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**ADVANCED
DEVELOPMENT
OF FINE COAL
DESULFURIZATION
AND RECOVERY TECHNOLOGY**

**For Division of Materials and
Exploratory Research**

MASTER

**Annual Technical Progress Report
Oct. 1, 1976-Sept. 30, 1977**

By

**Thomas D. Wheelock, Raymond T. Greer,
Richard Markuszewski, and Ray W. Fisher**

Under Contract No. W-7405-eng-82

AMES LABORATORY DOE

IOWA STATE UNIVERSITY

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ABSTRACT

During the first year of this project, work was carried out to develop and improve several promising methods for desulfurizing and recovering fine-size coal. These methods included froth flotation, selective oil agglomeration, pelletization, and a chemical desulfurization process which involves leaching fine coal with a hot dilute solution of sodium carbonate containing dissolved oxygen or air under pressure. This process is an oxydesulfurization process which utilizes an alkaline solution instead of an acidic solution for leaching coal.

The results of experiments with a small autoclave showed that more sulfur, both organic and inorganic, was removed from several high-sulfur bituminous coals when a dilute solution of alkali was used than when a dilute acid solution was used for leaching under the same conditions of time, temperature, and oxygen partial pressure. On the other hand, the heating value recovery was somewhat higher when acidic solutions were used. Also it was shown that pure oxygen is more effective than air, even though the oxygen partial pressure was kept the same, for oxydesulfurization of coal in either acidic or alkaline solutions. In addition it was found that the removal of organic sulfur by alkaline solutions increased as the oxygen partial pressure was raised. Although small concentrations of alkali were beneficial, large concentrations were detrimental.

The results of leaching pyrite isolated from coal in a fixed-bed, tubular reactor showed that the pyritic iron is converted to ferric oxide or hematite as the sulfur is extracted by the alkaline solution. Moreover the hematite particles are similar in size and shape to the original pyrite particles. The leaching rate of an individual particle appears to be controlled by diffusion of leachant through the hematite shell which forms around a core of unreacted material. Therefore the leaching time should vary directly as the square of the particle diameter and inversely as the dissolved oxygen concentration. Also the leaching rate should increase moderately with temperature because of the effect of temperature on the rate of diffusion of dissolved oxygen within the pore structure. On the other hand, the rate should be independent of liquid flow rate or alkali concentration as long as excess alkali is present. Most of these features were confirmed experimentally.

In order to improve the physical separation of coal and pyrite particles by froth flotation or oil agglomeration, various surface chemical treatments were tested. The most successful treatment involved treating the coal or pyrite particles with a warm, dilute alkaline solution which was aerated to provide mildly oxidizing conditions. By this means the floatability of pyrite was reduced markedly while the floatability of coal was hardly affected. This treatment also greatly improved the selectivity of the oil agglomeration process so that the inorganic sulfur content of a high-sulfur bituminous coal was reduced as much as 87% with good recovery.

The design of the first phase of a large bench-scale flow system for demonstrating various methods of cleaning and recovering fine-size coal was completed and construction started. The system will initially include equipment for grinding and chemically pretreating 1000 lb. batches of coal and for continuously cleaning the pretreated coal by froth flotation or oil agglomeration at a rate of several hundred pounds per hour. It will also include a rotating, inclined-pan pelletizer for balling coal fines.

Scanning electron microscope and energy dispersive X-ray analysis techniques showed that a significant portion of the pyrite in the high-sulfur bituminous coals used in this investigation was in the form of microcrystallites. The pyrite content of channel samples from several Iowa coal mines was characterized with regard to pyrite form and size distribution. Also it was confirmed that the ASTM method of determining pyritic sulfur is suitable for Iowa coals.

OBJECTIVES AND SCOPE OF WORK

Background

An important 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 in existence 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 first year of the project and provides a summary of all of 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.

Task G. - Neutron Source for Sulfur Monitoring Instrument

As originally conceived this task was to develop a neutron source based on the D-D reaction for a coal process stream sulfur monitoring instrument. Work on the task was halted when it became apparent that commercial interests had succeeded in developing such a device. An alternative approach which could lead to the development of a superior instrument for monitoring both sulfur and moisture is under consideration. The alternative method would utilize neutrons from a ^{252}Cf source which are moderated to thermal energies by zirconium hydride.

SUMMARY OF PROGRESS TO DATE

Several methods which hold great but largely unrealized promise for desulfurizing and recovering fine-size coal were selected for technical development. These methods included froth flotation, selective oil agglomeration, pelletization, and chemical desulfurization by a unique process. During the past year, a preliminary assessment of these methods was made and a program of laboratory and bench-scale work was launched to achieve the stated objectives.

The chemical desulfurization process selected for development involves leaching fine-size coal with a hot solution of sodium carbonate containing dissolved oxygen or air under pressure. Pyritic sulfur is converted to soluble sulfate which is extracted along with other mineral sulfates present in coal. Also some organic sulfur is extracted. On the other hand, pyritic iron is converted to insoluble ferric oxide or hematite. Two types of reaction systems are being utilized to demonstrate the leaching step in the laboratory. One type utilizes a stirred autoclave and the other a fixed bed tubular reactor through which the leachant is passed. The first type is being used to leach fine-size coal while the second is being used to measure the rate of reaction of pyrite particles which have been isolated from coal.

Preliminary experiments with the stirred autoclave showed that the rate of desulfurization of coal increases with speed up to a point and then for larger speeds the rate is independent of speed. Below this point the rate seems limited by the availability of oxygen at the surface of the particles while above this point it appears limited by the kinetic mechanism within the particles. The speed corresponding to this transition is about 1200 r.p.m. for an oxygen partial pressure of 50 psia and about 1800 r.p.m. for an oxygen partial

pressure of 200 psia. Further experiments showed that most of the inorganic sulfur was removed from several high-sulfur bituminous coals by leaching the ground materials for 1 to 2 hr. under rather mild conditions (temperatures of 150 to 180°C, oxygen partial pressures of 50 to 100 psia). Also a significant amount of organic sulfur was removed from some coals. In the case of a Western Kentucky coal the removal of organic sulfur increased as the oxygen partial pressure was raised. Experiments were also conducted to compare oxydesulfurization with acidic as well as basic solutions and with air as well as with pure oxygen. The results showed clearly that all forms of sulfur were reduced more in 1 hr. by an alkaline solution than by an acidic solution. On the other hand, the heating value recovery was somewhat higher when acidic solutions were used. But with either type of solution, more sulfur was extracted when pure oxygen was used than when air was used, the oxygen partial pressure being the same (50 psia) in both cases. Although small concentrations of alkali (e.g., 0.2M Na_2CO_3) proved beneficial, larger concentrations proved detrimental by reducing the heating value recovery and increasing the ash content of the coal while not improving desulfurization.

Experiments with the tubular reactor system have provided an indication of the mechanism which controls the leaching rate of individual pyrite particles. Thus the rate appears to be controlled by the rate of diffusion of leachant through a shell of reacted material surrounding an unreacted core of pyrite in the case of each particle. Consequently the time required to completely desulfurize the material should vary directly as the square of the particle diameter and inversely as the dissolved oxygen concentration which in turn depends on the oxygen partial pressure and temperature. The rate of desulfurization appears to increase with temperature in accordance with the Arrhenius law, the activation energy being about 8 kcal./mole. On the other hand, the rate is essentially independent of liquid flow rate and alkali concentration as long as excess alkali is present. The rate of desulfurization proved to be strongly dependent on the oxygen flow rate with the rate of desulfurization rising to a peak and then declining as the flow rate was raised. At lower oxygen flow rates there may not have been sufficient oxygen to supply the reaction while at higher rates the excess gas may have interfered with good contact between the liquid and solids.

Since poor rejection of pyritic sulfur has hampered the application of froth flotation in the industrial field of coal preparation, this problem is being addressed specifically. To help define the problem, a series of laboratory flotation tests was applied to a high-sulfur bituminous coal from Iowa. Although the recovery of coal was high with methyl isobutyl carbinol (MIBC) being the only reagent required, the separation of coal from pyrite was poor. Also the degree of separation did not appear to depend very much on the concentration of MIBC, particle size, slurry concentration, or other obvious factors. These results further emphasize the need to develop surface chemical treatments which selectively reduce the floatability of iron pyrites. Toward this end two series of measurements were made to rapidly screen various potential pyrite depressants. In one series the floatability of pyrite or coal particles in the presence of possible depressants was measured with a modified Hallimond tube micro-flotation cell. In the other series the zeta potential of coal or pyrite suspensions containing small amounts of the reagents was determined. Potential depressants which were tested included ammonium thiocyanate, calcium hydroxide,

diammonium citrate, ferric chloride, disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA), sodium carbonate, sodium cyanide, sodium phosphate, sodium silicate, and sodium sulfite. Among these compounds only ammonium thiocyanate seemed to depress selectively the floatability of freshly ground pyrite in the presence of MIBC but even the depressing action of this compound was not great. Although ferric chloride seemed to depress slightly freshly ground pyrite at lower pH, it also depressed coal. Fortunately a more promising surface chemical treatment was demonstrated. This involved treating the coal or pyrite particles with a warm, dilute alkaline solution which was aerated to provide mildly oxidizing conditions. By means of this treatment the floatability of the pyrite was reduced appreciably while the floatability of the coal was not affected noticeably.

Several ways to improve the technical and economic viability of the selective oil agglomeration method of beneficiating fine coal have been identified and demonstrated. Thus it has been shown that it is possible to use relatively inexpensive, heavy residual fuel oils for agglomeration provided that suitable techniques are used. One technique is to incorporate an emulsifying agent with the oil, another is to cut the heavy oil with some light oil. Also it has been found that the oxidative chemical pretreatment process which reduces the floatability of pyrite also improves the selectivity of the oil agglomeration method. Therefore even though heavy fuel oils are not as selective as light oils, it may be possible to improve the selectivity of the method by chemical pretreatment to the point where light oils no longer have an overriding advantage. In this regard it was shown that the inorganic sulfur content of a high-sulfur bituminous coal was reduced 87% by oil agglomerating the finely ground and chemically pretreated coal with an oil mixture composed largely of No. 6 fuel oil. The yield of coal on an ash-, moisture-, and oil-free basis was 83%. Omitting the chemical pretreatment step resulted in an inorganic sulfur reduction of only 44% while not improving the yield.

A technical assessment of various pelletization and briquetting methods indicated that one of the most promising size enlargement processes for coal fines is a tumbling or balling process carried out with a rotating, inclined-pan. This assessment also revealed that the cost of suitable binders for coal is a problem as well as the large number of variables which must be controlled. In order to resolve these problems, a bench-scale pelletizer has been designed and fabricated. This unit will be installed in the facility described below and will be used in coming months for testing various binders and methods of applying these binders.

A large bench-scale flow system for demonstrating various methods of cleaning and recovering fine-size coal is under construction at the Ames coal preparation facility. This system will include equipment for grinding and chemical 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. In addition it will include the pelletizer mentioned above. The pelletizer will be capable of pelletizing the full output of beneficiated coal. Construction of this system should be completed by April, 1978.

The microstructure-microchemistry of coal was studied to provide information bearing on the development of methods of desulfurizing and recovering fine coal. The relation of pyrite and other inorganic phases to coal macerals was developed by scanning electron microscope/energy dispersive X-ray analyses. The distribution of various forms of pyrite by size and by crystal structure has been determined for several coal seams on a micrometer size basis. Scanning electron microscope studies confirmed that the high volatile C bituminous coal of Iowa is well characterized for pyritic sulfur by the standard ASTM chemical tests. Microstructural features of coal treated by several processes have been compiled and utilized in support of improvement and technical development of methods for desulfurization of coal.

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Chemical Desulfurization

The development of a very promising chemical desulfurization process which will remove most of the inorganic sulfur and a significant portion of the organic sulfur from coal is underway. The process involves leaching fine-size coal with a hot, dilute solution of sodium carbonate containing dissolved oxygen or air under pressure which converts the sulfur in coal into water soluble sulfates. The overall reaction of pyrite appears to be as follows:

Sulfuric acid produced by the preceding reaction is neutralized immediately as shown below:

As a consequence of these reactions pyrite is converted to a soluble sulfate and insoluble ferric oxide or hematite. This sulfate is extracted along with other sulfates already present in coal. The mechanism whereby organic sulfur is extracted has not been established.

It is proposed to regenerate the leachant by employing the following reactions:

As indicated above, lime is added to precipitate calcium sulfate which is removed by filtration, and carbon dioxide is added next to recarbonate the alkali.

A schematic diagram of the process as presently conceived is presented in Figure 1. As shown in this diagram, run of mine coal is first crushed and separated by a heavy media unit to eliminate coarse pyrite and other refuse. The float fraction is wet-ground in a ball mill and mixed with a dilute sodium carbonate solution. The resulting slurry is heated and then reacted with oxygen or air under pressure in one or more mixed flow reactors in series. The reacted material is cooled, and if desired, the iron oxide is removed magnetically. The coal is recovered by oil agglomeration and dewatered. To recover the spent alkali, hydrated lime is added to the spent leachant. The precipitated calcium sulfate is removed by filtration along with other fine refuse. The alkali solution is recarbonated and the rejuvenated leachant recycled.

In comparison with other chemical leaching processes under development, this process offers several important advantages (1). Thus it extracts both inorganic and organic sulfur; not all other processes under development remove organic sulfur. It also involves relatively rapid leaching reactions so that lower temperatures and pressures can be employed than in most other processes. In addition it involves the use of a relatively noncorrosive leachant so that cheaper materials of construction can be used than for other processes.

For the past year the present experimental program was directed towards the laboratory development and demonstration of the leaching step. Experiments were conducted with two types of reaction systems. One system utilized a stirred autoclave to study the removal of different forms of sulfur from coal whereas the other system employed a fixed bed tubular reactor to measure the rate of extraction of sulfur from pyrite particles which had been isolated from coal.

Stirred Autoclave System

The 1.0-liter stirred autoclave has been demonstrated as an efficient batch reactor for the leaching of most of the inorganic and some of the organic sulfur from coal with hot dilute solutions of sodium carbonate containing dissolved oxygen under pressure. The contents of the autoclave are stirred by a gas dispersing turbine agitator operated by a magnetic drive. The reactor is designed for operation at elevated pressures (up to 5000 psi.) and elevated temperatures (up to 340°C). The reactor is jacketed by an electric heater which is controlled by a proportioning-type temperature controller. The temperature is measured accurately by means of a thermocouple. The reactor body and fittings are made of Type 316 stainless steel. The reactor cavity is protected by one of two removable liners; one is made of Type 316 stainless steel, and the other of Inconel 600.

For each run, the autoclave reactor was charged with 40 g. of coal and 400 ml. of the leach solution. After the autoclave was closed, the desired agitator speed was established and the autoclave was purged with nitrogen gas while being heated to the required temperature. When the desired temperature was reached, the flow of nitrogen was stopped and oxygen was introduced into the autoclave. The oxygen partial pressure (psia), the total pressure within the autoclave (psig.), the temperature, and the stirring rate were kept constant for a measured time period. Some gas was bled continuously from the reactor to avoid any concentration

build-up of gaseous products within the system. At the end of a run, the flow of oxygen was discontinued, the system was purged with nitrogen, and cold water was pumped through the cooling coil of the reactor to lower the temperature of the system. After cooling, the contents of the reactor were removed and filtered to recover the solid coal. The coal was dried in an oven, weighed to determine the recovery, and analyzed for the various chemical forms of sulfur, ash content, and heating value.

The initial task was to establish the effect of the stirring rate of the turbine agitator on the amount of sulfur removed by leaching. For this study coal from the Scott site of the Iowa State University Demonstration Mine (called Scott coal from here on) was leached for 1 hr. by 0.2M sodium carbonate solution at 150°C and 50 psia. oxygen pressure. The results of this series of experiments are listed in Table 1 and presented graphically in Figure 2. The amount of pyritic and of total sulfur extracted from the coal by leaching increased steadily

Table 1. Effect of agitator speed on pyritic and total sulfur reduction of Scott Coal (-200 mesh).^a

Speed r.p.m.	Yield %	Ash, wt.%	Sulfur Distribution, wt.%				Total S Reduction, %	Pyritic S Reduction, %
			Pyritic	Sulfate	Organic	Total		
(Scott Coal) ^b		15.4	5.68	0.79	2.90	9.37	----	----
200	95.3	17.0	5.47	0.24	2.78	8.49	9.4	3.7
350	95.8	16.8	5.18	0.17	2.73	8.08	13.8	8.8
400	95.5	17.8	5.33	0.26	2.79	8.38	10.6	6.2
500	94.8	16.8	4.53	0.22	3.12	7.87	16.0	20.2
600	96.3	17.8	4.48	0.01	3.38	7.87	16.0	21.1
700	95.8	17.5	4.76	0.06	2.76	7.58	19.1	16.2
800	95.5	16.7	4.71	0.02	3.02	7.75	17.3	17.1
1000	96.0	18.1	3.80	0.08	2.75	6.63	29.2	33.1
1200	96.0	18.5	3.92	0.07	2.62	6.61	29.5	30.9
1400	94.5	18.3	0.96	0.13	2.72	3.81	59.3	83.1
1600	94.5	17.5	1.09	0.14	2.70	3.93	58.1	80.8
1800	93.5	16.9	0.80	0.13	2.55	3.48	62.9	85.9
2100	93.5	17.5	0.57	0.13	2.79	3.49	62.8	90.0

^aLeached for 1 hr. by 0.2M Na₂CO₃ at 150°C and 50 psia O₂ pressure.

^bAsh and sulfur content of unleached coal.

Figure 2. Effect of agitator speed on the removal of sulfur from coal for 50 psia oxygen partial pressure.

