selective oxidation, in addition to removing large amounts of sulfur from coal, also shows potential as a pretreatment step for the removal of even more organic sulfur. One product derived from the IBC 101 coal using this approach had a sulfur content of only 0.47%, a sulfur reduction of nearly 90%.

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

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

EXECUTIVE SUMMARY

The combustion of high sulfur coals contributes substantially to the problems associated with acid rain. Current and pending clean air legislation is designed to reduce this problem by cutting the levels of sulfur dioxide that may be released into the atmosphere. These new laws prevent the direct and efficient utilization of many important Illinois coals reserves which, unfortunately are high in sulfur. This may present the already troubled Illinois coal industry with a difficult future if solutions to the sulfur problem are not found.

Removing sulfur from Illinois coals prior to combustion will reduce the acid rain problem and increase the marketability of Illinois coal. Sulfur dioxide emissions can be reduced by post combustion scrubbers but these are very expensive. Consequently precombustion coal cleaning strategies including physical, chemical and microbial methods have been investigated. Although some success has been achieved in the liberation of inorganic sulfur species from coal, no satisfactory technique for the removal of organic sulfur has been found.

The primary objective of this study is to investigate the removal of both mineral and organic sulfur from Illinois coals using low temperature selective oxidation. This overall objective is relevant to priority P.1.1: identified in the CRSC RFP89-2 under coal cleaning.

For the chemical desulfurization of coal to become a viable exercise the use of low temperatures, low pressures and inexpensive and recyclable reagents that can remove both organic and inorganic sulfur are necessary. Many chemical desulfurization processes can remove pyritic sulfur and some of the organic sulfur, but all too often only at the expense of high reaction temperatures and detrimental effects to desired coal properties (Btu content, volatile matter content and caking ability).

Peroxyacetic acid oxidation has been used at SIUC for the past two years as a method for selectively oxidizing and preserving organic sulfur compounds in coal. This is necessary for their characterization in our laboratories. Support for this project has and is being provided by the CRSC and EPRI. Results obtained from this ongoing study have suggested that the organic sulfur chemistry of coal is not as complicated as pyrolysis and extraction data have suggested, with only nine significant sulfur species being detected. In addition the sulfur compounds that have been identified reveal only one position of bonding to the coal macromolecular matrix suggesting that they are pendant or terminal structures. This supports the observation that much or the organic sulfur species are present at the surfaces of maceral components. If this is true then desulfurization may not be as difficult as many believe.

The chemical desulfurization procedure under investigation in this study is significant because it uses low temperatures, it is rapid, uses inexpensive reagents, addresses both inorganic and organic sulfur simultaneously and is designed to be used in conjunction with advanced physical coal cleaning methods and microbial desulfurization strategies.

Samples of -60 mesh and -400 mesh from the IBCSP 101 and 106 coals were studied together with a sample of the 101 coal that had been cryogenically treated prior to grinding. Reaction variables that were studied include reaction time, reaction temperature and reactant concentration. Examination of the soluble oxidation products for organic sulfur compounds were made and the only organic sulfur compound to be detected in significant concentrations was methyl sulfonic acid (MSA). The examination of the oxidation of pyrite with peroxyacetic acid at room temperature, 50°C and 104°C revealed that the primary product was sulfate, although some other soluble form of sulfur (probably methyl sulfonic acid) was formed. Obviously some methyl group migration from the acetic acid must have taken place in order for methyl sulfonic acid to have formed from pyrite.

In view of the difficulty in removing organic sulfur without dissolving large portions of the coal it was decided to investigate the whole process of selective oxidation as a pretreatment for other desulfurization processes. These studies were of a preliminary nature and were intended to demonstrate the feasibility of selective oxidation as both a partial desulfurization process and a pretreatment process for other subsequent desulfurization strategies.

The studies completed support the following conclusions:

1. No or very little improvement in the levels of desulfurization were achieved by grinding to very small particle sizes. This significant conclusion is based on both room temperature and 50°C results and indicates that expensive grinding to very small particle sizes may not be necessary.
2. Cryogenically treating the coal prior to grinding did not improve the selectivity of sulfur removal. It had been hoped that fracturing the coal along maceral boundaries by cryogenic treatment would result in a product more susceptible to desulfurization.
3. The sulfur contents of IBC 101 and 106 samples can be reduced by 40% and 50% respectively at room temperature, by 54% and 63% at 50°C and by 69% and 71% at 104°C.
4. Although sulfur removal is greater and more selective at higher reaction temperatures the yield of solid coal is reduced and hence the potential as a useful desulfurization process is diminished.
5. Nearly 80% of the total sulfur can be removed from both the 101 and 106 coals if one is willing to sacrifice about 30% of the weight of the coal. Similarly if one sets a limit of 10% for the maximum allowable coal weight loss then about 60% of the sulfur in the IBC 106 coal and about 40% of the sulfur in the IBC 101 coal can be removed using the peroxyacetic acid procedure.
6. Although much of the sulfur removal can be attributed to pyrite dissolution, significant amounts of organic sulfur removal has also been observed.

