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ADVANCED DEVELOPMENT OF FINE COAL DESULFURIZATION AND RECOVERY TECHNOLOGY

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By

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TABLE OF CONTENTS

DESCRIPTION OF TECHNICAL PROGRESS

LIST OF FIGURES

LIST OF TABLES

ABSTRACT

During the past year, progress was made in the development and improvement of several promising methods for the desulfurization and recovery of fine-size coal. The methods include froth flotation, selective oil agglomeration, pelletization, and a unique chemical desulfurization process based on leaching the fine coal with a hot dilute solution of sodium carbonate containing dissolved oxygen under pressure. The latter is a form of wet oxidation process which converts both organic and inorganic sulfur into soluble sulfates.

In order to establish optimum conditions for the leaching process, numerous laboratory experiments were carried out with a 1-liter stirred reactor. Several bituminous coals from Iowa, Illinois, and Appalachia were leached at different conditions of temperature, oxygen partial pressure, alkali concentration, slurry density, and reaction time. Also in some experiments no alkali at all was used, and in others an acid solution was employed. In general more sulfur (both organic and inorganic) was removed but slightly less combustible matter was recovered with an alkaline solution than with an acidic solution. Sodium carbonate was the alkali employed, and as long as some was present the extent of sulfur removal was about the same regardless of alkali concentration. However, the recovery of combustible matter declined at higher alkali concentrations. Increased oxygen partial pressure increased the removal of both pyritic and organic sulfur while it did not affect the recovery of combustible organic matter. When temperature was varied, coal desulfurization passed through a maximum somewhere between 120 and 160°C depending on the oxygen partial pressure whereas the recovery of combustible matter declined steadily with increasing temperature. When the concentration of solids in the reaction mixture was varied between 9 and 14%, no effect on sulfur removal was observed but a higher recovery of combustible matter was achieved at the higher concentration than at the lower. Increased leaching time increased sulfur removal but also reduced combustible matter recovery.

A modification of the chemical desulfurization process was also demonstrated in the laboratory. The modified process involves adding a second leaching step in which the alkaline coal slurry is simply heated to a higher temperature (230°C and above) in an inert atmosphere to decompose oxidized organic sulfur compounds. From 50 to 70% of the organic sulfur was apparently removed from an Iowa coal by the two-step treatment as compared to only about 15% by the unmodified one-step process.

Experiments on leaching of coal-derived pyrite were continued in a small packed-bed, tubular reactor in order to study the mechanism whereby individual pyrite particles are desulfurized. A gradual decrease was observed in the percent desulfurization as a function of packing length. On the basis of data obtained from experiments with different liquid flow rates and oxygen partial pressures, this decrease was linked to the pressure drop across the reactor and the corresponding change in oxygen partial pressure.

In order to improve the froth flotation method of separating bituminous coal and iron pyrites, the basic floatability of isolated coal and pyrite particles was investigated with a modified Hallimond tube microflotation cell. In the presence of methyl isobutyl carbinol (MIBC), a commonly used frothing agent, the floatability of bituminous coal particles and pyrite particles which had been cleaned with hot hydrochloric acid was relatively high. Although the floatability of both materials was reduced by various alkaline and alkaline earth compounds and by ferric chloride, the floatability of pyrite was affected more than the floatability of coal. The depressing action of various alkaline compounds on the floatability of either coal or pyrite increased with the basicity of the compound. Among various compounds tested, those which supplied calcium or magnesium ions appeared more selective for depressing pyrite rather than coal. Calcium hydroxide was found to be an exceptionally strong depressant for pyrite. Another promising method of depressing pyrite was demonstrated. This method involves mild wet oxidation of the pyrite surface with a warm, alkaline solution containing dissolved air. The method was observed to depress pyrite more than an alkaline solution by itself while not depressing coal any further.

The oil agglomeration process for cleaning and recovering fine coal was developed further by determining the effect of various process parameters and by applying the wet oxidation surface treatment described above. Small batches of bituminous coal suspended in water were agglomerated with various grades of fuel oil in a kitchen-type blender. The agglomerates were recovered by sieving. Coal from various mines in Iowa, Illinois and Western Kentucky was utilized. Some of this coal was ground to fine size (60 mesh x 0) and some to ultrafine size (400 mesh x 0). In general the recovery of fine coal was greater than the recovery of ultrafine coal but less inorganic sulfur was removed from the fine coal than from the ultrafine coal. While the recovery of fine coal was relatively independent of the grade of oil, the recovery of ultrafine coal was very dependent on the grade. The wet oxidation treatment proved very effective in reducing the tendency for pyrite particles to be agglomerated. Therefore when this treatment was applied to coal from various mines in Iowa, Illinois and Western Kentucky, the subsequent separation of coal and pyrite by oil agglomeration was improved significantly.

The construction of a large bench-scale flow system for demonstrating various methods of cleaning and recovering fine coal was completed and the system tested. This system includes equipment for grinding and chemically pretreating 1000 lb. batches of coal and for continuously processing the pretreated coal by froth flotation or oil agglomeration at a rate of several hundred pounds per hour. Also it includes a rotating, inclined-pan pelletizer for pelletizing the final product. Although preliminary testing and operation of the system revealed a number of mechanical and operation problems, the system generally met design expectations. Most of the problems were relatively minor and easily corrected. Other more serious problems are being solved by modifying the system.

Possible sources of error in the ASTM methods for determining forms of sulfur in coal were scrutinized by employing scanning electron microscope and energy dispersive X-ray analysis techniques. This work showed that maceral encapsulation of pyrite can lead to errors in the reported organic sulfur content of some coals. If pyrite encapsulation is corrected for, less sulfur will be attributed to the organic form. In some coals, elemental sulfur may be present in amounts ranging up to a few tenths weight percent. In one sample of Lower Freeport coal the elemental sulfur accounted for more than 50% of the sulfur reported as organic sulfur by the ASTM method. However, in most coals, crystalline elemental sulfur is found in a range from zero to a few tens of parts per million. Among potential methods for directly determining the organic sulfur content of raw and processed coals, a method based on sulfur K_α X-ray line shifts and intensities appears promising.

OBJECTIVES AND SCOPE OF WORK

Background

With the increasing value of coal as a source of energy and with the increasingly stringent regulations aimed at controlling sulfurous emissions into the atmosphere during the combustion of coal, the development of technology for coal cleaning is gaining in importance.

A great need exists for the improvement and development of certain promising methods which can be utilized to desulfurize and recover fine-size coal. These methods include froth flotation, selective oil agglomeration, pelletization, and chemical desulfurization. Although several of these methods have been known for some time, they have not been adopted widely in the field of coal preparation because of various shortcomings. The present investigation is directed towards overcoming these shortcomings and towards the development of a unique chemical desulfurization process.

This report documents the second year of the project and provides a summary of all the important results obtained during the year.

Objectives

The primary objective of this investigation is to improve and develop the following methods for desulfurizing and recovering fine-size coal: froth flotation, selective oil agglomeration, pelletization, and chemical leaching with a unique system. This objective is to be attained by accomplishing the major tasks which are outlined below.

Task A. - Chemical Desulfurization

A unique process for removing both inorganic and organic sulfur from coal is to be developed and demonstrated with small-scale laboratory reaction systems. This process involves leaching fine-size coal with a hot, dilute solution of sodium carbonate containing dissolved oxygen or air under pressure.

Task B. - Froth Flotation

The froth flotation method of separating coal and iron pyrites is to be improved and developed by applying surface chemical treatments which selectively reduce the floatability of the iron pyrites.

Task C. - Selective Oil Agglomeration

The selective oil agglomeration method of beneficiating fine coal is to be improved and developed in order to increase the efficiency of separation of coal and iron pyrites and to produce agglomerates with minimum oil consumption which are easily dewatered and have good handling properties.

Task D. - Pelletization

The pelletization of coal fines to produce pellets with suitable storage, handling, and utilization characteristics is to be demonstrated with a laboratory pelletizer.

Task E. - Continuous Processing

The continuous processing of fine coal by froth flotation, selective oil agglomeration, and pelletization either individually or in concert is to be demonstrated with a large bench-scale system designed for continuous flow, steady-state operation.

Task F. - Coal Microstructure

The microstructure of coal used in the preceding tasks is to be determined and characterized by scanning electron microscope techniques to assist the development of promising methods for desulfurizing and recovering fine coal.

DESCRIPTION OF TECHNICAL PROGRESS

Chemical Desulfurization

A unique and very promising chemical desulfurization process is under development. The process is based on leaching fine-size coal with a hot, dilute solution of sodium carbonate containing dissolved oxygen or air under pressure. In this process, most of the inorganic sulfur and a significant portion of the organic sulfur are extracted from coal by conversion into soluble sulfates. The overall reaction for the dissolution of pyrite appears to be as follows:

$$2FeS_2 + 7.5O_2 + 4H_2O = Fe_2O_3 + 4H_2SO_4$$

The pyritic iron remains as an insoluble iron oxide or hematite. The sulfuric acid generated by the preceding reaction is immediately neutralized by the alkali as shown below:

$$H_2SO_4 + Na_2CO_3 = Na_2SO_4 + CO_2 + H_2O$$

The sulfate from the conversion of pyrite is extracted along with other sulfates already present in the coal. The mechanism for the extraction of the organic sulfur has not been established, but it is suspected that an oxygenated sulfur intermediate may be involved.

The chemical leaching process under development presents several important advantages over other chemical desulfurization methods. There is good evidence that in this process both inorganic and organic sulfur components of coals are extracted; in many of the other chemical methods, organic sulfur is not affected. Also, in this process, a relatively mild and inexpensive alkaline leachant is used so that corrosion of materials is not a problem, and thus the cost of construction and maintenance can be kept at a competitive level. In addition, the normal operating temperature and pressure are relatively low, and the leaching process is rapid. However, it appears that increasing either the temperature or the pressure can significantly improve the removal of organic sulfur. Several experiments described in this report bear evidence for this conclusion.

During the past year, the experimental program was directed toward the laboratory development and demonstration of this leaching process by using two types of reaction systems. In one system, a stirred autoclave was used to study the extraction of the different forms of sulfur from coal as a function of various important parameters such as leaching time, temperature, oxygen partial pressure, and alkalinity. The object was to establish the optimum conditions for the removal of sulfur and especially for increasing the extraction of organic sulfur. In a modified version of the desulfurization process, involving two leaching steps, a significant improvement was observed in the removal of organic sulfur. This promising two-step leaching method will be studied more intensively in future experiments.

In the other system, a fixed bed tubular reactor was used to measure the rate of extraction of sulfur from pyrite particles which had been isolated from coal by mechanical means in a coal preparation plant. The leaching conditions were similar to those of the stirred autoclave system, employing hot solutions of sodium carbonate containing dissolved oxygen under pressure.

In the process under development, it is proposed to regenerate the leaching solution by using lime. The overall reactions are as follows:

$$Na_2SO_4 + Ca(OH)_2 = CaSO_4 + 2NaOH$$

$$2NaOH + CO_2 = Na_2CO_3 + H_2O$$

The added lime would precipitate calcium sulfate which is removed by filtration. In the subsequent step, carbon dioxide is added to recarbonate the alkaline solution.

Stirred Autoclave System

The coal leaching experiments were conducted in a 1-liter stirred reactor (Autoclave Engineers, Inc., Model AFP1005) made of Type 316 stainless steel. The reactor was furnished with a removable, protective stainless-steel liner, an electric heating jacket, a proportional temperature controller with digital read-out that was precise to ± 1°F, an internal coil for cooling water, and a pressure gauge. The contents of the autoclave were stirred by a gas-dispersing turbine agitator operated by a magnetic drive.

For each experiment, the autoclave reactor was charged with 40 g. of coal in 400 ml. of the leach solution and sealed. The desired agitator speed (2000 r.p.m.) was established, and the autoclave was purged with nitrogen gas while being heated. When the desired temperature was reached, the flow of nitrogen was stopped, the autoclave was vented, and oxygen was introduced into the reactor. The oxygen partial pressure (psia), the total pressure within the autoclave (psig), the temperature, and the stirring rate were kept constant for the duration of the experiment. Some oxygen was bled continuously from the reactor to prevent any build-up of gaseous reaction products, while fresh oxygen was supplied on demand to keep the system pressure constant. At the end of a run, the flow of oxygen was stopped,the system purged with nitrogen, and the reactor cooled. The leached coal was then recovered by filtration, dried at 90°C for 1 day, weighed, and analyzed for ash content. Each sample was split in two using a riffle splitter, and each half was analyzed for the various forms of sulfur by standard ASTM procedures. The reported data for sulfur distribution are averages of the two determinations. In most cases, the heating value of the leached coal was calculated from the ash-free heating value of the starting coal, determined by the ASTM method. The basis for this calculation was a mass of analytical data which indicated that the ash-free heating value was fairly constant, regardless of the treatment of the coal. Thus the heating values (H.V.) calculated by the following equation,

$$\text{H.V.} = (\text{H.V.})_{\text{ash-free}} \times \frac{(100 - \%\text{Ash})}{100} ,$$

were in good agreement with heating values actually determined.

The heating value recovery, in percent, was calculated by the following equation:

$$\text{H.V. Recovery (\%)} = \frac{(\text{wt. coal recovered}) \times \text{H.V. final} \times 100}{(\text{wt. coal started}) \times \text{H.V. started}} .$$

The specific sulfur content of the coal (lb. $S/10^6$ Btu) was determined as follows:

$$\text{Specific S content} = \frac{\text{wt. percent sulfur} \times 10^6}{100 \times \text{heating value (in Btu/lb.)}}$$

The coals used for leaching were: Lovilia coal (from Lovilia No. 4 mine in Monroe Co., Iowa), Western Kentucky coal (from Fies Mine, No. 9 seam, in Hopkins Co., Ky.), Illinois No. 5 coal (from Rapatee Mine in Middle Grove, Ill.) and Pittsburgh No. 8 and Lower Kittaning coals from Pennsylvania. The coals were dried at 90°C for 1 day, ground and sieved to the desired mesh size. Each batch of coal used for a set of experiments was analyzed prior to leaching.

Effect of Alkaline Conditions. The relative effectiveness of alkaline versus acidic leaching conditions and of oxygen versus air as the oxidant was compared previously for four coals, namely Lovilia, Big Ben, Scott, and Western Kentucky coals (1). In order to extend this examination to other coals, the same experiments were performed on three additional coals: Pittsburgh No. 8, Illinois No. 5, and Lower Kittaning coal. As before, the -200 mesh coals were leached for 1 hr. at 150°C and 50 psia oxygen partial pressure. For alkaline conditions, 0.2M sodium carbonate was used. For acidic conditions, pure water was used; the acidity was provided by the sulfuric acid produced by the oxidation of pyrite. The oxygen partial pressure was kept constant at 50 psia, regardless of whether air or pure oxygen was fed to the autoclave.

The results of these experiments are presented in Table 1. The values are averages of duplicate runs. The results are comparable to those obtained previously with other coals. Under alkaline conditions, more total sulfur was removed than under acidic conditions. The difference was more apparent for the Pittsburgh and Lower Kittaning coals; for the Illinois coal the difference was small. Also under alkaline conditions the heating value recovery was slightly lower for all three coals than under acidic conditions. The difference in heating value recovery was most pronounced for Illinois coal and least pronounced for Lower Kittaning coal. It seemed to make little difference with these coals whether air or pure oxygen was used for the process under either acidic or basic conditions.

To study the effect of alkali concentration on desulfurization, Lovilia coal was leached for 1 hr. at 150°C and 50 psia oxygen partial pressure with sodium carbonate solutions of various strengths. The results are depicted in Figure 1. For leach solutions without any sodium carbonate the reduction in total sulfur content was only about 56%. But even a small amount of alkali (0.05M sodium carbonate) present in the leach solution improved the reduction noticeably. Further increases in the alkali concentration produced only slight improvements, while at much higher concentrations the reduction of total sulfur even declined. A concentration of 0.15 to 0.20M sodium carbonate seemed to be optimum, resulting in a total sulfur reduction of about 71%. Higher concentrations of alkali were also detrimental to the heating value recovery. The recovery declined from 93 to 79% by increasing the sodium carbonate concentration from 0.05 to 0.5M. Thus, for most of the subsequent experiments, 0.2M sodium carbonate was chosen as the standard concentration of alkali.

The beneficial effect of sodium carbonate on the desulfurization of coal can be seen also in Figure 2 and Table 2. The data are for Western Kentucky coal, leached for 1 hr. at 150°C and various partial pressures of oxygen with alkaline, neutral, and acidic solution. It should be pointed out that the initially neutral leachant consisting only of water became acidic during the leaching process because of the production of sulfuric acid. Thus when water was used as the leachant, the reduction of total sulfur increased almost linearly with increasing oxygen pressure from 40.6 to 49.4% at 50 and 200 psia oxygen partial pressure, respectively. When the leachant was initially acidic (0.2N sulfuric acid), the reduction of total sulfur was less favorable, ranging from 36.7% at 100 psia, through 42.4% at 150 psia, to 41.8% at 200 psia oxygen partial pressure.

When the sodium carbonate solution was the leachant, the total sulfur reduction was much higher at 53.1 - 55.3%; it seemed to increase only slightly with increasing pressure. The amount of organic sulfur in the residue was less than that for the other leachants and appeared to decrease with increasing pressure. The heating value recovery, on the other hand, was lower under alkaline conditions (87 - 90%) than under acidic conditions (96 - 99%). The effect of increased oxygen partial pressure was examined further in subsequent experiments which are described below.

Effect of Oxygen Partial Pressure. In Table 3, the results are presented for leaching Lovilia, Pittsburgh, and Illinois coals with a sodium carbonate solution at 150°C as a function of the oxygen partial pressure from 50 to 200 psia. In each case, the reduction of total sulfur showed improvement

Table 1. Leaching run-of-mine coals (-200 mesh) with and without alkali using air or pure oxygen.[a]

Na_2CO_3 M	Gas Type	H.V., Btu/lb.	Ash %	Sulfur Distribution, lb/10^6Btu				Total S Redn.,%	H.V. Recov.,%
				Pyr.	Sulf.	Org.	Tot.		
(Pittsburgh No. 8 Coal)[b]		12,916	12.65	1.01	0.07	1.13	2.21	----	----
0	O_2	13,194	10.77	0.43	0.03	1.13	1.59	28.1	99.6
0	Air	13,193	10.78	0.43	0.03	1.12	1.58	28.3	99.3
0.2	O_2	12,925	12.59	0.18	0	1.09	1.27	42.5	92.2
0.2	Air	12,942	12.47	0.24	0.10	1.07	1.32	40.5	95.8
(Illinois No. 5 coal)[b]		11,899	13.65	1.26	0.14	1.28	2.68	----	----
0	O_2	12,332	10.55	0.42	0.07	1.33	1.82	32.3	97.9
0	Air	12,343	10.43	0.42	0.06	1.32	1.80	33.0	98.9
0.2	O_2	11,190	18.80	0.32	0.04	1.37	1.73	35.6	88.3
0.2	Air	11,317	17.87	0.37	0.04	1.38	1.79	33.0	91.3
(Lower Kittaning coal)[b]		12,481	18.91	1.86	0.14	0.44	2.44	----	----
0	O_2	12,642	17.87	0.07	0.10	0.94	1.11	54.5	99.3
0	Air	12,643	17.86	0.17	0.07	0.95	1.19	51.0	98.3
0.2	O_2	12,436	19.20	0.40	0.06	0.47	0.93	61.9	97.5
0.2	Air	12,447	19.13	0.34	0.06	0.49	0.89	63.5	97.1

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[a] Leached 1 hr. at 150°C and 50 psia O_2 partial pressure. Results are averages of duplicate runs.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

Table 2. Effect of oxygen partial pressure on the leaching of coal with alkaline, neutral or acidic solutions.[a]

O_2 Press. psia	H.V. Btu/lb.	Ash %	Sulfur Distribution lb./10^6Btu				Total S Redn.,%	H.V. Recov.,%
			Pyr.	Sulf.	Org.	Tot.		
	10,890[b]	18.3	0.89	0.86	1.43	3.18	----	----
$0.2\underline{M}$ Na_2CO_3								
50	10,322	21.7	0.10	0.07	1.32	1.49	53.1	90.0
100	10,368	21.9	0.15	0.07	1.21	1.43	55.0	87.8
150	10,344	22.1	0.20	0.09	1.13	1.42	55.3	86.9
200	10,230	22.9	0.13	0.13	1.19	1.45	54.4	90.2
water[c]								
50	10,885	16.8	0.12	0.28	1.49	1.89	40.6	97.2
100	11,090	16.4	0.13	0.27	1.41	1.81	43.1	95.0
150	11,138	16.1	0.16	0.22	1.29	1.67	47.5	96.7
200	11,148	16.0	0.14	0.20	1.27	1.61	49.4	96.2
$0.2\underline{N}$ H_2SO_4								
100	11,212	15.5	0.10	0.44	1.41	1.95	36.7	98.5
150	11,204	15.6	0.11	0.38	1.34	1.83	42.4	95.9
200	11,185	15.7	0.11	0.43	1.31	1.85	41.8	96.8

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[a] Western Kentucky coal (-200 mesh), leached 1 hr. at 150°C.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

[c] Initial solution, becomes acidic as leaching proceeds.

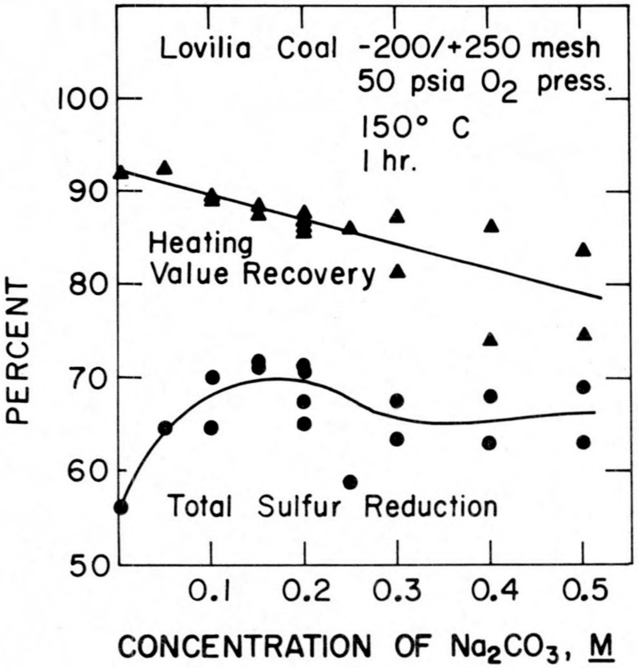

Figure 1. Effect of sodium carbonate concentration on the desulfurization of coal.

