ADVANCED DEVELOPMENT OF FINE COAL
DESULFURIZATION AND RECOVERY TECHNOLOGY

Quarterly Technical Progress Report
October 1, 1976 to December 31, 1976

Division of Materials & Exploratory Research

By

Ray W. Fisher and Thomas D. Wheelock

Ames, Laboratory, ERDA
Iowa State University
Ames, Iowa 50011

MASTER

Date Published - February 1977

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights

PREPARED FOR THE ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
UNDER CONTRACT NO. W-7405-eng-82

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

pg

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Available from: National Technical Information Service
U. S. Department of Commerce
P.O. Box 1553
Springfield, VA 22161

Price: Microfiche \$3.00
Paper Copy \$4.50

TABLE OF CONTENTS

	<u>page</u>
ABSTRACT	1
OBJECTIVES AND SCOPE OF WORK	2
Background	2
Objectives	2
Task A. - Chemical Desulfurization	3
Task B. - Froth Flotation	3
Task C. - Selective Oil Agglomeration	3
Task D. - Pelletization	3
Task E. - Continuous Processing	3
Task F. - Coal Microstructure	4
Task G. - Neutron Source for Sulfur Monitoring Instrument	4
SUMMARY OF PROGRESS TO DATE	4
DETAILED DESCRIPTION OF TECHNICAL PROGRESS	6
Chemical Desulfurization	6
Technical Assessment	6
Experimental Program	9
Froth Flotation	11
Technical Assessment	12
Experimental Program	13
Froth Flotation Tests	13
Zeta Potential	18
Zeta Potential Measurements	19
Microflotation Experiments	24
Flotation After Chemical Pretreatment	30
Selective Oil Agglomeration	31
Technical Assessment	31
Experimental Program	33
Pelletization	34
Technical Assessment	35
Demonstration	36
Continuous Processing of Fine Coal	36
System Description	37
Construction Schedule	39
Experimental Program	39
Neutron Source for Sulfur Monitoring Instrument	39
Characterization of Coal Microstructure	41
CONCLUSIONS	56
LITERATURE CITED	57

FIGURES

	<u>page</u>
Figure 1. Tubular reactor system for investigating chemical desulfurization.	10
Figure 2. Effect of frother concentration on the recovery of coal by froth flotation.	15
Figure 3. Cumulative results of froth fractionation experiments.	16
Figure 4. Average ash content of cumulative fractions recovered during froth fractionation experiments.	17
Figure 5. Zeta potential of coal and of pyrite isolated from coal in aqueous suspensions.	20
Figure 6. Different pH regulators affected the zeta potential of pyrite differently.	20
Figure 7. Ferric chloride had a greater effect on the zeta potential of pyrite than on that of coal.	22
Figure 8. Sodium cyanide seemed to affect the zeta potential of coal and pyrite similarly.	22
Figure 9. Sodium carbonate affected the zeta potential of pyrite much more than it affected the zeta potential of coal.	23
Figure 10. These results indicate that a negative anion of EDTA was adsorbed equally well over a wide pH range.	23
Figure 11. Ammonium thiocyanate affected the zeta potential of coal and pyrite differently whereas diammonium citrate affected the zeta potential of both similarly.	25
Figure 12. Modified Hallimond tube microflotation cell used for measuring the floatability of coal or pyrite.	26
Figure 13. The relative recovery of pyrite in microflotation experiments exhibited the same trends with pH as the zeta potential exhibited with pH.	28
Figure 14. Ferric chloride suppressed the flotation of pyrite in the pH range of 5 to 10.	28
Figure 15. Sodium cyanide served to suppress the flotation of pyrite.	29
Figure 16. The disodium salt of EDTA tended to suppress the flotation of pyrite over a pH range of 3 to 7.	29

Figure 17.	Ammonium thiocyanate suppressed the flotation of pyrite over a pH range of 4 to 8.	29
Figure 18.	Bench-scale system for demonstrating the continuous processing of fine coal.	38
Figure 19.	Distribution of pyrite in the Lovilia mine seam among three forms: single crystals, framboids, and other larger, massive forms.	43
Figure 20.	Distribution of pyrite in the Star strip mine seam among three forms: single crystals, framboids, and other larger, massive forms.	44
Figure 21.	Proportionation of pyrite for the various size ranges observed for the Lovilia mine.	46
Figure 22.	Proportionation of pyrite for the various size ranges observed for the Star mine.	46
Figure 23.	The distribution of single crystals of pyrite in the Lovilia mine with depth in the seam.	47
Figure 24.	The distribution of framboidal formations of pyrite in the Lovilia mine with depth in the seam.	48
Figure 25.	The distribution of the pyrite category, "other larger, massive forms", in the Lovilia mine with depth in the seam.	49
Figure 26.	The distribution of total pyrite (total contribution of the three forms: single crystal, framboids, and other larger, massive forms) in the Lovilia mine with depth.	50
Figure 27.	The distribution of single crystals of pyrite in the Star mine with depth in the seam.	51
Figure 28.	The distribution of framboidal formations of pyrite in the Star mine with depth in the seam.	52
Figure 29.	The distribution of the pyrite category, "other larger, massive forms", in the Star mine with depth in the seam.	53
Figure 30.	The distribution of total pyrite (total contribution of the three forms: single crystal, framboids, and other larger, massive forms) in the Star mine with depth.	54

TABLES

	<u>page</u>
Table 1. Design and construction schedule for flow system.	40
Table 2. Distribution of pyrite among various forms.	42
Table 3. Proportion of pyrite in certain size ranges.	45

ABSTRACT

The improvement and technical development of several promising methods for desulfurizing and recovering fine coal are well underway. 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 under pressure. A preliminary assessment of the state of the art has been made through field visits and review of the technical literature. Equipment and apparatus have been assembled for small-scale laboratory experiments in the areas of froth flotation, oil agglomeration and chemical desulfurization, and experimental work in these areas has been initiated. Preliminary froth flotation tests have been carried out on an Iowa coal with a sulfur content to establish baseline data. Quite unexpectedly these tests indicated that aluminum nitrate may be an activator for coal because it served to increase the recovery of coal. Several potential flotation depressants for pyrite have been screened by measurement of the zeta potential and floatability of pyrite or coal in aqueous suspensions containing the potential depressants. The following reagents show some promise as pyrite depressants: ferric chloride, sodium cyanide, ammonium thiocyanate, and the disodium salt of ethylenediaminetetraacetic acid. Preliminary plans have been prepared for a continuous flow bench-scale system to demonstrate the improved physical beneficiation and recovery of fine coal. This system will include equipment for grinding and pretreating the coal as well as equipment for demonstrating froth flotation, selective oil agglomeration and pelletization. An investigation of coal microstructure as it relates to coal beneficiation methods has also been initiated. The distribution of various forms of pyrite by size and crystal structure has been determined for two channel samples of coal through application of scanning electron microscope techniques.

OBJECTIVES AND SCOPE OF WORK

Background

The development of technology for desulfurizing and recovering fine coal is needed for the economical utilization of most of the high sulfur coal in the United States. Present coal preparation methods are simply inadequate for dealing with fine coal and yet it appears that much high sulfur coal could be more thoroughly desulfurized by first reducing it to a fine size. Such size reduction is required to liberate finely disseminated mineral particles including sulfur-bearing pyrites so that these impurities can be removed by physical means or to render the various forms of sulfur in coal accessible to chemical attack. But due to the present state of technology, the processing of fine coal is avoided as much as possible. In present coal preparation plants, fine coal is often lost or wasted, and if it is recovered, it is not adequately desulfurized.

Several methods have been identified as holding great promise for the desulfurization and recovery of fine coal. These methods include froth flotation, selective oil agglomeration, pelletization, and chemical desulfurization by a unique process. There is a strong possibility that froth flotation and oil agglomeration can be improved and developed to the point where they can be used in conjunction with other physical separation methods to remove most of the inorganic sulfur and ash from very dirty coals while recovering most of the combustible matter. Also there is a strong possibility that chemical desulfurization can be developed to remove a significant portion of the organic sulfur as well as virtually all of the inorganic sulfur in coal. With the advent of such developments it should become possible to prepare a much higher percentage of U.S. coals for direct combustion use than is now possible and obviate the need for stack gas scrubbing and other special means of controlling air pollution. Furthermore, such developments could lead to the more economical conversion of coal into liquid and gaseous fuels. Thus the extraction of most of the sulfur and mineral matter ahead of typical coal conversion processes could greatly reduce the burden of separating ash and sulfur at later stages in these processes.

The present investigation deals with the improvement and development of the specific methods cited above for desulfurizing and recovering fine coal as well as with the development of a neutron source for a coal sulfur monitoring instrument which can be used for the control of coal preparation plants. The investigation also involves characterization of the coal microstructure as it relates to the development of improved desulfurization methods.

Objectives

The primary objective of this project is to improve and develop specific methods and processes for the industrial desulfurization and recovery of fine coal. These methods include froth flotation, selective oil agglomeration, pelletization, and a unique process for chemical desulfurization. A secondary objective is to develop a neutron source for a coal sulfur monitoring instrument. These objectives are 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 in small-scale laboratory reaction systems. This process involves leaching fine-size coal with a hot, dilute solution of sodium carbonate containing dissolved oxygen under pressure. Experiments are to be conducted to measure the conversion and extraction of various forms of coal sulfur, rate of desulfurization, and recovery of combustible matter. The effects of important process parameters such as temperature, oxygen partial pressure, alkali concentration, and particle size are to be investigated. The applicability of the process to various types of coal and lignite is to be tested.

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 increase the dissimilarity in surface properties of coal and pyrite and by improving the liberation of pyrite through selective grinding or chemical comminution. A number of chemical reagents which may alter the surface of pyrite through selective adsorption and thereby serve to depress the pyrite in flotation practice are to be screened by measurement of the zeta potential and floatability of treated particles. The floatability is to be determined with a microflotation cell. Also a promising chemical treatment which appears to convert the surface of pyrite to a water avid surface and thereby serve to depress the pyrite is to be tested. Promising treatments are to be applied to various types of coal which are then processed in a laboratory flotation cell to measure the effectiveness of the treatment.

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. Laboratory tests are to be conducted to determine the factors which control the separation of coal and pyrite and to determine the factors which control agglomerate size, strength, and propensity for dewatering. A promising chemical treatment which appears to convert the surface of pyrite to a water avid surface and thereby make the pyrite less likely to be agglomerated with the coal is to be tested. Promising techniques are to be applied to various types of coal to demonstrate general utility.

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. Different binders and methods of applying these binders are to be tested. Also the effects of various operating parameters such as binder concentration, coal particle size, moisture content and feed rate, on resultant pellet size, strength, and moisture content are to be determined.

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. This system is to include equipment for grinding and chemically pretreating coal as well as for demonstrating the other operations. Basic improvements in the indicated beneficiation methods which are developed through smaller scale laboratory experiments are to be demonstrated with the continuous flow system.

