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PHYSICAL DESULFURIZATION
of
IOWA COAL

MASTER

Seongwoo Min

March 1977

IOWA STATE UNIVERSITY Ames, Iowa - 50011

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R. S. Hansen, Director

Iowa State University
Ames, Iowa 50011

Preface

This report was prepared as an account of work sponsored by the Iowa Coal Project and conducted in the Energy and Mineral Resources Research Institute at Iowa State University. Financial support for the research was provided by an appropriation from the Iowa Legislature in June 1974.

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ABSTRACT

An experimental investigation was carried out to determine the effectiveness of several different physical beneficiation methods for desulfurizing Iowa coals. These methods included separation and recovery of clean coal by (1) float-sink (gravity) separation in dense liquids, (2) froth flotation, and (3) selective oil agglomeration. Since the effectiveness of these separation methods depends on first liberating or freeing the mineral matter from the organic matter through fragmentation or breakage, the effects of size reduction and method of comminution on the separation achieved by these methods were also investigated. Comminution methods included chemical comminution as well as mechanical crushing and grinding. The effects of other parameters on the separation efficiency of these methods were also studied. In addition to application and testing of these methods individually, various combinations of comminution and separation methods were applied to some Iowa coals in order to determine the overall effectiveness of different treatment sequences.

Since a significant percentage of the pyrites in some Iowa coals consists of finely disseminated crystallites, it was found that these coals have to be ground rather finely to free and subsequently separate the crystallites in order to obtain a large reduction in pyritic sulfur. It proved helpful for subsequent separation to first chemically comminute the coal by soaking it in liquid anhydrous ammonia before crushing and grinding the coal to fine size. One of the most effective treatment sequences which was demonstrated involved soaking lump coal in liquid ammonia, crushing to 1/4 in. top size, separating float and sink fractions at a gravity of 1.6, pulverizing and grinding the float fraction, and recovering the fine-size coal from the ground float fraction by selective oil agglomeration. As a result of this treatment sequence the pyritic sulfur content of two Iowa coals was reduced 85-86% and the ash content 70-84% while obtaining an overall weight yield of 82-84%.

The separation of coal and pyrite by either froth flotation or selective oil agglomeration was improved significantly by chemically pretreating the pulverized coal in a manner designed to oxidize the surface of the pyrite so as to render the surface hydrophillic and distinctly different from the hydrophobic surface of the coal. The pretreatment involved wet oxidation of an aqueous, alkaline suspension of coal with air. This approach proved much more effective than the application of pyrite depressants which are chemical agents designed to alter the pyrite surface through adsorption.

I. INTRODUCTION

The development of a practical process for reducing the sulfur content of coal is of great importance owing to the scarcity of low sulfur coal and the stringent standards for sulfur dioxide emissions from coal burning power plants. In particular, coal is Iowa's only fossil fuel resource which occurs in large enough reserves to be of much interest as an energy source to meet the growing demand for energy within the state. Iowa coals, however, are high in sulfur and thus are not environmentally acceptable in the unbeneficiated state.

Sulfur in coal is chiefly present as organic sulfur and pyritic sulfur. Although the organic sulfur, being molecularly bound to the coal matrix, cannot be removed by any mechanical cleaning method, it is possible to remove liberated pyritic sulfur by various mineral beneficiation methods.

The theory and practice of modern methods of coal preparation have been described by Leonard and Mitchell (1). Although there are a large number of potential methods which can be utilized for removing pyritic sulfur from coal, the applicability of various methods is heavily dependent on the particle size of the coal to be treated. The degree of pyritic sulfur reduction depends upon the amount of free pyrite liberated by comminution prior to cleaning.

Most commercial coal cleaning methods rely on the difference in specific gravity between coal and its impurities, and they are effective only on relatively coarse coal, i.e., +35 mesh (2). Many high sulfur coals, however, contain finely disseminated pyrites which can only be liberated by very fine grinding. Several methods including those based on dense medium cyclones, hydrocyclones and froth flotation are used commercially for washing fine-size coal. Their effectiveness, however, varies widely with the particular coal to be washed. In general, physical cleaning of coal is practically limited to removing approximately one-third of the sulfur and one-half of the mineral matter (3).

Among the commercially applied coal cleaning methods, froth flotation is the only one where the separation is not based upon a difference in specific gravity. In froth flotation, the separation is based on the difference in surface characteristics of coal and inorganic minerals. The underlying principles of froth flotation have been described by Gaudin (4). Although there is a large body of technical literature about froth flotation, the mechanism of coal flotation is not fully understood and the potential for improvement of this method appears to be great.

Another method which utilizes the difference in surface properties between coal and mineral matter to effect a separation is one involving selective oil agglomeration of fine-size coal particles suspended in water (5-7). The relatively large coal and oil agglomerates can be separated readily from the unagglomerated mineral particles by screening. Although the effectiveness of this method has been demonstrated experimentally, it is not presently used commercially.

In order to effect a better separation of coal and mineral matter, chemical comminution has been proposed as a more effective means of liberating the mineral matter than mechanical crushing (8,9). This method of comminution involves soaking coal in liquid anhydrous ammonia or other suitable chemical agents so that the coal comes "unglued" along bedding planes and boundaries between coal and mineral matter and literally falls apart.

The work described in this report was undertaken to compare and evaluate the effectiveness of different coal preparation and cleaning methods including gravity separation, froth flotation, oil agglomeration, chemical comminution, and mechanical crushing and grinding to see which ones offer the greatest potential for use in desulfurizing Iowa coal. In addition the oil agglomeration and froth flotation processes were selected for more intensive research and further development.

II. MATERIALS AND EQUIPMENT USED

The coal samples used in this work were collected from several Iowa coal mines. The proximate analysis and sulfur distribution of these coal samples are given in Table 1. The proximate analysis was determined by ASTM method D271 and the sulfur distribution by ASTM method D2492 (10).

Table 1. Chemical analysis of Iowa coals

	Proximate Analysis, %				Sulfur Distribution, %			
Coal Mine	Moisture	Ash	Volatile Matter	Fixed Carbon	Pyritic	Organic	Sulfate	Total
Star	0.92	10.81	43.26	45.01	3.33	2.26	0.16	5.75
Big Ben	1.18	12.52	37.50	48.80	2.05	0.87	0.16	3.08
[a]ICO	4.51	8.92	43.98	42.59	2.41	0.99	0.05	3.45
Jude	8.79	14.18	39.42	37.61	2.97	3.53	0.44	6.94
[b]Scott	8.26	14.31	34.52	42.91	3.64	4.00	0.59	8.23

[a] Channel sample

[b] Sample from ISU Demonstration Mine #1

Most of the samples were "grab" samples which were not necessarily representative of the coal in the mines where they were obtained. In experimental studies of these coals, our practice was to prepare kilogram quantities of the coals with the particle size consists of interest. Representative samples of these kilogram quantities were then taken and analyzed to establish controls for the studies.

Throughout this investigation, Iowa State University tap water was used for all experiments except where otherwise noted. A chemical analysis of this water is shown in Table 2.

For the size reduction and separation experiments, the following equipment was used:

1. Bench-scale double roll crusher (Smith Engineering Works, Milwaukee, WI). Fifty pounds of coal per hour could be crushed

Table 2. Analysis of Iowa State University tap water from Malik (11)

Impurity	Concentration, mg./l.
Total solids	680
Total hardness as $CaCO_3$	400
Calcium hardness as $CaCO_3$	278
Magnesium hardness as $CaCO_3$	122
Total alkalinity as $CaCO_3$	270
Calcium as Ca^{++}	111
Magnesium as Mg^{++}	29.8
Bicarbonate as HCO_3^-	330
Chloride as Cl^-	17.5
Sulphate as SO_4^{--}	160
Fluoride as F^-	0.9
Manganese as Mn^{++}	0.0
Iron as Fe^{++}	0.03

to 1/4 in. top size with this machine.

2. Mikro-Samplmill (Pulverizing Machinery Division, American-Marietta Co., Summit, NJ). Five pounds of coal per hour could be pulverized to -35 mesh size with this device. The size distribution of the pulverized coal is shown in Table 3.
3. Disk Mill (BICO Inc., Burbank, CA). Four pounds of coal per hour could be pulverized to -100 mesh size with the disk mill.
4. Blender (Sears Insta-Blend Model No. 400). One thousand milliliters of slurry could be agitated at a speed of up to 20,000 rpm with the 14 speed blender.
5. Wemco Flotation Machine (Western Machinery Co.). Two liters of slurry could be agitated at a speed of 1725 rpm and processed by froth flotation in this unit.
6. Benco Agitator (Bench Scale Equipment Co., Dayton, OH). Up to 6 gallons of slurry could be agitated at different speeds in the range of 0 to 1100 rpm with this unit.

Table 3. Size distribution by weight of coals pulverized by Mikro-Samplmill

Size, Tyler Mesh	Distribution, %			
	Star	Big Ben	Jude	Scott
-35+65	4.33	7.78	16.20	20.20
-65+100	36.90	34.50	24.39	31.73
-100+200	30.33	35.30	30.05	19.62
-200	28.44	22.40	29.34	28.45

III. OIL AGGLOMERATION

Oil agglomeration provides a method for collecting coal fines in an aqueous suspension. When a small amount of oil is added to a coal slurry under vigorous agitation, the oil selectively collects hydrophobic coal particles to form agglomerates which can be separated from the aqueous mixture. The water wetting minerals remain suspended in the water and can be rejected. Sirianni _et_ _al_. (5) reported that agglomerates could be produced in a wide variety of equipment such as blenders, paint shakers, and simple agitated tanks. Capes _et_ _al_. (6) found that the reduction of pyritic sulfur accomplished by this process was up to 90% when the coal was pretreated with the iron-oxidizing bacterium, thiobacillus ferroxidan. Recently, investigators at the National Research Council of Canada (7) described a selective oil agglomeration process for cleaning coal fines in two steps, flocculation followed by balling.

In order to evaluate the potential of the oil agglomeration process for cleaning Iowa coal and to further develop and perfect the process, a series of experiments was carried out to demonstrate the process under different conditions. The effectiveness of the process was evaluated in terms of the following quantities which were determined for each run:

$$\text{Yield (\%)} = \frac{\text{weight of dry product}}{\text{weight of dry feed}} \times 100$$

$$\text{Ash reduction (\%)} = \frac{\text{\% ash in feed} - \text{\% ash in product}}{\text{\% ash in feed}} \times 100$$

$$\text{Sulfur reduction (\%)} = \frac{\text{\% sulfur in feed} - \text{\% sulfur in product}}{\text{\% sulfur in feed}} \times 100$$

$$\text{Oil consumption (\%)} = \frac{\text{weight of oil used}}{\text{weight of feed}} \times 100$$

Effect of Oil

Preliminary experiments indicated that the effectiveness of the oil agglomeration method is sensitive to the type and amount of oil used as well as the method of adding the oil to the coal-water slurry.

Method of adding oil. Tests were made to compare adding oil directly to the aqueous coal slurry with adding it as an oil-water emulsion. Twenty grams of pulverized Scott coal (-35 mesh) were slurried with deionized water in a cylindrical container (2 1/2 in. diameter by 5 in. height). Two hundred milliliters of water were used for the straight oil experiments, and 100 ml. of water for the emulsified oil experiments. After the slurry was agitated for 5 min. at a speed of 350 rpm with the Benco agitator using a 2 1/2 in. diameter pitched blade turbine impeller, a measured amount of kerosene - No. 5 heavy fuel oil mixture (Sp.Gr. = 0.83) was added either directly or as an emulsion of oil in 100 ml. of deionized water prepared with an ultrasonic vibrator. The agitation was continued for a specified time and speed. The coal slurry was then poured onto a 60 mesh screen to recover the coal. The collected coal was dried overnight at 100°C, weighed, and analyzed for ash and sulfur content.

The results are summarized in Table 4 and also are plotted as functions of agitator speed and retention time in Figures 1 and 2, respectively. The results show that when an emulsion of oil and water was used, a high yield of agglomerated coal was obtained over the whole range of agitator speed and/or retention time. On the other hand, when straight oil was used, an agitator speed of 1150 rpm and retention time of 3 min. or more were needed to obtain a high yield. Use of emulsified oil did not have much effect on ash and sulfur reduction. It could well be that an oil and

Table 4. Oil agglomeration test with 20 g. Scott[a] coal (-35 mesh) using Benco agitator to compare straight oil and emulsified oil

Operating Conditions			Product Using Straight Oil			Product Using Emulsified Oil		
Oil, ml.	Speed, r.p.m.	Time, min.	Yield, %	Ash, %	Total Sulfur, %	Yield, %	Ash, %	Total Sulfur, %
1	350	5	42.1	14.12	7.21	82.5	13.87	7.13
1	750	5	66.7	12.81	6.67	75.3	12.53	7.11
1	1050	5	81.7	13.05	7.24	80.2	12.99	7.18
2	350	5	46.3	14.92	7.53	92.7	13.86	7.35
2	750	5	83.6	13.02	6.74	89.9	12.69	7.24
2	1050	5	90.5	12.75	7.27	90.2	12.14	6.88
3	350	5	46.3	14.06	7.37	90.7	13.88	7.45
3	750	5	76.5	12.68	7.11	87.4	12.42	7.17
3	1050	5	91.1	11.84	6.72	97.8	12.61	7.09
2	1050	0.5	35.2	13.19	6.91	82.0	12.78	6.36
2	1050	1	44.7	11.78	6.37	82.6	12.46	6.60
2	1050	3	83.0	12.21	6.78	84.4	11.95	6.18
2	1050	5	89.7	12.28	7.15	83.1	11.78	6.85
2	1050	10	88.5	12.07	7.06	81.3	11.58	6.95
2	1050	20	83.1	11.35	6.97	84.8	11.27	6.88
2	1050	30	83.7	11.63	7.17	83.4	11.44	6.76

[a] Untreated Scott coal contained 15.83% ash and 7.58% total sulfur

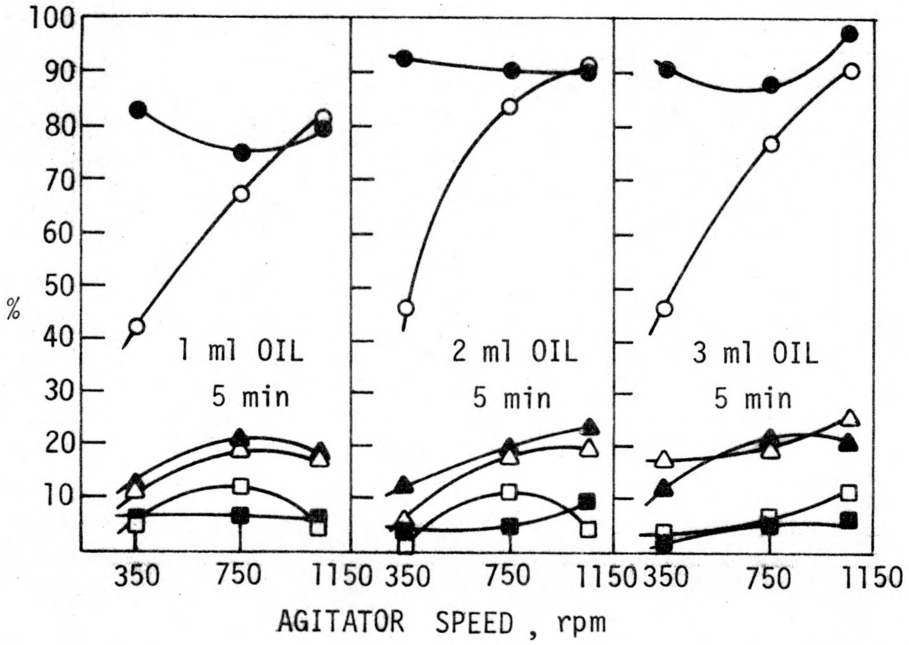

Figure 1. Effect of agitator speed and oil emulsification on agglomeration of -35 mesh Scott coal.

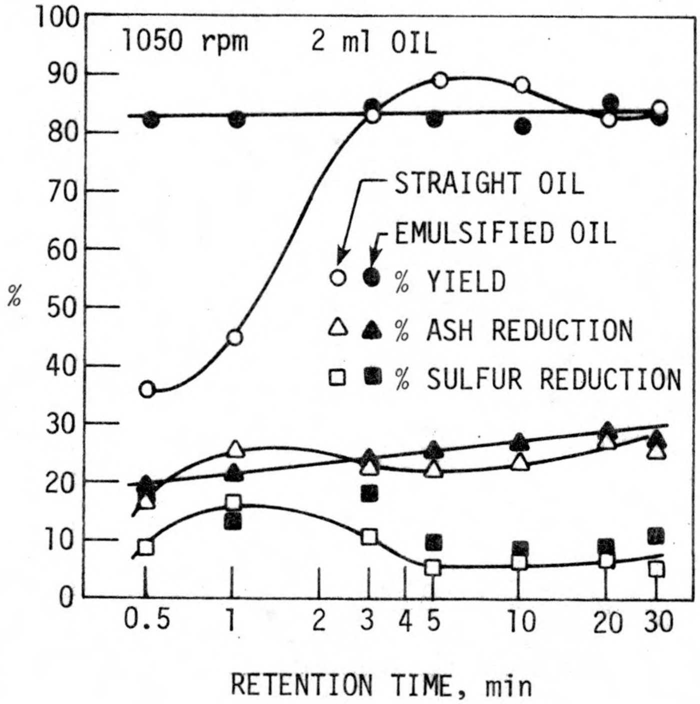

Figure 2. Effect of retention time and oil emulsification on agglomeration of -35 mesh Scott coal.

water emulsion is a necessary prerequisite for agglomeration of coal because even where straight oil is used the conditions necessary for agglomeration are likely to produce an emulsion.

Type of oil. The effectiveness of eight different petroleum oils (Table 5) for agglomerating coal was studied with another series of experiments.

The oil was added as an oil-water emulsion produced from one part of oil and 40 parts of tap water with an ultrasonic vibrator. Kerosene, heater oil, and furnace oil were readily emulsified without any emulsifying agent, but heavier oils required a small amount of silicon surfactant (L520, Union Carbide Corp.) as an emulsifying agent. For No. 6 fuel oils, 50 vol.% kerosene was added to reduce the viscosity of the oil.

Table 5. Specifications of petroleum oils[a] used for agglomerating coal

Oil	Specific Gravity at 60°F	Viscosity, Centistokes	Pour Point, °F
Kerosene	0.807	---	---
Heater Oil	0.811	---	---
Furnace Oil	0.855	2.08	-20
No. 200 Fuel Oil, LLS	0.916	13.11	-20
No. 5 Light Fuel Oil, LLS	0.934	49.70	-10
No. 5 Heavy Fuel Oil, LLS	0.946	58.89	0
No. 6 Fuel Oil, LLS	0.959	350.43	+30
No. 6 Fuel Oil	0.973	297.17	+30

[a] Source of oils and data was Amoco Oil Co.

Fifteen grams of pulverized coal (-35 mesh) were slurried with 500 ml. of tap water in the blender, and the pH of the slurry was adjusted to 6-7 by adding small amounts of 1 N. potassium hydroxide solution. Twenty milliliters of an oil-water emulsion were added to the slurry and the blender was operated for 10 min. at the lowest speed. If agglomerates formed and floated, the float product was skimmed off onto a 100 mesh sieve to recover the agglomerated coal. If the agglomerates were too small, more of the oil-water emulsion was added until stable agglomerates formed. The recovered coal was dried, weighed and analyzed for ash and sulfur contents.

The experimental results are given in Table 6 and plotted as a function of specific gravity of oil in Figure 3. The curves show that the oil consumption decreased with an increase in the specific gravity but the yield appeared to be constant. Since it appeared that maximum ash and sulfur reductions could be obtained with oil having a specific gravity of 0.82 - 0.84, further tests were made with several oil mixtures having a specific gravity of 0.83.

