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ADVANCED DEVELOPMENT OF FINE COAL
DESULFURIZATION AND RECOVERY TECHNOLOGY

Quarterly Technical Progress Report
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Division of Materials & Exploratory Research

By

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- (b) distribution among each form with respect to size (in micrometer intervals) for the range of sizes observed. Fields of single crystals are considered as units of a particular size, e.g., units of 300 μ m to 1200 μ m in diameter are comprized of single crystals. The sizes of the single crystals as constituents are usually submicrometer to 15 μ m in diameter.

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ABSTRACT

The improvement and technical development of several promising methods for desulfurizing and recovering fine coal was continued. These methods include froth flotation, selective oil agglomeration, pelletization, and a chemical desulfurization process which involves leaching fine coal with a hot dilute solution of sodium carbonate containing dissolved oxygen or air under pressure. Numerous laboratory experiments and measurements were conducted in the areas of froth flotation, selective oil agglomeration and chemical desulfurization. The results of this work showed that when pyrites are leached with an alkaline solution containing dissolved oxygen, the sulfur is extracted in the form of soluble sulfates and the iron is converted to ferric oxide or hematite. It was also shown that the rate of conversion of pyritic sulfur to soluble sulfates depends on the oxygen partial pressure with the rate increasing as the partial pressure is raised. Results which could lead to major improvements in the froth flotation method of separating coal and pyrites included the successful demonstration of an oxidative chemical pretreatment process which would greatly reduce the floatability of pyrite particles without greatly affecting the floatability of coal. Also conditions were identified which would aid in the selection of suitable cationic and anionic flotation collectors for effecting a better separation of coal and pyrite. The discovery that it may be possible to utilize relatively inexpensive, heavy residual fuel oils instead of light distillates for the selective agglomeration of fine coal enhances the economic viability of this method of coal beneficiation. The successful application of heavy residual oils seems to depend on the incorporation of a suitable emulsifying agent such as castile soap with the oils. A major part of the detailed design and specifications were prepared for a bench-scale flow system which will demonstrate the beneficiation and recovery of fine-size coal by various methods. The construction schedule for this system was revised and a completion date of December, 1977, established. The distribution of various forms of pyrite by size and by crystal structure has been determined for additional coal seams through application of scanning electron microscope techniques.

OBJECTIVES AND SCOPE OF WORK

Background

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

Objectives

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

Task A. - Chemical Desulfurization

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

Task B. - Froth Flotation

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

Task C. - Selective Oil Agglomeration

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

Task D. - Pelletization

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

Task E. - Continuous Processing

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

Task F. - Coal Microstructure

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

Task G. - Neutron Source for Sulfur Monitoring Instrument

The task of constructing and developing an electronic neutron source for a sulfur monitoring instrument is being reconsidered in light of the recent commercial availability of such an instrument.

SUMMARY OF PROGRESS TO DATE

Several methods which hold great but commercially unrealized 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 best development course to pursue. As a result of this assessment, an experimental program has been devised and launched to achieve the stated objective.

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 solution of sodium carbonate containing dissolved oxygen or air under pressure. Two laboratory reaction systems have been set up to demonstrate and develop the leaching step. One system utilizes a fixed bed tubular reactor through which the leaching 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 shown that most of the sulfur which is extracted is converted to soluble sodium sulfate. The pyritic iron, on the other hand, is converted to insoluble ferric oxide or hematite. The rate of conversion of pyrite particles which were isolated from coal has been measured under a variety of conditions by using the tubular reaction system. Thus the rate has been found to increase with increasing oxygen partial pressure but to decrease with increasing oxygen flow rate and increasing pyrite charge size. It does not seem to be affected by liquid flow rate under the conditions utilized. The stirred autoclave has been used to leach fine-size coal. Preliminary experiments have been conducted to determine the role of agitator speed.

Since poor rejection of pyritic sulfur has hampered the application of froth flotation in the industrial field of coal preparation, this problem is being addressed specifically. A number of potential flotation depressants for pyrite have been screened by measuring the floatability of pyrite in the presence of these reagents with a modified Hallimond tube microflotation cell. Although several reagents have been found to suppress the flotation of pyrite when used alone, these reagents have not proven to be good depressants when used in conjunction with methyl isobutyl carbinol (MIBC), a commonly employed

frothing agent in the field of coal flotation. Measurement of the zeta potential of coal or pyrite suspensions containing small amounts of these reagents has identified conditions where it may be possible to employ suitable cationic or anionic collectors to effect a good separation of coal and pyrite. In addition it has been shown that the floatability of pyrite can be greatly reduced by applying an oxidative chemical pretreatment process. Fortunately this process has only a slight effect on the floatability of coal.

Several ways to improve the technical and economic viability of the selective oil agglomeration method of beneficiating fine coal have been identified. Thus it has been found that it may be possible to use relatively inexpensive, heavy residual fuel oils for agglomeration provided that a suitable emulsifying agent is incorporated with the oils. Of various emulsifying agents tested, castile soap seems to be the best for this purpose. Also it has been found that the oxidative chemical pretreatment process which reduces the floatability of pyrite will greatly improve the selectivity of the oil agglomeration method.

Various types of pelletizers have been assessed in order to select a bench-scale unit for demonstrating the pelletization of coal fines. As a result of this assessment, a variable diameter, inclined, rotating disc pelletizer has been selected. Since a unit of this design does not appear to be manufactured commercially, the unit is being designed for fabrication in house.

A major part of the detailed design and specifications 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. Construction of this system is now scheduled to be completed by December, 1977.

The development of efficient methods for desulfurizing coal depends on the way sulfur is distributed in the coal. In order to gain some understanding of this distribution, channel samples of coal from three Iowa coal mines have been analyzed by scanning electron microscopy and associated energy dispersive x-ray analysis techniques. The distribution of pyrite among colloidal size single crystals, framboids, and larger massive forms has been determined as a function of depth from top to bottom of various coal seams as well as the distribution of total pyrite with depth. The relative proportions of the three forms of pyrite and the proportion of pyrite in various size ranges have also been determined for each of the channel samples as a whole.

