

DOE/PC/91

DOE/PC/91334--T32

DE92 007860

TECHNICAL REPORT

September 1 through November 30th, 1991

NOV 03 1992

Project Title: MILD PYROLYSIS OF SELECTIVELY OXIDIZED COALS.

DE-FG22-91PC91334

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Abstract

The combustion of high sulfur coals contributes substantially to the environmental problems associated with acid rain. Current 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. Although some clean coal technologies can remove much of the mineral sulfur from coal a satisfactory process that can remove organic sulfur has yet to be discovered.

The primary objective of this study is to investigate the removal of organic sulfur from selectively oxidized Illinois coals using mild thermal/chemical processes. Work completed this quarter includes the investigation of the mild pyrolysis of unoxidized coals plus a selection of selectively oxidized coals. In addition the effect of particle size and extent of oxidation on pyrolysis was investigated. Some preliminary data concerning pyrolysis under vacuum and ambient pressure was also obtained. Work completed this quarter supports the following conclusions: 1. Desulfurization of unoxidized coals increases with increasing pyrolysis temperature and correlates with the loss of volatile matter. 2. Particle size did not influence the extent of desulfurization significantly. 3. Removing pyrite prior to pyrolysis helps to achieve a lower sulfur product beyond that expected from the removal of pyrite alone. 4. The extent of selective oxidation in the pretreatment step did not effect the level of desulfurization obtained by pyrolysis alone. However this factor was important in the desulfurization obtained with supercritical methanol (SCM)/base. 5. Up to 84% of the sulfur has been removed from the IBC 101 coal by combining selective oxidation and SCM/base reactions. 6. Evidence for regressive reactions between volatilized sulfur compounds and partially desulfurized products was obtained by studying how changes in pyrolysis pressure effected the product sulfur content.

MASTER

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

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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.

For the 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).

In this study chemically desulfurized coals produced from a previously funded CRSC project entitled, "Chemical coal cleaning using selective oxidation", are examined for further desulfurization using mild pyrolysis and chemical techniques. This desulfurization procedure is significant because it uses relatively 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 chemical desulfurization strategies, both of which are currently under investigation in our laboratories.

As part of our previous CRSC project (Chemical coal cleaning using selective oxidation), Illinois Basin Coal Sample Program (IBCSP) coals Nos. 101 and 106 were ground to various particle sizes and then selectively oxidized with peroxyacetic acid to various extents in an attempt to find optimum oxidative conditions for sulfur removal. Although very encouraging desulfurization were obtained (40-55%), complete sulfur removal is not possible via selective oxidation alone. For this reason these partially desulfurized products are being examined further and their enhanced desulfurization attempted. Since the sulfur that remains is in a selectively oxidized form in which the carbon to sulfur bond is weakened, this sulfur should be more easily removed by a subsequent thermal process or chemical treatment. Thus it is possible that very high desulfurization levels may be achieved by

combining the desulfurization strategies of selective oxidation with a mild thermal or chemical process.

Using selective oxidation it has been established that all mineral forms of sulfur and between 10-25% of the organic sulfur can be removed from these coals using temperatures as low as 50°C and times of only a few hours. If temperatures of 100°C are used then the desulfurization takes less than 5 minutes. These reactions have led to desulfurized products for the IBCSP 101 and 106 coals that have 2.60 and 1.70 % sulfur respectively. This represents a sulfur reduction of 40% for the 101 coal and 55% for the 106 coal. If these levels of desulfurization can be combined with those established under a separated study using mild pyrolysis alone (63% organic sulfur removal for a pyrite-free Illinois No.6 coal), then almost 90% removal of sulfur may be possible.

The specific goals and objectives of this study are:-

1. To optimize sulfur removal from Illinois coals by combining selective oxidation with mild pyrolysis.
2. To determine the rate of desulfurization by varying the time and temperature of pyrolysis.
3. To study the desulfurization mechanism of selectively oxidized sulfur containing model compounds under mild pyrolysis conditions.
4. To establish the effect of additives on the level of desulfurization obtained during pyrolysis.
5. To investigate desulfurization of selectively oxidized coals during enclosed, open and vacuum pyrolysis.
6. To determine the effects of mild pyrolytic desulfurization on the Btu recovery of desulfurized coal.
7. To monitor the levels of nitrogen in the desulfurized products to determine if any nitrogen removal is effected.

Work completed this quarter includes the investigation of the mild pyrolysis of unoxidized coals plus a selection of selectively oxidized coals. In addition the effect of coal particle size and extent of selective oxidation on pyrolysis was investigated. Some preliminary data concerning pyrolysis under vacuum and ambient pressure inert gas were also obtained. Work completed supports the following conclusions: 1. Desulfurization of unoxidized coals increases with increasing pyrolysis temperature and correlated fairly well with the loss of volatile matter. 2. Particle size did not influence the extent of desulfurization significantly. 3. Removing pyrite prior to pyrolysis helps to achieve a lower sulfur product beyond that expected from the removal of pyrite alone. 4. The extent of selective oxidation in the pretreatment step did not effect the level of desulfurization obtained by pyrolysis alone. However this factor was important in the desulfurization obtained with supercritical methanol (SCM)/base. 5. Up to 84% of the sulfur has been removed from the IBC 101 coal by combining selective oxidation and SCM/base reactions. 6. Evidence for regressive reactions between volatilized sulfur compounds and partially desulfurized products was obtained by studying how changes in pyrolysis pressure effected the product sulfur content.