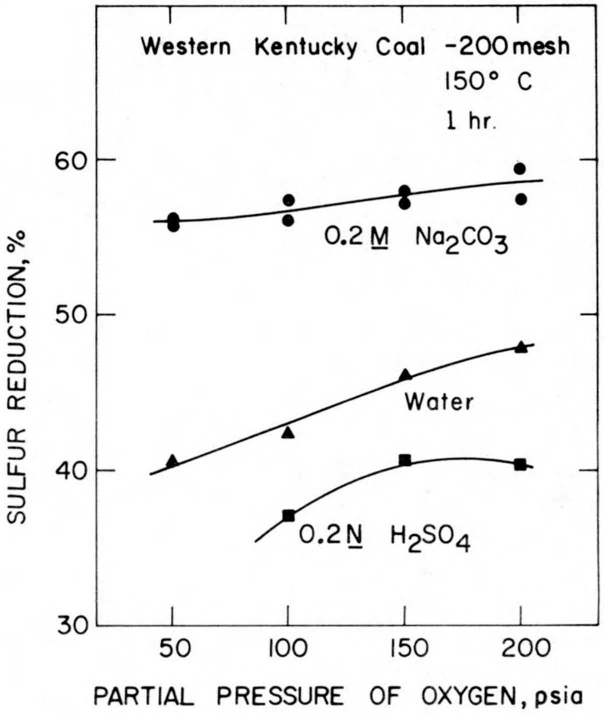

Figure 2. Effect of oxygen partial pressure on the desulfurization of coal by leaching with alkaline, neutral or acidic solutions.

Table 3. Effect of oxygen partial pressure on alkaline leaching of coal.[a]

O_2 Press. psia	H.V. Btu/lb.	Ash %	Sulfur Distribution lb./10^6Btu				Total S Redn.,%	H.V. Recov.,%
			Pyr.	Sulf.	Org.	Tot.		
(Lovilia coal, -200/+250 mesh)								
-[b]	10,175	18.63	3.84	0.92	1.02	5.78	----	----
50	9,600	23.22	0.76	0.15	0.87	1.78	69.2	86.1
100	9,619	23.07	0.57	0.25	0.83	1.65	71.5	86.3
150	9,716	22.30	0.34	0.22	0.76	1.32	77.2	86.9
200	9,618	23.08	0.36	0.23	0.78	1.37	76.3	84.1
(Pittsburgh No. 8 coal, -200 mesh)								
-[b]	12,916	12.65	1.01	0.07	1.13	2.21	----	----
50	12,925	12.59	0.18	0	1.09	1.27	42.5	92.2
100	12,948	12.43	0.18	0.01	0.99	1.18	46.6	93.7
150	12,882	12.88	0.13	0.01	1.01	1.15	48.0	94.8
200	12,895	12.79	0.15	0	1.01	1.16	47.5	93.1
(Illinois No. 5 coal, -200 mesh)								
-[b]	11,899	13.65	1.26	0.14	1.28	2.68	----	----
50	11,190	18.80	0.32	0.03	1.36	1.71	36.0	88.3
100	11.209	18.66	0.33	0.08	1.12	1.53	42.9	87.1
150	11,199	18.73	0.42	0.10	0.94	1.46	45.5	87.5
200	11,236	18.46	0.25	0.07	1.07	1.39	48.1	85.7

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[a] Leached 1 hr. with 0.2M Na_2CO_3 at 150°C.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

with increasing pressure. The overall reduction in total sulfur was best for Lovilia coal, approaching 77%. However, the residual levels of pyritic sulfur seemed to linger around 0.3 - 0.4 lb./10^6 Btu. For Illinois coal, the residual pyritic sulfur levels were similar to those for Lovilia coal, although the total sulfur reduction was not nearly as high, amounting to only 48%, at best. For Pittsburgh coal, the best reduction in total sulfur was also only 48%, but the pyritic sulfur levels dropped to as low as 0.13 lb./10^6 Btu. For all three coals, however, the heating value recovery was relatively good (84 - 95%) and did not seem to be affected by increased oxygen partial pressure. The reduction in organic sulfur content was best for Lovilia coal; it seemed to improve with increasing oxygen partial pressure. The organic sulfur reduction was less for Illinois coal and least for Pittsburgh coal. The difference may be related to the nature of the organic sulfur compounds in the three coals.

Effect of Temperature. The effect of temperature on the desulfurization of coal is described by the results presented in Table 4 and Figures 3 and 4. The data are for Lovilia coal, at both 50 and 200 psia oxygen partial pressure. Under both conditions, the total sulfur reduction increased first with increasing temperature, then passed through a broad maximum, and finally decreased at an increasing rate. The temperature range of the maximum was approximately 120 - 150°C at 50 psia oxygen and approximately 140 - 160°C at 200 psia oxygen. The greatest amount of sulfur extracted was 71% at 50 psia oxygen and 79% at 200 psia oxygen. At 200°C the total sulfur reduction was only 32% at 50 psia oxygen and 44% at 200 psia oxygen.

At both partial pressures of oxygen, the relative reductions in pyritic and organic sulfur seemed to parallel the reduction curve for total sulfur, reaching optimum values in the same temperature ranges. The removal of organic sulfur seemed minimal, if any, at the lower and at the higher temperatures. Only sulfate sulfur appeared to have a constant residual value, invariant with temperature. The heating value recovery, on the other hand, declined steadily with increasing temperature. The decline was much more rapid at the higher pressure, the heating value recovery dropping to about 35% at 200°C for 200 psia oxygen partial pressure but only to about 78% for 50 psia.

At the present time, it is not certain what causes this unusual temperature effect resulting in a maximum in the sulfur removal data. There may be a decrease in the solubility of oxygen in the sodium carbonate solution at higher temperatures. This can occur even at the higher oxygen partial pressure. Alternatively, there may be a change in the reaction mechanism or kinetics possibly caused by the decomposition of a reactive but thermally unstable intermediate. Or perhaps, the observed phenomenon may be caused by a heat-induced change in the structure of coal itself. In any case, the effect of temperature on the desulfurization of coal warrants further investigation in order to optimize the process.

Effect of Leaching Time. The effect of leaching time on the desulfurization of Lovilia coal is shown in Table 5. The coal was leached at 150°C and at oxygen partial pressures of 50 to 200 psia. In both cases, prolonged leaching with 0.2M sodium carbonate improved the extraction of total sulfur at first. But after about 1.5 hr., the reduction in total sulfur leveled off at about 76 - 79% for the lower and about 76 - 80% for the higher oxygen partial pressure. The initial increase in extraction seemed to be caused by the removal of additional pyritic sulfur, since the amount of organic sulfur removed appeared fairly

Table 4. Effect of temperature on alkaline leaching of coal.[a]

Temp., °C	H.V. Btu./lb.	Ash %	Sulfur Distribution, lb./10^6Btu Pyr.	Sulf.	Org.	Tot.	Total S. Redn.,%	H.V. Recov.,%
(At 50 psia O_2)								
–[b]	10,047	19.57	3.90	0.94	0.93	5.77	----	----
100	9,666	22.62	1.25	0.28	0.69	2.22	61.5	89.7
120	9,634	22.87	0.80	0.29	0.56	1.65	71.4	88.2
130	9,662	22.65	0.88	0.23	0.64	1.75	69.7	89.2
150	9,268	25.90	1.42	0.20	0.70	2.32	59.4	83.6
170	9,205	26.31	1.51	0.27	0.59	2.37	58.9	80.2
180	9,016	27.82	1.71	0.22	0.98	2.91	49.7	75.9
200	8,950	28.35	2.69	0.23	0.98	3.90	32.4	78.2
(At 200 psia O_2)								
–[b]	10,545	17.09	2.80	1.04	0.63	4.47	----	----
120	10,272	19.24	0.39	0.10	0.67	1.16	74.1	88.6
140	10,316	18.89	0.42	0.07	0.55	1.04	76.7	85.4
150	10,243	19.47	0.50	0.06	0.38	0.94	79.0	81.6
160	10,258	19.35	0.37	0.05	0.57	0.99	77.9	77.6
180	9,872	22.38	0.75	0.01	0.57	1.33	70.3	63.0
200	8,407	33.90	1.94	0.13	0.42	2.49	44.3	34.7

---

[a] Lovilia coal (-200/+250 mesh), uncleaned; leached 1 hr. with 0.2$\underline{M}$ Na_2CO_3

[b] Heating value, ash content, and sulfur distribution of unleached coal.

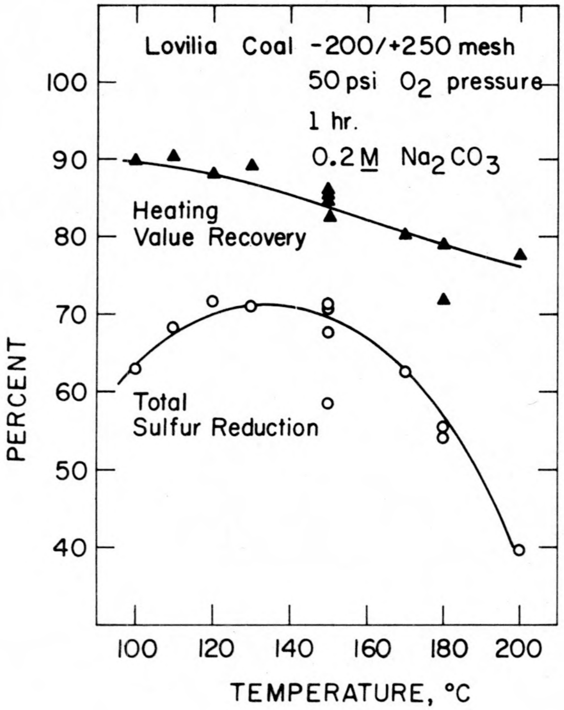

Figure 3. Desulfurization of coal as a function of temperature at 50 psia oxygen.

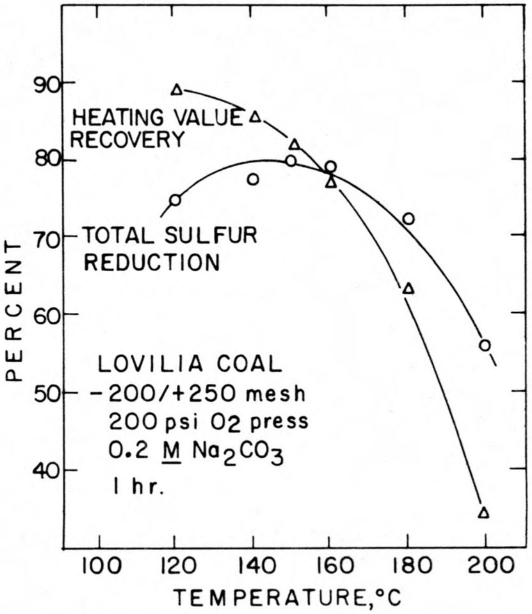

Figure 4. Desulfurization of coal as a function of temperature at 200 psia oxygen.

Table 5. Leaching of coal as a function of time.[a]

Temp., °C	H.V. Btu./lb.	Ash %	Sulfur Distribution, lb./10^6Btu				Total S Redn.,%	H.V. Recov.,%
			Pyr.	Sulf.	Org.	Tot.		
(At 50 psia O_2)								
-[b]	10,175	18.63	3.84	0.92	1.02	5.78	----	----
0.5	9,686	22.53	0.92	0.24	0.67	1.83	68.3	86.9
1.0	9,601	23.22	0.76	0.15	0.87	1.78	69.2	86.1
1.5	9,674	22.63	0.56	0.25	0.55	1.36	76.5	81.2
2.0	9,706	22.38	0.39	0.22	0.74	1.35	76.6	81.6
2.5	9,414	24.71	1.03	0.34	0.70	2.07	64.2	76.6
3.0	9,651	22.81	0.53	0.22	0.48	1.23	78.7	80.9
(At 200 psia O_2)								
-[b]	10,726	17.95	3.37	0.94	0.90	5.21	----	----
0.5	10,228	21.76	0.47	0.23	0.72	1.42	72.7	88.7
1.0	10,226	21.77	0.44	0.22	0.66	1.32	74.7	86.5
1.5	10,265	21.47	0.39	0.21	0.67	1.27	75.6	85.7
2.0	10,256	21.54	0.33	0.22	0.60	1.15	77.9	83.2
2.5	10,241	21.66	0.36	0.28	0.69	1.33	74.5	81.6
3.0	10,314	21.10	0.35	0.20	0.51	1.06	79.7	79.1

---

[a] Lovilia coal (-200/+250 mesh), uncleaned; leached with 0.2M Na_2CO_3 at 150°C.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

constant at both pressures. On the other hand, the heating value recovery decreased with increasing time. The decrease was approximately the same at both the lower and the higher pressure. Thus, the relatively small advantage of removing the little additional pyritic sulfur was offset by an increased loss in the heating value.

The desulfurization of Lovilia coal as a function of leaching time was repeated at 50 psia oxygen and lower temperatures (110 and 130°C). The results are summarized in Table 6. At 110°C, there seemed to be a steady improvement in the total sulfur reduction with increased time, all due to the additional removal of pyritic sulfur. However, after 0.5 hr. the sulfur reduction was rather low (56.2%), and after 3 hr. the sulfur reduction reached a maximum value (71%), which was comparable to that achieved in 1 hr. at 150°C. On the other hand, at 110°C the heating value recovery was relatively high (about 93%), and it did not decrease with prolonged leaching.

At 130°C, leaching for 1 hr. resulted in a total sulfur reduction of 70.5%, which was comparable to the reduction achieved at 150°C. Further leaching did not produce much improvement; both the pyritic and the organic sulfur contents approached constant values. At 130°C the heating value recovery (91 - 92%) was better than that at 150°C (82 - 86%). Thus, there are some advantages in using a lower temperature and a relatively short time for leaching.

Effect of Pulp Density. In each of the previous coal leaching experiments, 40 g. of coal and 400 ml. of leach solution were used. In order to study the possible effect of pulp density on desulfurization, a series of experiments was run with different concentrations of solids in the slurry. The results are portrayed by Figure 5. It is evident that the total sulfur reduction was not affected by the pulp density. The heating value recovery, however, increased with pulp density. This increase may have been due to more complete recovery of the leached solids by filtration and to smaller losses in handling the solids.

Effect of Oxygen Flow Rate. Another aspect of the described procedure was investigated by varying the oxygen flow rate during a series of experiments in which Lovilia coal was leached at 150°C and 50 psia oxygen partial pressure for 1 hr. Because the system was bled continuously throughout each run to prevent any build-up of gaseous reaction products, oxygen was supplied on demand to keep the system pressure constant at the desired level. The experiments were designed to test the effect, if any, of the rate of oxygen flow through the pressurized autoclave on desulfurization. The data are presented in Table 7. The oxygen flow was varied from 1.5 to 8.0 cu. ft./hr., as measured with a rotameter. There was apparently no effect either on the total sulfur reduction or on the heating value recovery. For all subsequent experiments, the oxygen flow rate was kept constant at 1.5 cu. ft./hr. just as a precaution to ensure that sufficient oxygen was supplied to the autoclave.

Effect of Acid Treatment. It had been observed previously (2) that during leaching of Lovilia coal, the residual pyritic sulfur levels rarely dropped below 0.3 - 0.4 lb./10^6Btu. In the work of Chen (3), it was postulated that a shell of hematite is formed around a shrinking core of unreacted pyrite as a particle of pyrite is oxidized by the leach solution. To test this postulate an experiment was conducted whereby some Lovilia coal was first leached with an

Table 6. Effect of time on leaching of coal at lower temperatures and low oxygen partial pressure.[a]

Time, hr.	H.V. Btu./lb.	Ash %	Sulfur Distribution, lb./10^6Btu Pyr.	Sulf.	Org.	Tot.	Total S Redn.,%	H.V. Recov.,%
(At 110°C and 50 psia O_2)								
-[b]	10,726	17.95	3.37	0.94	0.90	5.21	----	----
0.5	10,344	20.87	1.32	0.23	0.73	2.28	56.2	93.1
1.0	10,303	21.18	0.94	0.26	0.67	1.87	64.1	93.2
2.0	10,275	21.40	0.55	0.26	0.79	1.60	69.3	93.2
3.0	10,222	21.80	0.43	0.30	0.78	1.51	71.0	93.4
(At 130°C and 50 psia O_2)								
-[b]	10,940	16.69	2.88	0.88	0.88	4.64	----	----
0.5	10,538	19.75	0.75	0.20	0.63	1.58	66.0	92.7
1.0	10,475	20.23	0.50	0.20	0.67	1.37	70.5	91.9
1.5	10,366	21.06	0.49	0.24	0.67	1.40	69.8	91.4
2.0	10,393	20.86	0.40	0.19	0.59	1.18	74.6	90.5
2.5	10,393	20.86	0.40	0.32	0.63	1.35	70.9	91.4
3.0	10,386	20.91	0.43	0.26	0.56	1.25	73.1	89.7

---

[a] Lovilia coal (-200/+250 mesh), uncleaned; leached with 0.2M Na_2CO_3 at 50 psia O_2.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

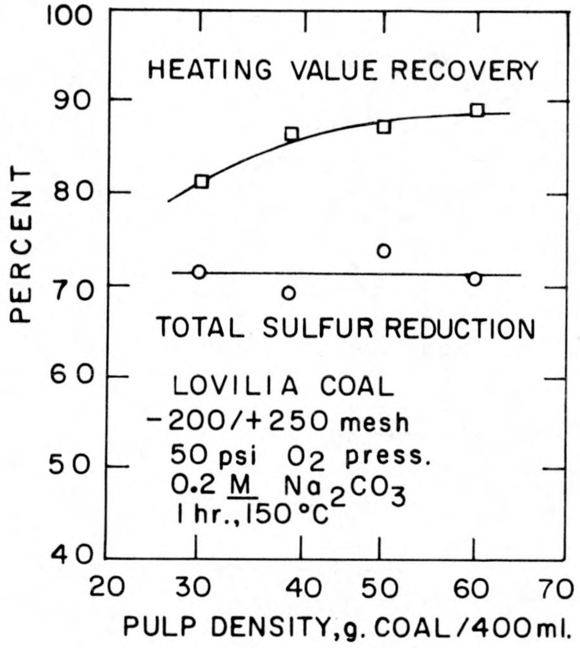

Figure 5. Effect of pulp density on leaching of coal.

Table 7. Effect of oxygen flow rate on leaching of coal.[a]

O_2 flow cu.ft./hr.	H.V. Btu./lb.	Ash %	Sulfur Distribution, lb./10^6Btu				Total S Redn.,%	H.V. Recov.,%
			Pyr.	Sulf.	Org.	Tot.		
-[b]	10,726	17.95	3.37	0.94	0.90	5.21	----	----
1.5	10,252	21.57	0.45	0.20	0.81	1.46	72.0	89.4
2.7	10,071	22.96	0.70	0.29	0.76	1.75	66.4	87.1
3.4	10,088	22.83	0.58	0.23	0.68	1.49	71.4	87.2
8.0	10,180	22.12	0.53	0.24	0.72	1.49	71.4	88.0

---

[a] Lovilia coal (-200/+250 mesh), uncleaned; leached 1 hr. with 0.2M Na_2CO_3 at 150°C and 50 psia O_2.

[b] Heating value, ash content, and sulfur distribution of unleached coal.

alkaline solution and next washed with hot hydrochloric acid to dissolve the anticipated iron oxide shell. The coal was then leached again with an alkaline solution to extract the remaining pyrite.

The results of this experiment are summarized in Table 8. The first leaching step reduced the pyritic sulfur content from 3.37 to 0.45 lb./10^6 Btu. Subsequent treatment with hot hydrochloric acid did not affect the pyritic sulfur content significantly. But the second alkaline leaching step did reduce the pyritic sulfur content to 0.14 lb./10^6Btu. Since the final pyritic sulfur content was much lower than was obtained previously after 2.0 hr. or even 3.0 hr. of leaching in a single treatment (see Table 5), the results did support the initial postulate. Therefore the results strongly suggest that the rate of pyritic sulfur removal from a single particle is slowed by the build-up of a shell of iron oxide around a reacting core of pyrite.

Table 8. Effect of acid treatment on repeated leaching of coal.[a]

Treatment	H.V. Btu./lb.	Ash %	Sulfur Distribution, lb./10^6Btu Pyr.	Sulf.	Org.	Tot.	Total S Redn.,%	H.V. Recov.,%
none	10,726	17.95	3.37	0.94	0.90	5.21	----	----
L[b]	10,537	19.39	0.45	0.09	0.76	1.30	75.0	
L + A[c]	11,929	8.76	0.43	0.05	0.77	1.25	76.0	
L + A + L	9,656	26.13	0.14	0.26	0.84	1.24	76.2	73.5

[a] Lovilia coal (-200/+250 mesh), uncleaned.

[b] L = leached 1 hr. with 0.2M Na_2CO_3 at 150°C and 50 psia O_2.

[c] A = acid treated for 1 hr. at 60°C with 300 ml. conc. HCl + 60 ml H_2O.

Two-Step Leaching. An attempt was made to improve the alkaline leaching process by adding a second step which was conducted under nonoxidizing conditions at a higher temperature than the first step. In the first step fine-size coal was leached for 1 hr. with 0.2M Na_2CO_3 at 150°C and 50 psia oxygen partial pressure. At the end of this step, the oxygen flow was interrupted, and the reactor was thoroughly flushed with nitrogen while the temperature was raised to 230 - 240°C. When this temperature was reached, the system was maintained constant for 1 hr. The total pressure was around 450 - 500 psig, while the oxygen partial pressure was essentially zero. It was hoped that the increase in temperature would remove additional organic sulfur. Furthermore, by removing all oxygen from the system, it was unlikely that the coal heating value would be affected.

Preliminary tests of the two-step process were performed on Lovilia and Western Kentucky coals. The results obtained with Lovilia coal are presented in Table 9. It can be seen that whereas the one-step method removed only 15% of the organic sulfur, the two-step method appeared to remove from 50 to 73%

Table 9. Two-step leaching of Lovilia coal (-200/+250 mesh).