DETAILED DESCRIPTION OF TECHNICAL PROGRESS

Chemical Desulfurization

The development of a very promising process for removing most of the inorganic sulfur and at least part of the organic sulfur from coal was continued. This process involves leaching fine-size coal with a hot, dilute solution of sodium carbonate containing dissolved oxygen under pressure. The

immediate goals of the present experimental program are to demonstrate the extraction of larger amounts of organic sulfur and faster rates of pyrite dissolution through the application of higher temperatures and/or oxygen partial pressures than used previously. Laboratory experiments are being conducted with two types of reaction systems. One system utilizes a fixed bed tubular reactor and the other a stirred tank reactor. The first reactor is more suitable for investigating the kinetics of pyrite dissolution while the second is more suitable for investigating the removal of different types of sulfur from coal.

Tubular Reactor System

A series of experiments involving the tubular reactor was initiated to determine the possible significance of various parameters on the rate of dissolution of pyrite particles and to see how the important parameters affect the rate. The reaction system is illustrated by Figure 1 and was described in the previous progress report (1).

For each run, a small measured quantity of ground and sized pyrite was placed in the tubular reactor. The loaded reactor was placed in the preheated fluidized sand bath and connected to the rest of the system (Figure 1). The system was next purged and pressurized with nitrogen and the feed pump was started. At first deionized water was pumped through the system. The flow of nitrogen was soon stopped and the feed pump was switched to pumping a dilute sodium carbonate solution. Almost concurrently a metered flow of oxygen was started. The back pressure valve located downstream from the reactor was adjusted to provide the desired system pressure. The run was then continued while maintaining constant conditions of temperature, pressure, and liquid and gaseous feed rates. During the run the liquid effluent was collected in a series of measured portions which later were analyzed separately for sulfur using the Fritz and Yamamura method (2). Before analyzing, the liquid samples were treated with hydrogen peroxide to insure that all of the soluble sulfur compounds were completely converted to sulfates. After a run was completed, the oxygen flow was interrupted, the feed pump stopped, and the reaction system purged with nitrogen gas. The reactor was then disconnected and emptied, and the solid residue weighed and analyzed for total sulfur.

The pyrite used for this series of experiments was recovered from Iowa coal by hand-picking. It was ground, sized and analyzed. It contained 41.94% iron and 39.82% total sulfur. Therefore, it was far from being pure pyrite. Also the atomic ratio of sulfur to iron was only 1.65 instead of the 2.0 required for FeS_2 . Therefore, not all of the iron was present in the form of pyrite.

The experimental conditions employed during the series of runs reported here are shown in Table 1. All of the runs were made with -120/+140 mesh (U.S. Standard Sieves) particles at a temperature of 150°C with a leachant containing 2.0 wt.% sodium carbonate. The pyrite charge, total system pressure, and liquid and gaseous feed rates were varied between runs. The total conversion of sulfur to soluble products was calculated two ways. The first was based

Figure 1. Tubular reactor system for investigating chemical desulfurization.

on a chemical analysis of the liquid effluent while the second was based on a chemical analysis of the solid residue. The total conversion determined by the first method was generally 10 to 15% lower than the total conversion determined by the second method (Table 1). It appears that either one of the methods of chemical analysis was slightly biased or not all of the solid residue was recovered.

The results presented in Table 1 show that the total sulfur extracted from the pyrite during the different runs was from 40 to 80% based on an analysis of the liquid extract or from 50 to 90% based on an analysis of the solid residue. This was the amount extracted in 1 hr. or less and depended on the experimental conditions employed. The best results were obtained in runs 16 and 30 which employed the lowest oxygen feed rates but highest oxygen partial pressure. Conversely the poorest results were obtained in run 19 which employed the highest oxygen feed rate and lowest partial pressure. It is suspected that higher gas flow rates prevented good contact between liquid and solids and thus resulted in a lower rate of extraction. On the other hand, increasing the oxygen partial pressure increased the rate of extraction because the rate of reaction depends on the concentration of this important reactant.

The progress of extraction during individual runs is illustrated by the diagrams of sulfur conversion versus time (Figures 2-7). These diagrams show that very little sulfur was extracted during the first 10 min. This was because it required that much time for the sodium carbonate solution and oxygen to reach the pyrite. However, once the leaching mixture contacted the pyrite, the rate of sulfur extraction was very rapid as shown by the large slope of the curves. As leaching proceeded, the rate gradually decreased.

For several runs the samples of liquid effluent were analyzed for iron as well as for sulfur. The iron content of the first sample was relatively high being in the range of 100 to 400 p.p.m. and this represented the soluble iron salts such as ferrous sulfate which were extracted by hot water alone. The iron content of the second sample was low being on the order of 1 p.p.m. However, the iron content of the third sample was higher being in the range of 4 to 18 p.p.m. while the iron content of all succeeding samples was about 1 p.p.m. Since the third sample was the first sample collected after the sodium carbonate solution contacted the solids, it appears that the solids contained a small amount of iron in some form which was more readily extracted than pyrite but which was not extracted by hot water.

The results presented in Figure 2 indicate that the rate of sulfur extraction increased as the charge size was reduced. There are several possible explanations for this effect. One possible explanation is that the larger the charge size, the larger the build-up in concentration of a rate-inhibiting reaction product in the leach solution. Another possible explanation is that the larger the charge size, the poorer the contact between the liquid and solids because of channeling or maldistribution of flow. Since a large excess of the leaching mixture was fed, it is doubtful that the concentration of leachant decreased enough to affect the rate regardless of charge size.

Table 1. Experimental conditions employed in chemical leaching of pyrite

Run No.	Pyrite Charge		Alkali Conc., wt. %	Liquid Rate, ml./sec.	O ₂ Rate, ^a ml./sec.	O ₂ Press., psia	Temp., °C	Press., psig	Rx. Time, min.	Total Conversion, %	
	wt., g.	size, mesh								Based on liquid	Based on solids
11	5.0	-120/+140	2% Na ₂ CO ₃	1.50	12.3	48	150	100	41	57	63
12	5.0	-120/+140	2% Na ₂ CO ₃	1.50	11.3	48	150	100	58	61	68
13	10.0	-120/+140	2% Na ₂ CO ₃	1.50	11.3	73	150	125	59	65	77
14	5.0	-120/+140	2% Na ₂ CO ₃	1.50	11.3	98	150	150	56	75	88
15	10.0	-120/+140	2% Na ₂ CO ₃	1.50	13.2	98	150	150	57	69	81
16	5.0	-120/+140	2% Na ₂ CO ₃	2.25	8.5	98	150	150	60	78	91
17	5.0	-120/+140	2% Na ₂ CO ₃	3.00	9.4	98	150	150	44	68	76
18	5.0	-120/+140	2% Na ₂ CO ₃	1.50	5.7	48	150	100	57	68	79
19	5.0	-120/+140	2% Na ₂ CO ₃	1.50	18.9	48	150	100	59	43	54
20	5.0	-120/+140	2% Na ₂ CO ₃	2.25	11.3	98	150	150	53	76	87
21	5.0	-120/+140	2% Na ₂ CO ₃	1.50	17.0	98	150	150	57	62	71
30	2.5	-120/+140	2% Na ₂ CO ₃	1.50	9.4	98	150	150	58	82	90

^a Measured at standard conditions of 1 atm. and 25°C.