Jude coal was pulverized to two different top sizes, -35 mesh with the Mikro-Samplmill and -100 mesh with the disk-mill. Twenty grams of pulverized coal was slurried with 200 ml. of tap water in the blender. At the same time, a specified oil mixture was emulsified with 200 ml. of tap water in another blender for 5 min. The oil-water emulsion was then poured into the coal slurry and the mixture was agitated for 5 min. The slurry was placed in a 1000 ml. separatory funnel and the floated coal was separated by draining off the water containing suspended ash. The recovered coal was filtered, dried and analyzed.

Table 6. Oil agglomeration tests using different oils with 15 g. pulverized coals (-35 mesh)

Amoco Oils	Product with Star Coal[a]				Product with Big Ben Coal[b]				Product with Jude Coal[c]			
	Oil, ml.	Yield, %	Ash, %	Total S, %	Oil, ml.	Yield, %	Ash, %	Total S, %	Oil, ml.	Yield, %	Ash, %	Total S, %
Kerosene	1.50	89.9	7.66	5.23	2.00	90.9	7.11	2.53	2.00	77.2	9.11	4.68
Heater	1.50	85.5	5.78	5.06	1.75	74.2	5.03	2.23	1.75	81.9	9.54	4.88
Furnace	1.13	85.7	6.33	4.73	1.50	86.4	5.76	2.10	1.25	81.5	10.0	4.75
No. 200	1.00	87.5	8.97	--	1.50	86.2	7.48	--	1.88	70.4	11.3	--
No. 5 Light	0.75	79.3	6.43	4.93	0.88	77.7	7.42	2.71	1.50	83.8	11.9	5.14
No. 5 Heavy	0.63	85.0	6.68	4.96	0.75	82.2	7.16	2.63	1.38	81.5	10.2	4.79
No. 6 Light (+ kerosene)	1.00	90.0	7.37	--	1.13	83.1	6.81	--	1.25	82.4	8.2	--
No. 6 Heavy (+ kerosene)	1.00	94.7	6.72	--	1.25	80.2	7.62	--	2.00	73.9	11.8	--

[a] Untreated Star coal contained 10.81% ash and 5.75% total sulfur

[b] Untreated Big Ben coal contained 12.52% ash and 3.08% total sulfur

[c] Untreated Jude coal contained 15.47% ash and 5.99% total sulfur

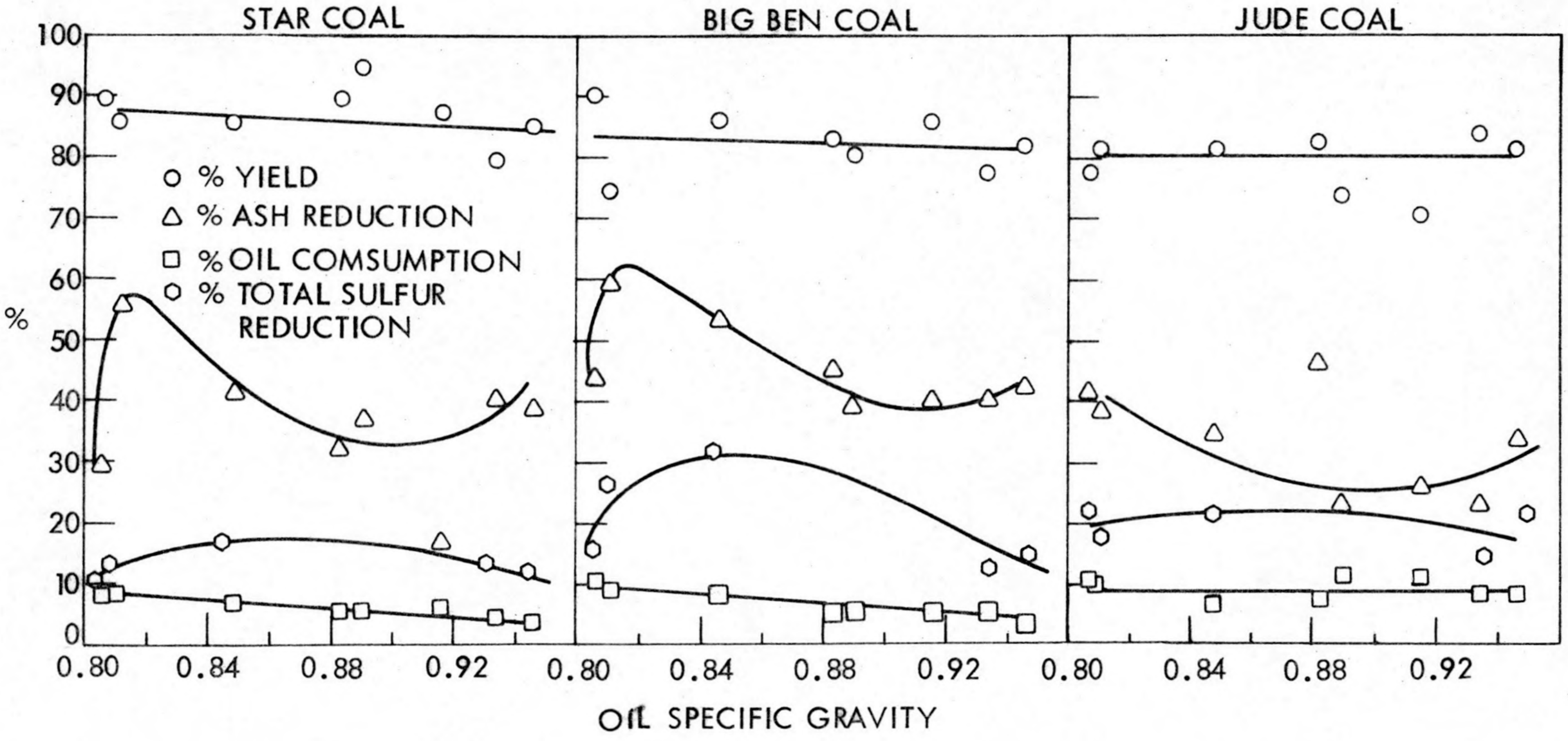

Fig. 3. Effect of different oils on agglomeration of -35 mesh coal.

For these tests either kerosene or heater oil was blended with one of the heavier oils to provide a blend having the desired specific gravity (0.83). The results of agglomerating two different size consists of Jude coal with these different blends are presented in Table 7. Although less oil was used than during the previous series of tests with -35 mesh Jude coal, the yield of agglomerated coal (about 80%) was generally as good as with either lighter or heavier oils. On the other hand, the ash and sulfur reductions were quite varied, evidently depending upon the particular heavy oil used in the blend. Thus the use of blends containing either light or heavy No. 6 fuel oils resulted in poor rejection of sulfur and ash in the case of -35 mesh coal. The blend of kerosene and No. 5 heavy fuel oil provided the greatest reduction in sulfur and ash but also gave the lowest yield for -35 mesh coal. The results with -100 mesh coal were less varied and the yield (about 90%) was uniformly higher than that obtained with the coarser material.

Amount of oil. A series of tests was carried out to examine the effect of oil concentration on the agglomeration process. Heater oil and two different coals were selected for the series. Star coal which had been ground with a disk-mill and screened through a 100 mesh sieve was one of the coals selected and Scott coal which had been ground for 16 hr. in a 1 1/2 gallon jar mill with 1900 g. of flint pebbles was the other. An aqueous slurry containing 40% solids was placed in the ceramic jar mill for the grinding operation; the product was -400 mesh. For the agglomeration of ground Star coal, 15 g. of coal were mixed with 500 ml. of tap water in the blender and a 1 N solution of potassium hydroxide was added to raise the pH to about 6. A measured amount of heater oil which had been emulsified with 200 ml. of tap water by using an ultrasonic vibrator was

Table 7. Oil agglomeration tests using oil mixtures of specific gravity 0.83 with 20 g. pulverized Jude coal[a]

	Product (-35 mesh coal, 1 ml. oil)					Product (-100 mesh coal, 2 ml. oil		
Oil Mixture (vol. ratio)	Yield, %	Ash, %	Total S, %	Ash Red., %	Sulfur Red., %	Yield, %	Ash, %	Ash Red., %
Kerosene + No. 6 heavy (86:14)	79.0	10.74	4.99	30.6	16.7	87.0	9.60	37.9
Kerosene + No. 6 light (85:15)	81.0	12.88	5.17	16.7	13.7	90.0	10.86	29.8
Kerosene + No. 5 heavy (83:17)	69.0	9.06	4.66	41.4	22.2	89.0	10.70	30.8
Kerosene + No. 5 light (82:18)	78.0	9.94	4.77	35.7	20.4	89.0	11.07	28.4
Heater + No. 6 heavy (88:12)	80.0	11.05	4.99	28.6	16.7	90.5	11.07	28.4
Heater + No. 6 light (87:13)	79.0	10.60	5.01	31.5	16.4	90.5	10.62	31.4
Heater + No. 5 heavy (86:14)	82.0	11.57	5.11	25.2	14.7	90.5	10.73	30.6
Heater + No. 5 light (85:15)	81.0	9.94	4.73	35.7	21.0	91.5	10.37	33.0

[a] Untreated Jude coal contained 15.47% ash and 5.99% total sulfur

added to the coal slurry. After blending the mixture for 5 min., the agglomerated coal was recovered by pouring the mixture onto a 100 mesh sieve.

For the agglomeration of ground Scott coal, 500 ml. of a 4 wt.% aqueous slurry of the coal was placed in the blender and a measured amount of heater oil was added directly to the slurry. After 5 min. agitation, the slurry was put in a 1000 ml. separatory funnel and the floated coal was recovered. The coal was then placed back in the blender and slurried again with 200 ml. of fresh tap water. After 2 min. of agitation, the slurry was again poured into the separatory funnel and the floated coal was recovered. This washing procedure was repeated once more, and the product was filtered, dried and analyzed.

The experimental results are shown in Table 8 and are plotted in Figure 4 as a function of the amount of heater oil used. The results for

Table 8. Oil agglomeration tests using different amounts of heater oil

	Star Coal[a] Product				Scott Coal[b] Product		
Oil, ml.	Yield, %	Ash, %	Total S, %	Oil, ml.	Yield, %	Ash, %	Total S, %
0.25	23.1	3.98	4.47	1	77.2	11.27	6.44
0.50	29.9	4.80	--	3	86.8	8.09	5.47
1.00	48.4	5.46	4.96	5	76.7	4.30	4.10
1.25	49.2	5.39	--	10	83.6	4.65	4.27
1.50	69.8	5.09	--	20	83.0	4.86	4.33
2.50	88.0	6.17	5.37	60	88.0	6.13	5.03
3.00	85.7	6.49	--				

[a] Untreated Star coal contained 10.81% ash and 5.75% total sulfur

[b] Untreated Scott coal contained 15.73% ash and 7.58% total sulfur

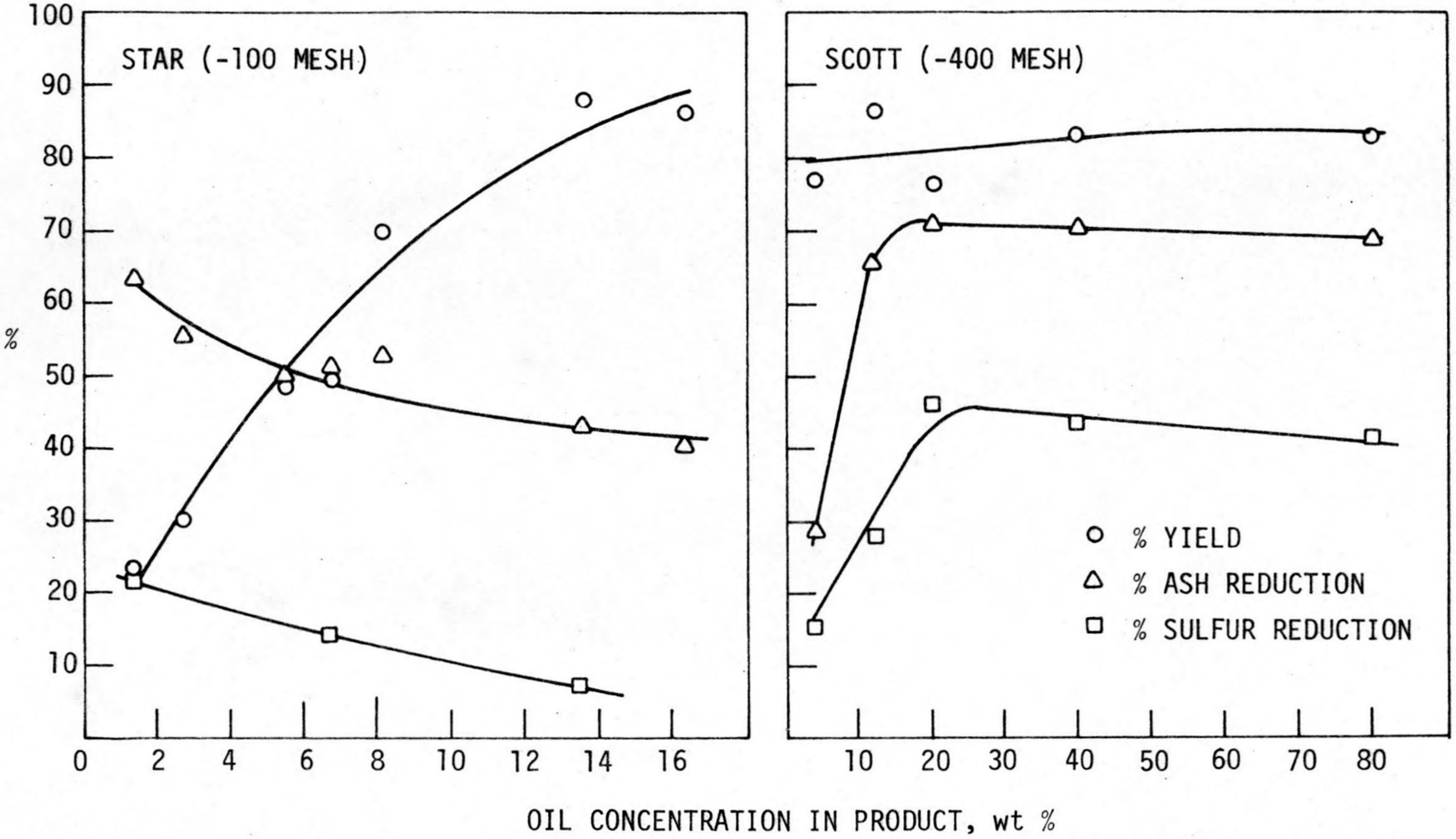

Figure 4. Effect of amount of heater oil on yield and reduction in ash and sulfur contents.

-100 mesh Star coal show that the yield increased with increasing oil concentrations in the product up to about 14% while the reduction in sulfur and ash contents declined. On the other hand, for -400 mesh Scott coal the yield appeared to be essentially independent of the amount of oil used over a wide range while the reduction in sulfur and ash contents increased sharply as the amount of oil used increased at first but above 20% oil in the product less sulfur and ash were rejected. However, the maximum reduction in sulfur and ash contents was much larger for Scott coal than for Star coal. This difference in behavior was due more likely to the difference in particle size than to some other difference in the properties of the two coals because the coals were quite similar in other respects.

Effect of Particle Size

Pulverized coal. In order to evaluate the effect of coal particle size on the oil agglomeration process, another series of experiments was carried out. First, the coal to be treated was pulverized with the Mikro-Samplmill and separated into four different particle size fractions (see Table 3). Fifteen grams of coal of a given size fraction was slurried with 500 ml. of tap water in the blender, and the pH was adjusted to 6-7. Twenty milliliters of an oil-water emulsion, which was prepared from one part of heater oil and 40 parts of water with the ultrasonic vibrator, was added to the coal slurry and the blender was operated for 10 min. at the lowest speed. If agglomerates formed and floated, the float product was skimmed off. If the agglomerates were too small to float, more of the oil-water emulsion was added until the agglomerates just floated. The results which are given in Table 9 and also shown in Figure 5 indicate

Table 9. Oil agglomeration tests using different size fractions of pulverized coal. (15 g. coal per test)

	Feed		Product			
Coal mesh size	Ash, %	Total S, %	Yield, %	Ash, %	Total S, %	Oil used, ml.
Star						
+65	6.03	4.49	93.4	4.50	3.54	0.9
-65+100	11.02	5.28	87.8	6.36	4.50	1.4
-100+200	12.70	5.26	91.2	7.15	4.76	2.2
-200	15.55	7.04	91.8	6.46	5.57	3.0
Big Ben						
+65	13.40	2.75	81.6	3.20	1.76	2.0
-65+100	13.10	2.44	83.8	6.62	1.83	3.0
-100+200	15.25	3.52	78.5	5.70	2.67	2.5
-200	17.10	4.68	80.2	6.20	2.89	3.2
Jude						
+65	16.00	5.69	79.5	10.0	4.40	1.0
-65+100	15.40	5.70	89.1	9.98	4.38	2.2
-100+200	17.99	5.42	87.4	10.50	4.99	3.2
-200	23.69	6.83	70.7	12.11	5.06	4.0

that the three different coals which were used behaved somewhat differently. Thus better yields were obtained with Star coal than with the other two coals and for both Star coal and Big Ben coal the yield was virtually independent of particle size whereas for Jude coal it changed with particle size. The oil consumption, however, increased as the particle size decreased for all three coals. Furthermore the maximum percentage reduction in sulfur and ash contents was generally obtained with the smallest particle size fraction. On the other hand, the minimum percentage reduction in sulfur content was obtained in every case with one of the intermediate size fractions (-100+200 mesh).

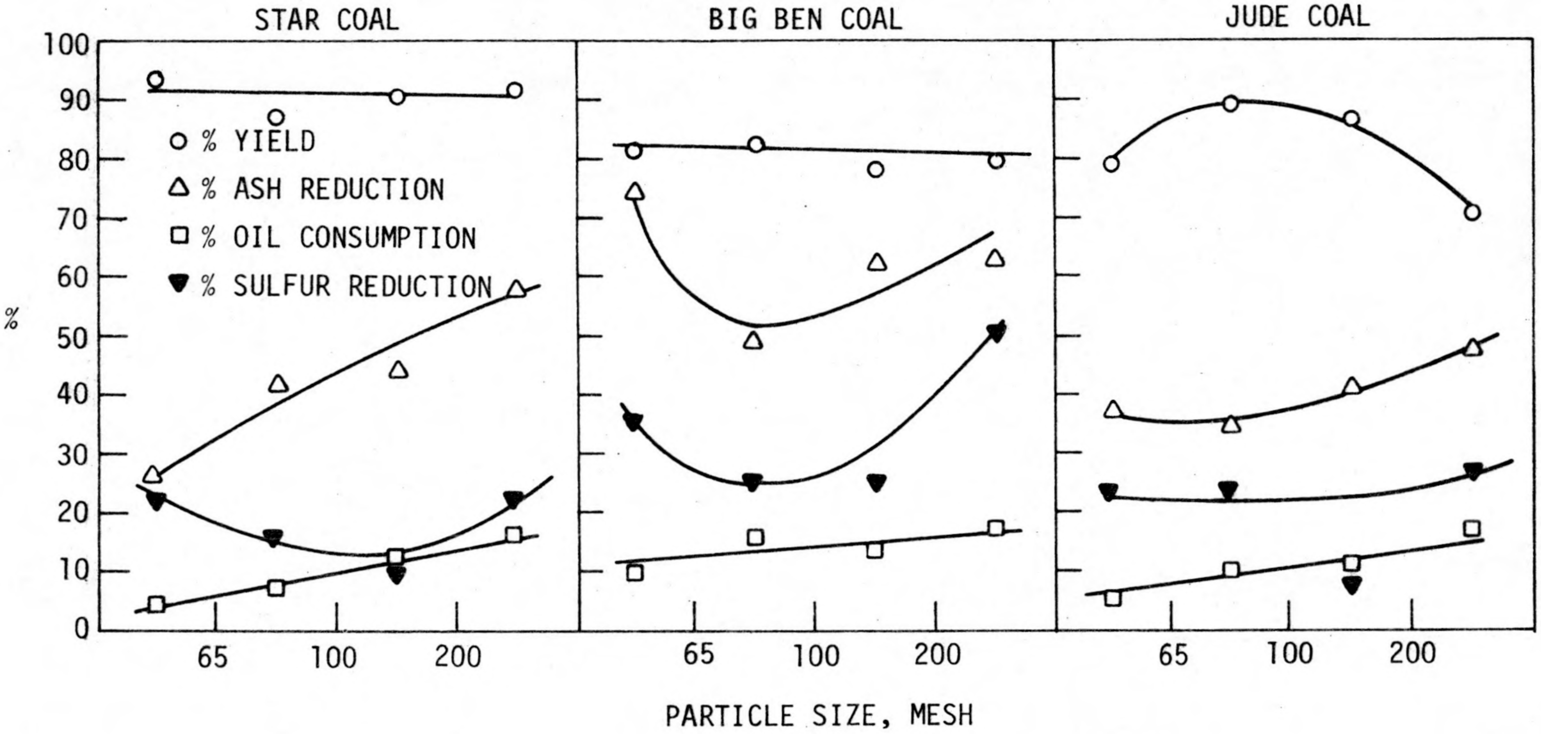

Figure 5. Effect of particle size on agglomeration of pulverized coal.