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. Microstructural information on a micrometer size scale is to be correlated with microchemical information determined by energy dispersive X-ray microanalysis to establish the presence and size distribution of pyrite.

Task G. - Neutron Source for Sulfur Monitoring Instrument

A neutron source is to be developed for a sulfur monitoring instrument which can be used for measuring the total sulfur content of a stream of coal such as would be encountered in a coal preparation plant. The source is to be based on the D-D reaction to provide long life with stable output. The unitized source assembly is to include a compact D-D accelerator-target assembly with extended output lifetime and a miniaturized electronic system to power the unit. In addition, an operating technique for a stable monitored output is to be developed.

SUMMARY OF PROGRESS TO DATE

Several methods which hold great promise for desulfurizing and recovering fine coal have been selected for development. These methods include froth flotation, selective oil agglomeration, pelletization, and chemical desulfurization. A preliminary assessment of these methods has been made to define the present state of technology, to identify problem areas, and to determine the most fruitful course to pursue. As a result of this assessment, an experimental program has been devised and launched to achieve the stated project objectives.

A very promising chemical desulfurization process has been identified which is capable of extracting virtually all of the inorganic sulfur from coal and at least part of the organic sulfur. The process involves leaching fine-size coal with a hot dilute solution of sodium carbonate containing dissolved oxygen under pressure. Two laboratory reaction systems have been acquired for investigating and developing the process. One system utilizes a fixed bed tubular reactor through which the aqueous solution is passed and the other system utilizes a 1.0 liter stirred autoclave. Both systems can be operated over a wide range of temperature and pressure. Preliminary experiments have been carried out with the tubular reactor to measure the rate of dissolution of pyrite particles which had been isolated from coal.

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. Preliminary laboratory froth flotation tests have been carried out with an Iowa coal having a very large pyritic sulfur content to obtain baseline data. A number of potential flotation depressants

for pyrite have been screened by measurement of the zeta potential of aqueous suspensions of pyrite containing small amounts of the potential depressants and by measurement of the floatability of pyrite in the presence of these potential depressants. A Hallimond tube microflotation cell has been utilized to measure the floatability of pyrite. By this means it was shown and/or verified that the following reagents tend to suppress the flotation of pyrite over specific ranges of pH: ferric chloride, sodium cyanide, ammonium thiocyanate, and the disodium salt of ethylenediaminetetraacetic acid. A promising chemical pretreatment for reducing the floatability of pyrite has been identified and is being developed further.

A technical assessment of selective oil agglomeration methods showed that several problems must be solved before these methods become technically and economically viable. A major difficulty is due to the incomplete separation of coal and pyrite provided by these methods. Another problem is the cost of the fuel oil which is not inconsequential. Furthermore, the technology has not advanced to the point where clean, relatively large, and easily dewatered agglomerates can be produced with minimum oil consumption. A promising chemical pretreatment which will greatly improve the selectivity of the process for coal and increase the rejection of pyrite has been identified. A program of laboratory experiments has been laid out and initiated to solve the major problems which have held up the industrial application of oil agglomeration.

A technical assessment of pelletizing methods showed that these methods are highly empirical, involve many different parameters, and require much individual tailoring. Various types of pelletizers are being assessed in order to select a bench-scale unit for pelletizing coal fines. A purchase order will be placed soon for such a unit. Plans have been laid for testing and demonstrating the pelletization of coal fines when the unit arrives.

Plans have been prepared for a bench-scale, continuous flow system which will demonstrate the beneficiation and recovery of fine-size coal by froth flotation, selective oil agglomeration and pelletization. It will also include equipment for grinding and chemically pretreating coal to improve the separation of coal and pyrite. The froth flotation cells have been acquired and purchase orders for the other equipment will be placed soon. Installation of equipment is scheduled to be completed by July, 1977.

Closely related to the development of industrial methods for beneficiating and recovering fine-size coal is the microstructural characterization of the coal itself. Scanning electron microscope and associated energy dispersive X-ray analysis techniques were used to measure the distribution of pyrite among the following forms: colloidal size single crystals, framboids, and larger pyrite masses in channel samples of coal from two Iowa mines. The vertical distribution from top to bottom of each of these forms was determined for two channel samples as well as the relative proportions of the three forms for the samples as a whole. Also the proportion of pyrite in various size ranges was determined for two channel samples.

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 at least part of the organic sulfur from coal is proceeding. This process seems particularly well suited for the extraction of finely disseminated pyrites which are very difficult to remove from coal by physical beneficiation. It involves leaching fine-size coal with a hot, dilute solution of sodium carbonate containing dissolved oxygen under pressure which converts the sulfur in coal into water soluble sodium sulfate. In comparison to other chemical leaching processes it offers a number of advantages which are described below in the technical assessment of various chemical desulfurization methods.

Plans have been prepared for the experimental development of the alkaline solution oxidation process and these are presented below.

Technical Assessment

Among a number of chemical extraction processes which have been proposed for desulfurizing coal, only a few such as the Battelle Hydrothermal, TRW-Meyers, and Ledgemont processes have received much notice and been actively developed in recent years. The Battelle hydrothermal process involves leaching pulverized coal with hot dilute caustic solutions which extract most of the inorganic sulfur but only part of the organic sulfur in the form of soluble sodium sulfide (1-3). If the leached coal is treated subsequently with dilute acid, the ash content is also reduced markedly. The product is reported to be completely noncaking and nonswelling. The leaching step has been demonstrated on small laboratory scale batch and continuous flow reactors and it has been found to take about 30 min. This step requires temperatures in the range of 25 to 350°C and pressures in the range of 350 to 2500 psi. At these conditions the hot caustic leachant causes stress corrosion cracking of many different metals which creates a very serious materials of construction problem. Another serious problem is due to the difficulty of regenerating the spent leachant. The scheme which has been proposed for regeneration is very complex and probably very costly (1-3).

In the TRW-Meyers process, inorganic sulfur is extracted from fine-size coal with a hot solution of ferric sulfate which is capable of oxidizing pyritic sulfur to soluble sulfates and elemental sulfur (4-7). Since the elemental sulfur is deposited within the coal matrix, a second treatment stage is required to remove the elemental sulfur either by extraction with a hot organic solvent or by heating and vaporization. The organic sulfur content, free-swelling index and other coking properties of the coal don't appear to be affected (7). Since the leaching step reduces ferric sulfate to ferrous sulfate, the spent leachant is regenerated by reoxidizing the ferrous sulfate back to ferric sulfate with air (4,6,7). The key steps in the process have been demonstrated extensively through laboratory and bench-scale testing. A process development unit for demonstrating these steps is under construction. One of the disadvantages of the process is that it does not extract any organic sulfur. Another is that leaching with ferric sulfate is a relatively

reaction. To achieve high conversions requires a number of hours. On the other hand, it is possible to extract as much as 70% of the pyritic sulfur from some coals in as little as 1 hr. (7). Since the hot acidic solution of ferric sulfate used for leaching is rather corrosive, special materials of construction must be used.

The Ledgemont process announced in 1974 by Agarwal *et al.* (9,10) of Kennecott Copper Corporation involved leaching pulverized coal with a hot aqueous solution containing dissolved oxygen under pressure which was capable of oxidizing iron pyrites and converting them into sulfuric acid and/or water soluble sulfates. In a subsequent patent, this group proposed several different versions of the oxygen solution leaching process (11). In one version coal is leached with a hot aqueous solution containing relatively little acid and the pyritic sulfur is converted to soluble sulfates as described above. After separating the coal and leach solution, lime is added to the solution to precipitate gypsum and iron oxide or hydroxide which are discarded and the water is recycled. In a second version, coal is leached under more acidic conditions and part of the pyritic sulfur is converted to soluble sulfates and part to elemental sulfur. The spent leach solution is treated as before while the coal is subsequently extracted with a hot organic solvent to remove elemental sulfur. In a third version, coal is leached with a hot solution containing ammonium hydroxide and the pyritic sulfur and part of the organic sulfur are converted to soluble sulfates. The spent leach solution is treated as before with the result that most of the ammonium hydroxide is recovered along with water which is recycled.

One or more versions of the Ledgemont process have been demonstrated in the laboratory. Sareen *et al.* (12) reported the results of numerous leaching experiments using conditions appropriate for the first version indicated above. Temperatures in the range of 80 to 130°C and oxygen partial pressures in the range of 100 to 300 psi were employed. Three different types of coal, semi-anthracite, high volatile B bituminous (Illinois No.6), and lignite, and two different size consists, -40 mesh and -100 mesh were utilized. The rate of pyrite extraction was found to be the same for all three types of coal, and required approximately 2 hr. to extract 90% of the pyritic sulfur from the finer size and 4 hr. for the coarser size at the highest temperature and oxygen partial pressure. The rate of extraction was observed to be temperature insensitive and proportional to the square root of the oxygen partial pressure. Some of the oxygen fed was also observed to react with the organic matter resulting in an increase in the oxygen content of the coal and in the formation of some carbon dioxide and a lesser amount of carbon monoxide. In this regard lignite was the most affected and semi-anthracite the least affected. The rate of formation of carbon dioxide was found to be directly proportional to the oxygen partial pressure and more sensitive to temperature than the rate of pyrite extraction. Therefore, the law of diminishing returns sets in as the temperature and pressure are increased. However, it was also noted that the oxygen uptake by Illinois No. 6 coal dropped precipitously when the pH was raised above 2.

Although the Ledgemont process appeared technically promising, development was halted by Kennecott Copper Corporation after the firm was ordered to divest itself of its coal mining subsidiary, Peabody Coal Co. However, development of a very similar process is continuing at the Pittsburgh Energy

Research Center of ERDA (13). Compressed air (in the range of 400 to 1000 psi) instead of oxygen and higher temperatures in the range of 150 to 200°C are being employed at PERC with interesting results. Most of the pyritic sulfur and up to 40% of the organic sulfur in coal have been converted into sulfuric acid with an overall Btu recovery of 93 to 98% in small scale laboratory experiments. Apparently higher temperatures have been instrumental in the extraction of part of the organic sulfur.

Even though the Ledge mont type processes are among the most promising chemical desulfurization methods, these processes are hampered by a relatively slow rate of extraction, the presence of relatively corrosive dilute sulfuric acid solutions, and operation at relatively high pressures. These problems were addressed by the Iowa Coal Research Project of the Energy and Mineral Resources Research Institute of Iowa State University with funds provided by the State of Iowa. As a result of this project, a major process improvement in coal desulfurization technology was developed (14). The improvement involves leaching coal with a dilute solution of sodium carbonate containing dissolved oxygen under pressure. The presence of sodium carbonate or some other alkali greatly accelerates the rate of reaction. Thus when pyrites recovered from Iowa coal by handpicking were leached at 150°C for 1.0 hr. with an oxygen bearing solution under an oxygen partial pressure of 50 psi, from 3 to 8 times as much pyrite was dissolved when the initial solution contained 5% sodium carbonate as compared to when it did not. Although other alkalis such as sodium hydroxide, sodium phosphate, or ammonium carbonate also increase the rate of dissolution of pyrite, they are generally not as effective as sodium carbonate. Furthermore, sodium carbonate has several other important advantages. It is very plentiful, readily available, and inexpensive. Moreover dilute solutions of sodium carbonate are not as corrosive as caustic solutions or sulfuric acid solutions.

