DOE/PC/92521--T291

FINAL TECHNICAL REPORT
September 1, 1995, through August 31, 1996

Project Title: **DESULFURIZATION OF ILLINOIS COALS WITH HYDROPEROXIDES OF VEGETABLE OILS AND ALKALI**

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 4)
ICCI Project Number: 95-1/1.1D-2P
Principal Investigator: Gerard V. Smith, SIU
Other Investigators: Ricky D. Gaston, SIU
Ruozhi Song, SIU
Jianjun Cheng, SIU
Feng Shi, SIU
Yaguang Wang, SIU
Project Manager: Ken K. Ho, ICCI

ABSTRACT

The goal of this project is to develop an inexpensive method to remove organic sulfur from pyrite-free and mineral-free coal using base, air, and readily available farm products. This is accomplished by treating coals with alkali, impregnating coals with polyunsaturated oils, converting the oils to their hydroperoxides, and heating. Since these oils are relatively inexpensive and easily applied, this project could lead to a cost effective method for removing organic sulfur from coals. Moreover, the oils are environmentally safe; they produce no noxious products and improve burning qualities of the solid products.

IBC-108 coal, (contains only 0.4% pyrite and 2.7% organic sulfur) was first treated with NaOH at two different concentrations and four different times, and with NH_4OH at two different concentrations and two different temperatures. Pretreating IBC-108 coal with bases removes 13% to 23% of the sulfur, and NaOH is a better treatment than NH_4OH in most of the experiments. Higher temperatures, higher base concentrations, and longer treatment times remove more sulfur. Na_2CO_3 is more effective than NaOH for oil extraction after the oil treatment.

To test for effectiveness of sulfur removal, eight coal samples were treated with NaOH (two concentrations at four different times) were further treated with linseed oil at three temperatures, four different times, and two oil to coal ratios. The combination of NaOH pretreatment, then oil treatment, followed by Na_2CO_3 extraction, removes 23% to 50% of the sulfur. The best result is achieved by pretreating with 5% NaOH for 20 hr (23% sulfur removal) followed by oil treatment at 100°C for 5 hr with a 1:1 oil to coal ratio (50% sulfur removal in total). More sulfur is removed with a 1:1 oil to coal ratio than a 1:10 ratio under most conditions. However, the effects of time of oil treatment are complex. Sulfur removal is favored by longer oil treatment in some cases, but disfavored in other cases. This demonstrates that other experimental parameters are important, such as temperature, concentration of base, time of base pretreatment, and oil to coal ratio.

EXECUTIVE SUMMARY

This project proposes to remove organic sulfur from coal, maintain its BTU, and increase its volatiles, by a new process of pretreating with alkali and impregnating with polyunsaturated vegetable oils. Catalyzed by coal, air converts these oils into their hydroperoxides which are powerful oxidizing agents. A similar agent, peroxyacetic acid, has shown in a previously funded ICCI project to desulfurize coal. But polyunsaturated vegetable oils have advantages which make them attractive for treating coal. First, these compounds are inexpensive, renewable natural products available from Illinois farms; second, they possess chemical properties which can be directed toward oxidizing organic sulfur; third, they furnish carbonaceous residues which will increase BTU's and volatiles; and fourth, they are environmentally safe and produce no noxious products.

Preliminary experiments at SIUC have shown that IBC-108 coal impregnated with linseed oil and heated in air at 50-100°C has its organic sulfur removed. The results show that coal catalyzes formation of hydroperoxides in the oil and these hydroperoxides oxidize the organic sulfur with minimum loss of BTU. Additionally, experiments have shown that pretreating IBC-108 coal with NaOH increases the amount of organic sulfur removed during subsequent treatment with linseed oil. This project proposes to build on this new evidence to aim at a technically feasible and economically viable process step.

Three tasks are proposed: **Task 1** will select the base for pretreating and extraction. Tests will examine NaOH and NH_4OH at two different concentrations followed by treatment with linseed oil at 100°C for 15 hours, then extraction with two different bases, NaOH and Na_2CO_3.. **Task 2** will determine the ability of the above selected base in combination with linseed oil to remove organic sulfur from IBC-108 coal. Tests of base pretreatment will be conducted at 25°C, two different concentrations, and four different times. Tests of oil treatment will be conducted at two different oil:coal ratios, three different reaction times, three different temperatures, and with two different extraction solutions. This task will produce 144 experiments with accompanying plots of sulfur removal as function of temperature and time and will be used to study reaction rates and the mechanism of sulfur removal. **Task 3** will determine the mass balance along with the volatiles and BTU changes from the experiments in Tasks 1 and 2 creating a data base of 152 analyses of mass balances, volatiles, and BTU's along with plots of their dependence on temperature and time. All of these data will be examined for clues to the mechanism of organic sulfur oxidation and removal from Illinois coals.

During the first quarter we completed screening of the bases for pretreating the coal and for extracting the oil after oil treatment. The bases selected for the pretreatment are NaOH and NH_4OH with two concentrations (5% and 1%) each and for the oil extraction are 5%NaOH ad 5%Na_2CO_3. The pretreatmets were carried out at either 25°C or 100°C for 15 hours.

Conclusions reached during the first quarter were that pretreating IBC-108 coal with bases removes 13% to 23% of the sulfur. NaOH is a better treatment than NH_4OH in

DISCLAIMER

most experiments and Na_2CO_3 is better than NaOH for the final extraction. Higher temperatures and higher base concentrations remove more sulfur. Thereby, treatments with 5% NH_4OH at 100°C in the presence of bubbling O_2 or with 5% NaOH at 25°C remove more sulfur (21-23%) than any other treatment with alkali alone. However, even more sulfur is removed from the pretreated coal by linseed oil treatment followed by base extraction. And the best results (about 40% sulfur removal) are obtained with the combinations of 5% NaOH-OIL-5%Na_2CO_3 (B-O-C), 1% NH_4OH-OIL-5%Na_2CO_3 (N1-O-C), and 5% NH_4OH (100°C)-OIL-5% Na_2CO_3 (N_{100}-O-C). Based on these results, NaOH was selected for pretreating the coal and Na_2CO_3 was selected for the oil extraction in the later experiments.

During the second quarter we tested the ability of the selected base (NaOH) in combination with linseed oil to remove organic sulfur from IBC-108 coal. Tests of NaOH pretreatment were performed at 25°C with two base concentrations (5% and 1% NaOH) at four different times (20hr, 10hr, 5hr, and 1hr). Tests of oil treatment were conducted at 125°C for three different times (20hr, 10hr and 5hr) with two different ratios of oil:coal (1:1 and 1:10).

The conclusions reached during the second quarter were that about 17% to 23% of sulfur is removed under these conditions, the sulfur removal is slightly favored by higher base concentration and longer time, more sulfur is removed from the NaOH pretreated coal by linseed oil treatment followed by Na_2CO_3 extraction. The best result (43% sulfur removal) is given by pretreating the coal with 1% NaOH for either 1hr or 5hr followed by oil treatment for 5hr with 1:1 oil to coal ratio.

During the third and the final quarters more experimental parameters were systematically varied to determine the effectiveness of linseed oil and NaOH for sulfur removal from IBC-108 coal. The eight coal samples pretreated with NaOH were further treated with linseed oil at 100°C and 75°C for three different times (20hr, 10hr, and 5hr) and two oil to coal ratios (1:1 and 1:10). The BTU's were measured for all the samples.

The combinations of NaOH pretreatment, then oil treatment followed by Na_2CO_3 extraction remove 23% to 50% sulfur form the IBC-108 coal. The best result is achieved by pretreating with 5% naOH for 20 hr (23% sulfur removal) followed by oil treatment at 100°C for 5 hr with a 1:1 oil to coal ratio (50% sulfur removal in total, exp.93). More sulfur is removed with a 1:1 oil to coal ratio than a 1:10 ratio under most conditions of the investigation. The effects of time of oil treatment are complex. Sulfur removal is favored by longer oil treatment in some cases, but disfavored in other cases. This demonstrates that other experimental parameters are important, such as temperature, concentration of base, time of base pretreatment, and oil to coal ratio.

The conclusions reached during the final two quarters were that up to 50% sulfur is removed from the IBC-108 coal, the BTU loss is minimal, sulfur removal is favored by high oil to coal ratio, but the effects of other experimental parameters is very complex.

OBJECTIVES

The goal of this project is to develop a cost effective method to remove organic sulfur from pyrite-free and mineral-free coal. The objective is to test the feasibility of using alkali and inexpensive, renewable farm products to desulfurize Illinois coals. The specific objectives of this project are:

1. determine the ability of alkali and oils to remove organic sulfur from Illinois coals,

2. establish the volatile and BTU changes from treating Illinois coals with alkali and oils,

3. establish the mass balance of solids, liquids, and gases resulting from treating Illinois coals with alkali and oils, and

4. study the reaction rate(s) and mechanism(s) of sulfur removal from Illinois coals treated with alkali and oils.

Briefly the tasks scheduled for the current year are:

Task 1. *Selection of base for pretreatment and extraction*

Task 2. *Determination of base and linseed oil ability to remove organic sulfur form IBC-108 coal*

Task 3. *Determination of mass balance, volatiles, and BTU*

INTRODUCTION AND BACKGROUND

Relevance to Illinois Basin Coal Problem and Unique Aspects

This project is relevant to solving the problem of high sulfur content of Illinois coals. Its significance rests on its use of inexpensive farm materials to neutralize organic sulfur in Illinois coals.

The potential importance of this project is its impact on the marketability of Illinois coals. Producing clean products from coal will add to the economic importance of coal. This project has the potential of utilizing cheap, renewable farm products for enhancing coal conversion process, especially for removing sulfur and thereby upgrading solid products.

