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Project Title: **DESULFURIZATION OF COAL: ENHANCED SELECTIVITY USING  
PHASE TRANSFER CATALYSTS**

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ABSTRACT

Due to environmental problems related to the combustion of high sulfur Illinois coal, there continues to be interest in the development of viable pre-combustion desulfurization processes. Recent studies by the authors have obtained very good sulfur removals but the reagents that are used are too expensive. Use of cheaper reagents leads to a loss of desired coal properties.

This study investigated the application of phase transfer catalysts to the selective oxidation of sulfur in coal using air and oxygen as oxidants. The phase transfer catalyst was expected to function as a selectivity moderator by permitting the use of milder reaction conditions than otherwise necessary. This would enhance the sulfur selectivity and help retain the heating value of the coal.

The use of certain coal combustion wastes for desulfurization, and the application of cerium (IV) catalyzed air oxidations for selective sulfur oxidation were also studied. If successful this project would have lead to the rapid development of a commercially viable desulfurization process. This would have significantly improved the marketability of Illinois coal. However, the phase transfer catalysts, the cerium and the scrubber sledge did not catalize the sulfur removal significantly.

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## EXECUTIVE SUMMARY

Due to environmental problems related to the combustion of high sulfur Illinois coal, there continues to be interest in the development of commercially viable pre-combustion desulfurization processes. These processes would allow the continued use of high sulfur Illinois coal for electricity generation, without the need for post combustion scrubbers.

Recent studies by the authors use a combination of a selective oxidation pretreatment reaction with a subsequent base desulfurization reaction to obtain very good sulfur removals (up to 95%). Unfortunately the cost of the chemical reagents used in the oxidative pretreatment is too high for commercial development and the use of cheaper oxidants results in too much carbon oxidation and hence Btu loss.

Although these studies failed to provide a cost effective desulfurization process, they do point us towards the types of chemical reactions needed for successful desulfurization. It is believed that the key to the success of the two-step process lies in the ability of the oxidant to selectively oxidize the organic sulfur species to their sulfoxides, sulfones or sulfonic acids in the pretreatment step. This selectively weakens the C-S bonds and therefore makes the subsequent removal of sulfur much easier.

The challenge that we face at this time is finding an inexpensive oxidant system that retains the desired sulfur selectivity and preserves the desired properties of the coal such as Btu value. Identifying this inexpensive oxidant system is the primary goal of this study. Specifically the application of phase transfer catalysts to the selective oxidation of sulfur over that of carbon, using air and oxygen as oxidants, is being investigated.

Phase transfer catalysts are substances that have the ability to transport chemical reagents across phase boundaries. This ability promotes chemical reactions in heterogeneous systems that would not otherwise take place or which would take place only very slowly. In this sense they are true catalysts and as such permit the formation of desired products under much milder, and therefore more selective, reaction conditions. It is these features that make phase transfer catalysts so attractive for reactions involving coal. It is anticipated that phase transfer catalysts would act as selectivity moderators in the oxidation of sulfur in coal.

Although the moderation of oxidative selectivity using phase transfer catalysts is the primary area for research in this project, a number of related features are also being examined. These include the potential use of coal combustion residues for the desulfurization step and the application of cerium (IV) catalyzed air oxidation to the selective oxidation of sulfur in coal.

Specific objectives have been identified for the completion of this project. These are:

1. Use physically cleaned coals from the Illinois Basin, to prepare a variety of selectively oxidized coals using air and oxygen under phase transfer catalysis conditions.

2. Test these selectively oxidized coals for enhanced desulfurization under standard desulfurization conditions.
3. Compare these desulfurization results with those obtained for oxidized coals prepared without the phase transfer catalyst.
4. Investigate the applicability of cerium (IV) catalyzed air oxidation for selective oxidation of sulfur in coal, both with and without phase transfer catalysts.
5. Examine the ability of alkaline coal combustion wastes (scrubber wastes and fly ash) to desulfurize selectively oxidized and unoxidized coals.
6. Investigate the kinetics and mechanism of desulfurization under these various conditions by varying the time and temperature of the treatments on coals and model compounds.
7. Measure Btu contents after both oxidation and desulfurization reactions to quantify Btu recoveries after each process.
8. Test selected products for trace element content to determine if these elements can also be removed by the process.
9. Investigate the influence of the amount of phase transfer catalyst on the level of selective oxidation and subsequent desulfurization.
10. Examine the recovery of phase transfer catalysts from the reaction media to see if recycling of the catalyst would be possible.

As far as the authors have been able to determine the application of phase transfer catalysts to the selective oxidation of sulfur in coal had not been investigated before. Similarly, the authors could not find reference to the application of the cerium (IV) catalyzed selective air oxidation of organic sulfur to the study of coal desulfurization. In addition, the use of coal combustion wastes for the precombustion desulfurization of coals appears to be another unique feature of this project.

From the data received, we can see that recovery of the coal oxidation product is high with yields approaching 95-97% in many cases. Unfortunately, if we compare the sulfur contents of the oxidation products we see that there is very little difference between them and the sulfur content of the blank sample (ie. No oxidant, no catalyst). This indicates that no or very little sulfur has been removed during the oxidation process.

The sulfur reductions obtained for all of the oxidized samples after base desulfurization are around 60 to 65%. Thus the use of the phase transfer catalysts and the cerium catalyst, under the oxidation conditions employed, does not appear to have significantly impacted the level of desulfurization obtained. However, it should be noted that the introduction of the cerium catalyst, by itself and in combination with TBAC, did improve the level of desulfurization by around 5%.

Attempts to optimize the level of desulfurization by employing other variables such as increased reaction time (1hr to 24hrs), increased catalyst loading (5% to 20%), introduction a catalyst soak time (1hr to 24hrs), changing the solvent to include methanol and THF, increased oxidant flow rates (200ml/min to 600ml/min), and the introduction of ultrasonic reaction conditions, have not been successful at this time.