As a consequence of the improvement in reaction rate obtained by adding sodium carbonate to the leachant, it is possible to employ relatively low oxygen partial pressures in leaching coal. Thus Tai (14) showed that most of the inorganic sulfur was extracted from various Iowa coals within 2 hr. by leaching with a 2% sodium carbonate solution containing oxygen dissolved under a partial pressure of only 20 psi and heated to a temperature of 120 to 150°C. Coarse pyrites were first removed from the coals by float-sink separation at a specific gravity of 1.60. The float product was finely ground in a ball mill and then leached. The sulfur distribution of the leached product is compared below with the sulfur distribution of the unleached float coal.

Coal	Temp., °C	P _{O₂} psi	Sulfur distribution, %			
			Pyritic	Sulfate	Organic	Total
ICO - float	---	---	0.89	0.26	0.79	1.94
ICO - leached	125	20	0.12	0.02	0.74	0.88
Scott - float	---	---	1.71	0.29	2.99	4.99
Scott - leached	120	21	0.15	0.07	2.73	2.95
Scott - leached	150	18	0.23	0.04	2.20	2.47

from these data it can be seen that most of the inorganic sulfur and a portion of the organic sulfur were removed under very mild treatment conditions. Also the percentage of organic sulfur removed was significantly greater at 150°C than at 120°C. Therefore, it is anticipated that with the application of higher temperatures, a large percentage of the organic sulfur would be extracted and a rapid rate of pyrite removal realized. Although coal treated with a sodium carbonate solution picks up some sodium, the sodium is easily removed by washing the coal with dilute acid.

Experimental Program

A program of laboratory experiments has been initiated to advance the development of the alkaline solution oxidation process for removing sulfur from coal. The immediate goals of this program are to demonstrate the extraction of larger amounts of organic sulfur and the realization of faster rates of pyrite dissolution through the use of higher temperatures and/or oxygen partial pressures than used heretofore. The effects of temperatures in the range of 150 to 200°C and oxygen partial pressures in the range of 50 to 300 psi will be explored as well as the effect of particle size. Another goal is to determine the applicability of the process for various types of coal from different regions of the country.

Laboratory experiments are being carried out with a fixed bed tubular reactor which has been acquired. This reactor has an inside diameter of 0.64 cm. and length of 15 cm. and it will accommodate approximately 15 g. of ground pyrite or 5 g. of pulverized coal. The reactor is made of Inconel 600 and is designed for operation at high pressures (up to 3000 psi) and high temperatures (up to 480°C). The reactor is heated by a fluidized bed of sand which in turn is heated by several electric heaters immersed in the sand bed. The reactor flow system is shown in Figure 1. An aqueous solution is delivered to the reactor at a controlled rate by a variable stroke plunger pump. Oxygen is drawn from a high pressure cylinder at a controlled rate and mixed with the aqueous solution ahead of the reactor. The mixture of liquid and gas is preheated to reactor temperature by passage through a coil of tubing which is immersed in the fluidized bed of sand and connected directly to the reactor. After the mixture of fluids has passed through the reactor, it is cooled by a heat exchanger and expanded through a pressure reducing valve. The gas and liquid are subsequently separated. The flow of gas is monitored with a wet test meter and the liquid is collected in measured portions which are chemically analysed later for sulfur content.

By monitoring the sulfur content of the effluent from the tubular reactor, a continuous curve of conversion versus time is generated for a sample of coal or pyrite. Since the slope of such a curve corresponds to the rate of reaction, the change in rate of reaction with conversion is also determined.

The tubular reactor system has been placed in operation and several preliminary runs made with it using ground pyrites recovered from an Iowa coal by handpicking. A number of additional runs will be made with pyrites to see whether the rate of dissolution is affected by the amount of material in the reactor and either the liquid or gas flow rates. More runs will be made to determine the effects of temperature, oxygen partial pressure, and particle size on the rate of extraction. After the pyrite runs, various samples of

Figure 1. Tubular reactor system for investigating chemical desulfurization.

coal will be leached in the reactor to see how the rate of sulfur removal differs from that of pyrites which were isolated from coal.

A stirred batch reactor has also been acquired and will be placed in operation in the near future. The batch reactor is a 1.0 liter autoclave with a gas dispersing turbine agitator operated by means of a magnetic drive and it is designed for operation at elevated pressures (up to 5000 psi) and elevated temperatures (up to 340°C). The reactor is surrounded by a jacket type electric heater which is controlled by a proportioning type temperature controller. The reactor body and fittings are made of type 316 stainless steel. Two removable liners are provided, one is made of type 316 stainless steel and the other of Inconel 600.

The batch reactor will be used primarily for leaching coal to determine the amounts of both organic and inorganic sulfur removed and the overall recovery of combustible matter in a given reaction time using specific operating conditions. From 50 to 100 g. of pulverized or ground coal and 300 ml. of a dilute sodium carbonate solution will be placed in the reactor for each run. The reactor will be connected to an oxygen cylinder and some gas will be bled from the reactor continuously to insure an adequate supply of oxygen for reaction and to maintain a constant oxygen partial pressure in the reactor at all times. After completing a run, the liquid and solids will be separated and analyzed. The total sulfur content of the liquid and the distribution of various forms of sulfur in the solids will be determined. The weight of coal recovered and its heating value will be measured.

A number of runs involving the batch reactor are planned. These runs will be made to investigate the effects of particle size, leachant concentration, oxygen partial pressure, and temperature. Also the possible effect of reaction products such as sodium sulfate on the rate of extraction will be studied. In addition the extraction of trace elements may be investigated. Several different kinds of coal will be leached to demonstrate the general utility of the process and to see how difficult it is to adapt the process to different coals.

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 (15,16). Also some sub-bituminous coals, lignite, and weathered or oxidized coals have not responded well to this treatment (17). 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 (17). In addition the clay slimes associated with some coals have interfered with good operating performance. Furthermore, 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 (18).

The present effort is focussed on improving the separation of coal and pyrites by froth flotation since such an improvement is sorely needed and a

breakthrough in this area would bring major benefits. As a first step the technology of froth flotation has been reviewed to assess the state of the art and a course of action chartered which can lead to the development of improved desulfurization methods. A specific program of experimentation has also been devised and initiated and preliminary results obtained.

Technical Assessment

The process of froth flotation is carried out by introducing air bubbles into an agitated suspension of fine particles in water in such a way that those particles with a particular surface characteristic become attached to the air bubbles and are buoyed to the surface of the suspension. Other particles without this surface characteristic remain behind. A frothing agent is added to reduce the surface tension of the water and produce a stable froth on the surface of the suspension; the froth is skimmed off or overflows the containing vessel to recover the adhering particles. Various reagents may be added to modify the surface characteristics of the particles being separated. Reagents which are selectively adsorbed on the surface of a particular species of particles are usually chosen. Thus a "collector" may be added to improve the floatability of one component and a "depressant" to reduce the floatability of another. Usually these reagents are operative over a specific pH range. In general particles with a hydrophobic surface are floated and particles with a hydrophilic surface are depressed. Unfortunately the surface of some particles may exhibit both hydrophobic and hydrophilic regions with the result that these particles are incompletely separated.

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 (17,19). Sun (20) 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 (19). A number of depressants for pyrite have been suggested including lime, cyanides, permanganates, aluminum chloride, ferric chloride, ferric sulfate, sodium sulfite, and various alkalis (17,19). In particular Baker and Miller (21) 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 U.S. Bureau of Mines 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 (22,23). 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% (23).

The laboratory test results obtained with several Iowa bituminous coals by Laros (24) and by Min (25) indicate that the two-stage flotation process may not be suitable for all kinds of coal. In general Min (25) 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.

The problem of depressing pyrite in coal flotation was addressed by the Iowa Coal Research Project of the Energy and Mineral Resources Research Institute of Iowa State University with funds provided by the State of Iowa. As a result of this project a major improvement in froth flotation technology was developed (25). This improvement involves chemically pretreating fine-size coal with an alkaline solution containing dissolved oxygen or air at elevated temperatures so as to oxidize the surface of the pyrite. Rather mild treatment conditions suffice. Thus the application of a dilute solution of sodium carbonate heated to 50 to 80°C and saturated with air at atmospheric pressure will have the desired effect within 5 to 30 min. For example, when a pulverized Iowa coal (~35 mesh size) was pretreated in this manner and then separated by single-stage froth flotation in a laboratory cell, a marked improvement in pyrite rejection was obtained over that obtained without the pretreatment step (25). This important development coincides with the observation of Glembotskii *et al.* (19) that the surface oxidation of pyrite in water leads to the formation of a film of hydrated ferric hydroxide which drastically reduces the floatability of the pyrite even up to the point of complete depression.

Experimental Program

A program of laboratory experiments has been initiated to develop improved methods of separating coal and pyrites by froth flotation. This program includes testing various techniques and treatments as well as extending the development and application of the pretreatment step described above. It also includes assessing the factors which control the separation of coal and pyrites such as surface properties, particle size, and degree of liberation of the components.

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. The coal selected was from the Iowa State University Demonstration Mine No. 1 in Mahaska county, Iowa. It 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. A typical sieve analysis of the coal selected for the flotation tests is shown below.

<u>Screen, mesh</u>	<u>Mat'l. Retained, wt.%</u>	<u>Mat'l. Passing, wt.%</u>
60	3.5	96.5
100	23.0	72.0
200	54.7	45.3
325	94.4	5.6

The flotation tests were carried out with a Denver D-1 laboratory Sub-A flotation cell fitted with a stainless steel bowl or tank. For each test 120 g. of coal and 2400 ml. of tap water were placed in the cell to provide a slurry with 5% solids. The pulp was conditioned for 5 to 10 min. by operating the agitator at 1000 r.p.m. to insure that the suspension was uniform. The pH of the pulp was adjusted to 5.5-5.6 by adding hydrochloric acid. Except where otherwise noted, 1.0 ml. of MIBC was added to the pulp and for some tests 0.5 ml. of a 1.0 wt.% solution of aluminum nitrate. After adding these reagents, the pH of the pulp was measured, the speed of the agitator was increased to 2000 r.p.m., and an air flow of 30 cu.ft./hr. 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, and analyzed for sulfur and ash. In some cases the heating value of the products was determined also.