The unique aspect of this project is its use of inexpensive farm products, such as linseed oil ($0.28/LB) and other vegetable oils, to achieve desulfurization and upgrade char. These farm products are cheap enough that they need not be recycled, rather, they enrich the coal conversion products. On an equivalent weight basis (gram molecular weight per hydroperoxy group), linseed oil with maximum hydroperoxy groups contains about 86% the oxidizing ability of peroxyacetic acid. Yet the cost of each hydroperoxy group in linseed oil is only 23% the cost of each hydroperoxy group in peracetic acid. Therefore this project has the unique aspects not only of being environmentally safe, disrupting the coal matrix, increasing volatiles, oxidizing the sulfur, and adding carbon, oxygen, and hydrogen to the char, but also of being less expensive than peroxyacetic acid.

Background

Each year Illinois farms produce millions of tons of usable and unusable materials which are easily collected, easily transported, and readily available near Illinois coal mining districts. These materials consist mainly of carbohydrates, fats, and oils, which contain hydrogen and oxygen, elements in low concentrations in coals. Therefore, these materials are potentially valuable for coal conversion processes.

There are good reasons for exploring carbohydrates, fats, and oils as participants in coal conversion reactions. First, these compounds are inexpensive and renewable natural products available from Illinois farms; second, they possess chemical properties which can be directed toward oxidizing organic sulfur; third, they furnish carbonaceous residues which will increase BTU's of coal char; and fourth, they are environmentally safe and produce no noxious products.

Hydrogen in some form is frequently added during coal conversion processes. Besides adding hydrogen as H_2 gas or as some readily dehydrogenatable molecule, such as tetralin, hydrogen has been added in the form of other hydrogen-rich organic molecules, such as ethanol and methane[1-3]. Other rich sources of hydrogen are fats and oils from vegetable and animal materials. Carbohydrates likewise contain hydrogen, although not as much on a molar basis as fats and oils. But, carbohydrates contain much more oxygen than fats and oils on a molar basis.

Using carbohydrates as well as fats and oils as sources of oxygen may be beneficial to pyrolysis and desulfurization because small amounts of oxygen seem to increase desulfurization. For example, ICCI funded coal treatments with methane/oxygen[2], ethanol[3], lignin[4], a proprietary oxidant[5], and air[5,6] are all processes in which oxygen, either added or present in the reactants, is beneficial to pyrolysis and desulfurization. Therefore, their oxygen contents make carbohydrates, fats, and oils likely candidates for enhancing coal conversion processes. Moreover, their oxygen may become incorporated into the products and increase their octane ratings. So using carbohydrates, fats, and oils makes chemical sense as sources of oxygen in coal conversion processes.

However, using carbohydrates, fats, and oils merely as sources of hydrogen, carbon, and oxygen is overlooking important coal desulfurization chemistry. For example, fats and oils contain labile allylic hydrogens which react with oxygen in air to form hydroperoxides. These hydroperoxides lead to rancidity, and some oils are so prone to this reaction that radical inhibitors are regularly added to preserve them for the food market. Thus oils can be converted into powerful oxidizing agents by forming hydroperoxides, and these can oxidize organic and inorganic sulfur in coals.

Formation of hydroperoxides in oils occurs from the reaction of singlet oxygen at allylic positions on unsaturated fatty acids. But singlet oxygen is not ordinary oxygen. Singlet oxygen is the excited state of ground-state oxygen (a triplet) and is formed in very low concentrations in air by action of light. Singlet oxygen is not formed in high concentrations because triplet oxygen does not readily absorb energy from light. Thus the rate of formation of hydroperoxides is ordinarily slow in air.

However, the rate of formation can be greatly increased by increasing the concentration of singlet oxygen through photosensitization. Photosensitization methods employ a photosensitizer molecule which absorbs energy from light and transfers that energy to triplet oxygen, raising it into the excited singlet state. Photosensitizers need be present in only low concentrations, so one of the tasks in the 1994-5 project was to test standard photosensitizers and **coal as a sensitizer**.

Results have shown that coal is indeed a sensitizer, perhaps because it contains radicals[7,8,9], which apparently directly convert triplet to siglet oxygen. During the first five months of the current funded project, we have found that coal alone amply catalyzes the formation of hydroperoxides in linseed oil. (We chose linseed oil for tests because it is readily available at the grocery store and relatively rich in polyunsaturated fats, such as glyceryl oleate, and glyceryl linoleate.) In fact, formation of hydroperoxides in the presence of coal equals that in the presence of a known photosensitizer and ultraviolet light. Apparently, coal is a very good singlet oxygen initiator.

We tested the ability of coal to sensitize oxygen in air and produce hydroperoxy groups in linseed oil because these hydroperoxy groups are powerful oxidizing agents. Similar powerful oxidizing agents, such as peroxyacetic acid, had been used in earlier ICCI funded projects to desulfurize coal[10,11]. Moreover, similar methods are well known for oxidizing organic sulfur to sulfate[12-15]. Since hydroperoxides possess about the same oxidizing ability as peracids, it is reasonable to investigate inexpensive hydroperoxides from vegetable oils for desulfurizing coals.

But do linseed oils actually desulfurize coals? To determine whether any coal desulfurization actually occurred we conducted the following experiments: A thin coat of linseed oil was placed on 5g of IBC-108 coal by making a slurry of the coal in a solution of the weighed oil in 30 mL of chloroform and then evaporating the chloroform. The oil-coal mixture was spread uniformly on a petri dish, which was floated on a constant temperature bath at either 100°C or 50°C with or without UV irradiation for 18hrs. The reaction mixture was extracted with 50 mL of tetrahydrofuran and chloroform, the coal was dried, and its sulfur content determined. Clearly, merely treating the coal with linseed oil removes some organic sulfur. Ultraviolet irradiation improves sulfur removal, but increasing the temperature removes more.

In order to remove the oil from the coals so sulfur analyses could be performed, we treated the reacted oil-coal mixture with NaOH. This hydrolyses the oil into the sodium salt of the fatty acids (soap) and glycerol, both of which are water soluble. During experimentation with various procedures, we discovered that pretreatment of the coal with NaOH resulted in subsequently better sulfur oxidation by the impregnated linseed oil. Clearly, pretreatment with NaOH influences the coal matrix such that it is more susceptible to oil impregnation and sulfur oxidation.

Bases, especially NH_4OH, are known to modify coal matrices by chemical comminution[17]. And NH_4OH has been used to pretreat coal before oxidation with NaOCl (sodium hypochlorite) followed by Na_2CO_3 extraction in a procedure for removing organic sulfur from coals[18]. Therefore, this project proposes to test both NaOH and NH_4OH as pretreatments of IBC-108 coal followed by treatment with the hydroperoxides of linseed oil and extracted with NaOH or Na_2CO_3.

Linseed oil has been and will continue to be preferentially used in this project because it is inexpensive, can be easily sprayed on coal, and possesses a high degree of unsaturation. Its main unsaturated groupings are the linolenate group (approximately 58%) which contains three double bonds and the linoleate group (approximately 27%) which contains two double bonds. So approximately 85% of linseed oil is composed of these highly unsaturated groupings.

In summary, adding oils to coals offers:

1. ***in situ* formation of hydroperoxides**, which are powerful oxidizing agents that can oxidize organic sulfur and lead to coal detoxification,

2. **environmental safety of zero discharge**; the oil need not be removed but can remain with the coal, and no noxious products will be formed,

3. **increased volatiles**; the oil will produce volatiles which will enhance the burning qualities of the treated coal,

4. **increased hydrogen content**; the high hydrogen content of the oils will be available to the coal,

5. **increased BTU**; the oils furnish carbon and hydrogen which will increase the heat content of the coal,

6. **decreased costs**; in pure form and truck load quantities these oils can be purchased for $0.28/LB; however, in raw form and tank car quantities the price will be much less. Eliminating purification steps necessary for current markets will reduce the cost of oils, and

7. **ease of use**; vegetable oils should be easily added to coals by simply spraying a thin film on finely divided coal.

EXPERIMENTAL PROCEDURES

Description of Work Proposed

Task 1. *Selection of base for pretreatment and extraction*

Screening of the base to use for pretreating the coal will be conducted in a systematic way: Eight 5 g portions (four pairs) for IBC-108 coal will be immersed for 10 hours at 25°C by pairs in one of the following aqueous solutions: 1% NaOH, 5% NaOH, 1% NH_4OH, or 5% NH_4OH. These eight pretreated portions of coal will each be washed with distilled water until the wash waters are neutral and the dried and treated with linseed oil for 20 hours at 100°C. One member of each pair will them be washed with a solution of 5% NaOH, followed by washings with water and organic solvents, and the other member of the pair will be washed with a solution of 5% Na_2CO_3, followed by washings with water and organic solvents. Sulfur analyses will be obtained on each sample before and after oil treatment, such that comparisons can be made between the samples treated with base only and the same samples receiving the full treatment. Based on which base produces the lowest sulfur content, one base, either NaOH or NH_4OH, will be chosen for pretreating coal and one washing solution, either *aq*NaOH or *aq*Na_2CO_3, will be chosen for washing the oil-treated samples in the next task.

Task 2. *Determination of base and linseed oil ability to remove organic sulfur from IBC-108 coal*

We will test different methods of using linseed oil to remove sulfur and IBC-108 coal. This is the coal from the Illinois Basin Coal Sample Program maintained in Champaign by the Illinois State Geological Survey. Its descriptions are shown in Table 1. Best conditions for the full treatment will be narrowed by a series of 144 experiments in which 5 g portions of IBC-108 coal are treated variously with two concentrations of base at four different temperatures followed by treatment with linseed oil (two different ratios of oil:coal) at three different temperatures for three different times, and finally washed in either NaOH or Na_2CO_3 (depending on which is chosen in Task1) and organic solvents. Mass balances will be obtained on all experiments; sulfur, volatiles, and BTU analyses will be obtained from the Department of Mechanical Engineering at SIUC.