7. In addition to removing sulfur peroxyacetic acid can be used to improve the ash contents of the coals.
8. Although Btu contents are lowered by selective oxidation the level of sulfur removal is much greater than the loss of heating value. Desulfurized products were obtained that still had higher heating values than many western coals.
9. The peroxyacetic acid oxidation of coal may be an alternative method for the determination of organic sulfur contents.
10. Extracting the coal prior to reaction with peroxyacetic acid improved the selectivity of the desulfurization reaction. It is anticipated that the removal of the mobile phase allowed better penetration of the reagents into the coal matrix.
11. The only quantitatively significant organic sulfur compound detected in the soluble oxidation products was methyl sulfonic acid.
12. Oxidation of pure pyrite gave sulfate as the primary product but it was anticipated that methylsulfonic acid was also formed via a rearrangement reaction between sulfate ion and the peroxyacetic acid or acetic acid.
13. Selective oxidation, in addition to removing large amounts of sulfur from coal, also shows potential as a pretreatment step for the removal of even more organic sulfur. One product derived from the IBC 101 coal using this approach had a sulfur content of only 0.47%, a sulfur reduction of nearly 90%.

Overall Objectives.

The primary objective of this study is to investigate the removal of both mineral and organic sulfur from Illinois coals using low temperature selective oxidation. This overall objective is relevant to priority P.1.1: identified in the CRSC RFP89-2 under coal cleaning.

"The priorities for physical/chemical or physical/microbial cleaning include the following:

P.1.1: Develop new methods for either physical/chemical or physical/microbial cleaning of Illinois coal. Innovative approaches to achieve deep cleaned products, containing both ash and sulfur contents less than 0.5 percent, should be considered. Experiments should focus on developing cost-effective methods for the removal of organic sulfur and finely disseminated mineral impurities, especially fine pyrite particles, from coal. Rates and mechanisms for organic sulfur removal should be studied. Chemical reagent recycling and/or reagent wastes handling should also be included. Bench scale studies are expected."

Specific Goals and Objectives.

The specific goals and objectives of this study are:-

1. To optimize the selective oxidation reaction conditions to yield maximum sulfur removal.
2. To determine the effects of particle size on desulfurization kinetics, thereby determining the extent of grinding required for effective desulfurization.
3. To investigate the desulfurization reactivity of sulfur at the surfaces of cryogenically fractured coal particles.
4. To screen the desulfurization wastes for organic sulfur compounds using the characterization strategy developed at SIUC.
5. To determine the effect of selective oxidation on Btu recovery of desulfurized coal.
6. To submit the selectively oxidized/chemically desulfurized coal for microbial desulfurization activity testing.
7. To establish the reaction of pyrite with peroxyacetic acid under organic desulfurization conditions.

Significance.

Removing sulfur from Illinois coals prior to combustion will reduce the acid rain problem and increase the marketability of Illinois coal. Sulfur dioxide emissions can be reduced by post combustion scrubbers but these are very expensive. Consequently precombustion coal cleaning strategies including physical, chemical and microbial methods have been investigated. Although some success has been achieved in the liberation of inorganic sulfur species from coal, no satisfactory technique for the removal of organic sulfur has been found. The chemical desulfurization procedure under investigation in this study is significant because it uses low temperatures, it is rapid, uses inexpensive reagents, addresses both inorganic and organic sulfur simultaneously and is designed to be used in conjunction with advanced physical coal cleaning methods and microbial desulfurization strategies.

Unique aspects of this work.

Unique aspects of this study include:-

- 1). Selective peroxyacetic acid (PAA) oxidation can remove significant amounts of organic sulfur from coal without serious detrimental effects.
- 2). The process is low temperature, rapid, involves ambient pressures, inexpensive chemicals, a simple single reaction step and removes organic sulfur.
- 3). Peroxyacetic acid (PAA) selective oxidation has never been investigated as a desulfurization strategy before.
- 4). Both organic and inorganic sulfur can be removed simultaneously and hence microdispersed pyrite presents no problems.
- 5). Cryogenically fractured coal products from an ongoing CRSC funded project will be used in this study to enhance organic sulfur desulfurization. Samples are already available at SIUC.
- 6). The products of this study will be tested for microbial desulfurization activity, and the potential for a combined chemical and microbial desulfurization strategy evaluated.
- 7). The combined experience of the investigators in the areas of coal cleaning, desulfurization, selective oxidation, analysis of organic sulfur compounds and the structure, reactivity and chemistry of coal in general. Of particular importance is the familiarity of the investigators with the selective oxidation technique and the behavior of the Illinois coals to be studied. For over two years the investigators have been using the selective oxidation method for the characterization of the organic sulfur compounds in Illinois coals. This work received funding from the CRSC and EPRI.