## OBJECTIVES

The overall objective of this study is to develop a cost-effective process for the removal of organic sulfur from high sulfur Illinois coals. This project focuses on the use of phase transfer catalysts to moderate the selective oxidation of organic sulfur in coal using air and oxygen. The desulfurization of coal treated this way would be significantly enhanced. In addition, the use of coal combustion wastes to aid the desulfurization of these selectively oxidized coals is being explored.

A number of specific goals and objectives can be identified for the successful completion of this project. These are:

1. Use physically cleaned coals from the Illinois Basin to prepare a variety of selectively oxidized coals using air and oxygen under phase transfer catalysis conditions.
2. Test these selectively oxidized coals for enhanced desulfurization under standard desulfurization conditions.
3. Compare these desulfurization results with those obtained for oxidized coals prepared without the phase transfer catalyst.
4. Investigate the applicability of cerium (IV) catalyzed air oxidation for selective oxidation of sulfur in coal, both with and without phase transfer catalysts.
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7. Measure Btu contents after both oxidation and desulfurization reactions to quantify Btu recoveries after each process.
8. Test selected products for trace element content to determine if these elements can also be removed by the process.
9. Investigate the influence of the amount of phase transfer catalyst on the level of selective oxidation and subsequent desulfurization.
10. Examine the recovery of phase transfer catalysts from the reaction media to see if recycling of the catalyst would be possible.

## INTRODUCTION AND BACKGROUND

To reduce coal derived sulfur oxide emissions the electricity generating industry has been forced to switch to low sulfur coal and to use flue gas scrubbers. This has led to high unemployment in areas where high sulfur coal is mined and to the generation of significant quantities of scrubber wastes.

Due to these considerations there continues to be interest in the development of pre-combustion desulfurization processes which would allow the continued use of high sulfur coal for electricity generation without the need for post combustion scrubbers.

Although some success has been achieved with the development of processes that can remove inorganic sulfur species from coal, an acceptable process for the removal of organic sulfur has yet to be found.

Laboratory studies have shown that very high levels of organic sulfur removal are technically possible. The problem has been that all of these processes have proven too expensive to become commercially viable.

Recent studies by the researchers used a combination of a selective oxidation pretreatment reaction with a subsequent base desulfurization reaction. Very good sulfur removals (up to 95%) were obtained but as with previous processes the cost of the reagents, especially those used in the selective oxidation step, inhibits the development of a commercial process (2-7). Use of cheaper oxidants were found to give similar levels of desulfurization but there are concerns regarding the selectivity of the oxidants and the possibility that too much carbon oxidation and therefore Btu loss occurs. The success of bases to desulfurize the oxidized coals raises the possibility that certain alkaline coal combustion wastes might be useful for desulfurization. If coal combustion wastes could be used for the desulfurization of coal, not only would process economics be influenced favorably, but a use for these problem wastes would be found. The possibility of using these waste materials for the desulfurization of coal is being investigated in this project.

Using XANES analysis it was found that oxidation with peroxyacetic acid converts most of the pyrite to sulfate and most of the sulfides and thiophenes to sulfoxides, sulfones and sulfonic acids.(8) This is the expected result. In addition the desulfurization treatment effectively removed the sulfoxides, sulfones and sulfonic acids that were formed by the oxidative pretreatment. Indeed, the only significant sulfur form still present after the combined treatment is thiophenic sulfur, and this has been reduced by some 70%. Both pyrite and organic sulfides were completely removed.

Although these studies failed to provide a cost effective desulfurization process, they do at least point us towards the kinds of processes that might become viable. It is believed that the key to the success of this process lies in the ability to selectively oxidize the organic sulfur species to their sulfoxides, sulfones or sulfonic acids in the pretreatment step. This selectively weakens the C-S bonds and therefore makes the subsequent removal of sulfur much easier.

The problem that we face at this time is finding an inexpensive oxidant system that retains the desired sulfur selectivity. Unfortunately the inexpensive oxidants such as air, oxygen, nitric acid, etc. are not known for their oxidative selectivity and excessive oxidation of carbon is often observed.

For reasons that will be explained later it is believed that the selective oxidation of sulfur over carbon can be performed using inexpensive oxidants by employing substances called phase transfer catalysts (PTC). It is anticipated that the PTC would act as a selectivity moderator in the oxidation of sulfur in coal.

Phase transfer catalysts are substances that have the ability to transport chemical reagents across phase boundaries. This ability promotes chemical reactions in heterogeneous systems that would not otherwise take place or which would take place only very slowly. In this sense they are true catalysts and as such permit the formation of desired products under much milder, and therefore more selective, reaction conditions. It is these features that make phase transfer catalysts so attractive for reactions involving coal.

Phase transfer catalysts such as tetrabutyl ammonium hydroxide (TBAH) have been found to aid the swelling of the coal structure thereby allowing the penetration of other reactants. Indeed, the rate of O-methylation was not limited by the mass transport of the chemical reagents into the coal structure. This result supports the proposed mechanism whereby the PTC promotes the penetration of reagents into the coal matrix.

It is believed that phase transfer catalysts could be used to enhance the accessibility of oxidants in coal thereby permitting the use of mild oxidation conditions which would only oxidize sulfur. A highly selective reaction should be the result because, in most situations, the divalent sulfur atom is inherently more reactive towards oxidants than the carbon atom.(9,10) This is because the divalent sulfur atom can easily accommodate oxygen atoms becoming tetravalent or hexavalent without having to break any bonds. Carbon on the other hand is usually unable to form bonds with the oxygen without first breaking a C-C or C-H bond. This is why the oxidation of sulfur containing model compounds usually results in the formation of the sulfoxides, sulfones or sulfonic acids in high yield with no or very little oxidation of the carbon in the molecules.

The ability of PTCs to promote oxidations with air and oxygen from the gas phase has been demonstrated with the development of a number of synthetic pathways for organic chemicals. (11-14) For instance, fluorenone can be formed from fluorene using air as the oxidant and tricaprylammonium chloride as a PTC. (11) Similarly 9,10 dihydroanthracene can be oxidized to anthraquinone by air with dicytyldiethylammonium chloride as the PTC. (12) In both these reactions the molar ratio of PTC to substrate was only 0.03 and the air pressure was 1 atm.