Figure 3. The interaction of agitator speed and oxygen partial pressure on pyritic sulfur removal.

with increasing rotation speed in the range 200-1200 r.p.m. The amount of extracted sulfur (both pyritic and total) increased sharply between 1200 and about 1400 r.p.m. For agitator speeds above 1400 r.p.m., the amount of pyritic and total sulfur extracted increased more and more slowly, finally leveling off between 1800 and 2100 r.p.m. Within this range of rotation speeds, the amount of sulfur extracted was highest, being about 90 and 63% for pyritic and total sulfur, respectively. At the same time, the amount of extracted sulfur became independent of the agitator speed, indicating that the rate of extraction is not limited by the mass transfer of oxygen to the reaction site. Thus by using the recommended agitator speed, e.g. 2000 r.p.m., any small deviation from the preset speed will have no effect on the extraction of sulfur.

The study of the effect of agitator speed on the amount of sulfur removed was repeated at a higher oxygen partial pressure, i.e. 200 psia. The data are shown in Table 2 and Figure 3. Beginning with 800 r.p.m., the reduction in total sulfur content increased more steeply and then leveled off sooner, at about 1200 r.p.m., and at a higher sulfur reduction value, approximately 67%, than that at the lower oxygen partial pressure of 50 psia. The reason for the steeper rise in sulfur removal may be the higher solubility of oxygen in the alkaline solution at the higher pressure. Thus, with increased stirring rate the mass transport is higher for the solution with the greater oxygen concentration, and, as more oxygen is transported to the reaction site, the reaction can proceed progressively faster. At the plateau, some mechanism other than mass transport is the rate-limiting step, and further increases in rotation speed do not increase the reaction rate.

Table 2. Influence of agitator speed on leaching uncleaned Scott Coal (-200 mesh) at high oxygen pressure.^a

Speed, r.p.m.	H.V. Btu/lb.	Ash, wt.%	Sulfur Distr., wt.%				Spec. Cont., lb.S/10 ⁶ Btu				H.V. Recovery, %
			Pyr.	Sulf.	Org.	Tot.	Pyr.	Sulf.	Org.	Tot.	
(Coal) ^b	10,270	16.9	6.41	1.91	2.60	10.92	6.24	1.86	2.53	10.63	----
800	10,410	19.0	5.13	0.26	2.35	7.74	4.93	0.25	2.26	7.44	93.8
1000	10,540	18.0	1.39	0.36	2.12	3.87	1.32	0.34	2.01	3.67	96.5
1200	10,600	17.6	0.96	0.20	2.25	3.41	0.91	0.19	2.12	3.22	93.1
1400	10,570	17.8	0.84	0.31	2.27	3.42	0.79	0.29	2.15	3.23	93.7
1600	10,530	18.1	0.92	0.31	2.37	3.60	0.87	0.29	2.25	3.41	93.0
1800	10,530	18.1	0.95	0.35	2.37	3.67	0.90	0.33	2.25	3.48	93.6
2000	10,540	18.0	0.88	0.31	2.33	3.52	0.84	0.29	2.21	3.34	93.6

^aLeached 1 hr. by 0.2M Na₂CO₃ at 150°C and 200 psia O₂ pressure.

^bHeating value, ash content, and sulfur distribution of unleached coal.

It is interesting to note that at this high pressure (200 psia O_2), there is a noticeable decrease in the organic sulfur content, a decrease that is not apparent at lower pressures. This observation was subjected to further study and will be discussed under the effect of partial pressure. A second item to note in Table 2 is the very high (93-96%) heating value recovery. Generally, the mechanical losses of coal during handling, filtration, etc., are not negligible and are reflected in an approximately 5% decrease in the heating value recovery. It has been observed that the losses are higher for finer mesh coal. The excellent recoveries in Table 2 were obtained with -200 mesh coal; in other experiments with -400 mesh coal, the recovery was not as good.

To study the possible effect of agitator speed on the further reduction of particle size of fine coal during leaching, three coal samples leached in the stirred autoclave at different speeds were subjected to particle size analysis using standard U.S. mesh sieves. The results are presented in Table 3. The differences in the three samples appear to be small. Particles passing through 400 mesh amounted to 45.5, 50.8, and 55.2% of samples leached at 200, 1000, and 2100 r.p.m., respectively. The slight increase indicates that during leaching some further reduction in particle size occurred at higher speeds, but the effect is not great.

The stirred autoclave system was used to study the effects of temperature, pressure, nature and concentration of leaching solution, and nature of the oxidizing gas on the chemical desulfurization of several coals. Besides Scott coal, the study included Iowa coals from the Lovilia and the Big Ben mines. In addition, a Western Kentucky coal from the Fies Mines (No. 9 seam) in Hopkins County was used. For the pre-cleaned coals, the run-of-mine coal was crushed to 1/4 in. or less and treated with 1,1,2-trichloroethylene (specific gravity = 1.45) by the float-sink method as a preliminary cleaning process. The cleaned coal was then pulverized and ball-milled to -400 mesh size. For uncleaned coals, no treatment with trichloroethylene was used. The coal was pulverized and screened to -200 mesh size.

Table 3. Particle size distribution of coal after leaching at different agitator speeds.^a

Screen mesh	200 r.p.m.		1000 r.p.m.		2100 r.p.m.	
	Retained, wt.%	Passed, wt.%	Retained, wt.%	Passed, wt.%	Retained, wt.%	Passed, wt.%
200	10.0	90.0	9.0	91.0	8.1	91.9
250	17.8	82.2	22.2	77.8	17.7	82.3
325	37.2	62.8	37.6	62.4	35.7	64.3
400	54.5	45.5	49.2	50.8	44.8	55.2

^aLeached for 1 hr. by 0.2M Na_2CO_3 at 150°C and 50 psia O_2 pressure.

Because many of the coals used in these experiments have been precleaned by the float-sink method using chlorinated hydrocarbons, any residual organic solvent adsorbed on the surface of the coal could possibly have an effect on the removal of sulfur compounds during leaching. This possibility was studied on raw coal and on coal that was wetted with 1,1,2-trichloroethylene, then air dried for two days, and finally dried in the oven for one day.

From the results shown in Table 4, it appears that the total specific sulfur content is decreased by about the same amount (52-55%) for both types of coals, and the reduction is not affected appreciably by treatment of the coal with trichloroethylene. However, the pyritic specific sulfur content is slightly higher and the organic specific sulfur content is slightly lower for the pretreated coal than for the raw coal. It is uncertain at this time whether this slight difference can be attributed to experimental error or to a bona fide effect of the action of the organic solvent. If the latter is true, one could presumably postulate an explanation in which the solvent somehow coats and protects the inorganic pyrite (remembering that unweathered pyrite is hydrophobic) while at the same time it renders the organic sulfur-bearing groups more susceptible to attack by the leaching solution. From the overall sulfur reduction, however, it appears that if some of the organic solvent from the pretreatment step remains adsorbed in residual amounts on the surface of the coal, the effect is slight.

In Table 5 the results are presented for removal of sulfur from the different pre-cleaned coals under four possible sets of experimental conditions, defined by two different temperatures (150 and 180°C) and two different partial pressures of oxygen (50 and 100 psia.). Every value in Table 5 represents an

Table 4. Results of leaching uncleaned Western Kentucky Coal (-200 mesh) with and without presoaking in trichloroethylene.^a

Treatment	H.V. Btu/lb.	Ash, wt.%	Specific S Cont., lb.S/10 ⁶ Btu				Total S Reduction, %	H.V. Recovery %
			Pyr.	Sulf.	Org.	Tot.		
None ^b	10,890	18.3	0.97	0.94	1.56	3.47	----	----
Leached	10,150	21.8	0.07	0.11	1.31	1.49	53.1	88.3
Leached	10,320	21.7	0.09	0.07	1.32	1.48	53.5	90.0
Leached ^c	10,080	21.9	0.21	0.10	1.23	1.54	51.6	91.6
Leached ^c	9,880	22.2	0.15	0.12	1.16	1.43	55.0	87.6

^aLeached 1 hr. by 0.2M Na₂CO₃ at 150°C and 50 psia O₂ pressure.

^bHeating value, ash content, and sulfur distribution of unleached coal.

^cCoal presoaked in trichloroethylene before leaching.

Table 5. Results of leaching precleaned coals (-400 mesh) at different temperatures and oxygen pressures.^a

Temp., °C	O ₂ Press., psia	H.V. Btu/lb.	Ash, wt. %	Specific S Cont., lb.S/10 ⁶ Btu				Total S Reduction %	H.V. Recovery %
				Pyr.	Sulf.	Org.	Tot.		
(Lovilia Coal) ^b		11,960	5.81	0.45	0.21	1.01	1.67	----	----
150	50	11,020	12.5	0.10	0.06	1.00	1.16	30.5	88.3
150	100	10,820	12.1	0.11	0.06	1.02	1.19	28.7	88.7
180	50	10,630	13.4	0.10	0.10	1.05	1.25	25.1	85.1
180	100	10,410	13.2	0.08	0.08	1.01	1.17	29.9	80.2
(Big Ben Coal) ^b		12,210	4.1	0.46	0.42	1.44	2.32	----	----
150	50	10,570	13.3	0.06	0.13	1.33	1.52	34.5	77.6
150	100	10,710	13.0	0.08	0.16	1.33	1.57	32.3	64.0
180	50	10,420	12.9	0.09	0.13	1.41	1.63	29.7	76.5
180	100	9,670	13.0	0.09	0.19	1.30	1.58	31.9	43.8
(Scott Coal) ^b		12,110	10.1	0.87	0.23	2.79	3.89	----	----
150	50	10,870	15.7	0.19	0.14	2.63	2.96	23.9	80.0
150	100	10,560	17.1	0.16	0.16	2.82	3.14	19.3	82.1
180	50	9,530	18.5	0.14	0.30	2.44	2.88	25.9	62.4
180	100	9,790	18.4	0.14	0.23	2.40	2.77	28.8	56.3
(West. Ky. Coal) ^b		13,020	5.6	0.33	0.14	1.44	1.91	----	----
150	50	10,810	13.2	0.06	0.05	1.44	1.55	18.8	82.2
150	100	10,930	11.7	0.06	0.04	1.37	1.47	23.0	83.0
180	50	10,580	13.6	0.05	0.05	1.46	1.56	18.3	80.0
180	100	10,220	14.5	0.06	0.10	1.44	1.60	16.2	54.2

^aLeached 2 hr. by 0.2M Na₂CO₃ at 2000 r.p.m.

^bHeating value, ash content, and sulfur distribution of unleached coal.

average of duplicate runs for each set of conditions. For Lovilia, Big Ben, and Western Kentucky coals, significant amounts of sulfur were leached; the reduction in the total specific sulfur content (expressed as lb. S/10⁶ Btu) was in the ranges 25-30, 30-35, and 18-23%, respectively. The reduction was most pronounced in the content of pyritic and sulfate sulfur. The residual level of pyritic sulfur was lowest for the Western Kentucky coal, being 0.05-0.06 lb. S/10⁶ Btu, and highest for Lovilia coal, 0.08-0.11 lb. S/10⁶ Btu. The residual level of sulfate sulfur was lowest for Western Kentucky coal also (0.04-0.10 lb. S/10⁶ Btu) and highest for Big Ben coal (0.13-0.19 lb. S/10⁶ Btu). By contrast to the inorganic sulfur content, the differences in the final organic sulfur content were less pronounced, initially indicating little or no significant reduction. For the three coals mentioned above, the effects caused by changes in the temperature or oxygen partial pressure had apparently no discernible trends.

For Scott coal, the reduction in the total specific sulfur content was in the range 19-29%. Again, substantial amounts of pyritic sulfur were removed, to residual levels of 0.14-0.19 lb. S/10⁶ Btu. The residual levels of sulfate sulfur were more variable, from 0.14 to 0.30 lb. S/10⁶ Btu. Unlike the other coals, Scott coal was characterized by some reduction in the organic sulfur content, especially at the higher temperature. Thus, at 180°C the organic specific sulfur content was reduced from the original value of 2.79 to 2.44 and 2.40 lb. S/10⁶ Btu at 50 and 100 psia, respectively. A similar improvement as a function of temperature is also apparent in the removal of total specific sulfur. At an oxygen pressure of 100 psia., increasing the temperature from 150 to 180°C improved the reduction in the total specific sulfur content from 19 to 29%. The greater effectiveness of higher temperature for leaching, observed in the case of Scott coal but not the other three coals, can be tied in possibly with the higher initial sulfur content (3.89 lb. S/10⁶ Btu total specific sulfur for Scott coal as compared to 1.67-2.32 lb. S/10⁶ Btu for other coals.)

The effect of increasing the partial pressure of oxygen on the reduction of sulfur was investigated further. Run-of-mine Western Kentucky coal that had not been precleaned was used for the experiments. The initial ash content was thus relatively high, namely 18.3%. Of the total sulfur content (3.47%), almost one-half (1.56%) was organic, with the rest being almost equally distributed between pyritic and sulfate sulfur (0.97 and 0.94%), respectively). The coal was leached for 1 hr. at 150°C by 0.2M sodium carbonate solution.

The results are presented in Table 6 and are depicted graphically in Figure 4. As the oxygen partial pressure was increased from 50 to 200 psia., the reduction in total sulfur increased only slightly, approximately from 53 to 57%. The interesting observation, however, is that the reduction in the organic sulfur content increased substantially (from about 8% to about 23%) with increasing pressure, while the removal of inorganic sulfur declined only slightly (from 89 to 85%). The temperature was relatively low, only 150°C; and the heating value recovery was excellent at about 87-92%. At the present time, the chemistry involved in the removal of organic sulfur from coal is not well understood, but the remarkable improvement with increasing oxygen partial pressure under relatively mild conditions warrants further investigation.

Figure 4. Effect of oxygen partial pressure on leaching of Western Kentucky coal.

Table 6. Results of leaching uncleaned Western Kentucky Coal (-200 mesh) at different oxygen pressures.^a

O ₂ Press., psia	H.V. Btu/lb.	Ash, wt.%	Specific S Cont., lb.S/10 ⁶ Btu				Total S Reduction, %	H.V. Recovery, %
			Pyr.	Sulf.	Org.	Tot.		
(Raw Coal) ^b	10,890	18.3	0.89	0.86	1.43	3.18	----	----
50	10,150	21.8	0.07	0.11	1.31	1.49	53.1	88.3
50	10,320	21.7	0.09	0.07	1.32	1.48	53.5	90.0
100	10,370 ^c	21.9	0.15	0.07	1.21	1.43	55.0	87.8
100	10,370 ^c	21.8	0.16	0.08	1.22	1.46	54.1	91.0
150	10,340 ^c	22.2	0.20	0.09	1.13	1.42	55.4	86.9
150	10,400 ^c	21.6	0.14	0.09	1.16	1.39	56.3	92.0
200	10,230 ^c	22.9	0.13	0.13	1.19	1.45	54.4	90.2
200	10,530 ^c	20.6	0.13	0.14	1.05	1.32	58.5	90.2

^a Leached 1 hr. by 0.2M Na₂CO₃ at 150°C.

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

^c Estimated from heating value of unleached coal.

The next set of experiments was designed to compare the relative effectiveness of alkaline versus acidic leaching conditions and of oxygen versus air as the oxidant. The four run-of-mine coals, -200 mesh size, were leached for one hour, at 150°C and 50 psia oxygen partial pressure. Alkaline conditions were produced by using an aqueous solution of 0.2M sodium carbonate. For acidic conditions, pure water was used; the sulfuric acid produced during the oxidation of pyrite provided the acidity. Under each condition, whether air or oxygen was supplied to the autoclave, the oxygen partial pressure was the same (50 psia.). Each experiment for each set of conditions was run in duplicate. The results were averaged for duplicate runs.

The results of these experiments are presented in Table 7. In each case, the recovery in heating value was high with the recovery being slightly greater for the acid leached material than for the alkali leached material. It can be seen at first glance that the percentage sulfur reduction is higher for alkaline than for acidic conditions. The relative merits of air versus oxygen are more difficult to discern. The data were therefore subjected to statistical analysis

Table 7. Results of leaching uncleaned coals (-200 mesh) with and without alkali and with air or pure oxygen.^a

Na ₂ CO ₃ , M	Gas Type	H.V. Btu/lb.	Ash, wt. %	Specific S Cont., lb.S/10 ⁶ Btu				Total S Reduction, %	H.V. Recovery %
				Pyr.	Sulf.	Org.	Tot.		
(Lovilia Coal) ^b		10,050	20.7	3.08	1.07	0.97	5.12	----	----
0	O ₂	10,320	17.1	0.92	0.51	1.15	2.58	49.6	95.3
0	Air	10,260	17.7	1.66	0.64	0.91	3.21	37.3	94.7
0.2	O ₂	9,520	23.5	0.56	0.22	0.71	1.49	70.9	86.9
0.2	Air	9,420	23.6	1.11	0.22	0.85	2.18	57.4	88.3
(Big Ben Coal) ^b		10,530	15.0	3.50	1.52	1.67	6.69	----	----
0	O ₂	11,003	11.3	1.18	0.38	1.66	3.22	51.9	97.1
0	Air	10,860	12.5	2.58	0.34	1.41	4.33	35.3	92.8
0.2	O ₂	10,260	17.3	0.72	0.34	0.97	2.03	69.7	88.2
0.2	Air	10,140	18.3	0.81	0.32	1.02	2.15	67.9	86.3
(Scott Coal) ^b		10,270	16.9	6.24	1.86	2.53	10.63	----	----
0	O ₂	11,260	12.4	1.42	0.34	3.21	4.97	53.2	93.9
0	Air	11,050	14.1	4.15	0.20	2.72	7.07	33.5	95.6
0.2	O ₂	10,520	18.2	1.93	0.22	1.94	4.09	61.5	93.2
0.2	Air	10,340	19.6	2.78	0.30	1.85	4.93	53.6	91.7
(West. Ky. Coal) ^b		10,890	18.3	0.89	0.86	1.43	3.18	----	----
0	O ₂	10,930	16.6	0.10	0.37	1.53	2.00	37.1	95.7
0	Air	11,180	16.3	0.13	0.33	1.63	2.09	34.3	95.7
0.2	O ₂	10,240	21.8	0.08	0.09	1.31	1.48	53.5	89.2
0.2	Air	10,730	20.6	0.09	0.10	1.37	1.56	50.9	92.9

^aLeached 1 hr. at 150°C and 50 psia O₂ pressure.