Sample No.	Treatment[a]	H.V., Btu./lb.	Ash %	Sulfur Distribution, lb./10^6Btu				Total S Redn.,%	Org. S Redn.,%	H.V. Recov.,%
				Pyr.	Sulf.	Org.	Tot.			
AK 55	Untreated	10,175	18.63	3.84	0.92	1.02	5.78	----	----	----
AK 57	Step I only	9,601	23.22	0.76	0.15	0.87	1.78	69.2	14.7	86.1
AK 70	Untreated	10,390	18.34	3.12	0.94	1.03	5.09	----	----	----
AK 99	Step I + Step II (210-235°C)	9,621	26.58	0.66	0.19	0.52	1.37	73.1	49.5	78.0
AK 110	Untreated	10,940	16.69	2.88	0.88	0.88	4.64	----	----	----
AK 126	Step I + Step II (230°C)	10,209	23.01	0.73	0.21	0.66	1.60	65.5	25.0	84.7
AK 127	Step I + Step II (230°C)	10,250	21.94	1.00	0.02	0.25	1.27	72.6	71.6	80.6
AK 128	Step I + Step II (240°C)	10,211	22.24	0.97	0.02	0.24	1.23	73.5	72.7	79.1
AK 129	Step I + Step II (240°C)	10,296	21.98	0.69	0.02	0.37	1.08	76.7	58.0	80.0

[a] Step I: Leached 1 hr. at 150°C and 50 psia O_2 with 0.2<u>M</u> Na_2CO_3.

Step II: Leached 1 hr. with 0.2<u>M</u> Na_2CO_3 at indicated temperature in N_2 atmosphere.

of the organic sulfur in most of the tests. On the other hand, the removal of pyritic sulfur was not improved by the two-step approach. The heating value recovery declined from 86% for the one-step treatment to about 80% for the two-step treatment.

The results of applying the two-step process to Western Kentucky coal are shown in Table 10. Again the two-step method appeared to increase the removal of organic sulfur because the two-step treatment reduced the organic sulfur content 15 - 30% while the one-step treatment reduced it only 8%. The heating value recovery was also reduced, from 90% for the one-step method to 85% for the two-step method.

Future work. Additional laboratory experiments with the stirred reactor are planned in order to establish optimum conditions for the desulfurization of coal. Specifically, the effect of higher temperatures and the relative effectiveness of alkalis other than sodium carbonate will be studied. Particular attention will be given to the removal of organic sulfur. The use of the two-step leaching method and its effect on the extraction of organic sulfur will be explored further in more detail.

Tubular Reactor System

In previous studies (1,3) using the packed bed tubular reactor, it was observed that the rate of pyrite conversion was affected not only by particle size but also by the amount of pyrite packed in the reactor. The greater the charge size, the lower was the percent conversion of pyrite. The effect was more pronounced for finer than for coarser particles of pyrite.

It was also observed (2) that the conversion of sulfur was not uniform along the length of the packed bed; the conversion decreased from the end where the leaching solution entered to the end where it exited. Several possible reasons for this decrease in sulfur conversion with bed length have been considered. One possibility, the presence of rate-inhibiting reaction products has been discounted because no effect was produced by introducing possible reaction products into the leach solution (3). Another possibility, the accumulation of finer particles in the downstream end of the reactor and partial blockage of the bed has also been considered. An additional possibility is that the leach solution becomes oxygen depleted as it passes through the packed bed which causes the rate of reaction to decrease toward the outlet end. Several experiments were conducted to investigate the last possibility and the results of these are described below.

The schematic flow diagram for the tubular reactor system is depicted in Figure 6. The flow system encompasses a delivery unit for the leaching solution, an oxygen feed system, the reactor proper, a gas-liquid separator, and the associated controls for temperature and pressure. The reactor tube itself (15 cm. long and 0.64 cm. inside diameter) is manufactured from Inconel 600. It can accommodate about 15 g. ground pyrite or about 5 g. pulverized coal. The system can be operated at pressures up to 3000 psi and temperatures up to 480°C. The reactor temperature is maintained by immersing the reactor in an electrically heated fluidized sand bed.

Table 10. Two-step leaching of Western Kentucky coal (-200 mesh).

Sample No.	Treatment[a]	H.V., Btu./lb.	Ash %	Sulfur Distribution, lb./10^6Btu				Total S Redn,%	Org. S Redn.,%	H.V. Recov.,%
				Pyr.	Sulf.	Org.	Tot.			
AH 21	Untreated	10,890	18.27	0.89	0.86	1.43	3.18	----	----	----
AH 24	Step I only	10,322	21.71	0.10	0.07	1.32	1.49	53.1	8.0	90.0
AH 50	Untreated	10,559	20.43	1.01	1.31	1.21	3.53	----	----	----
AH 51	Step I + Step II	9,936	26.36	0.30	0.13	1.03	1.46	58.4	14.9	83.5
AH 52	Step I + Step II	10,013	25.79	0.47	0.15	0.83	1.45	58.1	31.4	86.8

[a] Step I: Leached 1 hr. at 150°C and 50 psia O_2 with 0.2$\underline{M}$ Na_2CO_3

Step II: Leached 1 hr. with 0.2$\underline{M}$ Na_2CO_3 at 230°C and 450 psig in N_2 atmosphere.

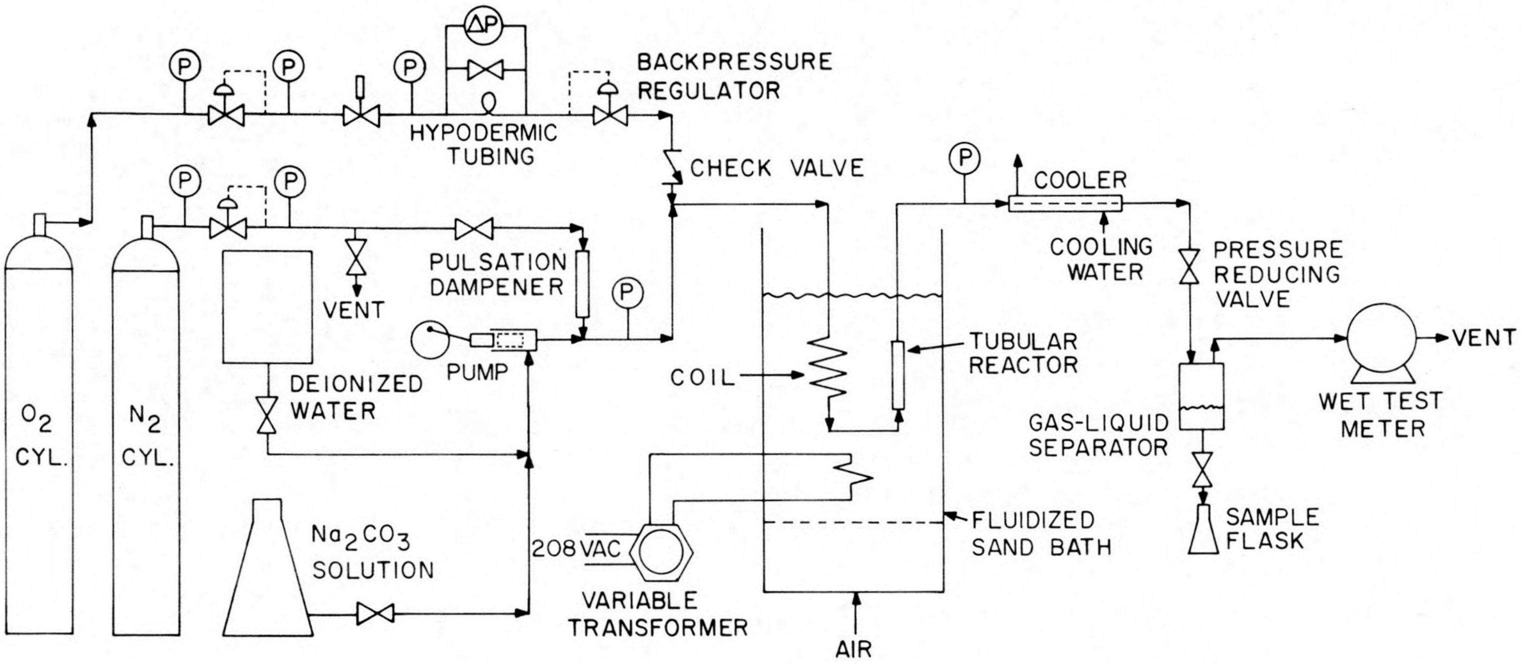

Figure 6. Schematic flow diagram of the tubular reactor system.

The aqueous leaching solution is delivered to the reactor at a controlled rate by a variable stroke plunger pump. Oxygen is supplied at a measured rate from a high-pressure cylinder through a flow restriction across which is a differential pressure gauge and is mixed with the leach solution at the desired pressure. The mixture of gas and liquid is heated up to the temperature of the reactor by passing through a coil of tubing immersed in the fluidized bed of sand just ahead of the reactor. The mixture is then fed directly into the reactor at the required temperature and pressure. The effluent coming out of the reactor is cooled by a heat exchanger, allowed to expand through a pressure reducing valve, and separated into the gas and liquid components. The gas is delivered to a wet test meter to monitor the flow rate, and the liquid is collected in measured portions for subsequent analysis for sulfur.

The experiments were performed using pyrite derived from Iowa coals during physical cleaning in the ISU coal preparation plant. The pyrite was ground, sized, and analyzed for iron and total sulfur. The analysis, 43.2% iron and 45.9% sulfur on the average, indicated an apparent purity of 86%. The atomic sulfur-to-iron ratio, being 1.85 instead of the theoretical 2.0 required by FeS_2, suggested that not all of the iron present was in the pyritic form. Similar conclusions were also reached based on the determination of iron in the liquid effluent from the reactor.

For each experiment, a weighed amount of the pyrite was packed into the tubular reactor, the loaded reactor was immersed in the preheated fluidized sand bath and connected to the rest of the system. The system was first purged and pressurized with nitrogen, and deionized water was pumped through it. Then the nitrogen flow was stopped, the feed was switched to the leach solution, and, almost simultaneously, the oxygen flow was started. The pressure of the system was adjusted to the desired level by a back pressure valve located downstream from the reactor. The pressure, temperature, and liquid and gas feed rates were maintained constant throughout the entire run. The gas flow rate was monitored by a wet test meter. For each run, the liquid effluent was collected in measured portions for subsequent analysis for sulfate. At the end of each run, the solid residue was removed from the reactor, weighed, and analyzed for total sulfur.

Several additional exploratory runs were made. The reactor was packed with 15 g. of pyrite (-80/+100 mesh), and the leach solution (2% sodium carbonate) was passed through the bed for 1 hr. at 150°C and at two different flow rates. The oxygen rate was maintained at 9.5 ml./sec., but the oxygen partial pressure was different for each run at a given liquid rate. At the end of each experiment, the insoluble bed residue was removed in three measured segments from the front, the middle, and the rear of the reactor. Each segment was analyzed separately for total sulfur and total iron, and the percent sulfur conversion was calculated for each segment, using the sulfur-to-iron ratios of the original sample and of the residue in each segment as the basis for the calculation. Thus, the conversion in each segment was calculated by this formula:

$$\text{conversion } (\%) = \frac{[(\%\text{Tot. S}/\%\text{Tot. Fe})_{\text{orig}} - (\%\text{Tot. S}/\%\text{Tot. Fe})_{\text{final}}] \times 100}{(\%\text{Tot. S}/\%\text{Tot. Fe})_{\text{orig.}}}$$

This was done to minimize the effect in the variation of sample size as each segment was removed from the reactor. The sulfur conversion of the whole bed continued to be calculated as before (3) on the basis of total sulfur removed.

The results are presented in Table 11. From the data, two effects are immediately evident. First of all, the different liquid flow rates did not produce much difference in the sulfur conversion for the reaction as a whole. This confirmed the previous results (1,3). However, at a given oxygen partial pressure, the difference in sulfur conversion between the front and the rear portion of the reactor bed was significantly lower for higher liquid rates. At 48 psia oxygen partial pressure, for example, the difference dropped from 12.9% to 3.8% by increasing the liquid flow rate from 1.5 to 3.0 ml./sec. The effect of increased oxygen partial pressure on the difference in sulfur conversion across the bed was less regular. But the total sulfur conversion for the whole reactor increased with increasing pressure, just as expected.

Several experiments were also carried out to investigate the possibility that the difference in sulfur removal from different segments of the bed was due to the hydrodynamic pressure drop across the bed and consequent reduction in oxygen partial pressure. Between individual experiments the oxygen partial pressure was changed, but the liquid flow rate and other conditions were not changed. After each experiment the bed was divided into three segments as before, and the total sulfur content of each segment was determined. From the results shown in Table 12 it can be seen that the pressure drop across the reactor was

Table 11. Effect of oxygen partial pressure and of liquid flow rate on total sulfur conversion for pyrite.[a]

Run No.	Liquid rate, ml./sec.	Total press., psig	O_2 press., psia	[b]Total sulfur conversion, %				
				Whole bed	Bed segments			Difference
					Front (F)	Middle	Rear (R)	(F) - (R)
10	1.5	100	48	63.1	67.7	61.5	54.8	12.9
2	1.5	148	96	71.7	79.1	65.6	58.3	20.8
6	1.5	244	192	86.7	89.7	84.8	82.3	7.4
9	3.0	100	48	65.8	69.3	67.4	65.5	3.8
11	3.0	148	96	71.8	76.4	70.9	64.4	12.0
12	3.0	244	192	84.3	85.9	84.3	81.4	4.5

[a] Pyrite (-80/+100 mesh), 15 g. charge, leached 1 hr. with 2% Na_2CO_3 at 150°C, 9.5 ml. O_2/sec.

[b] Sulfur conversion based on analysis of solids.

Table 12. Effect of pressure drop across reactor on sulfur removal from pyrite in packed bed.[a]

Total press., psig		O_2 press., psia		ΔP_{O_2}	[b]Total sulfur conversion,%				
						Bed segments			
Inlet	Outlet	Inlet	Outlet	%	Whole bed	F	M	R	F-R
150	100	98	48	51	83.6	84.7	81.7	76.6	8.1
200	155	148	103	30	90.3	91.8	90.0	87.0	4.8
300	250	248	198	20	95.9	96.7	96.1	94.4	2.3
400	350	348	298	14	96.5	97.0	96.7	94.4	2.6

[a] Pyrite (-60/+80 mesh), 14 g. charge, leached 1 hr. at 150°C with 2% Na_2CO_3, 1.5 ml. liquid/sec., 9.5 ml.O_2/sec.

[b] Sulfur conversion based on analysis of solids.

50 psia during most of the runs, regardless of the total pressure. But the relative change in oxygen partial pressure expressed as a percent of the inlet oxygen partial pressure decreased with increased oxygen partial pressure. Thus when the inlet partial pressure was 98 psia, the outlet partial pressure was 51% lower, but when the inlet partial pressure was raised to 348 psia, the outlet partial pressure was only 14% lower. It appeared that as a consequence of reducing the relative change in oxygen partial pressure across the bed, the difference in sulfur conversion between the various segments of the bed was reduced. Thus at the lowest oxygen partial pressure the difference in sulfur conversion between the front and rear segments of the bed was 8.1% while at the highest partial pressure it was only 2.6%. Although these results did not prove conclusively that the change in pyrite conversion across the bed was due to the change in oxygen partial pressure, they did tend to support this possibility.

In the future, further consideration will be given to the cause of the relative high pressure drop across the bed and its possible effect on the rate of sulfur removal.

Froth Flotation

Although froth flotation is being used industrially to recover fine-size coal, in its present state of development it does not generally provide a good separation between coal and iron pyrites, particularly where the pyrite particles are finely disseminated microcrystallites. Part of the problem appears due to the similarity in surface properties of unweathered bituminous coal and clean unoxidized pyrite. Both materials tend to be naturally hydrophobic and float readily in the presence of a frother such as methyl isobutyl carbinol (MIBC). In the past various chemical agents have been suggested as selective flotation depressants for pyrite but none appear to have been adopted in commercial coal flotation practice (4).

Since the present investigation is seeking to improve the technology of coal flotation, further consideration is being given to potential methods of depressing pyrite. In the work described below, several of these methods were evaluated by applying them to coal-derived pyrites and beneficiated coal fines, after which the relative floatability of the materials was measured with a modified Hallimond tube microflotation cell. This cell was described in a previous report (1). The measurement technique involved placing 1 g. of coal or pyrite particles and 100 ml. of water in the cell together with a frothing agent and measuring the percentage of solids by weight which was floated and recovered in 4 min. when the suspension was aerated with nitrogen.

Materials

Coal used for this series of experiments was obtained from the Childers site adjacent to the Iowa State University Demonstration Mine in Mahaska County, Iowa. This material, which appeared to be high volatile C in rank, was first crushed and screened in the laboratory to produce a quantity of 3/8 in. x 4 mesh size particles. These particles were cleaned subsequently by float/sink separation in a magnetite suspension having a specific gravity of 1.29. The coal which floated was further crushed, ground, and wet screened to produce the 80 mesh x 100 mesh particles used for the floatability measurements. This material was stored under water until needed to minimize surface oxidation. As indicated by Table 13, the impurity content of the prepared coal (3.5% ash) was relatively low.

Pyrite used for this series of experiments was recovered in the form of nodules from the refuse produced by the ISU coal preparation plant while cleaning coal from the Childers site. The nodules were cleaned and then in the dry state they were crushed, pulverized, and screened to produce the

Table 13. Impurity content of precleaned coal.

Component		wt.%
Ash		3.46
Sulfur		
Pyritic	0.62	
Sulfate	0.09	
Organic	4.58	
Total	5.29	5.29
Calcium		0.08
Iron		0.73

115 mesh x 150 mesh particles required for the floatability measurements. The composition of the raw sized pyrite is shown in Table 14; the data indicate that the material contained about 74% FeS_2 based on the pyritic sulfur content of the sample as determined by the standard ASTM procedure for determining pyritic sulfur in coal. Analysis of the material by X-ray diffraction showed that it contained a small amount of marcasite (less than 1%), a trace of bassanite, and about 5% calcite in addition to iron pyrite.

Table 14. Composition of the raw sized pyrites and acid cleaned pyrites.

Component	Ray pyrites	Acid cleaned pyrites	
		cold HCl	hot HCl
Pyritic sulfur, wt.%	39.7	46.6	47.0
Total sulfur, wt.%	40.2	47.2	47.9
Iron, wt.%	38.3	43.6	43.9
Calcium, wt.%	4.8	0.2	0.2
Iron pyrites, wt.%	74.3	87.2	87.9
Sulfur : iron ratio	1.81	1.86	1.86

Effect of Surface Cleaning

Since the impurities present in the raw pyrites could have affected the floatability of the material, different portions of sized pyrites were cleaned by different methods before testing. The first method involved washing the pyrites with water to remove soluble sulfates. The second method involved soaking the pyrites in cold 5% hydrochloric acid for 8 hr. and rinsing with water to remove calcium carbonate and some forms of iron oxide in addition to soluble sulfates. The third method involved soaking the pyrites in boiling 5% hydrochloric acid for 2 hr. and rinsing with water to remove the less soluble iron oxides, sulfates, and carbonates. The cleaned materials were stored under water to minimize contact with the air. The composition of the acid cleaned and of the raw pyrites reported in Table 14 shows that acid cleaning increased the pyrite (FeS_2) content of the material from 74% to either 87 or 88% depending on whether cold or hot acid was used. Also acid cleaning removed most of the calcium. However, the composition data do not indicate any major differences between the pyrites cleaned with cold acid and those cleaned with hot acid. X-ray diffraction analysis of the hot acid cleaned pyrite indicated that the material was principally pyrite with only a trace of marcasite.

Examination of the raw pyrites and hot acid cleaned pyrites with a scanning electron microscope revealed some important differences in the appearance of the surface of the two kinds of particles. Whereas the raw pyrite particles were coated with very fine debris, the acid cleaned particles were not coated. Moreover the surface of the acid cleaned particles was etched while that of the raw pyrite particles was not. In addition several small clusters of needle-shaped crystals (probably gypsum) were present on the surface of some of the raw pyrite particles but not on the surface of the acid cleaned particles.

Measurement of the floatability of the raw pyrites and of the pyrites cleaned by the different methods described above revealed important differences in the floatability of the particles receiving the various treatments (Table 15). Thus when 10 μl MIBC was employed, 53% of the hot acid cleaned pyrites, 22% of the cold acid cleaned pyrites, or 11% of either the water washed or raw pyrites were floated and recovered in the Hallimond cell. When 1 μl MIBC was used, much less pyrite was floated and recovered in all cases, and the hot acid cleaned pyrite was the only material recovered in a larger amount than the raw pyrites. When no MIBC was used, the recovery of pyrite was uniformly low (1 - 3%) regardless of surface preparation. Each value of the relative recovery listed in Table 15 is an average of two or more determinations; the standard deviation of each set of determinations is indicated. Since the standard deviation was small in most cases, the measurements were fairly reproducible.

Table 15. Floatability of pyrites cleaned by different procedures and effect of different concentrations of MIBC.

Cleaning procedure	Relative recovery, %			Standard deviation, %		
	0 μl MIBC	1 μl MIBC	10 μl MIBC	0 μl MIBC	1 μl MIBC	10 μl MIBC
None	2.6	3.8	11.4	0.18	0.13	2.25
Water washed	1.2	3.2	11.3	0.35	0.62	1.35
Cold acid cleaned	2.4	3.5	21.5	0.53	0.06	0.94
Hot acid cleaned	2.2	7.2	53.1	0.13	0.48	7.56

These results showed that the acid soluble impurities present in the raw pyrites affected the floatability of the material markedly. Since calcite was one of the principal impurities and would have been removed by either hot or cold acid, it is likely to have been one of the impurities affecting the floatability of pyrite. However, the fact that hot acid was more effective than cold acid points to the presence of additional impurities such as one of the less soluble iron oxides. In any case the results showed that floatable pyrites could be produced by the hot acid treatment. These pyrites would then be suitable for testing the effectiveness of various flotation depressants.

Since the recovery of clean pyrites was more pronounced when the higher concentration of MIBC was used, 10 μl MIBC was employed for most of the subsequent floatability measurements even though this amount was 20 to 30 times greater than would be used in commercial practice.

Tests of Potential Pyrite Depressants

A series of inorganic chemicals which might possibly depress pyrite in coal flotation was investigated with the microflotation cell. For each measurement one of the pure chemicals was added to a suspension of washed coal or hot acid cleaned pyrites in the cell together with 10 μl MIBC. In most cases the concentration of potential depressant ranged from 0.5 to 4.0 wt.% but in the case of calcium hydroxide it ranged from 0.03 to 0.15 wt.% because of the limited solubility of this material. The results are presented in Figures 7 and 8 and Table 16. Each point in these figures is an average of two measurements while each mean value in Table 16 is an average of 10 measurements over the indicated range of concentration. In Table 16 the results are arranged in order of effectiveness of the various chemicals for depressing pyrite.

From Table 16 it can be seen that calcium hydroxide was the most effective depressant for pyrite of all the chemicals tested. However, all of the chemicals reduced the floatability of pyrite to some extent. Also most of the chemicals reduced the floatability of coal but to a lesser extent than they reduced the floatability of pyrite. Figures 7 and 8 indicate that for most chemicals a concentration of 0.5 to 1.0 wt.% was as effective as much higher concentrations. In the case of calcium hydroxide a concentration as small as 0.03 wt.% appeared to be as effective for depressing pyrite as larger concentrations.