In addition, a new selective oxidation process has recently been developed for the conversion of sulfides into sulfoxides using air as the oxidant. This process uses a cerium catalyst  $[(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6]$  to promote a single electron transfer from the sulfur species to molecular oxygen forming the radical cation and the superoxide anion, followed by triplet oxygen

trapping of the radical cation. This catalytic air oxidation is also being investigated for the selective oxidation of sulfur in coal under PTC conditions.

## EXPERIMENTAL PROCEDURES

The work that has been undertaken during this project is outlined in the following text as a number of tasks.

### Task 1. Sample selection and preparation

IBCSP coal sample No. 101 was selected for use in this study. These coals were used because they have relatively high, but different, organic sulfur contents, and therefore provide the best challenge to the desulfurization process.

Each coal was riffled into suitable aliquot sizes and excessive deterioration prevented by storage under nitrogen. To provide beneficiated coal fines samples, aliquots of each coal was micronized using a nitrogen gas powered micronizer in order to liberate the very fine minerals found in these coals. Since previous results imply that pyrite removal prior to oxidation and desulfurization is essential, extra effort was applied towards pyrite removal. To this end aliquots of coal have been passed through the micronizer up to three times while other aliquots have been treated with liquid nitrogen prior to micronization. The micronized coals were centrifuged in a  $1.6 \text{ g/cm}^3$  cesium chloride solution to establish the extent of pyrite liberation. After centrifugation the mineral-attenuated float material were washed with 1N HCl and distilled water, and finally dried under vacuum below  $40^\circ\text{C}$ . Coals treated in this way typically have less than 1% ash and very little residual pyrite. Analysis of these various products determined the extent of physical pretreatment necessary to obtain optimum pyrite liberation. This level of coal preparation is required to provide a physically clean coal of very high quality. This enabled the desulfurization study to focus on organic sulfur removal, without worrying about any complications resulting from pyrite reactions or interactions.

Aliquots of each coal, both before and after physical cleaning, were submitted for analysis including proximate, ultimate, Btu and particle size determination.

All solvents, reagents and catalysts were obtained from chemical supply houses. Coal combustion wastes have been obtained from the Coal Combustion Residues Management (CCRM) Program Sample Bank maintained by the mining engineering department at SIUC.

### Task 2. Selective oxidation using phase transfer catalysts

Two phase transfer catalysts were examined in this study. These were tetrabutylammonium hydroxide (TBAH) and tetrabutylammonium chloride (TBAC). These PTC's were chosen because they have been used in coal related studies before and because one is a base while the other is a neutral salt. Comparison of the two helped to establish the role of pH in these oxidations.



Three oxidant systems were evaluated under PTC conditions. These were air oxidation, oxygen oxidation and cerium (IV) catalyzed air oxidation. Each was studied in the presence of each PTC and also in the absence of any PTC. Four temperatures with a standard reaction time of 1 hour were investigated for each PTC/oxidant combination. This reaction matrix is shown in Table 1.

For these initial investigations the oxidant flow rate were held constant at 20 ml/min and the PTC concentration maintained at 5% (wt% based on coal). Each experiment was conducted on 5 grams of coal. This provided sufficient sample for the subsequent desulfurization reaction, and for the Btu and proximate analysis of products both after oxidation and again after desulfurization.

### Task 3. Optimization of pretreatment reaction

At this point, other oxidative pretreatment processes were selected for further detailed study. This study investigated variations in PTC concentration, other oxidant flow rates and different reaction times and temperatures. Many of these variables were to be determined from an analysis of the results obtained in Task 2. Since little sulfur was removed in Task 2, harsher conditions were employed in Task 3. This new data was used to help identify any reasonable oxidation conditions that lead to improved levels of sulfur removal with subsequent desulfurization reactions. In addition, the recovery of the phase transfer catalysts from the reaction medium would be examined under this task.

### Task 4. Standard desulfurization reaction

Each selectively oxidized coal and unoxidized control coal were desulfurized under standard desulfurization conditions. A typical desulfurization experiment involves dispersing 2 grams of coal (oxidized or unoxidized) in 4 mL of methanol with 1 gram of sodium hydroxide. This slurry is placed in a 10 mL stainless steel microreactor. The microreactor is purged with argon, sealed and then placed in a fluidized sand bath maintained at a temperature of 350°C for 60 minutes. After this time the reactor is cooled to room temperature and the contents collected. The product is washed with dil. HCl then distilled water and finally dried overnight in a vacuum oven. Products are then submitted for analysis as described in Task 7.

### Task 5. Desulfurization with coal combustion residues

To test the ability of scrubber sludge and fly ash for the desulfurization of coal, up to five selectively oxidized samples and the unoxidized sample from each coal were selected. The desulfurization reaction conditions were used, but the sodium hydroxide was replaced with an equal quantity of the combustion waste. Products were tested as described in Task 7.

### Task 6. Studies involving sulfur model compounds

A set of sulfur compounds comprising of phenyl-thiol, diphenyl sulfide, benzo-phenyl-sulfide, dibenzo-sulfide, dithiophene, dibenzo-disulfide, diphenyl-disulfide, and

dibenzothiophene were oxidized in the presence of cerium, TBAH, and TBAC. Reactions were conducted in aqueous solution at the boiling point for 24 hours. These reactions were conducted with a tenth of a gram of each compound in the same apparatus used in the coal oxidations. About 100 mls of water was used. a blank was mixed up in which the compounds were mixed with water and let stood for 24 hours. The blank and the oxidized solutions were then extracted with 100 mls of chloroform in a seperatory funnel. If unoxidized, the sulfur compounds should report to the chloroform phase. If oxidized the sulfur compounds would be less soluble in the chloroform and might not be extracted at all. The extracted solutions were then diluted by micropipeting 0.1 mls of the sample into 100 mls of chloroform. This diluted solution was rediluted in the same manner. The product of that dilution was rediluted again. The final dilution was then passed through a Hewlett-Packard GC-MS. The height of the peaks as a function of time were compared to those of the blank. Pyrite was also oxidized following the methods used for the coal. The pyrite was obtained from a pyrite parting removed from the Illinois #6 coal seam. It was ground in the laboratory micronizer to a 3 micron mean size. It was then washed in HCl to remove any sulfate form during storage and grinding. Oxidation was carried out in TBAH, TBAC, and Cerium. After oxidation the remaining residue was filtered dried and weighed. It was then washed in HCl, dried ,and weighed again. The filtrate was collected, top to liter in a volumetric flask, and the concentration of iron was determined by ICPEs.