A number of flotation tests were conducted to determine the effect of frother (MIBC) concentration on the total weight of coal recovered. The results in terms of the percentage of the feed recovered in the froth product are shown in Figure 2. The results show that only 0.5 ml. of MIBC per batch was needed to recover 89% of the solids and increasing the amount of MIBC to 1.0 ml. only increased the recovery to 90.5% which is hardly a significant increase. Further flotation tests were made in which a small amount of aluminum nitrate was added to each batch. The addition of aluminum nitrate had the effect of increasing the recovery over the whole range of frother concentration but the effect was most pronounced at the lower end of the range (Figure 2). Thus with aluminum nitrate present only 0.25 ml. of MIBC per batch was needed to recover 90% of the solids in the froth. It appears that the aluminum salt served as an activator for the coal since it enhanced the recovery. This was an unexpected result since the aluminum salt was added to depress the pyrite.

Several flotation tests were run using a froth fractionation technique which involved collecting the froth product in a number of separate portions. The solids in each portion were separately recovered, dried, weighed, and analyzed for total sulfur, ash, and heating value. One pair of tests was conducted using only 1.0 ml. of MIBC and another pair of tests using 1.0 ml. of MIBC plus 0.5 ml. of a 1.0 wt.% aluminum nitrate solution. Within each pair of tests the results were virtually the same. Also there was very little difference in the results between the tests which involved addition of aluminum nitrate and those which did not (Figures 3 and 4). In every case the sulfur and ash contents increased and the heating value of the product decreased with each additional increment of froth collected. In Figures 3 and 4 the average ash and sulfur contents and the average heating value of the cumulative product are plotted against the corresponding cumulative recovery. Thus for a 70% recovery, the average sulfur content of the float product was 5.2-5.5%, the average ash content 16.5%, and average heating value 11,700 Btu/lb.

In the future, tests will be carried out using smaller concentrations of MIBC since the results presented in Figure 2 indicate that an excessive amount of MIBC was used for the froth fractionation experiments. In general, an excessive amount of frother reduces selectivity. Also pH and particle size will be varied to see if an optimum combination of conditions will provide a float product with much lower sulfur content than noted above.

Figure 2. Effect of frother concentration on the recovery of coal by froth flotation.

Figure 3. Cumulative results of froth fractionation experiments.

Figure 4. Average ash content of cumulative fractions recovered during froth fractionation experiments.

Zeta Potential. 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 (26,27). 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 (28). 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.

Campbell and Sun (29) utilized zeta potential measurements to investigate the adsorption by Pittsburgh seam coal of various flotation reagents including collectors, frothers, depressants and electrolytes. These investigators found that the adsorption of hydronium or hydroxyl ions on the hydrolyzed coal surface seemed to determine the zeta potential of coal particles at different pH. For values of pH less than 4.0-4.5 the zeta potential was positive and for values greater than this the zeta potential was negative with the zeta potential decreasing (the negative charge increasing) as the pH increased. Since the zeta potential was not affected by the presence of sodium chloride in dilute concentrations, it appeared that neither sodium nor chloride ions were adsorbed to any significant degree. On the other hand, the zeta potential was affected markedly by the chlorides of tin, aluminum, and calcium in descending order indicating that the multivalent cations were strongly adsorbed. The adsorption of tin or aluminum cations was sufficient to change the zeta potential from a negative value to a positive value. Zeta potential measurements also indicated that dodecylamine acetate, a cationic collector, was strongly adsorbed by coal whereas several anionic collectors were not adsorbed unless the coal surface was first activated through adsorption of aluminum cations. The evidence suggested that the adsorption of heteropolar collectors is governed by electrostatic forces. The zeta potential of coal particles was not affected significantly by the presence of nonionic frothers such as MIBC. However, it was affected by the depressants sodium silicate and sodium cyanide which both made the zeta potential more negative. On the other hand, another depressant quebracho which is anionic in character had no effect on the zeta potential indicating that it was not adsorbed. Since quebracho is a known depressant for sulfides, it would appear to be potentially useful for depressing pyrite during the flotation of coal.

Baker and Miller (21) used zeta potential measurements to study the adsorption of several potential depressants by both Pittsburgh seam coal and pyrites isolated from the coal. The depressants included the hydrolysis

products of both ferric and aluminum chlorides. In the case of ferric chloride, the adsorption of positively charged hydrolysis products such as Fe(OH)_2^+ and Fe(OH)^{++} at pH below 5 and of positively charged Fe(OH)_3 colloids at pH above 5 raised the zeta potential of both the coal and pyrite particles. However, the zeta potential of the pyrite was affected more than the zeta potential of the coal indicating that more adsorption took place on the pyrite. Subsequent laboratory flotation tests using MIBC showed that the hydrolysis products of ferric and aluminum chlorides in low concentrations did exert a selective depressing action on pyrites but in higher concentrations both coal and pyrite were depressed.

Zeta Potential Measurements. In the present investigation the zeta potential of coal and pyrite particles in an aqueous suspension is being measured with a model 400 Laser Zee Meter (Pen Kem Company) in order to screen a number of potential flotation depressants for pyrite. Coal obtained from the Iowa State University Demonstration Mine No. 1 in Mahaska County, Iowa, has been used for the measurements made up until now. 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, dried, and ground to a size of 5 to 50 μm . The pyrite was carefully hand-picked from University preparation plant tailings produced in treating similar coal. The pyrite was also ground to a size of 5 to 50 μm . Both the coal and pyrite were stored under nitrogen to minimize oxidation. 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 5 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 in general. For both coal and pyrite the zeta potential increases as the pH of the suspension decreases. Presumably at high pH, hydroxyl ions are adsorbed by coal or pyrite to make the zeta potential negative while at low pH hydronium ions are adsorbed to make the zeta potential positive or at least less negative. 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 in place of hydrochloric acid and sodium hydroxide, the results shown in Figure 6 were obtained. 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.* (19) 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.

Figure 5. Zeta potential of coal and of pyrite isolated from coal in aqueous suspensions.

Figure 6. Different pH regulators affected the zeta potential of pyrite differently.

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 7. For pyrite the results are similar in general to those reported by Baker and Miller (21); 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 (21) 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.

Cyanides have long been used to selectively depress pyrite where anionic collectors such as xanthates have been employed to recover other sulfide minerals. Iron is known to form very stable complex cyanides. According to Moeller (30) the ions of many transition metals react with alkali cyanides to form highly insoluble, gelatinous precipitates which commonly contain alkali metal ions and which are very stable toward acids. Measurements of the zeta potential show the effect of adding small amounts of sodium cyanide to a suspension of iron pyrite (Figure 8). At a very low concentration of sodium cyanide (10^{-5} mole/liter) and pH below 7.5, the zeta potential was raised to a positive value indicating the adsorption of some positive species. On the other hand, at high concentrations the zeta potential was lowered indicating the adsorption of some negative species such as CN^- , although in acidic solutions cyanide would exist mainly as HCN or as a complex metal cyanide. Interestingly enough, the effect of the lowest concentration of sodium cyanide on the zeta potential of coal was similar to that noted for pyrite (Figure 8) indicating the adsorption of a similar species in both cases. Since both pyrite and coal contain some acid soluble iron compounds, it seems possible that enough iron was leached out of the particles in both cases to react with the cyanide to form a positively charged hydrosol which was adsorbed by the coal or pyrite. Unfortunately since sodium cyanide appears to have had about the same effect on both coal and pyrite, it does not offer much promise of serving as a selective depressant for one or the other.

The addition of small amounts of sodium carbonate had a pronounced effect on the zeta potential of pyrite (Figure 9). The results indicate the adsorption of a positively charged species. Although adsorption of sodium ions may have accounted for part of the effect, it seems doubtful that they accounted for the total effect since the addition of other sodium salts did not produce the same effect. Another possibility is the adsorption of a positively charged iron carbonate. Figure 9 shows that the zeta potential of coal was affected in the same way by the addition of sodium carbonate. At higher

Figure 7. Ferric chloride had a greater effect on the zeta potential of pyrite than on that of coal.

Figure 8. Sodium cyanide seemed to affect the zeta potential of coal and pyrite similarly.

Figure 9. Sodium carbonate affected the zeta potential of pyrite much more than it affected the zeta potential of coal.

Figure 10. These results indicate that a negative anion of EDTA was adsorbed equally well over a wide pH range.

pH there was a tendency for the zeta potential to be reduced indicating the adsorption of a negative species such as CO_3^{2-} or HCO_3^- . Since sodium carbonate had different effects on coal and pyrite, it might serve as a selective depressant. Glembotskii *et al.* (19) reported that soda ash can serve both as a depressant and as an activator for pyrite depending on the state of surface oxidation of the pyrite. If the surface is oxidized very little, soda ash serves as a depressant, but if the surface is highly oxidized, it serves as an activator.

The zeta potential of pyrite and coal in aqueous suspensions containing small amounts of various sequestering agents was investigated. Agents which are known to form stable complexes with iron were utilized to see if they might be adsorbed selectively by the pyrite and thereby serve to depress the pyrite. the disodium salt of ethylenediaminetetraacetic acid (EDTA) was one of the agents used; the zeta potential of pyrite in very dilute solutions of this material was found to be independent of pH (Figure 10). Since the zeta potential was negative and the negative charge increased as the concentration of the salt increased, it appears that the negative anion was adsorbed by the pyrite.

Ammonium thiocyanate is another agent which was tested. At low pH (below 6) it appeared to have a large effect on the zeta potential of pyrite in as much as it changed the potential from a negative value to a positive value (Figure 11) which indicated adsorption of a positive species. It is also noteworthy that at a pH of 5-6 the agent seemed to have a much different effect on coal than on pyrite. Whereas it caused charge reversal in the case of pyrite, it caused the zeta potential to become more negative in the case of coal. This difference indicates that the coal and pyrite adsorbed different species which might augur well for subsequent separation.

Diammonium citrate had about the same effect on the zeta potential of both coal and pyrite (Figure 11). The results indicate that negative anions were adsorbed by both coal and pyrite at low pH since the zeta potential of each one became more negative.

In the future several other potential depressants for pyrite will be investigated to see what is revealed about their adsorption characteristics through measurement of the zeta potential.

Microflotation Experiments. 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 12 is a diagram of the cell. The cell offers several advantages according to Fuerstenau *et al.* (31). 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 not necessary 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 same stock of materials prepared for the zeta potential measurements. The 5 to 50 μm size of these materials was probably not a good choice as will be discussed later.

Figure 11. Ammonium thiocyanate affected the zeta potential of coal and pyrite differently whereas diammonium citrate affected the zeta potential of both similarly.

Figure 12. Modified Hallimond tube microflotation cell used for measuring the floatability of coal or pyrite.

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 tube along with 1.0 g. of coal or pyrite. The pH of the solution was adjusted next by adding a small amount of either 0.1 N hydrochloric acid or 0.1 N sodium hydroxide solutions. The suspension was conditioned subsequently for 10 min. During this interval the magnetic stirrer was used to stir the suspension and nitrogen was allowed to bubble through the mixture. 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 reagent solution was added. The floatability test was then carried out by bubbling nitrogen at a flow rate of 27 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 weight of solids charged to determine the relative flotation recovery.