Figure 2. Increasing the pyrite charge had an adverse effect on the rate of conversion.

Figure 3. Liquid flow rate had little effect on the rate of conversion.

Figure 4. Increasing gas flow rate had an adverse effect on the rate of conversion.

Figure 5. Increasing gas flow rate had an adverse effect on the rate of conversion.

Figure 6. Increasing the oxygen pressure increased the rate of conversion.

Figure 7. Increasing the oxygen pressure increased the rate of conversion.

Over the range of liquid flow rate investigated (1.5 to 3.0 ml./sec.), it appeared that this parameter had very little if any effect on the rate of extraction (Figure 3). On the other hand, the oxygen flow rate had a large effect on the rate of extraction (Figures 4 and 5). As the oxygen flow rate increased, the rate of extraction clearly decreased. Since a large excess of oxygen was fed even at the lowest flow rate, it appears as though the extra gas may have interfered with good contact between liquid and solids.

Increasing the oxygen partial pressure increased the rate of extraction (Figures 6 and 7). This was to be expected since oxygen was one of the primary reactants.

Some of the leached particles as well as some of the unleached particles were examined with a scanning electron microscope. Photomicrographs representing two levels of magnification of leached particles are presented in Figure 8. Both the size and shape of the leached particles were similar to those of the unleached particles. However, closer examination of the two types of particles revealed microscopic differences (Figure 9). Thus the grain size of the leached material was much finer than that of the unleached material. Only a portion of the surface of a single leached particle is shown in the lower photomicrograph of Figure 9 but it shows that the particle was made up of submicron size grains. Further examination of the leached particles by means of x-ray diffraction showed them to be largely hematite (Fe_2O_3).

Since very little iron was extracted from the solids by the leachant, it appears that most of the iron was converted to hematite. The evidence provided by scanning electron microscope examination of the particles indicates a recrystallization process which involves transformation of small pyrite crystallites within individual particles to even smaller hematite crystallites without alteration of the over-all size and shape of the particles.

Additional experiments will be carried out with the tubular reactor to further study the effects of different parameters on the rate of extraction of sulfur from pyrite. The effects of temperature, alkali concentration, and particle size will be included. Runs will also be made in which small amounts of reaction products, such as sodium sulfate, are added to the leach solution to determine the effect of these products on the rate of extraction.

Stirred Autoclave System

Although a 1.0 liter autoclave with a gas dispersing turbine agitator coupled to a magnetic drive was obtained some time ago for coal leaching experiments, the use of this device was delayed because the Rulon sleeve bearings which were supplied with the unit did not perform satisfactorily. These bearings were replaced with graphite bearings which have performed well.

A preliminary series of experiments has been completed with the stirred autoclave to demonstrate the effect of agitator speed on the quantity of sulfur extracted from a high-sulfur content coal in 1.0 hr. Run of mine coal from the Iowa State University Demonstration Mine No. 1 was used for this series of experiments. The coal was pulverized to -200 mesh size. For each

100 μ

25 μ

Figure 8. Photomicrographs of leached particles.

UNLEACHED PYRITE

LEACHED PYRITE

2 μ

Figure 9. The grain structure of leached particles was much finer than that of unleached particles.

run the autoclave was charged with 40 g. of coal and 400 ml. of 0.20 M sodium carbonate solution. After the autoclave was closed, the desired agitator speed was established and the heater was turned on. The autoclave was purged with nitrogen while being heated to the desired temperature. When the system reached operating temperature (150°C), the flow of nitrogen was stopped and oxygen introduced. Some gas was bled continuously from the reactor to avoid any build-up in concentration of gaseous products within the system. The temperature (150°C), total pressure (104 psig), oxygen partial pressure (50 psia), and stirring rate were kept constant for 1.0 hr. after which the reaction was stopped by discontinuing the flow of oxygen into the system and purging with nitrogen. Cold water was conducted through the cooling coil in the reactor to lower the temperature of the system. After cooling, the contents of the reactor were filtered to recover the coal. The coal was dried in an oven, weighed, and chemically analyzed for various forms of sulfur.

The results of this series of experiments are presented in Table 2 and Figure 10. It can be seen that the reduction in pyritic sulfur content of the treated coal, and consequently the total sulfur content as well, depended greatly on the speed of the turbine agitator. Thus the rate of extraction increased over the entire speed range from 200 to 1800 r.p.m. with the greatest increase taking place between 1200 and 1400 r.p.m. Above 1400 r.p.m. the changes in pyritic and total sulfur contents with agitator speed appeared to be smaller. This effect will be verified with further experiments conducted with higher agitator speeds.

In the future experiments will be conducted to investigate the effects of other parameters such as coal particle size, oxygen partial pressure, and temperature. Preferably these experiments will be conducted in a kinetically controlled regime where the rate of reaction is independent of agitator speed.

Table 2. Preliminary results of leaching experiments with the stirred autoclave

Run No.	Speed r.p.m.	Yield, %	Ash, wt. %	Sulfur Distribution, wt. %				Total S Reduction, %
				Pyritic	Sulfate	Organic	Total	
Coal ^a	---	---	15.4	5.68	0.79	2.90	9.37	---
AE01	200	95.3	17.0	5.47	0.24	2.78	8.49	9.4
AC01	350	95.8	16.8	5.18	0.17	2.73	8.08	13.8
AE02	400	95.5	17.8	5.33	0.26	2.79	8.38	10.6
AE03	500	94.8	16.8	4.53	0.22	3.12	7.87	16.0
AE04	600	96.3	17.8	4.48	0.01	3.38	7.87	16.0
AE05	700	95.8	17.5	4.76	0.06	2.76	7.58	19.1
AE06	800	95.5	16.7	4.71	0.02	3.02	7.75	17.3
AE07	1000	96.0	18.1	3.80	0.08	2.75	6.63	29.2
AE08	1200	96.0	18.5	3.92	0.07	2.62	6.61	29.5
AE09	1400	94.5	18.3	0.96	0.13	2.72	3.81	59.3
AE10	1600	94.5	17.5	1.09	0.14	2.70	3.93	58.1
AE11	1800	93.5	16.9	0.80	0.13	2.55	3.48	62.9

^a Ash and sulfur distribution of unleached coal is shown.