Table 16. Relative recovery of precleaned coal and hot acid washed pyrites in the presence of various reagents and 10 μl MIBC.

Reagent	Concentration wt.%	Relative recovery, %		Std. deviation, %	
		Pyrite	Coal	Pyrite	Coal
none	------	53.1	92.1	7.56	2.10
NaCl	0.5 - 4	30.2	90.0	1.95	1.74
$NaHCO_3$	1 - 4	26.6	86.9	3.11	1.56
$MgCl_2$	0.5 - 4	23.8	91.3	2.68	1.21
Na_2CO_3	0.5 - 4	22.2	85.4	2.37	3.37
$FeCl_3$	0.5 - 4	16.8	79.3	2.43	3.75
$CaCl_2$	1 - 4	15.7	85.9	2.60	2.29
NaOH	0.5 - 4	14.0	80.0	1.48	0.95
$Ca(OH)_2$	0.03 - 0.15	8.1	80.9	1.51	1.36

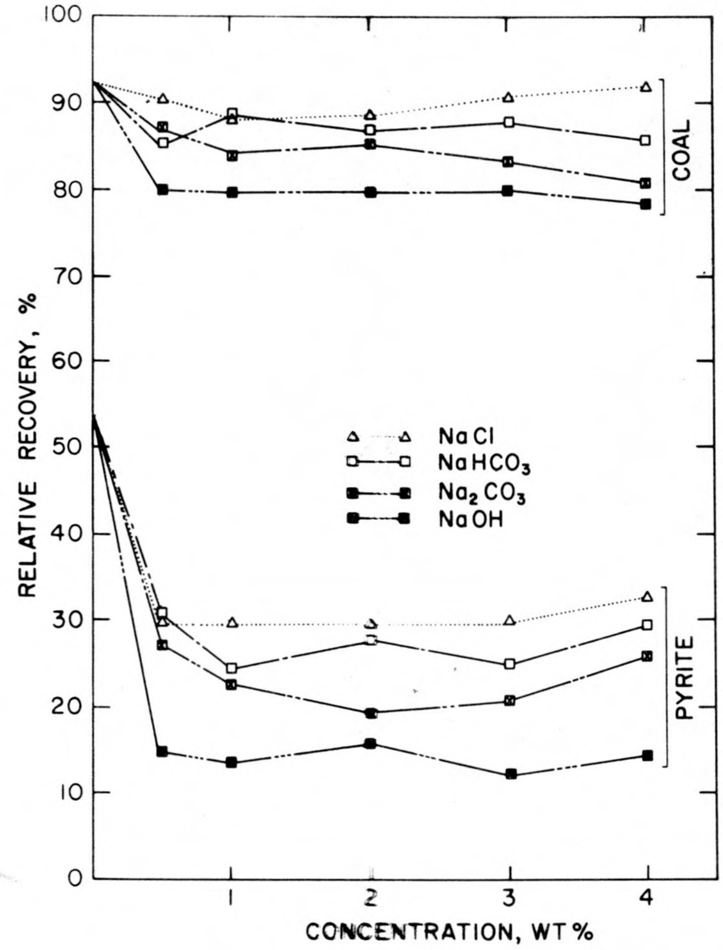

Figure 7. Effect of different alkalis on the floatability of coal and pyrite.

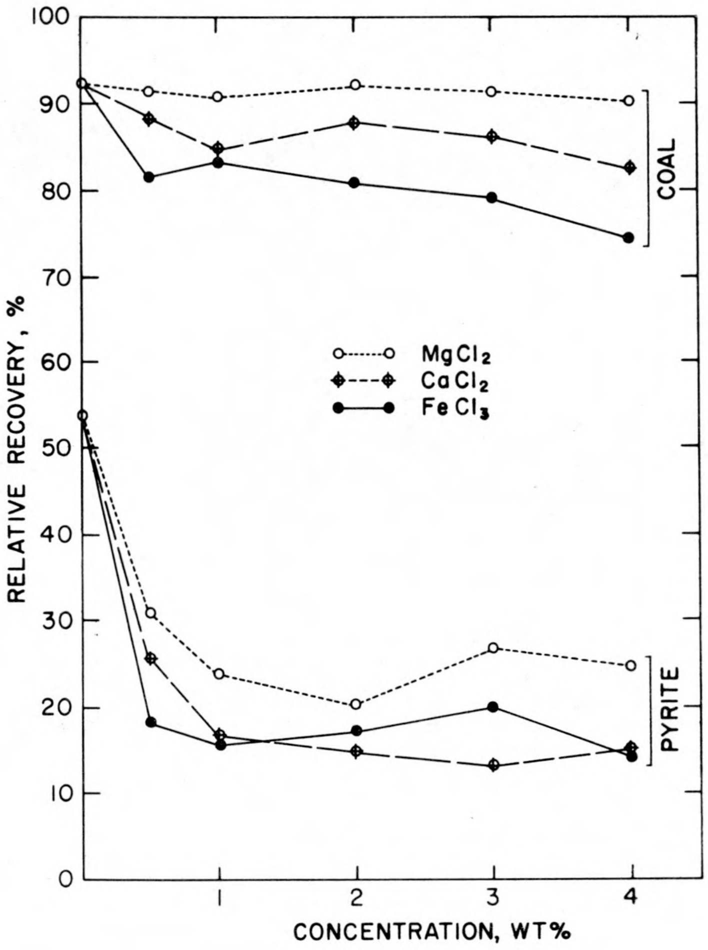

Figure 8. Effect of other reagents on the floatability of coal and pyrite.

The depressing action of the four sodium compounds was particularly interesting because the effectiveness of these compounds increased in proportion to their basicity, that is, in the following order; NaCl, $NaHCO_3$ Na_2CO_3 and NaOH. In other words, the relative recovery of both coal and pyrite decreased as the concentration of hydroxyl ions increased as a result of employing increasingly basic alkalis. This trend supports the suggestions of Glembotskii *et al.* (5) that pyrite is depressed by the adsorption of hydroxyl ions. However, the depressing action of sodium chloride which is a neutral salt suggests a different mechanism such as the adsorption of sodium ions. This possibility is supported by the work of Gaudin and Charles (6) which showed that pyrite adsorbs sodium ions in proportion to both the pH and concentration of sodium ions in solution. In actuality the adsorption of both sodium ions and hydroxyl ions may be involved in depressing pyrite.

The depressing action of calcium chloride and magnesium chloride on pyrite is also interesting. Calcium chloride proved nearly as strong a depressant as sodium hydroxide while magnesium chloride proved somewhat weaker. It seems likely that the depressing action of these compounds is due to the adsorption of calcium and magnesium ions by pyrite. Gaudin and Charles (6) showed that pyrite adsorbs calcium ions more strongly than sodium ions and, of course, calcium and magnesium tend to behave similarly.

The exceptional depressing action of calcium hydroxide on pyrite is probably due to the adsorption of both calcium ions and hydroxyl ions as Glembotskii *et al.* (5) suggested. These authors also suggested that calcium combines with various pyrite oxidation products forming hydrated films of calcium sulfate and/or carbonate on the pyrite surface.

Ferric chloride also proved to be a relatively strong depressant for pyrite, and at higher concentrations it proved to be the strongest depressant for coal among the chemicals tested. The action of ferric chloride seems due to the hydrolysis of the ferric ions and precipitation of colloidal ferric hydroxide which is adsorbed by the pyrite or coal. Baker and Miller (7) suggested such a mechanism in the case of pyrite.

Pyrite Depression by Wet Oxidation

Further experiments were conducted to develop and demonstrate the wet oxidation method of depressing pyrites in coal flotation which was described previously(1). For these experiments 115 mesh x 150 mesh pyrite particles which had been cleaned with hot hydrochloric acid as described above were treated with an aerated alkaline solution at 80°C for 15 min. to oxidize the surface of the particles. The suspension was cooled subsequently and transferred to the Hallimond cell where the floatability of the particles was determined using 10 μl MIBC. This treatment was also applied to precleaned 80 mesh x 100 mesh coal particles to see whether it would affect the floatability of coal as well.

The relative recovery of coal or pyrite particles which had been wet oxidized and floated in sodium carbonate solutions of various concentrations is indicated by Figure 9. The recovery of coal or pyrite particles which had not been wet oxidized is also shown for comparison. Each point plotted in this and subsequent

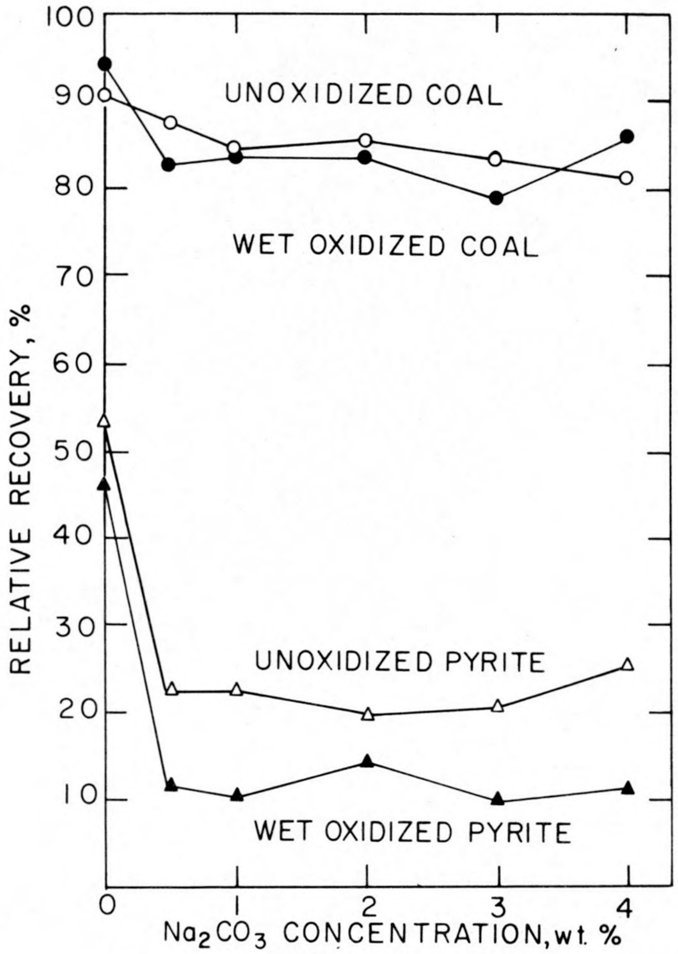

Figure 9. Effect of wet oxidation in Na_2CO_3 solutions on the floatability of coal and pyrite.

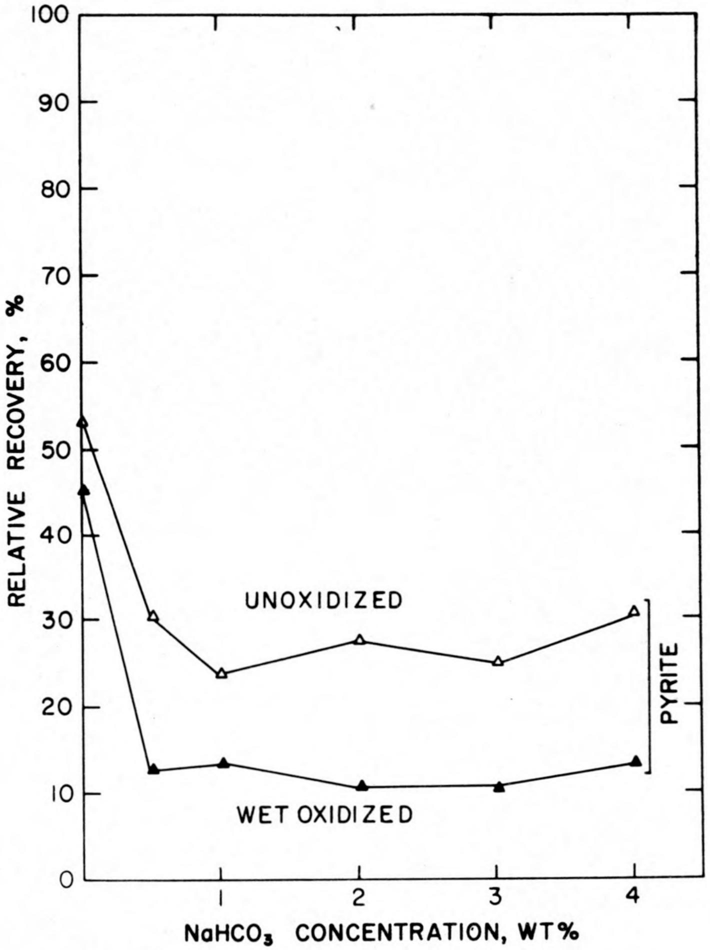

Figure 10. Effect of wet oxidation in $NaHCO_3$ solutions on the floatability of coal and pyrite.

diagrams represents an average of two or more floatability determinations. From these results it can be seen that wet oxidation reduced the floatability of the pyrite significantly below that achieved by the use of sodium carbonate solutions alone. Also wet oxidation seemed to exert little additional effect beyond that of the alkaline solutions on the floatability of the coal.

Similar results were obtained when other alkalis were used for the wet oxidation treatment and floatability determination. Thus the floatability of pyrite oxidized in sodium bicarbonate solutions (Figure 10) was nearly the same as that of pyrite oxidized in sodium carbonate solutions (Figure 9). Since the depressing action of sodium bicarbonate alone was less than that of sodium carbonate, the effect of wet oxidation was even more pronounced in the sodium bicarbonate solutions than in the sodium carbonate solutions.

When sodium hydroxide was used for the wet oxidation treatment, the floatability of the treated pyrite was also significantly less than the floatability of unoxidized pyrite in similar solutions (Figure 11). Also the floatability of pyrite which had been wet oxidized in sodium hydroxide solutions was less than that of pyrite which had been wet oxidized in either sodium carbonate or sodium bicarbonate solutions. On the other hand, the floatability of coal in sodium hydroxide solutions did not appear to be changed significantly by wet oxidation (Figure 11).

Although the floatability of pyrite in calcium hydroxide solutions was reduced somewhat by wet oxidation, the absolute difference in the floatability of oxidized and unoxidized pyrite was small because in these solutions the floatability of even the unoxidized pyrite was very small (Figure 12). Again as with the other alkalis, the floatability of coal in calcium hydroxide solutions was not affected significantly by wet oxidation.

Future Work

Pyrite depression in coal flotation will be developed further by applying various chemical depressants and/or wet oxidation in alkaline solutions to coal and carrying out laboratory-scale froth flotation tests. These test will show whether potential pyrite depressants are effective when applied to the actual separation of coal and pyrite. For these tests MIBC will be used as a frother and in some cases fuel oil will be added as a collector for coal. The depression of pyrite in various kinds of coal will also be studied.

Selective Oil Agglomeration

Even though the oil agglomeration method of cleaning and recovering fine-size coal has been known for a long time, it has not been used commercially because it has not given a good separation between coal and iron pyrites and the cost of the agglomerating oil has not been justified by the value of the product. As with froth flotation, part of the separation problem appears to be due to the similarity in surface properties of unweathered coal and clean pyrite. Both materials tend to be naturally hydrophobic and wetted by oil (5,8). Fortunately, the wet oxidation method described above seems to overcome this tendency

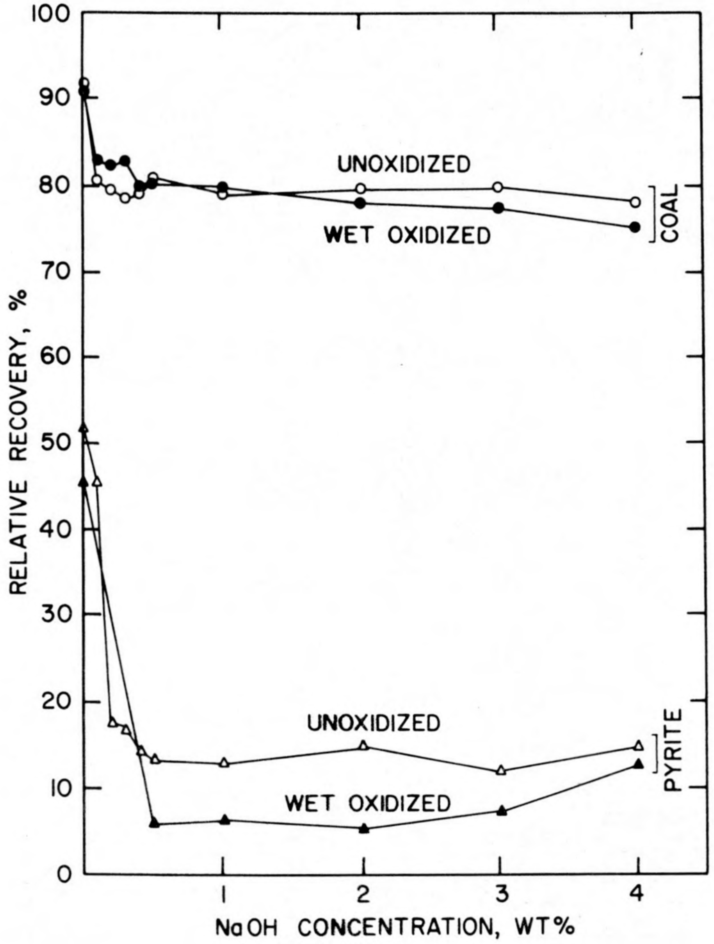

Figure 11. Effect of wet oxidation in NaOH solutions on the floatability of coal and pyrite.

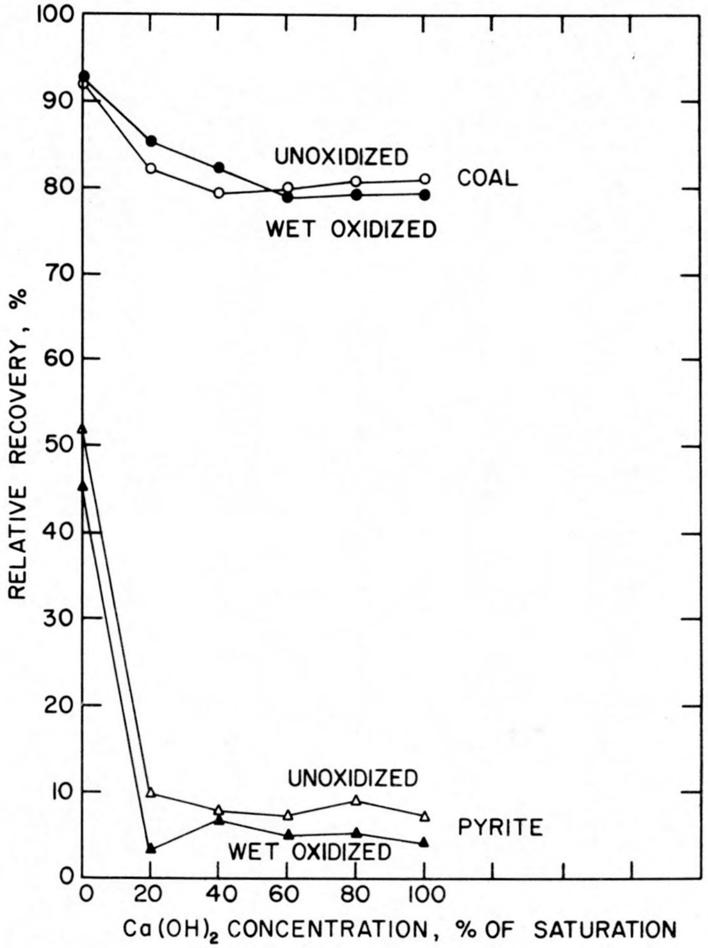

Figure. 12. Effect of wet oxidation in $Ca(OH)_2$ solutions on the floatability of coal and pyrite.

in the case of pyrite so that a mixture of coal and pyrite particles can be separated more completely by oil agglomeration after application of the method.

The results of several preliminary experiments involving pretreatment of fine-size bituminous coal by wet oxidation followed by agglomeration with various grades of fuel oil were reported previously (1). These results showed that wet oxidation in warm solutions of sodium carbonate improved the subsequent removal of inorganic sulfur from coal by oil agglomeration. Also more sulfur and ash were removed when the coal was agglomerated in the alkaline pretreatment medium than in fresh water. In addition, it was shown that 400 mesh x 0 size coal could be agglomerated and recovered as well as coarser 100 mesh x 0 size coal. However, the finer size coal could not be recovered with No. 6 fuel oil alone; the heavier oil had to be cut with a lighter oil. The addition of 25% No. 200 LLS fuel oil worked well. On the other hand, the coarser coal was recovered in high yield with any of the following fuel oils: No. 1, No. 2, No. 200 LLS, No. 5, and No. 6. The lighter oils produced a product with somewhat less sulfur than the heavier oils produced.

This work has been extended to further develop the wet oxidation pretreatment step and oil agglomeration process. The results reported below are for a number of experiments designed to explore the effects of different pretreatment conditions, fuel oils and particle sizes. Also reported are the results of pretreating and agglomerating bituminous coal from various sources in Iowa, Illinois and Western Kentucky and pyrite which had been isolated from an Iowa coal by hand picking.

Materials

Samples of run-of-mine high volatile bituminous coal were obtained from various mines in Iowa, Illinois and Western Kentucky. Each sample was crushed and then pulverized to 60 mesh x 0 size with a Mikro-Samplmill (Pulverizing Machinery Division, American-Marietta Co.). A typical cumulative size distribution for the pulverized material is given below.

U.S. Std. Sieve, No.	Coal retained, wt.%
100	11
140	30
200	49
270	59
400	92

Although this size consist was used for some experiments, much of the coal was ground subsequently in a ceramic jar mill for 24 hr. to produce 400 mesh x 0 size material. The ground coal was dried in an oven at 90°C for 24 hr. and used within two or three days. Typical values of the inorganic sulfur and ash contents of the different coals are given in Table 17.

Table 17. Source and composition of high volatile bituminous coal used for oil agglomeration experiments.

Coal	Source	Ash, wt.%	Inorganic Sulfur, wt.%
ISU	Demo. Mine, Mahaska Co., IA	15.7	4.96
Lovilia	Lovilia No. 4 Mine, Monroe Co., IA	15.2	2.99
Ky. No. 9	Fies Mines, Hopkins Co., KY	20.6	1.77
Ill. No. 5	Rapatee Mine, Middle Grove, IL	13.2	1.39

Pyrite in the form of nodules was recovered from the refuse produced in cleaning coal from the Iowa State University demonstration mine. The nodules were cleaned, pulverized, and screened to provide 230 mesh x 0 size material which had the following composition:

Component	wt.%
Pyritic sulfur	45.9
Total sulfur	47.3
Iron	43.2
Calcium	2.1

This material contained 86 wt.% FeS_2 based on the pyritic sulfur content as determined by the standard ASTM method for determining pyritic sulfur in coal. In addition to pyrite, the material contained significant amounts of other iron, sulfur, and calcium minerals.