PROJECT DESCRIPTION

Introduction.

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.

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.

For the 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).

Overall Objective.

The primary objective of this study is to investigate the removal of organic and inorganic sulfur from selectively oxidized Illinois coals using mild thermal/chemical processes. This overall objective is relevant to priority 2.2A: identified in the CRSC RFP91-1 under coal cleaning.

"The priorities for chemical cleaning include the following:

2.2A: Development of cost effective methods to remove organic sulfur from coal.

- > This should be a bench-scale study. Emphasis will be given on research schemes that may ultimately lead to a successful process for demonstration and commercialization.
- > Work should be done both with model sulfur compounds and coal. Physically cleaned coal should preferably be used as the starting material for chemical treatment.
- > Reaction rates and mechanism of sulfur removal should be studied.
- > The duration of this activity may be up to 24 months.

Relevance and significance.

This study is extremely relevant to the objectives outlined in CRSC RFP91-1 because it focuses on the removal of both inorganic and organic sulfur forms, but especially organic sulfur forms. The high organic sulfur content of many Illinois coals is a severe hindrance to their full exploitation and utilization and hence any process that would remove organic sulfur from these coals in an economic way, would have a pronounced beneficial impact on the marketability of Illinois coal.

This study is significant because it represents the first time that this particular combination of desulfurization strategies will have been tried. In addition it has the potential to produce high quality products with very low sulfur contents without the need for expensive operating conditions such as exceptionally high temperatures, and expensive chemical reagents. The process is designed to be used in conjunction with physically cleaned coal as well as chemically cleaned coal, processes that are currently being investigated in our laboratories at SIUC under funding from the CRSC.

Previous Work

In this study chemically desulfurized coals produced from a previously funded CRSC project entitled "Chemical coal cleaning using selective oxidation", are examined for further desulfurization using mild thermal/chemical techniques. The combination of these procedures may well lead to high quality products with very low sulfur contents.

Previously, IBCSP coals Nos. 101 and 106 had been ground to various particle sizes and then selectively oxidized with peroxyacetic acid to various extents in an attempt to find optimum oxidative conditions for sulfur removal. Although very encouraging desulfurization were obtained (40-55%), complete sulfur removal was not possible via selective oxidation alone. For this reason these partially desulfurized products are being examined further and their enhanced desulfurization attempted. Since the sulfur that remains in the desulfurized products is in a selectively oxidized form in which the carbon to sulfur bond is weakened, this sulfur should be more easily removed by thermal and/or chemical processes. Thus it is possible that very high desulfurization levels may be achieved by combining selective oxidation with other desulfurization strategies.

The term selective oxidation is used because in typical organic structures thought to be present in coal organic peroxy acids such as peroxyacetic acid oxidize sulfur functional groups faster than most carbon structures. As long as the oxidation conditions are controlled the result is a product where organic sulfur species have been converted to their sulfones and sulfonic acids but most of the carbon structures remain unoxidized. Hence the term selective oxidation. The faster rate of oxidation of sulfur over carbon is due to the strong electrophilic nature of the oxidizing species (hydroxyl cation) and the fact that sulfur is a stronger nucleophile than carbon.

Using selective oxidation it has been established that all mineral forms of sulfur and between 10-25% of the organic sulfur can be removed from these coals using temperatures as low as 50°C and times of only a few hours. If temperatures of 100°C are used then the desulfurization takes less than 5 minutes. These reactions have led to desulfurized products for the IBCSP 101 and 106 coals that have 2.60 and 1.70 % sulfur respectively. This represents a sulfur reduction of 40% for the 101 coal and 55% for the 106 coal. If these levels of desulfurization can be combined with those established under a separated study using mild pyrolysis alone (63% organic sulfur removal for a pyrite-free Illinois No.6), then almost 90% removal of sulfur may be possible. At present it is not known if the levels of desulfurization for the two processes will be additive, but the possibility that they are should be investigated.

Specific Goals and Objectives.

The specific goals and objectives of this study are:-

1. To optimize sulfur removal from Illinois coals by combining selective oxidation with mild pyrolysis.
2. To determine the rate of desulfurization by varying the time and temperature of pyrolysis.
3. To study the desulfurization mechanism of selectively oxidized sulfur containing model compounds under mild pyrolysis conditions.
4. To establish the effect of additives on the level of desulfurization obtained during pyrolysis.
5. To investigate desulfurization of selectively oxidized coals during enclosed, open and vacuum pyrolysis thereby probing for the presence of regressive reactions.
6. To determine the effects of the combined desulfurization strategies on the Btu recovery and volatile matter content of desulfurized coal.
7. To monitor the levels of nitrogen in the desulfurized products to determine if any nitrogen removal is effected.

Work completed this quarter.

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

Sample Preparation.

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 and Btu analysis. Sulfur forms analyses were performed on one sample of each coal also. 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.

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

Table 1. Proximate, ultimate, 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	68.41	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

Although there is slight variability in elemental composition between the aliquots of the same coal ground to different particle size, this variation is largely within experimental error. Thus good agreement is obtained between the data for the various particle size fractions of the same coal. 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.

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 1. Mild pyrolysis of unoxidized coal samples.

a) Variation of sulfur content with pyrolysis time and temperature.