Ground coal. A study of coal microstructure with a scanning electron microscope by Greer (12) revealed the presence of much finely disseminated pyrite in Iowa coals. Therefore, it appeared that very fine grinding would be required to liberate this pyrite so that it could be separated. Hence, another series of experiments were conducted to see if oil agglomeration of finely ground coal would produce a cleaner product than oil agglomeration of somewhat coarser material. In addition the effect of grinding finer and finer on the separation obtained with oil agglomeration was examined.

To prepare the coal for the oil agglomeration tests, 200 g. of pulverized (-35 mesh) Jude coal in a 20 wt.% aqueous slurry (or 400 g. of pulverized Scott coal in a 40 wt.% slurry) were ground in a jar mill containing 1900 g. of flint pebbles. The size distribution of the ground coal was determined with a Coulter Counter (Model TAII, Coulter Electronics, Inc., Lenexa, KS) and is shown in Table 10 and Figure 6. The data show that after 4 hr. of grinding, most of the particles were finer than 38μ (400 mesh) and as grinding time increased, the particles became smaller and the size distribution became narrower.

Oil agglomeration experiments of Jude coal were conducted in the blender using 300 ml. of a 6 wt.% aqueous slurry of ground coal. The coal was agglomerated with an oil-water emulsion containing 1 ml. of a mixture of heater oil and No. 5 light fuel oil (sp.gr. = 0.83) and 200 ml. of tap water. The agglomerated coal was placed in a separatory funnel and recovered. The recovered coal was then put back into the blender and washed twice with 200 ml. of fresh tap water.

Table 11 and Figure 7 summarize the experimental results obtained with Jude coal. These results indicate that the cleanest product was obtained with coal which had been ground for 4 hr. This product not only

Table 10. Particle size distribution of Jude coal ground in a jar mill for various time intervals

	4 hr.		6 hr.		12 hr.		24 hr.		48 hr.		72 hr.	
Particle Size μ	Pop., %	Vol., %	Pop., %	Vol., %	Pop., %	Vol., %	Pop., %	Vol., %	Pop., %	Vol., %	Pop., %	Vol., %
1.59-2.00	37.93	2.44	48.95	1.80	41.15	5.66	39.87	8.36	46.65	16.28	44.63	16.45
2.00-2.52	26.57	3.43	15.11	1.11	27.19	7.50	28.98	12.17	32.43	22.59	34.10	25.14
2.52-3.17	13.61	3.51	12.38	1.82	14.69	8.12	16.30	13.70	13.39	18.60	14.16	20.92
3.17-4.00	8.38	4.33	8.17	2.39	8.06	8.91	8.35	14.03	4.79	13.29	4.77	14.10
4.00-5.04	5.48	5.64	5.97	3.50	4.58	10.09	3.96	13.30	1.78	9.86	1.61	9.52
5.04-6.35	3.38	6.98	3.83	4.49	2.31	10.18	1.59	10.70	0.63	6.98	0.50	5.88
6.35-8.00	2.14	8.82	2.40	5.63	1.13	9.96	0.61	8.22	0.22	4.87	0.16	3.76
8.00-10.08	1.26	10.40	1.36	6.38	0.50	8.82	0.21	5.61	0.07	3.10	0.05	2.35
10.08-12.70	0.66	10.89	0.81	7.59	0.23	8.12	0.08	4.28	0.03	2.66	0.02	1.88
12.70-16.0	0.32	10.57	0.52	9.75	0.10	7.06	0.03	3.21	0.01	1.77	0	
16.0-20.2	0.16	10.57	0.24	9.00	0.03	4.26	0.01	2.14	0		0	
20.2-25.4	0.07	9.23	0.14	10.50	0.02	5.66	0.01	4.28	0		0	
25.4-32.0	0.03	7.92	0.08	12.01	0.01	5.66	0	0	0		0	
32.0-40.3	0.01	5.27	0.02	6.01	0	0	0	0	0		0	
40.3-50.8	0	0	0.01	6.01	0	0	0	0	0		0	
50.8-64.0	0	0	0.01	12.01	0	0	0	0	0		0	

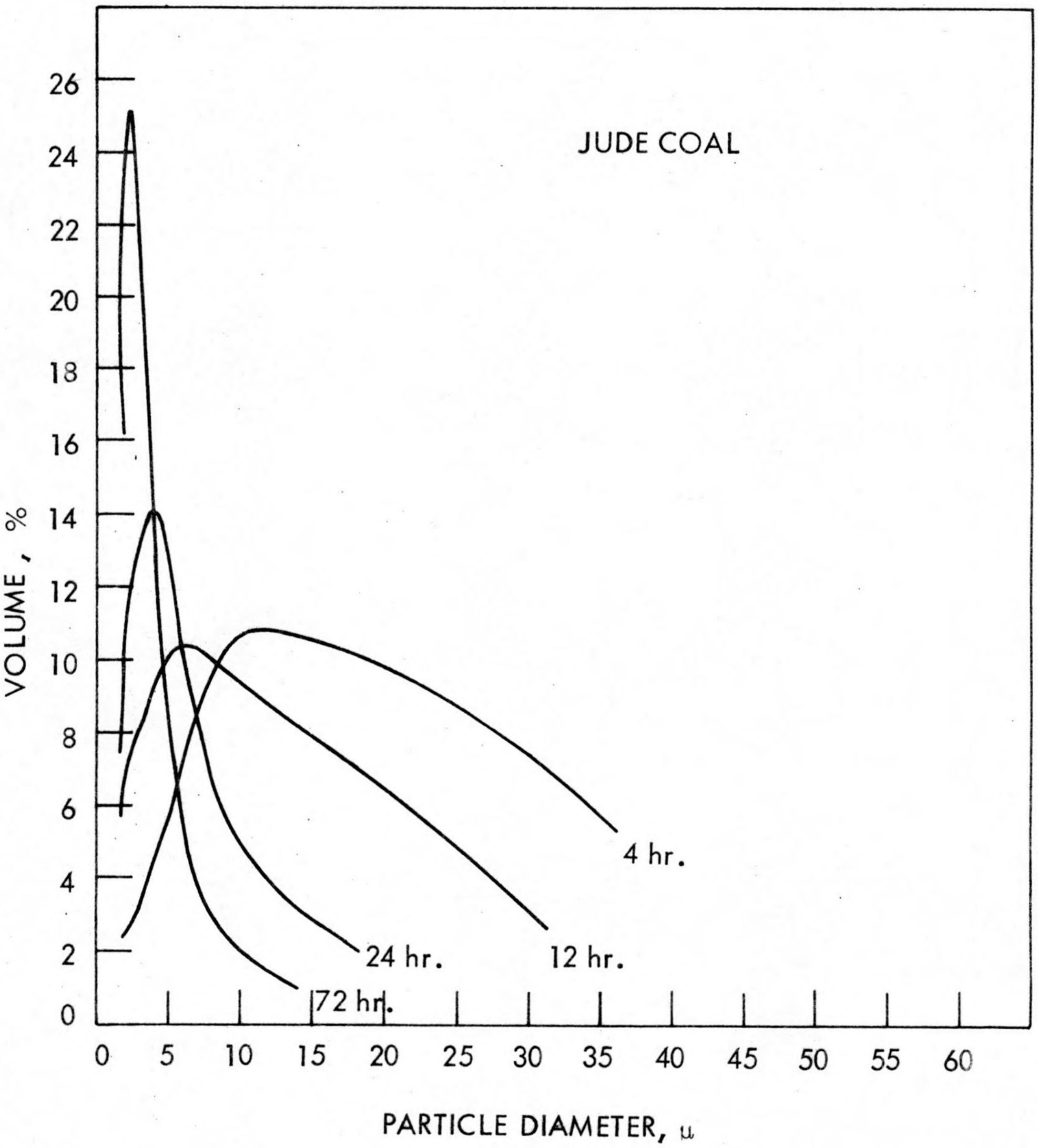

Figure 6. Size distribution of Jude coal ground for different periods of time.

contained the least sulfur and ash but it also was obtained in greater yield than that provided by the agglomeration of pulverized but unground coal or coal which had been ground for 6 hr. Prolonged grinding for up to 22 hr. resulted in larger yields of agglomerated coal at the expense of increased ash and sulfur in the agglomerated product.

Similar experiments were carried out with Scott coal. Five hundred milliliters of a 4 wt.% aqueous slurry of ground Scott coal were placed in the blender and mixed with an emulsion containing 1 ml. of blended heater oil and No. 5 light fuel oil (sp.gr. = 0.83) and 200 ml. of tap water. The agglomerated coal was recovered in a separatory funnel and washed twice with fresh tap water as described above. The results which are presented in Table 12 and also in Figure 8 were similar in some respects to those obtained with Jude coal but different in other respects. Thus a cleaner product in higher yield was obtained in both cases when the coal was ground for several hours before agglomeration than when it was only pulverized in the Mikro-Samplmill. Also prolonged grinding was detrimental

Table 11. Oil agglomeration tests of ball milled Jude coal[a] of different particle sizes

Coal	Feed Ash, %	Product Yield, %	Product Ash, %	Product Sulfur, %	Refuse Ash %
Pulverized (-35 mesh)	15.60	68.3	8.25	5.52	35.87
4 hr. ball mill	16.21	82.1	5.27	4.97	54.79
6 hr. ball mill	15.81	79.6	5.99	5.30	52.61
12 hr. ball mill	15.84	94.7	11.29	6.28	75.19
24 hr. ball mill[b]	15.85	86.2	6.83	5.30	72.30
48 hr. ball mill[b]	16.35	93.8	12.21	6.20	69.50
72 hr. ball mill[b]	15.97	97.4	14.28	6.47	57.44

[a] The untreated Jude coal contained 15.60% ash and 6.80% total sulfur.

[b] The agglomerated coal was floated by adding 0.1 ml. of methyl isobutyl carbinol.

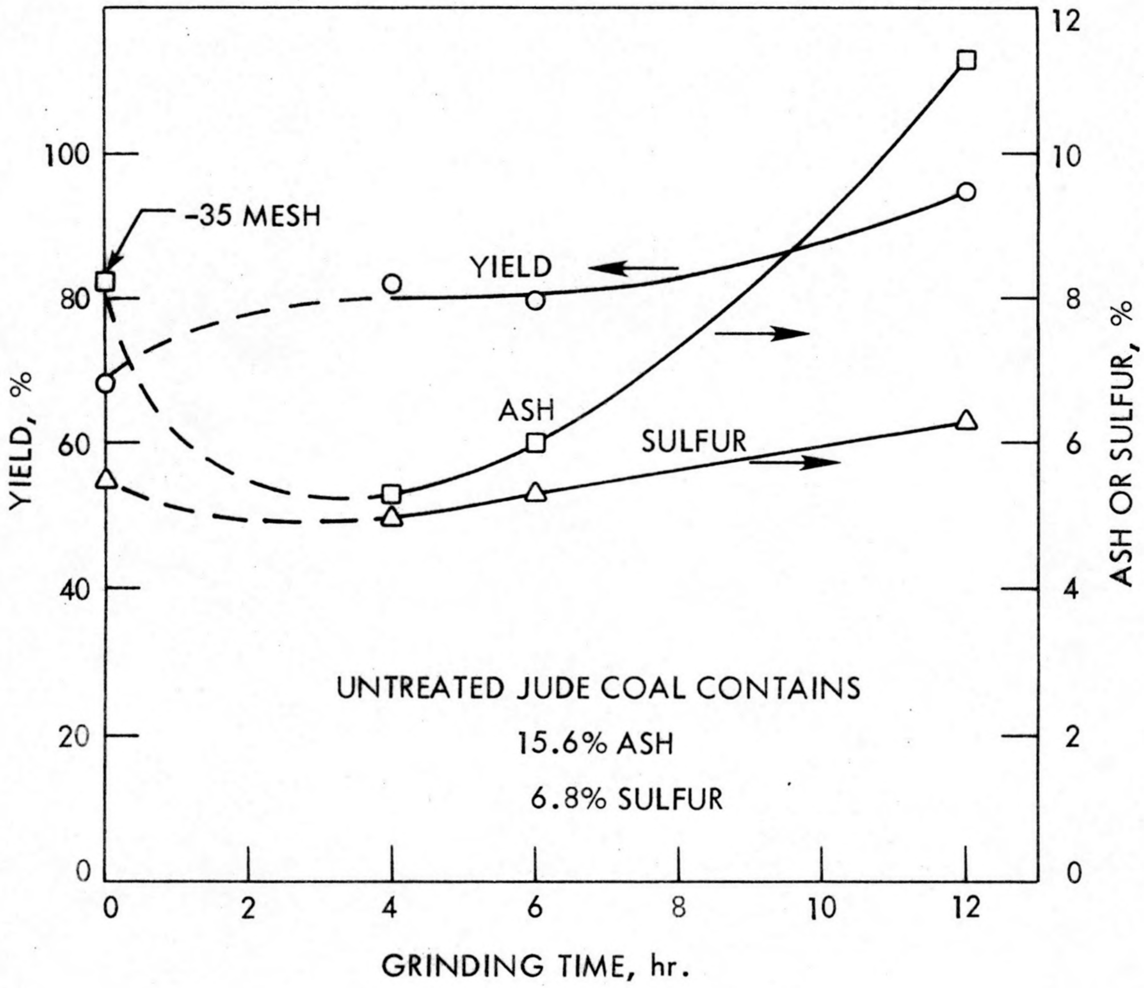

Figure 7. Effect of grinding time on oil agglomeration of Jude coal.

Table 12. Oil agglomeration test of ball milled Scott coal of different particle sizes

	Feed		Product			Refuse
Coal	Ash, %	Sulfur, %	Yield, %	Ash, %	Sulfur, %	Ash, %
Pulverized (135 mesh)	14.42	7.67	80.66	10.66	5.46	33.17
6 hr. ball mill	15.72	7.80	77.14	7.89	4.92	39.93
16 hr. ball mill	15.73	7.58	84.87	7.40	5.17	56.52
63 hr. ball mill	16.28	7.62	91.03	9.89	5.99	64.88

to product quality in both cases. On the other hand, the optimum grinding time appeared to be somewhat longer for Scott coal than for Jude coal. However, this result could have been due to differences in experimental conditions as well as a difference in the two materials. Since twice as much coal was charged in the jar mill when Scott coal was ground as when Jude coal was ground, it may have required longer to reduce Scott coal to the same size as Jude coal. Also the lower slurry concentration used while agglomerating Scott coal may have had some effect on the results.

Effect of Slurry Concentration

Using the blender. A series of experiments was carried out to determine the effect of slurry concentration on the oil agglomeration process. A measured amount of pulverized coal (-35 mesh) was slurried with 500 ml. of tap water in a blender and agitated for 5 min. Then, an emulsion of heater oil and water, equivalent to 8 wt.% oil based on dry coal, was added to the slurry and the blender was operated for 5 min. at the lowest speed. The agglomerated coal was recovered by pouring the

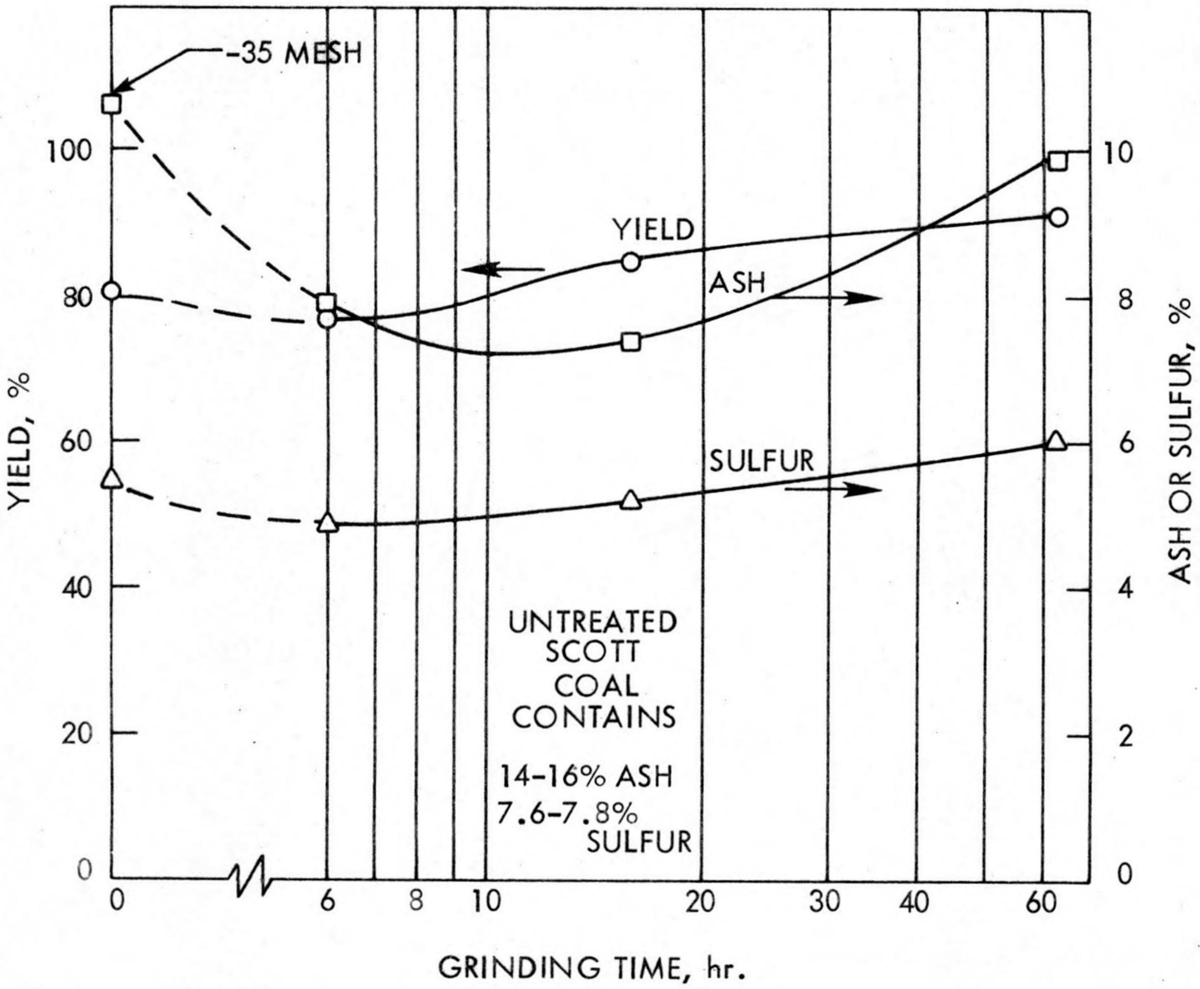

Figure 8. Effect of grinding time on oil agglomeration of Scott coal.

slurry onto a 100 mesh sieve. The product was dried, weighed and analyzed for ash and total sulfur. The results which are reported in Table 13 and also in Figure 9 indicate that the yield increased as the slurry concentration increased for each of the three coals tested. The reduction in total sulfur content, however, declined as the concentration increased and the reduction in ash content rose at first and then declined. In other words, the product contained the minimum amount of ash when a slurry concentration of 4-5% was employed.