Figure 10. The rate of sulfur removal depended greatly on agitator speed.

Froth Flotation

Experimental work was conducted in several areas in order to improve the froth flotation method of desulfurizing coal. Thus flotation tests were conducted with a high-sulfur content Iowa coal to obtain baseline data. Also the zeta potential of coal or pyrite suspensions was measured to screen various chemical reagents which might modify the surface properties of coal or pyrite. In addition, the relative floatability of coal on pyrite particles in the presence of various surface modifying reagents was determined.

Froth Flotation Tests

The series of froth flotation tests designed to obtain baseline data on an Iowa bituminous coal with a very high sulfur content was continued. The coal was from the Iowa State University Demonstration Mine No. 1 in Mahaska County, Iowa. The sample of coal fines used for the tests reported here contained 7.0% pyritic sulfur, 8.9% total sulfur, and 23.5% ash and had the following size distribution:

Screen, mesh	Mat'l. Retained, wt.%	Mat'l. Passing, wt.%
48	----	100.0
60	6.1	93.9
100	33.2	66.8
200	65.5	34.5
325	92.2	7.8

The sample was collected at the Iowa State University coal preparation plant and represented some of the fines produced during crushing. The flotation tests were carried out as before 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 by operating the agitator at 1000 r.p.m. for 10 min. to insure a uniform suspension. The pH of the pulp was adjusted to 5.5-5.6 by adding hydrochloric acid. A measured amount of MIBC was added next, the agitator speed increased to 2000 r.p.m., and an air flow of 30 cu.ft./hr. started. The froth was collected in a series of fractions until most of the coal had been recovered. The solids in each fraction were recovered separately, dried, weighed and analyzed for total sulfur, pyritic sulfur, and ash.

In the series of tests reported here, the quantity of MIBC was varied to see if the concentration of this reagent had an effect on flotation selectivity. Different runs were made using 1.0, 0.25, 0.10, and 0.05 ml. of MIBC per batch. The results presented in Figures 11 and 12 show that the concentration of MIBC had only a small effect on the selectivity of the separation process as practiced here. The surprising aspect of these results is that the selectivity seemed to increase as the concentration of MIBC was raised which is opposite to anticipated results. Thus for a given recovery such as 70%, the cleanest float product with respect to both sulfur and ash was produced when the highest concentration of MIBC was used. The total recovery of float product also increased with increasing concentration of MIBC (Figure 13).

Figure 11. The average sulfur content of the cumulative fractions was not greatly affected by the amount of MIBC used.

Figure 12. The selectivity of the flotation process increased with increasing amounts of MIBC.

Figure 13. The recovery of float product increased with increasing amounts of MIBC.

The greater selectivity which resulted from the use of larger concentrations of MIBC may have been due to the increased rate of frothing caused by the larger amounts of MIBC. As the concentration of MIBC was raised, the time required to complete a batch run was reduced and consequently the opportunity for floating the less floatable minerals was reduced.

Further tests will be conducted to investigate the effect of particle size and pulp density on the selectivity of the flotation process.

Zeta Potential

The screening of various chemical reagents which have some potential for modifying the surface properties of coal and/or pyrite particles in aqueous suspensions was continued. Reagents which can serve as pyrite depressants in froth flotation practice were specifically sought. For screening purposes the zeta potential of coal and/or pyrite suspensions was measured as described in the last progress report (1). Iowa coal and pyrite were drawn from the same stock of materials prepared for the previously reported measurements (1). The coal had been prepared by crushing and then floating in a solution of tetrachloroethylene and hexane having a specific gravity of 1.30. The composition of the raw coal and of the float fraction is shown in Table 3. A portion of the float fraction was ground to a size of 5 to 50 μ m and stored under nitrogen until used for the zeta potential measurements. The pyrite had been crushed to about 1/4 in. size and then split into two batches, pyrite I and pyrite II. The sulfur distribution of these two batches is shown in Table 3. The first batch (pyrite I) was pulverized and then screened to provide -80/+100 mesh material. A portion of this material was ground to 5-50 μ m size for the zeta potential measurements.

Measured values of the zeta potential of coal and/or pyrite suspensions adjusted with various pH modifiers are presented in Figure 14. In the case of coal, it appears that the electrical charge on the particles is determined by adsorption of hydrogen ions or hydroxyl ions and not by adsorption of other

Table 3. Chemical analysis of the Iowa coal and pyrite

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

ions present in the system. On the other hand, in the case of pyrite it appears that the adsorption of calcium ions plays an important role. When these are present, the surface charge on the pyrite particles changes from negative to positive.

Adding small amounts of sodium chloride to suspensions of coal or pyrite had little effect on the zeta potential (Figure 15). However, it should be noted that even when sodium chloride was not added to the suspensions, some sodium was present at high pH because sodium hydroxide was added to raise the pH. Also at low pH some chloride was always present because hydrochloric acid was used to lower the pH. In any event the evidence indicates that neither coal nor pyrite adsorb sodium or chloride ions to a great extent.

The effect of adding small amounts of the disodium salt of ethylenediaminetetraacetic acid ($\text{Na}_2\text{H}_2\text{EDTA}$) to a pyrite suspension was noted in the last report (1). The effect of adding this salt to a coal suspension is shown here for comparison (Figure 16). It can be seen that in the case of coal this salt only affects the zeta potential at high pH whereas in the case of pyrite it affects the zeta potential over the entire pH range which was studied.

The effects on the zeta potential of coal or pyrite suspensions of small amounts of sodium sulfite, sodium silicate, and sodium phosphate are shown in Figure 17. None of these reagents seemed to have a large effect on the zeta potential of coal. Although they all appeared to lower the zeta potential of coal equally well, the apparent effect may have been due more to a change in the coal itself rather than to the addition of these various salts. Thus the coal surface may have become oxidized between the time of the first measurement without any added reagents and subsequent measurements with the various salts. Among these salts, only sodium silicate had a unique effect on the zeta potential of pyrite (Figure 17). Thus this salt tended to raise the zeta potential whereas both sodium sulfite and sodium phosphate tended to lower it.