To establish the levels of sulfur removal obtained by mild pyrolysis alone each of the unoxidized coals was placed into the pyrolysis chamber, purged with nitrogen, sealed and then immersed for the desired length of time in a fluidized sand bath maintained at the desired pyrolysis temperature. Upon completion of the reaction period the pyrolysis chamber was withdrawn from the sand bath and cooled in cold water. When completely cool the pyrolysis chamber was opened (with caution) and the contents removed and weighed. The dry pyrolysis product was submitted for proximate, ultimate, Btu and sulfur forms analysis.

Pyrolysis temperatures of 250, 300, 350, 400 and 450°C were investigated. Pyrolysis times ranged from 15 min. to 2 hours with sampling times at 15, 30, 60 and 90 minutes.

The results from these baseline pyrolysis experiments are shown in Figures 1 through 4. Figures 1 shows how the sulfur content of the pyrolysis products from the IBC 101 coal vary with pyrolysis time and temperature. Figure 2 shows similar data obtained from the IBC 106 coal. Figures 3 and 4 show how the volatile matter contents of the pyrolysis products vary under the same pyrolysis conditions. (IBC 101 and 106 respectively).

From this data it is clear that thermally treating these coals can remove at least part of their sulfur. Although some of the data

points behave erratically, there are a number of general trends that can be observed. Firstly, the level of sulfur removal, as measured by the sulfur contents of the solid products, increases with increasing temperature. This increase in sulfur removal is fairly modest until temperatures over 350°C are used, at which point the level of sulfur removal increases rapidly. It is interesting to note that the level of volatile matter loss correlates fairly well with the level of sulfur removal (Figure 5). This suggests that much of the sulfur that is removed is contained in the volatile matter that is lost from the coal upon pyrolysis.

Most of the sulfur removal occurs in the first 15 minutes of thermal treatment, after which, in general, it continues to decline but at a slower rate. There are a number of data points which suggest that the sulfur content of the pyrolyzed coals actually increase slightly after the initial drop in sulfur content. This may be an indication of regressive reactions taking place between the sulfur initially released and the partially desulfurized product. It could also indicate that non-sulfur containing material is removed from the coal after the initial removal of sulfur containing material. However, this phenomena is not observed in all cases and it is difficult to be conclusive with regards to the possibility of regressive reactions at this point.

Thus, in summarizing this data we can say that the amount of desulfurization obtained by pyrolysis alone is both time and temperature dependent. At temperatures at or below 350°C only 2% of the sulfur in the IBC 101 coal was removed while 11% was removed from the IBC 106 coal. However at temperatures of 400°C and above the levels of sulfur removal increase to 14.3% for the IBC 101 coal and 23.6% for the IBC 106 coal. However, at these higher temperatures much of the volatile matter content of these coals has been lost.

b) Variation of sulfur content of pyrolysis products with particle size and physical pretreatment.

Having established how pyrolysis time and temperature affect the sulfur content of the two coals, the effect of varying the particle size and physical pretreatment of the samples was investigated. In addition to the -400 mesh samples already studied, samples of each coal at -60 mesh, -100 mesh and -200 mesh were also examined. A floated sample, an extracted floated sample and a cryogenically treated sample all derived from the IBC 101 were also studied. The pyrolysis time was held constant at 1 hour while two pyrolysis temperatures (350°C and 400°C) were chosen for use in this set of experiments. The results of this set of experiments are shown in table 3.

Table 3. Effect of varying particle size on pyrolytic desulfurization.

	Dry Sulfur Contents					
	IBC 101			IBC 106		
	No. py.	350 C	400 C	No py.	350 C	400 C
-60 mesh	4.43	4.02	3.55	3.63	3.41	3.19
-100 mesh	4.43	4.24	3.61	3.68	3.53	3.15
-200 mesh	4.47	4.13	3.95	3.61	3.34	3.08
-400 mesh	4.17	4.21	3.61	4.04	3.64	3.03
cryogenic	4.41	4.16	4.17			
floated	3.42	3.45	2.42			
extd. floated	3.44	2.93	2.33			

Although there are fluctuations in individual data points the underlying trend indicates that the removal of sulfur using pyrolysis conditions is not significantly effected by the particle size of the coal. Indeed, with a few exception, the levels of sulfur removal for each of the particle size samples, agree very well. With the exception of the cryogenically treated coal, the higher temperature removes more sulfur. The reason for the anomalous behavior of this sample is not clear at this time and this experiment will be repeated to check the data.

The floated IBC 101 coals behave differently. It is clear that both floated samples have a much lower sulfur content after pyrolysis than any of the un-floated samples. Although this can be explained in part by their lower sulfur content prior to pyrolysis, it would appear that removing the mineral component from these coals enhances there desulfurization under pyrolysis conditions. Indeed, the average amount of sulfur removed by pyrolysis at 400°C from the un-floated coals is 0.60%, but for the floated samples it is 1.05%. It is suspected that the removal of the majority of the pyrite from these samples is responsible for the lower sulfur contents obtained for these samples. This is because it has been established that under thermal treatment sulfur from pyrite can react with the organic matter in the coal forming organic sulfur compounds that are extremely difficult to desulfurize. Thus removing pyrite before pyrolysis prevents the formation of additional organo-sulfur compounds.

Extracting the coal prior to pyrolysis also improves the extent of sulfur removal. It is proposed that by removing the mobile phase from the pores in the coal, the sulfur compounds released upon pyrolysis may be able to escape the coal more easily. This would reduce the chances of regressive reactions and the reincorporation of sulfur before it could escape the coal matrix. More studies on extracted coals will be required to establish this.