Table 1. Descriptions of IBC-108 Coals

IBC 108. This is a micronized blend of Herrin and Springfield coals (80% and 20%, respectively) cleaned by an advanced froth flotation process (microbubble column flotation) in 1988. It is delivered to requesters as a filter cake (approximately 45% moisture). It is ideal for investigators wishing to use a deep-cleaned Illinois coal with low pyrite content.

Coal analyses (%, moisture free basis except moisture).

	Avg.	SD
Vol. Matter	41.6	0.57
Fixed Carbon	54.7	0.58
H-T Ash	3.7	0.19
Carbon	76.0	0.34
Hydrogen	5.2	0.31
Nitrogen	1.5	0.11
Oxygen	10.9	0.59
Total C	0.0	0.03
Total Sulfur	2.7	0.07
Sulfatic	0.0	0.03
Pyritic	0.4	0.07
Organic	2.3	0.09
TU/lb	13726	66.33
FSI	3.2	0.78

Task 3. *Determination of mass balance, volatiles, and BTU*

Task 3 will furnish information about how mass balance, volatiles, and BTU vary with the conditions in Task 2. This information will tell how much coal is extracted in the process and furnish a way to correct sulfur, volatiles and BTU analyses for changes in mass of the coal during the process. By comparing the rates of change of mass, sulfur contents, volatiles, and BTU it will be possible to evaluate the feasibility of the process.

RESULTS AND DISCUSSION

IBC-108 coal was pretreated with alkali solutions by suspending 20 g of the coal in 150 mL of 5% or 1% aqueous NaOH solution at 25°C for 1hr, 5hr, 10hr, or 20hr, and the suspension was stirred constantly. Then the coal sample was collected *via* vacuum filtration, thoroughly washed with distilled water until the filtrate is neutral, and then dried at 120°C for 24 hours. A portion of the sample was submitted for sulfur and BTU analyses and the rest of the sample was treated with linseed oil. The sulfur contents for the NaOH treated coal are listed in Table 2 (exps. 1,2, 19-27).

Testing for effectiveness of sulfur removal consisted of the following procedure: a thin layer of linseed oil was placed on the coal in a petri dish first by making a slurry of the base-pretreated coal in a solution of oil in hexane and then by evaporating the hexane.

Table 2. % S Remaining in IBC-108 Coal After Pretreatment with NaOH Followed by Linseed Oil Treatment

	NaOH PRETREATMENT			OIL TREATMENT				RESULTS	
Exp. No	NaOH (%)	Time (hr)	Temp (°C)	Oil:Coal	Time (hr)	Temp (°C)	Sulfur (%)	% Removal	BTU (/lb.)
1	5%	15	25				2.04	22.7	11,800
2	1%	15	25				2.14	18.9	12,251
3	5%NH_3	15	25				2.19	17.0	12,905
4	1%NH_3	15	25				2.29	13.3	13,045
5	5%NH_3	15	100				2.08	21.2	12,047
6	5%NH_3/O_2	15	100				2.04	22.7	11,985
7*	5%	15	25	1:1	20	100	1.80	31.8	11,809
8	5%	15	25	1:1	20	100	1.60	39.4	12,089
9*	5%NH_3/O_2	15	100	1:1	20	100	1.77	33.0	11,676
10	5%NH_3/O_2	15	100	1:1	20	100	1.66	37.1	11,835
11*	5%NH_3	15	25	1:1	20	100	1.92	27.3	11,825
12	5%NH_3	15	25	1:1	20	100	1.79	32.2	12,258
13*	1%	15	25	1:1	20	100	1.95	26.1	11,986
14	1%	15	25	1:1	20	100	1.79	32.2	12,369
15*	1%NH_3	15	25	1:1	20	100	1.96	25.8	12,964
16	1%NH_3	15	25	1:1	20	100	1.61	39.0	13,125
17*	5%NH_3	15	100	1:1	20	100	1.80	31.8	11,948
18	5%NH_3	15	100	1:1	20	100	1.58	40.2	12,136
19	5%	20	100				2.06	22.0	11,578
20	5%	20	25				2.03	23.1	11,986
21	5%	10	25				2.05	22.3	12,137
22	5%	5	25				2.09	20.8	12,096
23	5%	1	25				2.16	18.2	12,375
24	1%	20	25				2.09	20.8	12.089
25	1%	10	25				2.15	18.6	12,253
26	1%	5	25				2.16	18.2	12,650
27	1%	1	25				2.20	16.7	13,005
28	5%	20	100	1:1	20	125	1.69	36.0	11,863
29	5%	20	25	1:1	20	125	1.85	29.9	11,985
30	5%	10	25	1:1	20	125	1.77	33.0	12,347
31	5%	5	25	1:1	20	125	1.77	33.0	12,156
32	5%	1	25	1:1	20	125	1.76	33.3	12,998
33	1%	20	25	1:1	20	125	1.83	30.7	12,036
34	1%	10	25	1:1	20	125	1.75	33.7	12,985
35	1%	5	25	1:1	20	125	1.71	35.2	12,794
36	1%	1	25	1:1	20	125	1.59	39.8	13,158
37	5%	20	25	1:1	10	125	1.90	28.0	12,653
38	5%	10	25	1:1	10	125	1.81	31.4	12,135
39	5%	5	25	1:1	10	125	1.83	30.7	12,634
40	5%	1	25	1:1	10	125	1.85	29.9	12,897
41	1%	20	25	1:1	10	125	1.89	28.4	11,761
42	1%	10	25	1:1	10	125	1.74	34.1	11,938
43	1%	5	25	1:1	10	125	1.73	34.5	12,937
44	1%	1	25	1:1	10	125	1.66	37.1	12,658

45	5%	20	25	1:1	5	125	1.81	31.4	13,169
46	5%	10	25	1:1	5	125	1.72	34.8	12,697
47	5%	5	25	1:1	5	125	1.68	36.4	12,875
48	5%	1	25	1:1	5	125	1.65	37.5	13,015
49	1%	20	25	1:1	5	125	1.80	31.8	11,669
50	1%	10	25	1:1	5	125	1.59	39.8	12,348
51	1%	5	25	1:1	5	125	1.51	42.8	13,251
52	1%	1	25	1:1	5	125	1.52	42.4	12,985
53	5%	20	25	1:10	20	125	1.82	31.1	13,057
54	5%	10	25	1:10	20	125	1.78	32.6	12,985
55	5%	5	25	1:10	20	125	1.78	32.6	12,369
56	5%	1	25	1:10	20	125	1.82	31.1	12,195
57	1%	20	25	1:10	20	125	1.89	28.4	12,087
58	1%	10	25	1:10	20	125	1.97	25.4	13,256
59	1%	5	25	1:10	20	125	1.90	28.0	12,348
60	1%	1	25	1:10	20	125	1.90	28.0	12,690
61	5%	20	25	1:10	10	125	1.87	29.2	11,895
62	5%	10	25	1:10	10	125	1.78	32.6	12,037
63	5%	5	25	1:10	10	125	1.83	30.7	12,945
64	5%	1	25	1:10	10	125	1.85	29.9	12,456
65	1%	20	25	1:10	10	125	1.78	32.6	12,621
66	1%	10	25	1:10	10	125	1.86	29.5	13,005
67	1%	5	25	1:10	10	125	1.81	31.4	12,453
68	1%	1	25	1:10	10	125	1.82	31.1	12,760
69	5%	20	25	1:10	5	125	1.89	28.4	13,010
70	5%	10	25	1:10	5	125	1.85	29.9	11,985
71	5%	5	25	1:10	5	125	1.85	29.9	12,798
72	5%	1	25	1:10	5	125	1.86	29.5	12,698
73	1%	20	25	1:10	5	125	1.67	36.7	12,649
74	1%	10	25	1:10	5	125	1.83	30.7	11,548
75	1%	5	25	1:10	5	125	1.76	33.3	12,679
76	1%	1	25	1:10	5	125	1.79	32.2	13,059
77	5%	20	25	1:1	20	100	1.73	34.5	13,198
78	5%	10	25	1:1	20	100	1.76	33.3	12,597
79	5%	5	25	1:1	20	100	1.46	44.7	12,364
80	5%	1	25	1:1	20	100	1.53	42.0	13,037
81	1%	20	25	1:1	20	100	1.62	38.6	12,789
82	1%	10	25	1:1	20	100	1.55	41.3	12,356
83	1%	5	25	1:1	20	100	1.46	44.7	11,942
84	1%	1	25	1:1	20	100	1.67	36.7	11,395
85	5%	20	25	1:1	10	100	1.53	42.0	12,616
86	5%	10	25	1:1	10	100	1.56	40.9	12,359
87	5%	5	25	1:1	10	100	1.61	39.0	12,895
88	5%	1	25	1:1	10	100	1.57	40.5	12,315
89	1%	20	25	1:1	10	100	1.61	39.0	12,988
90	1%	10	25	1:1	10	100	1.84	30.3	12,693
91	1%	5	25	1:1	10	100	1.48	43.9	12,535
92	1%	1	25	1:1	10	100	1.74	34.1	13,029
93	5%	20	25	1:1	5	100	1.32	50.0	11,965
94	5%	10	25	1:1	5	100	1.47	44.3	12,196