PROJECT DESCRIPTION

Introduction and Background.

The combustion of high sulfur coals contributes substantially to the problems associated with acid rain. Current and pending clean air legislation is designed to reduce this problem by cutting the levels of sulfur dioxide that may be released into the atmosphere. These new laws prevent the direct and efficient utilization of many important Illinois coals reserves which, unfortunately are high in sulfur. This may present the already troubled Illinois coal industry with a difficult future if solutions to the sulfur problem are not found.

This study investigates the removal of both mineral and organic sulfur from coal using low temperature chemical cleaning strategies. Some preliminary results obtained for an Illinois No.6 coal using mixtures of acetic acid, water and hydrogen peroxide had shown that it was possible to remove nearly 25% of it's organic sulfur within 5 minutes at only 60°C with no significant loss of carbon. This extent of sulfur removal is very encouraging especially if the low temperatures and inexpensive reagents that were used are considered. Some dewatering of the desulfurized coal product would have to be performed in order to obtain a useful product. However, since the procedure uses glacial acetic acid as the solvent system, considerably less dewatering would be necessary than for a water based desulfurization strategy.

For the chemical desulfurization of coal to become a viable exercise the use of low temperatures, low pressures and inexpensive and recyclable reagents that can remove both organic and inorganic sulfur are necessary. Many chemical desulfurization processes can remove pyritic sulfur and some of the organic sulfur, but all too often, only at the expense of high reaction temperatures and detrimental effects to desired coal properties (Btu content, volatile matter content and caking ability). The work here involves low temperatures, ambient pressures, inexpensive reagents and addresses both the organic and inorganic sulfur simultaneously.

Desulfurization with peroxyacetic acid.

Although aqueous hydrogen peroxide has been used to investigate the desulfurization of coal, no reported use of peroxy organic acids for this purpose has been found. Aqueous hydrogen peroxide was found to oxidize pyrite to sulfate which could then be leached out of the coal. Very little removal of organic sulfur was effected. However, at SIUC peroxyacetic acid has shown effectiveness for the removal of organic sulfur.

Under a project supported in part by the CRSC, peroxyacetic acid oxidation has been used at SIUC for the past three years as a method for selectively oxidizing and preserving organic sulfur compounds in coal for their characterization. Results obtained from this ongoing study have suggested that the organic sulfur chemistry of coal is not as complicated as pyrolysis and extraction data have suggested, with only nine significant sulfur species being detected. In addition the

sulfur compounds that have been identified reveal only one position of bonding to the coal macromolecular matrix suggesting that they are pendant or terminal structures. This supports the observation that many of the organic sulfur species are present at the surfaces of maceral components. If this is true then desulfurization may not be as difficult as many believe.

Work completed this year.

The work completed this year is set out by task in the following text. Tasks are described in the proposal to the CRSC.

Task 1. Sample Preparation.

Samples of IBC-101 and IBC-106 from the IBCSP bank were obtained for use in this study. These coals were used because they have high organic sulfur contents and, in the case of IBC-106, the pyritic to organic sulfur ratio is approximately 1:1.

Experimental procedures.

Two kilograms of each coal was riffled into two 1 kg aliquots one of which is being kept in storage. The remaining 1 kg aliquot from each coal was riffled into five 200g aliquots. Four of these 200g aliquots were stage ground to -60 mesh, -100 mesh, -200 mesh and -400 mesh respectively. The fifth 200g aliquot was ground to -400 mesh, treated with HF and HCl and then sink/floated in a solution of CsCl of specific gravity 1.6. This was done to provide a sample with little pyritic or sulfatic sulfur. All coal samples were stored under nitrogen until required for the desulfurization studies. A sample of cryogenically treated IBC-101 was been obtained from Dr. E. Hippo at the Mechanical Engineering and Energy Processes department at SIUC. All ground coal aliquots and the cryogenically treated coal were submitted for proximate, ultimate, Btu and sulfur forms analysis. In addition, particle size distributions of each sample were determined. For the -60 and -100 mesh samples this was done by the wet sieving technique. For the finer coal samples, a Microtrac laser light scattering device was used.

Results and discussion.

Proximate, total sulfur and BTU results are shown below in Table 1. Particle size data is shown in Table 2.

Although there is slight variability in the elemental composition, it can be seen from Table 1 that the data agree very well for the same coal, ground to different sizes. This illustrates that no preferential loss of some coal components occurred during grinding and that levels of oxidation (if any occurred) are very similar for each sample regardless of its extent of grinding. This means that all samples of the same coal should be identical with the exception of their particle size distribution. This allows for more control of the variables associated with desulfurization and hence data interpretation should be easier.

Table 1. Proximate, total sulfur and btu content.