^bHeating value, ash content, and sulfur distribution of unleached coal.

by the Department of Statistics at Iowa State University.

Several important conclusions were drawn from the statistical analysis. In general, the nature of the leaching solution (alkaline or acidic) has a greater effect on the desulfurization efficiency than the nature of the oxidant (air or oxygen). Specifically, it can be stated that desulfurization is more effective, at the 99.5% confidence level, with alkaline than with acidic solutions. Also, at a slightly lower confidence level, 95%, oxygen can be said to be a better oxidant than air.

Closer screening of Table 7 reveals also that in almost every case the pyritic and organic sulfur contents were significantly lower for the alkaline leaching conditions. For the organic sulfur content, no discernible difference can be seen between using air or oxygen. For the pyritic sulfur content, use of oxygen tends to result in lower values than use of air.

Because alkaline leaching solutions were shown to be more effective than acidic solutions, the concentration of alkali was varied to study its effect on the extent of sulfur removal. The experiments were performed on Western Kentucky and Lovilia coals, -400 mesh size, both precleaned by treatment with trichloroethylene. The leaching was done for two hours at a mild temperature of 130°C but at a higher oxygen partial pressure of 275 psia. The concentration of sodium carbonate in the leaching solution was 0.2, 1.0 or 2.0M.

From the data shown in Table 8, it appears that increasing the concentration of alkali did not improve the reduction of total, organic, or pyritic sulfur. Thus there is no significant advantage in using more concentrated alkali solutions. In fact, because the ash content increases and the heating value recovery decreases with increasing alkali concentration, it is more advantageous to use the lowest possible concentration that still provides the same sulfur reduction.

In summary, use of the stirred autoclave has provided some interesting results in the study of desulfurization of coal by hot alkaline solutions containing dissolved oxygen under pressure. First of all, it has been shown that desulfurization becomes independent of the stirring rate at approximately 2000 r.p.m. At higher oxygen partial pressures, the desulfurization becomes independent of the stirring rate at a much lower speed, approximately 1200 r.p.m. It has also been observed that at higher oxygen partial pressures, the leaching process removes up to about 25% of organic sulfur with a relatively high Btu recovery of about 94%. This is in addition to removal of 85-90% of the inorganic sulfur. It has also been established, by statistical analysis, that the alkaline conditions employed in this process are more effective than acidic conditions. The removal of organic and pyritic sulfur was significantly better when an alkaline leachant was used. The use of air or oxygen as the oxidant has resulted in no discernible difference in the removal of organic sulfur; however, for the removal of pyritic sulfur, oxygen is apparently better than air. Thus the overall process has been shown to be effective in removing almost all of the inorganic sulfur and a significant portion of the organic sulfur under relatively mild conditions. Future experiments will be conducted to establish the optimum temperature for the process.

Table 8. Effect of alkali concentration on leaching of cleaned coals (-400 mesh).^a

Na ₂ CO ₃ , M	H.V., Btu/lb.	Ash, wt. %	Specific S Cont., lb.S/10 ⁶ Btu				Total S Reduction, %	H.V. Recovery, %
			Pyr.	Sulf.	Org.	Tot.		
(Lovilia) ^b	12,330	6.3	0.28	0.22	1.09	1.59	----	----
0.2	10,620	14.0	0.03	0.08	0.94	1.05	34.0	70.4
0.2	10,670	13.6	0.03	0.07	0.94	1.04	34.6	78.3
1.0	8,750	29.1	0.03	0.14	0.96	1.13	28.9	86.9
1.0	8,360	32.3	0.13	0.10	0.93	1.16	27.0	61.0
2.0	6,590	46.6	0.05	0.19	0.87	1.11	30.2	66.1
2.0	9,300	24.6 ^c	0.09	0.05	0.88	1.02	35.9	34.7
(West. Ky.) ^b	13,020	5.6	0.33	0.14	1.44	1.91	----	----
0.2	11,490	12.3	0.07	0.08	1.37	1.52	20.4	74.5
0.2	11,540	12.0	0.10	0.07	1.29	1.46	23.6	81.3
1.0	9,310	24.1	0.09	0.12	1.52	1.73	9.4	57.2
1.0	9,250	25.5	0.12	0.14	1.21	1.47	23.0	62.5
2.0	7,630	38.6	0.10	0.14	1.61	1.85	3.1	68.4
2.0	7,900	36.4	0.05	0.12	1.35	1.52	20.4	66.9

^aLeached 2 hr. at 130°C and 275 psia O₂ pressure.^bHeating value, ash content, and sulfur distribution of unleached coal.^cProduct was washed twice with water.

Tubular Reactor System

The desulfurization of pyrite particles under different leaching conditions has been studied by using the tubular reactor system illustrated in Figure 5. The reactor tube is manufactured from Inconel 600 and has a length of 15 cm. and an inside diameter of 0.64 cm. It can accommodate approximately 15 g. of ground pyrite or 5 g. of pulverized coal. The system can be operated at high pressures (up to 3000 psi) and high temperatures (up to 480°C). The temperature of the reactor is maintained by immersing it in a fluidized bed of sand which is heated electrically by coils within the sand bed.

Figure 5. Schematic flow diagram of tubular reactor system.

The reactor flow system (Figure 5) consists of a delivery unit for the leaching solution, an oxygen feed system, the reactor proper, a gas-liquid separator, and associated temperature and pressure controls. 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 tubular reactor system has been used to study the effects of temperature, oxygen pressure and flow rate, the nature and concentration of leaching alkali, the liquid flow rate, and the amount (charge size) and particle size of pyrite on the rate of conversion of pyritic sulfur into soluble sulfur forms. The experiments have been performed using pyrite that was recovered from Iowa coals by hand-picking. The pyrite was ground, sized, and analyzed for iron and total sulfur. The analysis, 42.3% iron and 40.3% sulfur on the average, indicated an apparent purity of 75%. The atomic sulfur-to-iron ratio, being 1.65 instead of the theoretical 2.0 required by FeS_2 , suggested that not all of the iron present was in the pyrite form. Similar conclusions were also reached based on the determination of iron in the liquid effluent from the reactor, as described below.

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 the feed pump was switched on to pump deionized water through it. The time was measured from this point on. Then, the flow of nitrogen was stopped, the feed pump was switched to pumping the leaching solution of dilute alkali, and, almost simultaneously, the measured flow of oxygen 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 which were subsequently analyzed for sulfate by a microtitration method (2). At the end of each run, the flow of oxygen and the pumping of the leaching solution were interrupted, the system was purged again with nitrogen and depressurized, and the reactor was disconnected. The solid residue was removed from the reactor, weighed, and subsequently analyzed for total sulfur. The entire system was then rinsed by pumping deionized water through it for some time.

The conversion of sulfur in the pyrite to soluble forms was calculated initially in two ways. One was based on the chemical analysis of the solid residue by the ASTM method for total sulfur and calculation of the decrease of sulfur content from the starting material. The second was based on titration of

the liquid effluent portions for sulfate after treatment with hydrogen peroxide to ensure that all the sulfur species present were converted to the sulfate form. The titration method yielded results that were generally 10-15% lower than those obtained by analysis of the solid residue, indicating a possible bias in one of the methods. For the purpose of estimating and comparing sulfur conversion rates, the titration data were selected rather arbitrarily.

For several runs, the sequential portions of the liquid effluent, each approximately 500 ml. in volume, were analyzed for total iron as well as for sulfate. The relatively high content of iron in the first portion, amounting to 100-400 p.p.m., represented the soluble iron salts such as ferrous sulfate which were extracted from the pyrite by hot water alone. The iron content of the second portion was low, approximately 1 p.p.m., indicating that most of the water soluble iron salts had been removed. The iron content of the third portion increased to 4-18 p.p.m. and then decreased to about 1 p.p.m. for all succeeding portions. Since the third effluent portion was the first sample collected after the alkali leaching solution contacted the pyrite, it appears that the pyrite contained also a small amount of iron in some form that was extractable by a hot sodium carbonate solution but not by hot water.

In Figure 6 the results of the titration of sequential portions of the effluent are plotted for a typical run in mg.S/l. versus time. The first, small peak corresponds to the leaching of soluble sulfate. The second, large peak marks the appearance of sulfur extracted from pyrites. After the initially high sulfur content, the following samples contained decreasing amounts of sulfur.

In Figure 7 the rate of extraction of sulfur from pyrite is illustrated for the same run. The total percent sulfur conversion is plotted versus time. From the diagram it is apparent that very little sulfur was extracted during, approximately, the first 10 min., the time required for the leaching solution with alkali and oxygen to reach the pyrite packed in the reactor tube. However, once the reaction between the leaching mixture and the pyrite started, the rate of sulfur extraction was very high as indicated by the steep slope of the initial segment of the curve. As the leaching proceeded and pyritic sulfur was used up, the slope and thus the rate gradually decreased.

At the end of each run, approximately one hour, the total conversion ranged from 35.8 to 93.2%, depending on the leaching condition. To help understand the effect of each parameter studied, a model is presented to describe the leaching process of pyrite by oxygen dissolved in aqueous alkali.

A shrinking core model was described by Levenspiel (3) for the reaction of solid particles with a fluid (either gas or liquid), given by the equation

In the shrinking core model, the assumption is made that the reacting solid consists of spherical particles of small, constant size. Each particle (Figure 8) of radius R is surrounded by a stagnant fluid film through which

Figure 6. Sulfur concentration of effluent samples from run 62 as a function of terminal collection time.

Figure 7. Conversion of total sulfur in impure pyrite as a function of effluent terminal sampling time for run 62.

reactant A must diffuse to react with the surface of the solid sphere. As the reaction proceeds and the products are carried away, a layer of reacted solid material remains as "ash." The ash layer continues to build up, while the unreacted core, with a radius r_c , shrinks. During the entire process, the overall particle size remains constant.

That these assumptions parallel physical reality has been demonstrated by Professor R. T. Greer who examined leached and unleached pyrite particles with a scanning electron microscope (Figures 9 and 10). He concluded that the size and shape of the leached particles are similar to those of the unleached particles. Upon closer examination, microscopic differences were revealed; the grain size within the leached material is much finer than that of the unleached pyrite. These submicron-size grains were shown by X-ray diffraction spectrometry to be largely hematite (Fe_2O_3). Thus the "ash" in reacted pyrite is hematite.

For the physical model described above, the reaction of the solid particle B with reactant A can be divided into the following steps:

- Step 1. Diffusion of reactant A through the stagnant fluid film surrounding the particle towards the solid surface.
- Step 2. Diffusion of A through the ash layer to the surface of the unreacted core.
- Step 3. Reaction of A with solid B at the core surface.
- Step 4. Diffusion of the fluid products through the ash layer to the surface of the particle.
- Step 5. Diffusion of the products through the fluid film into the bulk of the fluid.

The kinetics of the reaction are defined by one or more of these steps which is the rate-limiting step.

Levenspiel (3) provided equations which describe the reaction kinetics of such a model under three different conditions, depending on whether the rate-controlling step is diffusion through the fluid film (step 1), diffusion through the ash layer (step 2), or the chemical reaction at the surface of the unreacted core (step 3). If X_B is the fraction of unreacted solid B, τ is the time necessary for the particle to react completely, and t is instantaneous time, the equations take on the following form when the reaction rate is controlled by:

Figure 8. Shrinking core model of a single reacting particle.

100 μ

25 μ

LEACHED PYRITE

Figure 9. Photomicrographs of leached particles.

UNLEACHED PYRITE

LEACHED PYRITE

2 μ

Figure 10. The grain structure of leached particles was much finer than that of unleached particles.

1. diffusion through fluid film

$$t/\tau = 1 - (r_c/R)^3 = X_B \quad (6)$$

$$\text{and } \tau = \rho_B R / (3 b k_g C_{AL}) \quad (7)$$

2. diffusion through ash layer

$$t/\tau = 1 - 3(1-X_B)^{2/3} + 2(1-X_B) = p(X_B) \quad (8)$$

$$\text{and } \tau = \rho_B R^2 / (6 b D_e C_{AL}) \quad (9)$$

- or 3. chemical reaction at core surface

$$t/\tau = 1 - (1-X_B)^{1/3} = g(X_B) \quad (10)$$

$$\text{and } \tau = \rho_B R / (b k_s C_{AL}) \quad (11)$$

where

ρ_B = molar density of the solid B

b = stoichiometric coefficient in equation (5)

k_g = mass transfer coefficient through the fluid film

D_e = effective diffusivity through the ash layer

k_s = rate constant for reaction at the surface

C_{AL} = concentration of reactant A in the liquid

For the reaction of solid pyrite with oxygen dissolved in aqueous sodium carbonate solution, equation (5) has the following stoichiometry:

To determine which is the rate-controlling step in the overall reaction described by equation (12), the functions X_B , $p(X_B)$, and $g(X_B)$ (equations 6, 8, and 10, respectively) were plotted against time for each run. In every case, the function $p(X_B)$ gave the best fit, suggesting that the diffusion of oxygen through the ash layer is the rate-determining step. Almost all the data fit this function in a straight line; for the other functions, the plots are curved. To illustrate, data for a typical run are plotted in Figure 11 for function X_B and in Figure 12 for functions $p(X_B)$ and $g(X_B)$. The best fit for each run was also determined by linear regression and correlation of coefficient analysis. In each case, function $p(X_B)$ gave the best results. For the sake of comparison, Figure 13 shows a run with the worst straight line fit. Yet even in this case, function $p(X_B)$ fits a straight line better than the other two functions.

The straight line fitting of function $p(X_B)$ permits the calculation of the effective diffusivity D_e for each run. From equation (8) it is evident that the slope of each straight line equals $1/\tau$, and by rearranging equation (9)

Figure 11. Sulfur conversion as a function of effluent sampling time for run 67.

Figure 12. Functions $p(X_B)$ and $g(X_B)$ plotted against actual leaching time for run 67. Straight lines were fitted by eye.

Figure 13. Function $p(X_B)$ plotted against actual leaching time for run 35. Straight line was fitted by eye.

D_e can be calculated from

$$D_e = \rho_B R^2 / (6 b C_{AL} \tau) \quad (13)$$

The molar density ρ_B of the impure, coal-derived pyrite was determined to be 0.0269 moles/cm³. R is the radius of an average particle defined by the mesh size; for example, $R = 0.00575$ cm. for -120/+140 mesh pyrite. The value of C_{AL} was estimated from the solubility of oxygen in water at 150°C (4) as 3.125×10^{-6} mole/cm³. The coefficient b , based on equation (12), is 15/4. The calculated D_e values fell in the range $(0.39-2.13) \times 10^{-5}$ cm²/sec. with the average being around 1.2×10^{-5} cm²/sec. This is within the anticipated range of diffusivity for oxygen in water.

In terms of the model, the ash product layer can be considered to be porous with each pore being filled with the leaching solution. The dissolved oxygen diffuses through the solution to reach the surface of the unreacted core. As the effects of various parameters on the reaction rate were studied, the model was examined at the same time, on the basis of D_e values, to check if it supports the observed data.

The effect of oxygen partial pressure on sulfur conversion can be deduced from Figure 14. As the pressure is increased, the reaction rate increases also. To show how the model accounts for the effect of partial pressure of oxygen, the effective diffusivity data are presented in Table 9.

Statistical analysis of the data in Table 9 shows that the effective diffusivity is essentially constant, and thus the increased pressure has no significant effect on D_e . On the basis of equation (9) the increase in the reaction rate, i.e. a decrease in the total reaction time τ , can therefore be

Table 9. Effect of oxygen partial pressure on D_e .
(5 g. charge, -120/+140 mesh, 150°C, 13.2 ml./sec. O₂ flow rate).

Run No.	Total press., psig	O ₂ press., psia	$D_e \times 10^5$, cm ² /sec.	Total Sulfur conversion, %
12	100	48	1.01	61.2
62	100	48	1.08	61.3
70	100	48	1.37	70.2
14	150	98	1.18	75.0
24	150	98	1.10	76.5
35	250	198	1.13	93.2

Figure 14. Effect of oxygen partial pressure on sulfur conversion.

Figure 15. An Arrhenius plot showing the effect of temperature on the effective diffusivity.

accounted for by the change in the dissolved oxygen concentration term, C_{AL} . The solubility of oxygen in water is a linear function of the partial pressure. Thus, from equation (9) it appears that the average rate of reaction is directly proportional to the oxygen partial pressure.

To study the effect of temperature on the sulfur conversion, the temperature was varied from 121° to 175°C while the other parameters were kept constant. The results, presented in Table 10, show that not only the sulfur conversion but also D_e increases with temperature.

This temperature effect can be seen from the plot of the logarithm of D_e versus $1000/T$ (Figure 15). From the Arrhenius equation, the slope of the straight line obtained can be used to calculate the activation energy E_a , yielding a value of 7.97 kcal./mole. This value falls somewhere above the 1-4 kcal./mole range normally encountered for simple diffusion-controlled reactions. Yet it is also much lower than the 20-40 kcal/mole range for chemical reaction controlled systems. Further study seems necessary to pinpoint the energy of activation more precisely.

In Figures 16 and 17 the sulfur conversion is presented as a function of time for different particle sizes at 150 and 100 psig total pressure, respectively. In each case, the total sulfur conversion is inversely proportional to the particle size. From equation (9) it follows that τ plotted versus R^2 should give a straight line. In Figure 18, a straight line is indeed obtained for the particle size effect at 100 psig but not at 150 psig.