#### Task 7. Product analysis and evaluation.

The product yield, the sulfur content and the ash/moisture content were obtained on all products. Other tests such as proximate analysis, Btu analysis, elemental analysis and sulfur forms analysis were performed throughout the project on selected samples. Selected products were examined by digestion and then ICP-ES analysis to monitor trace element concentrations. The information provided will be used to evaluate the processes under investigation and to indicate the direction of future experiments.

## RESULTS AND DISCUSSION

### Sample Preparation (Task 1)

Data for the physically cleaned coals are shown in Table 2.

As expected there is increased particle size reduction with increasing passes through the micronizer. This is true both with and without the cryogenic pretreatment. It is surprising however, that the particle sizes for the cryogenically treated sample are larger than those produced without the freeze-thaw cycle provided by the addition of the liquid nitrogen. It was expected that the cracks resulting from the cryogenic pretreatment would have led to smaller particle sizes upon subsequent micronization. The fact that the cryogenic pretreatment followed by micronization does not produce smaller particle sizes than micronization alone does not mean that the liquid nitrogen treatment failed to give enhanced pyrite/mineral liberation. This information was provided by the sink/float tests.

The Btu values decline slightly (see 1st quarterly report) with increased grinding indicating that there is some oxidation during repeated micronization. However, the change in the Btu value is small and the levels of oxidation are not considered sufficient to influence subsequent reactions.

In general the elemental, proximate and Btu data agree very well with that provided by the Illinois Basin Coal Sample Program. It can be seen that the micronizer has a drying effect in that the moisture contents decline on repeated passes through the micronizer. As expected there are no major differences in the elemental composition of the various aliquots of the IBC-101 coal. This indicates that the various physical pretreatments have not resulted in the fractionation of the sample and that each aliquot is a true representation of the original coal.

These results are not as good as those reported earlier by Hippo and Crelling(15). One reason for the lower efficiency in the present study may have to do with the micronizer employed. In the earlier study a small laboratory unit was used. This unit has a larger linear gas velocity in the micronizer but the batch nature of the process allows lower gas velocities in the collection zone. Thus, more fines can be recovered. In the current work only 85% recoveries were obtained while in the earlier work 95% recoveries were experienced. The mean size in the earlier work was less than 1 micron. Smaller than in the current work. The larger unit was used because its design is very close to the type of unit which would be employed commercially. Most of the material loss occurred in the collection of sample from the bag house and from entrained particles which do not get collected by the bag house. The lost material was probably finer than that collected but the analysis indicate that the collected sample is representative of original composition. Thus, the actual liberation is slightly greater than that reported.

Although there did not appear to be any increased particle size reduction with the cryogenic (liquid nitrogen) pretreatment, it was hoped that improved mineral matter liberation would be achieved through the application of this technique. To test this, each of the samples was centrifuged at  $1.6\text{g/cm}^3$  to provide sink and float material at that density. The ultimate data for the floated materials are shown in Table 2. All six samples gave approximately the same ash content, indicating that the cryogenic treatment and the additional passes through the micronizer failed to give additional mineral liberation. Thus, even though increased micronizer treatment effectively reduced the average particle size, no additional mineral liberation was obtained.

The goal of these physical pretreatments was to provide a mineral free coal, so that the desulfurization reactions could be studied without significant interferences from mineral matter. Since this goal could not be realized using physical methods alone a decision was made to attenuate the mineral matter using a combination of chemical methods including HF/HCl demineralization and lithium aluminium hydride (LAH) reduction. LAH reduction has been shown to effectively remove pyrite and could significantly enhance the levels of desulfurization obtained during subsequent oxidation.

The effect of HF/HCl and the LAH treatments on the ash contents on the IBC 101 coal are shown in Table 3.

It is clear that the HF/HCl treatment significantly reduces the ash content, although more than one treatment under these conditions is recommended to ensure good mineral dissolution. The mineral that is not dissolved in HF/HCL after two treatments is probably pyrite with a few other minor minerals that are also resistant to HF. The drop in ash content upon LAH reduction of the HF/HCl treated coal of about 2% corresponds very well with the measured pyrite content for this coal. It is anticipated that ash contents down to the 1.5% to 1.0% level or perhaps even better will be obtained consistently using the combined HF/HCl and LAH treatment.

The results demonstrate that even after extensive physical and chemical treatments, the remaining ash is substantial when considering the demineralized coal as a potential feedstock for a direct fired turbine.

The elemental composition for sample number six in the Table 3 is listed in Table 4 along with the elemental composition for the micronized coal. Both compositions are reported on a "dry ash free basis". within experimental error both compositions are similar. The sulfur content for the micronized coal was corrected by backing out the pyrite sulfur from the overall composition. The data indicate that the chemical composition is identical for the two coal once the pyritic sulfur and ash differences have been accounted for.

It is not known if staged cleaning between passes could improve liberation performance. The applicability of these results to other samples from the basin is unknown, but these coals are notorious for poor cleaning performance. The elastic nature of the coal may play a role in the lack of liberation. Also these coals are known for the highly dispersed mineral impurities. It is not known if solvent extraction pretreatments would make the coal more brittle, or if the lack of liberation is limited by particle behavior in the micronizer.

#### Oxidation experiments using phase transfer catalysts. (Task 2)

A list of the oxidation experiments conducted together with the available yield and ultimate data for the products, is given in Table 5.