Petroleum based fuel oils used for the agglomeration of coal were supplied by Amoco Oil Co. The physical properties of these oils as determined by the manufacturer are shown in Table 18.

Table 18. Physical properties of fuel oils used for agglomerating coal.

Fuel Oil No.	Specific gravity at 60°F	Viscosity, centistokes	Pour point, °F
1 (heater)	0.811	-----	-----
200, LLS	0.916	13.1	-20
5 Light, LLS	0.934	49.7	-10
6, LLS	0.959	350.4	+30

Pretreatment and Agglomeration Methods

The pretreatment step involved wet oxidation of the particles in a warm aqueous suspension through which air was bubbled. Generally the suspension consisted of 50 g. of coal and 500 ml. of solution or 50 g. of pyrite and 250 ml. of solution. Usually an alkaline solution was employed. The suspension was placed in a 1-liter, three-neck Pyrex flask fitted with a reflux condenser, mechanical stirrer, thermometer, electric heating mantle, and gas sparger made of fritted glass. The suspension was treated subsequently at a selected temperature while air was introduced through the sparger at a rate of 0.3 to 0.5 cu. ft./min. for the desired treatment time. After this treatment the suspension was cooled rapidly and used directly for the oil agglomeration step.

To agglomerate coal or pyrite particles, either a pretreated suspension or an equivalent suspension (50 g. coal and 500 ml. water or 50 g. pyrite and 250 ml. water) was placed in a kitchen blender (Sears Insta-Blend Model No. 400). The suspension was agitated for 1 min., and while the agitation was continued, 5.0 ml. of a selected fuel oil was added. The agitation was continued for another 5 min. at the highest possible speed to agglomerate the coal and/or pyrite. The suspension was then poured onto either a 60 or a 140 mesh sieve to collect the agglomerates; these were allowed to drain. In the case of pyrite the agglomerates were recovered at this point whereas in the case of coal, the agglomerates were returned to the blender along with 500 ml. of deionized water. The suspension of coal agglomerates was agitated at high speed for 5 min. and screened. The recovered solids were dried overnight in an oven at 75-90°C and extracted with hexane to remove the fuel oil. The solids were then redried to remove the hexane and weighed. Coal recovered in this manner was analyzed for ash and total inorganic sulfur (sulfate plus pyritic forms).

The results of agglomerating coal were evaluated in terms of the recovery of coal combustible matter and the reductions in both ash content and total inorganic sulfur content. These quantities were determined as follows:

$$\text{Recovery }(\%) = \frac{(WP)(100 - AP)}{(WF)(100 - AF)} \times 100$$

$$\text{Ash Reduc. }(\%) = \frac{AF - AP}{AF} \times 100$$

$$\text{S Reduc. }(\%) = \frac{SF - SP}{SF} \times 100$$

where AF = ash content of dry feed
AP = ash content of dry, oil-free product
SF = inorganic sulfur content of dry feed
SP = inorganic sulfur content of dry, oil-free product
WF = weight of dry feed
WP = weight of dry, oil-free product

Agglomeration of Untreated Coal

The results of agglomerating 60 mesh x 0 size coal with various grades of fuel oil were reported previously (1). This coal was from the Iowa State University (ISU) Demonstration Mine in Mahaska County, Iowa, and was precleaned by float/sink separation in trichloroethylene. However, it was not pretreated by the wet oxidation method. This work was extended subsequently when similar coal of 400 mesh x 0 size was also agglomerated with different oils. The results for both sizes of material are shown in Table 19. With one exception, each value represents an average of several determinations. Although the results indicate that for both sizes of coal a high recovery of coal combustible matter of reduced sulfur content was obtained with almost any of the different grades of oil, there were noticeable differences in both product yield and sulfur content which seemed to depend more on both particle size and oil grade. Thus the recovery of 400 mesh x 0 size material seemed to depend more on oil grade than the recovery of the 60 mesh x 0 size material. At both ends of the oil grade spectrum, the recovery of the finer-size coal declined. No. 6 and No. 6 LLS oils were particularly troublesome because of their high viscosity which

Table 19. Results of agglomerating precleaned[a] and untreated ISU mine coal with different fuel oils.

Coal	Fuel oil no.	Recovery %	Composition, wt.%		Reduction, %	
			Inorg.S	Ash	Inorg.S	Ash
60 mesh x 0						
Untreated	---	---	1.71	9.65	---	---
Agglomerated	1	95.9	1.02	7.82	40.2	18.9
Agglomerated	2	98.3	1.02	7.95	40.4	17.7
Agglomerated	200 LLS	100.0	1.12	7.78	34.7	19.3
Agglomerated	5 LLS	91.7	1.20	7.93	30.0	17.8
Agglomerated	6	98.7	1.21	8.20	29.2	15.0
400 mesh x 0						
Untreated	---	---	1.82	9.97	---	---
Agglomerated	1	74.8	0.96	8.56	47.5	14.1
Agglomerated	2	88.2	0.99	7.76	45.3	22.2
Agglomerated	200 LLS	94.1	1.04	8.34	42.9	16.3
Agglomerated	5 LLS	95.4	0.78	8.22	57.1	17.6
Agglomerated	6 LLS	89.7	0.62	8.21	65.9	17.7

[a] Precleaned by float/sink separation in trichloroethylene.

made them difficult to disperse. Several attempts to recover the finer-size coal with No. 6 oil failed and only one attempt to recover this material with No. 6 LLS oil was successful. Whereas the recovery of 60 mesh x 0 size coal was generally higher than the recovery of 400 mesh x 0 coal with almost any of the oils, there was a notable exception in the case where No. 5 LLS oil was used. As might be expected, the sulfur content of the agglomerated 400 mesh x 0 size coal was lower than that of the agglomerated 60 mesh x 0 size coal with any given oil. On the other hand, the different trends in product sulfur content with oil grade for the two sizes of material were unexpected. In the case of the finer-size coal, the lighter oils produced large, shapeless, weak flocs which clogged the openings in the 140 mesh dewatering screen and interfered with the removal of both water and mineral matter, while the heavier oils formed microspherical agglomerates which were more completely dewatered and freed of mineral water.

Agglomeration of Pretreated Coal

In order to further develop the wet oxidation method of pretreatment, a series of experiments was carried out in which 60 mesh x 0 size coal from the ISU mine was pretreated with different alkalis and then agglomerated with a mixture of No. 1 (86 vol.%) and No. 6 (14 vol.%) fuel oils. During the pretreatment step,the coal was exposed to oxidizing conditions for 15 min. at 50°C in the presence of 2.0 wt.% concentration of alkali. For the agglomeration step,100 g. coal was agglomerated with 10 ml of oil. The results presented in Table 20 show that pretreatment with almost any of the alkalis listed followed by agglomeration reduced the inorganic sulfur content of the coal more than oil agglomeration by itself. On the other hand, pretreatment also lowered the recovery of coal combustible matter. While the recovery was reduced only slightly by pretreatment with sodium carbonate or magnesium carbonate, it was reduced markedly by pretreatment with calcium carbonate or calcium hydroxide and reduced to zero by pretreatment with sodium hydroxide.

The best combination of sulfur reduction and recovery of combustible matter was achieved with magnesium carbonate but the results with sodium carbonate were nearly as good. A comparison of the alkali metal content of the product with that of the feed indicates that the coal adsorbed some alkali from the pretreatment solution.

Additional experiments were conducted to establish the importance of other pretreatment conditions on the recovery of combustible matter and reductions in ash and sulfur contents achieved by oil agglomeration. For these experiments 400 mesh x 0 size coal from the ISU mine was pretreated and then agglomerated with a mixture of No. 200 LLS (25 vol.%) and No. 6 LLS (75 vol.%) fuel oils. This mixture was chosen because it gave consistent results and utilized a high proportion of the less costly No. 6 LLS fuel oil. The results achieved when the coal was pretreated at 80°C for 15 min. with various concentrations of sodium carbonate are indicated by Figure 13. These results show that the greatest reduction in sulfur content (88%) was obtained with a concentration of 2.0 wt.% sodium carbonate. While the removal of sulfur and ash varied greatly with alkali concentration, the

Table 20. Results of oil agglomerating 60 mesh x 0 size ISU coal pretreated with different alkalis.

Treatment	Alkali	Recovery, %	Composition, wt.%			Reduction,%	
			Inorg. S	Ash	Alkali	Inorg. S	Ash
None (ISU coal)	----	----	4.56	15.7	0.05 Na 0.17 Ca 0.02 Mg	----	----
Oil Aggl. only	----	87.4	3.93	12.8	0.05 Na 0.10 Ca 0.05 Mg	18.4	13.8
Chem./Oil Aggl.	Na_2CO_3	83.9	1.88	10.2	0.28 Na	58.9	35.3
Chem./Oil Aggl.	$MgCO_3$	86.8	1.66	11.2	0.16 Mg	63.7	28.7
Chem./Oil Aggl.	$CaCO_3$	69.4	2.56	11.4	0.31 Ca	43.8	27.7
Chem./Oil Aggl.	$Ca(OH)_2$	50.7	2.04	11.5	0.43 Ca	55.3	26.6
Chem./Oil Aggl.	Na_3PO_4	82.0	2.54	11.7	0.21 Na	44.3	25.6
Chem./Oil Aggl.	KOH	0	----	----	----	----	----

recovery of combustible matter varied slightly. The effect of alkali concentration is further illustrated by Figure 14 as well as the effect of pretreatment time. This diagram shows that a treatment time of 15 min. was best when the optimum alkali concentration of 2.0 wt.% was used. However, a longer treatment was beneficial when less than the optimum concentration was employed. The effect of pretreatment temperature on the results is indicated by Figure 15. This diagram shows that pretreatment for 15 min. at 50°C or higher temperatures with an aerated solution containing 2.0 wt.% sodium carbonate was very effective whereas similar pretreatment at room temperature was not effective.

Several experiments were also carried out in which No. 1 fuel oil was substituted for the mixture of No. 200 LLS and No. 6 LLS fuel oils. For these experiments 400 mesh x 0 size coal from the ISU mine was pretreated at 80°C for 15 min. with aerated solutions containing different concentrations of sodium carbonate. The results presented in Figure 16 show that while the recovery of combustible matter through oil agglomeration was nearly as great as that achieved with the mixture of heavier oils, the reductions in ash and sulfur contents were not nearly as large. Therefore the effect of oil grade on sulfur reduction was similar to that noted in Table 19 for the finer-size material. Alkali concentration in the range of 1 to 4% seemed to have less effect on sulfur removal than noted in Figure 13 for the mixture of heavier oils.

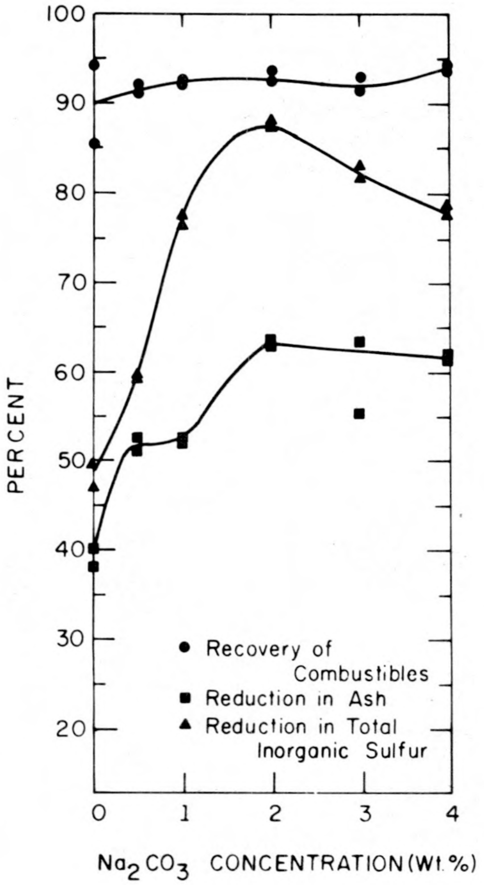

Figure 13. Results of oil agglomerating -400 M ISU coal pretreated for 15 min. at 80°C.

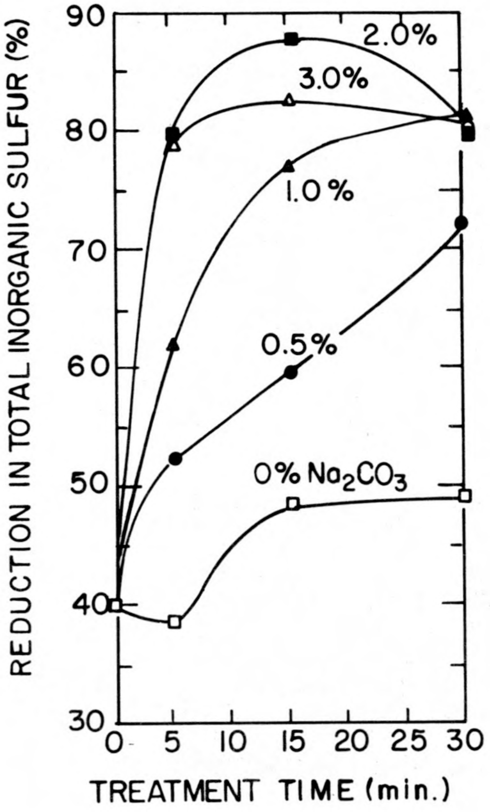

Figure 14. Effect of pretreatment time and alkali concentration on oil agglomeration of -400 M ISU coal. Pretreatment at 80°C.

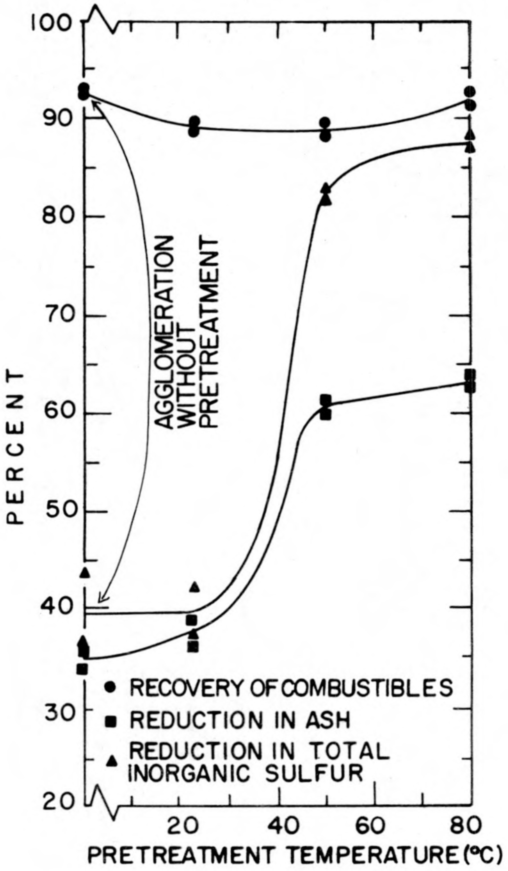

Figure 15. Results of oil agglomerating -400 M ISU coal pretreated for 15 min. with 2.0 wt.% Na_2CO_3 at different temperatures.

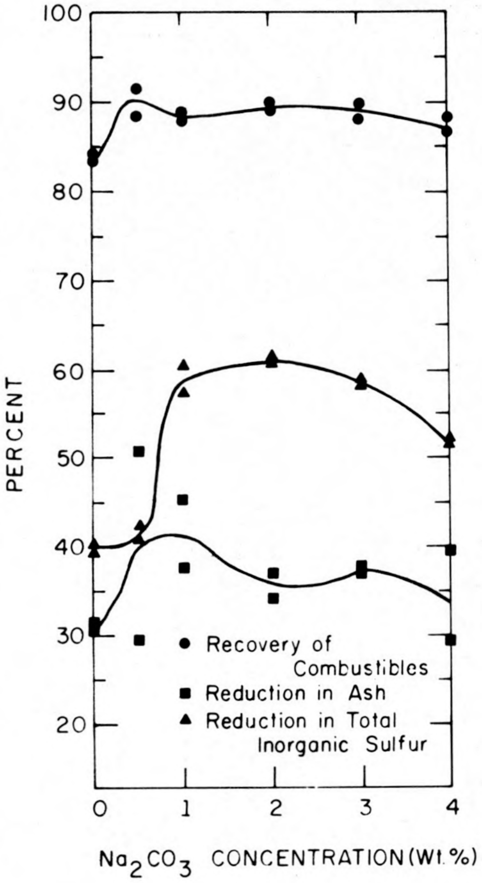

Figure 16. Results of agglomerating pretreated 400 M x 0 size ISU coal with No. 1 fuel oil.

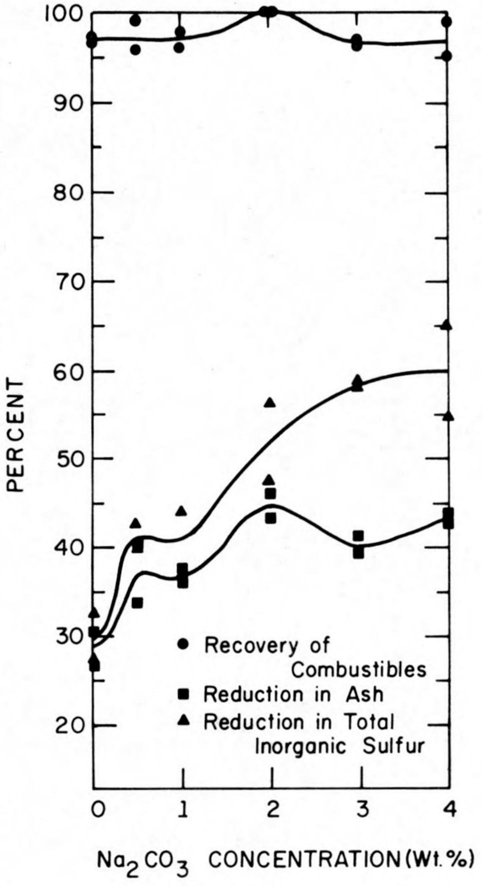

Figure 17. Results of agglomerating 60 M x 0 size ISU coal pretreated for 15 min. at 80°C.

A series of experiments was also conducted with 60 mesh x 0 size coal from the ISU mine to see how the coarser material would respond to pretreatment with solutions of different alkali concentration and agglomeration with the mixture of No. 200 LLS and No. 6 LLS fuel oils. For these experiments the coal was pretreated at 80°C for 15 min. and then agglomerated. The results presented in Figure 17 indicate that the recovery of combustible matter was over 96% which was higher than that realized with the finer-size coal (Figure 13). However, the maximum sulfur reduction was about 60% which was considerably less than achieved with the finer-size material. Furthermore the effect of alkali concentration was noticeably different for the two sizes of coal. Whereas for the finer-size coal the greatest sulfur reduction was achieved with 2.0 wt.% sodium carbonate, for the coarser coal the greatest sulfur reduction was achieved with 3 - 4 wt.%.

Further experiments were conducted to determine the response of coals from various sources to pretreatment and agglomeration. These coals were ground to 400 mesh x 0 size, pretreated for 15 min. at 80°C, and agglomerated with the mixture of No. 200 LLS and No. 6 LLS fuel oils. The results obtained with Kentucky No. 9 coal are illustrated by Figure 18. These results indicate that a high recovery of combustible matter (99%) and large reduction in sulfur content (86%) were achieved over a wide range of alkali concentration (1 to 4 wt.%). The results obtained with coal from the Lovilia No. 4 mine in Iowa are shown in Figure 19. While the recovery of combustible matter (96%) was high, the maximum inorganic sulfur reduction (70%) was poorer than achieved with the two previous coals. The greatest sulfur reduction was realized with 1.0 wt.% sodium carbonate. Finally the results obtained with Illinois No. 5 coal are shown in Figure 20. This coal had been precleaned by a jig washing plant and responded least of all. Although the recovery (95%) was high, the maximum reduction in inorganic sulfur content (52%) was lower than that realized with the other coals. Again as with the Lovilia mine coal, the greatest sulfur reduction was achieved with 1.0 wt.% sodium carbonate.

Future Work

Additional experiments will be conducted in the future to optimize the wet oxidation pretreatment step. Various alkalis and alkali concentrations will be tested to determine the best alkali and optimum concentration for this step. The application of both the pretreatment and agglomerated steps to various kinds of coal will also be studied.

Agglomeration of Pyrite

In order to further demonstrate wet oxidation as a means of suppressing the agglomeration of pyrite by fuel oil several experiments were conducted to compare the results of agglomerating pretreated pyrite with the results of agglomerating untreated pyrite. The 230 mesh x 0 size pyrite described above was used for these experiments. A solution containing 2.0 wt.% sodium carbonate was used for the pretreatment step and the same solution was used for the subsequent agglomeration step. When untreated pyrite was agglomerated, the material was suspended in deionized water for this step. Various pretreatment conditions and grades of fuel oil were tested as well as two

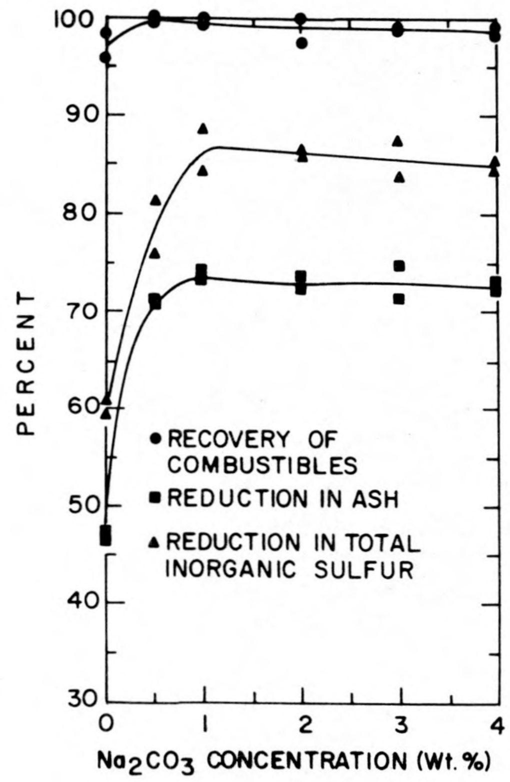

Figure 18. Results of oil agglomerating 400 M x 0 Kentucky No. 9 coal pretreated at 80°C for 15 min.