The data on the effect of particle size are summarized in Table 11. The effective diffusivity should be independent of particle size. Statistical analysis of the data reveals that at 100 psig the effect of particle size on D_e is not significant at the 25-50% confidence level. At 150 psig, however, the effect of particle size on D_e is significant at the 99.5% confidence level. Thus, since D_e depends on particle size at higher but not at lower pressures, it seems that the model represents the reaction mechanism more closely at lower pressures than at higher pressures.

Table 10. Effect of temperature.

(5 g. charge, -120/+140 mesh, 48 psia O_2 , 13.2 ml. O_2 /sec).

Run No.	Temp., °C	$1000/T$, $1/^\circ K$	$D_e \times 10^5$, $cm^2./sec.$	Total Sulfur conversion, %
81	121	2.54	0.53	50.0
82	135	2.45	0.71	52.0
62	150	2.36	1.08	61.3
83	160	2.31	1.48	72.4
80	175	2.23	1.84	75.7

Figure 16. Effect of particle size on sulfur conversion at 150 psig.

Figure 17. Effect of particle size on sulfur conversion at 100 psig.

Figure 18. Test of equation 9 by particle size.

Table 11. Effect of particle size (150°C, 13.2 ml./sec. O₂ flow rate).

Run No.	Particle Size, mesh	Total Pressure, psig	$D_e \times 10^5$, cm ² /sec.	Total Sulfur conversion, %
45	-60/+80	100	0.92	35.8
43	-60/+80	150	2.13	61.9
65	-60/+80	150	1.70	56.0
46	-80/+100	100	1.10	48.6
44	-80/+100	150	1.45	65.1
12	-120/+140	100	1.01	61.2
62	-120/+140	100	1.08	61.3
70	-120/+140	100	1.37	70.2
14	-120/+140	150	1.18	75.0
24	-120/+140	150	1.10	76.5

The effect of flow rate of the leaching solution on the sulfur conversion was investigated. The data are presented in Table 12 and plotted in Figure 19. It is apparent that in the range of 1.5 to 3.0 ml./sec., the flow rate of the leaching solution had very little, if any, effect on the rate of extraction. The effective diffusivity is also essentially constant at different flow rates. This fact is further evidence supporting the ash layer diffusion model. If the rate-determining step, for example, were film diffusion controlled, then the reaction rate would be affected by changes in the liquid flow rate. For most of the subsequent runs, a flow rate of 1.5 ml./sec. was used.

The oxygen flow rate had a large effect on the rate of sulfur extraction, as seen from the kinetic curves in Figure 20 and 21. A series of runs was made to determine the optimum oxygen flow rate. A plot of total sulfur conversion versus oxygen flow rate in Figure 22 reveals an optimum flow rate at approximately 0.004 cu.ft./min., i.e. 3 ml./sec., for which the amount of sulfur converted is maximum. For either higher or lower oxygen flow rates the sulfur conversion drops off sharply. The decreasing sulfur conversion at increasing oxygen flow rate may be attributed to interference of the gas with good contact between the solid pyrite and the liquid leachant. The surface of the solid may not be totally wetted, and thus the reaction may not be complete. Below the optimum value of the oxygen flow rate, the decline in sulfur conversion may be caused by insufficient oxygen for effective oxidation of the pyritic sulfur.

The data presented in Figure 23 show the effect of the concentration and nature of alkali in the leaching solution on the total sulfur conversion. For

Figure 19. Liquid flow rate had little effect on the rate of conversion

Figure 20. High gas flow rates had an adverse effect on the rate of reaction at 100 psig.

Figure 21. High gas flow rates also had an adverse effect at 150 psig.

Figure 22. The optimum gas flow rate was about 0.004 std.cu.ft./min. for leaching at 100 psig.

Table 12. Effect of liquid flow rate.
(5 g. charge, -120/+140 mesh, 150°C, 150 psig).

Run No.	Liq. flow rate, ml./sec.	$D_e \times 10^5$, cm ² /sec.	Total Sulfur conversion, %
14	1.5	1.18	75.0
24	1.5	1.10	76.5
20	2.25	1.16	75.6
17	3.0	1.05	68.1

solutions of sodium carbonate in the concentration range of 0.25-6%, the effect does not appear great; the total sulfur conversions all fall between 61.5 and 70.8%, perhaps because for this concentration range the pH changed only from 11.12 to 11.55. However, the conversion seems to be maximum at approximately 2%. The slight increase in conversion up to this point may be due to the additional alkali available for neutralization of the sulfuric acid produced during the oxidation of pyrite. The slight decrease beyond the optimum may be caused by lower solubility of oxygen with increasing alkalinity. Drescher *et al.* (5) observed a decrease in the solubility of oxygen in potassium hydroxide solutions with increasing alkali concentration.

For solutions containing 1-4% sodium bicarbonate, the total sulfur conversion was quite different from that of sodium carbonate solutions. For 1% sodium bicarbonate, the sulfur conversion was only slightly lower than that for 1% sodium carbonate. But then, in contrast to the sodium carbonate solutions, the sulfur conversion declined considerably for increasing sodium bicarbonate concentrations. The reason for this sizeable decline cannot be explained entirely by lower solubility of oxygen with increasing alkali concentration, by the lower molecular weight of sodium bicarbonate (compared with sodium carbonate) and, hence, higher molarity of solutions based on weight percent, nor by the difference in acid neutralization equivalents (one versus two equivalents per mole for sodium bicarbonate and sodium carbonate, respectively). Perhaps the carbonate ion itself plays a role in the oxidation mechanism, in addition to its role in the neutralization step. When the nature of the reaction of carbonate in the leaching process is better understood, maybe then these differences can be explained better.

It is known, however, that the presence of alkali is a necessary condition for effective desulfurization of pyrite. In one run, for example, in which only water was used to leach pyrite (at 150°C and 48 psia. oxygen partial pressure), the total sulfur conversion was only 12.8%. From the discussion above it appears that at lower concentrations, sodium bicarbonate is only slightly less efficient than sodium carbonate. The addition of another alkali, sodium formate, to a solution containing sodium carbonate did not have a significant effect on the sulfur conversion.

Figure 23. Effect of alkali concentration on sulfur conversion.

Figure 24. Effect of charge size on sulfur conversion.

The effect of charge size, i.e. the amount of pyrite packed into the tubular reactor, on the total sulfur conversion is evident in Figure 24. With increasing charge size, the amount of sulfur dissolved decreased. The effect was more pronounced for finer than for coarser particles. There are several possible explanations for this phenomenon, but none can be offered as the definite one at this time.

One of the possible explanations for the decrease in sulfur conversion with increased pyrite charge may be the presence of some soluble reaction products which inhibit the reaction. With greater charge size the accumulation of these products would be greater and thus the overall conversion would be smaller. To test this hypothesis, a series of runs was made in which small amounts of possible reaction products were introduced into the liquid leachant feed. The results are summarized in Table 13. It is evident that the total sulfur conversion remained essentially constant (within experimental error) and did not decrease as expected.

Another possibility would be the retention of an insoluble reaction product, such as the highly gelatinous ferrous and ferric hydroxides, for example. The retention would be greater with greater charge size. In addition, since such insoluble substances would be held more firmly by a bed packed with fine particles than with coarse particles, the decrease in conversion should be greater for fine particles, just as observed.

It is also possible that the finer particles become compacted more easily, causing poor flow distribution and channelling. The overall effect would be a decrease in total sulfur conversion. For coarser particles the compaction would be less. Thus for coarser particles the charge size would have less effect on the flow pattern, and the decrease in sulfur conversion would not be as great.

The greater effect of charge size for smaller particles may also indicate that this phenomenon is due to hydrodynamic factors. The flow pattern could be affected by charge size and could influence more the overall reaction rate of smaller particles for which boundary layer diffusion is more likely to be important. In other words, the overall reaction rate for larger particles is more likely to be controlled by the rate of diffusion within the pores of the individual particles which is not affected by the hydrodynamics of the system.

Table 13. Effect of possible reaction products
(5 g. charge, -120/+140 mesh, 150°C, 98 psia O₂ partial pressure).

Run No.	Leachant, 2% Na ₂ CO ₃ plus	D _e x 10 ⁵ cm ² /sec.	Total Sulfur conversion, %
26	0.05% Na ₂ SO ₄	1.15	74.4
27	0.1% Na ₂ SO ₄	1.16	75.0
28	0.1% Na ₂ SO ₃	1.18	75.3
29	0.1% Na ₂ S ₂ O ₃	1.10	71.2
24	no additives	1.10	76.5

In conclusion, the shrinking core model with the reaction rate controlled by diffusion through the ash or product layer seems to fit well the kinetics of leaching of pyrite by hot solutions of sodium carbonate containing dissolved oxygen under pressure. The effective diffusivity of about 10^{-5} cm²/sec. is about the right order for molecular diffusion of oxygen in water, indicating that oxygen is probably diffusing through the liquid-filled pores of pyrite particles. The model accounts well for the effect of oxygen concentration and liquid flow rate. For the effect of temperature, it yields an apparent energy of activation within the expected order of magnitude. It holds well for the effect of particle size at lower pressure but not at higher pressure. This discrepancy needs to be investigated further. In addition, measurements over a wider temperature range need to be taken. Also, the charge size and particle size effects need to be studied closer. Overall, the model represents an effective, working tool for studying the kinetics of the chemical desulfurization of pyrite. It may also prove to be a useful tool for reactor design.

Froth Flotation

Froth flotation has long been used for the treatment and recovery of fine-size coal. However, the general adoption of this beneficiation method has been held back by several technical limitations. Thus in most cases it has not provided a good separation between coal and iron pyrites (6,7). Also some sub-bituminous coals, lignite, and weathered or oxidized coals have not responded well to this treatment (8). Moreover, the optimum particle size for coal flotation has appeared to be in the range of 60 to 150 mesh and ultrafine size coal has proved difficult to treat (8). In addition the clay slimes associated with some coals have interfered with good operating performance and ultrafine particles have been difficult to dewater. Although these are serious limitations, they are not all insurmountable and some exist because they have not been the subject of an intensive, major research and development effort (9).

The present effort is focussed on improving the separation of coal and pyrites by froth flotation since a significant improvement in this area could have a major impact. The technology of coal flotation has been reviewed to assess the state of the art. An experimental program to improve the separation of coal and pyrite is underway and preliminary results are encouraging. This program involves conducting laboratory flotation tests with bench scale machines which model industrial practice, measurement of the relative floatability of coal and pyrite particles with a microflotation cell, and measurement of the zeta potential of coal and pyrite suspensions to study the effects of various flotation reagents.

Preliminary Technical Assessment

To separate a mixture of fine particles by froth flotation it is necessary to suspend the particles in water which is aerated with fine gas bubbles that become attached to some of the particles but not others. Those particles which become attached to gas bubbles are buoyed to the surface of the suspension where they can be removed while the other particles remain in suspension. In general, particles with a hydrophobic surface are floated and particles with a hydrophilic surface are not. Unfortunately, the surface of some particles may exhibit both

regions with the result that these particles are incompletely separated. Various reagents may be added to modify the surface characteristics of one or the other species of particles. Thus a "collector" may be added to improve the floatability of one component or a "depressant" to reduce the floatability of another. Generally these reagents are operative over a specific pH range. Usually a frothing agent is added to reduce the surface tension of the water and produce a stable froth on the surface of the suspension to hold the floated particles. The froth may be skimmed off to recover the adhering particles or it may simply overflow the containing vessel.

Many bituminous coals are naturally hydrophobic and easily floated with the addition of only a frothing agent such as methyl isobutyl carbinol (MIBC) or pine oil to the flotation system. Although MIBC is primarily a frother, it also tends to act as a collector for coal. On the other hand, some kinds of coal, particularly oxidized coals, are not so easy to float and require the use of special collectors such as kerosene or fuel oil in addition to a frother (8,10). Sun (11) found certain cationic organic compounds to be effective collectors for oxidized coals. Pyrites in coal are troublesome because they also tend to be hydrophobic and are readily floated using only a frother (10). A number of depressants for pyrite have been suggested including lime, cyanides, permanganates, aluminum chloride, ferric chloride, ferric sulfate, sodium sulfite, and various alkalis (8,10). In particular Baker and Miller (12) found ferric chloride in small concentrations (less than 2 ppm) to be an effective depressant for pyrite in laboratory flotation tests of Lower Freeport bed coal.

In commercial flotation practice the separation of coal and pyrites has continued to be a problem. The Pittsburgh Mining Operations Center is developing a two-stage flotation process which may provide a possible solution to the problem. In this process the bulk of the coal is floated away from the coarse pyrites and other heavy refuse particles in the first stage followed by depression of the coal and floating of the fine pyrites away from the clean coal in the second stage (13,14). A small amount of MIBC is added ahead of the first stage and a coal depressant such as Aero Depressant 633 and a pyrite collector such as potassium amyl xanthate are added ahead of the second stage. The pH of the feed to the second stage is adjusted to 6.5 and more MIBC may be added to the feed. This process has been demonstrated with a continuous flow system which is capable of treating 300 lb./hr. of coal. About 70% of the pyrite has been removed from Pittsburgh bed coal and 90% from Lower Freeport bed coal with an overall recovery of combustible material close to 80% (14).

The laboratory test results obtained with several Iowa bituminous coals by Laros (15) and by Min (16) indicate that the two-stage flotation process may not be suitable for all kinds of coal. In general Min (16) found that relatively large amounts of frothing and depressing agents were required for Iowa coals with the recovery of clean coal ranging between 40 and 80%. The pyritic sulfur content was reduced 15-55% depending on the coal source. The Iowa coals seemed particularly difficult to depress in the second stage.

Glembotskii et al. (10) noted that pyrite is readily floated, the unoxidized or very slightly oxidized material being recovered with only a frother. Pyrite which is oxidized slightly more is floated by fatty acid and soap type collectors and xanthates. On the other hand, these investigators also reported that oxidation

of the pyrite surface and formation of a ferric hydroxide film on this surface can lead to complete suppression of floatability. They also suggested that pyrite oxidation in an alkaline medium is very rapid.

The possibility of depressing pyrite in coal flotation through chemical oxidation of the pyrite surface was demonstrated by Min (16) at Iowa State University. Thus significantly greater sulfur rejection was achieved by floating an Iowa coal which had been pretreated with a hot alkaline solution containing dissolved air than by floating the untreated coal. This appears to be one of the most promising avenues for improving the separation of coal and pyrite.

Froth Flotation Tests

A series of froth flotation tests was carried out to obtain baseline data on an Iowa bituminous coal with a very high sulfur content. These tests were designed to show whether or not the coal floated readily and whether or not a good separation of coal from sulfur and ash-forming minerals could be obtained by conventional flotation methods. The coal selected was from the Iowa State University Demonstration Mine No. 1 in Mahaska County Iowa. Rather than conducting tests on ground whole coal, several samples of natural fines produced in mining and primary crushing operations were collected and used. Sample I had a total sulfur content of 6.3% and ash content of 24%. About half of the sulfur was present in the form of iron pyrites. Sample II contained 7.0% pyritic sulfur, 8.9% total sulfur, and about 24% ash. The size distribution of these natural fines is presented in Table 14. Although material from either sample was used as is for some of the flotation tests, part of the material from Sample II was separated by screening into various size fractions for use in other flotation tests. The composition of these different size fractions is indicated by Table 15. The data indicate that the pyrite tended to concentrate in the smaller size fractions.

The flotation tests were carried out with a Denver D-1 laboratory Sub-A flotation cell fitted with a stainless steel tank which held 3100 ml. For most tests, 120 g. coal and 2400 ml. of tap water were placed in the cell to provide a slurry with 5% solids. The pulp was conditioned by operating the agitator at 1000 r.p.m. for 5 to 10 min. to insure a uniform suspension. The pH of the pulp was adjusted to 5.5-5.6 by adding hydrochloric acid. A measured amount of methyl isobutyl carbinol (MIBC) was added next, the agitator speed increased to 2000 r.p.m., and an air flow of 0.5 cu.ft./min. started. The froth was collected until it appeared that most of the coal had been recovered. The solids in the froth and tailings were subsequently recovered, dried, weighed, and analyzed for sulfur and ash. In some cases the heating value of the products was determined also.

The results of a number of tests showed that the only flotation reagent needed to recover Iowa coal was MIBC. This reagent is one of the frothers which is commonly used in coal flotation. With as little as 0.5 ml. MIBC/batch almost 90% of the coal was recovered (Figure 25). Doubling the concentration of MIBC had only a slight effect on the recovery but reducing the concentration resulted in a lower recovery. The addition of a small amount of aluminum nitrate seemed to enhance the recovery of coal, particularly when small concen-

Table 14. Size distribution of coal fines used in froth flotation tests.

Tyler Screen, Mesh	Sample I		Sample II	
	Retained, wt.%	Passing, wt.%	Retained, wt.%	Passing, wt.%
48		100.0		100.0
60	3.5	96.5	6.1	93.9
100	23.0	72.0	33.2	66.8
200	54.7	45.3	65.5	34.5
325	94.4	5.6	92.2	7.8

Table 15. Composition of some individual size fractions of Sample II coal.

Size Fraction, Tyler Mesh	Ash, wt.%	Sulfur, wt.%	
		Pyritic	Total
48 x 100	21.0	4.9	6.9
100 x 200	22.6	5.6	7.6
200 x 0	23.8	7.8	9.7

trations of MIBC were employed (Figure 25). The activator role of aluminum nitrate was unexpected since it was added to see if it would depress pyrite.