Using froth flotation cell. Pulverized coal was agglomerated in a Wemco froth flotation cell in another series of experiments conducted to investigate the effect of slurry concentration. One thousand milliliters of tap water were placed in the bowl of the flotation cell and a measured amount of pulverized Scott coal (-35 mesh) was added. After 5 min. of agitation, an emulsion of heater oil and water, equivalent to 8 wt.% oil based on the dry coal, was added and the slurry was agitated for 10 min. The agglomerated coal was then floated by introducing air bubbles and was recovered by skimming. The product was poured back into the bowl and washed twice with fresh tap water. The results (Table 14 and Figure 10) were similar to those obtained with the blender (Table 13 and Figure 9) in that the yield of agglomerated coal increased as the slurry concentration increased and also the reduction in ash content at first increased and then decreased. On the other hand, the results with the froth flotation cell were different in that the yield of agglomerated coal was much lower and the reduction in sulfur content much greater for small slurry concentrations. Also the product contained the least sulfur and ash when a larger slurry concentration (10 wt.%) was used in the froth flotation cell.

Table 13. Oil agglomeration tests using different slurry concentrations with pulverized coals (-35 mesh) in a blender

Slurry Conc., wt.%	Product with Star[a] Coal, %			Product with Big Ben[b] Coal, %			Product with Jude[c] Coal, %		
	Yield	Ash	Total S	Yield	Ash	Total S	Yield	Ash	Total S
2	83.6	7.84	4.86	81.3	7.53	1.98	84.7	11.86	5.07
3	80.2	6.64	--	75.0	8.04	--	86.4	11.13	--
5	88.1	6.43	4.89	82.3	6.66	2.13	86.4	11.17	4.97
7	90.6	7.76	--	84.9	7.17	--	71.7	11.69	--
10	90.0	7.84	5.43	86.2	7.80	2.72	84.1	11.81	4.81
12	92.2	8.68	--	89.7	8.26	--	85.9	12.29	--
15	90.6	7.76	5.24	90.6	8.65	2.52	88.7	12.27	5.15

[a] Untreated Star coal contained 10.81% ash and 5.75% total sulfur

[b] Untreated Big Ben coal contained 12.52% ash and 3.08% total sulfur

[c] Untreated Jude coal contained 15.47% ash and 5.99% total sulfur

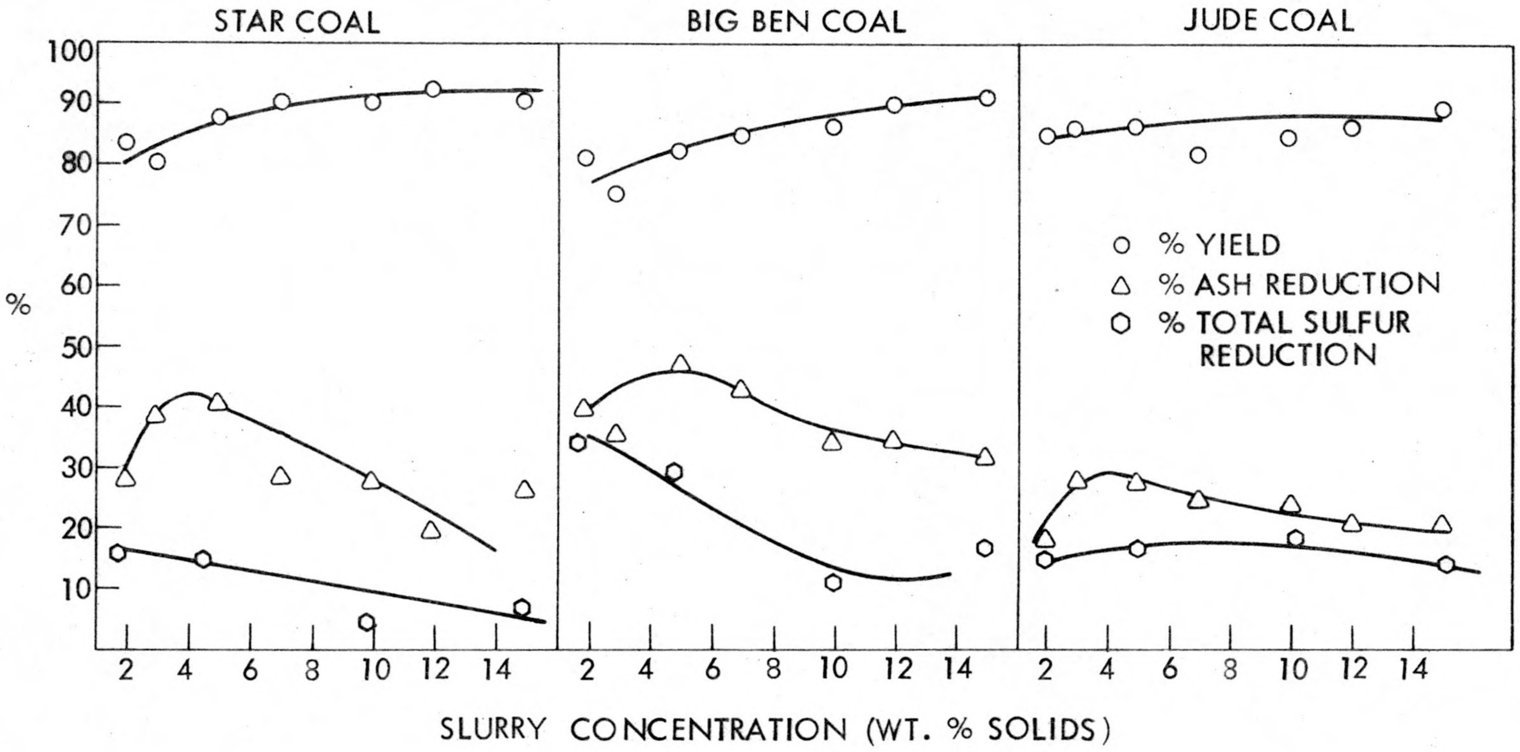

Fig. 9. Effect of slurry concentration on oil agglomeration of -35 mesh coal.

Table 14. Oil agglomeration tests of Scott coal[a] (-35 mesh) in a Wemco flotation cell

Slurry Concentration, wt.%	Product		
	Yield, wt.%	Ash, wt.%	Sulfur, wt.%
2	48.4	10.13	4.75
4	58.9	9.97	5.00
10	67.1	8.09	4.06
20	92.1	9.91	5.22
36	96.6	11.25	6.78
50	97.5	11.90	6.40

[a] The untreated Scott coal contained 15.73% ash and 7.58% total sulfur.

These results seem to indicate that in dilute slurries the distance between particles is too great for interactions which produce agglomerates. Although this problem may be alleviated by using more concentrated slurries, mechanical entrapment of refuse particles in the agglomerates may then become a problem. Hence, it may be necessary to balance one factor against the other.

Effect of pH and Different Chemical Agents

Since the separation of coal and pyrite particles was far from perfect in previous oil agglomeration experiments, an attempt was made to improve the separation by changing the pH or adding different chemical agents which might modify the surface of the pyrite. Thus if the surface of the pyrite could be made uniformly hydrophillic through adsorption of some chemical species, there would be less likelyhood of the pyrite particles being agglomerated with the hydrophobic coal particles.

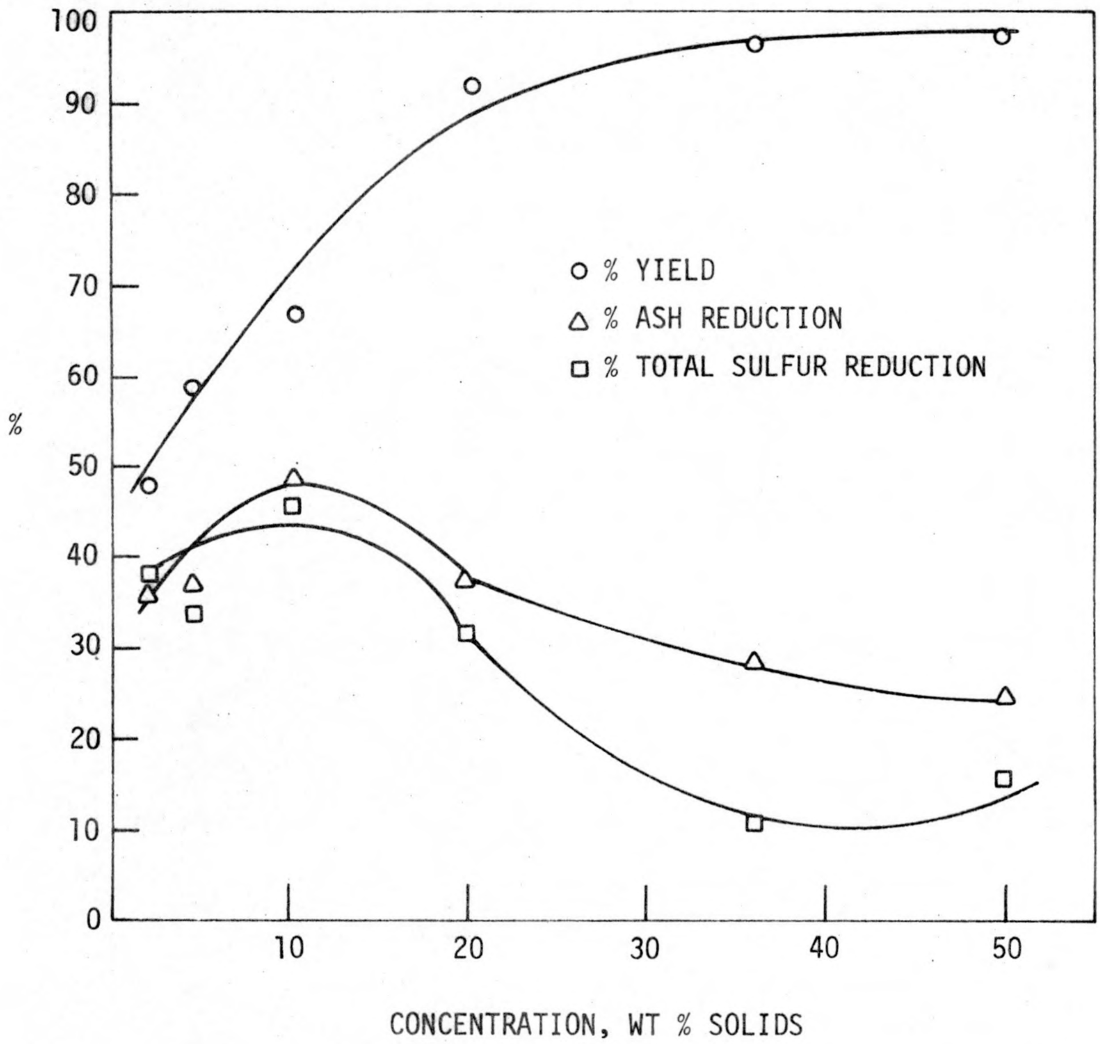

Figure 10. Effect of slurry concentration on oil agglomeration of pulverized (-35 mesh) Scott coal in a Wemco froth flotation cell.

Effect of pH. A number of experiments were carried out to examine the effect of the initial pH of the water employed for preparing the coal slurries used for oil agglomeration. For these experiments 500 ml. of tap water were placed in the blender and the pH was adjusted to the desired level by adding a 1 N solution of either hydrochloric acid or potassium hydroxide. Then, 15 g. of pulverized coal (-35 mesh) were mixed with the water for 5 min. at the lowest speed. Twenty milliliters of an oil-water emulsion, which was made from one part of heater oil and 40 parts of water with the ultrasonic vibrator, were added to the slurry and the blender was operated for 10 min. If agglomerates formed and floated, the float product was ladled onto a 100 mesh screen. If the agglomerates were too small to float, more of the oil-water emulsion was added and agitation was continued. This operation was repeated until suitable agglomerates were produced. Interestingly enough, the pH of the slurry was always in the range of 7.5 to 8.5 after the agglomerates were produced regardless of the initial pH of the water. Even though the buffering action of the coal was large enough to control the ultimate pH of the slurry, the initial pH of the water seemed to have an effect on the results which are shown in Table 15 and also in Figure 11. Thus for all three coals tested, the pyritic sulfur left in the product declined as the initial pH of the water was increased. Also for both Star coal and Big Ben coal the ash content and yield of agglomerated material declined as the pH was raised.

Different chemical agents. A series of tests was carried out to determine the effects of various chemical agents at different concentrations on the results of oil agglomerating pulverized (-35 mesh) Star coal and

Table 15. Oil agglomeration tests with 15 g. pulverized (-35 mesh) coal, the initial pH of the water being varied

Coal	Initial pH	Oil, ml.	Product, wt.%			
			Yield	Ash	Total S.	Pyritic S.
Star[a]	2.8	1.75	93.0	6.46	5.24	2.97
	3.8	1.25	92.6	7.01	--	--
	5.2	0.88	91.9	6.09	4.94	2.68
	6.0	1.00	85.3	6.17	--	--
	6.8	1.50	88.5	5.41	--	2.30
	8.3	0.88	90.4	7.33	--	--
	9.0	1.25	90.6	6.54	--	--
	10.0	1.50	81.3	4.66	4.27	1.93
Big Ben[b]	3.2	2.50	93.7	6.68	--	1.48
	4.0	1.75	90.2	6.18	2.28	1.28
	5.2	1.38	88.2	4.86	--	--
	5.8	1.13	86.5	5.75	1.98	1.36
	7.2	1.62	75.4	6.00	--	--
	8.5	1.88	79.2	5.17	1.93	0.99
	9.3	1.50	82.2	5.43	--	1.11
Jude[c]	3.3	2.00	87.3	10.29	--	2.45
	4.0	2.00	84.8	10.43	--	--
	5.2	1.60	81.3	10.61	--	--
	6.2	1.50	73.3	9.58	--	--
	7.5	2.00	82.5	10.12	--	2.04
	8.2	2.30	82.7	10.27	--	--
	9.1	2.00	89.3	9.47	--	2.05

[a] Untreated Star coal contained 10.81% ash and 3.33% pyritic sulfur

[b] Untreated Big Ben coal contained 12.52% ash and 2.05% pyritic sulfur

[c] Untreated Jude coal contained 15.47% ash and 3.12% pyritic sulfur

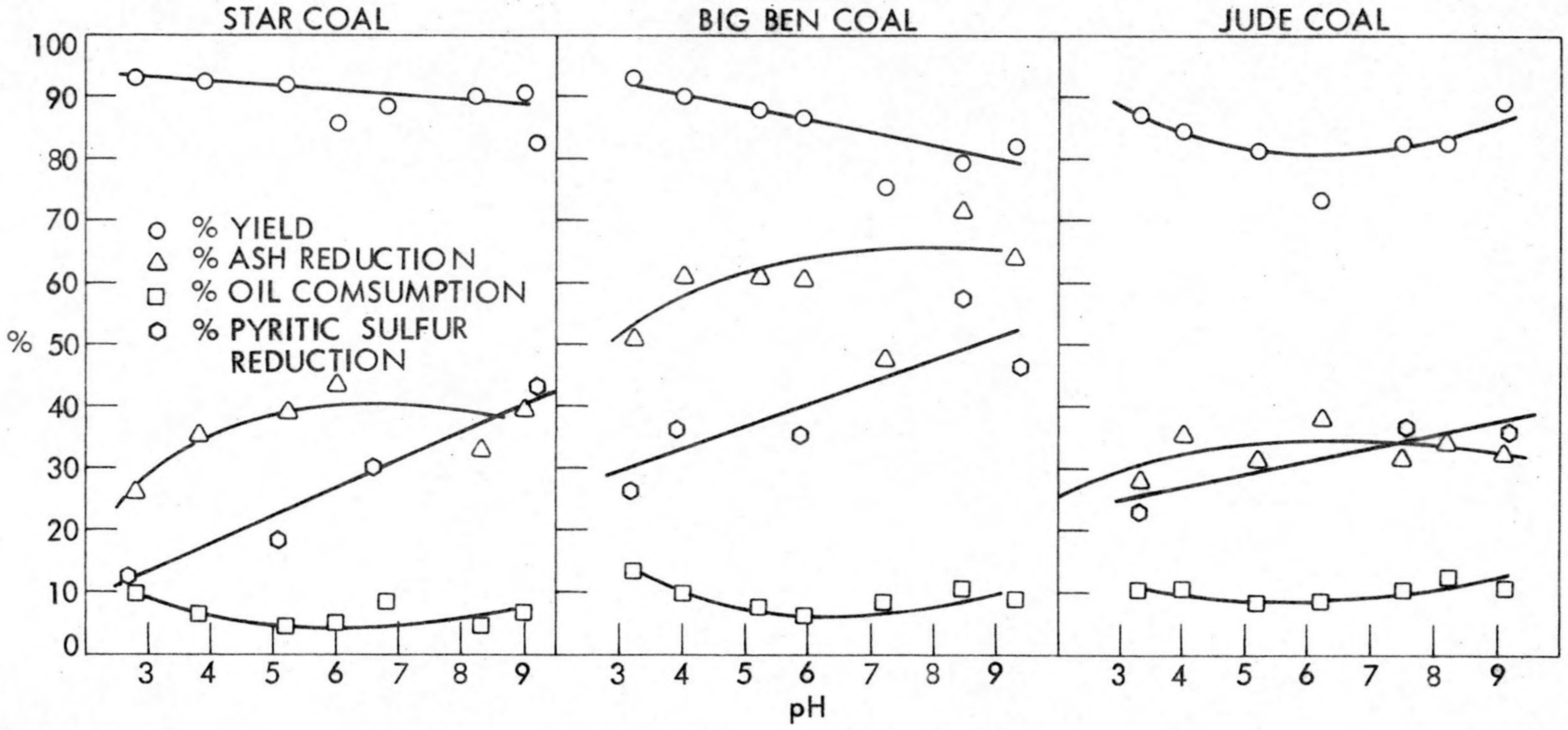

Fig. 11. Effect of initial pH on oil agglomeration of -35 mesh coal.

Jude coal. For these tests 15 g. of coal were mixed with 400 ml. of tap water in the blender and the desired amount of a 0.2 wt.% solution of the chemical agent was added. After 5 min. of agitation, the pH of the slurry was adjusted to 6-7 by adding a 1 N solution of either hydrochloric acid or potassium hydroxide. The oil agglomeration and recovery procedure were exactly the same as described above in the preceding section. The results (Table 16) were somewhat erratic and rather inconclusive.

Effect of chemical agents at different pH. Since the effect of any given chemical agent might well depend on the pH of its solution, a series of tests was made to determine the effect of various agents at different pH levels on the oil agglomeration process. For these tests 20 g. of pulverized coal were mixed with 400 ml. of tap water and 10 ml. of a 0.2 wt.% solution of the chemical agent. After 5 min. of agitation in the blender, the pH was adjusted to the desired level by adding a 1 N solution of either hydrochloric acid or potassium hydroxide. Then an emulsion composed of 2.0 ml. of a kerosene-No. 6 heavy fuel oil mixture (sp.gr. = 0.83) and 40 ml. of tap water was added. The emulsion was prepared with the ultrasonic vibrator. The slurry was agitated for 5 min. and the coal was recovered by ladling onto a 100 mesh sieve. The results which are presented in Table 17 and also in Figure 12 indicate that more sulfur was rejected from ICO coal by the oil agglomeration process when a small amount of ferric chloride was added to the coal slurry then when either sodium carbonate or sodium silicate were added. Moreover, ferric chloride appeared to have a beneficial effect over a pH range of 5 to 10. However, at higher pH levels the yield of agglomerated coal declined.

