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ADVANCED DEVELOPMENT OF FINE COAL DESULFURIZATION AND RECOVERY TECHNOLOGY

Quarterly Technical Progress Report

April 1, 1977 — June 30, 1977

For Division of Materials and Exploratory Research

By

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

Prepared for the U.S. Department of Energy

Under Contract No. W-7405 eng-82

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ABSTRACT

The improvement and technical development of several promising methods for desulfurizing and recovering fine coal were continued. These methods include 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. Numerous laboratory experiments and measurements were carried out to advance the state of this technology. As a result it was shown that the chemical leaching process removed most of the inorganic sulfur from several high sulfur coals as well as a significant amount of organic sulfur from some of the coals. Higher temperatures and/or oxygen partial pressures resulted in more organic sulfur being removed in some instances. Also it was shown that the rate of conversion of pyrite to soluble sulfates depends on particle size and alkali concentration as well as oxygen partial pressure and flow rate. In addition the effectiveness of a chemical pretreatment step for improving the separation of coal and pyrite by oil agglomeration was demonstrated. Among various fuel oils tested for agglomerating coal, No. 1 or 2 provided greater sulfur reduction than No. 5 or 6. Also the lighter fuel oils seemed better suited to agglomerating finely ground coal. However, No. 6 fuel oil was adapted to the agglomeration of ball milled coal by diluting it with a lighter oil. Construction was started on a bench-scale flow system for demonstrating the beneficiation and recovery of fine-size coal by various methods. Furthermore the suitability of the ASTM method for determining pyritic sulfur in coal was confirmed for certain high volatile C bituminous coals. Confirmation was obtained by scanning electron microscope/energy dispersive X-ray analyses.

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.

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 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

Work on the development of a neutron source based on the D-D reaction has been halted. At this time we find that the state of the art of this type of instrumentation has been developed by commercial vendors.

The Ames Laboratory is presently considering the development of a neutron monitor which addresses the process stream directly with neutrons which are released on the fission of ^{252}Cf and are then moderated with zirconium hydride to thermal energies. The thermal neutron monitor has the advantages of not requiring the use of a side stream and of not being affected by variations in the moisture and mineral content of the sample.

SUMMARY OF PROGRESS TO DATE

Several methods which hold great but largely unrealized promise for desulfurizing and recovering fine coal have been selected for technical development. These methods include froth flotation, selective oil agglomeration, pelletization and chemical desulfurization by a unique process. A preliminary assessment of these methods has been made to define the present state of development, to identify problem areas, and to design an appropriate experimental program to achieve the stated objective.

The chemical desulfurization process which has been 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 have shown that the rate of extraction of sulfur from coal increases with agitator speed up to about 2000 r.p.m. in the stirred autoclave. Beyond this speed the rate appears to become independent of speed. Further experiments have shown 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 3.4 to 6.8 atm.). Also for some coals a significant amount of organic sulfur was removed, particularly at higher temperatures and/or oxygen partial pressures.

Experiments with the tubular reactor system have indicated that the rate of conversion of pyrite particles increases with increasing oxygen partial pressure and decreasing particle size. The rate is also affected by oxygen

flow rate and alkali concentration. Starting with very low levels of either of these parameters and progressively increasing them, the rate of conversion has been observed to increase, reach a maximum, and then decline. In other words, there are optimum levels of these parameters which provide the maximum rate of reaction. The rate has also been observed to decline with increasing charge size, more so in the case of smaller particles than in the case of larger ones.

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. A number of potential flotation depressants for pyrite have been screened by measuring the floatability of pyrite in the presence of these reagents with a modified Hallimond tube microflotation cell. Although several reagents have been found to suppress the flotation of pyrite when used alone, these reagents have not proven to be good depressants when used in conjunction with methyl isobutyl carbinol (MIBC), a commonly employed frothing agent in the field of coal flotation. Measurement of the zeta potential of coal or pyrite suspensions containing small amounts of these reagents has identified conditions where it may be possible to employ suitable cationic or ionic collectors to effect a good separation of coal and pyrite. In addition it has been shown that the floatability of pyrite but not coal can be greatly reduced by applying an oxidative chemical pretreatment process.

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.

An inclined, variable diameter, rotating disc pelletizer has been selected for pelletizing coal fines. A bench-scale pelletizer has been designed and is being fabricated in house.

A bench-scale, continuous flow system has been designed to demonstrate the beneficiation and recovery of fine-size coal by froth flotation, selective oil agglomeration and pelletization. The system will also include a section for grinding and chemically pretreating coal. Construction of the system is underway and should be completed by December, 1977.

To better assess the problem of removing sulfur from coal, channel samples from several Iowa coal mines have been analyzed by scanning electron microscopy and associated energy dispersive X-ray analysis techniques. As a consequence, the distribution of pyrite among various crystalline forms has been determined as a function of location within specific coal seams. Also the relative pro-

portions of the various forms and proportion of pyrite in various size ranges have been determined for each of the channel samples as a whole. Finally, the accuracy and suitability of the ASTM method for determining pyritic sulfur in coal has been verified for several high volatile C bituminous coals.

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Chemical Desulfurization

The development of a promising process for extracting sulfur from coal was continued. This process involves leaching fine-size coal with a hot, dilute solution of sodium carbonate containing dissolved oxygen under pressure. Under the proposed leaching conditions pyrite appears to react 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 the coal. In addition some of the organic sulfur is extracted.

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.

The overall process is shown schematically in Figure 1. The 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.

Figure 1. Schematic flow diagram of proposed industrial process for desulfurizing coal.

The present experimental program is directed towards the laboratory development and demonstration of the leaching step. Experiments are being conducted with two types of reaction systems. One system utilizes a fixed bed tubular reactor and is being used to measure the rate of extraction of pyrite particles whereas the other system employs a stirred tank reactor and is being used to study the removal of different forms of sulfur from coal.

Attention is also being given to regeneration of the spent leachant. A theoretical analysis of the proposed method of regeneration is being made. This analysis is based on thermodynamic equilibrium and will serve as a guide for future experimentation and demonstration.

Stirred Autoclave System

A 1.0-liter stirred autoclave with a gas-dispersing turbine agitator has been demonstrated as an efficient device for studying the leaching of sulfur from coal with a dilute solution of sodium carbonate containing oxygen under various pressures and temperatures. During preliminary experiments described in the previous report (1), it has been observed that the amount of sulfur leached in 1 hr. from high-sulfur coal is highly dependent on the rotation speed of the turbine agitator. This effect of agitator speed on the quantity of sulfur extracted has been verified, and the range has been extended to include higher agitator speeds.

The final 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 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. 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.

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 2. 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 effect of temperature, oxygen pressure, and concentration of leaching solution on the chemical desulfurization of several pre-cleaned Iowa coals, including Big Ben coal, Lovilia coal, and coal from the Scott site of the I.S.U. Demonstration Mine (called

Table 1. Effect of agitator speed on pyritic and total sulfur reduction.^a

Speed r.p.m.	Yield, %	Ash, wt.%	Sulfur Distribution, wt.%				Total S Reduction, %	Pyritic S Reduction, %
			Pyritic	Sulfate	Organic	Total		
---	----	15.4 ^b	5.68 ^b	0.79 ^b	2.90 ^b	9.37 ^b	----	----
200	95.3	17.6	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

^aLeaching 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.