In many of the flotation tests which were run, the froth from a single batch was collected in several portions. The solids in each portion were recovered separately, dried, weighed, and analyzed for sulfur, ash and sometimes heating value. Thus it was possible to follow the change in composition of the float product as the run progressed. Typical results of such an experiment are presented in Figures 26 and 27 where the sulfur and ash contents and heating value of the cumulative float product are plotted versus the cumulative recovery

Figure 25. Effect of frother concentration on the recovery of coal by froth flotation.

of product. It should be noted that the points representing 100% recovery in these diagrams include the material left in the flotation cell at the end of the experiment. It can be seen that the earliest fraction was the cleanest with the highest heating value and the last fraction (corresponding to about 90% cumulative recovery) the dirtiest with the lowest heating value. Therefore, as more and more of the coal was recovered the average sulfur and ash contents of the accumulated product became higher and higher. Unfortunately the results indicate that only a modest reduction in sulfur and ash contents could be achieved with a reasonable recovery of coal. For example, for a 70% recovery, the average ash content of the product would be reduced by one-third and the total sulfur content by one-sixth.

The results shown in Figures 26 and 27 show that the addition of a small amount of aluminum nitrate did not improve the separation of coal from pyrite or other mineral matter. The results of other tests employing different concentrations of MIBC in the range of 0.05 to 1.0 ml./batch both with and without the addition of aluminum nitrate indicated little effect on the separation of coal from mineral impurities. Also the results of further tests made with various concentrations of solids in the water suspension showed that concentrations

Figure 26. Cumulative results of froth flotation experiment.

Figure 27. Average ash content of cumulative fractions recovered during froth fractionation experiments.

in the range of 2 to 10 wt.% all gave nearly the same degree of separation of coal and mineral matter. However, with a solids concentration of only 1 wt.%, the separation was considerably poorer (Figure 28).

When separate flotation tests were carried out on the three different size fractions of coal listed in Table 15, the percentage reduction in ash content was somewhat greater in the case of the 200 mesh x 0 fraction than in the case of the coarser fractions. However, the percentage reduction in total sulfur content was about the same for all three fractions. Although these results showed some benefit in floating finer size material, further size reduction of Sample II material proved counterproductive. Thus when some of the 48 mesh x 0 coal was ground with a Raymond laboratory mill until all of the material was smaller than 325 mesh, the ensuing separation of coal and mineral matter by froth flotation was worse than was achieved with the unground material (Figure 29). These results suggest that fine grinding may produce more colloidal size mineral matter which is entrapped by the froth.

While all of the preceding results show that coal from the Iowa State University Demonstration mine is readily floated with MIBC being the only required reagent, they also indicate that conventional froth flotation does not provide an adequate separation of coal from pyrite or from other ash-forming minerals. Therefore in the future more emphasis will be placed on chemical pretreatment to enhance the separation of coal and pyrite.

Zeta Potential Measurements

The electrical surface charge on different species of solid particles in an aqueous suspension can play an important role in the separation of such species by froth flotation because the surface charge can determine whether some types of flotation collectors are adsorbed or not by a particular species (17,18). Many collectors are organic compounds which ionize in water to provide either organic anions or cations. Positively charged cationic collectors tend to be adsorbed on negatively charged surfaces and negatively charged anionic collectors on positively charged surfaces (19). Also neutral organic molecules tend to be adsorbed on neutral surfaces. The surface charge on most particles tends to vary with pH with the charge increasing (becoming less negative or more positive) as the pH is reduced. Through appropriate adjustment and control of the pH it is sometimes possible to obtain significant differences in the surface charge on various components of a particle suspension and thereby create conditions such that a given flotation collector is adsorbed selectively on one of the particle species. Although the total surface charge on a small particle suspended in water can not be measured readily, a related quantity, the zeta potential, can be measured easily. Therefore, the zeta potential is used as a measure of the surface charge in flotation research.

In the present investigation the zeta potential of coal and pyrite particles in an aqueous suspension was measured with a model 400 Laser Zee Meter (Pen Kem Co.) in order to screen various chemical reagents which might modify the surface properties of coal and/or pyrite particles in aqueous suspensions. Coal from the Iowa State University Demonstration Mine was used. The coal was crushed and separated with a solution of tetrachloroethylene and hexane having a specific gravity of 1.30. The float fraction was recovered,

Figure 28. Effect of solids concentration on selectivity.

Figure 29. Fine grinding resulted in poorer selectivity.

dried, and pulverized to -60 mesh. The composition of the raw coal and of the float fraction is shown in Table 16. One portion of the float fraction was screened to provide -60/+100 mesh material for measurement of relative floatability while another portion was ground to a size of 5 to 50 μm for zeta potential measurements.

Pyrites were carefully hand-picked from University preparation plant tailings produced in treating similar coal. The pyrites were crushed to 1/4 in. top size and then split into two batches, pyrite I and pyrite II. The sulfur content of these batches is shown in Table 16. The pyrites were impure and probably a mixture of pyrite and marcasite. Pyrite I was pulverized and screened to provide -80/+100 mesh material for measurement of relative floatability. Some of the pulverized material was ground to 5-50 μm size for zeta potential measurements. Pyrite II was stored until ready for use in the floatability measurements. It was then ground and screened to provide -80/+100 mesh material.

For zeta potential measurement an aqueous suspension was prepared by mixing 0.05 g. of ground coal or 0.1 g. of ground pyrite with 500 ml. of deionized water. The pH of the suspension was adjusted by adding either 0.1 N hydrochloric acid or 0.1 N sodium hydroxide solutions. For a single determination, 25 ml. of the aqueous suspension was placed in the measurement cell of the Laser Zee Meter and a reading was taken. Three determinations were made on each suspension using a fresh portion of the suspension for each determination.

The measured zeta potential for an Iowa coal and for the pyrite extracted from the coal is shown in Figure 30 along with similar data reported by others for a Pittsburgh seam coal. Although the absolute values reported by various investigators differ, the trend of the zeta potential with pH is similar. For both coal and pyrite the zeta potential increases as the pH of the suspension decreases.

Table 16. Chemical analysis of the Iowa coal and pyrite

Material	Proximate Analysis, wt.%				Sulfur Distribution, wt.%			
	Moisture	Ash	Volatile Matter	Fixed Carbon	Pyritic	Organic	Sulfate	Total
Untreated coal	8.26	14.31	34.52	42.91	3.64	4.00	0.59	8.23
Float fraction	1.72	3.51	44.92	49.85	0.55	3.96	0.16	4.35
Pyrite I					45.77		0.89	49.55
Pyrite II					48.31		0.66	49.39

Figure 30. Zeta potential of coal and of pyrite isolated from coal in aqueous suspensions.

Figure 31. The surface charge on pyrite, but not on coal, was strongly affected by calcium ions.

Campbell and Sun (20) suggested that the adsorption of hydroxyl ions by the particles places a negative charge on the particles at high pH and the adsorption of hydronium ions at low pH places a positive charge on them. The change in trend for Iowa pyrite at pH below 4.5 must reflect some other potential determining phenomenon.

When sulfuric acid and calcium hydroxide were used to regulate the pH of the pyrite suspension, the results were different than when hydrochloric acid and sodium hydroxide were used (Figure 31). On the other hand, the different pH modifiers did not appear to affect the zeta potential of coal much differently, suggesting that only the hydroxyl and hydronium ions are adsorbed by the coal in these particular systems. However, in the case of pyrite the positive values of the zeta potential which were measured for pH greater than 5 appear to reflect the adsorption of positive calcium ions. Glembotskii *et al.* (10) noted that calcium ions are strongly adsorbed by pyrite surfaces and that in an alkaline medium calcium ions form insoluble compounds with the products of sulfide oxidation and suggested that a film of calcium sulfate may be formed on the pyrite surface. These effects were suggested to account for the depressing action which lime exerts on pyrite in froth flotation practice.

Since the addition of small amounts of sodium chloride to suspensions of coal or pyrite had little effect on the zeta potential (Figure 32), it appears that neither sodium nor chloride ions are strongly adsorbed by these solids. A similar observation was made by Campbell and Sun (20). Therefore the use of hydrochloric acid and sodium hydroxide to regulate the pH of the coal or pyrite suspensions should provide a minimum of interference when investigating the action of other surface active agents.

A series of measurements was made to investigate the effects of a number of potential pyrite flotation depressants on the zeta potential of coal and pyrite. For these measurements the pH was regulated with either sodium hydroxide or hydrochloric acid and only a small amount of the potential depressant was added to the coal or pyrite suspension. To investigate the effect of ferric chloride, three different concentrations of this material were used and the results are shown in Figure 33. For pyrite the results are similar in general to those reported by Baker and Miller (12); the addition of small amounts of ferric chloride raised the zeta potential supposedly because of adsorption of positively charged hydrolysis products such as $\text{Fe}(\text{OH})^{++}$ and $\text{Fe}(\text{OH})_2^+$. The effect tended to increase with increases in concentration. For coal the results were not as consistent. At the lowest concentration of ferric chloride, the zeta potential appeared to be reduced, which is difficult to explain, and at the higher concentrations, the zeta potential was only slightly greater than the zeta potential measured without any ferric chloride present. These results are not quite like those of Baker and Miller (12) for Pittsburgh seam coal which showed a larger effect and more consistent trend due to the adsorption of the hydrolysis products. Nevertheless it is apparent that over a pH range of 6 to 8, the addition of ferric chloride had a more pronounced effect on pyrite than on coal and therefore could act as a selective depressant for pyrite which is essentially what Baker and Miller were able to demonstrate.

Figure 32. The surface charge on coal and pyrite was not greatly affected by sodium chloride.

Figure 33. Ferric chloride had a greater effect on the zeta potential of pyrite than on that of coal.

The addition of small amounts of sodium carbonate to a pyrite suspension increased markedly the zeta potential of the particles at all pH levels (1). With a sodium carbonate concentration of 0.0001 M the increase in zeta potential was sufficient to make the zeta potential positive for all pH less than 8.0. The results were rather similar to those observed when ferric chloride was added. It appears then that a positively charged species was adsorbed by the particles but, of course, the species was not identified. One possibility is that a positively charged film of iron carbonate was adsorbed. Small additions of sodium carbonate affected the zeta potential of a coal suspension only to a small extent. It appeared that with a concentration of 0.0001 M the zeta potential of the coal particles was reduced somewhat at higher pH indicating the adsorption of some negative species such as HCO_3^- or CO_3^{2-} .

The addition of a small amount of ammonium thiocyanate to a pyrite suspension also produced results similar to those produced by ferric chloride (1). Thus with an ammonium thiocyanate concentration of 0.0001 M the zeta potential became positive for all pH less than 6.0. The adsorption of a positively charged complex such as FeCNS^{++} may account for the observed effect. Ammonium thiocyanate seemed to have little influence on the zeta potential of a coal suspension.

Small concentrations of sodium silicate also increased the zeta potential of pyrite suspensions (21). A concentration of 0.001 M caused the zeta potential to be positive for all pH below 7.0. The same concentration appeared to reduce somewhat the zeta potential of a coal suspension over most of the pH range.

The addition of small amounts of the disodium salt of ethylenediaminetetraacetic acid (Na_2EDTA) to a pyrite suspension had a marked effect on the zeta potential (1). The zeta potential became independent of pH over the pH range from 3 to 10 and as the concentration of Na_2EDTA was raised the zeta potential was reduced. Thus with a concentration of 0.0001 M the zeta potential was -20 mv. and with a concentration of 0.0002 M the zeta potential was -40 mv. The results indicate adsorption of some negatively charged species which may have been an iron-EDTA complex since such a complex is very stable. The addition of Na_2EDTA to a coal suspension seemed to reduce the zeta potential of the suspended particles at high pH but had no effect at low pH.

A review of the preceding results shows that the zeta potentials of coal and pyrite are of opposite sign when these materials are suspended in dilute solutions of the following reagents at the indicated pH:

Reagent	pH	Zeta Potential	
		Coal	Pyrite
$\text{Ca}(\text{OH})_2$	6-10	-	+
FeCl_3	7-8	-	+
Na_2CO_3	7-8	-	+
NH_4SCN	5-6	-	+
Na_2SiO_3	5-7	-	+
Na_2EDTA	3-5	+	-

These results indicate that cationic collectors might be used advantageously for the selective flotation of coal under the conditions indicated above where the coal particles bear a negative charge or anionic collectors where the coal particles bear a positive charge. Conversely cationic collectors might be used advantageously for the selective flotation of pyrite where it bears a negative charge or anionic collectors where it bears a positive charge.

The effect of several other reagents on the zeta potential of coal or pyrite suspensions was also investigated. When small amounts of either sodium sulfite, sodium phosphate, or ammonium citrate were added to these suspensions, the effect on the zeta potential was slight.

Floatability of Coal or Pyrite

A modified Hallimond tube microflotation cell was used to measure the relative floatability of coal or pyrite in the presence of various potential pyrite depressants and other flotation reagents. Figure 34 is a diagram of the cell. The cell offers several advantages according to Fuerstenau *et al.* (22). First, reproducible results can be obtained with very small samples (1-3 g.). Second, operating conditions can be controlled accurately. Third, the amount of liquid in the cell and the reagent concentration remain constant during the test. In addition a flotation test can be conducted either with or without a frother because it is unnecessary to produce a stable froth in order to have bubble attachment and particle flotation and deposition in the concentrate collecting stem.

Coal and pyrite for the floatability experiments were taken from the stock of materials prepared for the zeta potential measurements except that the -60/+100 mesh coal fraction and -80/+100 mesh pyrite fraction were used for the microflotation work. To conduct a floatability test, 25 ml. of deionized water or of a reagent solution was first placed in the lower part of the Hallimond

Figure 34.

Modified Hallimond tube microflotation cell.

tube and while the magnetic stirrer was operating and a small stream of nitrogen was flowing, 2.0 g. of coal or pyrite was added. The pH of the suspension was adjusted next by adding a small amount of either 0.1 N hydrochloric acid or 0.1 N sodium hydroxide solutions. If MIBC was to be used, it was introduced at this point. The suspension was then conditioned for 10 min. while stirring and aerating with nitrogen. After the conditioning period, the upper part of the Hallimond tube was connected to the lower part and 75 ml. of deionized water or of the reagent solution was added. The floatability measurement was then made by bubbling nitrogen at a flow rate of 35 ml./min. through the stirred suspension for 4.0 min. Particles which became attached to air bubbles were carried to the surface of the suspension and when the bubbles burst, the particles dropped into the concentrate collecting stem. After the test, the solids which had collected in the stem were recovered, dried, and weighed. The pH of the suspension remaining in the Hallimond tube was measured and the remaining solids were recovered, dried, and weighed. The weight of solids which floated and collected in the stem was divided by the total weight of concentrate and tailings to determine the relative recovery.

The percentage of relative recovery of both pyrite I and pyrite II obtained in a series of microflotation experiments conducted at different pH without any flotation reagents other than pH modifiers is shown in Figure 35 along with the relative recovery obtained in another series of experiments involving the addition of a small amount of methyl isobutyl carbinol (MIBC), a commonly used frothing agent. The relative recovery seemed to depend on the pH, the presence or absence of MIBC, and the particular batch of pyrite. All three factors appeared to interact. However, in the absence of MIBC, the relative recovery was about the same for both batches of pyrite, although the recovery of pyrite I seemed more dependent on pH than the recovery of pyrite II. The addition of MIBC increased significantly the recovery of both pyrite I and pyrite II over the entire pH range. The difference in behavior of pyrite I and II may have been due to a difference in state of oxidation of the pyrite surface. Pyrite I had been ground and stored for several months before the floatability measurements were made whereas pyrite II had been freshly ground shortly before the time of measurement.

The results of microflotation experiments which utilized sulfuric acid or calcium hydroxide for pH adjustment are shown in Figure 36 together with the results of similar experiments which utilized hydrochloric acid or sodium hydroxide. In all cases, a small amount of MIBC was added. While the type of acid seemed to have little effect on the relative recovery of either kind of pyrite, the type of base did seem to affect the recovery of pyrite I but not of pyrite II. Thus calcium hydroxide seemed to improve the recovery of pyrite I at higher pH which is surprising inasmuch as this reagent is generally regarded as a pyrite depressant (10).

Additional microflotation experiments were conducted to investigate the effects of various potential depressants on the relative recovery of pyrite. In all cases, a small amount of MIBC was used. Strangely enough all of the potential depressants including ferric chloride, sodium carbonate, sodium silicate, Na_2EDTA , and ammonium thiocyanate seemed to increase the relative recovery of pyrite I as indicated by Figures 37 and 38. On the other hand, most of these

Figure 35. Addition of MIBC improved the relative recovery of pyrite.

Figure 36. The relative recovery of pyrite I seemed to depend on whether the pH was controlled with sodium hydroxide or calcium hydroxide.

Figure 37. Ferric chloride appeared to activate pyrite I but had little effect on pyrite II.

Figure 38. Ammonium thiocyanate activated pyrite I and depressed pyrite II.

reagents with the exception of ammonium thiocyanate had little effect on the recovery of pyrite II. As can be seen from Figure 38, ammonium thiocyanate did reduce the recovery of pyrite II over most of the pH range. Also ferric chloride appeared to have a slight depressing effect on pyrite II at lower pH but not at higher pH (Figure 37). But pyrite II seemed indifferent to the other reagents.

The preceding results show that the effect of various chemical agents on the floatability of pyrite depends on the pH and the presence (or absence) of other flotation reagents such as MIBC as well as the nature or state of the pyrite itself. Thus various agents such as calcium hydroxide and ferric chloride which are reputed to depress pyrite had little effect as in the case of pyrite II or the opposite of the desired effect as in the case of pyrite I.

In a series of microflotation experiments with coal, the relative recovery was increased greatly by the addition of MIBC (Figure 39). The recovery of coal was increased much more than the recovery of pyrite was increased by MIBC. Therefore, the claim that MIBC serves as a collector for coal as well as a frothing agent seems well founded.