IBC #	part. size	moist. %	ASH dry	%C dry	%H dry	%N dry	VM dry	FC dry	TS dry	BTU dry
101	-60	7.68	9.32	74.95	4.06	1.32	40.67	50.01	4.43	13003
	-100	3.62	10.16	58.41	4.33	1.22	40.12	49.72	4.43	12634
	-200	2.92	10.54	65.78	3.98	1.22	39.63	49.83	4.47	12635
	-400	3.86	9.87	75.31	4.36	1.31	39.75	49.93	4.18	12192
	-400F	4.78	1.01	75.71	4.84	1.33	42.88	56.10	3.64	13027
	cryo	7.71	10.79	72.33	4.53	1.31	40.11	49.10	4.40	11884
106	-60	8.72	8.76	73.95	4.21	1.61	39.64	51.60	3.63	12340
	-100	7.91	8.70	74.11	3.80	1.66	39.86	51.44	3.68	12417
	-200	6.09	8.83	73.94	4.23	1.66	39.14	52.03	3.61	12604
	-400	3.63	8.86	71.36	4.06	1.58	39.32	51.82	4.05	12969

F = floated coal

cryo = cryogenically treated coal

It is clear that the floated coal has a very low ash content. This is the result of mineral matter being removed by the acid treatment and the flotation process. However the total sulfur for this floated coal is too high for the sulfur to be all organic. Thus it appears that about one third of the pyrite in the coal has not been liberated and subsequently separated by the sink/float process.

Table 2. Summarized particle size analysis data.

Coal type/top size	%16	%50	%84	MV	CS
IBCSP 101 -200 mesh	10.88	29.36	62.95	35.97	0.392
101 -400 mesh	6.36	16.82	34.68	20.59	0.581
106 -200 mesh	7.88	24.80	56.66	31.33	0.467
106 -400 mesh	5.45	14.11	27.91	16.48	0.672

%16, %50, %84 are the 16th, the 50th and 84th percentile respectively. Ie the percentage of the total sample which is below that particular particle size.

MV = Volume mean diameter in microns

CS = Calculated surface area in meters squared per cc.

Task 2. Desulfurization Studies.

Samples of -60 mesh and -400 mesh from each coal were studied together with a sample of the 101 coal that had been cryogenically treated prior to grinding. Reaction variables that were studied include reaction time, reaction temperature and reactant concentration. Studies were also performed that investigated selective oxidation as a pretreatment step for further desulfurization processes. These are described in the section entitled , 'Selective oxidation as a pretreatment'.

Experimental procedures.

Reaction times were varied from five minutes to a maximum of three days, with typical sampling times of 5, 15 and 30 minutes, plus 1, 6, 24 and 72 hours. Reaction temperatures studied include room temperature, 50°C and 104°C. The concentration of the oxidant was varied by changing the strength of the hydrogen peroxide solution added to the acetic acid. The strength of the hydrogen peroxide was varied from 30 w/v % to 5 w/v %.

Typical desulfurization runs involve dispersing 2g of the ground coal sample in 60 mL of glacial acetic acid, warming to the desired reaction temperature via a water bath and adding 20 mL of hydrogen peroxide solution of the desired strength. After completion of the designated reaction time the contents of the flask were cooled if necessary and immediately filtered to recover the desulfurized solid coal products. The filter is washed with 100mL hot distilled water and then dried in a vacuum oven at 110°C overnight. A small portion (10-20mg) of platinum on carbon is added to the filtrate to quench any excess peroxides. The filtrate is then refiltered and finally isolated on a rotary evaporator. In an industrial setting, the quenching of excess peroxide would not be necessary since the peroxide would be used to continue the desulfurization of more coal. Recycling of the acetic acid would also reduce processing costs.

Both solid and filtrate desulfurization products were examined by proximate, ultimate, sulfur and Btu analysis where the product was suitable and sufficient material was available.

Results and Discussion.

Figure 1 shows the desulfurization of the IBC 101 and IBC 106 coal samples at room temperature (21°C) as a function of reaction time. As is quite clear from Figure 1 there is rapid desulfurization in the early stages of the reaction followed by a more sedate level of desulfurization in the latter stages of the reaction. The levels of sulfur removal after three days, based solely on sulfur contents, are approximately 40% for the IBC 101 sample and 50% for the IBC 106 sample. These percentages are above those that would be produced if only mineral forms of sulfur were being removed and therefore these results show that some part of the organic sulfur is also being removed.

Indeed sulfur forms analysis of products from these coals obtained after reaction for only six hours at room temperature indicate organic sulfur forms as well as inorganic sulfur forms have been attacked. From the data in Table 3 it is clear that dissolution of pyrite is the most important contributing factor governing the removal of sulfur from these coals. However, organic sulfur removal is also observed. This is especially true for the IBC 101 coal where nearly 18% of the organic sulfur has been removed. Sulfate concentration increase after oxidation which can be attributed to the formation of sulfate as the pyrite oxidizes. However the increase in sulfate sulfur does not account for all of the pyritic sulfur that dissolves.