Table 2. Particle size distribution of coal after leaching at different agitator speeds.

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

Scott coal in this study). In addition, a Western Kentucky coal from the Fies Mines (No. 9 seam) in Hopkins County was used. The raw, run-of-mine coal was crushed to 1/4 in. or less and treated first with 1,1,2-trichloroethylene (specific gravity = 1.45) by the float-sink separation process as preliminary cleaning. The cleaned coal was then pulverized and ball-milled to -400 mesh size.

A sample of 40 g. of a given coal was used to charge the autoclave for each experimental run. After the addition of 400 ml. of 0.20M sodium carbonate solution, the autoclave was closed, and the desired agitator speed (2000 r.p.m.) was attained. The autoclave was purged with nitrogen while being heated to the required temperature. When the system reached operating temperature, the flow of nitrogen was stopped, and oxygen was introduced into the autoclave. Some gas was bled continuously from the reactor in order to avoid any build-up of gaseous products within the system. The reaction temperature, oxygen partial pressure, total pressure, and the stirring rate were kept constant for 2 hr., after which the reaction was stopped by discontinuing the flow of oxygen into the system and purging with nitrogen. After cooling by passing cold water through the cooling coil, the contents of the reactor were filtered to recover the coal. The coal was dried in an oven, weighed, and chemically analyzed for the various forms of sulfur and for its heating value.

In Tables 3-6 the results are presented for removal of sulfur from the various 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.). For Lovilia, Big Ben, and Western Kentucky coals (Tables 3, 4, and 5, respectively) significant amounts of sulfur were leached; the reduction in the total specific sulfur content (expressed as lb. S/10⁶ Btu) was in the ranges 22.16-33.53, 26.29-37.07, and 13.09-24.61%, 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 0.05-0.08 lb. S/10⁶ Btu, and highest for Lovilia coal, 0.07-0.13 lb. S/10⁶ Btu. The residual level of sulfate sulfur was lowest for Western Kentucky coal also (0.04-0.06 lb. S/10⁶ Btu) and highest for Big Ben coal (0.12-0.19 lb. S/10⁶ Btu). By contrast to the inorganic sulfur content,

Table 3. Leaching of Lovilia coal.^a

Sample No.	Temp., °C	O ₂ Press., psia	Ash, wt. %	Sulf. Distribution, wt. %				Redn. Total S. by wt., %	H.V. Btu/lb	Spec. Sulf. Cont., lb.S/10 ⁶ Btu				Redn. Tot. Spec. S. %
				Pyr.	Sulf.	Org.	Tot.			Pyr.	Sulf.	Org.	Tot.	
AK01 ^b	---	---	5.81	0.54	0.26	1.21	2.01	----	11,960	0.45	0.21	1.01	1.67	-----
AK02	150	50	11.88	0.15	0.07	1.09	1.31	34.8	11,489	0.13	0.06	0.95	1.14	31.74
AK06	150	50	13.08	0.07	0.06	1.11	1.24	38.3	10,543	0.07	0.06	1.05	1.18	29.34
AK03	180	50	12.15	0.14	0.10	1.08	1.32	34.3	11,139	0.13	0.09	0.97	1.19	28.74
AK07	180	50	14.69	0.07	0.10	1.14	1.31	34.8	10,113	0.07	0.10	1.13	1.30	22.16
AK04	150	100	11.70	0.13	0.07	1.19	1.39	30.8	10,819	0.12	0.06	1.09	1.27	23.95
AK08	150	100	12.55	0.11	0.07	1.03	1.21	39.8	10,826	0.10	0.06	0.95	1.11	33.53
AK05	180	100	12.55	0.11	0.08	1.03	1.22	39.3	10,924	0.10	0.07	0.94	1.11	33.53
AK09	180	100	13.84	0.07	0.09	1.07	1.23	38.8	9,900	0.07	0.09	1.08	1.24	25.75

^aPre-cleaned (-400 mesh); leached 2 hr. by 0.2M Na₂CO₃ at 2000 r.p.m.

^bAsh content, sulfur distribution, and heating value of unleached coal.

Table 4. Leaching of Big Ben coal.^a

Sample No.	Temp., °C	O ₂ Press., psia	Ash, wt.%	Sulf. Distribution, wt.%				Redn. Total S. by wt., %	H.V. Btu/lb	Spec. Sulf. Cont., lb.S/10 ⁶ Btu				Redn. Tot. Spec. S. %
				Pyr.	Sulf.	Org.	Tot.			Pyr.	Sulf.	Org.	Tot.	
AI01 ^b	---	---	4.44	0.56	0.52	1.76	2.84	-----	12,210	0.46	0.42	1.44	2.32	-----
AI02	150	50	13.72	0.05	0.14	1.45	1.64	42.25	10,322	0.05	0.13	1.40	1.58	31.90
AI06	150	50	12.90	0.07	0.15	1.36	1.58	44.37	10,814	0.06	0.14	1.26	1.46	37.07
AI03	180	50	12.63	0.09	0.15	1.45	1.69	41.19	10,837	0.08	0.14	1.34	1.56	32.76
AI07	180	50	13.23	0.11	0.12	1.48	1.72	39.44	10,009	0.11	0.12	1.48	1.71	26.29
AI04	150	100	12.54	0.10	0.15	1.50	1.75	38.38	10,740	0.09	0.14	1.39	1.62	30.17
AI08	150	100	13.42	0.07	0.21	1.35	1.63	42.60	10,674	0.06	0.19	1.27	1.52	34.48
AI05	180	100	12.97	0.09	0.19	1.26	1.54	45.77	9,670	0.09	0.19	1.30	1.58	31.90
AI10 ^b	---	---	4.09	0.52	0.46	1.91	2.89	-----	12,303	0.42	0.37	1.55	2.34	-----
AI09 ^c	180	100	13.57	0.05	0.17	1.49	1.71	40.83	10,356	0.05	0.16	1.44	1.65	29.49

^aPre-cleaned (-400 mesh); leached 2 hr. by 0.2M Na₂CO₃ at 2000 r.p.m.

^bAsh content, sulfur distribution, and heating value of unleached coal.

^cControl sample for AI09 is AI10.

Table 5. Leaching of Western Kentucky coal.^a

Sample No.	Temp., °C	O ₂ Press., psia	Ash, wt. %	Sulf. Distribution, wt. %				Redn. Total S. by wt., %	H.V. Btu/lb	Spec. Sulf. Cont., lb.S/10 ⁶ Btu				Redn. Tot. Spec. S. %
				Pyr.	Sulf.	Org.	Tot.			Pyr.	Sulf.	Org.	Tot.	
AH06 ^b	---	---	5.57	0.43	0.18	1.87	2.48	----	13,024	0.33	0.14	1.44	1.91	-----
AH07	150	50	13.25	0.05	0.06	1.46	1.57	36.7	10,880	0.05	0.05	1.34	1.44	24.61
AH11	150	50	13.20	0.07	0.07	1.65	1.79	37.8	10,749	0.06	0.06	1.54	1.66	13.09
AH08	180	50	13.43	0.07	0.06	1.60	1.73	30.2	10,554	0.07	0.05	1.52	1.64	14.14
AH12	180	50	13.78	0.05	0.07	1.64	1.76	29.0	10,603	0.05	0.06	1.55	1.66	13.09
AH09	150	100	11.90	0.06	0.04	1.50	1.60	35.5	10,966	0.05	0.04	1.37	1.46	23.56
AH13	150	100	11.54	0.07	0.05	1.49	1.61	35.1	10,892	0.06	0.04	1.37	1.47	23.04
AH10	180	100	14.43	0.05	0.14	1.42	1.61	35.1	9,918	0.05	0.14	1.43	1.47	23.04
AH14	180	100	14.49	0.08	0.07	1.54	1.69	31.9	10,519	0.08	0.06	1.46	1.60	16.23

^aPre-cleaned (-400 mesh); leached 2 hr. by 0.2M Na₂CO₃ at 2000 r.p.m.