Task 2. Mild pyrolysis of selectively oxidized coals.

Before the effect of pyrolysis and additives etc. on the selectively oxidized coals can be studied, it is necessary to

established the level of selective oxidation that has the greatest potential to provide low sulfur products. As reported in our previous work the level of product recovery as well as the level of desulfurization is largely dependent upon the extent of selective oxidation. For our studies here we are interested in a selective oxidation pretreatment that removes as much sulfur as possible but does not dissolve too much of the coal. To provide a variety of selectively oxidized coals the IBC 101 -400 mesh samples was oxidized using six different sets of conditions. These are:

- a) Room temperature for 1 hour
- b) Room temperature for 6 hours
- c) Room temperature for 24 hours
- d) Room temperature for 72 hours
- e) 50 °C for 6 hours
- f) 104 °C for 5 minutes.

These conditions were chosen because they all produced yields of selectively oxidized coal of around 80% and better. These yields are based on the weight of solid residue obtained after oxidation. If the weight of the solubilized coal is taken into account then yields approach 100%. Desulfurization of the selectively oxidized coal without prior separation of the solubilized coal and insoluble residue will be investigated later in this project. Each selectively oxidized coal was submitted for total sulfur and ash/moisture analysis and then pyrolyzed for 1 hour at 350°C. Each coal was also treated with NaOH in supercritical methanol (SCM) for 1 hour at 350°C. Samples were also submitted for sulfur and ash/moisture analysis after pyrolysis and SCM/base treatment. The results of these treatments obtained to date are summarized below in table 4.

Table 4. Effect of extent of oxidation on desulfurization using pyrolysis conditions for the IBC 101 -400 mesh sample.

Treatment	Yield ⁺⁺	Dry sulfur contents		
		Before PY	After PY	SCM/Base ⁺
a	94.0	3.41	3.42	1.94
b	93.3	3.05	3.09	1.49
c	93.2	2.86	2.75	1.22
d	85.5	2.63	2.78	0.86
e	78.9	2.49	2.83	0.68
f	79.5	2.48	2.43	1.46
none	100.0	4.14	4.20	1.75*

++ Yields based on weight of oxidation residue only.

+ Data not corrected for moisture. Awaiting results of moisture analysis.

* SCM/base reaction on untreated samples performed under slightly different conditions. This experiment will be repeated using identical condition used for the oxidized coals.

From table 4 it is clear that the extent of selective oxidation has little effect on the amount of sulfur removed under pyrolysis conditions alone. However, under the conditions of the SCM/base reaction, the extent of oxidation in the pretreatment step has a pronounced effect and large variations in the sulfur contents of the products can be seen. It appears that as the level of oxidation in the pretreatment step increases (as measured by the yield after oxidation) the greater the desulfurization obtained in the SCM/Base treatment. Although the moisture data for the SCM/base products are unavailable at this time and hence the sulfur contents cannot be normalized for moisture, it is clear that very low sulfur content products can be obtained via this treatment. Indeed, on a concentration basis up to 84% of the sulfur in the IBC 101 coal has been removed. From this data a selective oxidation pretreatment with peroxyacetic acid at 50°C for 6 hours gives the best results. Unless data for the IBC 106 coal contradicts this observation, all subsequent desulfurization studies in this project involving additives will use this pretreatment.

From previous work with SCM alone it was found that the methanol or its degradation products can react directly with the sulfur in the coal. Even though the C-S bond is weakened by selective oxidation it is normally not broken by it. Therefore, the enhanced desulfurization that we see with the SCM system must be due to either C-S bond breaking by the methanol and/or its degradation products, or to the methanol or its degradation products reacting with and stabilizing the sulfur species as they are liberated thermally. Thus, although the SCM/base data show the effect of selective oxidation as a pretreatment for desulfurization they leave a very important question open. Is the desulfurization limited by the C-S bond breaking or are regressive reactions so rapid that the sulfur products cannot escape the coal particle regardless of the particle size employed.

Clearly these results are preliminary and many more experiments are required before any conclusion can be made, but these levels of desulfurization and the enhancement in desulfurization obtained using selective oxidation pretreatment are very encouraging.

Task 3. Effect of additives and pyrolysis pressure on desulfurization.

As mentioned in task 2 above SCM/base treatment on the oxidized coal have been performed this quarter. This was done in part to establish the level of selective oxidation necessary in the pretreatment step. In addition some initial experiments have been performed in which the pyrolysis pressure was varied. So far only unoxidized coals have been studied. The results of this set of experiments is shown in table 5 below.

Table 5. Effect of pyrolysis pressure on desulfurization.

Temperature	% dry Sulfur		
	Pressure		
	Confined	Vacuum	Ambient'
250	4.209	3.898	4.009
300	4.165	3.959	3.987
350	4.206	3.864	3.952
400	3.609	3.393	3.400
450	3.471		

Although the effect of varying the pressure of the pyrolysis chamber is small, it is clear that lower sulfur contents are obtained by lowering the pressure. This is evidence for the regressive reaction of volatile sulfur components, initially released by pyrolysis, with the remaining coal matrix. It is proposed that in the enclosed system the volatilized sulfur compounds, which cannot escape the pyrolysis chamber, react with the partially desulfurized coal forming new sulfur compounds.

Task 4. Studies involving sulfur model compounds.