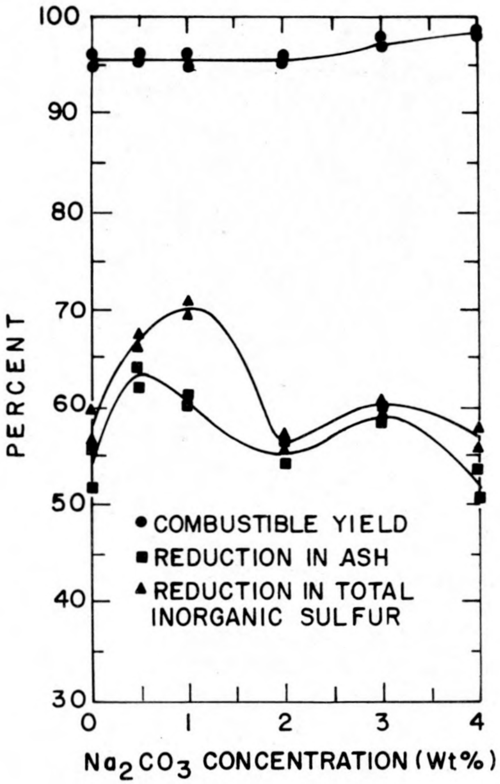

Figure 19. Results of oil agglomerating 400 M x 0 size Lovilia mine coal pretreated at 80°C for 15 min.

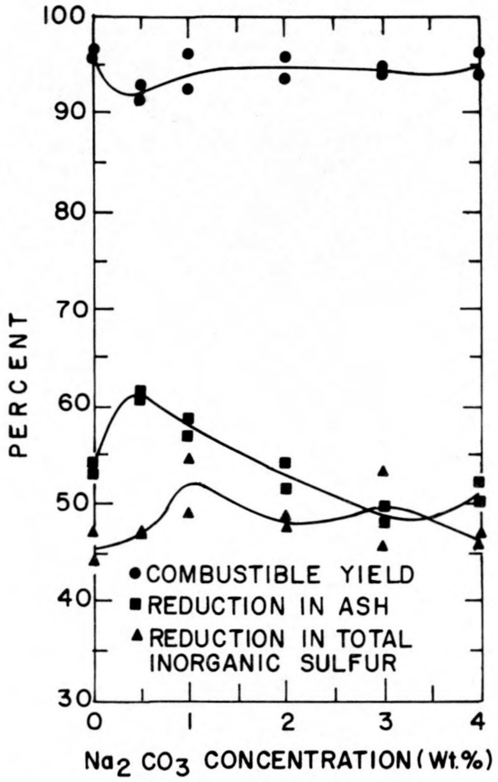

Figure 20. Results of oil agglomerating 400 M x 0 size Illinois No. 5 coal pretreated at 80°C for 15 min.

different methods of introducing the fuel oil. The first method involved adding the oil directly to the agitated suspension of pyrite particles and water while the second method involved adding an emulsion of oil and water to the suspension. The emulsion was prepared by treating 5.0 ml. of oil and 45 ml. of deionized water with an ultrasonic transducer. The agglomerated pyrite was recovered by pouring the final suspension through a 140 mesh screen. The weight of pyrite recovered on an oil-free and moisture-free basis divided by the weight of dry pyrite charged is reported as the pyrite recovery.

A few preliminary experiments indicated that untreated pyrite particles could not be recovered by agglomeration with No. 1 fuel oil. However, subsequent experiments showed that untreated pyrite was readily agglomerated and recovered by either No. 200 LLS or No. 5 LLS fuel oils with the greatest recovery being obtained in either case when the oil was emulsified before use (Table 21). Thus with emulsified No. 200 LLS oil the recovery of untreated pyrite was 92% (Case II) but with unemulsified oil the recovery was only 64% (Case I). Similarly with emulsified No. 5 LLS fuel oil the recovery was 75% (Case V) but with unemulsified oil the recovery was only 46% (Case IV). On the other hand, when the pyrite was wet oxidized with air at 80°C for 15 min. and then agglomerated with either of these oils in the emulsified state, the recovery dropped to 8 - 9% (Cases III and VI). Pretreatment

Table 21. Results of agglomerating untreated and pretreated 230 mesh x 0 pyrite with different fuel oils.

Case No.	Pretreatment Conditions			Agglomerating Oil		Pyrite recovered, wt.%
	Gas type	Temp., °C	Time, min.	No.	State	
I	----	----	----	200 LLS	unemulsified	63.8
II	----	----	----	200 LLS	emulsified	91.7
III	Air	80	15	200 LLS	emulsified	8.8
IV	----	----	----	5 LLS	unemulsified	46.4
V	----	----	----	5 LLS	emulsified	74.9
VI	Air	80	15	5 LLS	emulsified	8.0
VII	N_2	80	15	200 LLS	emulsified	84.5
VIII	Air	23	15	200 LLS	emulsified	87.9
IX	Air	50	5	200 LLS	emulsified	9.5
X	Air	50	15	200 LLS	emulsified	10.1

with nitrogen instead of air (Case VII) had little effect on pyrite recovery as did pretreatment at room temperature with air (Case VIII). But pretreatment with air at 50°C for either 5 min. (Case IX) or 15 min. (Case X) reduced the recovery to 10%. Therefore the results showed that wet oxidation with air in an alkaline solution at 50°C or higher temperatures and for 5 min. or longer was very effective in suppressing the oil agglomeration of pyrite.

Pelletization

A rotating, inclined-pan pelletizer (Figure 21) was installed in the large bench-scale flow system which is described below. The diameter of the pelletizer pan can be varied from 14 to 36 in. to accommodate a wide range of feed rates. At maximum diameter the pelletizer should have a capacity of 300 to 500 lb./hr. of coal. Both the speed and angle of inclination of the pan can be varied. The pelletizer is installed to process coal recovered by the oil agglomeration circuit of the flow system.

Continuous Processing of Fine Coal

Construction of a large bench-scale flow system for demonstrating various methods of cleaning and recovering fine-size coal was completed and tested. This system is located at the Ames coal preparation facility (Figure 22) and includes equipment for grinding and chemically pretreating 1000 lb. batches of coal and for continuously beneficiating the pretreated coal by froth flotation or oil agglomeration at a rate of several hundred pounds of coal per hour. It also includes the pelletizer described above.

System Description

Figure 23 is a schematic diagram of the flow system. Coal fines suspended in water are supplied to the system from the main Ames coal preparation facility. The feed slurry is placed in either one of two agitated tanks which serve for both storage and chemical pretreatment (Figure 24). Each of these tanks has a working volume of 2000 gal. and is fitted with a panel coil heating/cooling jacket. If the feed is coarser than required, the coal can be ground with a 16 in. diameter by 4 ft. long ball mill (Figure 25) which is in closed circuit with a cyclone separator. This separator classifies and dewaters the feed to the mill so that it is free of undersize particles and excess water. After the feed has been reduced to the proper size, it can be pretreated by wet oxidation to enhance the subsequent separation of coal and pyrite. For the pretreatment step, an alkali is added to the coal slurry which is then heated to the necessary temperature. Air is introduced next to oxidize the surface of the pyrite particles. After the oxidation step, the slurry is cooled to the proper temperature for the next step.

Once the feed has been pretreated, it is pumped at a controlled rate to either a froth flotation unit or an oil agglomeration unit. The froth flotation unit (Figure 26) includes a conditioning tank where various flotation reagents may be added and a bank of four flotation cells, each cell having a volume of 5 cu. ft. The float product from these cells is either stored in a 750 gal. agitated tank to await further processing or added to the fine coal recovery circuit of the main coal preparation facility. The tailings from the flotation cells are added to the fine refuse circuit of the main facility.

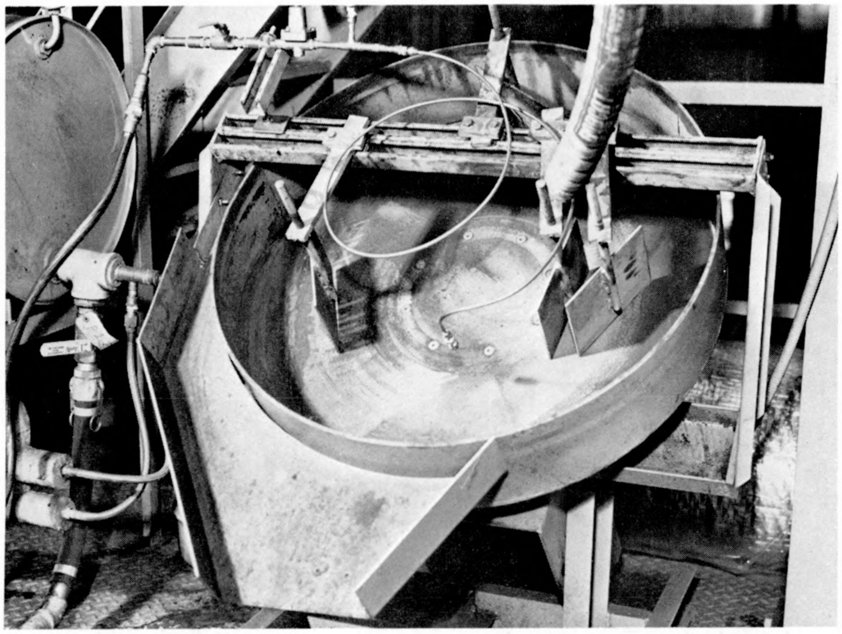

Figure 21. Rotating, inclined-pan pelletizer.

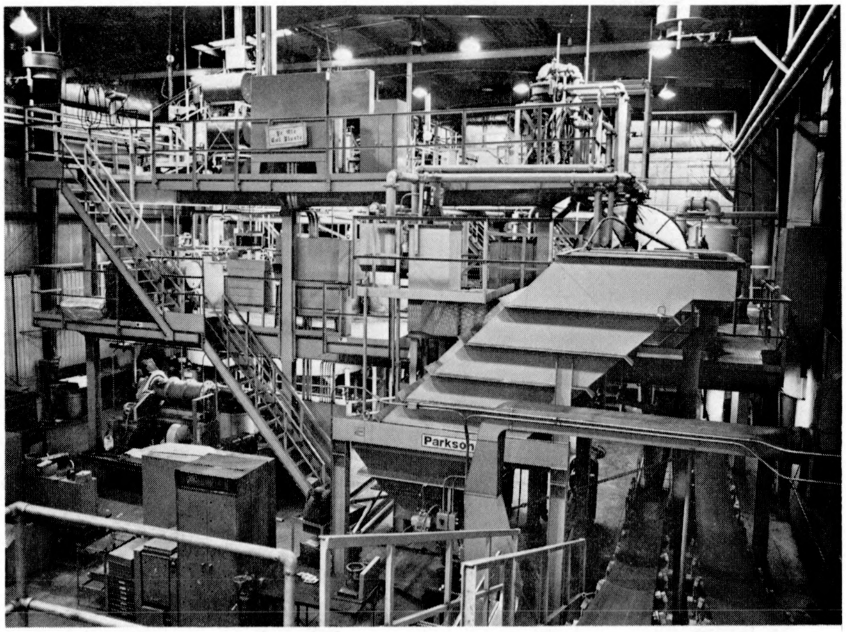

Figure 22. Ames coal preparation facility.

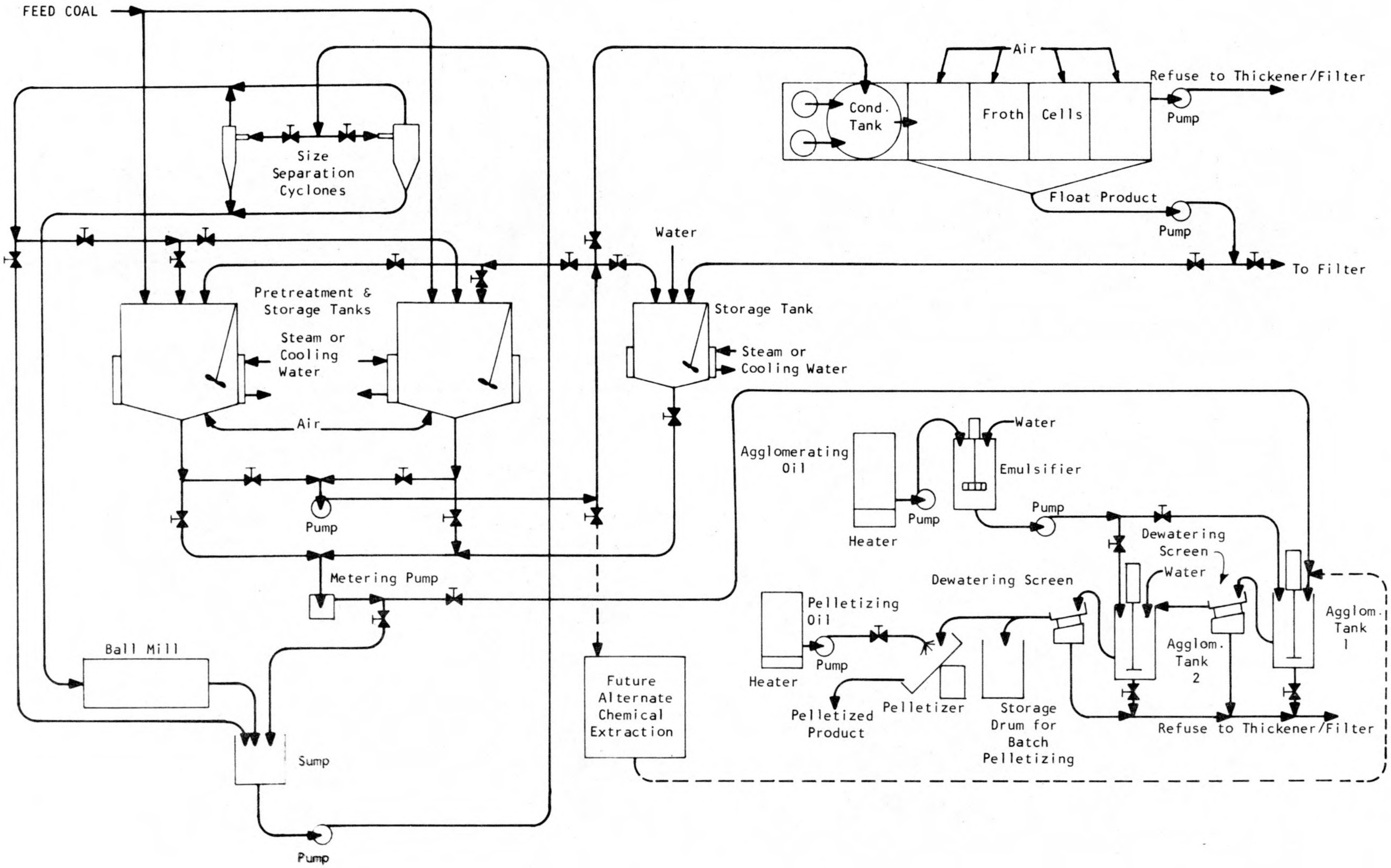

Figure 23. Bench-scale flow system for demonstrating continuous processing of fine coal.

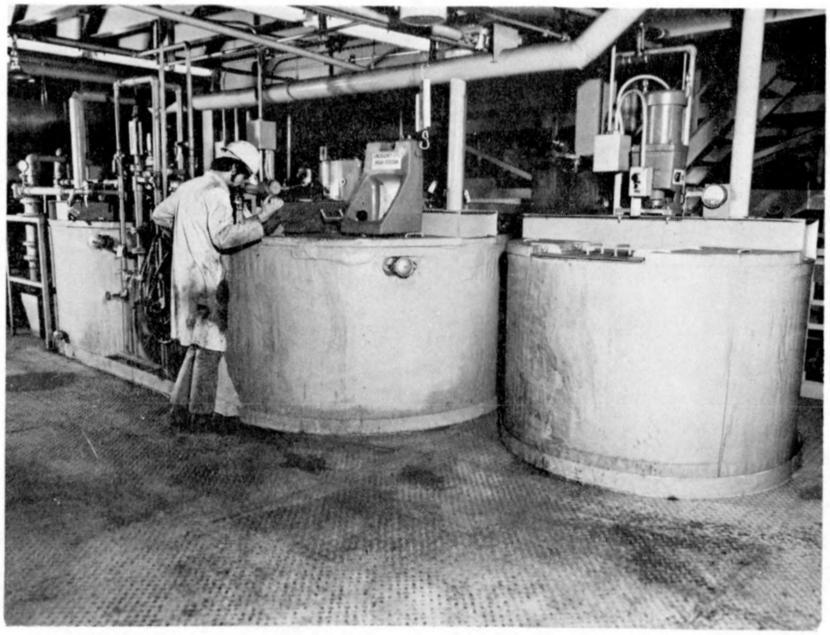

Figure 24. A slurry of fine coal can be stored, heated, and chemically pretreated in the two larger tanks on the left.

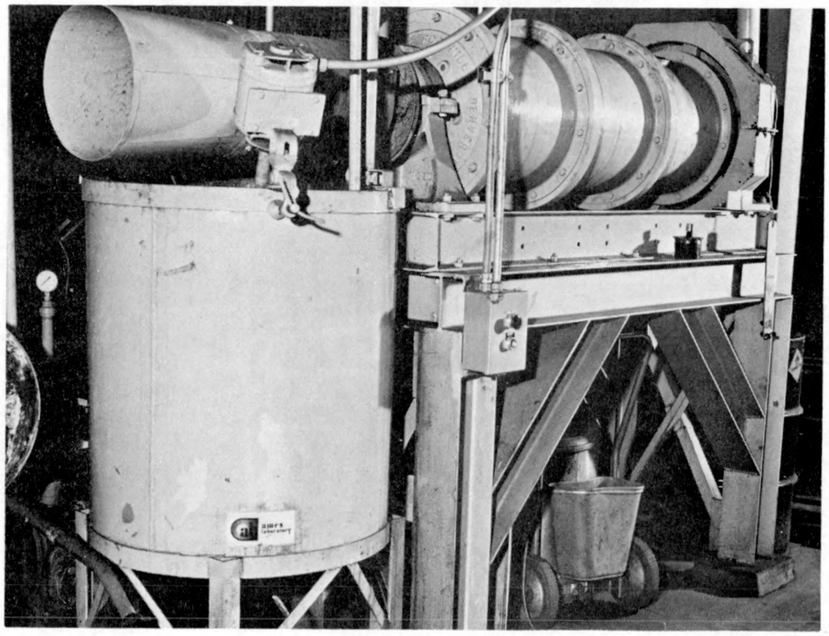

Figure 25. Ball mill for fine grinding of coal.

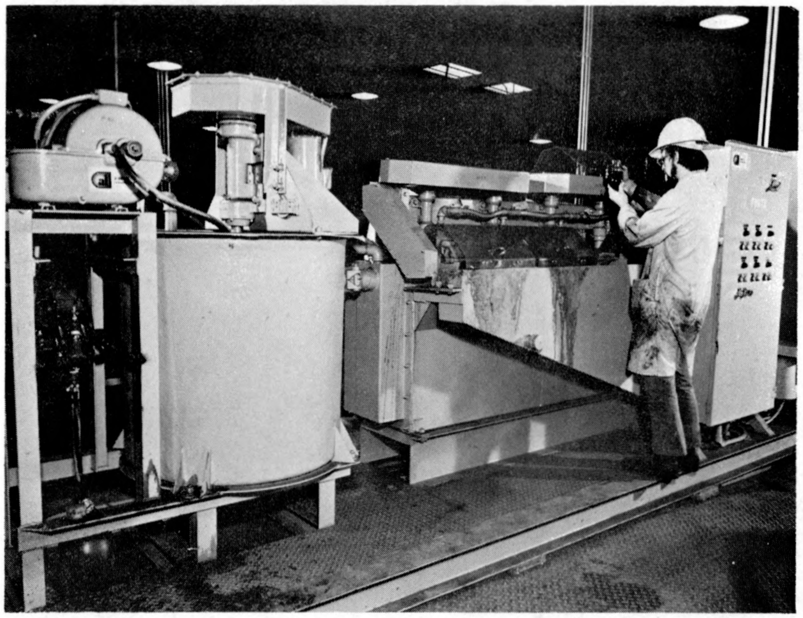

Figure 26. Reagent feeder, conditioning tank and bank of froth flotation cells.

Figure 27. Two-stage oil agglomeration unit consisting of two agitated tanks and two vibrating screens.

The oil agglomeration unit (Figure 27) includes an oil emulsifier and two agglomeration and separation stages. The emulsifier is designed to prepare one batch at a time of an oil-water emulsion for use in the agglomerators. Emulsification is accomplished by a rotor-stator assembly which produces an extremely high shearing action. The assembly is located in a 100 gal. tank which can store sufficient emulsion for 3 to 30 hr. of operation. The tank is fitted with a panel coil heating jacket so that hot emulsions can be prepared as well as cold emulsions.

Each agglomerator consists of a 100 gal. flat-bottom tank and a variable speed agitator driven by a 3/4 h.p. motor. The agitator in the first stage employs a 4 in. diameter bar turbine impeller 6 in. above the bottom of the tank and 4 in. diameter marine propeller located 12 in. above the turbine. The agitator in the second stage employs only a 6 in. diameter axial flow impeller, 6 in. above the bottom of the tank. Each tank is fitted with four vertical baffles; each baffle is 2 1/2 in. wide and runs from top to bottom of the tank. Each tank is also fitted with a panel coil heating jacket and is insulated so that oil agglomeration can be carried out hot as well as cold. In addition each tank is furnished with three overflow lines so that the liquid level can be maintained at either 8.5, 15.8, or 25.5 in. above the bottom by selection of the appropriate line.

A single-deck vibrating screen which is 30 in. in diameter is located after each agglomerator. The stainless steel screen cloth can be replaced easily so that screens with openings of different sizes can be utilized.

To operate the oil agglomeration unit, a coal slurry is drawn from one of the pretreatment tanks or from the float product storage tank and is fed continuously at a constant rate to the first agglomerator along with either emulsified or unemulsified oil. The first agglomerator utilizes relatively high-shear mixing to disperse the oil and produce microagglomerates. The mixture of agglomerated coal, water, and refuse particles is removed through one of the overflow lines from the first agglomerator and deposited on the first vibrating screen which recovers the microagglomerates and passes the water and refuse. The microagglomerates are conducted from the screen to the second agglomerator which utilizes low-shear mixing to produce larger agglomerates. Make-up water and additional oil, if necessary, are added to the second agglomerator. The slurry of agglomerates overflows onto the second vibrating screen for dewatering and removing additional refuse. The agglomerated coal can be collected at this point or it can be conducted to a rotary, inclined-pan pelletizer for further size enlargement. The refuse is added to the fine refuse circuit of the main facility.