^bAsh content, sulfur distribution, and heating value of unleached coal.

Table 6. Leaching of Scott coal.^a

Sample No.	Temp., °C	O ₂ Press., psia	Ash, wt. %	Sulf. Distribution, wt. %				Redn. Total S. by wt., %	H.V. Btu/lb	Spec. Sulf. Cont., lb.S/10 ⁶ Btu				Redn. Tot. Spec. S. %
				Pyr.	Sulf.	Crg.	Tot.			Pyr.	Sulf.	Org.	Tot.	
AG21 ^b	---	---	10.12	1.05	0.28	3.38	4.71	-----	12,108	0.87	0.23	2.79	3.89	-----
AG25	150	50	14.94	0.23	0.13	3.01	3.37	28.45	10,875	0.21	0.12	2.76	3.09	20.57
AG29	150	50	16.37	0.20	0.18	2.72	3.10	34.18	10,864	0.18	0.16	2.50	2.84	26.99
AG26	180	50	17.95	0.13	0.27	2.32	2.72	42.25	9,528	0.14	0.28	2.43	2.85	26.74
AG30	180	50	19.00	0.12	0.31	2.34	2.77	41.19	9,524	0.13	0.32	2.45	2.90	25.45
AG27	150	100	16.87	0.19	0.17	3.11	3.47	26.33	10,645	0.18	0.15	2.92	3.25	16.45
AG31	150	100	17.42	0.14	0.19	2.84	3.17	32.70	10,475	0.13	0.18	2.71	3.02	22.37
AG28	180	100	18.49	0.16	0.23	2.33	2.72	42.25	9,816	0.16	0.23	2.37	2.76	29.05
AG32	180	100	18.39	0.13	0.23	2.37	2.73	42.04	9,757	0.13	0.23	2.43	2.79	28.28

^aPre-cleaned (-400 mesh); leached 2 hr. by 0.2M Na₂CO₃ at 2000 r.p.m.

^bAsh content, sulfur distribution, and heating value of unleached coal.

the differences in the final organic sulfur content were less pronounced, 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 no discernible trends.

For Scott coal, the reduction in the total specific sulfur content was in the range 16.45-29.05% (Table 6). Again, substantial amounts of pyritic sulfur were removed, to residual levels of 0.13-0.21 lb. S/10⁶ Btu. The residual levels of sulfate sulfur varied somewhat and seemed to be connected with the amount of organic sulfur remaining in the coal. Unlike the other coals, Scott coal was characterized by some reduction in the organic sulfur content, especially at the higher temperature. Thus, at 180° the organic specific sulfur content was reduced from the original value of 2.79 to 2.43-2.45 and 2.37-2.43 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 16.45-22.37 to 28.28-29.05%. 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 (4.71 wt.% total sulfur for Scott coal as compared to 2.01-2.84 wt.% total sulfur for the other coals).

The effect of different concentrations of sodium carbonate in the leaching solution on the amount of sulfur extracted from Big Ben coal is presented in Table 7. By increasing the concentration of sodium carbonate from 0.2 to 2.0M, the amount of total sulfur removed was seemingly increased from 39.79-40.14% to 56.79-64.70%, and the apparent content of organic sulfur was more than halved. However, at the same time, the ash content increased to 47.50-56.51 wt.% from 4.09 wt.% for the untreated coal, and the heating value dropped from 12,303 Btu/lb. to 4,835-6,494 Btu/lb. By using the less concentrated leaching solution, the heating value decreased only slightly (by less than 9%) while the ash content increased only to 11.73-12.84 wt.%. When the effectiveness of the two solutions is compared on the basis of the percent reduction in the total specific sulfur content, the 0.2M solution is much better than the 2.0M solution (reductions of 33.76-35.04% and 10.26-20.09%, respectively). Similar results are obtained when calculations are performed using sulfur contents and heating values corrected to an ash-free basis.

It should be noted that the low heating values of the coal treated with the 2.0M sodium carbonate solution resulted from the increase in ash content of the product. Expressed on an ash-free basis, the heating values were only slightly less than that of the original coal.

The results reported in Table 7 also indicate that a significant amount of organic sulfur was removed from Big Ben coal leached with the 0.2M sodium carbonate solution. This improvement over the results reported in Table 4 appears due to either the employment of a higher oxygen partial pressure in the case of Sample No. A111 and A113 or a higher temperature in the case of Sample No. A116.

Table 7. Leaching of Big Ben coal.^a

Sample No.	Temp., °C	O ₂ Press., psia	Na ₂ CO ₃ concn., M	Ash, wt. %	Sulf. distribution, wt. %				Redn. Total S. by wt., %	H.V. Btu/lb	Spec. Sulf. Cont., lb.S/10 ⁶ Btu				Redn. Tot. Spec. S. %
					Pyr.	Sulf.	Org.	Tot.			Pyr.	Sulf.	Org.	Tot.	
AI10 ^b	---	-----	---	4.09	0.52	0.46	1.91	2.89	-----	12,303	0.42	0.37	1.55	2.34	-----
AI11	130	275.5	0.2	12.84	0.11	0.15	1.48	1.74	39.79	11,216	0.10	0.13	1.32	1.55	33.76
AI13	130	275.5	0.2	11.73	0.14	0.14	1.45	1.73	40.14	11,362	0.12	0.12	1.28	1.52	35.04
AI12	130	275.5	2.0	56.51	0.07	0.20	0.75	1.02	64.70	4,835	0.14	0.41	1.55	2.10	10.26
AI14	130	275.5	2.0	47.50	0.05	0.24	0.92	1.21	56.79	6,494	0.08	0.37	1.42	1.87	20.09
AI15 ^b	---	-----	---	4.53	0.53	0.45	1.82	2.80	-----	12,754	0.42	0.35	1.43	2.20	-----
AI16 ^c	240	0	0.2	11.64	0.52	0.105	1.41	2.04	27.14	11,908	0.43	0.09	1.19	1.71	22.27

^aPre-cleaned (-400 mesh); leached 2 hr. at 2000 r.p.m.^bAsh content, sulfur distribution, and heating value of unleached coal^cControl sample for AI16 is AI15.

Preliminary studies on the leaching of uncleaned coals have also been performed; the possibly interesting developments will be studied further. Specifically, the heating values will be obtained so that the specific sulfur content can be calculated and used as a basis for comparison. In addition, the effect of oxygen partial pressure, temperature, and the size of the coal particles on the removal of sulfur, especially organic sulfur, will be investigated. All future experiments will be also conducted in a controlled regime of constant agitator speed in which the rate of sulfur removal is independent of the speed.