95	5%	5	25	1:1	5	100	1.64	37.9	12,227
96	5%	1	25	1:1	5	100	1.63	38.3	12,385
97	1%	20	25	1:1	5	100	1.49	43.6	11,856
98	1%	10	25	1:1	5	100	1.83	30.7	12,317
99	1%	5	25	1:1	5	100	1.43	45.8	12,109
100	1%	1	25	1:1	5	100	1.41	46.6	11,896
101	5%	20	25	1:10	20	100	1.68	36.4	12,054
102	5%	10	25	1:10	20	100	1.83	30.7	11,990
103	5%	5	25	1:10	20	100	1.65	37.5	12,555
104	5%	1	25	1:10	20	100	1.74	34.1	11,819
105	1%	20	25	1:10	20	100	1.76	33.3	12,198
106	1%	10	25	1:10	20	100	1.98	25.0	13,063
107	1%	5	25	1:10	20	100	1.71	35.2	12,995
108	1%	1	25	1:10	20	100	1.78	32.6	12,918
109	5%	20	25	1:10	10	100	1.79	32.2	12,279
110	5%	10	25	1:10	10	100	1.89	28.4	12,595
111	5%	5	25	1:10	10	100	1.71	35.2	12,323
112	5%	1	25	1:10	10	100	1.68	36.4	12,650
113	1%	20	25	1:10	10	100	1.92	27.3	12,587
114	1%	10	25	1:10	10	100	2.03	23.1	11,809
115	1%	5	25	1:10	10	100	1.70	35.6	12,332
116	1%	1	25	1:10	10	100	1.82	31.1	12,364
117	5%	20	25	1:10	5	100	1.84	30.3	12,640
118	5%	10	25	1:10	5	100	2.01	23.9	12,213
119	5%	5	25	1:10	5	100	1.72	34.8	12,298
120	5%	1	25	1:10	5	100	1.74	34.1	12,919
121	1%	20	25	1:10	5	100	1.70	35.6	12,995
122	1%	10	25	1:10	5	100	1.94	26.5	12,905
123	1%	5	25	1:10	5	100	1.65	37.5	12,078
124	1%	1	25	1:10	5	100	1.74	34.1	12,494
125	5%	20	25	1:1	20	75	1.65	37.5	13,131
126	5%	10	25	1:1	20	75	1.64	37.9	12,378
127	5%	5	25	1:1	20	75	1.72	34.8	11,980
128	5%	1	25	1:1	20	75	1.62	38.6	12,336
129	1%	20	25	1:1	20	75	1.51	42.8	12,389
130	1%	10	25	1:1	20	75	1.98	25.0	12,415
131	1%	5	25	1:1	20	75	1.85	29.9	12,698
132	1%	1	25	1:1	20	75	1.52	42.4	12,736
133	5%	20	25	1:1	10	75	1.64	37.9	11,673
134	5%	10	25	1:1	10	75	1.56	40.9	12,351
135	5%	5	25	1:1	10	75	1.53	42.0	12,506
136	5%	1	25	1:1	10	75	1.62	38.6	12,694
137	1%	20	25	1:1	10	75	1.53	42.0	12,169
138	1%	10	25	1:1	10	75	1.67	36.7	12,363
139	1%	5	25	1:1	10	75	1.64	37.9	12,594
140	1%	1	25	1:1	10	75	1.51	42.8	12,865
141	5%	20	25	1:1	5	75	1.71	35.2	11,670
142	5%	10	25	1:1	5	75	1.44	45.5	12,346
143	5%	5	25	1:1	5	75	1.51	42.8	12,862
144	5%	1	25	1:1	5	75	1.46	44.7	12,697

145	1%	20	25	1:1	5	75	1.36	48.5	12,364
146	1%	10	25	1:1	5	75	1.43	45.8	12,485
147	1%	5	25	1:1	5	75	1.38	47.7	12,159
148	1%	1	25	1:1	5	75	1.45	45.1	13.047
149	5%	20	25	1:10	20	75	1.98	25.0	11,695
150	5%	10	25	1:10	20	75	1.93	26.9	12,046
151	5%	5	25	1:10	20	75	1.74	34.1	12,498
152	5%	1	25	1:10	20	75	1.91	27.7	12,872
153	1%	20	25	1:10	20	75	1.76	33.3	12,396
154	1%	10	25	1:10	20	75	2.09	20.8	12,581
155	1%	5	25	1:10	20	75	1.72	34.8	12,762
156	1%	1	25	1:10	20	75	2.08	21.2	12,699
157	5%	20	25	1:10	10	75	2.01	23.9	11,963
158	5%	10	25	1:10	10	75	2.04	22.7	12,461
159	5%	5	25	1:10	10	75	1.72	34.8	12,257
160	5%	1	25	1:10	10	75	2.01	23.9	12,312
161	1%	20	25	1:10	10	75	1.77	33.0	12,653
162	1%	10	25	1:10	10	75	2.00	24.2	12,578
163	1%	5	25	1:10	10	75	1.43	45.8	12,379
164	1%	1	25	1:10	10	75	2.03	23.1	12,916
165	5%	20	25	1:10	5	75	1.94	26.5	12,671
166	5%	10	25	1:10	5	75	1.92	27.3	13,088
167	5%	5	25	1:10	5	75	1.77	33.0	12,950
168	5%	1	25	1:10	5	75	2.02	23.5	12,378
169	1%	20	25	1:10	5	75	1.83	30.7	11,876
170	1%	10	25	1:10	5	75	2.04	22.7	12,643
171	1%	5	25	1:10	5	75	2.03	23.1	12,967
172	1%	1	25	1:10	5	75	2.04	22.7	12,379
173	0.5%						2.30	12.9	12,995
174	0.5%	1	25	1:1	20	125	1.68	36.4	12,579
175	.05%						2.46	6.8	13,096
176	.05%	1	25	1:1	20	125	1.78	32.6	12,358

* 5%NaOH used for oil extraction instead of 5%Na_2CO_3

The oil-coal mixture on the petri dish was heated at the reaction temperature by floating it in a constant temperature bath for certain times as described in Table 2.. After reaction, the oil-coal mixture was treated with 5% Na_2CO_3 at 80°C for 2 hours to saponify the oil and to leach out some sulfur compounds from coal matrices. After the oil extraction, the coal samples were thoroughly washed with water and 50 mL of methanol, then dried and submitted for sulfur and BTU analyses. The results are listed in Table 2.

In all experiments, the chlorinated solvents, such as chloroform and tetrachloroethylene, were completely eliminated because of the possible interference of chlorine with sulfur analyses as suggested by the project monitor.

Effects of different base treatment on sulfur removal: Figure 1 shows results of pretreating IBC-108 coal with NaOH and NH_4OH under different conditions. The sulfur removal ranges from 13% to 23%. Sulfur removal is favored by higher base concentrations and higher temperatures, and the presence of oxygen has little effect on sulfur removal (compare N_{100} with $N_{100/Ox}$). NaOH is more effective than NH_4OH under the same conditions (compare B with N, and Bl with N1).

Effects of different base for pretreatment and extraction on sulfur removal: Figures 2 and 3 show the effects on sulfur removal of oil treatment and base extractions after the oil treatment. Clearly, more sulfur is removed from the pretreated coals. After oil treatment, extraction with Na_2CO_3 is more effective than extraction with NaOH. For example, pretreating with 5% NaOH alone removes 23% of the sulfur, pretreating with 5% NaOH, then linseed oil, and finally 5% NaOH (B-O-B) removes 32% of the sulfur, and pretreating with 5% NaOH, then linseed oil, and finally 5% Na_2CO_3 (B-O-C) removes 39% of the sulfur.

Sulfur removal as a function NaOH concentrations: Figure 4 shows the results of treating IBC-108 coal with four different NaOH concentrations for the pretreatment and followed by linseed oil treatment. It is clearly shown that sulfur removal is favored by higher base concentration when treated with NaOH alone. After linseed oil treatment, however, most sulfur is removed with 1% NaOH and least sulfur is removed with 5% NaOH under the conditions of the investigation.

Sulfur removal as a function of time of NaOH pretreatment: Figures 5 and 6 show results of pretreating IBC-108 coal with 5%NaOH and 1%NaOH for four different times (1hr, 5hr, 10hr, and 20hr). Sulfur removal ranges from 21% to 23% for 5% NaOH and from 17% to 21% for 1%NaOH. Increasing the impregnating time with NaOH from 1hr to 20hr results in more sulfur removal under both concentrations. It is also shown that sulfur removal is slightly favored by higher base concentrations.

Sulfur removal as a function of time of oil treatment: Figures 7 and 8 show the percent sulfur remaining in IBC-108 coal after pretreatment with 5% NaOH (Figure 7) or 1% NaOH (Figure 8) for four different times (1hr, 5hr, 10hr, and 20hr) followed by linseed oil treatment at 125°C for three different times (5hr, 10hr, and 20hr) with 1:1 oil to coal ratio. In each figure the percent sulfur remained was plotted against the times of NaOH pretreatment so that the time effects of NaOH pretreatment on the subsequent sulfur removal can be directly compared. Also results from the same coal sample but treated with oil at different times are grouped together so that the time effects of the oil treatment on sulfur removal can also be compared by examining each individual groups.

Comparing each individual groups in Figures 7 and 8 revealed that the most sulfur is removed with 5hr oil treatment and the least sulfur is removed with 10hr oil treatment regardless the time difference in NaOH pretreatment. These results were obtained at 125°C with 1:1 oil to coal ratio. Under some other conditions, however, the effects of the time for the oil treatment on the sulfur removal is different. The sulfur removal is favored by longer oil treatment in some cases, but disfavored in some other cases. That means it also depending on other experimental parameters such as temperature, base concentration and time for pretreatment, and oil to coal ratio.

Sulfur removal as a function of temperature of oil treatment: Figures 9 and 10 show the percent sulfur remaining in IBC-108 coal after pretreatment with 1% NaOH for four different times (1hr, 5hr, 10hr, and 20hr) followed by linseed oil treatment at three different temperatures (75°C, 100°C, and 125°C) for 5hr. The oil to coal ratio is 1:1 In figure 9 and 1:10 in finger 10. Once again, in each figure the percent sulfur remained was plotted against the times of NaOH pretreatment so that the time effects of NaOH pretreatment on the subsequent sulfur removal can be directly compared. The results from the same coal sample but treated with oil at different temperatures are grouped together so that effects of temperature for the oil treatment on sulfur removal can be compared by examining each individual groups.