From the data received, we can see that recovery of the coal product is high with yields approaching 95-97% in many cases. This indicates that the oxidation conditions are mild and hence carbon loss via conversion to carbon dioxide is minimal. This is also supported by the carbon contents of the products which show very little change from the unoxidized coal.

If we compare the sulfur contents of the oxidation products, we see that there is very little difference between them and the sulfur content of the blank sample (ie. No oxidant, no catalyst). This indicates that no or very little sulfur has been removed during the oxidation process. This does not necessarily mean that the sulfur was not oxidized, just that it was not removed by the oxidative process. If the sulfur has been selectively oxidized but not

removed, then we should have seen enhanced desulfurization when these products were reacted under the base/methanol desulfurization conditions. This will be discussed in the following section.

#### Optimization of PTC oxidation reaction (Task 3)

To investigate the PTC assisted oxidation of coal further a number of additional reaction variables were investigated under this task. These include increasing the reaction time (1hr to 24hrs), increasing the catalyst loading (5% to 20%), introducing a catalyst soak time (1hr to 24hrs), changing the solvent to include methanol and THF, increased oxidant flow rates (200ml/min to 600ml/min), and the introduction of ultrasonic reaction conditions.

The results of the oxidation experiments are presented in Table 6. For the most part, the increased severity of the oxidations did not effect the resulting sulfur content of the oxidized residues. In a few cases the 101 3 pass micronized sample showed a slight decrease in sulfur content; but the LAH treated samples showed no corresponding decrease under the exact same conditions. The more severe conditions appear to oxidize the pyrite. However, even these results were obtained under conditions which would be considered unattractive for commercial considerations. The results for the three tests conducted under ultrasonic conditions did not improve these results. They are listed in Table 7. The ultrasonic tests were conducted with LAH treated coal.

#### Base desulfurization of oxidation products (Task 4)

Yield and ultimate data for the subsequently desulfurized oxidation products generated in Task 2 is reported in Table 8.

The sulfur reductions obtained for all of the samples analyzed so far are around 60 to 65%. Thus the use of the phase transfer catalysts and the cerium catalyst, under the oxidation conditions employed, does not appear to have significantly impacted the level of desulfurization obtained. However, it should be noted that the introduction of the cerium catalyst, by itself and in combination with TBAC, did improve the level of desulfurization by around 5%.

The results of the subsequent desulfurization of these products is presented in Table 9. The cultrugonic treatment results are shown in Table 10. At this time we have seen very little improvement in the levels of desulfurization obtained in Task 2.

#### Fly ash and scrubber sludge desulfurizations (Task 5)

The results for the preliminary desulfurizations using fly ash and scrubber sludge that had been performed in the previous quarter are listed in Table 11. At this time only standard conditions of 350°C for 60 minutes have been examined. In all of these reactions the IBC 101 coal that recieved three passes through the micronizer was used.

It can be seen from Table 11 that performing the desulfurization reaction using water without any other reagent or additive results in a sulfur reduction of only 15%. If we add a small amount of sodium hydroxide the desulfurization improves to around 26%. Adding fly ash in place of the sodium hydroxide does not appear to aid sulfur removal. Indeed, water alone appears to be better. The results for the scrubber sludge in an aqueous environment are even poorer, with the sulfur contents of the product increasing significantly. In the case of the aqueous scrubber sludge reaction the product received a second acid washing to see if any residual scrubber sludge was retained in the original product and therefore was responsible for giving a falsely high sulfur content. No change was found in either the sulfur content or the ash content after this second acid washing. Since we know the scrubber sludge to be almost completely soluble in acid, it can be concluded that sulfur in the scrubber sludge is incorporated chemically into the product coal. Clearly this is not the goal of a desulfurization reaction, and the use of scrubber sludge under these conditions for desulfurization does not look promising.

Similar desulfurization reactions using methanol in place of water gave improved levels of desulfurization, but again the presence of fly ash or scrubber sludge hindered the removal of sulfur from the coal. The incorporation of sulfur into the coal product from the scrubber sludge was not observed in the methanol environment. This indicates that the species in the scrubber sludge that is responsible for this reaction is probably soluble in water but insoluble in methanol.

#### SEM-EDAX analysis of fly ash

Analysis of the fluorescent X-rays produced by the defocussed electron beam in the SEM was used to establish the bulk chemistry of the fly ash in terms of the oxide content. Based upon previous determinations of this type Si, Al, Fe, Na, Ca, K, Ti, Mg, S and Mn were determined as their oxides. The results are given in Table 12.

Bulk chemical analysis of the fly ash using semi-quantitative SEM-EDAX indicates that there are oxides of sodium, potassium and calcium, among others, all of which may take part in base desulfurization reactions. Of course the SEM-EDAX results are reported as oxide contents and these elements may not necessarily be in the oxide form. However, a water slurry of the fly ash is strongly alkaline with a pH of around 12-13., suggesting oxides are present.

#### Model compound work (Task 6)

The results of the model compound work showed that no significantly detectable amount of oxidation occurred for any of the compounds in the presence of the TBAH or TBAC. The results from the Cerium oxidation indicates that most of the thiol and about half of the sulfides were oxidized. This is interesting in that the cerium oxidation of the coal showed some indication of decrease sulfur content in the desulfurized residue. However, based on the extent of oxidation of these model compounds the Cerium oxidation of the coal samples would have been expected to show a larger effect after desulfurization. This indicates that the thiol and sulfides in the coal are probably being removed by the base

desulfurization anyway. Thus, the oxidation is really required for the thiophenic sulfur forms in the coals. which have not been touched by the current oxidation methods employed.