Tubular Reactor System

In order to understand better the process of leaching pyritic sulfur from coal, the kinetics of dissolution of pyrite in a flow-through tubular reactor are being studied. The apparatus and procedure for the tubular reactor system were described in the previous report (1). The apparatus was slightly modified by including a differential pressure gauge to determine the pressure drop across the orifice used to measure the oxygen flow rate. The system was used in a series of continuing experiments to explore the possible effects of different parameters on the rate of dissolution of pyrite particles by hot leaching solutions containing sodium carbonate and oxygen under pressure.

The studies included the effect of total pressure, oxygen flow rate, concentration of sodium carbonate, the amount of pyrite in the reactor (charge size), and the particle size of the pyrite on the rate of sulfur conversion. In addition, the possibility of an effect of sodium formate in the leachant on the dissolution rate was investigated.

The reaction was monitored by analyzing the effluent from the reactor for total soluble sulfur compounds and calculating the percent sulfur conversion from the original pyrite charge. The results of the experiments under different conditions are summarized in Table 8. The conversions ranged from 35.8 to 93.2%. The rate of dissolution of pyrite as a function of various parameters can be deduced from Figures 3-6 in which the percent sulfur conversion is plotted versus time.

The diagram in Figure 3 depicts the rate of sulfur conversion in the presence and absence of sodium formate in the leaching solution. The two dissolution curves are very similar, indicating that a mixture of sodium formate and sodium carbonate is not significantly more effective than sodium carbonate alone.

The effect of total pressure on the rate of dissolution is shown in Figure 4. As expected, an increase in pressure increased the dissolution rate. At 250 psig. the total sulfur conversion was best, amounting to 93.2% in 1.0 hr.

In Figures 5 and 6 the dissolution of pyrite is presented as a function of particle size at two different pressures. In all cases, a decrease in particle size improved the dissolution rate considerably. This is the normal effect observed in dissolution processes, that the finer the particles the faster the dissolution rate.

Table 8. Chemical leaching of pyrite in a tubular flow-through reactor.
(1.50 ml./sec. flow rate, 150°C, 1 hr. reaction time)

Run No.	Pyrite Charge		Na ₂ CO ₃ Conc., wt.%	O ₂ Rate ml./sec.	O ₂ Press., psia	Total Press., psig	Total Sulfur Conversion, %
	wt., g	Particle Size, Mesh					
22	5	-120/+140	0	13.2	48	100	12.8
33	5	-120/+140	1 ^a	13.2	98	150	81.1
35	5	-120/+140	2	13.2	198	250	93.2
43	5	-60/+80	2	13.2	98	150	61.9
44	5	-80/+100	2	13.2	98	150	65.1
45	5	-60/+80	2	13.2	48	100	35.8
46	5	-80/+100	2	13.2	48	100	48.6
47	5	-120/+140	2	7.9	48	100	65.6
48	5	-120/+140	2	4.4	48	100	69.9
49	5	-120/+140	2	3.04	48	100	72.4
50	10	-60/+80	2	13.2	98	150	56.5
51	25	-60/+80	2	13.2	98	150	57.0
52	10	-80/+100	2	13.2	98	150	67.9
53	25	-80/+100	2	13.2	98	150	72.6
54	5	-120/+140	2	2.0	48	100	65.9
55	5	-120/+140	1.75	13.2	48	100	67.7
56	5	-120/+140	1.5	13.2	48	100	65.3
57	5	-120/+140	1.25	13.2	48	100	64.8
58	5	-120/+140	1.0	13.2	48	100	56.2
59	5	-120/+140	0.75	13.2	48	100	63.5
60	5	-120/+140	0.5	13.2	48	100	61.5
61	5	-120/+140	4	13.2	48	100	63.3
62	5	-120/+140	2	13.2	48	100	61.3
63	5	-120/+140	6	13.2	48	100	62.2
64	2.5	-60/+80	2	13.2	98	150	57.3
65	5	-60/+80	2	13.2	98	150	56.0
66	10	-60/+80	2	13.2	98	150	53.5
67	5	-120/+140	1	13.2	48	100	65.3
68	5	-120/+140	0.75	13.2	48	100	67.3
69	5	-120/+140	0.25	13.2	48	100	62.6
70	5	-120/+140	2	13.2	48	100	70.2
71	5	-120/+140	1.75	13.2	48	100	68.1

^a0.1M Na₂CO₃ + 0.1M NaHCO₂

Figure 3. Effect of substituting sodium formate for part of the sodium carbonate.

Figure 4. Effect of total pressure on sulfur conversion.

Figure 5. Effect of particle size on sulfur conversion at 150 psig.

Figure 6. Effect of particle size on sulfur conversion at 100 psig.

The effect of charge size on the total sulfur conversion is evident in Figure 7. With increasing charge size, the amount of sulfur dissolved decreased. The effect was more pronounced for finer than for coarser particles. Although several possible explanations of this phenomenon are offered below, a definite explanation cannot be offered at this time.

The greater effect of charge size in the case of smaller particles may indicate that the charge size phenomenon is due to hydrodynamic factors. Thus the flow pattern would be affected by charge size and the flow pattern could have more effect on the overall rate of reaction in the case of smaller particles where boundary layer diffusion is more likely to be important. In other words, in the case of larger particles the overall rate of reaction is more likely to be controlled by the rate of diffusion within the individual particles which is not affected by the hydrodynamics of the system.

It is possible that since the leaching solution has better access to finer particles because of greater contact and uniform flow, the fine particles are more readily attacked to form upon leaching even finer, more easily compacted particles. By increasing the charge size, more and more of the leached particles can be compacted into denser aggregates causing a collapse of the flow-through structure of the charge and blocking uniform flow. Thus the overall effect would be a decrease in total sulfur conversion. For coarser particles, on the other hand, where the contact with the solution is poorer to begin with and a non-uniform or channeled flow is initially possible, increasing the charge size would not affect the flow that much more and, hence, the decrease in dissolution rate would not be as great.

Another possible explanation is that with greater charge size any accumulation of inhibiting reaction products within the charge can become greater. In this case, the retention of such products may be better for the finer particles than for the coarser particles; hence the effect of charge size is greater for fine than for coarse particles. A useful experiment would be the analysis of several segments of the residue within the tubular reactor to confirm any differences in the content of pyritic sulfur or the presence of reaction products over the length of the charge in the tube.

The effect of oxygen flow rate on the total sulfur dissolved is shown in Figure 8. From this study, it appears that the optimum oxygen flow rate is approximately 0.004 cu.ft./min., i.e. 3 ml./sec., at which the amount of sulfur converted is maximum. For either higher or lower oxygen flow rates the total sulfur conversion drops off sharply. The decreasing rate of dissolution with increasing oxygen flow rate has been reported previously (1) and attributed to the interference of the gas with good contact between the solid pyrite and the liquid leachant. Below the optimum value of oxygen flow rate, the decrease in sulfur conversion may be caused by a lack of sufficient oxygen to oxidize effectively the pyritic sulfur.

The data presented in Figure 9 show the effect of the concentration of sodium carbonate on the total sulfur conversion. For concentrations ranging from 0.25 to 6% sodium carbonate, the effect does not seem great; the conversions all fall in the range 61.5-70.8%. But the conversion seems to be maximum for

Figure 7. Effect of charge size on sulfur conversion.

Figure 8. Effect of oxygen flow rate on sulfur conversion.