The type of acid or base used to adjust the pH of the coal suspensions for the microflotation experiments involving MIBC seemed to make little difference (Figure 40). On the other hand, the addition of ferric chloride to the coal suspensions seemed to reduce the relative recovery of coal at either high or low pH (Figure 41). Also the addition of ammonium thiocyanate increased the recovery of coal at intermediate pH (Figure 42). Moreover the addition of sodium carbonate had about the same effect as ammonium thiocyanate. Both sodium silicate and Na_2EDTA increased the recovery of coal more than the other salts when used in conjunction with MIBC over the pH range of 3 to 10.

Floatability of Chemically Pretreated Coal or Pyrite

An oxidative chemical pretreatment was applied to coal or pyrite to determine if it would reduce the floatability of pyrite without reducing the floatability of coal. For this treatment 50 g. of the -60/+100 mesh float fraction of coal (Table 16) prepared for the previously described floatability tests or 50 g. of the -80/+100 mesh pyrite II also prepared for these tests was mixed with 500 ml. of solution containing 10% by weight of sodium carbonate. The mixture was heated to 80°C and held at this temperature in a stirred flask while air was introduced continuously into the suspension through a diffuser for 30 min. at atmospheric pressure. The flask was then cooled to room temperature and the solids recovered by filtration. The unwashed solids were dried in an oven at 100°C for 3 hr. Two grams of the solids were used for each of the microflotation experiments with the modified Hallimond tube. The procedure used for these experiments was similar to that employed for the previously described floatability tests. For each test, 0.01 ml. of MIBC was added to the suspension of coal or pyrite placed in the microflotation cell. The results are presented in Table 17. A comparison of these results with those shown in Figures 35 and 39 for untreated pyrite or coal indicate that the chemical pretreatment step greatly reduced the floatability of pyrite while only slightly reducing the floatability of coal. An examination of both the treated and untreated pyrite particles with a scanning

Figure 39. MIBC greatly increased the recovery of coal.

Figure 40. The recovery of coal was indifferent to the type of acid or base used.

Figure 41. $FeCl_3$ depressed coal at high pH.

Figure 42. NH_4SCN improved the recovery of coal at medium pH.

Table 17. Floatability of chemically pretreated coal and pyrite.

Coal		Pyrite	
pH	Relative Recovery, %	pH	Relative Recovery, %
3.2	60.02	3.3	2.65
4.4	60.25	4.8	3.17
6.5	64.67	6.4	3.54
7.5	58.02	7.8	3.32
9.7	63.70	9.0	4.39

electron microscope revealed no marked differences between the two types of particles. Hence, it would appear that the chemical treatment only affected the surface of the particles.

In the future an effort will be made to optimize the chemical pretreatment step by investigating the effects of several potentially important parameters such as temperature, alkali concentration, and reaction time on the resulting floatability of coal or pyrite.

Selective Oil Agglomeration

The principles of recovering coal fines from an aqueous suspension through selective agglomeration with oil and subsequent sieving were outlined many years ago by Perrott and Kinney (23). Since the surface of most kinds of coal is hydrophobic whereas the surface of most inorganic minerals in coal is hydrophilic, coal particles are selectively coated by oil when a suspension of coal, oil and water is agitated vigorously. The oil-coated particles stick together forming agglomerates which are much larger than the individual particles. These agglomerates can then be recovered by screening the mixture.

A preliminary technical assessment of oil agglomeration technology has been made and problem areas identified. An experimental program to further develop this technology has been launched and as a consequence some of the more serious problems are being solved.

Technical Assessment

Over the past 60 years several coal beneficiation processes based on selective oil agglomeration were proposed and developed to some degree although apparently not to the point of both technical and economic viability. One of the earliest proposals was made by Walter E. Trent during the first World War (23). Experimental development of the Trent process was first undertaken by the Bureau

of Standards and later the development was transferred to the Bureau of Mines. The Trent process required a large amount of oil, about 30% based on the weight of coal, and appears not to have advanced beyond the laboratory stage of development.

Following the second World War, the Convertol process appeared in Germany (24). This process employed a Pallman phase inversion mill and required less oil, only 2 to 7% based on the weight of solids. A pilot plant for demonstrating this process was built at the Hanover Colliery near Essen. Later another pilot plant was built at Gary, West Virginia, and operated by U.S. Steel Corporation (25). The plant at Gary was subsequently modified and enlarged until it assumed the proportions of a commercial prototype (26). The plant was operated for several years to clean and recover fine-size coking coal. Although the operation was a technical success, the economics of the operation did not justify continued work and the plant was closed in 1963.

In recent years various research organizations have become involved in developing oil agglomeration methods. Thus the National Research Council of Canada has become involved in developing the "Spherical Agglomeration Process" (27-29). Bergbau-Forschung GMBH of Germany is developing the Olifloc process and is operating a 3 ton/hr. pilot plant near Essen (30). Shell International Petroleum Company Limited is interested in the development of the Shell pelletizing separator which is a unique device for conducting oil agglomeration (31). A prototype of this device was tested by the National Coal Board in England and a larger unit (10 ton/hr.) was constructed in Japan by Nagata Engineering and is being used by Mitsui Mining. The Central Fuel Research Institute of India has also carried out bench-scale work which has led to the installation of a 2 ton/hr. oil agglomeration plant for upgrading a coal slurry from the Lodna washery of the Bharat Coking Coal Ltd. (India) (32).

The use of oil agglomeration to desulfurize Iowa coals was investigated recently by Min and Wheelock (33). Oil agglomeration was applied alone and in combination with gravity separation and froth flotation to coal samples which had been comminuted in various ways. Oil agglomeration proved more effective in removing pyrites from samples which had been ground to -400 mesh size in a ball mill than from samples which had been pulverized to -35 mesh in a hammer mill. The method proved even more effective in removing pyrites from samples which had been chemically comminuted first by soaking in anhydrous liquid ammonia before pulverizing or grinding. In addition to providing greater sulfur removal, fine grinding resulted in a higher recovery of agglomerated coal (on an oil-free basis). Oil agglomeration was also found to complement the other methods of separation. By employing the following treatment combination, the pyritic sulfur content of two Iowa coals was reduced by more than 85% while recovering over 82% of the weight of coal. The coal was soaked in liquid ammonia, crushed to 1/4 in. top size, and gravity separated with a liquid having a specific gravity of 1.61; the float product was recovered, ground, and oil agglomerated.

In order for selective oil agglomeration to become both technically and economically viable, several major problems must be solved. One of these problems is due to an incomplete separation of coal and pyrite because the

surface of pyrite like the surface of coal tends to be hydrophobic and the two materials are agglomerated together (23). Capes et al. (34,35) proposed to solve this problem through bacterial oxidation of the pyrite surface thereby changing its character from hydrophobic to hydrophilic. However, bacterial oxidation is slow, apparently requiring 1 to 3 days, which could translate into a high capital cost. Another approach which appears more promising involves oxidation of the pyrite surface with a hot alkaline solution containing dissolved air or oxygen (16). Preliminary work at the Energy and Mineral Resources Research Institute of Iowa State University showed this treatment to be very rapid and quite effective.

Another major problem arises from the relatively high cost of the agglomerating oil. Capes et al. (28) showed that this cost is the preponderant component of the total processing cost of oil agglomeration. Although this cost can be minimized by using relatively low cost heavy residual fuel oils such as Bunker C, the heavy oils are not as selective as the more expensive light distillate oils and therefore will not produce as clean a product. On the other hand, the heavy oils should provide somewhat stronger agglomerates than the lighter oils and the heavy oils would not be lost through vaporization even if the agglomerated coal were thermally dried.

Another problem is due to the difficulty of producing relatively large and easily dewatered agglomerates; the larger their size, the easier it is to dewater them. According to Capes et al. (27,36), agglomerates larger than 2mm. across can be dewatered by mechanical means alone to a moisture content of 10% or less. Agglomerate size seems to be determined both by the agglomerating equipment and amount of oil used. High-shear mixers employing rapidly rotating blades disperse the oil well but tend to produce small agglomerates perhaps because the agitator blades cut up the larger agglomerates. Mixers with more slowly revolving paddles tend to produce larger agglomerates but have poor oil dispersion capabilities. Capes et al. (28) suggested using a series of two mixing vessels; the first vessel would be equipped with a high-shear mixer for good oil dispersion and coating of the coal particles and the second vessel would be equipped with a lower speed agitator. Microagglomerates would be formed in the first vessel and these would combine to form larger agglomerates in the second vessel. The Shell pelletizing separator may be the only device developed specifically for oil agglomerating coal. It produces relatively large spherical agglomerates; Verschur and Davis (31) reported that 1mm. diameter pellets were produced with an amount of oil equivalent to 10% of the weight of coal and 5-6mm. diameter pellets with an amount equivalent to 18% of the weight. They also reported producing a relatively clean (low ash content) product even though a heavy fuel oil was employed.

Experimental Program

A program of laboratory experiments was initiated to advance the basic technology of selective oil agglomeration so that it can become a useful and economically viable method of cleaning and recovering fine coal. The goal of this program was to develop a practical means of agglomeration which provides clean, pyrite-free agglomerates which are easily dewatered, stored and transported while at the same time utilizing a relatively inexpensive fuel oil in minimal amount. To achieve this goal several steps were proposed including chemical pretreatment, the use of heavy residual fuel oils or mixtures of these oils and

lighter fuel oils, pre-emulsification of the oil and water, and optimization of equipment and methods. Considerable progress which is described below was made in several of these areas.

The greatest progress was made in the application of chemical pretreatment and in the use of heavy fuel oils. For the following experiments, a run-of-mine coal from the Iowa State University Demonstration Mine was used. This coal was first crushed to 1/4 in. top size by passing it through a bench-scale double roll crusher.

The first set of experiments was conducted to compare the effectiveness of different grades of fuel oil for agglomerating both chemically pretreated and untreated coal. Raw coal containing 19.7% ash and 6.47 total inorganic sulfur (pyritic plus sulfate forms) was precleaned by gravity separation using trichloroethylene (specific gravity = 1.47) as the heavy medium. The float product recovered in 60% yield was dried overnight in an oven at 75°C, ground to -100 mesh with a Mikro-Samplmill, and analyzed; it contained 9.59% ash and 1.70% total inorganic sulfur. Part of the material was agglomerated directly with various grades of fuel oil and part was chemically pretreated before being agglomerated. For the pretreatment step, 50 g. of coal was mixed with 500 ml. of an aqueous solution containing 2.0 wt.% sodium carbonate. The suspension was heated to 80°C and aerated for 15 min. to oxidize the surface of the pyrite. It was then cooled and agglomerated. For the agglomeration step, either the pretreated alkaline suspension or a similar suspension of untreated coal and deionized water was placed in a kitchen blender (Sears Insta-Blend Model No. 400) and agitated for 1 min. whereupon 5.0 ml. of the specified fuel oil was added. The agitation was continued for another 5 min. at the highest possible speed. The agglomerated coal was poured onto a 60 mesh sieve and allowed to drain. The solids were then returned to the blender along with 500 ml. of deionized water. The pH of the suspension was adjusted to 2.0 by adding a 10% solution of hydrochloric acid. The suspension was agitated at high speed for 5 min. and screened. The recovered coal was dried overnight in an oven at 75°C and extracted with hexane to remove the fuel oil. It was redried to remove the hexane, weighed, and analyzed.

The results of the first set of experiments are listed in Table 18. Each value listed represents an average of the results of three separate runs. The results were quite reproducible since there was little variation in them between runs made under the same conditions. The results indicate that coal with the lowest sulfur content was produced by chemically pretreating the coal and agglomerating it with No. 1 fuel oil. This combination reduced the total inorganic sulfur content of the precleaned coal 63% and precleaning and oil agglomeration together reduced the inorganic sulfur content 90%. Omitting the chemical pretreatment step reduced the effectiveness of the separation step as did also the use of lower grade fuel oils. Thus oil agglomeration alone with either No. 1 or No. 2 fuel oil reduced the inorganic sulfur content of the precleaned coal 40% and oil agglomeration alone with No. 6 fuel oil only reduced the inorganic sulfur content of the precleaned coal 29%. On the other hand, with chemical pretreatment, oil agglomeration with No. 6 fuel oil reduced the inorganic sulfur content of the precleaned coal 49%. The experiments with No. 6 heavy fuel oil were noteworthy in as much as coal was agglomerated successfully

Table 18. Results of oil agglomeration tests with different types of fuel oil.

Treatment	Fuel Oil No.	Yield, ^b %	Na, %	Ash, wt.%	Inorg. S, wt.%	Reduction, %	
						Ash	Inorg. S
Feed Coal ^a	---	----	---	9.59	1.70	----	----
Oil Aggl.	1	94.0	0.029	7.82	1.02	18.5	40.0
	2	97.4	0.026	7.95	1.02	17.1	40.0
	200 LLS	96.5	0.027	7.78	1.12	18.9	34.1
	6 heavy	97.0	0.026	8.20	1.21	14.5	28.8
Chem/Oil Aggl.	1	94.9	0.055	8.08	0.63	15.7	62.9
	2	95.7	0.057	7.69	0.75	19.8	55.9
	200 LLS	95.1	0.061	8.01	0.70	16.5	58.8
	5 heavy	96.2	0.065	7.63	0.84	20.4	50.6
	6 heavy	95.0	0.066	7.72	0.86	19.5	49.4

^aPrecleaned by float/sink separation in trichloroethylene.

^bYield of coal on an oil and moisture free basis.

with this material and high yields were obtained without resorting to emulsifying agents or special techniques. Although chemical pretreatment greatly improved the removal of inorganic sulfur from coal by oil agglomeration, it also resulted in a small increase in the sodium content of the coal. Thus the pretreated and agglomerated product contained 0.06% sodium whereas the untreated run of mine coal contained 0.03%.

Since previous work (33) had shown that oil agglomeration is a more effective beneficiation method when applied to very finely ground coal than when applied to somewhat coarser material, several attempts were made to substitute heavy No. 6 fuel oil for the lighter fuel oil which had been used successfully before to agglomerate finely ground coal. These attempts were not successful. In other words, the finely ground material proved more difficult to agglomerate than the coarser material. However, it was discovered that the finely ground material could be agglomerated with a mixture of No. 6 and No. 200 LLS fuel oils. Therefore the following set of experiments was carried out using this mixture.

For the second set of experiments, the crushed run of mine coal containing 19.7% ash and 6.47% inorganic sulfur was pulverized to -100 mesh with the Mikro-Samplmill and ground to -400 mesh with a ball mill. The coal was then chemically pretreated as before except that a treatment time of 30 min. was used and the concentration of sodium carbonate was varied between runs. After pretreatment, the hot suspension was filtered and the recovered coal was placed in the blender

along with 500 ml. of deionized water. The mixture was agitated for 5 min. at the highest possible speed and as agitation was continued 5.0 ml. of fuel oil was added. The fuel oil was a mixture of No. 200 LLS (25 vol.%) and No. 6 (75 vol.%). The suspension was agitated for 5 min. to agglomerate the coal and then poured onto a 100 mesh sieve to recover the agglomerates. The agglomerates were placed back in the blender along with 500 ml. of deionized water and agitated for 5 min. more. The agglomerates were recovered by screening and then transferred to a Buchner funnel where they were washed with 200 ml. of hydrochloric acid (5%). The product was dried overnight at 75°C, extracted with hexane, redried, weighed, and analyzed.

The results of the second set of experiments showed that finely ground and chemically pretreated coal could be recovered in relatively high yield by agglomeration with the mixture of No. 6 and No. 200 LLS fuel oils. The results also showed that the concentration of sodium carbonate used in the chemical pretreatment step had an important effect on the removal of inorganic sulfur by oil agglomeration with the greatest removal occurring when a concentration of 1.0 wt.% was used (Figure 43). Again the results of duplicate runs carried out under the same conditions were quite close. Also the sodium content of the product was the same as that obtained in the first set of experiments (0.06 wt.%) even though the product was washed with acid in the second set. While the total sulfur reduction obtained by chemical pretreatment and oil agglomeration was not as great as that obtained in the first set, by combining these operations with gravity separation, the overall product yield was much higher.

In the second set of experiments the coal suspension had been filtered following the chemical pretreatment step and the coal had been resuspended in deionized water for the oil agglomeration step. In order to see whether the filtration step could be eliminated, a third set of experiments was conducted without this step. For this set of experiments another sample of coal from the Iowa State University Demonstration Mine was used; it contained 4.96% inorganic sulfur and 15.7% ash. The experimental procedure was similar to that used for the second set of experiments except that a chemical treatment time of 15 min. was used and the pretreatment reactor was purged with nitrogen before and after the treatment to insure that oxidation did not occur either before or after the specified period. After pretreatment and cooling, the contents of the reactor were transferred directly to the blender for agglomeration.

The results of the third set of experiments (Figure 44) were much better than the results of the second set indicating it is better to practice oil agglomeration in the chemical pretreatment medium rather than in fresh water. Thus, by employing the simpler and better method, the inorganic sulfur content of the coal was reduced by 87% and the ash content by 63% under the best pretreatment conditions which were employed. Of course, the product yield (83%) was a little lower than before. In the case of these experiments the optimum concentration of sodium carbonate was 2.0 wt.%. The final product contained 0.15 wt.% sodium when the optimum concentration of sodium carbonate was employed as compared to 0.016 wt.% in the untreated coal. Two oil agglomeration experiments which did not include the chemical pretreatment step were also conducted on the same coal. These resulted in an average reduction in both the inorganic sulfur content of 44% and ash content of 36% and in an average yield of 83%.

Figure 43. Results of agglomerating coal in fresh water after pretreatment. Yield expressed on moisture- and ash-free basis.

Figure 44. Results of agglomerating coal in alkaline pre-treatment solution. Yield expressed on moisture- and ash-free basis.

Hence, these data provide a dramatic illustration of the importance of the chemical pretreatment step. Since the large change in the ash content which seemed to result from applying the pretreatment was greater than can be attributed to the corresponding change in pyrite content, it appears as though some of the other minerals besides pyrite might also be affected by the pretreatment.