Table 16. Oil agglomeration tests using different chemical agents with 15 g. pulverized coal (-35 mesh)

		Star Coal[a]				Jude Coal[b]			
Chemical Agent	Amount, g.	Yield, %	Oil, ml.	Product Ash, %	Ash Red., %	Yield, %	Oil, ml.	Product Ash, %	Ash Red., %
Sodium Carbonate	0.01	92.73	0.75	7.87	27.20	87.02	1.0	10.90	29.54
	0.02	92.28	0.75	7.10	34.32	86.72	1.0	10.80	30.19
	0.03	95.77	1.00	8.90	17.67	88.45	1.25	11.70	24.37
	0.06	93.81	1.38	6.79	37.19	90.79	1.38	11.00	28.89
	0.10	90.29	1.00	7.50	30.62	87.38	1.38	11.50	25.66
Ferric Chloride	0.01	86.98	1.38	6.47	40.15	87.03	1.50	11.30	26.96
	0.03	91.15	1.50	7.60	29.69	82.91	1.63	10.10	34.71
	0.06	88.49	1.38	6.90	36.17	86.27	1.75	13.20	14.67
	0.10	88.12	1.50	6.88	36.36	83.01	1.75	10.70	30.83
Sodium Cyanide	0.01	89.44	1.00	6.78	37.28	83.71	1.38	10.50	32.13
	0.03	85.99	1.38	7.02	33.40	88.93	1.63	11.23	27.41
	0.06	89.44	1.63	7.18	33.36	87.46	1.50	11.40	26.31
	0.10	89.11	1.50	6.99	35.34	86.08	1.75	12.08	21.91
Calcium Carbonate	0.01	88.59	1.25	6.67	38.30	81.94	1.13	10.58	31.61
	0.03	72.61	1.50	7.15	33.86	81.84	1.38	10.90	29.54
	0.06	96.76	1.50	8.50	21.37	89.43	1.63	11.50	25.66
	0.10	75.73	1.25	6.86	36.54	93.38	1.50	11.30	26.96
Lithium Carbonate	0.01	82.85	1.25	6.16	43.02	85.65	1.75	11.58	25.15
	0.03	90.55	1.38	5.98	44.68	84.43	1.88	10.90	29.54
	0.06	85.37	1.38	6.42	40.61	87.62	2.00	11.70	24.37
	0.10	92.79	1.38	8.67	19.80	83.49	2.13	10.40	32.77

[a] Untreated Star coal contained 10.81% ash

[b] Untreated Jude coal contained 15.47% ash

Unfortunately a similar beneficial effect was not found when ferric chloride was used in conjunction with the oil agglomeration of Jude coal. The addition of various chemical agents and the simultaneous control of pH also affected the yield of agglomerated coal. Thus a very high yield of agglomerated ICO coal was obtained when sodium carbonate was added to the system and relatively high yields of either agglomerated ICO or Jude coal were obtained when sodium silicate was added.

Another series of experiments was carried out to determine the effect of various chemical agents. For this series the chemical agent

Table 17. Oil agglomeration tests with 20 g. pulverized (-35 mesh) coal and 0.02 g. of the indicated chemical agent

	ICO Coal[a]				Jude Coal[b]			
Chemical agent	pH	Yield, %	Ash, %	Total S, %	pH	Yield, %	Ash, %	Total S, %
Sodium Carbonate	2.1	90.8	8.95	3.09	4.0	83.0	10.00	5.10
	3.0	96.5	9.50	--	5.7	73.6	10.02	4.83
	7.4	97.6	7.84	3.29	7.5	88.0	10.88	5.07
	9.0	96.0	8.46	3.00	8.9	88.0	11.25	5.04
	10.0	94.3	8.19	3.01	11.2	63.5	11.36	--
Ferric Chloride	2.9	86.0	7.99	3.12	2.2	84.0	10.05	5.42
	4.9	87.0	7.89	2.62	4.2	85.0	10.36	5.29
	7.1	92.5	7.39	2.65	6.0	82.5	10.78	5.18
	8.9	88.0	7.79	2.64	8.8	76.0	11.39	5.19
	9.8	86.8	7.37	2.55	11.0	71.1	10.50	4.76
Sodium Silicate	2.1	98.8	8.50	2.96	3.2	91.5	12.33	--
	5.6	95.3	7.87	2.79	4.9	91.0	11.26	--
	7.4	91.5	7.70	2.59	8.2	90.0	11.22	--
	9.2	96.5	8.10	2.70	9.9	88.5	11.90	--
	11.6	91.8	8.34	2.60				

[a] Untreated ICO coal contained 10.09% ash and 3.79% total sulfur

[b] Untreated Jude coal contained 15.47% ash and 5.99% total sulfur

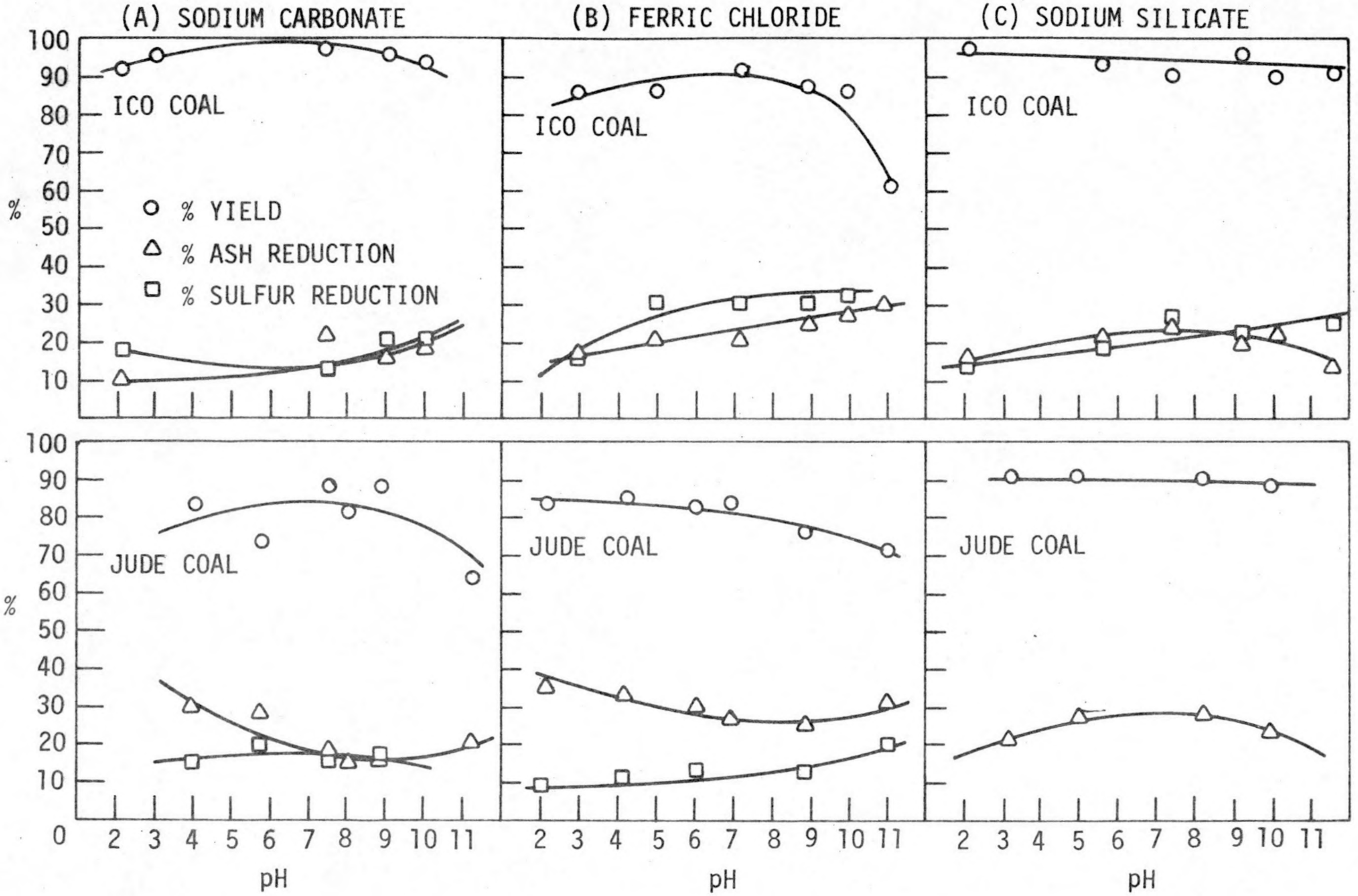

Figure 12. Effect of pH and different chemical agents on the agglomeration of pulverized (-35 mesh) coal.

was ground with Scott coal in the ceramic jar mill before oil agglomeration. To prepare the coal, 400 g. of pulverized Scott coal (-35 mesh) and 4 g. of chemical agent were ground for 16 hr. in the jar mill with 1000 ml. of tap water and 1900 g. of flint pebbles. The ground coal slurry was diluted with tap water to a slurry concentration of 4 wt.%. Five hundred milliliters of the diluted slurry were placed in the blender and a small amount of a 1 N solution of either sulfuric acid or sodium hydroxide was added. After 5 min. of agitation, the pH of the slurry was measured. The coal was then agglomerated with an emulsion composed of 1 ml. of kerosene-No. 5 heavy fuel oil mixture (sp.gr. = 0.83) and 200 ml. of tap water. The emulsion was prepared with the ultrasonic vibrator. The agglomerated coal was recovered in a separatory funnel and washed twice with fresh tap water. The results which are summarized in Table 18 and also in Figure 13 show that a large percentage of sulfur and ash was removed at an optimum pH of 8 without any chemical agent at all. None of the chemical agents improved the separation of coal and mineral matter very much. Slightly more sulfur was removed at optimum pH when either ferric chloride or sodium silicate were added to the coal than when no agent was added. Although coal with the lowest sulfur content was produced when potassium permanganate was added, the yield was also very low.

Effect of Chemical Pretreatment

Another approach which was utilized to modify the surface properties of pyrite in order to improve the separation of pyrite and coal was to oxidize the surface of the pyrite. Presumably an oxide coating would be hydrophillic whereas the unoxidized pyrite surface tends to be hydrophobic. To oxidize the pyrite surface, coal was pretreated with an aqueous solution

Table 18. Effect of different chemical agents and pH on oil agglomeration of ball milled (16 hr.) Scott coal (15.6 to 17.0% Ash, 7.4 to 7.8% S)

Chemical agent	Measured factor	Results for different acid or base addition				
		4 ml. acid[a]	1 ml. acid[a]	None	1 ml. base[b]	4 ml. base[b]
None	pH	3.3	5.7	6.5	7.8	9.9
	Yield, %	91.0	85.9	84.9	84.3	85.0
	Ash, %	10.3	6.9	7.4	6.2	7.5
	Total S, %	7.2	5.2	5.2	4.9	4.9
$Fe_2(SO_4)_3$	pH	3.8	5.6	6.3	8.2	9.0
	Yield, %	88.7	84.3	85.1	85.2	86.3
	Ash, %	9.2	6.5	7.1	6.9	7.5
	Total S, %	6.8	4.8	4.9	4.8	5.1
CaO	pH	6.4	7.8	8.3	8.5	10.6
	Yield, %	87.0	87.8	86.0	89.3	76.2
	Ash, %	8.6	8.7	9.0	10.7	9.5
	Total S, %	5.5	5.4	5.2	5.7	4.7
Na_2CO_3	pH	4.8	7.1	7.6	8.4	10.1
	Yield, %	84.1	85.0	85.1	85.0	81.9
	Ash, %	7.2	6.8	7.2	6.8	7.7
	Total S, %	5.3	4.9	4.9	4.8	4.7
$FeCl_3$	pH	2.7	5.0	5.7	6.3	8.0
	Yield, %	91.1	81.2	84.0	85.2	88.1
	Ash, %	10.5	6.4	7.1	7.2	9.3
	Total S, %	7.6	4.4	4.7	4.7	5.6
Na_2SiO_3	pH	3.2	6.8	7.4	8.4	10.0
	Yield, %	86.4	84.6	84.5	84.7	83.8
	Ash, %	7.8	6.9	6.8	6.6	7.2
	Total S, %	5.7	5.1	4.9	4.8	4.7
$KMnO_4$	pH	3.6	6.9	7.4	8.2	9.5
	Yield, %	78.5	59.6	77.2	76.3	57.1
	Ash, %	8.3	6.9	7.6	7.7	6.3
	Total S, %	5.6	4.3	4.9	4.8	4.2

[a] Sulfuric acid (1.0 N)

[b] Sodium hydroxide (1.0 N)

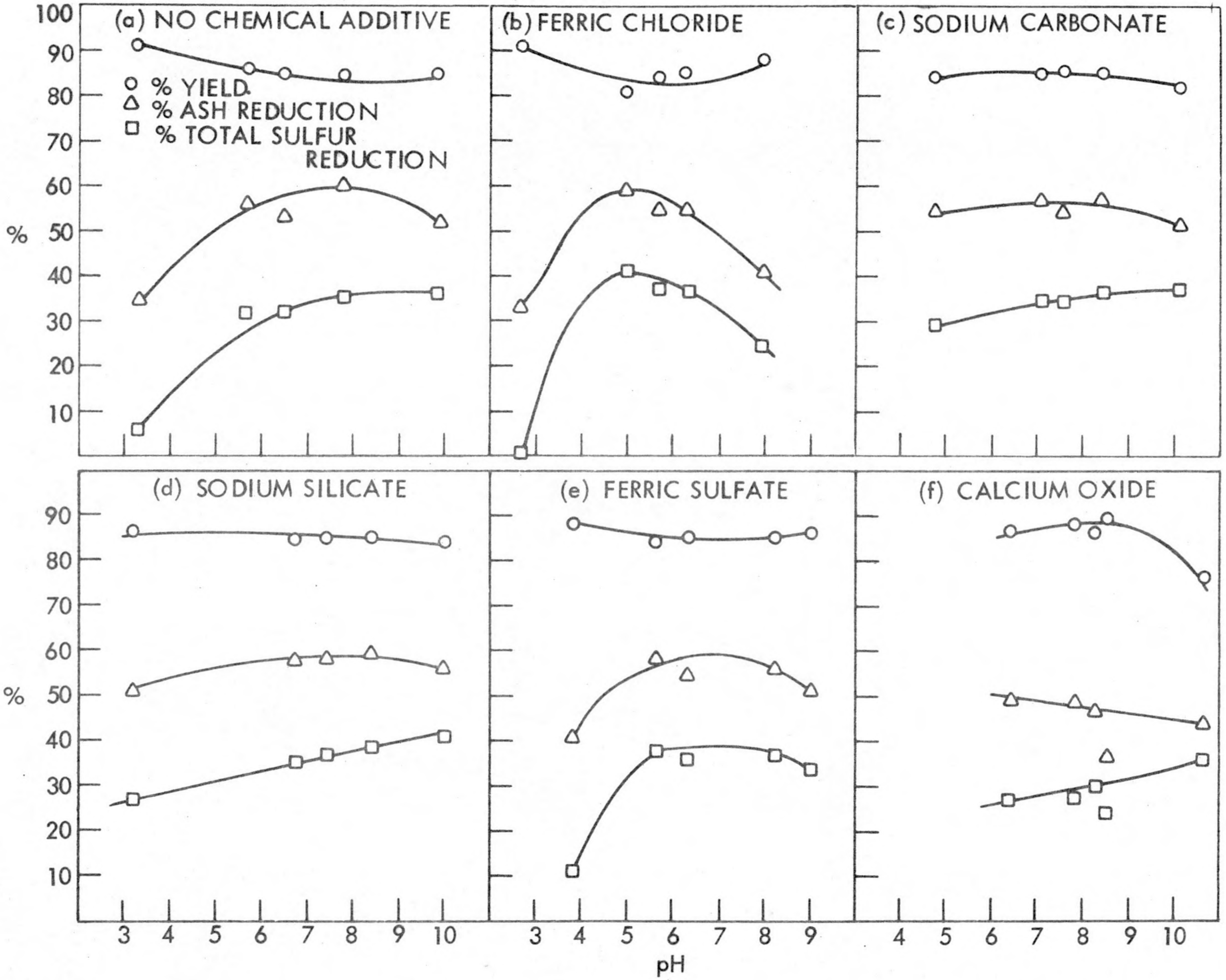

Figure 13. Oil agglomeration of Scott coal ground for 16 hr. with different chemical additives.

containing dissolved oxygen and an alkali. For the pretreatment step 100 g. of pulverized (-35 mesh) Scott coal was mixed with 500 ml. of deionized water in a 1000 ml. reaction flask (Figure 14). A small quantity of an alkali such as sodium carbonate was added to the slurry and the mixture was heated to boiling. Air was then introduced through a sparger at a flow rate of 0.33 cu.ft./min. and the treatment was continued for a specified time at 80°C. After this treatment the slurry was diluted to 1000 ml. by adding more deionized water and cooled to room temperature. A portion of the coal was then agglomerated by placing 200 ml. of the slurry in the blender and mixing it for 5 min. with an emulsion composed of 2 ml. of a kerosene-No. 5 heavy fuel oil mixture (sp.gr. = 0.83) and 200 ml. of deionized water. The slurry was then poured onto a 100 mesh sieve to recover the product. The results are summarized in Table 19. The first run represented a blank run where a coal slurry containing a small amount of sodium carbonate was agglomerated without the oxidizing pretreatment. For the second run the coal was chemically pretreated for 5 min. and for the rest of the runs for 30 min. It can be seen that even with the 5 min. pretreatment, the results were improved significantly. Although the greatest reduction in sulfur content was obtained in run 7, the results of run 6 were nearly as good. The results of run 5 were marred by a relatively poor yield.

Effect of a Third Component

The effect of adding another solid component to a coal slurry undergoing oil agglomeration was investigated. Both relatively coarse (+30 mesh) silica sand and finer loess (-200 mesh) were utilized for this purpose. The loess came from Monona County, Iowa.

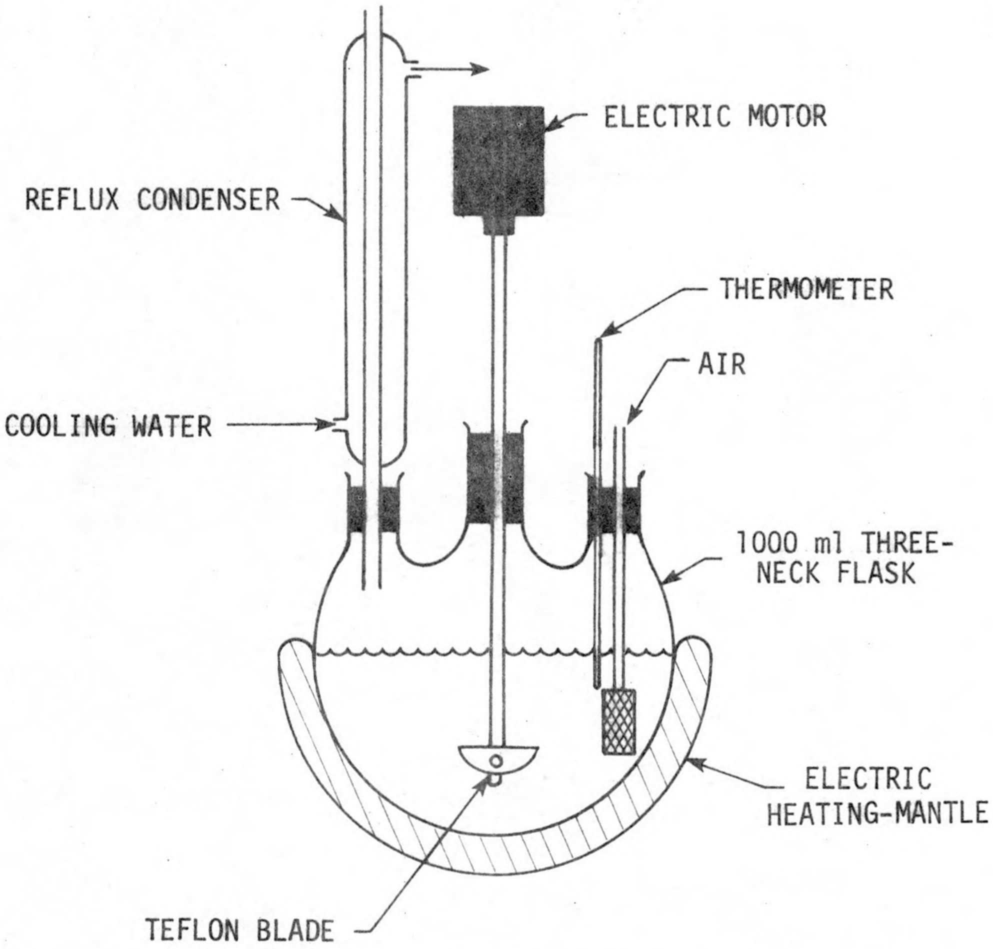

Figure 14. Equipment for chemical pretreatment of a coal slurry.