Table 3. Sulfur forms analysis, before and after selective oxidation.

	SO ₄	FeS ₂	Organic	Total
Raw coal IBC 101	0.30	1.00	3.13	4.43
Oxidized IBC 101	0.34	0.19	2.57	3.10
% change	+13.3	-81.0	-17.9	-30.0
Raw coal IBC 106	0.21	1.56	1.84	3.61
Oxidized IBC 106	0.37	0.05	1.74	2.16
% change	+76.2	-96.8	-5.43	-40.2

The Btu contents of the oxidized coals show a reduction of about 7% after oxidation for 24 hours at room temperature. This reduction in the Btu content is to be expected for an oxidative process because some of the chemical bonds are oxidized prior to combustion. This will reduce the amount of energy released when the coal is burnt. Although the loss of heating value is a negative aspect of the selective oxidation process the reduction in Btu content is much smaller than the reduction in sulfur content. In addition the desulfurized product still has more heating value than typical western coals.

In addition to plotting sulfur content vs reaction time we can also plot ash content vs reaction time. The results of this are shown in Figure 2 for the IBC 101 samples and in Figure 3 for the IBC 106 samples. As was observed for the sulfur contents, the ash contents fall rapidly during the early stages of the reaction. However, unlike the sulfur contents the ash contents reach a minimum and then start to increase with increasing reaction time. This phenomena is explained by the simultaneous dissolution of the mineral and organic parts of the coal. Initially reactive mineral matter dissolves faster than the organic coal. As a result the ash content goes down. At some point all the reactive mineral will have been removed and no more mineral will dissolve. At this point the ash content is at its minimum. The increase in the ash level after this point is explained by the dissolution of the organic portion of the coal which results in the residual mineral matter becoming more concentrated in the final product.

The fact that both ash contents and sulfur contents decrease rapidly during the early stages of the reaction strongly suggest that a mineral form of sulfur is being removed. The relationship between ash content and sulfur content for the desulfurized products is shown in Figures 4 and 5. (IBC 101 -400 mesh and IBC 101 cryogenically ground respectively). Although a perfect straight line relationship is not observed the level of sulfur removal and ash reduction is consistent with pyrite being dissolved from the coals. This confirms the dissolution of pyrite detected by the sulfur forms analysis. The point in Figures 4 and 5 where the ash contents begin to increase yet the sulfur content continue to fall is probably the point at which the dominant sulfur removal process switches from inorganic to organic sulfur. It can be seen that this happens at about 2.8-2.9 %S which is very close to the level of organic sulfur reported in this coal. Indeed this type of plot may be a more reliable way of determining the organic sulfur contents of coal.

Particle size effects.

It is interesting to note that the particle size of the samples does not influence the rate or level of desulfurization to any significant extent. One might have expected the finer particle sizes to have reacted faster because of the increased surface area they exhibit and because of better reagent penetration. Since no difference in sulfur removal was observed between the -60 mesh and the -400 mesh samples it was decided that examination of the intermediate particle sizes would serve little purpose. The cryogenically treated sample was also expected to behave differently from the other samples. This is because the cryogenically treated coal fractures along particle interfaces and these interfaces have been shown to have higher sulfur concentration than the bulk of the sample. However neither of these expected differences in desulfurization were evident at room temperature (Figure 6.) or 50°C (Figure 7.). This very important observation indicates that grinding to very small particle sizes is unnecessary. This would help to keep process costs down.

Reaction temperature effects.

To establish the relationship between reaction temperature and desulfurization, experiments have been performed at both 50°C and at the boiling point of the reaction mixture (104 °C) as well as at room temperature. Figures 8 and 9 show the effects of increasing the reaction temperature from room temperature to 50°C and then to 104 °C on the desulfurization of IBC 101 -400 mesh and IBC 106 -400 mesh respectively. These figures suggest that by increasing the reaction temperature, both the rate and level of desulfurization can be enhanced. This apparent enhancement in desulfurization shown by these graphs can be misleading because this type of graph does not consider the amount of coal that is dissolved by the oxidation procedure nor does it take into account the addition of oxygen as oxidation proceeds. Oxygen addition dilutes the remaining sulfur. Thus it is necessary to examine the yield of solid product and the actual sulfur to carbon atomic ratios (the only true measure of effective desulfurization) of the solid products.

Figures 10 and 11 show the relationship between the amount of coal dissolved and the amount of sulfur removed for the IBC 101 and 106 coals respectively. Both coals were -400 mesh and were reacted at 50°C. It is clear that during the early stages of coal dissolution sulfur is released from the coal at a faster rate than the coal dissolves. This is primarily a result of the pyrite dissolving. However, these results show that in both coals nearly 80% of the total sulfur can be removed if one is willing to sacrifice about 30% of the weight of the coal. Similarly if one sets a limit of 10% for the maximum allowable coal weight loss then about 60% of the sulfur in the IBC 106 coal and about 40% of the sulfur in the IBC 101 coal can be removed using the peroxyacetic acid procedure.