The percentage recovery of pyrite in a series of microflotation experiments conducted at different pH without any flotation reagents other than pH modifiers is shown in Figure 13 together with the previously measured zeta potential. For this series of experiments the pyrite suspension had a pH of about 4.5 without the pH modifiers. To raise the pH, a sodium hydroxide solution was added and to lower the pH, a hydrochloric acid solution. The results indicate that flotation of pyrite was suppressed by raising the pH which is in agreement with the views of Glembotskii *et al.* (19) that hydroxyl ions exert a depressing action through adsorption on the pyrite surface. The similar trends in pyrite recovery and zeta potential with pH as shown by Figure 13 seem to indicate a direct correlation between recovery and zeta potential.

Additional microflotation experiments were conducted to test different potential pyrite depressants. The results obtained when small amounts of ferric chloride were added to a pyrite suspension are shown in Figure 14. These results indicate that flotation of pyrite was suppressed over a pH range of 5 to 10 which is not surprising since previous measurements of the zeta potential indicated that the hydrolysis products of ferric chloride were adsorbed by pyrite over this range of pH. On the other hand, there is no ready explanation for the sharp increase in pyrite recovery at low pH (below 4) because this increase can not be accounted for by a corresponding change in zeta potential.

The results obtained when small amounts of sodium cyanide were tested as a pyrite depressant are shown in Figure 15. These indicate that cyanide did tend to suppress the flotation of pyrite particularly at high pH. Also the degree of suppression increased when the concentration of cyanide was increased. The disodium salt of EDTA also tended to suppress the flotation of pyrite under certain conditions (Figure 16). A concentration of 0.0001-0.0002 mole/liter seemed to have a depressing action over a pH range of 3 to 7. Ammonium thiocyanate also seemed to suppress the flotation of pyrite somewhat over a range of 4 to 8 (Figure 17). On the other hand, at low pH (below 4) it seemed to result in greater floatability of pyrite.

Figure 13. The relative recovery of pyrite in microflotation experiments exhibited the same trends with pH as the zeta potential exhibited with pH.

Figure 14. Ferric chloride suppressed the flotation of pyrite in the pH range of 5 to 10.

Figure 15. Sodium cyanide served to suppress the flotation of pyrite.

Figure 16. The disodium salt of EDTA tended to suppress the flotation of pyrite over a pH range of 3 to 7.

Figure 17. Ammonium thiocyanate suppressed the flotation of pyrite over a pH range of 4 to 8.

When an attempt was made to measure the floatability of coal with the microflotation cell, the results were scattered and inconsistent. It appears that the particles may have been so small and light that they were suspended too readily by mechanical agitation in the Hallimond tube and were carried over into the collecting stem without being attached to gas bubbles. In the future, larger size particles will be utilized.

Further microflotation experiments will be carried out in the future to compare the floatability of coal and pyrite in the presence of some of the chemical agents which seem to depress pyrite. In some of these experiments a small amount of MIBC will be employed to see whether it interacts with any of the pyrite depressants either for better or for worse.

Flotation After Chemical Pretreatment. Since chemical pretreatment with a hot sodium carbonate solution containing dissolved oxygen under pressure appears to be one of the most effective ways to reduce the floatability of pyrites mixed with coal, this technique will be further developed and applied to different kinds of coal. The effectiveness of the pretreatment will be determined by applying a standard flotation test to the treated coal. For the pretreatment step, pulverized and/or ground coal will be mixed with a dilute alkaline solution in a stirred laboratory flask while air or oxygen is introduced continuously into the suspension through a diffuser. Atmospheric pressure and elevated temperatures below the boiling point will be employed. For the flotation step, the coal will be transferred to either a Wemco or Denver D-1 laboratory flotation cell. In some experiments the entire suspension from the pretreatment step may be transferred to the flotation cell whereas in others only the solids may be transferred, in which case they will be repulped with fresh water. A frother such as MIBC (and sometimes other reagents) will be added to the pulp and the coal floated. The product yield will be determined, and samples of the product and tailings will be collected, dried, and analyzed for ash and pyritic sulfur.

The effects of several parameters on the overall results obtained by pretreatment and froth flotation will be investigated to optimize the conditions for the process. Thus the effect of initial particle size and method of comminution will be studied as well as the effects of pretreatment conditions and flotation conditions. Pretreatment conditions to be investigated include temperature and alkali concentration. Flotation conditions to be studied include slurry concentration, frother type and concentration, and pH. In addition, a comparison of using the whole pulp from the pretreatment step for the flotation step versus separating the pretreated solids and repulping them with fresh water before applying the flotation step will be investigated. The overall process will be applied to several representative coals of high pyritic sulfur content from both the Eastern and Midwestern regions of the United States to see how well different coals respond to the method and to see whether each coal requires a unique set of operating conditions for optimum results. In addition the effect of removing coarse pyrites by gravity separation before applying chemical pretreatment and froth flotation may be studied.

Flow Systems. As improvements in the technology of froth flotation of coal are developed through the program of experiments described above, the improvements will be demonstrated with a continuous flow system which is

described in a later section of this report. This system will utilize bench-scale equipment which is many times larger than the laboratory equipment and which can be operated under steady state conditions so that it will more closely simulate industrial practice.

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 (32). 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. Unfortunately many pyrite particles also are agglomerated because the surface of pyrite tends to be hydrophobic (32). Within the last few years Capes et al. (33,34) discovered that a larger percentage of the pyrites are rejected if the coal is first treated by an iron-oxidizing bacterium, *thiobacillus-ferrooxidans*. Apparently the bacteria are capable of oxidizing the pyrite surface and changing its character from hydrophobic to hydrophilic.

A preliminary technical assessment of selective oil agglomeration technology has been made and problem areas identified. Further development of the method appears warranted and preliminary plans for an experimental program to accomplish this development have been prepared. The assessment and program are outlined below.

Technical Assessment

Several industrial coal beneficiation processes based on selective oil agglomeration have been 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 (32). 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 (35). 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. After another pilot plant was built at Gary, West Virginia, and operated by U.S. Steel Corporation (36). The plant at Gary was subsequently modified and enlarged until it assumed the proportions of a commercial prototype (37). 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"

(38-40). Bergbau-Forschung GMBH of Germany is developing the Olifloc process and is operating a 3 ton/hr. pilot plant near Essen (41). Shell International Petroleum Company Limited is interested in the development of the Shell pelletizing separator which is a unique device for conducting oil agglomeration (42). 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) (43).

The use of oil agglomeration to desulfurize Iowa coals was investigated recently by Min and Wheelock (44). 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 compliment 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 already noted above is due to the incomplete separation of coal and pyrite. Although Capes *et al.* (33-34) have proposed a solution which involves bacterial oxidation of the pyrite surface, the treatment is slow, apparently requiring 1 to 3 days, which could translate into a high capital cost. Another major problem is due to the high cost of the agglomerating oil. Capes *et al.* (39) have shown 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 light distillate oils such as kerosene or No. 1 fuel oil. Hence, the best separation is obtained with the light oils. On the other hand, the agglomerates produced with light oils are fragile, and some of the light oil may be lost through vaporization if the agglomerates are left in the open for any great length of time. Needless to say the light oil agglomerates could experience a substantial loss of oil if dried thermally.

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.* (38,45), agglomerates larger than 2mm. gross 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.* (39) 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 (42) 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.

Several of the problems described above were addressed by the Iowa Coal Research Project of the Energy and Mineral Resources Research Institute of Iowa State University with fund provided by the State of Iowa. As a result of this project, two major improvements in oil agglomeration technology were developed (25). The first improvement involves the use of an oil-water emulsion for agglomerating coal. By first emulsifying the oil before adding it to an aqueous suspension of coal, much less time is required to agglomerate the coal with a given level of agitation or less agitation is required to agglomerate the coal in a given period of time. The implications of this discovery are far ranging and can lead to the use of simpler and less demanding equipment for the agglomeration of coal itself. The second improvement involves the application of the chemical pretreatment step which is described above in the section on Froth Flotation. By applying this pretreatment step to a sample of Iowa coal which had been pulverized to -35 mesh size, the percentage of pyritic sulfur rejected by the subsequent oil agglomeration step was increased from less than 40% to over 70%. The advantage of this pretreatment step over the bacterial oxidation treatment proposed by Capes *et al.* (33,34) is that it is much quicker requiring only a few minutes.

Experimental Program

A program of laboratory experiments will be carried out to advance the basic technology of selective oil agglomeration so that it may become a truly useful and economically viable method of cleaning and recovering fine coal. The immediate goal of this program is to develop a practical means of agglomeration which will provide clean, pyrite-free agglomerates which are relatively large (that is, 1-2mm. in diameter), easily dewatered, and sufficiently durable to be readily stored and handled while at the same time utilizing a relatively inexpensive fuel oil in minimal amount. Several steps will be taken to achieve these goals. First, to obtain good separation of coal and pyrite, we will be made of the chemical pretreatment step involving oxidation of the pyrite surfaces with an alkaline solution containing dissolved air. Second, to obtain durable agglomerates at low cost, use will be made of the lowest cost, heavy residual fuel oils or mixtures of these heavy oils and lighter fuel oils. Third, to make efficient use of these heavy oils, the oil will be emulsified just before adding it to the coal suspension and the suspension will be stirred to reduce the oil viscosity. Fourth, to determine the optimum means for forming relatively large, durable pellets with the least amount of oil and

With the least amount of entrapped refuse material, different types of mixing equipment and hydrodynamic conditions will be utilized.

Relatively simple experimental techniques will be utilized. For the chemical pretreatment step, pulverized and/or ground samples of coal will be mixed with a dilute alkaline solution in a stirred and heated laboratory flask while air or oxygen is introduced continuously into the suspension through a diffuser. Atmospheric pressure and elevated temperatures below the boiling point will be employed. For the agglomeration step, an aqueous suspension of the pretreated coal will be mixed with an emulsified oil by one of the several types of mixers to be tested. These mixers will include a Waring-type blender, laboratory flask equipped with either a flat-bladed paddle or turbine agitator, and paint shaker. The agglomerates will be recovered by pouring the final suspension through a sieve. A sample of the agglomerates will be dewatered with a centrifuge and the moisture content of the dewatered product determined. The average agglomerate size will be measured and the durability of the agglomerates determined by a technique which has yet to be selected. Another sample will be dried, extracted with hexane to remove the oil, and analyzed for ash and sulfur.

The effects of several parameters on the results obtained by oil agglomeration will be investigated in order to optimize the conditions for the process. Thus the effect of initial particle size and method of comminution will be studied as well as the effects of oil type and amount, agglomeration temperature, type of mixer and level of agitation. Heavy residual oils such as No. 5 and No. 6 fuel oils will be utilized; these may be blended with lighter distillate oils such as No. 1 and No. 2 fuel oils. In some experiments agglomeration will be carried out in two stages with a high-shear mixer such as the Waring-type blender employed for the first stage and a low-shear mixer employed for the second stage. The agglomeration process will be applied to several representative coals of high pyritic sulfur content from both the Eastern and Midwestern regions of the country to see how well different coals respond to the method and to see whether each coal requires a unique set of operating conditions for optimum results. In addition the effect of removing coarse pyrites by gravity separation before applying oil agglomeration may be studied.