To study the effect of sand, Scott coal was first ball milled for 16 hr. to reduce its size to -400 mesh. For the agglomeration tests 500 ml. of a slurry containing 20 g. of the ground coal were mixed in the blender for 5 min. with an emulsion composed of 1 ml. of a kerosene-No. 5 heavy fuel oil mixture (sp.gr. = 0.83) and 200 ml. of tap water. The emulsion was prepared with the ultrasonic vibrator. The agglomerated coal was recovered in a separatory funnel and washed twice with fresh tap water as described before. A blank run was made first in which no sand was added. In the next run 10 g. of sand were added to the already agglomerated coal

Table 19. Oil agglomeration tests of chemically pretreated, pulverized (-35 mesh) Scott[a] coal

Run No.	Alkali, (g)	Temp. °C	Reaction Time, min.	pH[b]	Product, %			Reduction, %	
					Yield	Ash	Total S	Ash	Total S
1[c]	Na_2CO_3(0.5)	20	--	8.5	93.2	10.61	5.63	32.5	25.7
2	Na_2CO_3(0.5)	80	5	6.0	94.0	9.54	4.75	39.4	37.3
3	Na_2CO_3(0.5)	80	30	5.5	93.6	9.33	4.78	40.7	36.9
4	NaOH(0.5)	80	30	6.5	93.1	9.43	5.02	40.1	33.8
5	CaO(0.5)	80	30	7.5	78.1	8.67	4.67	44.9	38.4
6	Na_2CO_3(0.5) + NaOH(0.5)	80	30	7.6	94.6	9.38	4.61	40.4	39.2
7	Na_2CO_3(0.5) +$Ca(OH)_2$(0.5)	80	30	8.0	94.1	9.18	4.36	41.6	42.5
8	NaOH(0.5) + CaO(0.5)	80	30	---	58.4	8.40	5.00	46.6	34.0

[a] Untreated Scott coal contained 15.73% ash and 7.58% total sulfur

[b] pH of coal slurry just before adding oil

[c] Coal was not pretreated

in the washing stage and in the final run 10 g. of sand were added to the coal slurry before it was agglomerated. The results (Table 20) show that adding sand during the agglomeration process was beneficial. The greatest benefit was obtained when the sand was added before agglomeration took place. Both the ash and sulfur content of the product were reduced by the addition of sand. It appears that sand particles, which are both hydrophillic and heavy, may adsorb pyrite and gangue mineral slimes and thereby reduce the entrapment of such particles in the coal agglomerates.

To study the effect of adding loess, 20 g. of pulverized (-35 mesh) Scott coal were mixed with 100 ml. of tap water and a specified amount of loess. Mixing and agglomeration were accomplished with the Benco agitator using a speed of 1050 rpm. An emulsion composed of 2 ml. of a kerosene-No. 5 heavy fuel oil mixture (sp.gr. = 0.83) and 100 ml. of tap water was prepared with the ultrasonic vibrator and used for agglomeration. Agglomeration was continued for 5 min. before the slurry was poured onto a 60 mesh sieve to recover the product. The results (Table 20) indicate that the addition of loess had a detrimental effect on both product yield and ash content. As increasing amounts of loess were added, the yield declined and the ash content increased. The corresponding decrease in the sulfur content of the product could be accounted for by the diluting effect of the increased ash content.

Production of Larger Agglomerates

For ease of drying and material handling it is generally advantageous to produce relatively large agglomerates of coal and oil. However, the particle diameter of coal agglomerated with a high speed blender is smaller than 1 mm. regardless of the amount or type of oil used. It is apparent that the high speed rotating blade prevents the growth of agglomerates above a certain size.

Some exploratory experiments were conducted to study different techniques for increasing the size of oil-coal agglomerates. Several different methods of agitation were tested. It was found that gentle agitation with a either paddle stirrer or a magnetic stirrer could increase the size of coal agglomerates. In addition, the cylindrical agitator shown in Figure 15 was built and tested for balling of agglomerated coal. With this device it was possible to increase the size of coal agglomerates up to 1 cm. in diameter.

Table 20. Oil agglomeration tests of Scott[a] coal using an added solid component

		Product, %			Reduction, %	
Coal	Extra Component	Yield	Ash	Total S	Ash	Total S
Ball milled	None	84.9	7.40	5.17	53.0	31.8
	10 g. of sand added in washing stage	85.4	7.08	4.86	55.0	35.9
	10 g. of sand added before agglomeration	84.4	7.09	4.60	54.9	39.3
Pulverized	None	90.2	12.14	6.88	22.8	9.2
	1 g. of loess	84.3	13.47	6.95	14.4	8.3
	2 g. of loess	86.3	15.43	6.85	1.9	9.6
	4 g. of loess	82.1	17.72	6.58	-12.7	13.2
	10 g. of loess	82.4	22.26	6.01	-41.5	20.7

[a] Untreated Scott coal contained 15.73% ash and 7.58% total sulfur.

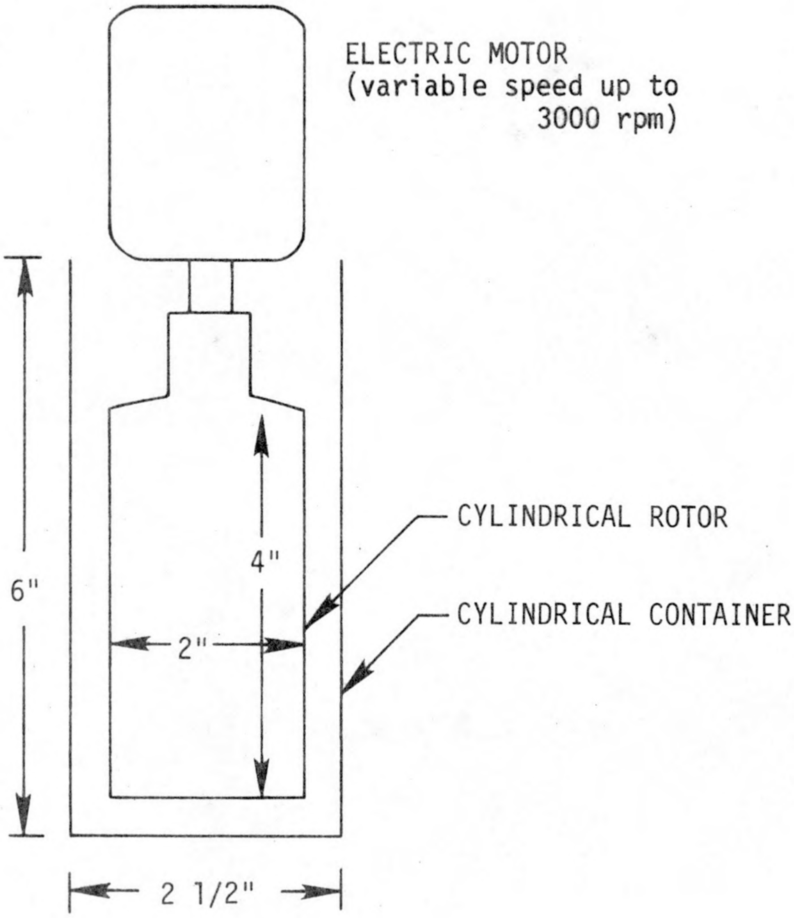

Figure 15. Cylindrical agitator used for oil agglomeration.

Table 21 shows some of the experimental results. This study indicated that heavier or more viscous oil was more effective than lighter oil for increasing the size and strength of agglomerates. However, the addition of heavy oil to the coal slurry was difficult. The coal could not be agglomerated by adding No. 6 heavy oil directly because the oil was so viscous that it could not be dispersed by simple agitation. Hence, the heavy oil had to be broken up into small droplets either by emulsification before it was added or by spraying it into the coal slurry. In order to facilitate emulsification or spraying, the heavy oil was heated in a boiling water bath. However, a completely satisfactory method has not been developed yet.

The optimum speed of the cylindrical agitator appeared to be 500 - 1000 rpm for an emulsified oil and 1500 - 2000 rpm for a straight oil depending on the viscosity of the oil. A larger cylindrical container (3 1/2 in. diameter) was tried but it was not as effective as a 2 1/2 in. diameter container.

IV. FROTH FLOTATION

In a modest way froth flotation has long been used as a beneficiation method for fine-size coal. To apply this method, finely divided coal is mixed with water and a frothing agent and sometimes other chemical reagents. Air bubbles are generated in the mixture and the hydrophobic coal particles become attached to the air bubbles and are buoyed to the surface where they are recovered in a froth. Since the ash forming mineral particles tend to be hydrophillic, they remain in the aqueous suspension.

Table 21. Size of agglomerates produced by various treatments starting with pulverized (-35 mesh) Scott coal

Treatment		Avg. Dia. mm.
50 g. coal was agglomerated with a paddle stirrer using 5 ml. of heated No. 6 heavy oil sprayed with an atomizer		1-2
50 g. coal was agglomerated in a blender with 5 ml. of heated and emulsified No. 6 heavy oil and then was agitated with a paddle stirrer		5
20 g. coal was agglomerated in a blender with 2 ml. of emulsified kerosene-No. 5 heavy oil mixture and balled with cylindrical agitator using 4 ml. of kerosene-No. 5 heavy oil mixture		5
20 g. coal was agglomerated with cylindrical agitator using 6 ml. of emulsified kerosene-No. 5 heavy oil mixture		2-3
20 g. coal was agglomerated with cylindrical agitator using 6 ml. of emulsified No. 1-No. 6 heavy oil mixture		5
100 g. coal was floated with 0.4 ml. MIBC and agglomerated with 10 ml. of emulsified heated No. 6 heavy oil in a froth flotation cell, and then agitated with a magnetic stirrer		2-3
100 g. coal was floated with 0.4 ml. MIBC and agglomerated with 10 ml. of No. 1 fuel oil in a froth flotation cell. The agglomerated coal was divided into four parts and balled with cylindrical agitator using different amounts of No. 1-No. 6 heavy oil mixture:		
	1 ml.	1-2
	2 ml.	3-4
	4 ml.	4-5
	6 ml.	5-10

The effectiveness of froth flotation varies widely with coal characteristics, particle size, pulp density, pH value and flotation agents (13). In particular, pyrite is frequently troublesome in the flotation of coal, owing to its tendency to float with coal. Yancy and Taylor (14) showed that the soluble oxidation products of pyrite were powerful depressants for pyrite. Baker and Miller (15) reported that the colloidal hydroxides precipitated from ferric chloride, aluminum chloride, and cupric sulfate solutions by sodium hydroxide would act as pyrite depressants under controlled conditions of pH and concentration. One of the most promising recent developments is a two-stage process which has been demonstrated by U.S. Bureau of Mines personnel (16). In the first stage, coal is floated while coarse, free pyrite and other minerals are rejected. In the second stage, coal is depressed while fine-size pyrite is floated.

In order to evaluate the desulfurization potential of the froth flotation method, a series of bench scale experiments was carried out with several Iowa coals. Some important results are presented below.

Evaluation of Two-Stage Froth Flotation Process

The Bureau of Mines two-stage froth flotation process was tested to evaluate its effectiveness for cleaning Iowa coal. Experiments were carried out with a Wemco laboratory froth flotation cell using the following steps, except where otherwise stated:

1. 200 g. of coal was placed in the bowl and 1300 ml. of tap water was added.
2. The coal slurry was agitated for 15 min. and 2.5 ml. of amyl alcohol was added.

3. After 30 sec. agitation, air was turned on at a flow rate of 0.33 cu.ft./min. and 1000 ml. of tap water was added.
4. Froth was collected until it looked clean (about 5 min.).
5. Tails were removed and filtered to collect refuse.
6. The first froth was poured back into the bowl and 1000 ml. of tap water was added.
7. Coal depressant (Aero depressant 633) and pyrite collector (potassium amyl xanthate) were added and the coal slurry was agitated for 10 min.
8. 1 ml. of amyl alcohol was added and the slurry was agitated for 30 sec. before air was turned on (0.33 cu.ft./min.).
9. The second froth was collected in 2 min.
10. The tails were filtered to recover clean coal.

The results are summarized in Table 22 and show that the two-stage froth flotation process reduced the ash content 15-50% and the pyritic sulfur centent 15-55% depending on the coal source. However, it was not as effective for Iowa coals as shown by Miller (16) for Pennsylvania coals. In particular, the yield was generally low and relatively large amounts of frothing and depressing agents were required for Iowa coals.

Effect of Different Frothing Agents

Several different frothing agents were tested for flotation of -35 mesh ICO coal with a Wemco laboratory froth flotation cell. The experimental procedure used is as follows:

1. 100 g. of pulverized coal was placed in the bowl and 1000 ml. of tap water was added.

Table 22. Two-stage froth flotation test of pulverized Iowa coals (-35 mesh)

Coal	Product	Weight, %	Ash, %	Pyritic S, %	Treatment
Big Ben	Clean coal	70.38	7.39	0.97	1st stage: 1 wt.% amyl alcohol
	Reject 2	19.36	9.29	3.91	
	Reject 1	10.26	64.52	8.14	2nd stage: 0.1 wt.% Aero 633
					0.05 wt.% xanthate
	Feed	100.00	13.62	2.27	0.4 wt.% amyl alcohol
Big Ben	Clean coal	73.87	6.45	0.90	1st stage: 1 wt.% amyl alcohol
	Reject 2	15.72	11.98	4.60	
	Reject 1	10.41	67.29		2nd stage: 0.15 wt.% Aero 633
					0.03 wt.% xanthate
	Feed	100.00	11.79	2.05	0.04 wt.% amyl alcohol
Jude	Clean coal	78.68	11.75	2.34	1st stage: 1 wt.% amyl alcohol
	Reject 2	9.80	12.80	4.24	
	Reject 1	11.52	74.27		2nd stage: 0.15 wt.% Aero 633
					0.03 wt.% xanthate
	Feed	100.00	19.00	3.12	0.04 wt.% amyl alcohol
Jude	Clean coal	79.06	12.17	2.18	1st stage: 1 wt.% amyl alcohol
	Reject 2	14.63	12.49	3.77	
	Reject 1	6.31	78.98		2nd stage: 0.25 wt.% Aero 633
					0.03 wt.% xanthate
	Feed	100.00	16.43	3.12	0.04 wt.% amyl alcohol
Star	Clean coal	40.08	6.89	1.63	1st stage: 0.32 wt.% amyl alcohol
	Reject 2	14.37	11.85	5.94	
	Reject 1	45.55	18.33	3.68	2nd stage: 0.05 wt.% Aero 633
					0.05 wt.% xanthate
	Feed	100.00	12.74	3.18	0.16 wt.% amyl alcohol
Star	Clean coal	57.47	6.02	2.14	1st stage: 1 wt.% amyl alcohol
	Reject 2	20.41	5.10	2.13	
	Reject 1	22.12	23.28	6.28	2nd stage: 0.25 wt.% Aero 633
					0.03 wt.% xanthate
	Feed	100.00	11.96	3.05	0.04 wt.% amyl alcohol

2. The coal slurry was agitated for 5 min. and 1 ml. of frothing agent was added.
3. After 30 sec. of agitation, air was turned on at a flow rate of 0.33 cu.ft./min. and 1000 ml. of tap water was added.
4. Froth was collected until the water phase looked clean (about 2-3 min.) and filtered.
5. The resultant filter-cake was dried, weighed and analyzed.

The results are shown in Table 23. Although there seemed to be no major differences in the results produced by different frothing agents, methyl isobutyl carbinol (MIBC) gave the best ash reduction, while Dow froth No. 1012 gave the greatest sulfur reduction.

Effect of pH

A series of tests was carried out to determine the effect of pH on froth flotation of Iowa coals. First, 100 g. of pulverized (-35 mesh) coal and 1000 ml. of tap water were placed in the bowl of the Wemco flotation cell, and the slurry was agitated for 5 min. The pH of the slurry was adjusted to the desired level and 0.4 ml. of kerosene was added. After 5 min. of agitation, the coal was floated with 0.05 ml. of MIBC using an air flow rate of 0.33 cu.ft./min. The froth was collected until the water phase appeared free of coal. Similar tests were conducted subsequently with deionized water to compare the effect of water quality.

The results of this series of tests are shown in Table 24 and Figure 16. The data indicate that the two coals which were used responded differently. Thus the yield of Scott coal was larger than the yield of ICO coal over the entire pH range. Also the sulfur and ash contents of ICO coal were reduced more than the sulfur and ash contents of Scott coal. In addition the greatest

Table 23. Single-stage froth flotation of pulverized ICO coal[a] (-35 mesh) with different frothing agents

Frother	Product			Reduction in	
	Yield, %	Ash, %	Total S, %	Ash, %	Total S, %
MIBC	89.4	6.73	2.21	26.45	32.83
Dowfroth #250	92.2	7.16	2.40	21.75	27.05
Dowfroth #1012	91.4	7.11	2.09	22.30	36.47
Dowfroth #1263	92.9	7.26	2.28	20.66	30.70

[a] Untreated ICO coal contained 9.15% ash and 3.29% total sulfur.

reduction in the ash content of ICO coal was obtained at a pH of 3-4 whereas the greatest reduction in the ash content of Scott coal was obtained at a pH of 7-8. Furthermore the reduction in sulfur content of ICO coal was relatively constant over the pH range from 3 to 10 while the reduction in sulfur content of Scott coal rose gradually over this pH range.

The results obtained when deionized water was used for the froth flotation of Scott coal were superior to those obtained when tap water was used (Table 24 and Figure 16). Thus the yield was larger over a pH range of 3 to 10 and the product had less sulfur and ash.

Wettability of Coal and Pyrite

A series of qualitative tests was carried out to determine the wettability of coal and pyrite particles over a pH range from 2 to 12 in solutions of various chemical reagents. Scott coal (-20+40 mesh) was cleaned by floating it in a liquid having a specific gravity of 1.3 and pulverized to provide a -200 mesh sample. Pyrite was carefully hand-picked from another portion of Scott coal and ground to -200 mesh.

Table 24. Single-stage froth flotation test of pulverized (-35 mesh) coals at different pH

ICO[a] in tap water				Scott[b] in tap water				Scott[b] in deionized water			
pH[c]	Yield, %	Ash, %	Total S, %	pH[d]	Yield, %	Ash, %	Total S, %	pH[d]	Yield, %	Ash, %	Total S, %
2.3	79.1	6.53	2.41	2.5	87.1	13.44	7.18	3.0	94.5	12.2	6.38
3.2	71.6	5.91	1.98	2.8	86.7	13.05	6.97	5.1	93.4	11.7	5.91
3.9	73.1	6.04	1.96	5.1	83.7	12.07	6.04	5.7	93.4	11.7	7.75
6.8	77.3	6.58	2.01	6.1	83.4	11.50	5.85	8.2	91.6	10.8	5.42
9.7	77.0	6.75	2.07	6.7	83.1	10.99	6.21	9.2	90.8	10.6	5.23
10.3	67.7	6.52	1.93	8.0	82.4	10.97	5.86	10.5	73.2	9.7	4.33
11.4	22.9	7.02	1.58	9.7	81.8	11.31	5.48	11.1	64.4	10.5	4.43

[a] Untreated ICO coal contained 9.15% ash and 3.29% total sulfur.

[b] Untreated Scott coal contained 14.42% ash and 7.58% total sulfur.

[c] pH was adjusted with 1 N HCl or 1 N KOH solutions.

[d] pH was adjusted with 1 N H_2SO_4 or 1 N NaOH solutions.