TBAC oxidation of the pyrite gave a 98.5% weight recovery; we believe the slight weight loss was due to loss of fine particles, there was no detectable Fe in the ICPES wash. The TBAH and Cerium oxidation gave a 90 and an 83 % recovery after oxidation. The filtrate contained 80 and 252 ppm of Fe for the TBAH and Cerium oxidation. These numbers are in fairly good agreement with those expected by the weight loss data. HCl washing decreased the recovered weight by another 10 % in these two cases but not for the blank water oxidation or the TBAC oxidation. ICP results indicate that iron is removed from the residue during the HCl wash. After the HCl wash of the pyrite, the sulfur content is 52.9% just slightly lower than the stoichiometric 53.4. Similar results were obtained for the oxidation residues after HCl washing (52.9% for the aqueous oxidation, 52.4% for the TBAC and TBAH oxidations, and 49% for the Cerium oxidation. The low sulfur in the cerium may indicate that some iron oxide was formed which diluted the sulfur slightly and was not dissolved in the HCl. The sulfur concentration in the oxidized sample before washing is slightly higher than expected and greater than stoichiometric pyrite. This result is somewhat surprising and indicates some elemental sulfur is formed. But why this should be removed by HCl is not understood at this time.

Samples of raw coal, floated coal, oxidized coal, and desulfurized coal are currently being extracted. in HCl and HF. Trace elements will be determined for these samples

## CONCLUSIONS AND RECOMMENDATIONS

Analysis of the six samples of IBC-101 coal that had undergone various physical pretreatments in order to liberate minerals revealed that the cryogenic pretreatment and the additional passes through the micronizer did not give superior liberation. Indeed, despite improved particle size reduction with increasing micronizer passes, the ash content of the subsequently floated material, was not reduced beyond the 4.5 to 4.9% level.

Preparation of a pyrite free coal sample was achieved using HF/HCl and then LAH treatment. This sample had an ash content of only 0.3%.

At this time we have not been able to identify oxidation and desulfurization conditions using PTC's which aid the desulfurization of coal. At best the levels of desulfurization achieved through the application of PTC's are only marginally better than those obtained without the addition of PTC. Some small improvements were obtained using Cerium as a catalysts but these improvements are slight

Model compound work confirmed that TBAH and TBAC do not catalyze oxidations of sulfur in coal. Cerium on the other hand oxidizes thiol and sulfide groups. However, these groups do not limit coal desulfurization. The Pyrite is oxidized slowly under the mild conditions employed.

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## REFERENCES

1. Philo, G.R and Covert, D.E. 1994. Outlook for the Illinois Coal Industry. Report of the Illinois Coal Development Board, Illinois Department of Energy and Natural Resources, Illinois.
2. Palmer, S.R., Hippo, E.J., Kruge, M.A and Crelling, J.C. 1992. "Characterization and Selective Removal of Organic Sulfur from Illinois Basin Coals." Coal Preparation, 10:93-106.
3. Hippo, E.J. and Palmer, S.R., 1990. Chemical coal cleaning using selective oxidation. CRSC Final Report, Center for Research on Sulfur in Coal, Carterville, Illinois.
4. Hippo, E.J. and Palmer S.R., 1991. Mild pyrolysis of selectively oxidized coals. CRSC Final Report, Center for Research on Sulfur in Coal, Carterville, Illinois.



5. Palmer, S.R., Hippo, E.J. and Dorai, X.A., 1992. Proceedings of the Ninth Annual International Pittsburgh Coal Conference. University of Pittsburgh, Pittsburgh, PA, October 12-16, p77.
6. Palmer S.R., Hippo, E.J. and Dorai, X.A. 1994. "Chemical coal cleaning using selective oxidation." Fuel. 73:161-169.
7. Palmer S.R., Hippo, E.J. and Dorai, X.A. 1995. "Selective Oxidation Pretreatments for the Enhanced Desulfurization of Coal." Fuel. 74:193-200.
8. Palmer, S.R. and Huffman, G.P. 1994. Analyzing organic sulfur in coal/char: Integrated mild degradation/XANES methods. Final Technical Report, Report No. 93-1/6.1A-1P, Illinois Clean Coal Institute, Carterville, Illinois.
9. Streitwieser, A. and Heathcock, C.H., 1981. Introduction to Organic Chemistry, Second Edition, Chapter 4. p51. Macmillan Publishing Co. New York.
10. Roberts, J.D. and Caserio, M.C. 1979. Basic Principles of Organic Chemistry, Second Edition, p14. Addison Wesley, Menlo Park CA.
11. Starks, C.M. and Liotta, C. 1978. Phase Transfer Catalysis. Principles and Techniques. Academic Press, New York.
12. Alneri, E., Bottaccio, G. and Carletti, V. 1977. Tetrahedron Letters, p2117.
13. Jarrouse, J. and Raulin, J.C. 1977. Acad. Sci. Paris, 284:503.
14. Dietrich, B. and Lehn, J.M. 1973. Tetrahedron Letters, p1225.
15. Crelling, J.C., and Hippo, E.J., 1992. "A Novel Technique for Evaluating Cleaned Fine and Ultrafine Coal." Final Technical Report to ICCI.

Table 1. Reaction matrix for PTC assisted oxidations

PTC/Oxidant Combination	0°C	20°C	50°C	100°C
no oxidant	X	X	X	X
air	X	X	X	X
oxygen	X	X	X	X
cerium/air	X	X	X	X
air/TBAH	X	X	X	X
air/TBAC	X	X	X	X
oxygen/TBAH	X	X	X	X
oxygen/TBAC	X	X	X	X
cerium/air/TBAH	X	X	X	X
cerium/air/TBAC	X	X	X	X

Table 2. Ultimate analysis data for physically treated coal samples.