A review of the results presented here and in the last report (1) shows that the zeta potentials of coal and pyrite are of opposite sign when these materials are suspended in solutions of the following reagents at the indicated pH:

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

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

Figure 14. The surface charge on pyrite but not coal was strongly affected by calcium ions.

Figure 15. The surface charge on coal and pyrite was not greatly affected by sodium chloride.

Figure 16. The surface charge on coal was only affected at higher pH by $\text{Na}_2\text{H}_2\text{EDTA}$ whereas the surface charge on pyrite was affected at all pH tested.

Figure 17. Sodium silicate tended to raise the zeta potential of pyrite.

advantageously for the selective flotation of pyrite where the pyrite particles bear a negative charge or anionic collectors where the pyrite particles bear a positive charge.

In the future, floatability tests will be conducted to study the practical application of these results. In other words, the floatability of coal and/or pyrite in the presence of various cationic and anionic collectors and the reagents listed above will be investigated to see whether a more efficient method of separating coal and pyrite can be developed.

Floatability of Coal or Pyrite

An investigation of the relative floatability of coal or pyrite in the presence of various potential pyrite depressants and other flotation reagents was continued. Measurement of the relative floatability was done with a modified Hallimond tube microflotation cell. The cell and experimental procedure used were described in the previous progress report (1). The coal was part of the float fraction prepared for the zeta potential measurements except that it was not finely ground. The composition of the float fraction is given in Table 3. The float fraction was pulverized and screened to provide -60/+100 mesh material for the floatability measurements. Two batches of pyrite (pyrite I and pyrite II) described above (see Table 3 for sulfur distribution) were also used for the floatability measurements. Each of these batches was ground and screened to provide -80/+100 mesh material for these measurements. However, pyrite I was ground and stored for several weeks before use while pyrite II was ground just before use.

The percentage or relative recovery of both pyrite I and pyrite II obtained in a series of microflotation experiments conducted at different pH without any flotation reagents other than pH modifiers is shown in Figure 18 along with the relative recovery obtained in another series of experiments involving the addition of a small amount of methyl isobutyl carbinol (MIBC), a commonly used frothing agent. The relative recovery seemed to depend on the pH, the presence or absence of MIBC, and the particular batch of pyrite. All three factors appeared to interact. However, in the absence of MIBC, the relative recovery was about the same for both batches of pyrite, although the recovery of pyrite I seemed more dependent on pH than the recovery of pyrite II. The addition of MIBC increased significantly the recovery of both pyrite I and pyrite II over the entire pH range.

The results of microflotation experiments which utilized sulfuric acid or calcium hydroxide for pH adjustment are shown in Figure 19 together with the results of similar experiments which utilized hydrochloric acid or sodium hydroxide. In all cases, a small amount of MIBC was added. While the type of acid seemed to have little effect on the relative recovery of either kind of pyrite, the type of base did seem to affect the recovery of pyrite I but not of pyrite II. Thus calcium hydroxide seemed to improve the recovery of pyrite I at higher pH which is surprising in as much as this reagent is generally regarded as a pyrite depressant (3).

The effect of a small amount of ferric chloride on the floatability of pyrite in the presence of MIBC proved interesting (Figure 20). Thus ferric

Figure 18. Addition of MIBC improved the relative recovery of pyrite.

Figure 19. The relative recovery of pyrite I seemed to depend on whether the pH was controlled with sodium hydroxide or calcium hydroxide.

Figure 20. Ferric chloride appeared to activate pyrite I but had little effect on pyrite II.

Figure 21. Ammonium thiocyanite activated pyrite I and depressed pyrite II.

chloride seemed to activate and enhance the floatability of pyrite I over the whole range of pH investigated which again was surprising since ferric chloride is supposed to be a pyrite depressant, and as noted in the last progress report (1), it did tend to depress pyrite I in the absence of MIBC. Also the effect of ferric chloride on pyrite II was much less pronounced than on pyrite I. Moreover, at lower pH ferric chloride did seem to reduce somewhat the floatability of pyrite II.

The action of ammonium thiocyanate on the floatability of pyrite also proved interesting. It was noted previously that this reagent tended to reduce the floatability of pyrite I in the absence of MIBC (1). However, in the presence of MIBC it seemed to increase the floatability of this material (Figure 21). On the other hand, it seemed to reduce the floatability of pyrite II in the presence of MIBC.

Several other reagents which were investigated had about the same effect on the floatability of pyrite. These reagents included sodium carbonate, sodium silicate and $\text{Na}_2\text{H}_2\text{EDTA}$. All of these reagents appeared to enhance the floatability of pyrite I in the presence of MIBC but seemed to have little effect on the floatability of pyrite II (Figures 22-24).

The preceding results show that the effect of various chemical agents on the floatability of pyrite depends on the pH and the presence (or absence) of other flotation reagents such as MIBC as well as on the nature or state of the pyrite itself. Thus various agents such as calcium hydroxide and ferric chloride which are reputed to depress the floatability of pyrite seemed to exert the opposite effect in the presence of MIBC. Since pyrite I and pyrite II behaved differently even though they came from the same source, it is suspected that the difference in behavior may have been due to a difference in the state of surface oxidation. Thus pyrite I was ground and then stored for a considerable period of time before use while pyrite II was freshly ground before use. Hence, the surface of the pyrite I particles could have been oxidized more than that of the pyrite II particles.

The relative recovery of coal was greatly increased by the addition of MIBC in a series of microflotation experiments (Figure 25). The effect of MIBC on coal was much greater than its effect on pyrite. Therefore, the claim that MIBC serves as a collector for coal as well as a frothing agent seems well founded.

The type of acid or base used to adjust the pH of the coal suspensions for the microflotation experiments involving MIBC seemed to make little difference (Figure 26). On the other hand, the addition of ferric chloride to the coal suspensions seemed to reduce the relative recovery of coal at high pH (Figure 27). However, the addition of small amounts of sodium carbonate, $\text{Na}_2\text{H}_2\text{EDTA}$, sodium silicate, or ammonium thiocyanate seemed to improve the relative recovery of coal in the presence of MIBC (Figures 28-31). Unfortunately none of the chemical agents tested had either the effect of greatly increasing the recovery of coal or the effect of greatly decreasing the recovery of pyrite when used in conjunction with MIBC.