A set of sulfur-containing model compounds comprising a thiol, an aliphatic sulfide, an alkyl aryl sulfide, an aryl aryl sulfide, an aliphatic disulfide, an aromatic disulfide, a thiophene, benzothiophene and dibenzothiophene will be oxidized using peroxyacetic acid later in this project. The oxidation products (sulfonic acids and sulfones) will then be pyrolyzed under the same conditions as used for coal studies. Confined pyrolysis will have to be used for the model compounds to prevent them from evaporating. GCMS and GC-FID/FPD analysis of the pyrolysis products will be used to identify any desulfurized products. Compounds identified in this way would be used in attempts to elucidate the mechanism of desulfurization and as a characterization tool for the organic sulfur in coal.

Conclusions:

Work completed this quarter supports the following conclusions:

1. Desulfurization of unoxidized coals increases with increasing pyrolysis temperature, but the volatile matter contents decline.
2. Particle size did not influence the extent of desulfurization significantly.
3. Removing pyrite prior to pyrolysis helps to achieve a lower sulfur product beyond that expected from the removal of pyrite alone.

4. The extent of selective oxidation in the pretreatment step did not affect the level of desulfurization obtained by pyrolysis alone. However this factor was important in the desulfurization obtained with SCM/base.

5. Up to 84% of the sulfur has been removed from the IBC 101 coal by combining selective oxidation and SCM/base reactions.

6. Evidence for regressive reactions between volatilized sulfur compounds and partially desulfurized products was obtained by studying how changes in pyrolysis pressure effected the product sulfur content.

DISCLAIMER

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FIGURE 1. Sulfur content vs pyrolysis