Figure 9. Effect of sodium carbonate concentration on sulfur conversion.

Figure 10. Effect of solids concentration on total recovery.

approximately 2% sodium carbonate, apparently the optimum concentration. Also with no sodium carbonate the conversion is only 13.5%.

Future experiments will include the study of the effect of oxygen flow rate on the dissolution of pyrite of different particle sizes. Also the effect of temperature on the rate of dissolution will be examined more closely. It is hoped that enough meaningful data can be obtained to provide sufficient information to aid in selecting optimum conditions for the conversion of pyritic sulfur into soluble sulfur species.

Froth Flotation

Further attention was devoted to evaluating and developing the froth flotation method of desulfurizing coal.

Froth Flotation Tests

The series of froth flotation tests designed to obtain baseline data on an Iowa bituminous coal with a very high sulfur content was continued. The coal was from the Iowa State University Demonstration Mine in Mahaska County, Iowa. The sample was collected at the Iowa State University coal preparation plant and represented some of the fines produced during crushing. This material contained 7.0% pyritic sulfur, 8.9% total sulfur, and 24% ash; it had the following size distribution:

<u>Tyler Screen, Mesh</u>	<u>Mat'l. Retained, wt.%</u>	<u>Mat'l. Passing, wt.%</u>
48	0.0	100.0
60	6.1	93.9
100	33.2	66.8
200	65.5	34.5
325	92.2	7.8

Although the 48 mesh x 0 material was used as is for some of the flotation tests, part of the material was separated by screening into various size fractions for use in other flotation tests. The composition of these different size fractions is shown below.

<u>Size Fraction, mesh</u>	<u>Ash, wt.%</u>	<u>Sulfur, wt.%</u>	
		<u>Pyritic</u>	<u>Total</u>
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

These data indicate that the pyrite tended to concentrate in the 200 mesh x 0 size fraction.

The flotation tests were carried out as before with a Denver D-1 laboratory-size 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 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 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 in a series of fractions until a clean froth was produced. The solids in each fraction were recovered separately, dried, weighed, and analyzed for total sulfur and ash.

In the first series of tests the pulp density was varied to determine its effect on coal recovery and flotation selectivity. Different runs were made using 1, 2, 5, and 10% solids in the pulp. The 48 mesh x 0 material was used for these runs. The amount of MIBC used in each run corresponded to 0.23% of the weight of coal used. For a pulp with 5% solids this amounted to 0.25 ml. MIBC. Most of the runs were made with a flotation cell tank which held 3100 ml., but for the run involving 1% solids, a tank which held 5700 ml. was used and correspondingly larger volume of pulp. The results of these runs show that the total recovery of coal increased with initial solids concentration (Figure 10). Thus 88% of the solids was recovered altogether in the float product during a run made with an initial solids concentration of 10% but only 67% was recovered during a run with an initial solids concentration of 1%. On the other hand, the initial solids concentration in the range of 2 to 10% seemed to have little effect on the selectivity of the separation (Figure 11). Although the results with 1% solids were noticeably different than with higher concentrations, the difference may not have been due altogether to a difference in pulp density since a larger volume of pulp was used in the case of the run made with 1% solids. While the data plotted in Figure 11 indicate that a reasonably good separation of coal from ash was obtained when the recovery of product was modest, they also indicate that the separation of coal from pyrite was very poor even when the recovery of product was low. In other words, the total sulfur content of the first fraction floated was not much lower than that of the feed and in the case of the 1% slurry it was the same as that of the feed.

In the second series of tests both the coal particle size and the concentration of MIBC were varied. Different runs were made with the three different size fractions of coal described above as well as with different amounts of MIBC. All of the runs were made with the same volume of pulp (2500 ml.) and pulp density (5% solids). The results of these runs were not much different than the results described above for the unsized material. Also there was little difference in the results between the various size fractions of material (Figures 12 and 13). However, the selectivity of the separation of coal from both pyrite and ash did improve slightly as the concentration of MIBC was reduced.

For the third series of tests 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. Different runs were made with this material using two different concentrations of MIBC. These runs were made under similar conditions starting with 2500 ml. of pulp and 5% solids in the pulp. The results of the runs with 325 mesh x 0

Figure 11. Effect of solids concentration on selectivity.

Figure 12. Effect of particle size and frother concentration on selectivity of sulfur removal.

Figure 13. Effect of particle size and frother concentration on selectivity of ash removal.

coal are shown together with the results obtained with 48 mesh x 0 coal in Figure 14. It can be seen that grinding the coal to a very fine size did not improve the separation of coal and pyrite by froth flotation and it decreased the separation of coal and ash. These results suggest that fine grinding may produce more colloidal size mineral matter which is entrapped by the froth and therefore it is counterproductive.

In the fourth series of tests the effects of adding a small amount of aluminum nitrate together with different concentrations of MIBC were investigated. For each run 0.5 ml. of a 1.0% solution of aluminum nitrate was added to the pulp before the MIBC was added. The unsized 48 mesh x 0 coal was used for this series of runs and an initial solids concentration of 5% and pulp volume of 2500 ml. were also used. The results of these runs (Figure 15) were similar to the results of earlier runs made without aluminum nitrate. Also for these runs, the results did not appear to be affected significantly by changes in the concentration of MIBC.

For the particular coal under investigation, none of the standard measures has resulted in an effective separation of coal and pyrite by froth flotation. Another possible variation in the method which merits testing is the application of milder agitation and aeration. However, the unpromising results obtained so far suggest that conventional froth flotation techniques are insufficient and that more sophisticated techniques are required.

Floatability of Coal or Pyrite

An investigation of the relative floatability of coal or pyrite in the presence of various flotation reagents was continued. Measurement of the relative floatability was done with a modified Hallimond tube microflotation cell. The cell and experimental procedure used were described in a previous report (2). The coal was from the Iowa State University Demonstration Mine in Mahaska County, Iowa, and the pyrite was recovered by hand-picking from the University preparation plant tailings produced in treating similar coal. The coal was prepared by crushing and then floating in a solution of tetrachloroethylene and hexane having a specific gravity of 1.30. The float fraction was ground and screened to provide -80/+100 mesh material for the floatability measurements. The hand-picked pyrite was also ground and screened to provide material of the same size.

Previous measurements of the zeta potential of coal and pyrite in the presence of a dilute solution of ferric chloride had indicated that a separation of these solid species might be obtained by using a cationic collector in an intermediate range of pH where the coal should bear a negative charge and the pyrite a positive charge (1). In order to test this hypothesis, the relative floatability of the prepared coal and pyrite in the presence of ferric chloride and pyridine (a potential cationic collector) was measured at different pH. For this series of measurements, 2.0 g. of coal or pyrite was first mixed with 25 ml. of a dilute solution of ferric chloride (10^{-4} mole/L.); the pH of the suspension was adjusted next by adding 0.2N sodium hydroxide. Then, 0.01 ml. of pyridine and 75 ml. of the dilute ferric chloride solution were added to the suspension. After this preparation, the suspension was treated in the microflotation cell for 4 min., and the percentage of the material which floated

Figure 14. Fine grinding resulted in poorer selectivity.

Figure 15. Results of froth flotation tests made with aluminum nitrate.

measured. Another series of measurements was made using similar conditions except that ferric chloride was omitted from the system.