As the basic technology of oil agglomeration unfolds through the program of experiments described above, the improved methods will be demonstrated with a continuous flow system which is described in a later section of this report. Although the flow system will utilize bench-scale equipment, the scale of operation will be many times larger than that used for the laboratory experiments and, of course, it will permit carrying out the oil agglomeration operation under steady state conditions so that it will more closely simulate industrial practice.

Pelletization

Since the removal of disseminated pyrites and organic sulfur from coal generally requires treating fine-size coal which is difficult to dewater, store, and handle, the pelletization of coal-fines to produce a material which is easier to dewater and handle is being investigated. Initially the technology of coal pelletization is being reviewed to assess the state of the art, to identify potential problems, and to determine which aspects of the technology

for further development. Subsequently the pelletization of coal fines was demonstrated with suitable bench-scale apparatus to test possible solution to existing problems and to further develop the technology.

General Assessment

In order to assess the state of the art, the technical literature on pelletization is being reviewed and visits are being made to other laboratories and research centers where work on pelletization is underway. Visits have already been made to the Bureau of Mines laboratory at Bruceton, Pennsylvania, Dravo Corporation research laboratory at Neville Island, Pennsylvania, and National Research Council research center in Ottawa, Canada. In the near future a visit will be made to the research laboratory of Ferro-Tech Inc., East Lake, Michigan. Both Dravo and Ferro-Tech are leading manufacturers of pelletizing equipment. The equipment manufactured by Dravo was demonstrated during the recent visit to their laboratory. A method of pelletizing lignite is being developed by the Bureau of Mines. The National Research Council of Canada has carried out small bench-scale development of a method of pelletizing coal recovered by selective oil agglomeration (38,46).

The National Research Council method seems particularly well suited for pelletizing wet or moist fines recovered by oil agglomeration or froth flotation. These fines are fed to a rotating, inclined balling disc along with coarse coal particles which serve as balling nuclei or "seed". A heavy hydrocarbon oil such as Bunker C fuel oil or coal tar is sprayed on the disc while it is being balled. This oil not only serves to bind the pellets but also displaces moisture from the surface of the coal. Pellets 1/4 in. diameter produced from a relatively wet feed by a 16 in. diameter balling disc had 12% surface moisture which was reduced to 1/2% moisture by air drying overnight (38). Thus it appears that thermal drying might be avoided by simply allowing the pellets to drain or by using a centrifugal dryer.

Pelletization poses several challenging problems. One of the major problems is the cost of a suitable binder. Heavy residual fuel oils, coal-tar, 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 usually greater than that of the coal. A preliminary economic analysis by Smith et al. (39) of a process for recovering coal fines by a combination of selective oil agglomeration and disc pelletization showed that the costs of agglomerating oil and pellet binder made up the bulk of the total overall processing cost.

Another difficulty which comes up in trying to use pelletization is the number of variables which must be controlled and/or optimized in producing pellets of suitable size, strength, and moisture content at the lowest cost or on the basis of some other economic measure. For example, if a rotating disc pelletizer were to be selected for pelletizing coal, the following parameters could affect system 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 will require experimental testing and verification.

Demonstration

After further technical assessment of the state of the art of pelletization, a small bench-scale pelletizer will be selected and acquired to demonstrate the pelletization of coal fines. One of the more likely choices is an inclined, rotary disc pelletizer; laboratory models are available with a disc diameter of 15 to 30 in. A program of experiments will be carried out with the selected device to produce pellets from coal fines under various conditions of operation. Different binders such as heavy residual fuel oils, coal-tar pitch, asphalt, and solvent refined coal will be tested. Also different methods of applying these binders will be tried to see what savings can be achieved through more efficient application. These methods may include application of the binder as a spray, foam, or water emulsion. Applying the binder as a foam seems especially promising in light of the success achieved by Csanyi (47-49) in utilizing foamed asphalt in bituminous paving mixes. He observed that foaming increases the volume of the 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. Other parameters such as disc speed and angle of inclination, feed rate and moisture content, diameter of balling nuclei, and feed ratio of coal fines to balling nuclei will also be investigated. 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, the pelletizer will be integrated with the continuous, bench-scale flow system for demonstrating froth flotation and selective oil agglomeration. The continuous cleaning and recovery of fine coal by froth flotation or oil agglomeration and subsequent pelletization of the product will then be demonstrated.

Continuous Processing of Fine Coal

A continuous flow system is being designed to demonstrate the methods described above for cleaning and recovering fine-size coal. Initially this system will include equipment for grinding and chemically pretreating coal, arating and recovering coal by froth flotation and oil agglomeration, and letizing coal. Equipment may be added later for demonstrating the chemical

extraction of sulfur from coal. Although this will be a bench-scale system, it will be large enough to closely simulate industrial practice. It will be located at the Iowa State University coal preparation plant in Ames, Iowa, and will be able to utilize the coal preparation and handling facilities of the plant. Thus it can be supplied with coal fines from different points in the plant including untreated fines and Deister table product, middlings, or rejects. A description of the flow system and the use which will be made of it will follow.

System Description

Figure 18 is a preliminary flowsheet of the continuous flow system. Coal fines from the Iowa State University coal preparation plant will be placed in an aqueous slurry in either of two tanks which will serve both for storage and chemical pretreatment. These tanks will be equipped with agitators and means for introducing both air and steam. For the pretreatment step, the coal slurry will be heated to the required reaction temperature either by injecting live steam or by recirculating the slurry through an external heat exchanger which will be heated by steam. An alkali will be added to the slurry and air will be introduced to oxidize the surface of the pyrite particles. If a finer particle size is required, the coal slurry may be conducted from one tank through a ball mill to the other tank or back to the same tank. Thus the grinding mill may be operated in either open loop or closed loop operation depending on how many passes through the mill are needed to achieve the desired particle size. The grinding operation may precede or be conducted concurrently with the chemical pretreatment step.

After the feed has been adequately ground and/or pretreated, it will be passed through the external heat exchanger, where it may be heated or cooled, to either a bank of froth flotation cells or to 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 18) does not include any filtration equipment since use will be made of filters which are planned for the Iowa State University coal preparation plant.

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 through 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 fines which will be treated.

The agglomerated and dewatered coal will be conveyed to a pelletizer for size enlargement. Although the type of pelletizer has not been selected, the more likely possibilities is an inclined, rotary disc pelletizer.

Figure 18. Bench-scale system for demonstrating the continuous processing of fine coal.

Additional oil will be added to the coal during the pelletizing step. The pelletizing oil may be the same or it may be different from the agglomerating oil.

The oil agglomeration circuit will be designed to treat about 100 lb./hr. of coal whereas the froth flotation circuit will be designed to process several hundred pounds per hour of coal. The oil agglomeration circuit will be smaller because of the greater uncertainty involved in the design of this circuit and its various components. In all likelihood the oil agglomerating equipment and sequence of steps will need to be revamped more than once in the course of the experimental program.

Sometime in the future, equipment may be added to the system to demonstrate the chemical extraction of sulfur from coal. This equipment would be fitted into the system as shown in Figure 18 and would include a high pressure reactor, feed pump, air compressor, and other items.

Design and Construction Schedule

The design and construction schedule for the continuous flow system is shown in Table 1. As indicated by this schedule, the construction phase should be completed and the system should be ready for testing about the middle of July, 1977.

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

Information for the design and specification of a neutron source for a sulfur monitoring instrument is being collected. The design should be completed during the first calendar quarter of 1977 and the neutron source should be fabricated and the auxiliary equipment assembled by summer. Testing and evaluation of the source will then be undertaken.

Table 1. Design and construction schedule for flow system

Week begin.	Engineering	Drafting	Sheet Metal	Electrical	Mechanical
Jan. 10	Finalize flowsheet				
17	Equipment specifi- cations			Equipment specifi- cations	
24	Order steel				
31	Orders out for bids			Orders out for bids	
Feb. 7	Modeling & equip. layout	Modeling & equip. layout			
14		Drafting			
21	Order equipment			Order equipment	
28					
Mar. 7			Fabricate		Fabricate structurals
14					
21					
28					
Apr. 4					
11					
18					
25					
May 2					
9					
16					
23					
30					
June 6	All equip. delivered			All equip. delivered	Begin installation
13					
20					
27					
July 4					
11					Complete installation Tryout testing
18					
25					
Aug. 1					

Characterization of Coal Microstructure

by

Raymond T. Greer

Scientific Background

Studies on Iowa coal (50-53) indicate a potential to synthesize micro-structural and microchemical data obtained from scanning electron microscope - energy dispersive analyses to provide a working approach to correlating important property - behavior parameters of interest in the following areas:

- (1) phyteral and maceral-mineral structural characteristics,
- (2) nature and distribution of pyrite,
- (3) aspects of mechanical and chemical comminution, beneficiation and conversion and associated desulfurization improvements, and
- (4) precision and accuracy of chemical determination of sulfur, especially organic sulfur, as these may be strongly influenced by the presence and abundance of micrometer size and colloidal pyrite (source of inorganic sulfur).

The recognition of the importance of different mixtures of macerals and minerals in affecting coal conversion liquefaction and gasification processes is broadly acknowledged. The details of these interrelations between physical and chemical characteristics and the behavior of the coal lithotypes are not known. The present investigation is concerned with developing certain micro-structural and microchemical data to enhance our understanding of the nature of coal as related to various methods of beneficiation, desulfurization and processing.

Objectives

The objectives of the present investigation are as follows:

- (1) the description of maceral organization and relation to mineral components for a variety of coals,
- (2) identification of microstructural and microchemical specifications as related to bonding, and
- (3) 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.

Technical Approach

The microstructure of coal is determined and characterized by combined scanning electron microscope - energy dispersive analysis techniques. Micro-structural information on a micrometer size scale is correlated with micro-chemical information developed by energy dispersive X-ray microanalyses to establish the presence and distribution of pyrite, the primary sulfur bearing phase in coal. Other complementary analytical techniques such as scanning transmission electron microscopy, X-ray diffraction, and conventional reflectance and petrographic microscope studies are employed as well. This evaluates particle size, shape and distribution factors which bear on decisions to try to remove additional sulfide particles to reduce the sulfur content.

Subsamples are obtained from complete channel samples or sources such as raw material prepared as appropriate to the major methods of coal conversion.

Experimental Results

The work has centered on developing microstructural-chemical information for coal and for pyrite in coal (presence, distribution, and relation to coal macerals). Scanning electron microscope (SEM) and associated energy dispersive X-ray analyses have provided the bulk of the data on microstructure and micro-chemistry. Complete channel samples have been obtained from Iowa mines and prepared for SEM analysis. In addition to general surveys of these samples, very detailed results have been obtained on a micrometer size basis for complete channel samples. This is very time consuming; however, the findings offer great insight into the presence and distribution of pyrite (the primary sulfur bearing phase in coal) as well as suggest the application of innovative techniques to remove this material from coal prior to combustion of the coal at a power plant.