IBCSP 101, -400 mesh

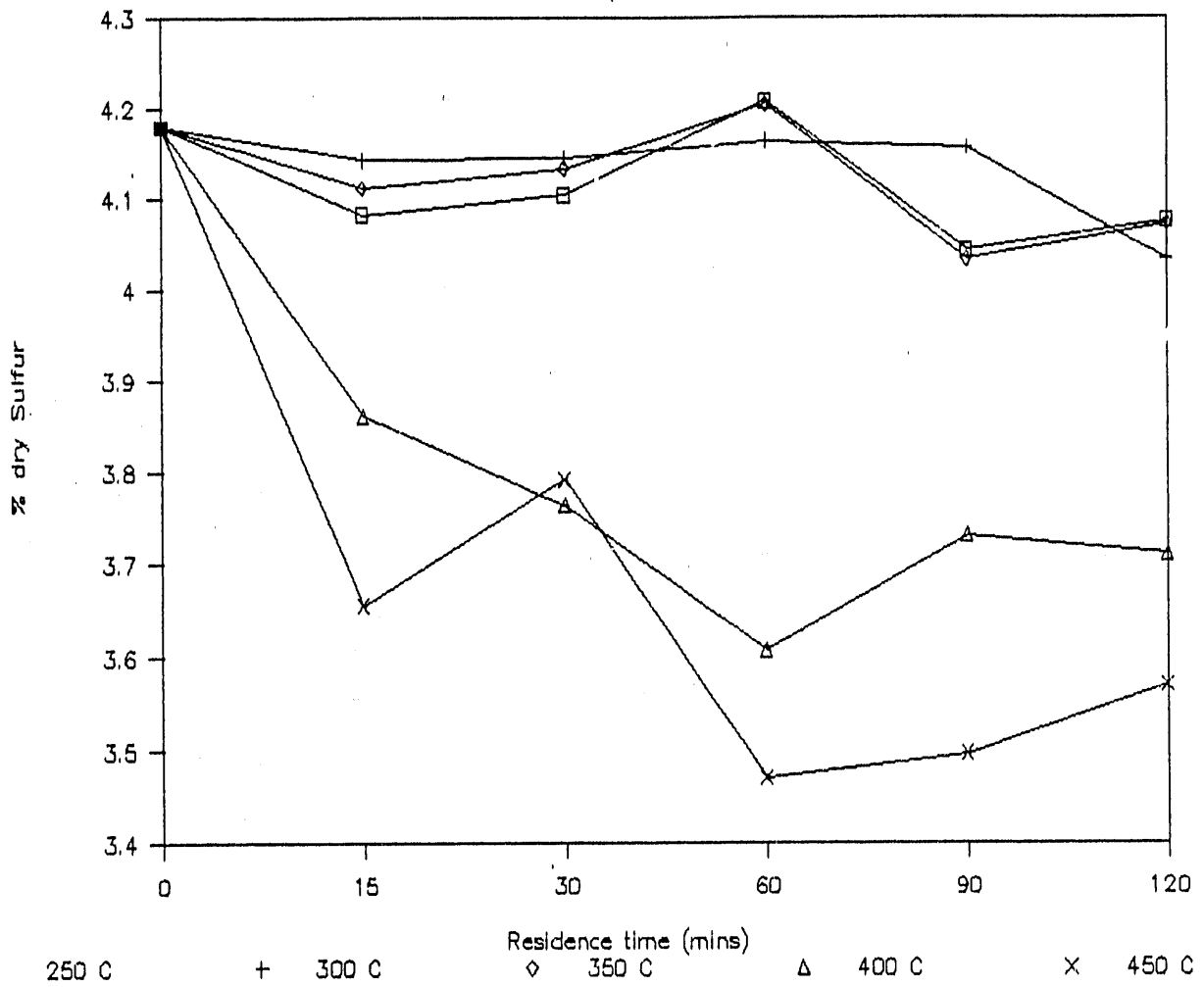


FIGURE 2. Sulfur content vs pyrolysis

IBCSP 106, -400 mesh

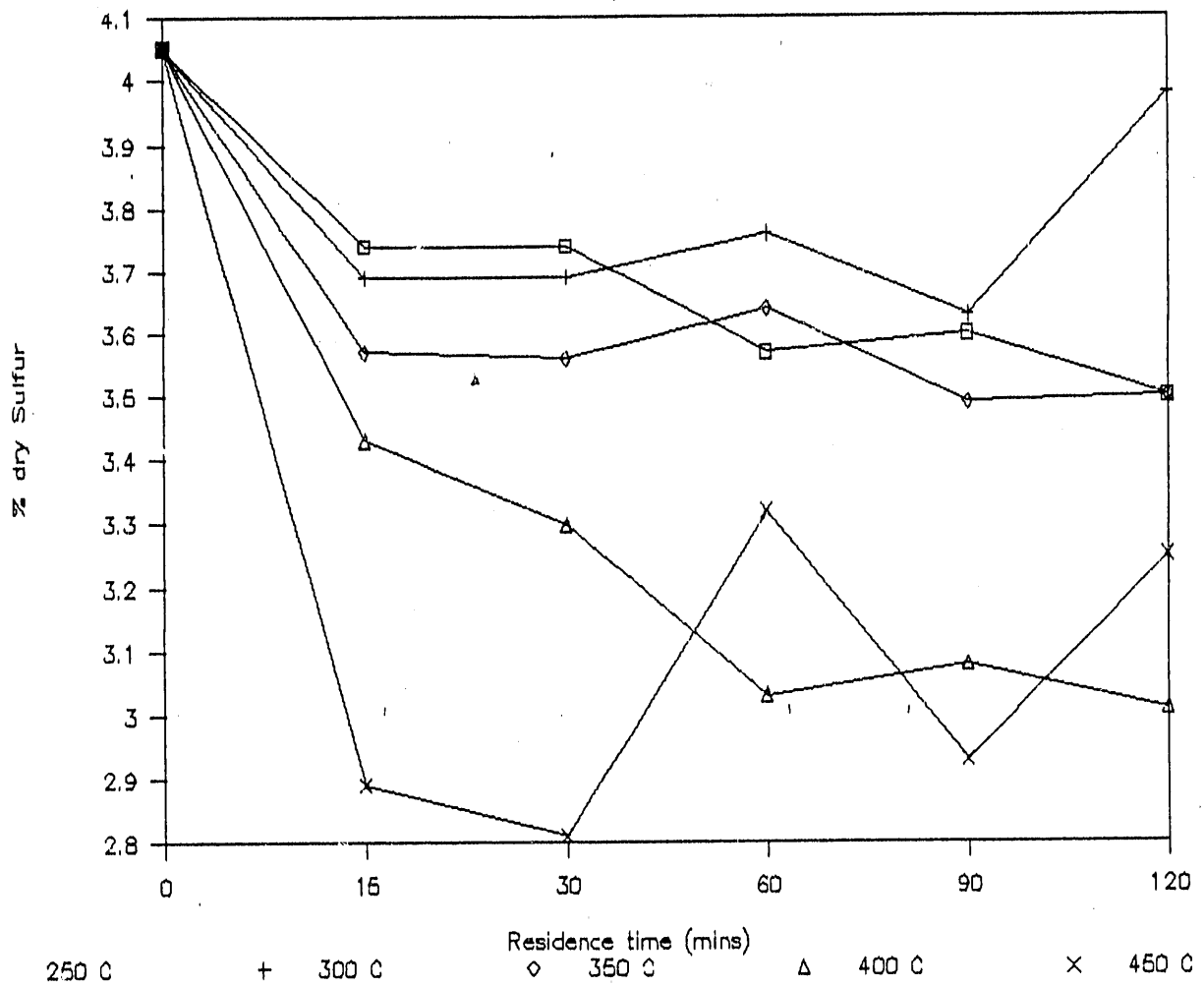


FIGURE 3. Volatile matter vs pyrolysis
IBCSP 101, -400 mesh