Since heavy fuel oils are difficult to disperse in aqueous suspensions of coal and do not exhibit the selectivity for coal which light oils do, the pre-emulsification of heavy oils and water was investigated to see if this would provide a means for overcoming these difficulties. In order to form a stable emulsion of No. 6 fuel oil and water, it was found necessary to incorporate an emulsifying agent in the mixture. The following emulsifying agents were tested:

Castile Soap, Fisher Scientific Co.

Mixture of Amyl Alcohol and Castile Soap

L-520 Silicone Surfactant, Union Carbide Co.

Polyacrylic Acid, K & K Laboratories, Inc.

These agents were combined with oil and water and then emulsified with an ultrasonic transducer (model A140, Sonifier Cell Disrupter, Heat Systems - Ultrasonics, Inc.). The emulsions were used to agglomerate run-of-mine coal from the Iowa State University Demonstration Mine No. 1. This coal had been pulverized to -60 mesh size.

In order to produce a relatively stable emulsion of oil and water, the following procedure was adopted: A mixture of 10 ml. of No. 6 fuel oil and 500 ml. of deionized water was placed in a beaker which was agitated with the ultrasonic transducer under full power while the emulsifying agent was added a little bit at a time. After each addition the mixture was agitated for a few minutes and then the ultrasonic generator was turned off to see if the oil and water would separate. When a relatively stable emulsion was formed, no more of the emulsifying agent was added and the emulsion was used to agglomerate coal. The amount of each emulsifying agent used is shown in Table 19 along with the results of the oil agglomeration experiments.

To conduct an oil agglomeration experiment, the emulsion of fuel oil and water was placed in a kitchen blender (Sears Insta-Blend Model No. 400) and agitated at the highest speed setting while 100 g. of pulverized coal was slowly added. After adding all of the coal, agitation was continued for about 5 min. more. The contents of the blender were then poured on to a 60 mesh sieve to collect the agglomerates. The recovered agglomerates were dried in an oven at 100-110°C for several hours, extracted with hexane to remove the agglomerating oil, and then redried in an oven to remove the hexane. The product was weighed to determine the yield of dry, oil-free coal and chemically analyzed to determine the ash content and total inorganic sulfur content.

In addition to the experiments which utilized various emulsifying agents, two experiments did not involve the use of these agents. In one case a light fuel oil (No. 200 LLS) was emulsified with water alone by vigorous agitation with

Table 19. Results of using different emulsifying agents in oil agglomerating an Iowa coal.^a

Oil Type	Emulsifying Agent		Yield %	Ash		Inorganic Sulfur	
	Type	Amount		wt. %	Reduction, %	wt. %	Reduction, %
No. 200 LLS	none	----	91	13.2	23.6	4.0	33.8
No. 6	none	----	74	16.0	7.6	5.1	15.2
No. 6	castile soap	0.083 g.	86	13.8	20.1	3.9	35.0
No. 6	castile soap + amyl alc.	0.015 g. 1.0 ml.	71	13.1	24.0	3.4	42.8
No. 6	L-520 silicone	1.0 ml.	62	12.6	27.2	3.9	35.0
No. 6	poly-acrylic acid	4.0 ml.	41	12.2	29.8	2.5	58.4

^aThe untreated coal contained 17.8% ash and 6.0% total inorganic sulfur.

the ultrasonic transducer before it was used for agglomeration. A relatively stable emulsion was produced in this case without the use of an emulsifying agent. In another case an unstable emulsion was prepared with the blender by mixing No. 6 fuel oil and water at high speed and the unstable emulsion was used for agglomerating coal.

The results of these experiments are presented in Table 19. The highest yield of product on a moisture and oil-free basis was obtained by using the light (No. 200 LLS) fuel oil without an emulsifying agent. The light oil also produced discrete, well-formed and relatively clean agglomerates. The results were nearly as good when coal was agglomerated with an emulsion of No. 6 fuel oil and water stabilized with castile soap. Fair results were also obtained with the emulsion of No. 6 fuel oil and water stabilized with a mixture of castile soap and amyl alcohol. However, the results obtained with the other emulsions were very poor; discrete, well-formed agglomerates were not produced so the recovery was low.

Although the results of these experiments were encouraging, subsequent experiments with castile soap as well as other emulsifying agents have given inconsistent results. It has proved difficult to reproduce the same state of emulsion. Also it appears that a very stable emulsion will not agglomerate coal. In other words, if the oil is too highly dispersed in the water phase it may not coat the coal particles.

Thus far the effect of chemical pretreatment on the yield and quality of the agglomerated product has been determined for a limited number of pretreatment conditions and only for one kind of coal. The investigation will be broadened to include other coals from Iowa, Illinois and Western Kentucky, and to characterize the effects of treatment time, temperature, and particle size. This work should lead to optimization of pretreatment conditions.

Pelletization

Since fine-size coal recovered by either froth flotation or oil agglomeration methods may be difficult to store and ship, consideration is being given to pelletization of this fine material in order to produce a product with better handling characteristics. The technology of coal pelletization has been reviewed to assess the state of the art, to identify potential problems, and to determine which aspects of the technology require further development. Subsequently the pelletization of coal fines will be demonstrated with suitable bench-scale apparatus to test possible solutions to existing problems and to further improve the technology.

Technical Assessment

Although many different size enlargement processes are used by industry, the two which seem to hold the most promise for coal fines are pelletization by tumbling and briquetting by roll pressing. The latter was used extensively in the past (37). From 8 to 10% coal-tar pitch or 6 to 8% petroleum asphalt was commonly used as the binder for the briquetts. Even though the briquetting of coal is a commercially proven method, it suffers several disadvantages compared to pelletizing. Briquetting equipment is heavier, more complex, and more costly to build and operate than pelletizing equipment (38,39). The size and, therefore, the production capacity of briquetting equipment also is more limited than that of pelletizing equipment. Furthermore coal supplied to a roll press for briquetting must be much drier than coal supplied to a pelletizer (39).

Pelletization by tumbling is generally carried out with either a rotating drum or rotating, inclined-pan. An inclined-pan or disk appears to have several advantages over a drum pelletizer. The inclined-pan is reputed to be lower in both capital cost and operating cost, to require less floor space, to produce pellets within a narrower size range, and to operate in a more nearly steady-state fashion (38,40). On the other hand, a drum pelletizer provides an enclosure which is more suitable for handling dusty materials.

A promising method of pelletizing wet or moist coal fines recovered by oil agglomeration or froth flotation has been demonstrated in small laboratory equipment at the National Research Council of Canada (27,41). The fines are fed to a rotating, inclined-pan along with clean coarse coal particles which serve as balling nuclei or "seed". A heavy oil such as No. 6 fuel oil or coal tar is sprayed on the coal while it is being balled. The oil not only serves to bind the pellets but it also displaces surface moisture from the coal. Pellets 1/4 in. in diameter made from a relatively wet feed in a 16 in. diameter balling

pan had 12% surface moisture which was reduced to 1/2% moisture by air drying overnight (27). Thus it appears that such pellets may be dried easily.

Pelletization poses several challenging problems. One of the major problems is the cost of a suitable binder. Heavy residual fuel oils, coal-tar pitch, or asphalt may serve as a binder in amounts ranging from 5 to 10% of the weight of the coal. Although any of these materials will contribute to the overall heating value of the product, their cost per unit of heating value is generally greater than that of the coal. A preliminary economic analysis by Capes et al. (28) of a process for recovering coal fines by a combination of selective oil agglomeration and disc pelletization showed that the costs of the agglomerating oil and pellet binder made up the bulk of the total overall processing cost.

A possible means of reducing the amount of binder required for pelletizing coal may lie in the development of a more efficient method of applying the binder. Application as a foam (rather than as a spray) seems especially promising in light of the success achieved by Csanyi (42-44) in utilizing foamed asphalt in bituminous paving mixes. He observed that foaming increases the volume of asphalt, reduces its viscosity, and alters its surface tension so that it sticks to solids very tenaciously. Furthermore foamed asphalt displaces moisture from the surface of the solids and coats the surface with a thin film.

Another problem with pelletization is the large number of variables which must be controlled and/or optimized in producing pellets of suitable size, strength, and moisture content at minimum cost. In the case of an inclined-pan pelletizer, the following parameters can affect its performance:

- (1) disc diameter,
- (2) depth of lip surrounding disc,
- (3) rotating speed of disc,
- (4) angle of inclination of disc,
- (5) feed point location,
- (6) solids retention time on disc,
- (7) feed ratio of coal fines to balling nuclei,
- (8) diameter of balling nuclei,
- (9) ratio of nuclei density to density of other particles,
- (10) moisture content of feed,
- (11) type and amount of binder.

Due to the large number of variables it appears that pelletization has not advanced much beyond the state of an industrial art. Hence, any application of this art requires a great deal of empirical testing. Moreover the technical know-how acquired in developing one application may not carry over to another application so each different application requires experimental testing and verification.

Demonstration

Because of the advantages described above, a rotating, inclined-pan was selected as a means for demonstrating and improving the pelletization of fine-size coal. The pelletizer shown in Figure 45 was built subsequently and it is being installed in the large bench-scale flow system which is under

Figure 45. Rotating, inclined-pan pelletizer.

Figure 46. Large bench-scale flow system is supported by structure in the foreground.

construction at the Ames coal preparation facility. The diameter of the pelletizer pan can be changed from 14 to 36 in. by placing cylindrical inserts of different diameter inside the outer pan. Therefore it will be possible to accommodate coal feed rates over a wide range, that is, from tens of pounds per hour up to several hundred pounds per hour. The pelletizer will be able to handle the output of either the froth flotation or oil agglomeration components of the bench-scale flow system. Alternatively the pelletizer can be supplied with fine-size coal from other sources. The pelletizer will be fitted with means for applying liquid binders as either a spray or foam.

After the pelletizer is installed, a program of experiments will be carried out to test various binders and methods of applying the binders and to optimize various system parameters such as disc speed and angle of inclination, coal moisture content and particle size, retention time, and ratio of binder to coal. The results of these experiments will be evaluated in terms of pellet size, strength and moisture content. When an effective method of pelletization has been developed, operation of the pelletizer will be integrated with operation of the oil agglomeration and/or froth flotation parts of the flow system.

Continuous Processing of Fine Coal

Construction of the first phase of a large bench-scale flow system for demonstrating various methods of cleaning and recovering fine-size coal is well along (Figure 46). This system will be located at the Ames coal preparation facility. Initially the system will include 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 will also include the rotating, inclined-pan pelletizer described above which is capable of pelletizing the full output of beneficiated coal. Equipment may be added in future years for further dewatering and drying oil agglomerated coal and for regenerating the spent pretreatment solution. In addition equipment may also be added in the future to demonstrate chemical leaching of coal by the alkaline oxydesulfurization method. Construction of the first phase of the system should be completed by April, 1978 (Table 20).

System Description

A schematic diagram of the flow system is presented in Figure 47. Coal fines from the Ames coal preparation facility will be placed as an aqueous slurry in either of two agitated tanks which will serve for both storage and chemical pretreatment. For the pretreatment step, an alkali will be added to the coal slurry which will then be heated to the required temperature. Air will be introduced next to oxidize the surface of the pyrite particles. After the oxidation step, the slurry can be cooled to whatever temperature is indicated for the subsequent separation steps. If a finer particle size is required, the coal can be ground with a ball mill before applying the chemical treatment. The ball mill circuit includes cyclones for both thickening the pulp supplied to the mill and classifying the particles according to size. Consequently only the coarser particles will enter the ball mill.

Table 20. Revised design and construction schedule for large bench-scale flow system.

	ENGINEERING	DRAFTING	STEEL FABRICATION	ELECTRICAL	ERECTION
1977					
Jan	conceptual analysis, flow sheet design				
Feb	structural de- sign, construct model	draft struct. steel ↓ ↓			↓
Mar	equipment specs. ↓ ↓	↓ ↓		equipment specs..	
Apr			begin struct. steel fabr. ↓ ↓		
May			↓ ↓		
June	equip. spec. deadline		steel fabr. complete		begin struct. steel erect. ↓ ↓
July	equip. order deadline				↓ ↓
Aug					↓ ↓
Sept					struct. steel erect. compl.
Oct		equipment delivery deadline 30 Sept. 1977			
Nov		draft special equip., elect. & piping	fabr. special equipment ↓ ↓		install piping and equipment ↓ ↓
Dec				install elect. equipment ↓ ↓	↓ ↓
1978					
Jan				↓ ↓	↓ ↓
Feb				↓ ↓	
Mar				↓ ↓	test ↓ ↓
Apr					↓ ↓

Figure 47. Bench-scale flow system for demonstrating continuous processing of fine coal.

After the feed has been adequately ground and/or pretreated, it will be pumped to either a bank of froth flotation cells or an oil agglomeration unit. If the feed is directed to the bank of flotation cells, it will first pass through a conditioning tank where a frothing agent will be added. The flotation cells will be operated to recover the clean coal in the float product and this product will be placed in a storage tank from which it can be conducted to a filter for dewatering or to the agglomeration unit for further cleaning. The flowsheet (Figure 47) does not include any filtration equipment since use will be made of filters which are part of the large Ames coal preparation facility.

Either coal fines cleaned by froth flotation or coal fines which have only been chemically pretreated can be oil agglomerated. A slurry of these fines will be delivered to the agglomeration unit which will include two stages. The first stage will utilize a high shear mixer for producing microagglomerates and the second stage a low shear mixer for producing larger agglomerates. Between stages and following the second stage the agglomerates will be passed over vibrating screens for dewatering and for removing refuse particles. The agglomerating oil will be emulsified with water and introduced into the first stage. Provisions will be made to heat the agglomerating oil and the coal slurry which will be treated.

The agglomerated and dewatered coal will be conveyed to a pelletizer for further size enlargement.

Experimental Program

A program of demonstration runs will be carried out with the continuous flow system described above. These runs will be designed to confirm and/or extend the results of earlier, small-scale laboratory experiments. Some of these runs will be designed to demonstrate chemical pretreatment of fine coal and recovery by froth flotation and others to demonstrate chemical pretreatment and recovery by oil agglomeration. Other runs will combine froth flotation and oil agglomeration or oil agglomeration and pelletization. The results will be evaluated in terms of the recovery of combustible matter; sulfur, ash, and moisture content of the product; and physical properties of the product. Samples of the product will be dewatered with a laboratory centrifuge to determine how low the moisture content is after applying this method of dewatering. The effects of important parameters such as residence time, slurry concentration, reagent concentration, and temperature will be investigated. Also the various treatments will be applied to several different representative coals from the Eastern and Midwestern regions of the country.

Neutron Source for Sulfur Monitoring Instrument

Although the development and construction of an electronic neutron source based on the D-D reaction was one of original tasks of this project, it became apparent that such a source was being developed by commercial interests so work was halted. In the meantime a more promising method of monitoring sulfur in coal was conceived. This method would address a coal process stream with thermal neutrons produced by moderating neutrons from a californium-252 source with

zirconium hydride. The advantage of this monitor over other monitors which employ californium-252 is derived from the pre-thermalization of the neutrons. Because of this feature, the determination of sulfur is not affected by coal moisture or bulk density and a coal process stream can be analyzed directly. With the other type of monitoring instrument both the moisture content and bulk density of the coal must be controlled so it is only practical to monitor a side stream. Furthermore with the pre-thermalized neutrons it is possible to monitor coal moisture and bulk density as well as sulfur. Even though this concept is very promising, further development of the concept can not proceed until additional funds become available.

Characterization of Coal Microstructure

by

Raymond T. Greer

Scientific Background

The microstructure of coal is of interest in understanding coal properties. Microstructural features may affect the selection of coal beneficiation methods for removing impurities. For example, in planning sulfur removal schemes for coal it is useful to understand the proportionment of inorganic sulfur compared with that of organic sulfur. Details of size, shape, orientation, and distribution factors for pyrite, certain pyrite and maceral groupings or fields, or other constituents (macerals and other inorganic components) are of importance in supporting rational designs of sulfur removal processes. Scanning electron microscope (SEM) investigations help to show the interrelations between macerals and inorganic phases such as pyrite (FeS_2 , the primary inorganic source of sulfur in coal) (45-51). Many significant coal features (such as cellular components) and impurity crystals occur in a size range of the order of hundreds and thousands of angstroms in diameter. Important features of coal constitution discovered by SEM are discussed below.

The first complete distribution data for pyrite in coal seams on a micrometer scale are presented for several strip and shaft mines. Significant amounts of pyrite can be present in coal as particles less than 50 micrometers in diameter.

Objectives

The objectives of the investigation are as follows:

- (1) maceral-mineral characterization; functional behavior of separable constituents,

- (2) identification of features of coal constitution which bear on ways to improve coal treatment schemes for removing sulfur and potential ash components,
- (3) determination of particle size, shape, and distribution to permit evaluation of factors bearing on decisions for developing methods to remove additional sulfide particles by optimum methods,
- (4) microstructural-chemical investigation of processed coal as this relates to the success of sulfur removal and to separation characteristics of sulfide material, and
- (5) clarification of the relative proportionment of organic and inorganic sulfur in coal as this influences subsequent choice of treatments in desulfurization and in conversion in the production fuel.

Technical Approach

Combined scanning electron microscope/energy dispersive X-ray analysis techniques are used to determine the microstructure of coal and the presence and distribution of pyrite. Complementary analyses such as X-ray diffraction are used for phase identification. Microstructural information on a submicrometer scale (generally for a size range of approximately a centimeter to as small as hundreds of angstroms for pyrite crystals of coal constituents, for example) is developed by the use of the SEM, and this textural information is correlated with associated microchemical information obtained from energy dispersive X-ray microanalyses to locate pyrite (and other inorganic phases). This permits an evaluation of particle size, shape and distribution factors which impact on decisions to try to remove additional sulfide particles to reduce the sulfur content.