The results presented in Figure 16 show that the relative recovery of coal was variable but reasonably good and the relative recovery of pyrite was fairly low over the applied range of pH. Since the recovery of coal was higher than obtained previously without a collector, it appears that pyridine may serve as a collector for coal. On the other hand, the recovery of coal with pyridine was not as good as that obtained previously with the same amount of MIBC (1). But whereas MIBC also enhanced the recovery of pyrite, pyridine did not. Moreover it appears that when pyridine was used in conjunction with ferric chloride, the recovery of coal was improved while the recovery of pyrite was diminished.

Although these preliminary results are interesting, further experiments must be performed to verify the apparent trends. Also other potential cationic flotation collectors should be tested.

Selective Oil Agglomeration

The experimental development of the selective oil agglomeration method of cleaning and recovering fine-size coal was continued. Small-scale laboratory experiments were conducted to demonstrate the effectiveness of a unique chemical pretreatment process for improving the separation of coal and pyrite by this method and to compare the efficiency of various grades of fuel oil for agglomeration. Run of mine coal from the Iowa State University Demonstration Mine was used for these experiments after it was crushed to 1/4 in. top size by passing it through a bench-scale double roll crusher. This material contained 19.7% ash and 6.47% total inorganic sulfur (pyritic plus sulfate forms).

For the first set of experiments the coal 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.

Figure 16. Relative recovery of coal or pyrite measured with a microflotation cell.

The results of the first set of experiments are listed in Table 9. 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 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%.

Table 9. Results of oil agglomeration tests with different types of fuel oil.

Treatment	Fuel Oil No.	Yield, %	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		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.

For the second set of experiments, the crushed run of mine coal 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 agglomerants. The agglomerants were placed back in the blender along with 500 ml. of deionized water and agitated for 5 min. more. The agglomerants 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 are shown in Figure 17. These indicate 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. Although the agglomeration of ball milled and chemically pretreated coal seemed more difficult than the agglomeration of coarser material, relatively high yields and good sulfur reductions were obtained. It should be noted, however, that the No. 6 heavy fuel oil was cut with some lighter No. 200 LLS fuel oil to facilitate the agglomeration operation. Even though the final product was washed with acid, it still had a higher sodium content (0.06 wt.%) than the feed (0.03 wt.%). Again the results of duplicate runs carried out under the same conditions were quite close (Figure 17). While the total sulfur reduction obtained by chemical pretreatment and oil agglomeration was not as great as that obtained above by combining these operations with gravity separation, the product yield was much higher.

Optimum yield and sulfur reduction for the given coal will likely result from conducting the initial float/sink separation at a higher specific gravity than was used in the first set of experiments followed by ball milling, chemical pretreatment, and oil agglomeration.

Further experiments are planned to study the effects of different parameters on both the chemical pretreatment and oil agglomeration steps.

Pelletization

A more extensive review of the technical literature on pelletization was completed. The same conclusion was reached as before that the disc pelletizer is the best suited type of pelletizer for coal fines. A variable diameter, rotating disc pelletizer is being fabricated in house. This unit will be installed in the bench-scale flow system for demonstrating the recovery and beneficiation of coal fines.

Figure 17. Yield and reduction in ash and inorganic sulfur contents of pretreated and agglomerated coal.

Continuous Processing of Fine Coal

Minor changes were made in the flow-sheet for the bench-scale flow system which is designed to demonstrate the froth flotation, selective oil agglomeration, and pelletization methods of cleaning and recovering fine coal. These changes are incorporated in Figure 18. The system includes a pretreatment section for grinding and chemically treating coal to enhance the separation of coal and pyrite.

The design and construction schedule for the system is presented in Table 10. Major items of equipment are on order and will be delivered before the end of September. Construction of the steel supporting structure is underway. Equipment will be installed as it is received and process piping and wiring will be installed during October and November. Construction should be completed during December.

Neutron Source for Sulfur Monitoring Instrument

Information for the design and specification of a thermal neutron sulfur monitoring instrument has been collected and the design could be completed by Spring, 1978, pending the availability of funds. The instrument could be assembled and placed in the Iowa State University Coal Preparation Plant during 1978. Preliminary results obtained with reactor thermal neutrons indicate that this type of instrumentation should be highly successful in a multi-stream operation. Moisture and bulk density measurements can be taken as well.

The advantage of this monitor over other neutron monitors which employ ^{252}Cf as the neutron source is derived from the pre-thermalization of the neutrons, which allows for the direct analysis of the process stream, rather than a side stream, and is not affected by variations in moisture or bulk density of the sample.

Further work on this part of the program is dependent on additional funding.

Figure 13. Bench-scale system for demonstrating the continuous processing of fine coal.

Table 10. Revised design and construction schedule for bench-scale flow system

	wk 77	Engineering	Drafting	Steel Fabrication	Electrical	Erection
Jan	10 17 24 31	Conceptual Analysis Flow Sheet Design				Froth Cells Del.
Feb	7 14 21 28	Structural Design Construct Model	Draft Struct. Steel			
Mar	7 14 21 28	Equipment Specs. ↓ ↓	↓ ↓		Equipment Spec. ↓ ↓	
Apr	4 11 18 25			Begin Steel Fabr.		
May	2 9 16 23 30	↓ ↓			↓ ↓	Steel Delivered Emulsifier Del.
Jun	6 13 20 27	90% of Major Equip. on Order Equip.Spec.Deadline	Begin Drafting Process Plumbing & Special Equip. ↓ ↓	Steel Fabr. Compl.	Equip. Specs. Deadline	Bgn. Erect. Steel and Tanks Initial Erect. Compl.
Jul	4 11 18 25	Equip. Order Dead.	↓ ↓	Fabricate Process Sheet Metal and Special Equip. ↓ ↓		Install Catwalks & Equip. Del. to Date ↓ ↓
Aug	1 8 15 22 29					
Sep	5 12 19 26					
Oct	3 10 17 24 31				Electrical Install	Install Remaining Process Equip. Install Process Plumbing ↓ ↓
Nov.	7 14 21 28					
Dec	5 12 19 26					Equip. Testing & Shakedown System Complete

Characterization of Coal Microstructure

by

Raymond T. Greer

Scientific Background

Studies on Iowa coal (2-6) have provided a basis for recognizing the presence and distribution of pyrite (the primary sulfur bearing phase in coal) in coal seams for pyrite particles as small as submicrometers in diameter. The significance of the sizes and occurrence of different forms of pyrite (colloidal size single crystals, framboids . . . various size agglomerations of single crystals, and larger pyrite masses) bears on the potential analytical uncertainties in sulfur analyses of coal. Distribution data of pyrite among various forms of pyrite and of pyrite particle sizes are available for two complete Iowa coal channel sample examples, the Lovilia mine and the Star mine (2). It will be shown that for this high volatile C bituminous coal the organic sulfur determination is well within the ASTM error tolerance levels and that the determinations are accurate and precise for this rank of coal. Uncertainties in the chemical analyses for any of the forms of sulfur take on great importance as they relate to standards which may actually vary throughout the U.S. depending on the coal burned and the way that the sulfur is distributed in the fuel.

Objectives

The objectives to be considered in this portion of the investigation include:

- (1) clarification of the relative proportionation of organic and inorganic sulfur in coal as this influences subsequent choice of treatments in desulfurization and in conversion in the production of fuel and
- (2) examination of how the presence and distribution of pyrite forms less than 250 μ m in diameter may influence the accuracy of standard ASTM tests for the determination of sulfur in coal.