Comparing each individual groups in figures 9 and 10 revealed that effects of temperature for the oil treatment on sulfur removal is significant. Most sulfur is removed at 75°C and 100°C and least sulfur is removed at 125°C with 1:1 oil to coal ratio as shown in figure 9. With 1:10 oil to coal ratio as figure 10, however, the sulfur removal is favored by higher temperature.

Effects of time of NaOH pretreatment on the subsequent sulfur removal: As pointed out earlier, Figures 7-10 also show the effects of time of NaOH pretreatment on the subsequent sulfur removal. Clearly, the time of NaOH pretreatment has noticeable effects on the subsequent sulfur removal in some cases and has little effects in the other cases. For example, more sulfur is removed from the pretreated coal by decreasing the time of NaOH treatment as shown in Figures 7 and 8. But changing the time of NaOH pretreatment has very little effect on the subsequent sulfur removal in Figure 10.

Sulfur removal as a function of oil to coal ratio: Figure 11 shows the effects of oil to coal ratio on the sulfur removal under various conditions. The percentages shown in parentheses represent the NaOH concentrations for the pretreatment. Apparently, the sulfur removal is favored by 1:1 oil to coal ratio regardless the other experimental parameters.

BTU changes Figure 12 shows BTU changes under various treatments. Pretreating with 5% NaOH causes loss of 11% BTU. However, pretreatment with base followed by first oil and then base again causes loss of only 10% (B-O-B) and 8% (B-O-C) BTU. Comparing these results to those in Figure 2 suggests that the base-oil-base treatments removes organic sulfur but only slightly removes other organics which do not contain sulfur. Perhaps oxidation by the linseed oil hydroperoxides converts organic sulfur into an inorganic form which is extracted by aqueous base. Thereby, the treatment selectively removes organic sulfur with minimum loss of BTU.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

- Pretreating IBC-108 coal with 5%NaOH and 1% NaOH removes 17% to 23% of the sulfur under the conditions of this investigation. Higher NaOH concentration and longer impregnation times remove more sulfur.

- More sulfur is removed by the treatment sequence: NaOH pretreatment, then linseed oil treatment, and finally Na_2CO_3 extraction.

- The combinations of NaOH pretreatment, then oil treatment followed by Na_2CO_3 extraction remove 23% to 50% sulfur. The best result is achieved by pretreating with 5% NaOH for 20 hr (23% sulfur removal) followed by oil treatment at 100°C for 5 hr with a 1:1 oil to coal ratio (50% sulfur removal in total, exp. 93). Table 3 lists the conditions under which 40-50% organic sulfur may be removed from IBC-108 coal. IBC-108 coal has the following sulfur analysis: Percent Total Sulfur, 2.7 ± 0.07% (Sulfatic, 0.0 ± 0.03; Pyritic, 0.4 ± 0.07; Organic, 2.3 ± 0.09).

- More sulfur is removed with a 1:1 oil to coal ratio than a 1:10 ratio under most conditions of the investigation.

- The effects of time and temperature for the oil treatment are complex. Sulfur removal is favored by longer time and lower temperaturs in some cases, but disfavored in other cases. This demonstrates that other experimental parameters are important, such as temperature, concentration of base, time of base pretreatment, and oil to coal ratio.

Table 3 The conditions under which 40-50% organic sulfur removed

	NaOH PRETREATMENT			OIL TREATMENT			RESULTS	
Exp. No	NaOH (%)	Time (hr)	Temp (°C)	oil:coal ratio	Time (hr)	Temp (°C)	Sulfur (%)	S% removed
93	5%	20	25	1:1	5	100	1.32	50.0
145	1%	20	25	1:1	5	75	1.36	48.5
147	1%	5	25	1:1	5	75	1.38	47.7
100	1%	1	25	1:1	5	100	1.41	46.6
99	1%	5	25	1:1	5	100	1.43	45.8
146	1%	10	25	1:1	5	75	1.43	45.8
163	1%	5	25	1:10	10	75	1.43	45.8
142	5%	10	25	1:1	5	75	1.44	45.5
148	1%	1	25	1:1	5	75	1.45	45.1
79	5%	5	25	1:1	20	100	1.46	44.7
83	1%	5	25	1:1	20	100	1.46	44.7
144	5%	1	25	1:1	5	75	1.46	44.7
94	5%	10	25	1:1	5	100	1.47	44.3
91	1%	5	25	1:1	10	100	1.48	43.9
97	1%	20	25	1:1	5	100	1.49	43.6
51	1%	5	25	1:1	5	125	1.51	42.8
129	1%	20	25	1:1	20	75	1.51	42.8
140	1%	1	25	1:1	10	75	1.51	42.8
143	5%	5	25	1:1	5	75	1.51	42.8
52	1%	1	25	1:1	5	125	1.52	42.4
132	1%	1	25	1:1	20	75	1.52	42.4
80	5%	1	25	1:1	20	100	1.53	42.0
85	5%	20	25	1:1	10	100	1.53	42.0
135	5%	5	25	1:1	10	75	1.53	42.0
137	1%	20	25	1:1	10	75	1.53	42.0
82	1%	10	25	1:1	20	100	1.55	41.3
86	5%	10	25	1:1	10	100	1.56	40.9
134	5%	10	25	1:1	10	75	1.56	40.9
88	5%	1	25	1:1	10	100	1.57	40.5

DISCLAIMER STATEMENT

REFERENCES

1. Webster, J. R., R.H. Shiley, R.E. Hughes, P.L. Lapish, D.K. Cowin, G.V. Smith, C.C. Hinckley, T. Nishizawa, N. Yoshida, T. Wiltowski, Y. Wada, and M. Saporoschencko, *Second Annual Pittsburgh Coal Conference, Proceedings*, 1985, p138.

2. Smith, G.V., T. Wiltowski, and J.B. Phillips, *Energy & Fuels*, **3**, 536 (1989)

3. Shiley, R.H., R.E. Hughes, J.R. Webster, C.C. Hinckley, G.V. Smith, and T. Wiltowski, U.S. 4,888,029 19 Dec 1989

4. Akash, B.A., C. B. Muchmore, J.A. Koropchak, J.W. Kim, and S.B. Lalvani, *Energy & Fuels*, **6**, 629 (1992)

5. Chou, M.-I.M., D.H. Buchanan, J.M. Lytle, R.R. Ruch, C. W. Kruse, C. Chaven, K.C. Hackley, R.E. Hughes, R.D. Harvey, J.K. Frost, J.W. Stucki, G.P. Huffman, and F.E.

Huggins, *1991-1992 Final Technical Report for the reporting period of September 1, 1991 through August 31, 1992*, Center For Research on Sulfur in Coal, September 1992 pp 16-1 to 16-3.

6. Chou, M.-I.M., J.M. Lytle, R.R. Ruch, C.W. Kruse, C. Chaven, K.C. Hackley, R.E. Hughes, R.D. Harvey, J.K. Frost, D.H. Buchanan, J.W. Stucki, G. P. Huffman, and F.E. Huggins, *Final Technical Report for the period September 1, 1992 through August 31, 1993*, Illinois Clean Coal Institute, September 30, 1993, pp. 12-1 to 12-4.

7. Petrakis, L., D.W. Grandy, *Anal. Chem.*, **50**, 303 (1978)

8. Petrakis, L., D.W. Grandy, *Fuel*, **59**, 227 (1980)

9. Petrakis, L., D.W. Grandy, *Nature*, **289**, (1981)

10. Hippo, E.J. and S.R. Palmer, *1991-1992 Final Technical Report*, Center for Research on Sulfur in Coal, 1992, pp 15-1 to 15-5.

11. Palmer, S.R. E.J. Hippo, M.A. Kruge, and J.C. Crelling, *Coal Preparation*, 1992, **10**, 93-106.

12. *ASTM Standard, D1266-64T, Part 17*, Amer. Soc. for Testing and Materials, Philadelphia, PA, 1966, p. 456

13. Hempel, W., *Z. Angew. Chem.*, **5**, 393 (1892)

14. Parr, S.W., W.F. Wheeler, and R. Berolzheimer, *J. Ind. Engl. Chem.*, **1**, 689 (1909)

15. Ailey-Trent, K.S., C.W. McGowan, W.Lachowicz, and R. Markuszewski, *ACS Division of Fuel, Preprints*, **36**, 1198 (1991)

16. For example, see Buchanan, D.H., M. Amin, R. Cunningham, J. Galyen, and Y.Tong, *First Quarter Technical Report for the period September 1, 1993 through November 30, 1993*, Illinois Clean Coal Institute, pp. 29-1 to 29-4, December 14, 1993.