Apparatus. A JSM-U3 SEM with an EDAX energy dispersive X-ray analysis system is used for the microscale structural and chemical studies. The resolution capabilities of the instrument on a day-to-day basis are somewhat better than 200 Å for microstructural information and submicrometer in a chemical analysis mode for localized crystal description. The system provides size, shape, orientation, and distribution information for inorganic phases and coal constituents (macerals).

Procedure. Samples for SEM studies are mounted in an orientation where the face and vertical position in the coal seam are maintained. The electron beam accelerating potential usually used in viewing the specimens is 25 kV. Samples receive a vacuum-deposited coating of approximately 200 Å gold (for microstructural studies; to minimize charging problems) or a vacuum-deposited graphite coating of 20-100 Å (for microchemical studies; to avoid possible interpretation difficulties of the sulfur and the gold X-ray fluorescence lines). Additional information about experimental technique appears in reference 48.

Materials. Samples of high-volatile C bituminous coal from both strip and shaft mines in Iowa form the primary materials of interest in this work.

Experimental Results

Microstructural Features. A number of representative microstructural features of maceral types, pyrite forms, and pyrite encapsulations; presence

and association of pyrite with external maceral boundaries and within macerals; association of potential ash components such as gypsum, quartz, and calcite next to and within macerals; and nature of cracks, cleats, cellular openings and, in certain cases, variations of infillings of these openings have been developed by the SEM studies and have been reported during this project period (45,46,50-54).

An important demonstration of determining carbon distributions has been made through the recording of electron microprobe micrographs for two-dimensional carbon K-alpha displays (for example, reference 46, page 422, figure 8c). In electron optical systems [(such as electron microscopes, Auger electron or ESCA (electron spectroscopy for chemical analysis) units, or other forms of microprobes)] carbon contamination during analysis is of great concern. In this work, electron microprobe wavelength dispersive X-ray analyses have been found to offer significant advantages compared with other techniques such as Auger analysis, for example. The curved crystal monochromator for the carbon studies is lead stearate decanoate. The primary analyzing line is the carbon K-alpha X-ray line (at 0.282 keV). The accelerating potential of the electron beam incident on the sample is 5 keV if the analysis is for carbon alone, or is 10 to 12 keV if several other elements of interest are present as well. It is important to emphasize that X-rays are analyzed rather than electrons. In the X-ray analysis, the range of the carbon X-rays in carbon is of the order of 8 to 10 μm in depth. The X-rays coming from the lower portion (deeper in the sample) are severely attenuated; however, for example at 10 keV, even with a 200 Å coating of carbon on coal, better than 90% of the coal carbon signal is available for analysis. By comparison, Auger electrons providing electron analytical signals for carbon originate in the top few angstroms of a surface. In an X-ray analysis, a region is scanned a single time and the associated initial carbon X-ray signal (point-by-point) is displayed as a two-dimensional image on an oscilloscope screen for photographic recording. The discrimination of a point A compared with a point B for the amount of carbon located at each point is still maintained even if many additional scans are performed because carbon or graphite deposit build-ups just add to the general total background level. The signal to noise ratio will decrease; however, the ability to discriminate carbon below such a layer remains even with a few hundred angstrom thick contamination layer.

In addition to carbon distribution displays, there is no particular major problem to obtaining oxygen displays. The problems for oxygen and carbon are similar. Analyzing crystal resolution is adequate and many crystals will work. A thallium acid phthalate analyzing crystal is used for the studies in this case. Consequently, this has permitted a highly localized investigation (on a scale of thousands of angstroms) to be performed for coal constituents and inorganic phase associations and distributions (for example, to delineate coal from calcite or gypsum).

Distribution Information. Complete distribution data for pyrite in the Mich. coal mine upper seam, Otley mine, Jude mine, and ICO mine (strip mines, Iowa) on a micrometer scale are presented. Data for the Star strip mine (49), Lovilia shaft mine (49), and Mich strip mine lower seam (50) were reported in previous quarterly reports during this project period. This information is for complete coal channel samples, and represents the first complete distribution data for pyrite in coal seams on a micrometer scale (accounting for essentially

all of the pyrite along continuous analyses paths from top to bottom of complete seams).

The distribution of pyrite among three forms in the mines (micrometer diameter of colloidal size single crystals; framboids...various size raspberry-like agglomerations of single crystals; and larger pyrite masses) is considered. Representative views of each of these forms are presented in Figure 33 of reference 50. For all of the mines analyzed to date, the distribution of pyrite among these forms is presented in Table 21. Additional distribution information for the Mich coal mine (upper seam) is shown in Figures 48 to 54, (see Appendix), for the Otley mine in Figures 55 to 61, for the ICO mine in Figures 62-68, and for the Jude mine in Figures 69 to 75. Common features are observed. The single crystal form of pyrite predominates below 1 μ m particle diameter, with isolated single crystals in size up to tens of micrometers in diameter. Fields of contacting single crystals occur over a wide range of sizes (Figures 49, 56, 63, and 70). Framboids are an important form of pyrite over a size range of a few micrometers to tens of micrometers in diameter for all of the seams analyzed. Referring again to Table 21, framboids are seen to comprise approximately 6 to 15% (by weight) of the total pyrite observed in the channel samples.

The proportion of pyrite in various size ranges suggests an insight into difficulties in pyrite removal by conventional separation techniques. A portion of this information is summarized in Table 22. These data indicate variations among mines as well as between seams in a particular mine. The pyrite material is extremely fine. Details of the proportionment of pyrite for the Mich mine (upper seam) are presented in Figures 49 and 50, for the Otley mine in Figures 56 and 57, for the ICO mine in Figures 63 and 64, and for the Jude mine in Figures 70 and 71.

Distribution information (as a volume percent pyrite based on total volume of material) for the three forms of pyrite (single crystals, framboids, and other larger massive forms) and the total of all pyrite forms is shown as a function of depth in the Mich mine (upper seam; Figures 51 to 54), in the Otley mine (Figure 58 to 61), in the ICO mine (Figures 65 to 68), and in the Jude mine (Figures 72-75). There are distinct differences in the way the three forms are distributed. Major trends of occurrence of pyrite are apparent for several mines. This can be seen in a comparison of the graphs designated "for all forms of pyrite" for each of the mines [Star, (49), Lovilia (49), Mich upper, Mich lower, (50), Otley, Jude, and ICO]]. For example, the data for the ICO and Mich upper seam show a concentration of pyrite in the lower half of the seam compared with data for the Star, Lovilia, and Mich lower seam where the pyrite is concentrated primarily in the upper half of the seams. The Otley and Jude graphs indicate a somewhat more uniform distribution of pyrite. Petrographic evidence supports groupings. More detailed correlations can be found at specific depths among certain mines; however, it is premature to offer comments at these early stages of the investigations. There are several possible sources for the pyrite.

Sulfur Determinations. A detailed investigation of the precision and accuracy of sulfur determinations on Iowa coal has been performed. Cross sections of untreated coals and residues from standard ASTM sulfur determinations were examined by combined energy dispersive X-ray microanalyses and scanning

Table 21. Distribution of pyrite among various forms.

Form of Pyrite	Distribution, wt. %						
	Lovilia Mine	Star Mine	Mich Mine (upper seam)	Mich Mine (lower seam)	Otley Mine	ICO Mine	Jude Mine
Single crystal	7.5	21.1	64.1	69.7	64.8	11.7	34.8
Framboids	6.1	10.9	7.9	12.3	14.5	12.4	9.2
Other larger, massive forms	<u>86.4</u>	<u>68.0</u>	<u>27.4</u>	<u>18.0</u>	<u>20.7</u>	<u>75.9</u>	<u>56.0</u>
	100.0	100.0	100.0	100.0	100.0	100.0	100.0

Note: Fields of individual crystals are taken as size units; single crystals within these fields as well as isolated single crystals are included in the single crystal category.

Table 22. Proportion of pyrite in certain size ranges.

Mine	50% of Pyrite Below Size Indicated	Amount < 200 Mesh
Lovilia	50% < 300 μ m	30% < 76 μ m
Star	50% < 45 μ m	57% < 76 μ m
Mich (upper seam)	50% < 150 μ m	42% < 76 μ m
Mich (lower seam)	50% < 12 μ m	75% < 76 μ m
Otley	50% < 7 μ m	91% < 76 μ m
ICO	50% < 100 μ m	47% < 76 μ m
Jude	50% < 22 μ m	80% < 76 μ m

Note: Fields of single crystals are considered as size units.

electron microscope analytical techniques. For Iowa coal (high volatile C bituminous) no significant errors were observed and the standard wet chemical analyses techniques were confirmed to be reliable (51,53). Pyrite was found in the residues in the form of undissolved framboids (spherical assemblies of individual micrometer sized pyrite single crystals). However, the amount of these framboids left after the nitric acid dissolution step in the ASTM procedures was well within the tolerance limits set in the standards. Studies are continuing to explain these observations in more detail as these may relate to other coals (ranks, maceral types, etc.).

Processed Coals. SEM characterization of fine-size coal has been performed for starting materials and products of chemical desulfurization processes. Of particular interest were the findings from a comparison of leached and unleached coal particles obtained from use of a process involving leaching coal with a hot, dilute solution of sodium carbonate containing dissolved oxygen under pressure (reference 50, pp.12-14). X-ray diffraction confirmed the nature of the phase transformations for the pyrite, and SEM observations revealed information of the mechanism of the reaction. Other SEM studies in support of process development have included characterization of various froth flotation specimens and of jet pulverized coal comminuted to a minimum size of the order of 6 to 10 micrometers in diameter (for both coal and coal-oil mixtures).

Conclusions

Microstructural-chemical information suggests a basis of coal cleaning variations to be expected from mine to mine. An analysis of channel samples from several Iowa coal mines has established that a significant proportion of pyrite in these samples was in the form of extremely small crystals and framboids. Major trends of occurrence of pyrite with depth are recognizable among specific mines. The claimed accuracy of ASTM chemical procedures for determining pyritic sulfur in coal has been confirmed for Iowa high volatile C bituminous coals by scanning electron microscope/energy dispersive analyses. Pyrite and the alteration products of pyrite have been monitored and characterized on a micrometer crystal size scale for coals treated in several sulfur removal processes.

GENERAL CONCLUSIONS

Several advances were made during the year in the development of various methods for desulfurizing and recovering fine-size coal. Thus it was demonstrated by means of small autoclave experiments that most of the inorganic sulfur and a significant part of the organic sulfur can be removed from high-sulfur bituminous coals by chemical leaching with hot aqueous solutions containing both dissolved oxygen and sodium carbonate. The removal of organic sulfur is favored by higher oxygen partial pressures. Omitting the alkali and leaching with acidic solutions results in less extraction of all forms of sulfur but high concentrations of alkali are detrimental. Supplying the leaching system with air instead of oxygen extracts less sulfur even though the same oxygen partial pressure is used.

Pyritic iron is converted to ferric oxide or hematite as sulfur is extracted from pyrite by a hot, alkaline solution containing dissolved oxygen. The leaching rate of an individual particle of pyrite appears to be controlled by diffusion of dissolved oxygen through the hematite shell which forms around the receding core of unreacted material. Consequently the leaching rate should be proportional to the dissolved oxygen concentration and inversely proportional to the square of the particle diameter. Moreover it should be independent of alkali concentration and liquid flow rate. These characteristics have been partially confirmed experimentally.

Although it was shown in laboratory froth flotation tests that Iowa bituminous coals are readily floated by methyl isobutyl carbinol, pyrite rejection was poor. Also various potential pyrite depressants such as lime, ferric chloride, and sodium cyanide proved ineffectual. On the other hand, a very promising surface chemical treatment was demonstrated which reduces the floatability of pyrite without affecting the floatability of coal. This treatment involves treating the coal or pyrite particles with a warm, dilute alkaline solution containing dissolved air. This treatment also improves the selectivity of the oil agglomeration process. Consequently heavier and less expensive fuel oils can be used for agglomerating coal without greatly penalizing pyrite rejection.

The construction of a large bench-scale flow system for demonstrating various methods of beneficiating and recovering fine-size coal was started and was well along by the end of the year. The first phase of the system which will include equipment for demonstrating chemical pretreatment, froth flotation, oil agglomeration, and pelletization should be completed by March, 1978.

An analysis of channel samples from several Iowa coal mines showed that a substantial proportion of the pyrites in these samples was in the form of very small crystallites and framboids. The claimed accuracy of the ASTM wet chemical method for determining pyritic sulfur in coal was confirmed for the Iowa high volatile C bituminous coals.

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APPENDIX

Pyrite Distribution Data for Iowa Bituminous Coals

Figure 48-75

MICH MINE (UPPER SEAM)
DISTRIBUTION OF PYRITE AMONG FORMS

Figure 48. Distribution of pyrite in the Mich mine (Upper Seam) among three forms: single crystals, framboids, and other larger, massive forms.

MICH MINE (UPPER SEAM)

PROPORTION OF PYRITE IN SIZE RANGES
PERCENTAGE OF PYRITE LESS THAN PARTICULAR SIZE

Figure 49. Proportionment of pyrite for the various size ranges observed for the Mich mine (Upper Seam). Units of agglomerated, recognizable single crystals are included in this presentation. Compare this with Figure 50.

MICH MINE (UPPER SEAM)

PROPORTION OF PYRITE IN SIZE RANGES
PERCENTAGE OF PYRITE LESS THAN PARTICULAR SIZE

Figure 50. Proportionment of pyrite on a constituent crystal size basis for the various size ranges observed for the Mich mine (Upper Seam).

Figure 51. The distribution of single crystals of pyrite in the Mich mine (Upper Seam) with depth in a seam. For example, in the top 1% of the seam, 0.2% of the material is small pyrite single crystals.

Figure 52. The distribution of framboidal formations of pyrite in the Mich mine (Upper Seam) with depth in a seam.

Figure 53. The distribution of the pyrite category, "other larger, massive forms," in the Mich mine (Upper Seam) with depth in a seam.

Figure 54. The distribution of total pyrite (total contribution of the three forms: single crystal, frambolds, and other larger, massive forms) in the Mich mine (Upper Seam) with depth in a seam.

OTLEY MINE
DISTRIBUTION OF PYRITE AMONG FORMS

Figure 55. Distribution of pyrite in the Otley mine among three forms: single crystals, framboids, and other larger, massive forms.

OTLEY MINE
PROPORTION OF PYRITE IN SIZE RANGES
PERCENTAGE OF PYRITE LESS THAN PARTICULAR SIZE

Figure 56. Proportionment of pyrite for the various size ranges observed for the Otley mine. Units of agglomerated, recognizable single crystals are included in this presentation. Compare this with Figure 57.

OTLEY MINE
PROPORTION OF PYRITE IN SIZE RANGES
PERCENTAGE OF PYRITE LESS THAN PARTICULAR SIZE

Figure 57. Proportionment of pyrite on a constituent crystal size basis for the various size ranges observed for the Otley mine.

Figure 58. The distribution of single crystals of pyrite in the Otley mine with depth in a seam.

Figure 59. The distribution of framboidal formations of pyrite in the Otley mine with depth in a seam.

Figure 60. The distribution of the pyrite category, "other larger, massive forms," in the Otley mine with depth in a seam.

Figure 61. The distribution of total pyrite (total contribution of the three forms: single crystal, frambolds, and other larger, massive forms) in the Otley mine with depth in a seam.

ICO MINE
DISTRIBUTION OF PYRITE AMONG FORMS

Figure 62. Distribution of pyrite in the ICO mine among three forms: single crystals, framboids, and other larger, massive forms.

ICO MINE

PROPORTION OF PYRITE IN SIZE RANGES
PERCENTAGE OF PYRITE LESS THAN PARTICULAR SIZE

Figure 63. Proportionment of pyrite for the various size ranges observed for the ICO mine. Units of agglomerated, recognizable single crystals are included in this presentation. Compare this with Figure 64.

ICO MINE

PROPORTION OF PYRITE IN SIZE RANGES
PERCENTAGE OF PYRITE LESS THAN PARTICULAR SIZE

Figure 64. Proportionment of pyrite on a constituent crystal size basis for the various size ranges observed for the ICO mine.

Figure 65. The distribution of single crystals of pyrite in the ICO mine with depth in a seam.

Figure 66. The distribution of framboidal formations of pyrite in the ICO mine with depth in a seam.

Figure 67. The distribution of the pyrite category, "other larger, massive forms," in the ICO mine with depth in a seam.

Figure 68. The distribution of total pyrite (total contribution of the three forms; single crystal, frambolds, and other larger, massive forms) in the ICO mine with depth in a seam.

JUDE MINE
DISTRIBUTION OF PYRITE AMONG FORMS

Figure 69. Distribution of pyrite in the Jude mine among three forms: single crystals, framboids, and other larger, massive forms.

JUDE MINE

PROPORTION OF PYRITE IN SIZE RANGES
PERCENTAGE OF PYRITE LESS THAN PARTICULAR SIZE

Figure 70. Proportionment of pyrite for the various size ranges observed for the Jude mine. Units of agglomerated, recognizable single crystals are included in this presentation. Compare this with Figure 71.

JUDE MINE

PROPORTION OF PYRITE IN SIZE RANGES
PERCENTAGE OF PYRITE LESS THAN PARTICULAR SIZE

Figure 71. Proportionment of pyrite on a constituent crystal size basis for the various size ranges observed for the Jude mine.

Figure 72. The distribution of single crystals of pyrite in the Jude mine with depth in a seam.

Figure 73. The distribution of framboidal formations of pyrite in the Jude mine with depth in a seam.

Figure 74. The distribution of the pyrite category, "other larger, massive forms," in the Jude mine with depth in a seam.

Figure 75. The distribution of total pyrite (total contribution of the three forms; single crystal, framboids, and other larger, massive forms) in the Jude mine with depth in a seam.