Technical Approach

Sulfur data have a high priority in the evaluation of coals. The total sulfur value is commonly specified, and three other types of sulfur values may be reported: pyrite sulfur, sulfate sulfur, and organic sulfur. Sulfate sulfur is generally very low. Organic sulfur is computed (not chemically determined) simply by subtracting the sum of the pyrite and sulfate sulfur from the total sulfur concentration (7) (American Society for Testing Materials D271, D2492-68; reapproved 1974). An outline of this analysis is presented in Figure 19. Two features are of particular interest: 1) the determinations are performed on 1 g. amounts of coal, and, 2) the coal is pulverized to pass a 60 mesh sieve, that is, a particulate size $\leq$ 200 μ m.

ANALYSIS OF SULFUR IN COAL
[ASTM D271, D2492-68 (REAPPROVED 1974)]

SULFATE SULFUR DETERMINATION:

SULFATE SULFUR IS SOLUBLE
IN DILUTE HCl (2:3 H₂O)

PYRITIC AND ORGANIC FORMS
OF SULFURS ARE INSOLUBLE
IN DILUTE HCl

PYRITIC SULFUR DETERMINATION:

BOTH SULFATE AND PYRITIC SULFUR
ARE DISSOLVED IN HNO₃ (1:7 H₂O);
THEREFORE THE TITRATION MUST BE
PERFORMED WITH RESPECT TO IRON.

THE DIFFERENCE BETWEEN THE NITRIC ACID
AND HYDROCHLORIC ACID SOLUBLE IRON IS
THE IRON COMBINED IN THE PYRITE FORM

TOTAL SULFUR DETERMINATION:

ESCHKA MIXTURE IS 2 MgO + Na₂CO₃

(1/2 to 3/4 HOUR; STIR)

TOTAL SULFUR IS CALCULATED FROM
THE WEIGHT OF THE BARIUM SULFATE
PRECIPITATE

ORGANIC SULFUR DETERMINATION:

$$\text{ORGANIC SULFUR} = \text{TOTAL SULFUR} - [\text{PYRITIC SULFUR} + \text{SULFATE SULFUR}]$$

* ALL COAL IS PULVERIZED TO PASS 60 MESH; THAT IS, PARTICULATE SIZE ≤ 250 μm

Figure 19. Summary of the ASTM methods for sulfur determination.

Total sulfur is determined by heating coal combined with Eschka's mixture. This mixture is then leached with hot water to remove sulfur. This solution is made acid. The sulfur is oxidized to sulfate with bromine water, and precipitated and weighed as barium sulfate. The total sulfur is calculated from the weight of barium sulfate.

Sulfate sulfur is determined by refluxing coal with hydrochloric acid. The sulfate dissolves in the acid. It is then precipitated with barium chloride and weighed as barium sulfate. Sulfate sulfur is soluble in hydrochloric acid; pyritic and organic forms of sulfur are insoluble.

Pyrite sulfur is determined by extracting a weighed sample of coal with nitric acid followed by a titrimetric determination of iron in the extract as a measure of pyritic sulfur.

Organic sulfur is determined by subtracting the sum of sulfate sulfur and pyritic sulfur from the total sulfur.

Limits of repeatability for the ASTM methods (7) for results of consecutive determinations carried out on the same sample in the same laboratory should not differ more than the following:

Sulfate sulfur	0.02
Pyritic sulfur, under 2%	0.05
Pyritic sulfur, 2% or more	0.10

However, a question of accuracy exists concerning the complete removal of finely-dispersed pyrite by extraction with nitric acid. Incomplete removal would yield low pyritic sulfur values and erroneously high organic sulfur values. Initial results to examine this question are presented in the following discussion.

In Figure 20, several continuous strips of micrographs are shown for the lower seam of the Mich mine (strip mine; Iowa). The photo columns are continuous, and should be considered from left to right as a series. Pyrite is distributed on a fine scale, and pyrite crystals and framboids are seen to occur at various locations with depth for this portion of the seam. The scale bar is 40 μ m, and in examining the seam over continuous regions of 250 μ m (60 mesh sieve passes particles $\leq$ 250 μ m in diameter) it is clear that the pyrite is distributed on a finer scale. It might not leach out (refer to pyritic sulfur determination in Figure 19), and if not, this would contribute to an erroneous organic sulfur determination. Figure 20 presents a basis to consider the significance of the details of the pyrite distribution with depth and the effectiveness of nitric acid dissolution of the pyrite.

Examination of the residue from samples which had been leached with nitric acid (ASTM method) show that potential uncertainties are associated with organic sulfur values. In Figure 21, for example, an incompletely leached framboid (agglomerate of pyrite crystals in a berry-like form) is seen (3,6). Other complementary detailed energy dispersive X-ray microanalyses have established the presence of pyrite in the residues on the basis of the $Fe_{K\alpha}$ and $S_{K\alpha}$

Figure 20. Microstructural features of coal in a Mich mine channel sample. At 16mm below the top of the lower coal seam (starting at the top left photo column), a region of little pyrite is seen, followed by pyrite concentrations of framboids and single crystals (the third column, for example). Scale bar is 40 μ m.

Figure 21. Scanning electron micrograph of residue of Star mine coal from HNO_3 treatment to dissolve pyrite (ASTM method). The spherical form in the lower left quarter of the micrograph is an incompletely leached pyrite framboid (3). Scale bar is $3\mu\text{m}$.

characteristic X-ray fluorescence radiation detected on a point-by-point basis from the specimen and correlated with microstructural evidence (scanning electron microscope images such as Figure 21).

To examine the effectiveness of the dissolution in more detail, residues of coals leached with nitric acid (ASTM method) were mounted in plastic, polished to reveal cross sections through the coal particles and examined with the scanning electron microscope and with an optical microscope (reflected light). In this way bright areas were subsequently located, indicating the possible presence of undissolved pyrite within coal particles. Further specific evidence to confirm that pyrite was present in a particular location was developed by energy dispersive X-ray microanalysis on a micrometer scale. This provided the capability to monitor both sulfur and iron at a point and to correlate this with the microstructural information provided by reflected light microscopy and scanning electron microscopy.

Figure 22. Coal particle from the Star strip mine in Iowa (2,6) which was treated with HNO_3 (ASTM method). This view is a polished cross section seen in reflected light in an optical microscope. The central bright spherical feature is an undissolved pyrite framboid. Scale bar is $9\mu\text{m}$.

In Figure 22, the central bright circular feature (approximately $7\mu\text{m}$ in diameter) is a framboid which was not leached by the HNO_3 . The particle is $54\mu\text{m}$ from the surface of the coal which was in contact with the nitric acid (this surface begins right at the lower left corner of the micrograph). In Figure 23, a pyrite framboid is seen in a cross sectional view where the framboid is located approximately $30\mu\text{m}$ from the surface which was in contact with nitric acid (ASTM method). Figure 24 shows the associated energy dispersive X-ray microanalysis for this pyrite framboid. The iron and sulfur peaks confirm the identification of pyrite (the Cu, Si, Al, etc. are associated with the polishing compounds or mounting material used in preparing the specimen mount).