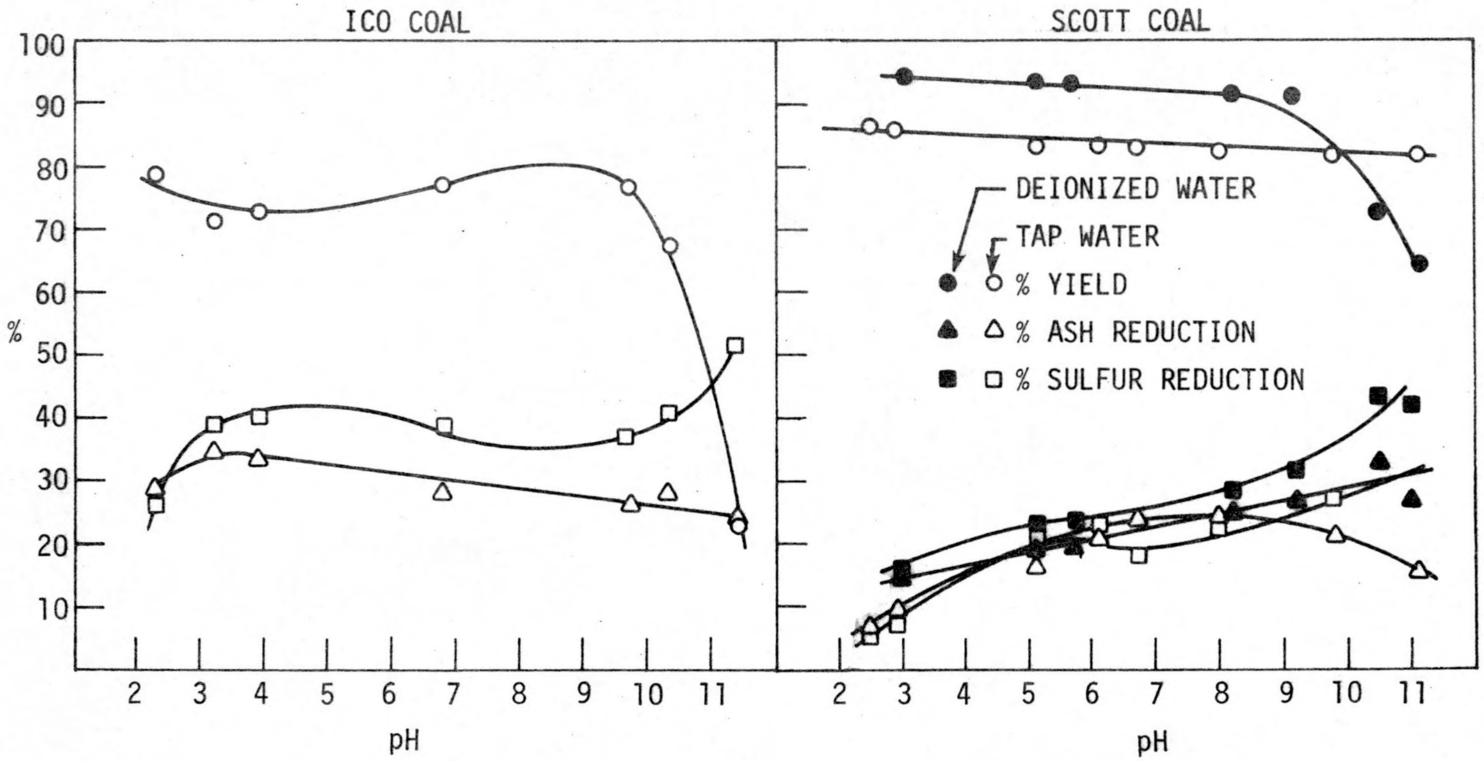

Figure 16. Effect of pH and water source on single-stage froth flotation of Iowa coals.

The wettability of coal and pyrite particles was determined by the following procedure:

1. 5 g. of coal or pyrite was slurried with 500 ml. of 0.001 mole/l. chemical solution for 10 min. in a blender. Deionized water was used to make the chemical solution.
2. 10 ml. of the slurry was placed in a glass test tube and the pH was adjusted to the desired value by adding 1 N hydrochloric acid or sodium hydroxide solution.
3. 5 ml. of No. 1 fuel oil was added to the test tube and the test tube was shaken vigorously.
4. The test tube was then allowed to stand still for a while and the distribution of coal or pyrite between oil and water phases was observed.

It was found that the coal stayed almost completely at the oil-water interface over the entire pH range regardless of the chemical solutions used. Hence, it can be concluded that the wettability of Scott coal is constant and unaffected by the pH or chemical additives tested. On the other hand, the pyrite behaved differently depending upon the pH and chemical environment. The results are summarized in Table 25, where the following letter symbols are used:

W - pyrite almost completely in water phase
WI - pyrite partly in water phase and partly at interface
W(I) - pyrite largely in water phase and some at interface
I(W) - pyrite largely at interface and some in water phase
I(O) - pyrite largely at interface and some in oil phase

The wettability tests discussed above indicated conditions where coal and pyrite have different wettability, and, hence, where they might be separated

Table 25. Wettability of pyrite in solutions of various reagents

pH	None	$FeCl_3$	Na_2CO_3	Na_2SiO_3	Na_2PO_4	Na_2SO_3	NaCN	EDTA	NH_4SCN
2 - 3	I(O)	W(I)	I(W)	I(W)	I(W)	I(O)	----	I(W)	I(O)
3 - 4	----	W	I(W)	I(W)	I(W)	I(O)	----	I(W)	I(O)
4 - 5	I(O)	W(I)	I(W)	I(W)	I(W)	I(O)	----	I(W)	I(O)
5 - 6	I(O)	I(W)	I(W)	I(W)	I(W)	I(O)	----	I(W)	WI
6 - 7	I(W)	I(W)	I(W)	WI	WI	I(W)	----	I(W)	WI
7 - 8	I(W)	I(W)	WI	W(I)	WI	I(W)	----	WI	W
8 - 9	WI	I(W)	WI	W(I)	W(I)	W(I)	W(I)	WI	W
9 - 10	WI	I(W)	I(W)	W(I)	W(I)	W(I)	W	W(I)	W
10 - 11	I(O)	----	W(I)	W(I)	W(I)	WI	W	W	W(I)
11 - 12	I(O)	W(I)	W(I)	W(I)	W(I)	I(O)	W	W	W(I)

effectively. These conditions were chosen and applied to the single stage froth flotation separation of pulverized Scott coal (-35 mesh).

One hundred grams of Scott coal were slurried in 1000 ml. of 0.001 mole/l. chemical solution and agitated for 10 min. in a Wemco froth flotation cell. Throughout this test, deionized water was used. The pH of the slurry was adjusted to the desired value by adding 1 N hydrochloric acid or sodium hydroxide solution. The coal was then floated by adding 0.4 ml. of No. 1 fuel oil and 0.2 ml. MIBC and using an air flow rate of 0.33 cu.ft./min. Table 26 summarizes the test results. The addition of various chemicals did not seem to make a significant improvement in sulfur reduction. In particular, the results obtained with ferric chloride was very poor and seemed to contradict what was expected from the wettability test. The poor separation may have been

Table 26. Single stage froth flotation of Scott coal[a] (-35 mesh)

Chemical	pH	Product		
		Yield, wt.%	Ash, wt.%	Sulfur, wt.%
None	9.2	90.8	10.95	5.23
$FeCl_3$	3.9	96.4	12.97	7.03
Na_2CO_3	7.8	92.3	11.45	5.45
Na_2SiO_3	9.2	90.5	10.71	5.08
Na_3PO_4	6.8	91.1	11.63	5.64
Na_2SO_3	9.7	91.9	10.96	5.09
NaCN	9.2	91.4	11.04	5.35
EDTA	9.5	72.2	9.86	5.75
NH_4CNS	7.2	86.1	8.98	6.05

[a] Untreated Scott coal contained 15.73% ash and 7.58% total sulfur.

due to the following reasons. Firstly, the pyrite in the pulverized Scott coal may not have been liberated sufficiently. Hence, a large portion of the pyrite may have been attached to coal particles which were carried into the froth product. Secondly, the soluble salts contained in the run of mine coal may have changed the chemical environment for the froth flotation tests from that of the wettability tests. Thirdly, the inner pore surface of the coal may have adsorbed the chemical reagents so that they were unavailable for depressing the pyrite.

Effect of Chemical Pretreatment

Pulverized (-35 mesh) Scott coal was subjected to a mild chemical pretreatment which was designed to oxidize the surface of the pyrite particles and thereby render the surface hydrophillic. After the pretreatment the coal was separated by the single stage froth flotation method. The pretreatment involved wet oxidation of a coal slurry. A small amount of alkali or other chemical reagent was added to the slurry (Table 27). For Runs 2 to 10 the pretreatment was carried out in the reactor shown in Figure 14 and the procedure described above for pretreating coal which had been subsequently oil agglomerated was used. For Runs 11 to 14 the pretreatment was carried out in the Wemco froth flotation cell at room temperature. For pretreatment in the flotation cell, 100 g. of coal and the chemical reagent were mixed with 1000 ml. of deionized water and the mixture was aerated for 3 hr. while introducing air at a rate of 0.33 cu.ft./min. After either type of pretreatment, the coal slurry diluted to 1000 ml. with deionized water was separated by the Wemco froth flotation cell. For this separation, 0.4 ml. of MIBC was added to the slurry and air was introduced at a rate of 0.33 cu.ft./min.

Table 27. Single stage froth flotation test with 100 g. of chemically pretreated Scott coal[a] (-35 mesh)

Run No.	Chemical (g.)	Temp., °C	Trt. time min.	pH[b]	Product, %			Reduction, %	
					Yield	Ash	Total S	Ash	Total S
1[c]	Na_2CO_3(0.5)	20	--	7.8	92.3	11.45	5.45	27.2	28.1
2	Na_2CO_3(0.5)	80	5	6.0	83.4	11.67	4.99	25.8	34.2
3	Na_2CO_3(2.5)	50	5	8.2	83.5	11.56	4.86	26.5	35.9
4	Na_2CO_3(0.5)	80	30	5.5	83.0	10.53	5.07	33.1	33.1
5	NaOH(0.5)	80	30	6.5	80.1	10.84	4.94	31.1	34.8
6	CaO(0.5)	80	30	7.5	78.0	10.81	4.93	31.3	35.0
7	Na_2CO_3(0.5) + NaOH(0.5)	80	30	7.6	86.1	11.35	5.41	27.8	28.6
8	Na_2CO_3(0.5) + $Ca(OH)_2$(0.5)	80	30	8.0	77.9	11.40	4.66	27.5	38.5
9	NaOH(0.5) + CaO(0.5)	80	30	---	84.2	10.67	5.18	32.2	31.7
10	$FeSO_3$(1.0)	80	30	7.0	62.9	10.70	5.48	32.0	27.7
11	CaO(1.0)	20	180	4.5	90.5	9.69	4.75	38.4	37.3
12	NaOH(1.0)	20	180	4.4	91.3	9.85	4.95	37.4	34.7
13	Na_2CO_3(1.0)	20	180	4.0	92.2	12.09	5.95	23.1	21.5
14	$KMnO_4$(1.0) + NaOH(1.0)	20	180	3.8	87.7	10.06	4.85	36.0	36.0

[a] Untreated Scott coal contained 15.73% ash and 7.58% total sulfur.

[b] The pH was measured just before the addition of frother.

[c] Coal was not pretreated.

The results (Table 27) show that in most cases chemical pretreatment improved the sulfur reduction obtained by froth flotation over that obtained in the first run where the coal was not pretreated. On the other hand, pretreatment also appeared to reduce the yield. Runs 11 and 12 provided about the best overall results with high yields and good reductions in both sulfur and ash.

V. CHEMICAL COMMINUTION

Chemical comminution involves fracturing or breaking coal by application of specific chemical agents such as anhydrous liquid ammonia rather than by application of mechanically applied forces. Chemical comminution seems to induce cleavage at coal-mineral interfaces and, hence, appears to be more selective in its action than mechanical breakage. Hence, it may be possible to liberate mineral particles through chemical comminution without resorting to the same degree of size reduction required with mechanical crushing.

To test the effectiveness of chemical comminution for liberating the minerals in Iowa coal, several experiments were conducted where coal was soaked in a known comminuting agent, dried, and then passed through a double roll crusher. After this treatment, the material was separated by a float-sink precedure and the results were compared with those obtained by mechanical crushing and float-sink separation. Two comminuting agents were utilized, anhydrous liquid ammonia and a 1 M solution of sodium hydroxide in methanol. For applying the treatment, 500 g. of lump coal (1 1/2 in. x 0) was placed in a 2 liter Erlenmeyer flask and the liquid comminuting agent was added until the lumps were completely covered. When liquid ammonia was used, the flask was kept in a cold bath (-70°C) consisting of dry ice and methanol. After the coal had soaked in the ammonia for 1 hr., the flask was removed from the cold bath and placed in a well ventilated hood where the ammonia evaporated. It was left in the hood until the oder of ammonia could no longer be detected. When the methanol solution of caustic was used as the comminuting agent, the coal was allowed to soak in the solution at room temperature for 2 hr. The solution was then decanted off and the coal was washed with warm water until the caustic was completely removed. The coal was subsequently dried.

The treated coal was passed through a double roll crusher to reduce it to 1/4 in. top size and next was mixed with 2 liters of tetrachloroethylene liquid (sp.gr. = 1.613). After standing for 30 min. to allow the material to separate, the float fraction was skimmed off into a 100 mesh sieve and the remaining suspension was filtered to recover the sink fraction. The two fractions were heated in a drying oven at 100°C for 4 hr. to evaporate the organic liquid and then were weighed and analyzed. Untreated coal was also reduced to 1/4 in. top size by the double roll crusher and then separated in the same manner.

The weight distribution and composition of the float and sink fractions of both treated and untreated Iowa coals are shown in Table 28. In the case of ICO coal it appears that chemical comminution resulted in somewhat lower yields of float coal and only slightly greater sulfur reductions than those obtained by straight mechanical crushing. But in the case of Jude coal, chemical comminution seemed to provide somewhat higher hields of float coal with a lower ash content than was provided by mechanical crushing. However, there was not much difference in the sulfur content. Since these results were rather inconclusive, it appears that either a different type of test or a more sensitive test is needed to show whatever advantages chemical comminution may have over mechanical crushing.

Table 28. Comparison of comminution methods followed by float-sink separation in tetrachloroethylene (sp.gr. = 1.613)

		ICO Coal				Jude Coal			
Comminution method	Product	Yield, %	Ash, %	Total S, %	Pyritic S, %	Yield, %	Ash, %	Total S, %	Pyritic S, %
Roll crush to 1/4 in. top size	Float	91.0	5.08	2.06	1.23	83.7	6.87	5.38	1.17
	Sink	9.0	44.44	----	----	16.3	50.33	----	----
	Feed	100.0	8.32	3.48	2.41	100.0	14.18	6.94	2.97
Liquid NH_3 & roll crush to 1/4 in. top size	Float	86.9	4.98	1.71	0.83	88.4	4.39	5.05	1.05
	Sink	13.1	46.72	----	----	11.6	50.59	----	----
	Feed	100.0	8.48	3.15	2.30	100.0	9.91	6.63	2.46
NaOH + CH_3OH & roll crush to 1/4 in. top size	Float	84.6	5.42	2.04	0.88	89.2	5.42	5.39	1.30
	Sink	15.4	26.95	----	----	10.8	45.52	----	----
	Feed	100.0	11.40	2.72	2.06	100.0	13.99	7.96	4.43

VI. COMPARISON OF DIFFERENT BENEFICIATION METHODS

In order to compare the relative effectiveness of various coal beneficiation methods and different combinations of these methods, a series of sixteen different coal beneficiation treatments was applied to two Iowa coals. These treatments involved different combinations of size reduction methods (crushing, pulverizing, grinding, and chemical comminution) and of physical separation methods (float-sink, froth flotation, and oil agglomeration). The results are compared on the basis of product yield and percentage reduction in sulfur and ash brought about by the treatment.

Experimental Methods

The following experimental methods and equipment were used in various combinations:

Roll crushing. Lump coal (1 1/2 min. x 0) was crushed to 1/4 in. top size by passing it through a bench-scale double roll crusher manufactured by Smith Engineering Works, Milwaukee, Wisconsin.

Pulverizing. Previously crushed coal was pulverized to -35 mesh by a Mikro-Samplmill manufactured by Pulverizing Machinery Division, American-Marietta Co., Summit, New Jersey.

Ball milling. Previously pulverized coal was ground to -400 mesh size in a ceramic jar mill. For this operation 200 g. of coal, 1000 g. of water, and 1900 g. of flint pebbles were placed in a 1.5 gal. jar mill and the mill was then run for 20 hr.

Chemical comminution. For this operation 500 g. of lump coal (1 1/2 in. x 0) were placed in a 2000 ml. Erlenmeyer flask which was then placed in a cold bath of dry ice and methanol and cooled to -70°C. Liquid anhydrous ammonia was then added to the flask until the coal was immersed in the liquid. After the coal had soaked for 1.0 hr., the flask was removed from the cold bath and placed in a well ventilated hood where the ammonia evaporated. When the odor of ammonia could no longer be detected, the comminution step was completed.

Gravity separation. To effect the gravity separation of coal and mineral matter, 500 g. of crushed coal (1/4 in. x 0) were added to 2000 ml. of tetrachloroethylene (specific gravity = 1.613) contained in a large beaker placed in a well ventilated hood. The mixture was stirred by hand to insure wetting of all particles and then it was allowed to stand for 30 min. The float product was subsequently skimmed off and placed on a 100 mesh sieve to allow any adhering liquid to drain away. The float product was then placed in a drying oven set at 100°C for 4 hr.

Froth flotation. To conduct a froth flotation test, 200 g. of pulverized coal (-35 mesh) were added to 2000 ml. of tap water placed in the bowl of a laboratory model Wemco Fagergren flotation cell. With the agitator running, the pH of the slurry was lowered below five by adding 10 ml. of an acid solution containing 10 vol.% concentrated hydrochloric acid. Both kerosene (1.0 ml.) and methyl isobutyl carbinol (0.5 ml.) were added to the agitated slurry and the air flow to the cell was set at 0.33 cu.ft./min. The resulting froth was collected until it appeared that no more coal was being recovered. The material remaining in the bowl was poured out and the froth product was put back in the bowl and fresh tap water was added to bring the slurry volume to 2000 ml. With the agitator running, the pH of the slurry was raised above nine by adding 40 ml. of base containing 5 wt.% potassium hydroxide. The coal was then refloated without adding further reagents and using the same air flow rate as before.

Oil agglomeration. Oil agglomeration tests were carried out with a 14 speed blender marketed by Sears Roebuck and Co. This blender is designed for home use and can hold up to 40 oz. of liquid. For an agglomeration test, 200 ml. of an aqueous slurry containing 10 wt.% coal was placed in the blender together with 10 ml. of a solution containing 0.2 wt.% sodium carbonate. The sodium carbonate not only increased the pH of the slurry but also served as a dispersing agent for the clay particles. The slurry was agitated for 5 min. at the lowest speed setting. An emulsion of fuel oil and water was then added to the coal slurry and the agitation continued for another 5 min. at the same speed setting. The emulsion was prepared by combining 2.0 ml. of a mixture of No. 1 fuel oil (86 vol.%) and No. 5 fuel oil (14 vol.%), the mixture having a specific gravity of 0.83, with 200 ml. of tap water and emulsifying the mixture with an ultrasonic vibrator. The coal slurry was poured into a 1000 ml. separatory funnel whereupon the agglomerated coal floated to the surface and the refuse particles settled to the bottom. The water and refuse were drained out through the bottom opening and the agglomerated coal was put back in the blender and mixed with 200 ml. of fresh tap water. After agitating the mixture for 2 min. at the lowest speed setting, the coal slurry was poured back into the separatory funnel where the agglomerated coal was recovered again. This washing operation was repeated once more to reduce entrapped impurities.

Chemical analysis. Coal samples were analyzed for sulfur and ash by the standard ASTM procedures (10). These procedures also gave the distribution of pyritic, sulfate, organic, and total sulfur.