Consider the following information obtained for a channel sample from the Lovilia mine ("deep" mine) and for a channel sample from the Star mine ("surface" mine). First, compare the distribution of pyrite between three forms in the mines (colloidal size single crystals, framboids ... various size agglomerations of single crystals, and larger pyrite masses) given in Table 2.

Table 2. Distribution of pyrite among various forms

Form of Pyrite	Distribution, wt. %	
	Lovilia mine	Star mine
Single crystal	7.5	21.1
Framboids	6.1	10.9
Other larger, massive forms	86.4	68.0
Total	100.0	100.0

Additional distribution results are presented in Figures 19 and 20. For example, for the Star mine the single crystal form of pyrite predominates below 1 μ m particle diameters; framboids are an important form of pyrite over a size range of a few micrometers to 30 μ m diameter, and slightly more than 50% of the pyrite present of a diameter of 5 to 10 μ m is of the framboidal form.

Second, the proportion of pyrite in various size ranges offers an insight into difficulties in pyrite removal by conventional techniques as well as considerations for establishing the degree of confidence in precision and accuracy of sulfur determinations in coal by conventional chemical analytical techniques. Some of this information is presented in Table 3.

LOVILIA MINE
DISTRIBUTION OF PYRITE AMONG FORMS

FOR ENTIRE CHANNEL SAMPLE

Figure 19. Distribution of pyrite in the Lovilia mine seam among three forms: single crystals, framboids, and other larger, massive forms. Data are presented in two ways:

- (1) fraction of total pyrite for the mine seam for each form, and
- (2) distribution among each form with respect to size (in micrometer intervals) for the range of sizes observed.

STAR MINE
DISTRIBUTION OF PYRITE AMONG FORMS

Figure 20. Distribution of pyrite in the Star strip mine seam among three forms: single crystals, framboids, and other larger, massive forms. Data are presented in two ways:

- (1) fraction of total pyrite for the mine seam for each form, and
- (2) distribution among each form with respect to size (in micrometer intervals) for the range of sizes observed. This information can be compared with that in Figure 19 for a shaft mine.

Table 3. Proportion of pyrite in certain size ranges

<u>Lovilia mine</u>	
50%	< 300 μ m
30%	< 76 μ m (i.e., 200 mesh)
<u>Star mine</u>	
50%	< 45 μ m
57%	< 76 μ m (i.e., 200 mesh)

In Table 3, two items are of primary interest: 1) the size (particle diameter) below which 50% of the pyrite is present in the seam, and 2) the amount of pyrite present that could pass through a 200 mesh sieve. From these data, it is not surprising that the Star mine coal would be difficult to clean with so much pyrite being present in a very small size range. The amount of pyrite present of a size of 76 μ m or less in diameter is of direct practical interest. Most utilities in the U.S. crush coal to -200 mesh size just prior to combustion. Thus, the significance of this information relates to the potential for additional sulfur removal at a power plant after final coal crushing. There may be a very important potential present to decrease the coal sulfur content by removal of the very fine sulfur bearing phases (predominantly pyrite) at this stage. Details of the proportionation of pyrite for these two mines for various size ranges are shown in Figures 21 and 22. From these figures, the percentage of pyrite (less than a particular size of pyrite) present can be obtained. This, coupled with how the various forms are distributed with depth in a particular mine, provides an interesting basis for some general comments. Most of the sulfur seems to be accounted for by the various forms of pyrite. For the Lovilia mine, the pyrite is highly concentrated at the top of the seam and this rapidly tapers off with depth in a seam (the bottom 50% exhibits almost no pyrite). In strong contrast, the Star mine pyrite is more widely distributed. A significant fraction of the pyrite is present as colloidal crystals and as framboids (generally < 40 micrometers in diameter). Distribution information (as 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 Lovilia mine (Figures 23-26) and in the Star mine (Figures 27-30). This represents the first complete energy dispersive X-ray analyses on a micrometer size scale for continuous seam series of face-channel coal specimens. These results indicate a clear difference in the way the three forms are distributed.

Several practical implications of the research findings can be summarized as follows:

TOTAL LOVILIA MINE

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

Figure 21. Proportionation of pyrite for the various size ranges observed for the Lovilia mine. For example, 30% of the pyrite is less than 76 μm in diameter (i.e., 200 mesh).

TOTAL STAR MINE

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

Figure 22. Proportionation of pyrite for the various size ranges observed for the Star mine. For example, 57% of the pyrite is less than 76 μm in diameter (i.e., 200 mesh).

Figure 23. The distribution of single crystals of pyrite in the Lovilia mine with depth in the seam. For example, in the top 1% of the seam; 5.5% of the material in this portion of the seam is small pyrite single crystals. The contributions of the other two forms of pyrite referred to in Figure 19 are given in Figures 24 and 25. The total pyrite contributions with depth are shown in Figure 26.

Figure 24. The distribution of framboidal formations of pyrite in the Lovilia mine with depth in the seam. For example, for the 1% interval at a depth of 39 to 40% of the thickness of the seam, almost 16% of the material in this portion of the seam is framboidal pyrite. The contributions of the other two forms of pyrite referred to in Figure 19 are given in Figures 23 and 25. The total pyrite contributions with depth are shown in Figure 26.

Figure 25. The distribution of the pyrite category, "other larger, massive forms", in the Lovilia mine with depth in the seam. For example, in the top 1% of the seam, slightly more than 2% of the material in this portion of the seam is in this category. The contributions of the other two forms (single crystal and framboidal) of pyrite referred to in Figure 19 are given in Figures 23 and 24. The total pyrite contributions with depth are shown in Figure 26.

Figure 26. The distribution of total pyrite (total contribution of the three forms: single crystal, framboids, and other larger, massive forms) in the Lovilia mine with depth. For example, in the top 1% of the seam, approximately 9% of the material is pyrite. The individual contributions of the three forms of pyrite with depth are given in Figures 23, 24 and 25.

Figure 27. The distribution of single crystals of pyrite in the Star mine with depth in the seam. For example, for the 1% interval at a depth of 42 to 43% of the thickness of the seam, approximately 1% of the material in this portion of the seam is small pyrite single crystals. The contributions of the other two forms of pyrite referred to in Figure 20 are given in Figures 28 and 29. The total contributions with depth are shown in Figure 30.

Figure 28. The distribution of framboidal formations of pyrite in the Star mine with depth in the seam. For example, for the 1% interval at a depth of 50 to 51% of the thickness of the seam, approximately 2% of the material in this portion of the seam is framboidal pyrite. The contributions of the other two forms of pyrite referred to in Figure 20 are given in Figures 27 and 29. The total pyrite contributions with depth are shown in Figure 30.

Figure 29. The distribution of the pyrite category, "other larger, massive forms", in the Star mine with depth in the seam. For example, in the 1% interval at a depth of 38 to 39% of the thickness of the seam, approximately 71% of the material in this portion of the seam is in this category. The contributions of the other two forms (single crystal and framboidal) of pyrite referred to in Figure 20 are given in Figures 27 and 28. The total pyrite contributions with depth are shown in Figure 30.

Figure 30. The distribution of total pyrite (total contribution of the three forms: single crystal, framboids, and other larger, massive forms) in the Star mine with depth. For example, in the 1% interval at a depth of 38 to 39% of the thickness of the seam, approximately 71% of the material is pyrite. The individual contributions of the three forms of pyrite with depth are given in Figures 27, 28 and 29.

- 1) useful insight has been gained in understanding the difficulty of sulfur removal using conventional techniques,
- 2) microstructural-chemical information suggests an important basis of coal cleaning variations to be expected from mine to mine,
- 3) large uncertainties are to be expected for standard sulfur chemical determinations (much of the pyrite may never get into solution and this can contribute to large inaccuracy in total sulfur, pyritic sulfur and "organic" sulfur values), and
- 4) coal is generally crushed to -200 mesh at most utilities, but is then burned directly without attempts to clean it at this stage and for this size (-76 μ m diameter particles) ... due to the presence of large amounts of pyrite at this stage, innovative cleaning techniques offer an important potential to upgrade the coal through additional sulfur removal.

Experimental Programs in Progress and Planned

Analyses of other Iowa mines are in progress; microstructural-chemical data for macerals and for pyrite should be completed for the Mich mine during this project period and information being developed for other Iowa mines (three mines) should contribute to the understanding of choice and improvement of processing and purification procedures. Channel samples from other states will be prepared for scanning electron microscope - energy dispersive X-ray analysis (SEM-ED analysis) during this period.

Arrangements are being completed to begin analyses of documented samples from three coal liquefaction processes: H-coal, Synthoil, and Solvent Refined Coal (SRC). Microstructural-chemical characterization by SEM-ED analysis will include specimens of feed coals, residues, and liquefaction solid product for presence of pyrite or sulfur reaction products such as pyrrhotite. The liquefaction solid product is of particular interest. Is inorganic sulfur from very small pyrite crystals carried over and found in the SRC coal product (e.g., in the form of a reaction product such as pyrrhotite), for example? This work will be coordinated with that of other groups such as the Illinois Geological Survey (S. Russell).

Microscale coal etching experiments and SEM-ED analyses of cross sections of these specimens will be performed to establish the effectiveness of nitric acid dissolution of pyrite in coals as this relates to the accuracy of current wet chemical analyses techniques used for total sulfur, pyritic sulfur and organic sulfur determinations. This is of particular interest for coals which contain large amounts of pyrite on a micrometer scale (especially below 50 μ m in size which would not be included in standard optical microscope characterization schemes and would be missed by conventional X-ray diffraction techniques). In this situation, the insoluble coal can encapsulate the pyrite crystals which would result in significant errors in the determination of sulfur and its distribution between inorganic and organic forms.

CONCLUSIONS

An investigation for the purpose of improving and developing several promising methods for desulfurizing and recovering fine coal is well underway. A preliminary assessment of the state of development of the applicable technology has been made through field visits and review of the technical literature. Laboratory equipment and apparatus have been collected and experimental work initiated. In this regard two laboratory-scale reaction systems have been acquired to investigate the chemical desulfurization of coal by a unique process. One of these systems has been tested and is being utilized to measure the rate of dissolution of pyrite separated from coal. Preliminary froth flotation tests have been conducted with a laboratory-scale flotation cell to obtain baseline data on an Iowa coal with a high sulfur content. Quite unexpectedly these tests indicated that aluminum nitrate may be an activator for coal because it served to increase the recovery of coal. Several potential pyrite depressants for improving the separation of coal and pyrite have been screened by measurement of the zeta potential and floatability. The following reagents show some promise as pyrite depressants: ferric chloride, sodium cyanide, ammonium thiocyanate, and the disodium salt of ethylenediaminetetraacetic acid. A preliminary design for a bench-scale flow system which will demonstrate the continuous processing of fine coal by the froth flotation, selective oil agglomeration and pelletization techniques has been prepared. Furthermore the distribution of various forms of pyrite by size and crystal structure has been determined for two channel samples of coal through application of scanning electron microscope techniques.