Initial Testing and Operation

After constructing the flow system, several batches of coal were processed to test the mechanical operation of the system. Although a number of start up problems were encountered, most of the system met design expectations. Some of the problems were due to the nature of the feed which was highly acidic and endowed with a small amount of oversize material. The acid corroded the mild steel equipment and the oversize coal plugged pump strainers and other narrow passages. These difficulties were overcome for the most part by screening the feed to remove the large particles and adding sodium carbonate to neutralize the acid. However, the mild steel impellers in the two pretreatment tanks continued to be corroded and/or eroded by the coal slurry, even under alkaline or basic conditions. An attempt will be made to overcome this problem by adding a protective coating to the impellers.

One of the more serious problems encountered arose because the two pretreatment tanks were out-of-round. Consequently the panel coil heaters attached to the outside did not make good contact with the walls of the tanks which resulted in poor heat transfer rates and long heat-up times. This problem will be corrected by installing a pipe coil within each tank to provide additional heat transfer surface.

Initial operation of the fine coal flow system also brought out certain operational problems caused by having the system coupled to the main coal preparation facility. Thus the fine coal sub-system could only operate when the main plant was running and could only process whatever coal was being treated by the main plant. Also it was not certain that the main plant could supply consistent feed material to the fine coal sub-system. In addition some of the chemical agents and oils used in the fine coal sub-system for experimental purposes could cause problems in the main plant. Therefore, to provide greater operating flexibility and a means for operating the fine coal flow system independently, several changes will be made in the system. One of the changes will be to install a separate coal feeder and crusher so that small batches of coal can be introduced directly into the system without operating the main plant. Another change will be to provide a separate means for handling and disposing of the refuse from the system.

Future Work

After correcting the problems described above, the fine coal flow system will be tested further to establish the principal operating characteristics of the system. After these characteristics are established, the system will be operated to demonstrate the improvements in froth flotation and oil agglomeration which are being developed in the laboratory.

Characterization of Coal Microstructure

by

Raymond T. Greer

Scientific Background

There are several major areas of interest in methods of determining the forms of sulfur in coal. These include the reliability and accuracy of the

ASTM technique for pyrite determination (ASTM standard D-2492), the proportionment of inorganic and organic sulfur in coal, the presence and nature of organic sulfur in coal, the significance and determination of the amounts of elemental sulfur present in coal, the possibility of determining organic sulfur directly using wavelength dispersive X-ray analysis, and the suitability of using the ASTM technique and the organic sulfur wavelength dispersive X-ray technique for sulfur determination in desulfurized coals. By combining the capabilities of newly available analytical techniques and examining coal on a micrometer size scale before and after ASTM analytical leaching treatments, valuable insight has been gained in several of these areas.

The specification of the type and amount of sulfur in coal is important in assessing sulfur removal capabilities of new sulfur removal processes. Of the major forms of sulfur in coal, organic sulfur is usually determined as a numerical difference of a total sulfur determination minus the sum of sulfatic and pyritic sulfur determinations. Work is reported for the application of a direct organic sulfur determination technique to raw and processed coals. This new method, based on the analysis of sulfur and iron X-rays, offers a significant improvement in the understanding of the way sulfur is distributed among various forms in coal, of differences on a maceral (coal constituent) level of the nature of the sulfur bonding in organic sulfur, and of the degree of selectivity of organic sulfur removal (from different macerals and from different types of organic sulfur compounds).

Recently, chemical shifts of X-ray spectra (for S K_α and K_β emissions) for sulfur in various organic and inorganic hosts have been reported. Using X-ray fluorescence spectrometers, shifts have been monitored for bulk specimens with a sensitivity permitting the distinction of organic sulfur from both sulfatic and pyritic sulfur. By adapting this technique to electron microprobe X-ray analysis, sufficient sensitivity remains to discriminate among the forms of sulfur through peak position (both the S K_α and K_β bands exhibit the shift), and the important capability of analyzing regions of the order of several micrometers in width in their smallest dimension, sulfur forms can be analyzed in association with specific maceral types which reflect particular molecular organizations. Desulfurized coals can be compared with starting material on a maceral level to see if organic sulfur is being removed or is being removed selectively (i.e., is a specific type of organic sulfur being removed more easily in a particular process than another).

Several of the features of the technique have been assessed, including a comparison of peak shift analyses on various coals and sulfur standards, the use of the sulfur K_α emissions compared with the sulfur K_β emissions, and the applicability of the technique to characterizing desulfurized coals.

Objectives

The proportionment of inorganic and organic sulfur in coal (for both raw and processed coal) is to be characterized.

Two sets of samples representing 43 different coals in the Pennsylvania State University Coal Bank were obtained for various tests. One set containing 38 samples was obtained directly from the Bank. Another set containing 28 samples was obtained through Los Alamos Scientific Laboratory. Analyses by standard ASTM techniques for sulfur (pyritic, sulfatic, organic, and total) were to provide data for comparisons. To assess the completeness of pyrite removal from residues obtained by following ASTM leaching procedures, scanning electron microscopy was to be used to locate crystals of interest for subsequent detailed microchemical analysis and identification. Electron microprobe X-ray analysis was to be used to identify pyrite by the presence of iron and sulfur. For microprobe analyses where iron was absent but sulfur was present, the results were to be used to quantify the amounts of organic or elemental sulfur. The presence of other cations associated with sulfides or sulfates were also to be monitored by microprobe analysis. Gas chromatography was to be used to specify the presence and amount of elemental sulfur present (in raw and desulfurized coal). X-ray diffraction was to be used for phase identification and for quantification of pyrite remaining in residues from ASTM leaching procedures.

An important form of sulfur to be characterized is organic sulfur. How much organic sulfur is removed from coals which have been desulfurized? Is organic sulfur removed more easily from a particular maceral type? To study this, a direct measure of organic sulfur is necessary. Electron microprobe analyses are utilized. The applicability of small sulfur K_α and sulfur K_β X-ray wavelength shifts (indicative of the type of sulfur present... pyritic, sulfatic, organic, elemental) and peak characteristics (peak height, area under peak, and full width at half maximum, for example... quantitative measure of the amount of sulfur present) in the determination of the amount of organic sulfur present is examined. These characteristics can be catalogued not only for coal before and after processing, but also for model organic compounds where the nature of the sulfur bonding is well characterized. This microprobe approach permits a study on a maceral level to contribute fundamental information of interest to improving sulfur removal schemes, as well as to provide a way to directly compare the effectiveness of various processes.

Technical Approach

For microstructural work, a JSM-U3 scanning electron microscope with an energy dispersive X-ray analyzer was used. An accelerating potential of the electron beam of 25 KeV at 10^{-11} to 10^{-10} amperes was chosen for the microstructural studies. Fracture surfaces of bulk coal and polished sections of individual particles (before and after ASTM analyses or oxydesulfurization processing) were examined in detail. The polished sections of coal particles in a copper diallyl phthalate mount were used to examine the extent of penetration of nitric acid into the -60 mesh coal particles to evaluate the degree of pyrite removal. Untreated coal particles (-60 mesh) were also examined to provide a basis for comparison. This permitted recognition of any crystalline phases down to a size of the order of hundreds of angstroms. These same treated (residue from the ASTM leaching procedure) and untreated polished section samples were then examined using an electron microprobe X-ray analyzer (Applied Research Laboratories) equipped with an energy dispersive X-ray analyzer. This combination permitted the assembly of information for a variety of possible cations of interest while the microprobe analysis was being performed for determining the specific presence, amounts, and distribution of sulfur, iron, or calcium within and among coal particles of a mounted sample.

Microprobe analyses were performed using an Applied Research Laboratories-EMX electron microprobe X-ray analysis system. An accelerating potential of 25 KeV for iron analysis and 17 KeV for sulfur analysis, a beam current of 3 nanoamperes, and an ammonium dihydrogen phosphate (ADP) analyzing crystal were utilized in the microprobe analysis. These parameters were satisfactory for the organic sulfur characterization work. In the case of coal samples in addition to sulfur, other elements were monitored, such as iron and calcium, to determine if pyrite or gypsum was present or just organic sulfur. Each sample was analyzed for the sulfur K_α and K_β emissions starting from known emission lines for a molybdenum standard. In this way both the S K_α and S K_β shifts could be recorded. Five complete spectra were recorded at each point of analysis, and several points on any particular particle of a sample were studied. The five spectra for any particular analysis location were added electronically and these data were then used in a spectrum identification program to identify a peak centroid, area under a peak (corrected for background), and the full width of a peak at its half maximum.

X-ray diffraction work on ASTM residues was performed on 2 g. of a sample mounted on a glass slide. Measurements of pyrite concentration were done by integrating counts from each of the two major pyrite peaks.

Elemental sulfur was extracted with cyclohexane from both raw coal samples and leached residues from the ASTM analytical procedure. Aliquots of the cyclohexane solution were subjected to gas chromatography (9). The detection limit for sulfur was less than 5×10^{-10}g.

Experimental Results

Microstructural Features. Scanning electron microscopy and energy-dispersive X-ray analysis have shown that coal rank and maceral type can affect the dissolution of pyrite by nitric acid. Encapsulation of the pyrite can control the penetration of nitric acid, resulting in incomplete dissolution of pyrite (2,10). This can affect the determination of sulfur by the ASTM procedure. Pyrite which was not dissolved would be reported as organic sulfur.

Sulfur Determinations. Data in Table 22 show significant variations in ASTM sulfur determinations for samples provided to Los Alamos (Ames Laboratory determinations) and to the Ames Laboratory directly compared with Penn State data tabulations. The ASTM Standard Method of Test for Forms of Sulfur in Coal (D-2492) sets repeatability limits (same laboratory, consecutive determinations) as follows:

sulfate sulfur	0.02 wt.%
pyritic sulfur, under 2%	0.05 wt.%
pyritic sulfur, 2% or more	0.10 wt.%

Reproducibility limits (duplicate determinations by different laboratories) are as follows:

sulfate sulfur	0.04 wt.%
pyritic sulfur, under 2%	0.30 wt.%
pyritic sulfur, 2% or more	0.40 wt.%

Table 22. ASTM sulfur determinations

Sample No.	Seam/State	Rank/Province	Sample Source[a]	Type of Sulfur, (DRY), wt.%			
				Pyr.	Sulf.	Org.	Total
PSOC-003	Upper Elkhorn #3/ KY	HVA/Eastern	1	0.01	0.0	0.61	0.62
			2	0.04	< 0.01	0.71	0.76
			3	0.04	< 0.01	0.49	0.54
PSOC-022	Illinois #6/IL	-/Eastern	1	0.89	0.07	1.63	2.59
			2	0.25	0.68	1.43	2.36
PSOC-065	Dietz/WY	Subbit. B/Northern Great Plains	1	0.01	0.03	0.25	0.29
			3	0.03	0.02	0.19	0.24
PSOC-081	Buck Mountain/ PA	Anthracite/Eastern	1	0.0	0.0	0.50	0.50
			3	0.04	< 0.01	0.45	0.46
PSOC-084	Pennsylvania #8/PA	Semi-Anthracite/ Eastern	1	0.55	0.06	0.60	1.21
			3	0.30	0.14	0.80	1.24
PSOC-119	Tioga/WV	Low Volatile/Eastern	1	0.04	0.0	0.26	0.30
			3	0.02	< 0.01	0.28	0.31
PSOC-128	Lower Kittanning/PA	Low Volatile/Eastern	1	1.67	0.02	0.38	2.07
			2	1.95	0.27	0.30	2.52
			3	1.54	0.46	0.48	2.48
PSOC-154	Cannel/UT (?)	HVC/Rocky Mountain (?)	1	0.42	0.08	0.69	1.19
			2	0.26	0.17	0.73	1.16
			3	0.22	0.20	0.68	1.10
PSOC-164	Tebo/MO	HVB/Interior	1	3.79	0.64	2.84	7.27
			2	2.28	2.22	2.04	6.54
			3	4.99	0.40	1.90	7.29
PSOC-176	Pittsburgh/WV	HVA/Eastern	1	0.83	0.0	2.10	2.93
			2	1.01	< 0.01	1.94	2.96
			3	0.88	0.06	1.82	2.76
PSOC-188	Illinois #2/IL	HVB/Interior	1	1.28	0.05	2.27	3.60
			2	0.32	0.96	2.22	3.50
			3	0.25	0.94	1.97	3.16

Sample No.	Seam/State	Rank/Province	Sample Source[a]	Type of Sulfur, (DRY), wt.%			
				Pyr.	Sulf.	Org.	Total
PSOC-193	Ohio #5/OH	Subbit. C/Eastern	1	0.01	0.0	0.92	0.93
	(?)	(?)	2	0.09	0.04	0.79	0.92
PSOC-212	Ohio #2/OH	HVC/Eastern	1	0.11	0.01	0.71	0.83
			2	0.06	0.02	0.64	0.72
			3	0.04	0.01	0.63	0.68
PSOC-216	Kentucky #14/KY	HVB/Interior	1	2.72	0.14	1.69	4.55
			2	2.29	1.16	1.43	4.88
PSOC-220	Kentucky #11/KY	HVB/Interior	1	1.32	0.04	2.66	4.02
			3	0.90	0.40	2.36	3.66
PSOC-255	Lower Kittanning (Bottom Bench)/PA	Medium Volatile/ Eastern	1	4.49	0.03	0.78	5.30
			3	4.49	0.20	0.43	5.12
PSOC-257	Upper Freeport/PA	Medium Volatile/ Eastern	1	1.06	0.0	0.56	1.62
			2	1.38	0.03	0.54	1.95
			3	1.18	0.03	0.35	1.56
PSOC-267	Clintwood/VA	HVA/Eastern	1	0.02	0.05	1.89	1.96
			2	1.00	0.34	0.81	2.15
			3	0.86	0.47	0.72	2.05
PSOC-270	American/AL	HVA/Eastern	1	0.02	0.04	2.28	2.34
			2	1.30	0.38	1.00	2.68
			3	1.13	0.42	0.88	2.43
PSOC-274	Sewell/WV	Medium Volatile/ Eastern	1	0.02	0.0	0.80	0.82
			2	0.27	0.14	0.55	0.96
			3	0.26	0.12	0.47	0.85
PSOC-275	Ohio #6A/OH	HVA/Eastern	1	1.41	0.0	0.73	2.14
			2	1.24	0.18	0.84	2.26
			3	1.08	0.26	0.88	2.22
PSOC-287	Bevier/MO	HVB/Interior	1	4.71	0.05	1.09	5.85
			2	3.94	1.21	1.73	6.88
PSOC-294	Pittsburgh/PA	HVA/Eastern	1	2.27	0.01	0.34	2.62
			2	2.52	0.02	0.75	3.29

Sample No.	Seam/State	Rank/Province	Sample Source[a]	Type of Sulfur, (DRY), wt.%			
				Pyr.	Sulf.	Org.	Total
PSOC-303	Callide/Australia	HVC/ -	1				0.14
			3	0.07	0.02	0.16	0.25
PSOC-309	New Mexico#8/NM	HVC/Rocky Mountain	1	0.34	0.0	0.47	0.81
			2	0.32	0.01	0.50	0.83
			3	0.27	0.06	0.33	0.66
PSOC-317	Lower Freeport/PA	Low Volatile/Eastern	1	5.87	0.09	0.48	6.44
			3	5.37	0.62	0.57	6.56
PSOC-319	Upper Kittanning/PA	Low Volatile/Eastern	1	5.85	0.06	0.08	6.01
			2	6.47	0.48	0.80	7.75
			3	5.08	0.75	0.65	6.48
PSOC-359	Lower Elkhorn/KY	HVA/Eastern	1	0.06	0.0	0.27	0.33
			3	0.04	< 0.01	0.28	0.33
PSOC-360	Lower Elkhorn/KY	HVA/Eastern	1	0.03	0.0	0.52	0.55
			2	0.08	0.01	0.51	0.60
			3	0.04	0.01	0.41	0.46
PSOC-370	Hazard #7/KY	HVA/Eastern	1	0.03	0.0	0.51	0.54
			2	0.10	0.02	0.59	0.71
			3	0.04	0.02	0.54	0.60
PSOC-380	P & M "B"/PA	Semi-Anthracite/Eastern	1	0.06	0.0	0.44	0.50
			3	0.03	< 0.01	0.56	0.60
PSOC-408	Upper Hartshorne/OK	Low Volatile/Interior	1	0.58	0.09	2.62	3.29
			2	0.34	0.30	0.76	1.40
			3	0.51	0.20	0.65	1.36
PSOC-413	Darco Lignite/TX	Lignite/Gulf	1	0.64	0.09	1.21	1.94
			2	0.56	0.17	0.61	1.34
PSOC-422	Wildcat/TX	Subbit.C/Gulf	1	0.35	0.04	1.39	1.78
			2	0.31	0.22	0.88	1.41
			3	0.16	0.27	0.81	1.24

Sample No.	Seam/State	Rank/Province	Sample Source[a]	Type of Sulfur, (DRY), wt.%			
				Pyr.	Sulf.	Org.	Total.
PSOC-458	Blind Canyon/UT	HVA/Rocky Mountain	1	0.13	0.0	0.33	0.46
			2	0.13	< 0.01	0.41	0.55
			3	0.10	0.02	0.34	0.46
PSOC-474	Adaville #2/WY	Subbit. B/Rocky Mountain	1	0.10	0.07	0.79	0.96
			3	0.06	0.08	0.71	0.85
PSOC-483	Bed #53/WY	-/Rocky Mountain	1	0.10	0.0	0.43	0.53
			2	0.27	< 0.01	0.35	0.68
			3	0.12	0.02	0.42	0.56
PSOC-491	Bed #80/WY	Subbit. A/Rocky Mountain	1	0.10	0.01	1.05	1.16
			3	0.08	0.08	0.57	0.73
PSOC-506	Upper Sunnyside/ UT	HVA/Rocky Mountain	1	0.06	0.0	0.59	0.65
			2	0.10	< 0.01	0.62	0.73
			3	0.10	< 0.01	0.63	0.74
PSOC-529	Dietz #3/WY	Subbit. B/Northern Great Plains	1	0.13	0.0	0.15	0.28
			2	0.06	< 0.01	0.23	0.30
			3	0.04	0.02	0.11	0.17
PSOC-538	Wadge/CO	HVC/Rocky Mountain	1	0.35	0.0	0.62	0.97
			2	0.40	0.05	0.54	0.99
			3	0.31	0.04	0.62	0.97
PSOC-556	Iowa #1/IA (Lucas County) (?)	HVC/Interior	1	8.37	0.23	3.66	12.26
			3	6.40	1.29	1.22	8.91
PSOC-584	Illinois #5/IL	HVB/Interior	1	6.38	0.08	1.95	8.41
			3	5.24	1.05	1.83	8.12

[a] Sample source designations:

1. Penn State Analyses; Coal Data Base Processor: Version 4.9 Feb. 1977 and Version 5.0 Feb. 1978.
2. Ames Laboratory Analyses (average of duplicate determinations); Sample source: Los Alamos.
3. Ames Laboratory Analyses (average of duplicate determinations); Sample source: Penn State.

In viewing the results in Table 22, it is obvious that major discrepancies are present for samples supplied to different laboratories. Reproducibility limits are exceeded in 25 of the 43 samples examined. (Also, repeatability is a problem for several samples.) Examples from the table indicate major differences in agreement among analyses in each type of sulfur determination. These include total sulfur in sample PSOC-164, -287, -319; organic sulfur in -270, -274, -319; pyritic sulfur in -164, -188, -267; and sulfate sulfur in -022, -164, -216... to specify a few.

The Penn State analyses were performed on fresh samples. These samples were sealed in containers by Penn State for storage until requested by investigators. In most cases the samples sent directly to the Ames Laboratory from Penn State were several years old (most were in the original sealed containers). The Los Alamos samples sent to the Ames Laboratory had been open to the atmosphere.

In many cases in Table 22 where the Ames Laboratory analyses have high sulfate values compared to those of Penn State, the sulfate increases and the sulfide decreases while total sulfur remains fairly consistent. This suggests oxidation. The Los Alamos samples are apparently more highly oxidized than the Ames Laboratory samples received directly from Penn State (still in sealed containers; subsequent grinding and handling of samples prior to wet chemical analyses were done under a nitrogen atmosphere). Of the 43 coals in Table 22, the 25 coals which exceed reproducibility limits probably do so primarily because there has been oxidation of some of the pyrite to sulfate. In a comparison of Penn State data on fresh coals with that of either set of Ames Laboratory data from Table 22, the few samples that show major pyrite discrepancies (assuming sulfate differences to be attributed to oxidation of pyrite) are high sulfur coals (PSOC-164, -267, -270, -319, and -556) where total sulfur exceeds 2 wt.% (pyritic sulfur > 1.2%). Both examples of significant pyritic sulfur and of significant total sulfur variations are seen in Table 22. Thus, sample representativeness can be a problem as well as the oxidation discussed. For the relatively low sulfur coals, the analytical problems appear to be minimal. In the coals that contain abundant pyrite, the chance for inhomogeneity in sample splits seems to be high.

In addition, a portion of the reported organic sulfur can be elemental sulfur. Specific data showing the magnitude of this error source to organic sulfur determinations are presented in a later section.

Direct Determination of Organic Sulfur. A direct analytical method for the determination of organic sulfur in coal based on the use of an electron microprobe has been described (11). This technique permits a comparison of ASTM organic sulfur determinations with direct electron microprobe determinations of organic sulfur to be made. In an assessment of the organic sulfur content of several of the coals in Table 22, it is convenient to present the sulfur determinations on a dry basis (DRY). By comparison, dry, ash free (DAF) values are strictly numerical calculations, and are susceptible to mineral variation (and are, therefore, less desirable).

In the method of Raymond and Gooley (11), organic sulfur values are obtained by electron microprobe X-ray analysis on a maceral level. Their approach is valuable. In their paper, computations are based on Penn State values. The Ames Laboratory analytical results in Table 22 on their subsamples permit a more detailed evaluation of the technique to be performed. The values from Table 22 for specimens received from Los Alamos correspond directly to those reported in reference 11 in Table 8 (PSOC-360, page 102), Table 9 (1. PSOC-003, 2. PSOC-193, 3. PSOC-360, 4. PSOC-370, 5. PSOC-506, 6. PSOC-458, 7.PSOC-529; page 102), and Table 10 (1. PSOC-274 , 2. PSOC-267, 3. PSOC-270, 4. PSOC-408, 5. PSOC-257, 6. PSOC-128, 7. PSOC-216, 8. PSOC-294, 9. PSOC-164, 10. PSOC-287, and 11. PSOC-319; page 103).