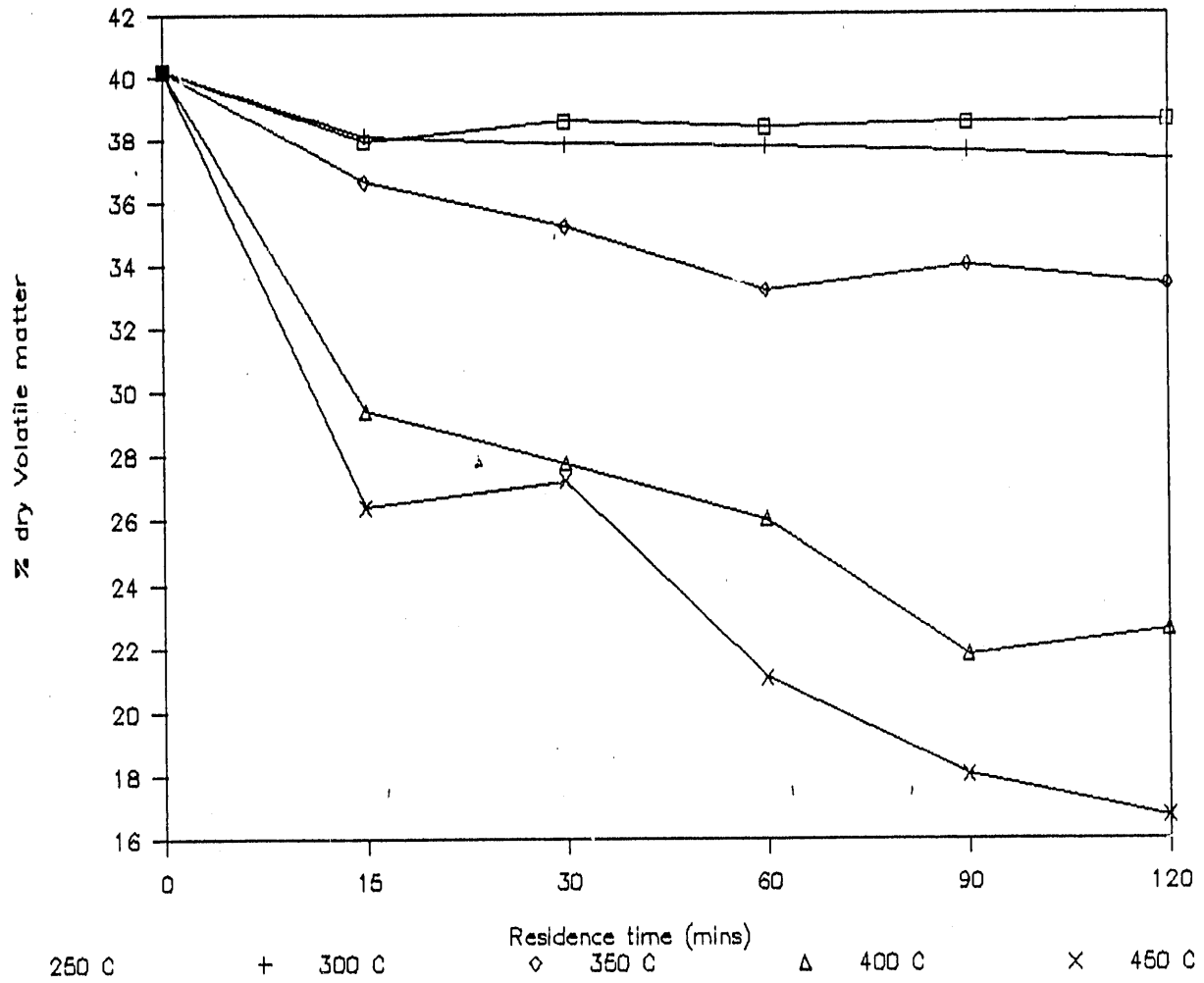


FIGURE 4. Volatile matter vs pyrolysis

IBCSP 106, -400 mesh

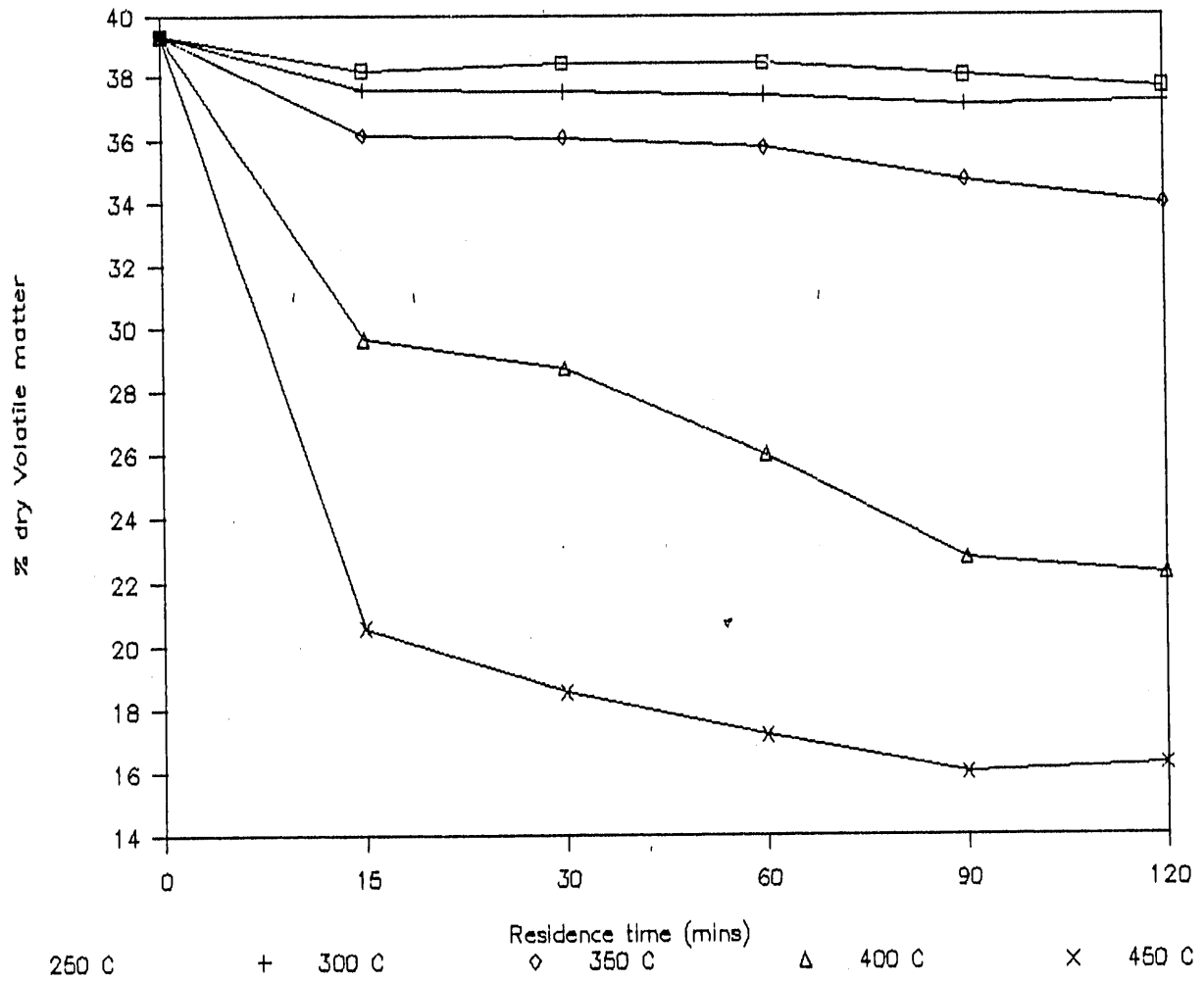
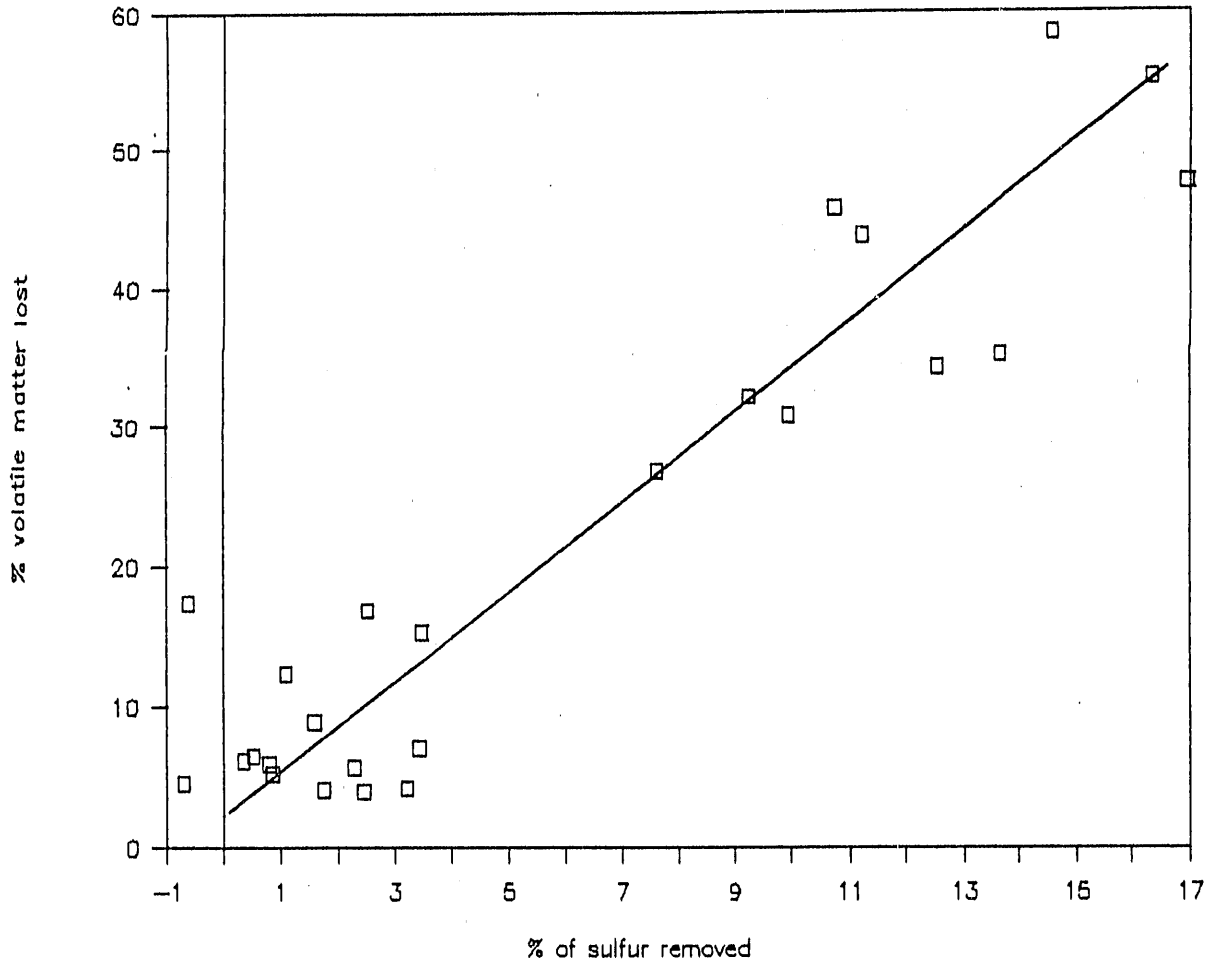


FIGURE 5. Volatile matter loss vs sulfur removed

IBCSP 101, -400 mesh



PROJECT MANAGEMENT REPORT
September 1 through November 30, 1991

Project Title: Mild Pyrolysis of Selectively Oxidized Coals

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