Figure 22. Sodium carbonate activated pyrite I but had little effect on pyrite II.

Figure 23. Sodium silicate tended to activate pyrite I but had little effect on pyrite II.

Figure 24. Na_2H_2EDTA activated pyrite I but had little effect on pyrite II.

Figure 25. MIBC increased the relative recovery of coal much more than it increased the relative recovery of pyrite.

Figure 26. The relative recovery of coal was indifferent to the type of acid or base used.

Figure 27. Ferric chloride exerted a depressing action on coal at high pH.

Figure 28. Sodium carbonate tended to improve the floatability of both coal and pyrite I.

Figure 29. Na₂H₂EDTA tended to improve the recovery of both coal and pyrite I.

Figure 30. Sodium silicate tended to improve the relative recovery of both coal and pyrite I.

Figure 31. Ammonium thiocyanate tended to improve the recovery of both coal and pyrite I.

Floatability of Chemically Pretreated Coal or Pyrite

An oxidative chemical pretreatment was applied to coal or pyrite to determine if it would reduce the floatability of pyrite without reducing the floatability of coal. For this treatment 50 g. of the -60/+100 mesh float fraction of coal (Table 3) prepared for the previously described floatability tests or 50 g. of -60/+100 mesh pyrite II also prepared for these tests was mixed with 500 ml. of a solution containing 10% by weight of sodium carbonate. The mixture was heated to 80°C and held at this temperature in a stirred flask while air was introduced continuously into the suspension through a diffuser for 30 min. at atmospheric pressure. The flask was then cooled to room temperature and the solids recovered by filtration. The unwashed solids were dried in an oven at 100°C for 3 hr. Two grams of the solids were used for each of the microflotation experiments with the modified Hallimond tube. The procedure used for these experiments was similar to that employed for the previously described floatability tests. For each test, 0.01 ml. of MIBC was added to the suspension of coal or pyrite placed in the microflotation cell. The results are presented in Table 4. A comparison of these results with those shown in Figure 25 for untreated coal and pyrite indicate that the chemical pretreatment step greatly reduced the floatability of pyrite while only slightly reducing the floatability of coal. An examination of both the treated and untreated pyrite particles with a scanning electron microscope revealed no marked differences between the two types of particles. Hence, it would appear that the chemical treatment only affected the surface of the particles.

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

Selective Oil Agglomeration

An experimental program was outlined in the previous progress report for developing the selective oil agglomeration method of cleaning and recovering fine-size coal. One of the objectives of this program is to develop an economical process which utilizes relatively inexpensive heavy residual fuel oils. Although such oils should yield agglomerates which are more stable (both mechanically and thermally) than light oils would yield, past work has indicated

Table 4. Floatability of chemically pretreated coal and pyrite

Coal		Pyrite	
pH	Relative Recovery, %	pH	Relative Recovery, %
3.2	60.02	3.3	2.65
4.4	60.25	4.8	3.17
5.5	64.67	6.4	3.54
7.5	58.02	7.8	3.32
9.7	63.70	9.0	4.39

that the heavy oils are not as selective in their agglomerating properties as light oils (4). Also it is more difficult to disperse the heavy oils in water.

A series of experiments was carried out to see if incorporating a suitable emulsifying agent with a heavy residual fuel oil (No. 6) would overcome these difficulties. The following emulsifying agents were tested:

Castile Soap, Fisher Scientific Co.

Mixture of Amyl Alcohol and Castile Soap

L-520 Silicone Surfactant, Union Carbide Co.

Polyacrylic Acid, K & K Laboratories, Inc.

These agents were combined with oil and water and then emulsified with an ultrasonic transducer (model Al40, Sonifier Cell Disrupter, Heat Systems - Ultrasonics, Inc.). The emulsions were used to agglomerate run-of-mine coal from the Iowa State University Demonstration Mine No. 1. This coal had been pulverized to -60 mesh size.

In order to produce a relatively stable emulsion of oil and water, the following procedure was adopted: A mixture of 10 ml. of No. 6 fuel oil and 500 ml. of deionized water was placed in a beaker which was agitated with the ultrasonic transducer under full power while the emulsifying agent was added a little bit at a time. After each addition the mixture was agitated for a few minutes and then the ultrasonic generator was turned off to see if the oil and water would separate. When a relatively stable emulsion was formed, no more of the emulsifying agent was added and the emulsion was used to agglomerate coal. The amount of each emulsifying agent used is shown in Table 5 along with the results of the oil agglomeration experiments.

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

In addition to the experiments which utilized various emulsifying agents, two experiments did not involve the use of these agents. In one case a light fuel oil (No. 200LLS) was emulsified with water alone by vigorous agitation with the ultrasonic transducer before it was used for agglomeration. A relatively stable emulsion was produced in this case without the use of an emulsifying agent. In another case an unstable emulsion was prepared with the blender by mixing No. 6 fuel oil and water at high speed and the unstable emulsion was used for agglomerating coal.

Table 5. Results of using different emulsifying agents in oil agglomerating an Iowa coal^a

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

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

The results of these experiments are presented in Table 5. The highest yield of product on a moisture and oil-free basis was obtained by using the light (No. 200LLS) fuel oil without an emulsifying agent. The light oil also produced discrete, well-formed and relatively clean agglomerates. The results were nearly as good when coal was agglomerated with an emulsion of No. 6 fuel oil and water stabilized with castile soap. Fair results were also obtained with the emulsion of No. 6 fuel oil and water stabilized with the mixture of castile soap and amyl alcohol. However, the results obtained with the other emulsions were very poor; discrete, well-formed agglomerates were not produced so the recovery was low.

The encouraging aspect of these results is the success obtained with the emulsion stabilized with castile soap. Thus it appears that by using this emulsifying agent it may be possible to utilize relatively inexpensive heavy fuel oils and still gain the advantage of the light oils. Of course, much more work needs to be done to demonstrate and develop this improvement.

The reduction in sulfur and ash achieved in these experiments was not remarkable but it can be improved by grinding the coal to a finer size to unlock the mineral matter and by chemically pretreating the coal to alter the surface of the pyrite particles so that it is uniformly hydrophilic. Also the oil agglomeration method can be used advantageously with gravity separation.