The best way to determine the level of desulfurization attained by a process is to calculate the S/C ratios for the original coal and compare it to S/C ratio in the desulfurized product. In this way the effects of changes in the composition of the coal such as moisture

content, mineral content and added oxygen for instance, are eliminated. The original S/C ratios for the IBC 101 and 106 coals are 236×10^{-4} and 196×10^{-4} respectively. To determine if organic sulfur is removed we also need to calculate the organic sulfur to carbon ratio for the original coals. The 101 and 106 coals have organic S/C ratios of 167×10^{-4} and 99.2×10^{-4} respectively. (These calculations were performed using the data provided by the Illinois Basin Coal Sample Program, IBCSP).

At room temperature the lowest S/C ratios obtained for the 101 and 106 desulfurized coals are 161×10^{-4} and 95×10^{-4} respectively. These results were obtained after three days. The 101 coal was the cryogenically treated sample while the 106 coal that gave the best result was the -60 mesh sample. However, in general the particle size, method of grinding and the reaction time had little effect on the S/C ratios.

Increasing the reaction temperature on the other hand gave significant improvements in the S/C ratios. At 50°C the best results obtained for the 101 coal were from the -400 mesh sample, the desulfurized product of which had a S/C ratio of 139×10^{-4} . The 106 sample which gave the best desulfurization at 50°C was the -400 mesh sample, the desulfurized product from which had a S/C ratio of 92×10^{-4} . Sulfur to carbon ratios for the desulfurized products obtained after 1 hour at 104°C were 112×10^{-4} for the IBC 101 -400 mesh coal and 80.3×10^{-4} for the IBC 106 coal.

In another experiment the floated IBC 101 coal was extracted with THF and the extraction residue reacted with peroxyacetic acid. The sulfur to carbon ratio of the oxidation product obtained after 1 hour at 104°C was only 86.4×10^{-4} . This is significantly lower than that for the unextracted coal. This suggests that extracting the coal prior to selective oxidation enhances the selectivity of the sulfur removal reaction. This increase in selectivity is probably brought about by the removal of the mobile phase which then allows for better penetration of the peroxyacetic acid into the coal. Further work is needed to confirm this.

In another set of experiments the concentration of the hydrogen peroxide used to prepare the peroxyacetic acid in situ was varied. This was done to investigate the possibility that the coal to reactant ratio might improve desulfurization selectivity. Figure 12 shows how changing the hydrogen peroxide concentration effects the sulfur content of the desulfurized IBC 101 -400 mesh sample at both room temperature and 50°C . It can be seen that increasing the concentration of hydrogen peroxide beyond 5-10% has only a marginally beneficial effect on the sulfur content. This is interesting because one might have expected the rate of sulfur removal to double if the oxidant concentration doubled (assuming a first order reaction with respect to peroxide). This may be the case at much lower oxidant concentrations than those used in these experiments, but is certainly not the case at the higher concentrations. The level of sulfur removal versus the amount of coal dissolved in these experiments was about the same as obtained in previous experiments in which reaction time and temperature were varied.

Thus it is clear that peroxyacetic acid can reduce the sulfur contents of coals considerably. Although most of this sulfur removal can be explained via the dissolution of pyrite, it is evident that removal of much of the organic sulfur has been effected also. Thus it would appear that increasing the reaction temperature improves the level of desulfurization obtained, including the amount of organic sulfur removed. However, the drawback of using higher temperatures is the fact that substantial coal dissolution occurs. For example the reactions at 50°C that resulted in the best S/C ratios, also resulted in 50% and 30% dissolution for the 101 and 106 coals respectively. At 104°C the levels of coal dissolution are even higher than this. Thus it would appear that high levels of organic sulfur removal using peroxyacetic acid involves an unacceptable level of coal dissolution. For this reason peroxyacetic acid oxidation was investigated as a potential pretreatment step for other desulfurization processes.

Selective oxidation as a pretreatment.

In view of the difficulty in removing organic sulfur without dissolving large portions of the coal it was decided to investigate the whole process of selective oxidation as a pretreatment for other desulfurization processes. These studies are of a preliminary nature and are intended to demonstrate the feasibility of selective oxidation as both a partial desulfurization process and a pretreatment process for other subsequent desulfurization strategies.

The reactions that were considered included reacting the selectively oxidized coal with mild reducing agents, phase transfer assisted reductions and displacement reactions, mild pyrolysis and mild pyrolysis in the presence of methanol and base. Indeed some reactions involving the methanol/base reagent system have produced a desulfurized coal from the IBC 101 coal that has only 0.47% sulfur and a good product recovery. Comparison with a control sample that had not been selectively oxidized showed that selective oxidation enhanced the level of desulfurization substantially. Table 4 belows shows some preliminary results for these desulfurization reactions.