17. Philip, H. H., and R. S. Datta, *Coal Desulfurization, Chemical and Physical Methods, ACS Symposium Series*, **64**, American Chemical Society, Washington D.C.,(1977) pp58-69

18. Brubaker, I. M., and T. Stoicos, *Coal Science and Technology* ***9***, *Processing and Utilization of High Sulfur Coals*, (Ed. Y.A.Attia) Elsevier, Amsterdam, (1985) pp 311-326

Fig. 1 % Sulfur Remaining After Treatment with Alkali Under Various Conditions

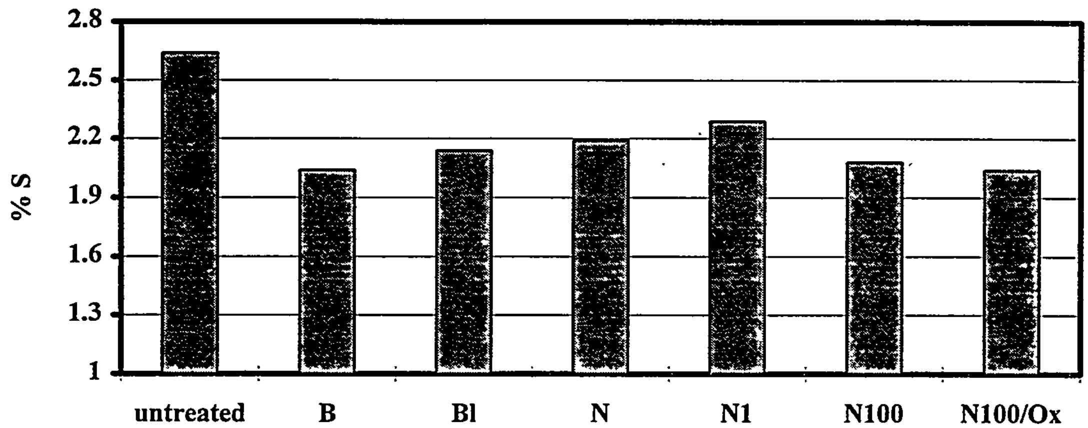


Fig.2 % Sulfur Remaining in IBC-108 Coal After Treatment with NaOH and Linseed Oil

(B: 5%NaOH, C: 5%Na_2CO_3, B1: 1%NaOH, O: Linseed Oil Treatment at 100°C for 15 hr with 1:1 Oil:Coal Ratio)

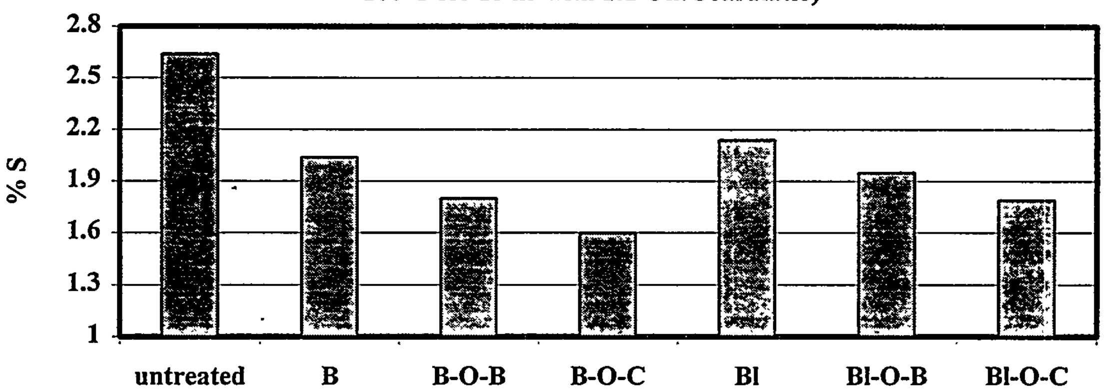


Fig.3 % Sulfur Remaining in IBC-108 Coal After Treatment with NH_4OH and Linseed Oil
(N: 5%NH_4OH, B: 5%NaOH, C: Na_2CO_3, N1: 1%NH_4OH, O: Linseed Oil Treatment at 100°C for 15hr with 1:1 Oil:Coal Ratio)

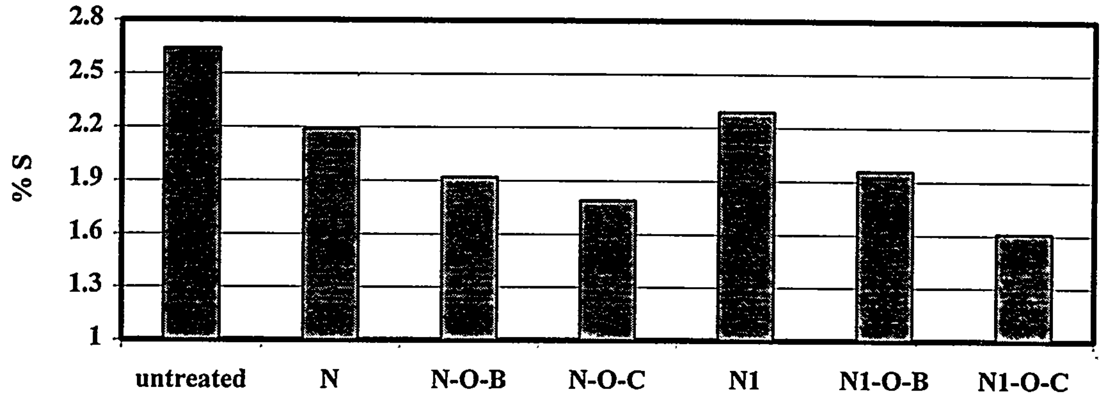


Fig.4 Effects of NaOH Concentration on the Sulfur Removal from IBC-108 Coal
(NaOH Pretreatment at 25°C for 1hr, then Oil Treatment at 125°C for 20*hr* with 1:1 Coal:Oil Ratio)

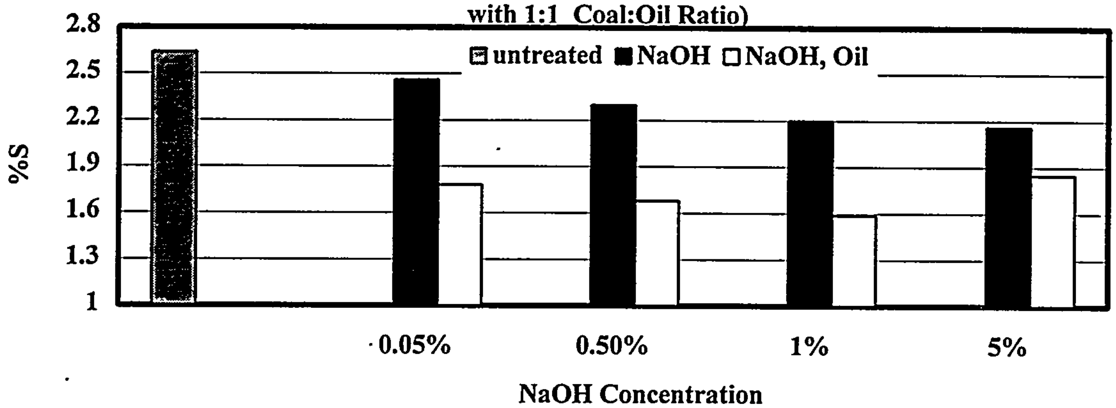


Fig.5 Effects of Time of *5%NaOH* Pretreatment on the Subsequent Sulfur Removal from IBC-108 Coal

(Oil Treatment at 125°C for 20hr with 1:1 Coal:Oil Ratio)

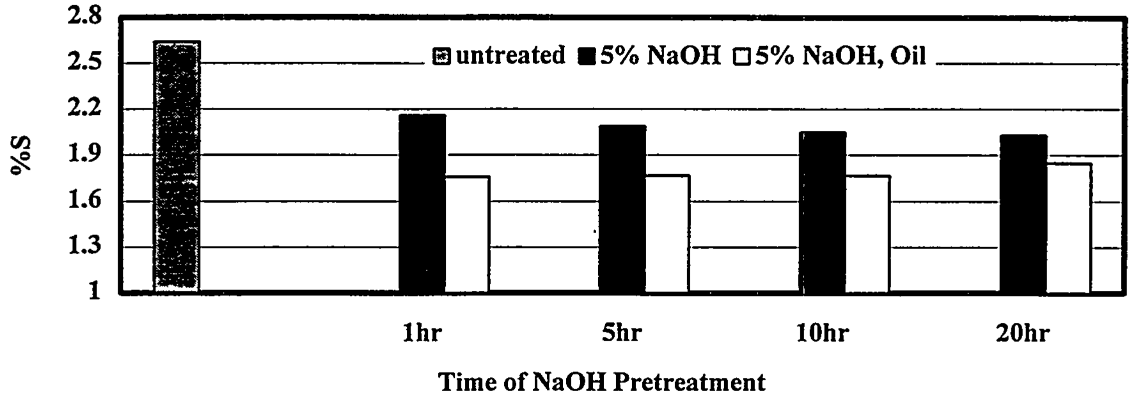


Fig.6 Effects of Time of *1%NaOH* Pretreatment on the Subsequent Sulfur Removal from IBC-108 Coal

(Oil Treatment at 125°C for 20hr with 1:1 Coal:Oil Ratio)

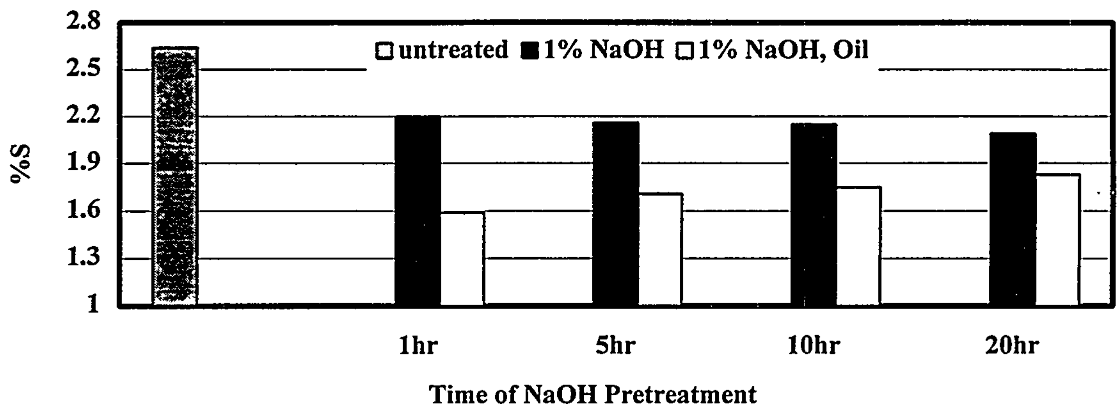


Fig.7 Effects of Time of Oil Treatments on Sulfur Removal from IBC-108 Coal

(Pretreatmet with 5% NaOH, Oil Treatment at 125°C with 1:1 Oil:Coal Ratio)