In the near future, a series of experiments will be carried out to compare the effectiveness of different types of fuel oils both with and without an emulsifying agent for agglomerating coal which has been precleaned by gravity separation and also chemically pretreated.

Pelletization

Further consideration was given to the selection and/or design of a suitable pelletizer for demonstrating the pelletization of coal fines. As a result of this consideration, a variable diameter, inclined, rotating disc pelletizer was selected for the proposed work. Since a pelletizer of this size with out special features does not seem to be available commercially, a unit is being designed which can be fabricated in house.

Continuous Processing of Fine Coal

A major portion of the detailed engineering design of a bench-scale flow system for demonstrating the froth flotation, selective oil agglomeration, and pelletization methods of cleaning and recovering fine coal was completed. A schematic flow-sheet of this system is presented as Figure 32. The system includes a pretreatment section for grinding and chemically treating coal to enhance the separation of coal and pyrite.

The design and construction schedule for the system was revised and now appears as shown in Table 6. Erection of the steel supporting structure is scheduled to begin about the middle of June. All of the major items of equipment should be delivered to the site by the end of September and construction should be completed by the end of November. System testing and shakedown should be finished by the end of December.

Neutron Source for Sulfur Monitoring Instrument

Although developing and constructing an electronic neutron source for a sulfur monitoring instrument was one of the original tasks of this project, it appears that such a device will soon become available commercially. Therefore, continued development of a neutron source by the Ames Laboratory may be an unnecessary duplication of effort. Further consideration is being given to the direction this task should take. It may be more cost effective for the Ames Laboratory to acquire and test one of the new commercial units.

Figure 32. Bench-scale system for demonstrating the continuous processing of fine coal.

Table 6. Revised design and construction schedule for bench-scale flow system

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

Characterization of Coal Microstructure

by

Raymond T. Greer

Scientific Background

The first complete distribution data for pyrite in coal seams on a micrometer scale have been presented (1,5). Significant amounts of pyrite can be present in coal as particles less than 50 micrometers in diameter. These can be missed or ignored using standard sulfur analysis techniques. The development of microstructural and microchemical data to improve our understanding of the nature of coal and of how different mixtures of macerals and minerals affect coal conversion liquefaction and gasification processes is of concern in the present investigation.

Objectives

- (1) maceral - mineral characterization; functional behavior of separable constituents,
- (2) identification of features of coal constitution which bear on ways to improve coal treatment schemes for removing sulfur and potential ash components, and,
- (3) precision and accuracy of chemical determination of sulfur as influenced by distribution factors of pyrite.

Technical Approach

Combined scanning electron microscopy/energy dispersive x-ray analysis techniques are used to determine the microstructure of coal and the presence and distribution of pyrite (FeS_2), the principal inorganic sulfur bearing phase. Microstructural information on a micrometer scale is developed by use of the scanning electron microscope, and this textural information is correlated with associated microchemical information obtained from energy dispersive x-ray microanalyses to locate pyrite (and other inorganic phases). This permits an evaluation of particle size, shape and distribution factors which impact on decisions to attempt removal of additional sulfide particles and thus reduce the sulfur content.

Experimental Results

Complete distribution data for pyrite in the Mich coal mine (strip mine, Iowa) on a micrometer scale are presented. Data for the Star mine (strip mine) and the Lovilia mine (shaft mine) were reported in the previous quarterly report (1). This information is for complete coal channel samples.

The distribution of pyrite among three forms in the mines (micrometer diameter or colloidal size single crystals; framboids. . . various size berry-like agglomerations of single crystals; and larger pyrite masses) is considered. Representative views of each of these forms are presented in Figure 33. For the

(a)

(b)

Figure 33. Scanning electron micrographs of pyrite in coal.

- a. micrometer size individual crystals and framboids (Otley Mine, Iowa)
- b. pyrite masses; intimate intergrowths of pyrite crystals (ISU Demonstration Mine No. 1)

Figure 33c. Pyrite masses; partial field of single crystals (and framboids); general lack of intergrowth characteristic such as in Figure 33b. These fields of view are considered both as units comprised of single crystals (e.g. Figure 34b), or as crystals on a constituent crystal basis (size of individual crystals independent of distribution fields). Framboids, if present, are treated as a single unit in both cases. (Mich Mine-Lower Seam, Iowa.) Scale bar is 10 micrometers.

Table 7. Distribution of pyrite among various forms

Form of Pyrite	Distribution, wt. %		
	Mich Mine ^a	Star Mine ^b	Lovilia Mine ^b
Single crystal	69.7	21.1	7.5
Framboids	12.3	10.9	6.1
Other larger, massive forms	<u>18.0</u>	<u>68.0</u>	<u>86.4</u>
	100.0	100.0	100.0

^aFields of individual crystals are taken as size units; note, single crystals within these fields as well as isolated single crystals are included in the single crystal category.

^bFrom reference 1. pg. 42

Mich mine (lower seam), the distribution of pyrite among these forms is presented in Table 7. Additional distribution information for the Mich mine is shown in Figure 34. The single crystal form of pyrite predominates below 1 μ m particle diameters, but is an important form over a wide range of sizes. In the case where all single crystal occurrences are seen (including fields of single crystals, Figure 34), the single crystals and units of single crystals are especially abundant for two size ranges: submicrometer to 150 μ m and 300 to 1200 μ m in diameter. The single crystals considered as constituents generally range from submicrometer in size to approximately 15 μ m in diameter with individual crystals seen as large as 150 μ m in diameter in these samples (Figure 35b). Framboids are an important form of pyrite over a size range of a few micrometers to tens of micrometers in diameter.

The proportion of pyrite in various size ranges suggests an insight into difficulties in pyrite removal by conventional separation techniques and by conventional chemical analytical techniques. A portion of this information is presented in Table 8. The Mich mine data are significantly different in comparison to the data for the other two mines. The pyrite material is extremely fine (Figure 35a and 35b), even when considered on an agglomerate basis where fields of single crystals are taken as particular sized units.