Earlier investigations (8-11) of higher rank coals (predominantly in Britain) did not have the microchemical-microstructural analytical capabilities which the current scanning electron microscope/energy dispersive X-ray analysis systems offer; however, several investigators (9) indicated the value of crushing coal specimens to less than $20\mu\text{m}$ to ensure complete decomposition of the pyrite. These instruments provide a distinct microscale analytical advantage. (The first commercial scanning electron microscopes were available in the United States in 1967; suitable high resolution energy dispersive X-ray

Figure 23. Cross section of a coal particle from the Star mine. Reflected light optical microscope image. Bright circular form is pyrite. Each small division corresponds to $3.3\mu\text{m}$. The pyrite framboid is approximately $30\mu\text{m}$ in the interior of the coal particle. The mounting material is on the left, and the coal is on the right.

Figure 24. Energy dispersive X-ray analysis spectrum showing the sulfur and iron peaks of the pyrite framboid seen in Figure 23. Point analysis. (High resolution X-ray analysis system utilized; 147 eV FWHM on Fe.)

analysis systems became available approximately 3 or 4 years ago.) The evidence indicates that a significant amount of pyrite may be missed (up to 20-30 wt.% in high rank coals). Subsequent recent work on U.S. coal by Levinson and Jacobs (12) at General Electric using Mössbauer spectroscopy (upper Freeport, Pennsylvania bituminous coal) indicates that the standard wet chemical technique may be inaccurate by up to 20%.

To test the level of uncertainty in organic sulfur determinations for the Iowa coals (high volatile C bituminous), the following detailed analyses were performed for strip mine and shaft mine specimens. In this case, two sets of specimens were of interest:

(1) Coal particles remaining as a residue after completion of the standard ASTM sulfur determinations, and (2) coal particles less than 60 mesh which were allowed to stand in nitric acid (1 HNO₃:7 H₂O) for 24 hr. (refer to Figure 19). Subsamples from these sets for several mines were then mounted in two ways: (1) in Lucite, and (2) in a copper-filled, diallyl phthalate mounting medium (provided a superior mount to avoid charging problems due to the interaction of the electron beam from either the scanning electron microscope or the electron microprobe X-ray analyzer). These mounts were then polished using 6, 1 and 1/4 μ m diamond paste to reveal cross sections through the particles. This polishing procedure was adopted to avoid Si or Al contamination from small particles of carbide (SiC) or oxide (Al₂O₃) polishing materials. The particle cross sections were numbered for identification and total areas were analyzed for coal compared with pyrite. Every crystal encountered on these polished surfaces was analyzed for the possibility of being pyrite down to the size of 0.5 μ m in diameter (or somewhat smaller).

For the level of pyrite shown to be present by standard ASTM analyses (a typical pyritic sulfur value was taken as 4 wt.% sulfur) a simple calculation shows that 1/40 of the pyrite crystals originally present can be left in the coal after the etching treatment and still fall within the analytical tolerance limits. If this pyrite is considered to be distributed throughout a centimeter cube of the coal, 5 μ m² of pyrite for each 10,000 μ m² of material could be detected in area analyses of the etched material as a maximum amount to still stay within the analytical limits of repeatability for the initial high level of sulfur.

Pyrite was found (for example, Figures 21-23); however, the amounts were of little importance. The amounts found were always below 1/50 of the limit of 5 μ m² of pyrite per 10⁴ μ m² of the material. Evidence for the complete removal of the pyrite is seen in the cross sectional polished sections. For example in Figures 25 and 26, the cast of a dissolved framboid is outlined in the coal. Several of the bright spots in the polished coal particles shown in Figure 25 correspond to empty cavities which contained pyrite framboids prior to nitric acid treatment. One of these is shown at higher magnification in Figure 26.

The high volatile C bituminous coal of Iowa is well characterized for sulfur (including organic sulfur) by the standard ASTM chemical tests. The analyses are well within the analytical tolerances. (This is consistent with the British findings (8,10) for this relatively low rank of coal.) The sulfur determinations are both accurate and precise when performed by competent analysts.

Figure 25. Polished coal samples from the Star mine, Iowa. Particles are < 60 mesh and prior to polishing to reveal cross sections, they were treated with nitric acid as specified in the ASTM test for pyritic sulfur. The particles are mounted in the copper filled diallyl phthalate mount. Several bright areas are seen, corresponding to cavities where pyrite framboids were removed due to the acid treatment. The central bright circular feature (framboid cavity) is seen at higher magnification in Figure 26. Scale bar is 50 μ m.

Figure 26. Framboid cavity. The surface detail shows the location of the other (micrometer size) pyrite crystals of the framboid prior to nitric acid treatment and removal. A lower magnification view is shown in Figure 25. Scale bar is 2 μ m.

Experimental Programs in Progress and Planned

Additional studies are in progress to assess the influence of maceral type surrounding the pyrite and of rank on the dissolution characteristics of the pyrite. Stains, such as malachite green (oxalate), may aid in discriminating the rim of penetration of the nitric acid into the coal particles. Pyrite distribution information will be assembled for a variety of higher rank U.S. coals to test the applicability of the British observations that there may be a significant uncertainty for sulfur analyses for high rank coals.

CONCLUSIONS

Several advances were made in the development of various methods for desulfurizing and recovering coal. Thus it was demonstrated by means of laboratory experiments that most of the inorganic sulfur was removed from several high sulfur bituminous coals by chemical leaching with hot aqueous solutions containing both dissolved oxygen and sodium carbonate. In some cases significant amounts of organic sulfur were also extracted, particularly at higher temperatures and/or higher oxygen partial pressures. In other experiments where pyrite particles alone were leached it was shown that the rate of conversion of pyrite to soluble sulfates is increased by increasing the oxygen partial pressure or reducing the particle size. Although the rate of conversion does not seem to be greatly affected by alkali concentration, the rate does appear to be a maximum when a concentration of 2.0 wt.% sodium carbonate is used. Also there appears to be an optimum flow rate of oxygen when pyrite particles are leached in a fixed bed tubular reactor.

The inadequacy of conventional froth flotation as a means for desulfurizing coal was further demonstrated by laboratory testing. On the other hand, preliminary measurements of the relative floatability of coal or pyrite particles in the presence of trace amounts of pyridine, a potential cationic collector for coal, were encouraging.

The effectiveness of an oxidative chemical pretreatment process as a means for improving the subsequent separation of coal and pyrite by selective oil agglomeration was demonstrated. The pretreatment mixture includes an alkali such as sodium carbonate. The optimum concentration of this alkali was shown to be about 1.0 wt.%. It was also shown that the relatively heavy No. 5 and No. 6 fuel oils as well as the lighter fuel oils can be used for agglomerating chemically pretreated coal. However, the heavier oils are not as effective with respect to sulfur removal as the lighter oils. Also the heavier oils seem to require some dilution with a lighter oil in order to agglomerate finely ground coal.

Major items of equipment were placed on order for the bench-scale flow system which will demonstrate the beneficiation and recovery of fine-size coal by various methods. Construction of the steel supporting structure was started. Construction of the entire system should be completed by December.

The claimed accuracy of the ASTM wet chemical method for determining pyritic sulfur in coal was confirmed for Iowa high volatile C bituminous coals. Confirmation was obtained by scanning electron microscope/energy dispersive X-ray analyses of appropriate specimens.

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