Table 8 (reference 11, page 102) shows how the electron microprobe organic sulfur values are calculated. Each weight percent maceral value (Penn State data) is multiplied by the average organic sulfur determined in the particular maceral type by the microprobe analyses, and these values are summed. Thus, an overall organic sulfur value for a coal is on a DRY basis. However, in this table and Tables 9 and 10 (reference 11) DRY values are compared directly with ASTM DAF values (Penn State data). An improvement is to compare microprobe DRY values with ASTM DRY values, preferably where the ASTM values are determined on the particular subsample that is studied by the microprobe technique. To show this, the last two columns in Tables 23 and 24 can be compared.

For relatively low sulfur coals reported in Table 23 (Total Sulfur (DRY) < 1%), the difference of ASTM and EPM values is of the order of 0.1 to 0.2 wt.% For relatively high sulfur coals reported in Table 24 (Total Sulfur (DRY) > 1%), the difference of ASTM and EPM values is of the order of 0.1 to 0.4 wt.%.

Table 23. Comparison of ASTM and electron microprobe (EPM) organic sulfur determination for selected coals.

Sample No.	EPM Org. Sulfur (DRY) wt.% (from ref. 11, Table 9, p. 102)	ASTM Org. Sulfur (DRY) wt.% (Ames Lab Analyses, Table 22[a])	Org. S [ASTM-EPM] wt.% (from ref.11, Table 9, p. 102)	Org. S [ASTM-EPM] wt.% (Ames Lab ASTM Values from Table 22[a])
PSOC-003	.78	.71	-.14	-.07
PSOC-193	.96	.79	.05	-.17
PSOC-360	.52	.51	.05	-.01
PSOC-370	.61	.59	.02	-.02
PSOC-506	.66	.62	-.03	-.04
PSOC-458	.39	.41	-.04	.02
PSOC-529	.22	.23	-.06	.01

[a] Sample Source: Los Alamos

Table 24. Comparison of ASTM and electron microprobe (EPM) organic sulfur determinations for selected high sulfur coals.

Sample No.	EPM Org. Sulfur (DRY) wt.% (from ref.11, Table 10, p. 103)	ASTM Org. Sulfur (DRY) wt.% (Ames Lab Analyses, Table 22[a])	Org. S [ASTM-EPM] wt.% (from ref.11, Table 10 p. 103)	Org. S [ASTM-EPM] wt.% (Ames Lab ASTM Values from Table 22[a])
PSOC-274	.55	.55	.33	0
PSOC-267	.69	.81	1.32	.12
PSOC-270	1.04	1.00	1.66	-.04
PSOC-408	.65	not analyzed	2.35	not avail.
PSOC-257	.39	.54	.25	.15
PSOC-128	.33	.30	.11	-.03
PSOC-216	1.18	1.43	.66	.25
PSOC-294	.60	.75	-.16	.15
PSOC-164	2.44	2.04	1.22	-.40
PSOC-287	1.86	1.73	-.45	-.13
PSOC-319	.56	.80	-.46	-.10

[a] Sample Source: Los Alamos

The elemental sulfur analyses for these 18 samples (Tables 23 and 24) are very low as will be seen in the next section.

Elemental Sulfur Recorded as Organic Sulfur. There are few data available in the literature to assess the importance of elemental sulfur to the organic sulfur problem. Many investigators feel that elemental sulfur is usually low in concentration in coal. Elemental sulfur values for coals in Table 22 are listed in Table 25 for both untreated and ASTM residue samples (-60 mesh).

The elemental sulfur content of these coals is generally very low, but ranges from 0 to 3435 μg/g. The higher levels of elemental sulfur may possibly be attributed to weathering of coal, since under certain conditions, elemental sulfur can be a product of the oxidation of pyrite (12). The Iowa coals are high in elemental sulfur. Also, note the high value for sample PSOC-317, and then compare this with the organic sulfur content for this same subsample as given in Table 22. In this case, more than 50% of the organic sulfur is actually elemental sulfur (i.e., organic S from Table 22 = 0.57 wt.% compared with elemental S from Table 25 = 0.34 wt.%).

Pyritic Sulfur Determination on ASTM Residues. Phase identification by sensitive X-ray diffraction techniques (13) shows that pyritic sulfur is present in certain ASTM residue samples (refer to Table 26).

Table 25. Elemental sulfur analyses (Ames Laboratory).

Sample No.	Sample Source	Untreated[a](μg./g.)	ASTM Residue[a](μg./g.)
PSOC-003	Los Alamos	n.a.[b]	41
PSOC-022	Los Alamos	n.a.	83
PSOC-065	Penn State	n.a.	33
PSOC-081	Penn State	n.a.	20
PSOC-084	Penn State	n.a.	228
PSOC-119	Penn State	n.a.	23
PSOC-128	Penn State	6	9
PSOC-154	Los Alamos	n.a.	81
PSOC-164	Penn State	8	8
PSOC-176	Penn State	n.a.	258
	Los Alamos	n.a.	396
PSOC-188	Penn State	13	1
PSOC-193	Los Alamos	n.a.	16
PSOC-212	Los Alamos	n.a.	0
PSOC-216	Los Alamos	14	13
PSOC-220	Penn State	5	9
PSOC-255	Penn State	n.a.	1601
PSOC-257	Penn State	0	4
PSOC-267	Penn State	14	8
PSOC-270	Penn State	6	9
PSOC-274	Penn State	2	1
PSOC-275	Los Alamos	n.a.	663
PSOC-287	Los Alamos	7	5
PSOC-294	Los Alamos	1	5
PSOC-303	Penn State	n.a.	84
PSOC-309	Los Alamos	n.a.	74
PSOC-317	Penn State	n.a.	3435
PSOC-319	Penn State	16	44
PSOC-359	Penn State	n.a.	53
PSOC-360	Los Alamos	n.a.	47
PSOC-370	Los Alamos	n.a.	83
PSOC-380	Penn State	n.a.	42
PSOC-408	Penn State	4	4
PSOC-413	Penn State	n.a.	222
PSOC-422	Penn State	n.a.	242
	Los Alamos	n.a.	242
PSOC-458	Los Alamos	n.a.	59
PSOC-474	Penn State	n.a.	7
PSOC-483	Los Alamos	n.a.	16
PSOC-491	Penn State	n.a.	16
PSOC-506	Los Alamos	n.a.	75
PSOC-529	Los Alamos	n.a.	40
PSOC-538	Los Alamos	n.a.	91
PSOC-556	Penn State	n.a.	1236
PSOC-584	Penn State	n.a.	1154

Sample No.	Sample Source	Untreated[a] (µg./g.)	ASTM Residue[a] (µg./g.)
Big Ben (Iowa; cleaned)	Ames Lab	841	n.a.
Big Ben (Iowa; cleaned)	Ames Lab	1094	n.a.
ICO (Iowa;raw)	Ames Lab	2075	n.a.
ICO (Iowa; cleaned)	Ames Lab	1610	n.a.
ISU (Iowa; raw)	Ames Lab	1718	n.a.
ISU (Iowa; raw)	Ames Lab	2087	n.a.
ISU (Iowa; mostly pyrite)	Ames Lab	491	n.a.
ISU (Iowa; cleaned)	Ames Lab	1050	n.a.
Lovilia (Iowa; raw)	Ames Lab	371	n.a.
Lovilia (Iowa; raw)	Ames Lab	532	n.a.
Lovilia (Iowa; cleaned)	Ames Lab	401	n.a.
Mich (Iowa; raw)	Ames Lab	924	n.a.
Mich (Iowa; cleaned)	Ames Lab	791	n.a.
Shinn (Iowa; raw, surface A)	Ames Lab	202	n.a.
Shinn (Iowa; raw, surface B)	Ames Lab	181	n.a.

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[a] Note: All test samples were -60 mesh.
Refer to reference 9 for analytical details: analysis by gas chromatography.
Residue samples are from HCl followed by HNO_3 leach procedure.

[b] n.a. = not analyzed

Several of the high sulfur samples listed in Table 24 are included in Table 26. Note that PSOC-216, -274, and -287 have detectable amounts of pyrite (∿ 0.2 wt.% FeS_2) in the residue from the ASTM determination for sulfatic and pyritic sulfur (on same sample).

Microprobe Estimates of Pyritic Sulfur in ASTM Residues. Results of detailed wavelength dispersive X-ray microprobe analyses for several ASTM residue samples are shown in Table 27. The information shows average iron amounts remaining in the various coal particles of a sample. If this iron is assumed to be in the form of pyrite the listed average weight percent of pyrite in all cases except PSOC-164 is less than 0.4 wt.% There is great variability in the iron content from coal particle to coal particle for these samples. Further studies are in progress to establish the identity of the iron-bearing phase(s) present.

Table 26. Pyritic sulfur determined by X-ray diffraction[a] (Ames Laboratory).

Sample Number	Sample Source	ASTM Residue[b], wt.%
PSOC-128	Penn State	< 0.1
PSOC-164	Los Alamos	< 0.1
PSOC-188	Penn State	< 0.1
PSOC-216	Los Alamos	0.1
PSOC-220	Penn State	< 0.1
PSOC-257	Penn State	< 0.1
PSOC-267	Penn State	< 0.1
PSOC-270	Los Alamos	< 0.1
PSOC-274	Penn State	0.1
PSOC-287	Los Alamos	0.1
PSOC-319	Penn State	< 0.1
PSOC-408	Penn State	< 0.1

[a] Note: Detection limit is approximately 0.1% pyritic sulfur.

[b] Residue samples are from HCl followed by HNO_3 leach procedure. Residue samples are ground for X-ray work (-200 mesh).

Table 27. Electron microprobe X-ray analyses[a]

Sample Number	Source	Weight Percent Iron		Estimated wt.% Pyrite[b]
		Mean	Standard Deviation	
PSOC-128	Los Alamos	0.17	0.14	.4
PSOC-257	Los Alamos	0.10	0.06	.2
PSOC-267	Los Alamos	0.16	0.07	.3
PSOC-274	Los Alamos	0.10	0.15	.2
PSOC-287	Los Alamos	0.32	0.20	.7
PSOC-319	Los Alamos	0.18	0.20	.4
PSOC-408	Los Alamos	0.04	0.03	.1
PSOC-164	Penn State	0.14	0.14	.3
PSOC-216	Los Alamos	0.01	0.03	0
PSOC-270	Penn State	0.08	0.16	.2

[a] Analyses performed on ASTM coal residues following hydrochloric followed by nitric acid treatment (ASTM). Iron and sulfur are monitored to establish the presence and amounts of pyrite remaining in the coal (-60 mesh).

[b] Assumes that the iron detected in the leached material is present as pyrite.

Direct Determination of Forms of Sulfur. The following samples were examined by a wavelength dispersive X-ray analyzer monitoring wavelength shifts and other features of the peaks:

Model compounds

Diphenyl sulfone (Aldrich Chemical Co.)

Dibenzothiophene sulfone (prepared in Ames Laboratory)

Dibenzothiophene sulfone (Aldrich Chemical Co.)

Organic sulfur

Organic sulfur standard (Los Alamos Scientific Laboratory)

ICO mine coal (float), (Iowa)

Coal treated by Ames chemical desulfurization process

Untreated coal samples (Kentucky)

1-step treatment (Kentucky)

2-step treatment (Lovilia mine, Iowa)

Sulfate sulfur

Gypsum ($CaSO_4 \cdot 2H_2O$)

Pyrite sulfur

ICO mine, (Iowa)

Sublimed (elemental) sulfur

J. T. Baker Chemical Co. (Phillipsburg, N.J., orthorhombic; lot 32,580)

Table 28 contains sulfur K_α peak position information for several sulfur forms as determined by microprobe analyses. All data were recorded relative to the Mo $L_{\alpha_{1,2}}$ emission at 5.4062 Å.

The sulfur K_α line can be used as an indicator of the amount of sulfur present in raw and processed coals, and of the form of sulfur present. The elemental sulfur band falls at the same location as that for organic sulfur. The sulfur K_β peak appears to fall at values related to the form of sulfur which may be of use in establishing organic sulfur or elemental sulfur. As the intensity of this peak is much less than that of the K_α peak, further studies are in progress to evaluate this. In some of the compounds, the S K_β peak seems to degrade under these conditions of analysis. However, the

Table 28. Sulfur peak positions based on the analysis of the sum of five analyses at a location.

Form of Sulfur	Sulfur K_α, Å
A. <u>Model compounds</u>	
Diphenyl sulfone (Aldrich Chemical Co.)	5.372
Dibenzothiophene sulfone (prepared in Ames Lab)	5.373
Dibenzothiophene sulfone (Aldrich Chemical Co.)	5.373
B. <u>Organic sulfur</u>	
Organic sulfur standard (provided by Los Alamos)	5.371
Organic sulfur standard (data on Los Alamos standard, reference 11)	5.371
ICO mine (float; organic sulfur in vitrinite)	5.371
C. <u>Chemically desulfurized by Ames process</u>	
#3638 - Control, Kentucky (pyrite and organic sulfur in vitrinite)	5.372
#3718 - 2-step treatment (Kentucky; mostly organic sulfur)	5.371
#3707 - 2-step treatment (Lovilia, Iowa; pyrite and organic sulfur)	5.373
D. <u>Sulfate sulfur</u>	
$BaSO_4$ (reference 11)	5.368
Gypsum ($CaSO_4 \cdot 2H_2O$)	5.369
E. <u>Pyritic sulfur</u>	
Pyrite (Iowa)	5.373
ICO (Raw; pyrite and organic sulfur in vitrinite)	5.372
F. Sublimed (elemental) sulfur	
J. T. Baker Chemical Co.	5.371

major tests center on the K_β peak use to discriminate organic sulfur from elemental sulfur directly. In certain low sulfur coals this may be very significant as recent work at the Ames Laboratory shows that occasionally most of the reported organic sulfur of a standard wet chemical analysis can actually be elemental sulfur (specific example: Lower Freeport Coal, PA; elemental sulfur = 0.34 wt.% whereas ASTM organic sulfur = 0.57 wt.%). This may require direct gas chromatography for elemental sulfur as well as microprobe analysis for organic sulfur as part of an analysis scheme.

The chemical shift in Table 28 for barium sulfate compared with gypsum is detectable. Model compounds can be catalogued by this technique; however, many organic sulfides of interest are liquids under the normal microprobe analytical conditions. Cold stage analyses of these compounds are in progress. Excellent agreement in the sulfur spectra for a laboratory prepared pure specimen and a commercially available specimen of dibenzothiophene sulfone was obtained.

Where pyrite and organic sulfur are present at the same analysis point (#3638), a value between that for pyrite and for organic sulfur is observed. In sample #3707, the pyrite contribution is much stronger than that for the organic sulfur, and thus the pyrite peak maximum is observed. For sample #3718, organic sulfur provides the major contribution to the peak observed. Also, organic sulfur alone is represented by the analysis for the ICO float specimen.

X-ray intensity of iron is continuously monitored at each analysis point. Iron intensities in excess of background levels are assumed to be pyrite. These results are rejected when specifically analyzing for organic sulfur. At the same time, other elements are monitored that might suggest the presence of other sulfides or sulfate minerals.

Conclusions

Microstructural features of coal such as maceral encapsulation of pyrite can inhibit nitric acid leaching of pyrite in standard sulfur determinations. When pyrite is not completely leached, reported organic sulfur values are high since the percentage of organic sulfur is obtained by subtracting the sum of the percentages of sulfatic and pyritic sulfur from the percentage of total sulfur as determined by the Eschka method described in ASTM Methods D271.

Another major source of error in reported organic sulfur values can result from the presence of elemental sulfur. This would be missed by the ASTM technique. An example of where this error can be more than 50% is shown for the Lower Freeport coal (PSOC-317).

X-ray wavelength shift information appears to be of value in determining the forms of sulfur in coal. Elemental sulfur should also be monitored in such analyses.

Special measures for preparing, storing, and dividing standard coals are required to insure that every user receives the same material in the same condition. It is recognized that in practice this is difficult to achieve. For example, the stability of sulfur compounds in coal may not be sufficiently high. Pyrite in coal oxidizes fairly rapidly.

GENERAL CONCLUSIONS

Progress was made during the past year in the development and improvement of various methods for desulfurizing and recovering fine-size coal. The development of an oxidative pressure leaching process was advanced by investigating the effects of various process conditions using a small stirred reactor. It was established that more sulfur, both organic and inorganic, was removed by leaching with alkaline (sodium carbonate) solutions than with acidic solutions. The heating value recovery, however, was slightly lower under alkaline conditions and declined with increasing alkali concentration. At higher oxygen partial pressures, the removal of pyritic and organic sulfur was improved without a significant decrease in the heating value recovery. With prolonged leaching time, the sulfur removal increased moderately, but the recovery in heating value declined. At higher concentrations of solids in the reaction mixture, the recovery of combustible matter was improved, but no effect of pulp density on sulfur removal was observed. When the temperature was increased, desulfurization of coal increased at first, passed through a maximum value, and then decreased. On the other hand, the heating value recovery declined steadily with increasing temperature. In a modified version of the desulfurization process, a second leaching step was added in which the coal from the first leaching step was heated at a higher temperature in a non-oxidizing environment. By this two-step process, more than half of the organic sulfur was apparently removed from an Iowa (Lovilia) bituminous coal.

The leaching of coal-derived pyrite, studied in a packed-bed, tubular reactor, showed that desulfurization decreased as a function of packing length. The decrease in desulfurization appeared to be linked to the change in oxygen partial pressure caused by the hydrodynamic pressure drop across the packed bed.

Measurement of the floatability of bituminous coal particles and pyrite particles isolated from coal and cleaned with hot hydrochloric acid, showed that both materials float readily in the presence of MIBC and that the floatability of either material is reduced by small concentrations of various alkaline and alkaline earth compounds and ferric chloride. While all of these compounds seemed to affect the floatability of pyrite more than that of coal, compounds which supply calcium and magnesium ions showed greater selectivity as pyrite depressants than others. Calcium hydroxide was found to be an exceptionally strong depressant for pyrite. Also wet oxidation of the pyrite surface with a warm alkaline solution containing dissolved air was shown to be a very effective method of reducing the floatability of pyrite. Moreover this method does not appear to reduce the floatability of coal more than an alkaline solution by itself.

Oil agglomeration experiments showed that fine (60 mesh x 0) coal was generally recovered in higher yield than ultrafine (400 mesh x 0) coal by various grades of fuel oil, but the inorganic sulfur content of the agglomerated fine coal was generally greater than that of the agglomerated ultrafine coal. Also the recovery of fine coal was uniformly high (92 - 100%) with any of the following grades of fuel oil: No. 1, No. 2, No. 200 LLS No. 5 LLS, and No. 6. While the recovery of ultrafine coal was high with No. 200 LLS and No. 5 LLS oils, it was lower with either lighter or heavier oils. No recovery of ultrafine coal was achieved with No. 6 oil. The removal of inorganic sulfur from coal by oil agglomeration was improved significantly by pretreating the coal with a warm alkaline solution containing dissolved air. This treatment reduced the tendency for pyrite particles to be oil agglomerated while not affecting the agglomeration of coal particles.

The construction of a large bench-scale flow system for demonstrating various methods of cleaning and recovering fine coal was completed and the system tested. Although a number of mechanical and operational problems became apparent, the system generally met design expectations. Most of the problems were corrected and the remainder are being solved.

Analysis of numerous samples of coals by scanning electron microscope and energy dispersive X-ray techniques showed that encapsulation of pyrite by coal macerals may result in errors for the reported values of sulfur forms as determined by ASTM methods. It was shown that the content of organic sulfur in particular may be subject to error. Part of the error may be caused by encapsulation of pyrite. Another part of the error may be due to the presence of elemental sulfur. A potentially promising method for the direct determination of organic sulfur in raw and processed coal is based on wavelength dispersive X-ray analysis.

LITERATURE CITED

1. Wheelock, T. D., Greer, R. T., Markuszewski, R., and Fisher, R. W., "Advanced Development of Fine Coal Desulfurization and Recovery Technology," Annual Technical Progress Report, Oct. 1, 1976 - Sept. 30, 1977, IS-4363, Ames Laboratory DOE, Iowa State University, Ames, Iowa, March 1978.

2. Wheelock, T. D., Greer, R. T., Markuszewski, R., and Fisher, R. W., "Advanced Development of Fine Coal Desulfurization and Recovery Technology," Quarterly Technical Progress Report, Oct. 1 - Dec. 30, 1977, IS-4536, Ames Laboratory DOE, Iowa State University, Ames, Iowa, October 1978.

3. Chen, M.-C., "Desulfurization of Coal-Derived Pyrite Using Solutions Containing Dissolved Oxygen," M.S. Thesis, Iowa State University, Ames, Iowa, 1978.

4. Aplan, F. F., "Use of the Flotation Process for the Desulfurization of Coal," Coal Desulfurization: Chemical and Physical Methods, T. D. Wheelock, ed., ACS Symposium Series 64, Am. Chem. Soc., Washington D.C., 1977, pp. 70-82.

5. Glembotskii, V. A., Klassen, V. I., and Plaksin, I. N., Flotation, Primary Sources, New York, 1972.

6. Gaudin, A. M., and Charles, W. D., "Adsorption of Calcium and Sodium on Pyrite," Transactions AIME, 196, 195-200 (Feb. 1953).

7. Baker, A. F., and Miller, K. J., "Hydrolyzed Metal Ions as Pyrite Depressants in Coal Flotation: A Laboratory Study,: R. I. 7518, U.S. Bureau of Mines, May 1971.

8. Perrott, G. St. J., and Kinney, S. P., "The Use of Oil in Cleaning Coal." Chem. and Met. Engr., 25 (5), 182 (1921).

9. Richard, J. J., Vick, R. D., and Junk, G. A.,"Determination of Elemental Sulfur by Gas Chromatography," Environ. Sci. Techn. 11 (12), 1084-6, 1977.

10. Greer, R. T., "Pyrite Distribution in Coal," Scanning Electron Microscopy/1978, I, O. Johari, ed., SEM Inc., AMF O'Hare, Illinois, 1978, pp. 621-6 and 610.

11. Raymond R., and Gooley, R., "A Review of Organic Sulfur Analysis in Coal and a New Procedure," Scanning Electron Microscopy/1978, I, O. Johari, ed., SEM Inc., AMF O'Hare, Illinois, 1978, pp. 93-107.

12. Bergholm, A., "Oxidation of Pyrite," Jernkontorets Ann. 139 (8), 531-49 (1955).

13. Benson, J., and Jacobson, R. A., "Rapid Analysis of Mineral Content of Coals: Development of an On-Line Monitoring Instrument for Pyrite and Ash in Coal," Quarterly Technical Progress Report, Oct. 1 - Dec. 31, 1978, IS-4655, Ames Laboratory DOE, Iowa State University, Ames, Iowa, March 1979.