LITERATURE CITED

1. Stambaugh, E. P., Miller, J. F., Tan, S. S., Chauhan, S. P., Feldman, H. F., Carlton, H. E., Foster, J. F., Nack, H., and Oxley, J. H., "Hydrothermal process produces clean fuel," *Hydrocarbon Processing* 54 (7), 115-116 (July 1975).
2. "Hydrothermal process cleans up coal," *Chemical and Engineering News* 53 (27), 24-25 (July 1, 1975).
3. "New process makes clean coal," *Chemical Week* 118 (1), 33-35 (January 7, 1976).
4. Lorenzi, L., Jr., Lord, J. S., Van Nice, L. J., Koutsoukos, E. P., and Meyers, R. A., "TRW zeroes in on leaching method to desulfurize pyritic coals," *Coal Age* 77 (11), 76-79 (Nov. 1972).
5. Hamersma, J. W., Kraft, M. L., Kendrick, W. P., and Meyers, R. A., "Chemical Desulfurization of Coal to Meet Pollution Control Standards," American Chemical Society, Division of Fuel Chemistry, Reprints of papers presented at 167 National Meeting, Los Angeles, April 1-5, 1974.
6. Hamersma, J. W., Kraft, M. L., Kendrick, W. P., and Meyers, R. A., "Meyers' Process cuts out 80% sulfur," *Coal Mining & Processing* 11 (8), 36-39 (Aug. 1974).
7. Meyers, R. A., "Desulfurize coal chemically," *Hydrocarbon Processing* 54 (6), 93-95 (June 1975).
8. Meyers, R. A., TRW Inc., personal communication (1976).
9. Agarwal, J. C., Giberti, R. A., Irminger, P. F., Petrovic, L. J., and Sareen, S. S., "Coal Desulfurization: Costs/Processes and Recommendations," presented at American Chemical Society meeting, Los Angeles, April, 1974.
10. Agarwal, J. C., Giberti, R. A., Irminger, P. F., Petrovic, L. F., and Sareen, S. S., "Chemical Desulfurization of Coal," *Mining Congress Journal* 61 (3), 40-43 (March 1975).
11. Agarwal, J. C., Giberti, R. A., and Petrovic, L. J., "Method for Removal of Sulfur from Coal," U.S. Patent 3,960,513 (June 1, 1976).
12. Sareen, S. S., Giberti, R. A., Irminger, P. F., and Petrovic, L. J., "The Use of Oxygen/Water for Removal of Sulfur from Coals," presented at 80th National Meeting of AIChE, Boston, Sept. 7-10, 1975.
13. Friedman, Sidney, Pittsburgh Energy Research Center, ERDA, personal communication (1976).
14. Tai, C. Y., "Extraction of Pyrites from Coal by Oxidation and Leaching," Energy and Mineral Resources Research Institute, Iowa State University, Ames, Iowa, in press.

15. Leonard, J. W., and Cockrell, C. F., "Basic Methods of Removing Sulfur from Coal," Mining Congress Journal 56 (12), 65-70 (Nov. 1970).
16. Gorin, E., and Lebowitz, H. E., "Removing Sulfur and Mineral Matter from Coal," in "Coal Processing Technology," pp. 64-68, Am. Inst. Chem. Engr., New York, 1974.
17. Zimmerman, R. E., "Froth Flotation in modern coal preparation plants," Mining Congress Journal 50 (5), 26-32 (May 1964).
18. Aplan, F. F., Bonner, C. M., Hirt, W. C., and Rastogi, R. C., "Recent Advances in Coal Flotation," presented at Second Symposium on Coal Preparation, NCA/BCR Coal Conference and Expo III, Louisville, KY, Oct. 19-21, 1976.
19. Glembotskii, V. A., Klassen, V. I., and Plaksin, I. N., "Flotation," English translation by R. E. Hammond, Primary Sources, New York, 1972.
20. Sun, S. C., "Effects of Oxidation of Coals on their Flotation Properties," Mining Engineering 6 (4), 396-401 (April 1954).
21. Baker, A. F., and Miller, K. J., "Hydrolyzed Metal Ions as Pyrite Depressants in Coal Flotation: A Laboratory Study," Bureau of Mines Report of Investigations 7518, U.S. Dept. of Interior, Washington, DC (May 1971).
22. Miller, K. J., "Flotation of Pyrite from Coal: Pilot Plant Study," Bureau of Mines Report of Investigations 7822, U.S. Dept. of Interior, Washington, DC (1973).
23. Miller, K. J., "Coal-Pyrite Flotation," Transactions Society of Mining Engineers, AIME 258 (1) 30-33 (March 1975).
24. Laros, T. J., "Froth Flotation," progress report June 1975-January 1976, Energy and Mineral Resources Research Institute, Iowa State University, Ames, Iowa.
25. Min, S., "Physical Desulfurization of Iowa Coal," IS-ICP-35, Energy and Mineral Resources Research Institute, Iowa State University, Ames, Iowa, in press.
26. Sennett, P., and Oliver, J. P., "Colloidal Dispersions, Electrokinetic Effects and the Concept of Zeta Potential," in "Chemistry and Physics of Interfaces," pp. 73-92, Am. Chem. Soc., Washington, DC, 1965.
27. Somasundaran, P., "Interfacial Chemistry of Particulate Flotation," AIChE Symposium Series No. 150, Vol. 71, 1-15 (1975).
28. Iwasaki, I., Cooke, S. R. B., and Colombo, A. F., Bureau of Mines Report of Investigations 5593, U.S. Dept. of Interior, Washington, DC (1960).
29. Campbell, J. A., and Sun, S. C., "An Electrokinetic Study of Bituminous Coal Froth Flotation and Flocculation," Special Research Report SR-74 Submitted to the Coal Research Board of the Commonwealth of Pennsylvania, Pennsylvania State University, University Park, PA (May 23, 1969).

30. Moeller, T., "Inorganic Chemistry," John Wiley & Sons, New York, 1952.
31. Fuerstenau, D. W., Metzger, P. H., and Seele, G. D., "How to Use this Modified Hallimond Tube for Better Flotation Testing," Engineering and Mining Journal 158 (no. 3), 93-95 (March 1957).
32. Perrott, G. St. J., and Kinney, S. P., "The Use of Oil in Cleaning Coal," Chemical and Metallurgical Engineering 25 (5), 182-188 (Aug. 1921).
33. Capes, C. E., McIlhenney, A. E., Sirianni, A. F., and Puddington, I. E., "Bacterial Oxidation in Upgrading Pyritic Coals," Canadian Mining and Metallurgical (CIM) Bulletin 66 (739), 88-91 (Nov. 1973).
34. McIlhinney, A. E., Sirianni, A. F., Capes, C. E., and Puddington, I. E., "Bacterial Oxidation in Upgrading Sulfide Ores and Coals," U.S. Patent 3,796,308 (March 12, 1974).
35. Fraser, T., "Convertol Process of Coal-Slurry Treatment," Bureau of Mines Information Circular 7660, U.S. Dept. of Interior, Washington, DC (April 1953).
36. Brisse, A. H., and McMorris, W. L., "Convertol Process," Transactions Society of Mining Engineers, AIME 211 258-261 (Feb. 1958).
37. Anderson, John, Manager of Preparation and Quality Control, U.S. Steel Corp., Pittsburgh, PA, personal communication (August 1976).
38. Capes, C. E., McIlhinney, A. E., and Coleman, R. E., "Beneficiation and Balling of Coal," Transactions Society of Mining Engineers AIME 247 233-237 (Sept. 1970).
39. Capes, C. E., Smith, A. E., and Puddington, I. E., "Economic Assessment of the Application of Oil Agglomeration to Coal Preparation," CIM Bulletin 67 (747), 115-119 (July 1974).
40. Capes, C. E., McIlhinney, A. E., McKeever, R. E., and Messer, L., "Application of Spherical Agglomeration to Coal Preparation," presented at 7th International Coal Preparation Congress, Sidney, Australia (May 23-28, 1976).
41. Pulsifer, A. H., Professor, Iowa State University, Ames, Iowa, personal communication (March 1976).
42. Verschuur, E., and Davis, G. R., "The Shell Pelletizing Separator: Key to a Novel Process for Dewatering and De-ashing Slurries of Coal Fines," presented at 7th International Coal Preparation Congress, Sidney, Australia (May 23-28, 1976).
43. Sarkar, G. G., Konar, B. B., Sakha, S., and Sinha, A. K., "Demineralization of Coals by Oil-Agglomeration Technique, Part I: Studies on the Applicability of Oil Agglomeration Technique to Various Coal Beneficiation Problems," paper presented at 7th International Coal Preparation Congress, Sidney, Australia (May 23-28, 1976).

44. Min, S., and Wheelock, T. D., "Cleaning High Sulfur Coal," presented at Second Symposium on Coal Preparation, NCA/BCR Coal Conference and Expo III, Louisville, KY, Oct. 19-21, 1976.
45. Capes, C. E., McIlhinney, A. E., Sirianni, A. F., and Puddington, I. E., "Agglomeration in Coal Preparation," Proceedings Institute for Briquetting and Agglomeration 12, 53-62 (Aug. 1971).
46. Capes, C. E., McIlhinney, A. E., and Coleman, R. D., "Beneficiation of Coals," U.S. Patent 3,665,066 (May 23, 1972).
47. Csanyi, L. H., "Method for Combining a Bituminous Binder with an Aggregate Material," U.S. Patent 2,917,395 (Dec. 15, 1959).
48. Csanyi, L. H., "Bituminous Mixes Prepared with Foamed Asphalt," Bulletin 189, Iowa Engineering Experiment Station, Iowa State University, Ames, Iowa, (Nov. 9, 1960).
49. Csanyi, L. H., "Foamed Asphalt for Economical Road Construction," Civil Engineering 32 (6), 66-68 (June 1962).
50. Greer, R., "Microstructural Characteristics of Iowa Coal," Working Paper No. 1 - October 3, 1974; Working Paper No. 2 - February 28, 1975; Working Paper No. 3 - May 31, 1975; Working Paper No. 4 - June 30, 1975; Iowa Coal Project, available from Document Library, Ames Laboratory ERDA, Iowa State University, Ames, Iowa 50011.
51. Greer, Raymond T., "Nature and Distribution of Pyrite in Iowa Coal," Proc. Electron Microscopy Society of American, G. W. Bailey, editor, Claitor's Press, Baton Rouge, pp. 620-621. 1976.
52. Greer, R. T., "Colloidal Pyrite Growth in Coal," Recent Advances in Colloid and Interface Science, Vol: 5, edited by Milton Kerker, Academic Press, New York, pp. 411-423, 1977.
53. Greer, R. T., "Coal Microstructure and the Significance of Pyrite Inclusion," Scanning Electron Microscopy/1977, O. Johari, editor, IIT Research Institute, Chicago, 11 pp., 1977, in press.