Table 4. Selective oxidation as a pretreatment.

% Dry Sulfur		
Reaction for 1 hour	No pretreatment	Selective oxidation Pretreatment.
Pyrolysis 350°C	3.94	2.72
aq NaOH reflux 24hrs	3.79	2.58
MeOH/NaOH/250°C	3.45	1.91
MeOH/NaOH/350°C	1.75	0.95
MeOH/NaOH/450°C	0.79	0.47
MeOH = methanol Original total sulfur = 4.43%		

Task 3. Analysis of dissolved organic sulfur.

Examination of the soluble oxidation products for organic sulfur compounds were made. This involved isolation of the soluble oxidation products, dispersion in methanol and methylating with diazomethane prior to GC-FID/FPD analysis. Products from the room temperature experiments were examined in a diluted form. The only organic sulfur compound to be detected was methyl sulfonic acid (MSA). The origins of this MSA can be a number of different species in the coals, both inorganic and organic. Since pyrite dissolution is observed during the reaction and that it is known that MSA can be formed from pyrite, we believe the MSA is produced primarily from the coal pyrite. The mechanism by which this occurs is not known but intermediate compounds such as sulfuric acid may be involved.

Other soluble products were taken from a variety of samples that represented the whole range of coal solubilities observed in this project. Each of these were methylated as mentioned above and the concentrated products analyzed by GC-FID/FPD. The sulfur compounds detected consisted of those found previously for these coals during characterization studies. No new sulfur compounds were detected but the distribution of the detected sulfur compounds did vary with the extent of coal dissolution suggesting that some sulfur structures may be buried deeper in the coal matrix than others.

Task 4. Oxidation kinetics of pyrite.

Pure coal derived pyrite was reacted with peroxyacetic acid at room temperature, 50°C and 104°C. Figure 13 shows the rate of pyrite dissolution at each of these temperatures. The amount of pyrite reacted with the peroxide was adjusted so the the pyrite to peroxide ratio was close to that used in the oxidation of the IBC 101 and 106 coals. From these experiment it is clear that the amount of pyrite in the 101 and 106 coals will take about 24 hours to dissolve at room temperature, about 1 hour at 50°C and about 5 minutes at 104°C assuming that in the coal it is not protected from the oxidant by organic matter. Indeed the rate at which sulfur is initially removed from the coal is comparable to the pyrite dissolution rates obtained with pure pyrite. This would suggest that the pyrite in the coal, or at least the majority of it, is not protected from the oxidant by the organic matter.

From sulfate determination of the pyrite oxidation products it appears that iron sulfate is a major product of pyrite oxidation. The quantity of sulfate produced increases as the pyrite is oxidized but does not account for all of the dissolved pyritic sulfur. Thus some of the sulfur remains unaccounted for. It is possible that some elemental sulfur may have been produced but it is anticipated that the missing sulfur is in the form of methylsulfonic acid. It has been determined previously that methylsulfonic acid is a product of pyrite oxidation with peroxyacetic acid. The mechanism by which this organic sulfur compound is produced from pyrite is not known but some kind of methyl group rearrangement from the peroxyacetic acid to the sulfate ion is suspected.

Task 5. Microbial Activity.

Some of the desulfurized coal products have been sent to Dr. Robert Kelly at the Department of Chemical Engineering, Johns Hopkins University, Baltimore, Maryland 21218. for their microbial activity to be measured. The samples sent show variable extents of desulfurization and oxidation. This was done so that how these parameters influence microbial desulfurization can be determined. The potential of combined chemical and microbial desulfurization as a two step process will be evaluated.

Conclusions.

The research completed during this project supports the following conclusions:

1. No or very little improvement in the levels of desulfurization were achieved by grinding to very small particle sizes. This significant conclusion is based on both room temperature and 50°C results and indicates that expensive grinding to very small particle sizes may not be necessary.
2. Cryogenically treating the coal prior to grinding did not improve the selectivity of sulfur removal. It had been hoped that fracturing the coal along maceral boundaries by cryogenic treatment would result in a product more susceptible to desulfurization.
3. The sulfur contents of IBC 101 and 106 samples can be reduced by 40% and 50% respectively at room temperature, by 54% and 63% at 50°C and by 69% and 71% at 104°C.
4. Although sulfur removal is greater and more selective and at higher reaction temperatures the yield of solid coal is reduced and hence the potential as a useful desulfurization process is diminished.
5. Nearly 80% of the total sulfur can be removed from both the 101 and 106 coals if one is willing to sacrifice about 30% of the weight of the coal. Similarly if one sets a limit of 10% for the maximum allowable coal weight loss then about 60% of the sulfur in the IBC 106 coal and about 40% of the sulfur in the IBC 101 coal can be removed using the peroxyacetic acid procedure.
6. Although much of the sulfur removal can be attributed to pyrite dissolution, significant amounts of organic sulfur removal has also been observed.
7. In addition to removing sulfur peroxyacetic acid can be used to improve the ash contents of the coals.
8. Although Btu contents are lowered by selective oxidation the level of sulfur removal is much greater than the loss of heating value. Desulfurized products were obtained that still had higher heating values than many western coals.
9. The peroxyacetic acid oxidation of coal may be an alternative

method for the determination of organic sulfur contents.