coal	cryogen treated	float Y/N	micro passes	particle size	moisture (wt%)	dry ash (wt%)	Dry Basis (wt%)			
							C	H	N	S
IBC 101	none	N	0	NA	11.4	10.3	69.8	4.4	1.2	4.4
IBC 101	none	N	1	9.9	5.9	12.4	66.8	4.3	1.0	4.5
<b>IBC 101</b>	<b>none</b>	<b>Y</b>	<b>1</b>	<b>9.9</b>	<b>2.2</b>	<b>4.7</b>	<b>73.4</b>	<b>5.1</b>	<b>1.2</b>	<b>3.3</b>
IBC 101	none	N	2	6.76	3.8	12.8	66.0	4.6	1.1	4.5
<b>IBC 101</b>	<b>none</b>	<b>Y</b>	<b>2</b>	<b>6.76</b>	<b>2.4</b>	<b>4.9</b>	<b>72.5</b>	<b>4.8</b>	<b>1.1</b>	<b>4.0</b>
IBC 101	none	N	3	4.49	3.3	12.6	65.3	4.2	1.0	4.4
<b>IBC 101</b>	<b>none</b>	<b>Y</b>	<b>3</b>	<b>4.49</b>	<b>1.6</b>	<b>5.8</b>	<b>71.6</b>	<b>4.8</b>	<b>1.1</b>	<b>3.5</b>
IBC 101	cryo	N	0	NA	12.2	9.6	70.4	3.9	1.1	4.3
IBC 101	cryo	N	1	11.79	8.1	10.8	69.9	4.1	1.1	4.4
<b>IBC 101</b>	<b>cryo</b>	<b>Y</b>	<b>1</b>	<b>11.79</b>	<b>4.1</b>	<b>5.0</b>	<b>74.3</b>	<b>4.9</b>	<b>1.2</b>	<b>3.5</b>
IBC 101	cryo	N	2	6.43	3.7	10.9	67.9	4.3	1.0	4.3
<b>IBC 101</b>	<b>cryo</b>	<b>Y</b>	<b>2</b>	<b>6.43</b>	<b>5.2</b>	<b>6.2</b>	<b>75.0</b>	<b>4.8</b>	<b>1.2</b>	<b>3.5</b>
IBC 101	cryo	N	3	4.85	3.6	10.7	66.8	4.2	0.9	4.3
<b>IBC 101</b>	<b>cryo</b>	<b>Y</b>	<b>3</b>	<b>4.85</b>	<b>3.6</b>	<b>4.9</b>	<b>73.9</b>	<b>4.9</b>	<b>1.2</b>	<b>3.5</b>

Table 3. Ash contents after HF/HCl and LAH treatments.

run #	Treatment type	dry ash %
1	none	10.8
2	HF/HCL one treatment (24hours at room temp.)	3.25
3	HF/HCL two treatments (24hours at room temp.)	1.77
4	HF/HCL (run 2) then LAH for 60 minutes at 67°C	1.29
5	HF/HCL (run 2) then LAH for 12 hours 67°C	1.25
6	Run 5 then HF/HCl (24hours at room temp.)	1.09

Table 4. Elemental composition of micronized and demineralized coal samples.

COAL	PRETREATMENT	C	H	N	S
101	MICRONIZED	77.8	5.0	1.3	3.5
101	DEMINERALIZED	78.1	5.2	1.2	3.6

Table 5. Oxidation conditions and results obtained in Task 2.

Table 6. Oxidation conditions and results obtained in Task 3.

Table 7. The influence of fultrasonic conditions introduced during the oxidation step

Run	Coal	Temp	Time (hr)	Flow rate ml/min	Oxidant	Catalyst	Catalyst Loading	Soak Time (hr)	Soak Temp	Media	Sample wt.	Moisture	S	Dry Ash	Dry Yield	S Dry	Dry S Ash Free
UL X1	101 LAH	b.p.	1	600	oxygen	TBAH	20%	NA	NA	water	5	7.1	3.3	0.4	96	3.6	3.6
UL X2	101 LAH	b.p.	1	600	oxygen	TBAH	20%	NA	NA	methanol	5	6.3	3.4	0.5	94	3.6	3.6
UL X3	101 LAH	b.p.	1	600	oxygen	TBAH	20%	NA	NA	THF	5	6.2	3.3	0.5	97	3.6	3.6

Table 8. Base desulfurization results for oxidation products formed in Task 2.

Run	temp (°C)	time (hr)	NaOH (g)	MeOH (ml)	moisture %	dry ash	dry yield	dry S	dry S ash free
BPD1R	350	1	1	7.5	1.9	10.1	84.6	2.08	2.31
BPD2	350	1	0.5	7.5	2.1	10.0	71.9	2.08	2.32
BPD3	350	1	1	7.5	3.9	7.4	69.7	2.09	2.26
BPD4R	350	1	1	7.5	2.9	8.1	74.3	2.06	2.24
BPD5	350	1	1	7.5	2.3	5.6	76.2	1.92	2.04
BPD6	350	1	1	7.5	5.2	9.0	73.9	1.91	2.10
BPD7	350	1	1	7.5	4.8	9.1	66.3	2.11	2.32
BPD8	350	1	0.15	7.5	2.1	8.9	73.9	2.02	2.22
BPD9	350	1	1	7.5					
BPD10	350	1	1	7.5	4.2	7.6	70.7	1.95	2.11
BPD 11	350	1	0.15	7.5	2.5	9.7	86.3	1.88	2.08
BPD 12	350	1	0.15	7.5	3.7	14.5	84.7	2.19	2.56
BPD 13	350	1	0.15	7.5	3.3	8.9	84.3	1.88	2.07
BPD 14	350	1	0.15	7.5	2.6	9.7	86.2	1.88	2.08
BPD 15	350	1	0.15	7.5	1.8	10.4	82.3	1.80	2.01
BPD 16	350	1	0.15	7.5	3.6	14.7	89.0	2.23	2.62
BPD 17	350	1	0.15	7.5	1.7	16.7	82.4	1.81	2.16
BPD 18	350	1	0.15	7.5	2.2	10.0	82.9	1.80	1.97
BPD 19	350	1	0.15	7.5	3.2	9.3	87.4	1.89	2.08
BPD 20	350	1	0.15	7.5	2.3	8.7	83.7	1.86	2.04
BPD 21	350	1	0.15	7.5	0.8	10.5	89.1	1.90	2.12
BPD 22	350	1	0.15	7.5	0.1	10.9	89.9	1.84	2.07
BPD 23	350	1	0.15	7.5	2.6	10.2	84.8	1.89	2.10
BPD 24	350	1	0.15	7.5	3.5	8.3	83.6	1.85	2.02
BPD 25	350	1	0.15	7.5	3.3	7.8	85.5	1.89	2.05
BPD 26	350	1	0.15	7.5	3.1	10.6	85.6	1.82	2.03
BPD 27	350	1	0.15	7.5	2.2		86.2	2.00	
BPD 28	350	1	0.15	7.5	3.1		84.1	1.92	
BPD 29	350	1	0.15	7.5	4.2		89.3	1.95	
BPD 30	350	1	0.15	7.5	3.3		80.0	2.00	
BPD 31	350	1	0.15	7.5	2.6		82.1	1.93	
BPD 32	350	1	0.15	7.5	3.6		81.6	2.10	
BPD 33	350	1	0.15	7.5	2.5		88.7	1.88	
BPD 34	350	1	0.15	7.5	1.1		86.5	1.85	
BPD 35	350	1	0.15	7.5	0.9		84.4	1.86	
BPD 36	350	1	0.15	7.5	2.1		86.7	1.96	
BPD 37	350	1	0.15	7.5	2.4		88.1	2.03	
BPD 38	350	1	0.15	7.5	2.3		90.1	2.02	