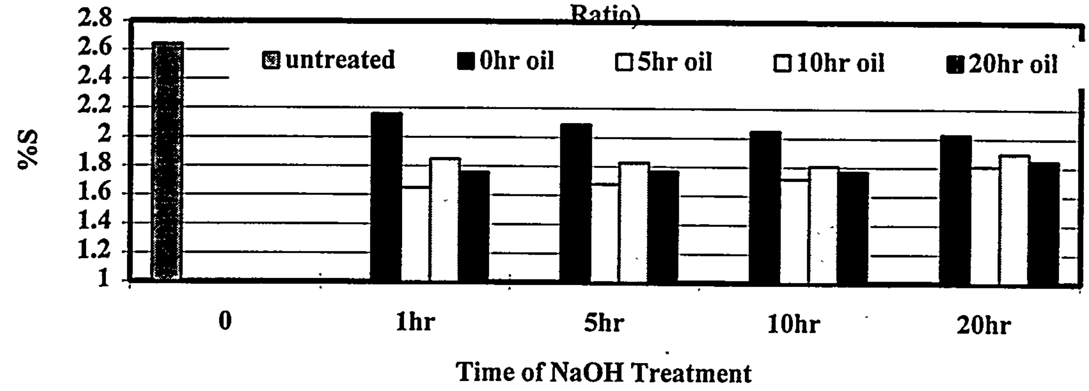


Fig.8 Effects of Time of Oil Treatment on Sulfur Removal from IBC-108 Coal

(Pretreatment with 1% NaOH and Oil Treatment at 125°C with 1:1 Oil:Coal Ratio)

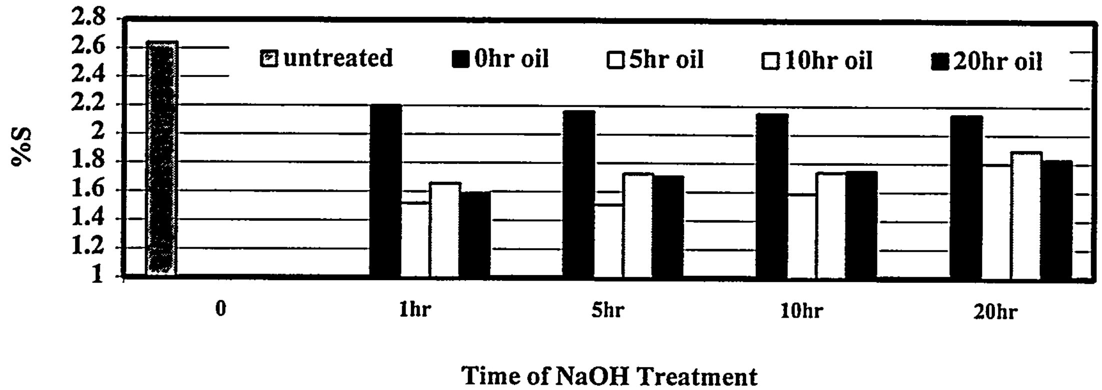


Fig.9 Effects of Temperature for Oil Treatment on Sulfur Removal from IBC-108 Coal
(Pretreatment with 1% NaOH, Oil Treatment with *1:1 Oil:Coal Ratio* for 5hr)

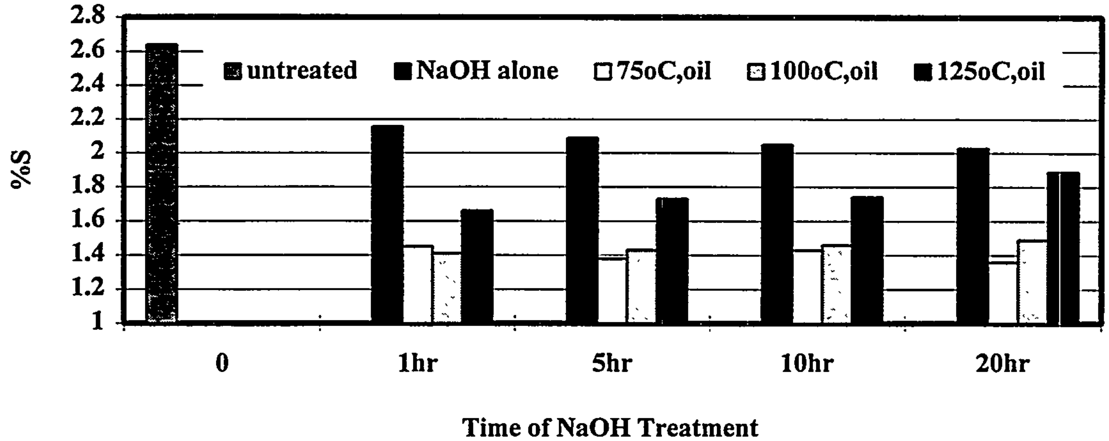


Fig.10 Effects of Temperature for Oil Treatment on Sulfur Removal from IBC-108 Coal
(Pretreatment with 1% NaOH and Oil Treatment with *1:10 Oil:Coal Ratio* for 5hr)

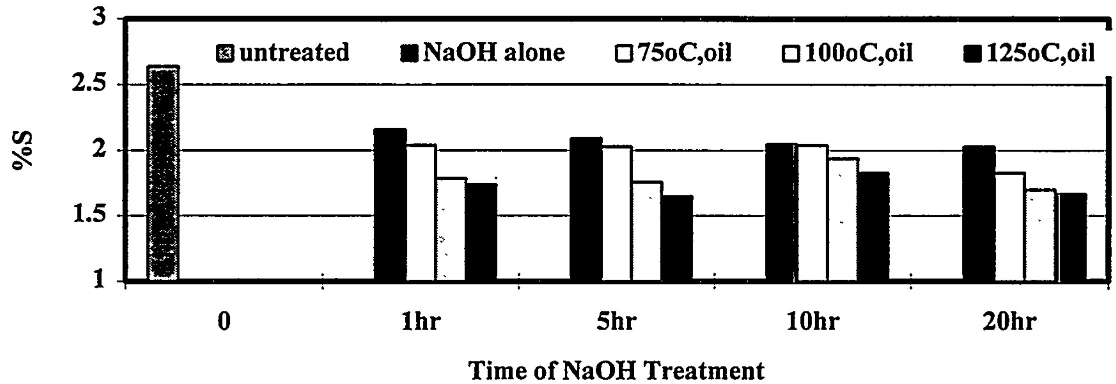


Fig.11 Effects of Different Oil to Coal Ratio in the Oil Treatment on Sulfur Removal from IBC-108 Coal

(Oil Treatment at 125°C for 20 hr)

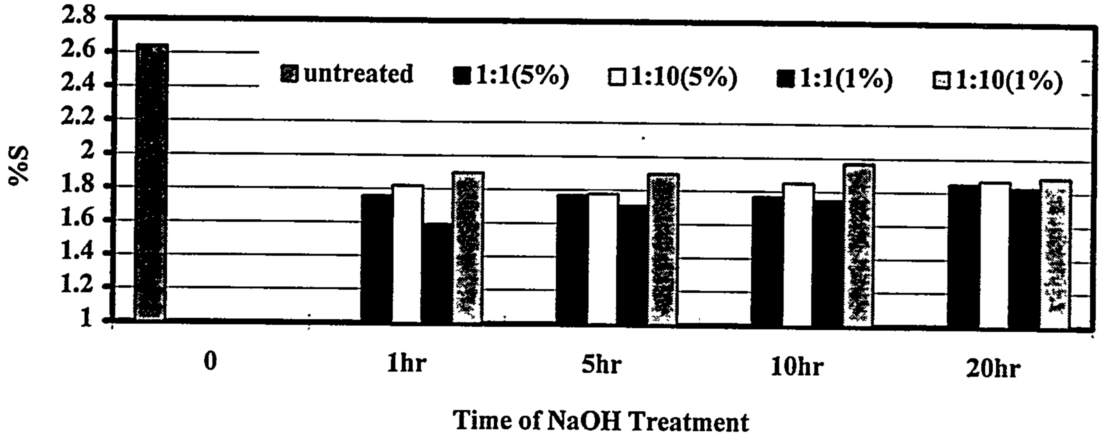
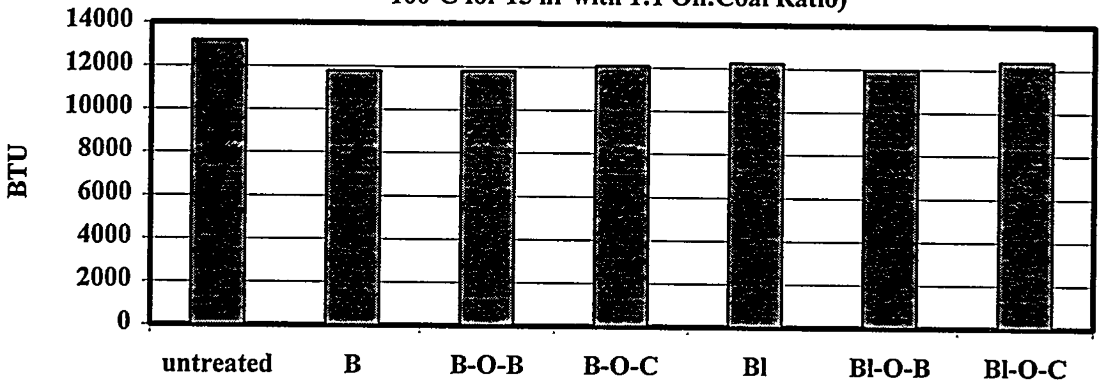


Fig.12 BTU Changes in IBC-108 Coal After Treatment with NaOH and Linseed Oil

(B: 5%NaOH, C: 5%Na2CO3, B1: 1%NaOH, O: Linseed Oil Treatment at 100°C for 15 hr with 1:1 Oil:Coal Ratio)



PROJECT MANAGEMENT REPORT
June 1, 1996, through August 31, 1996

Project Title: **DESULFURIZATION OF ILLINOIS COALS WITH HYDROPEROXIDES OF VEGETABLE OILS AND ALKALI**

DOE Cooperative Agreement Number:	DE-FC22-92PC92521 (Year 4)
ICCI Project Number:	95-1/1.1D-2P
Principal Investigator:	Gerard V. Smith, SIUC
Other Investigators:	Ricky D. Gaston, SIUC Ruozhi Song, SIUC Jianjun Cheng, SIUC Feng Shi, SIUC Yaguang Wang, SIUC
Project Manager:	Ken Ho, ICCI

COMMENTS

Expenditures are proceeding approximately as projected. No unusual problems have occured.