10. Extracting the coal prior to reaction with peroxyacetic acid improved the selectivity of the desulfurization reaction. It is anticipated that the removal of the mobile phase allowed better penetration of the reagents into the coal matrix.

11. The only quantitatively significant organic sulfur compound detected in the soluble oxidation products was methyl sulfonic acid.

12. Oxidation of pure pyrite gave sulfate as the primary product but it was anticipated that methylsulfonic acid was also formed via a rearrangement reaction between sulfate ion and the peroxyacetic acid or acetic acid.

13. Selective oxidation, in addition to removing large amounts of sulfur from coal, also shows potential as a pretreatment step for the removal of even more organic sulfur. One product derived from the IBC 101 coal using this approach had a sulfur content of only 0.47%, a sulfur reduction of nearly 90%.

FIGURE 1. Desulfurization at Room Temperature

FIGURE 2. DEMINERALIZATION - ROOM TEMPERATURE
PARTICLE SIZE EFFECTS

FIGURE 3. DEMINERALIZATION AT ROOM TEMPERATURE
PARTICLE SIZE EFFECTS

FIGURE 4. SULFUR VS ASH REMOVAL AT ROOM TEMP.
IBC 101 -400 MESH

FIGURE 5. SULFUR VS ASH REMOVAL AT ROOM TEMP.
IBC 101 -CRYOGEN. GRND.

**FIGURE 6. DESULFURIZATION - ROOM TEMPERATURE
PARTICLE SIZE EFFECTS**

FIGURE 7.

**DESULFURIZATION AT 50 DEG.C
PARTICLE SIZE EFFECTS**

FIGURE 8. DESULFURIZATION - IBC 101 -400 MESH
TEMPERATURE EFFECTS

FIGURE 9. DESULFURIZATION - IBC106 -400 MESH
TEMPERATURE EFFECTS

FIGURE 10. COAL DISSOLVED VS SULFUR DISSOLVED
IBC 101 -400 MESH (50 DEG.C)

FIGURE 11. COAL DISSOLVED VS SULFUR DISSOLVED
IBC 106 -400 MESH (50 DEG.C)

FIGURE 12. DESULFURIZATION -IBC101 -400 MESH
CONCENTRATION EFFECTS

FIGURE 13.

KINETIC STUDY RATE OF PYRITE DISSOLUTION

PROJECT MANAGEMENT REPORT

1st June 1991 through 31st August 1991

Project Title: CHEMICAL COAL CLEANING USING SELECTIVE
OXIDATION

Principal Investigator: Edwin J Hippo, Associate Professor
Department of Mechanical Engineering
and Energy Processes
Southern Illinois University at
Carbondale, Carbondale, IL 62901
(618) 536-2396

Co-Investigator: Stephen R Palmer, Adjunct Asst. Professor
Department of Geology
Southern Illinois University at
Carbondale, Carbondale IL 62901
(618) 453-7324

Project Monitor: Daniel D. Banerjee, CRSC

COMMENTS: None.

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

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	Projected	10,604	1,438	0	0	1,750	2,758	16,550
to Nov. 30, 1990	Estimated Actual	8,921	432	0	0	900	2,050	12,303
Sept. 1, 1990	Projected	21,207	2,875	0	0	3,500	5,516	33,098
to Feb. 28, 1991	Estimated Actual	19,683	683	0	0	1,269	4,327	25,962
Sept. 1, 1990	Projected	31,811	4,313	0	0	5,250	8,275	49,649
to May 31, 1991	Estimated Actual	32,171	3,806	712	0	5,444	8,427	50,560
Sept. 1, 1990	Projected	48,710	5,750	1,000	0	7,000	12,492	74,952
to Aug. 31, 1991	Estimated Actual	48,710	5,750	973	0	7,000	12,427	74,860

*Cumulative by quarter.

COSTS BY QUARTER - EXHIBIT C

Chemical Coal Cleaning Using Selective Oxidation

Cumulative \$
(thousands)

O = Projected Expenditures -----

Δ = Actual Expenditures _____

Total CRSC Award \$ 74,952

PROJECT MILESTONES

Chemical Coal Cleaning Using Selective Oxidation

Milestones:

- A. Coal preparation and analyses.
- B. Desulfurization studies.
- C. Dissolved organic sulfur characterization.
- D. Kinetics of pyrite dissolution.
- E. Microbial activity testing.
- F. Reporting.

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
01/30/92

I