Details of the proportionation of pyrite for the Mich mine (Lower Seam) for various size ranges are presented in Figures 35a and 35b. Figure 35a indicates that the pyrite crystal assemblies (units of crystals), framboids and individual crystals range from submicrometer in size up to approximately 1200 micrometers in diameter. By comparison, when the pyrite is considered on a constituent size basis, the largest are of the order of 150 μ m in diameter, with most of the pyrite less than 5 μ m 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

MICH MINE , (LOWER SEAM)
DISTRIBUTION OF PYRITE AMONG FORMS

(a)

(b)

Figure 34. Distribution of pyrite in the Mich mine (Lower Seam) among three forms: single crystals, framboids, and other larger, massive forms. Data are presented two ways:

- (a) fraction of total pyrite for the mine seam for each form, and,
- (b) distribution among each form with respect to size (in micrometer intervals) for the range of sizes observed. Fields of single crystals are considered as units of a particular size, e.g., units of 300μm to 1200μm in diameter are comprised of single crystals. The sizes of the single crystals as constituents are usually sub-micrometer to 15μm in diameter.

MICH MINE (LOWER SEAM)

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

(a)

MICH MINE (LOWER SEAM)

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

(b)

Figure 35a. Proportionation of pyrite for the various size ranges observed for the Mich mine (Lower Seam). For example, 75% of the pyrite is less than 76μm in diameter (i.e., 200 mesh). Units of agglomerated, recognizable single crystals are included in this presentation. Compare this with Figure 35b.

35b. Proportionation of pyrite on a constituent size basis for the various size ranges observed for the Mich mine (Lower Seam). For example, 96% of the pyrite is less than 76μm in diameter (i.e., 200 mesh).

Table 8. Proportion of pyrite in certain size ranges

Mich Mine^a

50% < 12 μ m
75% < 76 μ m (i.e., 200 mesh)

Mich Mine^b

50% < 2 μ m
96% < 76 μ m (i.e., 200 mesh)

Star Mine^c

50% < 45 μ m
57% < 76 μ m (i.e., 200 mesh)

Lovilia Mine^c

50% < 300 μ m
30% < 76 μ m (i.e., 200 mesh)

^a(with extensive fields of single crystals considered as size units, Figure 34)

^b(single crystals considered on a constituent crystal basis)

^cfrom reference 1, pg. 45

larger, massive forms) and the total of all pyrite forms is shown as a function of depth in the Mich mine (Lower Seam; Figures 36-39). There are distinct differences in the way the three forms are distributed.

Complete pyrite removal would be difficult for these samples, and a primary constituent size of the order of a micrometer in diameter is observed.

Experimental Programs in Progress and Planned

Scanning electron microscopy/energy dispersive x-ray analyses of other Iowa mines are in progress. Complete channel samples for these mines are being described.

To assess the effectiveness of nitric acid dissolution of pyrite in these coals, cross sections of treated and untreated specimens are being examined on a micrometer scale basis. Initial etching, staining and characterization studies should be completed during this project period. This work is providing information on the accuracy of current wet chemical analyses techniques used for total sulfur, pyritic sulfur and organic sulfur determinations.

Figure 36. The distribution of single crystals of pyrite in Mich mine (Lower Seam) with depth in a seam. For example, in the top 1% of the seam, 3% of the material is small pyrite single crystals. The contributions of the other two forms of pyrite referred to in Figures 33 and 34 are given in Figures 37 and 38. The total pyrite contributions with depth are shown in Figure 39.

Figure 37. The distribution of framboidal formations of pyrite in the Mich mine (Lower Seam) with depth in a seam. For example, for the 1% interval at a depth of 7 to 8% of the thickness of the seam, approximately 1% of the material is framboidal pyrite. The contributions of two other forms of pyrite referred to in Figures 33 and 34 are given in Figures 36 and 38. The total pyrite contributions with depth are shown in Figure 39.

Figure 38. The distribution of the pyrite category, "other larger, massive forms", in the Mich mine (Lower Seam) with depth in the seam. For example, for the 1% interval at a depth of 21 to 22% of the thickness of the seam, approximately 3% of the material is in this form. The contributions of the two other forms of pyrite referred to in Figures 33 and 34 are given in Figures 36 and 37. The total pyrite contributions with depth are shown in Figure 39.

Figure 39. The distribution of total pyrite (total contribution of the three forms; single crystal, framboids, and other larger, massive forms) in the Mich mine (Lower Seam) with depth. For example, in the top 1% of the seam, approximately 6% of the material is pyrite. The individual contributions of the three forms of pyrite with depth are given in Figures 36, 37, and 38.

CONCLUSIONS

The improvement and development of several promising methods for desulfurizing and recovering fine coal was continued. The chemical desulfurization of coal and of pyrites extracted from coal was demonstrated with laboratory reaction systems. In this method of desulfurization, iron pyrites are oxidized by oxygen dissolved in an alkaline solution. Experimental evidence indicates that most of the iron is converted to insoluble ferric oxide or hematite while the sulfur is converted to soluble sulfates. The rate of conversion of pyritic sulfur to soluble sulfates was shown to depend on oxygen partial pressure with the rate increasing as the partial pressure was raised. When pyrite particles were leached in fixed bed tubular reaction systems, the rate of sulfur extraction was not affected by liquid flow rate but it was adversely affected by oxygen flow rate since the rate of extraction declined as the oxygen feed rate was raised. This adverse effect may have been due to interference of the excess gas with proper liquid-solids contact. The rate of sulfur extraction from pyrites in a tubular reactor was also affected adversely by increasing charge size. This effect could have been due to a buildup in concentration of some soluble reaction product or to channeling and maldistribution of flow.

Results which could lead to major improvements in the froth flotation method of separating coal and pyrites included a demonstration of an oxidative chemical pretreatment process which greatly reduced the floatability of pyrite while only slightly affecting the floatability of coal. In addition conditions were identified which could lead to the selection of suitable cationic or anionic flotation collectors which would effect a good separation of coal and pyrite.

The economic viability of the selective oil agglomeration process for beneficiating fine coal was enhanced by the discovery that it may be possible to utilize relatively inexpensive, heavy residual fuel oils for this process providing a suitable emulsifying agent is incorporated with the oil. Castile soap was found to be a promising emulsifying agent for this application.

A major part of the detailed design and specifications was prepared for a bench-scale flow system which will demonstrate the beneficiation and recovery of fine-size coal by various methods. The construction schedule for this system was revised and a completion date of December, 1977, established.

An analysis of channel samples from several Iowa coal mines showed that a substantial proportion of the pyrites in these samples was in the form of very small crystallites and framboids.

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