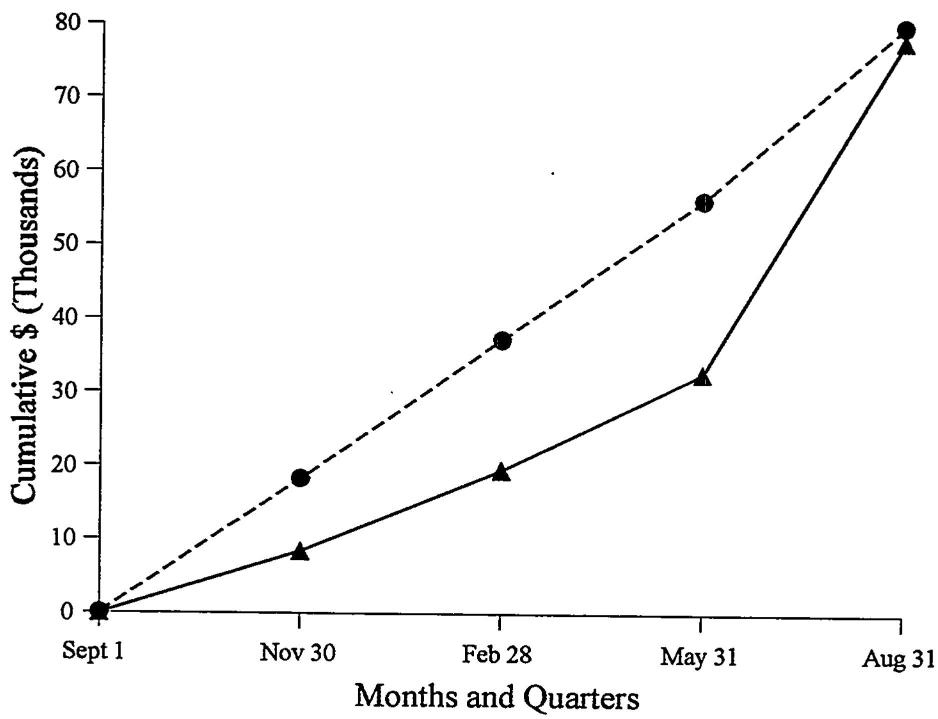
PROJECTED AND ESTIMATED EXPENDITURES BY QUARTER

Quarter*	Types of Cost	Direct Labor	Fringe Benefits	Materials and Supplies	Travel	Major Equipment	Other Direct Costs	Indirect Cost	Total
Sept. 1, 1995 to Nov. 30,1995	Projected	12,717	1,730	750	0	0	1,426	1,662	18,285
	Estimated	6,000	641	568	0	0	384	759	8,352
Sept. 1, 1995 to Feb. 28, 1996	Projected	25,434	3,461	1,500	600	0	2,852	3,385	37,232
	Estimated	12,974	1,648	1,689	0	0	1,394	1,771	19,476
Sept. 1, 1995 to May 31, 1996	Projected	38,151	5,191	2,250	1,200	0	4,279	5,107	56,178
	Estimated	22,410	3,094	2,511	0	0	1,731	2,975	32,721
Sept. 1, 1995 to Aug. 31, 1996	Projected	57,832	8,068	3,000	500	0	3,325	7,273	79,998
	Estimated	51,606	7,347	7,435	316	0	3,958	7,273	77,934

*Cumulative by Quarter

CUMULATIVE COSTS BY QUARTER

Desulfurization of Illinois Coals with Hydroperoxides of Vegetable Oils and Alkali

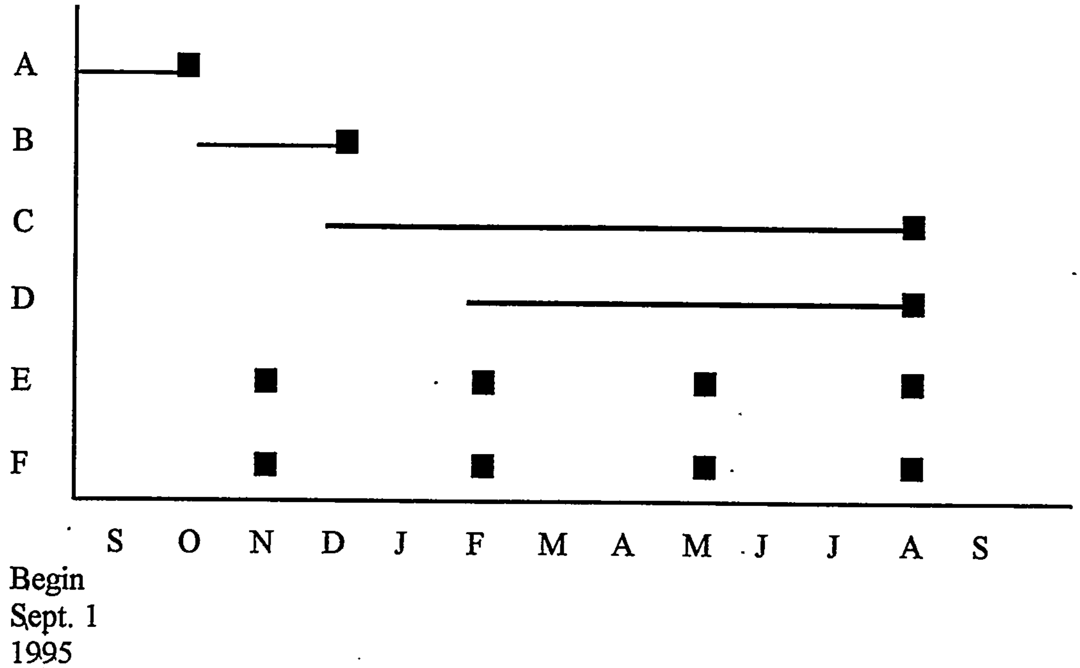


● = Projected Expenditures - - - - - - -

▲ = Actual Expenditures ______________

Total Illinois Clean Coal Instutute Award $79,998

SCHEDULE OF PROJECT MILESTONES



Hypothetical Milestones:

A: Research personnel employed
B: Task 1, selection of base for pretreatment and extraction
C: Task 2, determination of base and linseed oil ability to remove organic sulfur from IBC-108 coal
D: Task 3, determination of mass balance, volatiles, and BTU
E: Project Technical Reports
F: Project Management Reports

LIST OF PUBLICATIONS AND PRESENTATIONS
September 1, 1995 through August 31, 1996

Project Title: **DESULFURIZATION OF ILLINOIS COALS WITH HYDROPEROXIDES OF VEGETABLE OILS AND ALKALI**

DOE Cooperative Agreement Number:	DE-FC22-92PC92521 (Year 4)
ICCI Project Number:	95-1/1.1D-2P
Principal Investigator:	Gerard V. Smith, SIUC
Other Investigators:	Ricky D. Gaston, SIUC Ruozhi Song, SIUC Jianjun Cheng, SIUC Feng Shi, SIUC Yaguang Wang, SIUC
Project Manager:	Ken Ho, ICCI

COMMENTS

Smith, G.V., Ricky D. Gaston, Ruozhi Song, Jianjun Cheng, Feng Shi , and Yaguang Wang. 1996. "Desulfurization of Illinois Coals with Hydroperoxides of Vegetable Oils and Alkali." Poster presentation at 14th Annual Contractors' Technical Meeting, July 30-31, 1996, Champaign, IL.

EQUIPMENT INVENTORY REPORT
September 1, 1995 through August 31, 1996

Project Title: **DESULFURIZATION OF ILLINOIS COALS WITH HYDROPEROXIDES OF VEGETABLE OILS AND ALKALI**

DOE Cooperative Agreement Number:	DE-FC22-92PC92521 (Year 4)
ICCI Project Number:	95-1/1.1D-2P
Principal Investigator:	Gerard V. Smith, SIUC
Other Investigators:	Ricky D. Gaston, SIUC
	Ruozhi Song, SIUC
	Jianjun Cheng, SIUC
	Feng Shi, SIUC
	Yaguang Wang, SIUC
Project Manager:	Ken Ho, ICCI

COMMENTS

No new equipment was purchased.

HAZARDOUS WASTE REPORT
September 1, 1995 through August 31, 1996

Project Title: **DESULFURIZATION OF ILLINOIS COALS WITH HYDROPEROXIDES OF VEGETABLE OILS AND ALKALI**

DOE Cooperative Agreement Number: DE-FC22-92PC92521 (Year 4)
ICCI Project Number: 95-1/1.1D-2P
Principal Investigator: Gerard V. Smith, SIUC
Other Investigators: Ricky D. Gaston, SIUC
Ruozhi Song, SIUC
Jianjun Cheng, SIUC
Feng Shi, SIUC
Yaguang Wang, SIUC
Project Manager: Ken Ho, ICCI

COMMENTS

All hazardous wastes were turned over to the SIUC Center for Environmental Health and Safety to be disposed of in accordance with the EPA/SIUC approved disposal plan. The following chemicals/solvents were utilized during this project:

EPA Hazardous Waste No.	Chemical/Solvent	Quantity	Hazard Code
U154	Methanol, CH_3OH	10 liters	3
D001	Hexane, C_6H_{14}	10 liters	3