Table 9. Base desulfurization results for oxidation products formed in Task 3.

Run	temp deg(C )	time (hr)	NaOH (g)	MeOH (ml)	moisture %	dry ash	dry yield	dry S	dry S ash free
APD1R	350	1	0.15	7.5	2.1	7.4	78.6	2.15	2.32
APD2	350	1	0.15	7.5	1.8	9.6	82.9	2.07	2.29
APD3	350	1	0.15	7.5	2.1	8.5	82.9	2.08	2.28
APD4R	350	1	0.15	7.5	1.6	9.0	81.4	2.15	2.37
APD5	350	1	0.15	7.5	1.5	10.4	79.6	2.05	2.29
APD6	350	1	0.15	7.5	2.3	10.2	79.7	2.14	2.38
APD7	350	1	0.15	7.5	1.5	10.8	81.5	2.07	2.32
APD8	350	1	0.15	7.5	2.3	8.5	80.5	2.09	2.28
APD9	350	1	0.15	7.5	2.7	9.4	77.1	2.11	2.32
APD10	350	1	0.15	7.5	2.6	8.5	79.9	2.16	2.36
APD 11	350	1	0.15	7.5	2.4	10.1	76.0	2.11	2.35
APD 12	350	1	0.15	7.5	2.3	9.5	80.9	2.09	2.31
APD 13	350	1	0.15	7.5	2.5	9.2	82.2	2.10	2.32
APD 14	350	1	0.15	7.5	1.6	8.5	78.6	1.99	2.18
APD 15	350	1	0.15	7.5	2.1	8.6	79.3	2.05	2.25
APD 16	350	1	0.15	7.5	1.6	8.9	82.2	2.11	2.32
APD 17	350	1	0.15	7.5	2.2	10.0	75.1	2.07	2.30
APD 18	350	1	0.15	7.5	1.7	10.6	81.8	2.07	2.31
APD 19	350	1	0.15	7.5	4.7	8.0	66.3	2.10	2.28
APD 20	350	1	0.15	7.5	3.8	1.0	76.3	2.20	2.23
APD21	350	1	0.15	7.5	4	8.8	75.2	2.10	2.31
APD 22	350	1	0.15	7.5	3.4	1.7	76.3	2.12	2.16
APD 23	350	1	0.15	7.5	3.2	3.0	82.6	2.40	2.47
APD 24	350	1	0.15	7.5	2.5	1.4	78.0	2.42	2.46
APD 25	350	1	0.15	7.5	3.6	5.4	69.7	2.21	2.34
APD 26	350	1	0.15	7.5	3.8	5.0	79.0	2.41	2.54
APD 27	350	1	0.15	7.5	2.7	1.2	78.1	2.28	2.31
APD 28	350	1	0.15	7.5	2.6	2.6	70.4	2.34	2.40
APD 30	350	1	0.15	7.5	2.7	1.5	77.6	2.29	2.32
APD 31	350	1	0.15	7.5	2.7	3.5	75.2	2.33	2.42

Table 10. Base desulfurization results for ultrasonically treated samples.

Run	Date	Temp (°C)	Time (hr)	NaOH (g)	Methanol (ml)	Moisture	Ash	S
ULD1		350	1	0.15	7.5	3.1	1.4	2.15
ULD2		350	1	0.15	7.5	3.7	1.9	2.16
ULD3		350	1	0.15	7.5	2.8	1.7	2.12



Table 11. Fly ash and scrubber sludge desulfurization conditions

run	agent	solution	moisture	dry ash	yield	S (%dry)	Sulfur reduction
SP1	none	water	2.2	11.1	81%	3.8	15%
SP2	NaOH	water	2.6	11.4	85%	3.3	26%
SP3	fly ash	water	1.9	18.6	96%	3.4	13%
SP4	scrub.s	water	2.1	10.8	81%	7.3	-64%
SP5	none	MeOH	1.2	11.7	82%	2.5	42%
SP6	NaOH	MeOH	12.1	8.0	93%	1.8	59%
SP7	fly ash	MeOH	17.8	25.6	97%	2.7	21%
SP8	scrub.s	MeOH	1.9	12.1	87%	3.3	25%

Table 12. Bulk chemical composition of fly ash determined by SEM-EDAX.

Element	Wt%	Formula	Oxide %
Na	0.86	Na <sub>2</sub> O	1.16
Mg	0.26	MgO	0.43
Al	10.32	Al <sub>2</sub> O <sub>3</sub>	19.50
Si	23.86	SiO <sub>2</sub>	51.04
S	1.18	SO <sub>3</sub>	2.94
K	1.86	K <sub>2</sub> O	2.24
Ca	3.17	CaO	4.44
Ti	0.84	TiO <sub>2</sub>	1.39
Fe	11.79	Fe <sub>2</sub> O <sub>3</sub>	16.85
O	45.87		