Materials

Coal from two Iowa strip mines was used for comparing different treatments. A channel sample from the ICO mine and a run of mine sample from the Jude mine were the source of the materials used. The proximate analysis and sulfur distribution of each of these samples are shown in Table 1. Although the sulfur and ash contents of these samples were widely different, the samples represented coal of the same rank (high volatile C). Investigation of the coal microstructure with a scanning electron microscope revealed substantial amounts of finely disseminated microcrystals of iron pyrites (12).

Each coal sample was crushed to 1 1/2 in. top size and then divided into three size fractions (1 1/2 in. x 3/8 in., 3/8 in. x 48M, and 48M x 0). Each size fraction was then float-sink tested at various specific gravities using organic liquids of known specific gravity. The standard Bureau of Mines procedure was employed for this test (17). The data for the different size fractions were combined to provide the composite washability analysis for 1 1/2 in. x 0 coal shown in Table 29.

Experimental Results

The sequence of steps involved in each of the sixteen treatments which were applied to each of the two coals is shown in Figure 17. Thus the first treatment was the simplest and involved crushing with the roll crusher, pulverizing with the Mikro-Samplmill, and oil agglomeration. The second treatment included a ball milling step in addition to the other steps. The third and fourth treatments included a froth flotation step. In the fifth through eighth treatments the crushed coal was subjected to gravity separation before being pulverized and otherwise treated as in the first four treatments. In the last eight treatments the coal was chemically comminuted before being conducted through the roll crusher. Following the chemical comminution step the pattern of treatments was the same as for the first eight treatments. The final step of each treatment was an oil agglomeration step.

After each separation step within any given treatment, the weight of coal recovered was measured after drying overnight in an oven at 80-100°C and a

Table 29. Composite washability analysis of coal (1 1/2 min. x 0) from ICO and Jude strip mines

Product Fraction	Direct Data, %			Cumulative Date, %		
	Weight	Ash	Total Sulfur	Weight	Ash	Total Sulfur
ICO Coal						
Float 1.30	78.7	5.36	1.80	78.7	5.36	1.80
1.30 - 1.35	6.3	11.98	2.74	85.0	5.85	1.87
1.35 - 1.40	2.8	15.63	3.66	87.8	6.16	1.93
1.40 - 1.45	2.9	16.84	4.18	90.7	6.50	2.00
1.45 - 1.50	2.0	20.47	4.83	92.7	6.80	2.06
1.50 - 1.55	1.5	22.50	4.01	94.2	7.05	2.09
1.55 - 1.60	0.5	25.39	6.46	94.7	7.15	2.11
Sink 1.60	5.3	42.05	17.57	100.0	9.00	2.93
Jude Coal						
Float 1.30	46.5	5.67	5.07	46.5	5.67	5.07
1.30 - 1.35	19.0	12.03	4.83	65.5	7.51	5.00
1.35 - 1.40	7.6	15.84	5.24	73.1	8.38	5.03
1.40 - 1.45	7.1	19.94	6.41	80.2	9.40	5.15
1.45 - 1.50	3.9	23.80	7.91	84.1	10.07	5.28
1.50 - 1.55	3.0	28.30	7.53	87.1	10.70	5.36
1.55 - 1.60	1.7	31.51	6.79	88.8	11.10	5.38
Sink 1.60	11.2	48.92	12.84	100.0	15.33	6.22

small sample was taken for analysis. The samples were subsequently analyzed for ash, pyritic sulfur and total sulfur. The composition of the dried product from each separation step for each treatment is shown in Tables 30 and 31 for ICO coal and Jude coal respectively. The yield of coal for each separation step and the total yield for the overall treatment were determined as follows:

$$\text{Yield (\%)} = \frac{\text{dry weight of product}}{\text{dry weight of feed}} \times 100$$

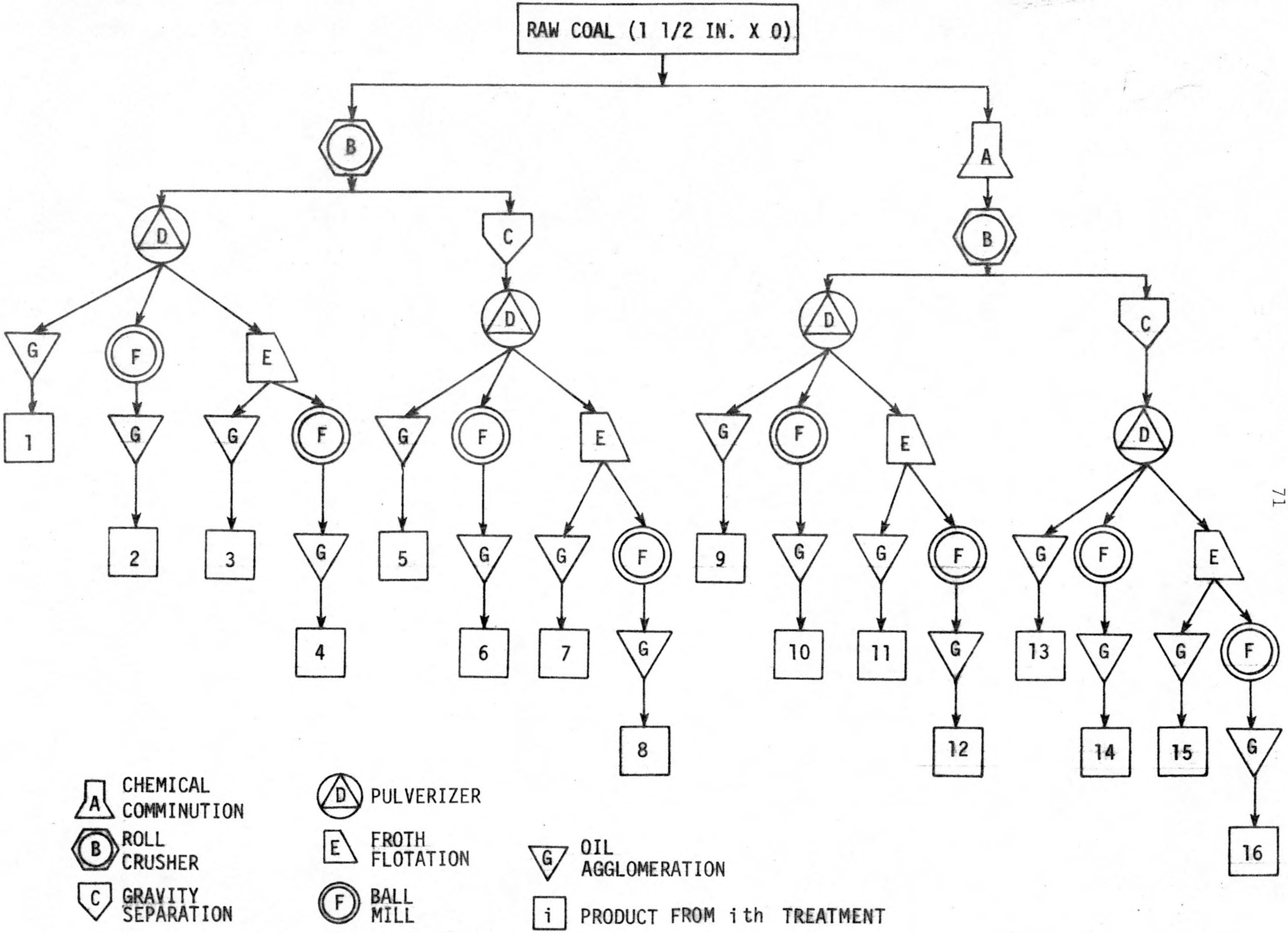

Figure 17. Flow diagram of 16 different treatments.

Table 30. Results of different treatments on ICO mine coal

		Product Composition, %			Reduction, %			
Treatment	Step	Ash	Pyritic Sulfur	Total Sulfur	Ash	Pyritic Sulfur	Total Sulfur	Yield %
1	G	6.24	2.11	2.82	25.0	12.4	18.3	94.7
(B-D-G)	Total				25.0	12.4	18.3	94.7
2	G	6.46	1.75	2.82	22.4	27.4	18.3	98.4
(B-D-F-G)	Total				22.4	27.4	18.3	98.4
3	E	4.75	1.03	1.99	42.9	57.3	42.3	89.9
(B-D-E-G)	G	3.74	0.90	1.74	21.3	12.6	12.6	98.9
	Total				55.0	62.7	49.6	88.9
4	E	4.75	1.03	1.99	42.9	57.3	42.3	89.9
(B-D-E-F-G)	G	3.37	0.84	1.81	29.1	18.4	9.0	97.7
	Total				59.5	65.1	47.5	87.8
5	C	5.08	1.23	2.06	38.9	49.0	40.3	91.0
(B-C-D-G)	G	4.29	1.14	1.99	15.5	7.3	3.4	94.5
	Total				48.4	52.7	42.3	87.8
6	C	5.08	1.23	2.06	38.9	49.0	40.3	91.0
(B-C-D-F-G)	G	3.56	0.91	1.76	36.5	26.0	14.6	99.4
	Total				57.2	62.2	49.0	90.5
7	C	5.08	1.23	2.06	38.9	49.0	40.3	91.0
(B-C-D-E-G)	E	3.74	0.69	1.51	26.4	43.9	26.7	95.7
	G	2.95	0.58	1.36	21.1	15.9	9.9	99.6
	Total				64.5	75.9	60.6	86.7
8	C	5.08	1.23	2.06	38.9	49.0	40.3	91.0
(B-C-D-E-F-G)	E	3.74	0.69	1.51	26.4	43.9	26.7	95.7
	G	2.55	0.48	1.37	31.8	30.4	9.3	98.8
	Total				69.4	80.1	60.3	86.0

Table 30. continued.....

		Product Composition, %			Reduction, %			
Treatment	Step	Ash	Pyritic Sulfur	Total Sulfur	Ash	Pyritic Sulfur	Total Sulfur	Yield %
9	G	6.45	1.46	2.19	22.5	39.4	36.5	87.5
(A-B-D-G)	Total				22.5	39.4	36.5	87.5
10	G	6.14	1.17	2.10	26.2	51.5	39.1	94.4
(A-B-D-F-G)	Total				26.2	51.5	39.1	94.4
11	E	5.22	0.82	1.59	37.3	66.0	53.9	90.7
(A-B-D-E-G)	G	4.05	0.67	1.50	22.4	18.3	5.7	86.5
	Total				51.3	72.2	56.5	78.5
12	E	5.22	0.82	1.59	37.3	66.0	53.9	90.7
(A-B-D-E-F-G)	G	3.14	0.53	1.28	39.8	35.4	19.5	97.4
	Total				62.3	78.0	62.9	88.3
13	C	4.98	0.83	1.71	40.1	65.6	50.4	86.9
(A-B-C-D-G)	G	4.15	0.79	1.63	16.7	4.8	4.7	87.5
	Total				50.1	67.2	52.8	76.0
14	C	4.98	0.83	1.71	40.1	65.6	50.4	86.9
(A-B-C-D-F-G)	G	2.47	0.36	1.25	50.4	56.6	26.9	96.7
	Total				70.3	85.1	63.8	84.0
15	C	4.98	0.83	1.71	40.1	65.6	50.4	86.9
(A-B-C-D-E-G)	E	2.47	0.53	1.31	14.3	36.1	23.4	94.8
	G	3.34	0.44	1.28	21.8	17.0	2.3	97.7
	Total				59.9	81.7	62.9	80.5
16	C	4.98	0.83	1.71	40.1	65.6	50.4	86.9
(A-B-C-D-E-F-G)	E	4.27	0.53	1.31	14.3	36.1	23.4	94.8
	G	2.29	0.31	1.09	46.4	41.5	16.8	97.4
	Total				72.5	87.1	68.4	80.2

Table 31. Results of different treatments on Jude mine coal

		Product Composition, %			Reduction, %			
Treatment	Step	Ash	Pyritic Sulfur	Total Sulfur	Ash	Pyritic Sulfur	Total Sulfur	Yield %
1	G	8.56	2.04	5.99	39.6	31.3	13.7	83.8
(B-D-G)	Total				39.6	31.3	13.7	83.8
2	G	9.32	2.02	5.86	34.3	32.0	15.6	94.3
(B-D-E-G)	Total				34.3	32.0	15.6	94.3
3	E	8.50	1.54	5.18	40.1	48.1	25.4	86.9
(B-D-E-G)	G	4.74	0.92	4.36	44.2	40.3	15.8	90.5
	Total				66.6	69.0	37.2	78.6
4	E	8.50	1.54	5.18	40.1	48.1	25.4	86.9
(B-D-E-F-G)	G	4.06	0.83	4.55	52.2	46.1	12.2	93.7
	Total				71.4	72.1	34.4	81.4
5	C	6.87	1.17	5.38	51.6	60.6	22.5	83.7
(B-C-D-G)	G	4.92	1.06	5.04	28.4	9.4	6.3	93.0
	Total				65.3	64.3	27.4	77.8
6	C	6.87	1.17	5.38	51.6	60.6	22.5	83.7
(B-C-D-F-G)	G	4.24	0.86	4.88	38.3	26.5	9.3	97.1
	Total				70.1	71.0	29.7	81.3
7	C	6.87	1.17	5.38	51.6	60.6	22.5	83.7
(B-C-D-E-G)	E	5.58	0.90	4.89	18.8	23.1	9.1	95.9
	G	3.93	0.73	4.68	29.6	18.9	4.3	98.0
	Total				72.3	75.4	32.6	78.7
8	C	6.87	1.17	5.38	51.6	60.6	22.5	83.7
(B-C-D-E-F-G)	E	5.58	0.90	4.89	18.8	23.1	9.1	95.9
	G	2.74	0.36	4.01	50.9	60.0	18.0	96.6
	Total				80.7	87.9	42.2	77.5

Table 31. continued.....

		Product Composition, %			Reduction, %			
Treatment	Step	Ash	Pyritic Sulfur	Total Sulfur	Ash	Pyritic Sulfur	Total Sulfur	Yield %
9	G	6.08	1.70	5.91	57.1	42.8	14.8	92.1
(A-B-D-G)	Total				57.1	42.8	14.8	92.1
10	G	4.78	1.34	5.14	66.3	54.9	25.9	92.7
(A-B-D-F-G)	Total				66.3	54.9	25.9	92.7
11	E	6.34	1.63	5.53	55.3	45.1	20.3	95.0
(A-B-D-E-G)	G	5.31	1.27	5.24	16.2	22.1	5.2	97.2
	Total				62.6	57.2	24.5	92.3
12	E	6.34	1.63	5.53	55.3	45.1	20.3	95.0
(A-B-D-E-F-G)	G	3.10	0.73	4.55	51.1	55.2	5.2	94.1
	Total				78.1	75.4	24.5	89.4
13	C	4.39	1.05	5.05	69.0	64.6	27.2	88.4
(A-B-C-D-G)	G	3.59	0.96	4.98	18.2	8.6	1.4	90.5
	Total				74.7	67.7	28.2	80.0
14	C	4.39	1.05	5.05	69.0	64.6	27.2	88.4
(A-B-C-D-F-G)	G	2.23	0.40	4.45	49.2	61.9	11.9	97.3
	Total				84.3	86.5	34.9	86.0
15	C	4.39	1.05	5.05	69.0	64.6	27.2	88.4
(A-B-C-D-E-G)	E	4.04	0.79	4.74	8.0	24.8	6.1	98.3
	G	2.98	0.69	4.55	26.2	12.7	4.0	98.2
	Total				79.0	76.8	34.4	85.3
16	C	4.39	1.05	5.05	69.0	64.6	27.2	88.4
(A-B-C-D-E-F-G)	E	4.04	0.79	4.74	8.0	24.8	6.1	98.3
	G	2.23	0.42	4.39	44.8	46.8	7.4	98.5
	Total				84.3	85.9	36.7	85.6

In the case of oil agglomerated coal, the the product yield determined in this manner represents the yield of coal and oil associated with it after drying. Unfortunately most of the oil was lost by evaporation during the drying step, so the reported yields include very little of the oil which was recovered with the coal before drying. The percentage reduction in either ash or sulfur content was found for each separation step and for the overall treatment by employing the relation

$$\text{Reduction (\%)} = \frac{\text{content of feed - content of product}}{\text{content of feed}} \times 100$$

These parameters are also shown in Tables 30 and 31.

With reference to Table 30, it can be seen that following the oil agglomeration step (G) of the first treatment the product contained 6.24% ash, 2.11% pyritic sulfur, and 2.82% total sulfur which corresponded to a reduction in ash content of 25.0%, reduction in pyritic sulfur content of 12.4% and reduction in total sulfur content of 18.3%. Also the product weight yield for this step was 94.7%. Since the first treatment involved only one separation step, the total reduction in ash and sulfur and total yield for the overall treatment were the same as for the oil agglomeration step. Losses of material in the crushing and pulverizing steps were assumed to be negligible.

The data in Tables 30 and 31 indicate that the yield of cleaned coal was uniformly high for most of the treatments. Thus the overall yield was above 80% for 14 out of 16 treatments applied to ICO coal and 12 out of 16 applied to Jude coal. On the other hand, the percentage reduction in ash and sulfur contents was more variable with the overall reduction in ash content between 22 and 72% for ICO coal and between 34 and 84% for Jude coal and the overall reduction in total sulfur content between 18 and 68% for ICO coal and between 14 and 42% for Jude coal. The overall percentage reduction in pyritic sulfur was also quite variable, ranging between 12 and 87% for ICO coal and between 31 and 88% for Jude coal.

In the case of ICO coal, Treatment 16 produced the cleanest product. This treatment was the most complex of all the treatments since it included all of the comminution and separation steps. The product from this treatment contained only 2.29% ash, 0.31% pyritic sulfur, and 1.09% total sulfur and it was recovered in 80% overall yield. This represented an overall reduction of 72.5% in ash content, 87.1% in pyritic sulfur content, and 68.4% in total sulfur content. In the case of Jude coal, Treatments 14 and 16 provided coal with the lowest ash content (2.23%) while Treatment 8 provided coal with the lowest sulfur content (0.36% pyritic sulfur and 4.01% total sulfur). The overall yield of cleaned coal was 86% for Treatments 14 and 16 and 78% for Treatment 8. The overall reduction in ash content was 84% for Treatments 14 and 16 and 81% for Treatment 8 and the overall reduction in pyritic sulfur content was 86% for Treatments 14 and 16 and 88% for Treatment 8. Finally the overall reduction in total sulfur content was 36% for Treatments 14 and 16 and 42% for Treatment 8.

Treatments 1 and 2 which involved only mechanical size reduction and oil agglomeration were the least effective for both ICO and Jude coal. Although the yield of the cleaned coal was high, the reduction in ash and sulfur contents was small for ICO coal and only somewhat greater for Jude coal.

Most of the treatments provided a cleaner product for a given yield than could be obtained by gravity separation alone of 1 1/2 in. x 0 size coal as indicated by the washability analysis of Table 29. Thus to obtain by gravity separation the same yields reported in Tables 30 and 31 for the various treatments would result in higher ash and sulfur contents than shown for all but a few of these treatments. For ICO coal only Treatment 9 resulted in a higher ash content (6.45%) than gravity separation of 1 1/2 in. x 0 size coal would provide (6.12%) at the corresponding yield of 87.5%. For Jude coal none of the treatments resulted in a higher ash content than would be obtained by gravity separation for a corresponding yield. But Treatments 1, 2, and 9 did result in a higher sulfur content than would be obtained at corresponding yields by gravity separation of either ICO or Jude coal and for ICO coal Treatment 5 also resulted in a higher sulfur content.

A comparison of the results in Tables 30 and 31 for individual steps of Treatments 3 and 5 indicates that gravity separation at 1.613 of crushed (1/4 in. x 0) ICO coal and froth flotation of pulverized (-35 mesh) ICO coal were equally effective. Thus either method resulted in a 90% yield and ash and sulfur reductions of about 40% (pyritic sulfur reductions of about 50%). Subjecting ICO coal to chemical comminution before applying gravity separation or froth flotation as in Treatments 11 and 13, resulted in greater sulfur reduction (50% in total sulfur and 66% in pyritic sulfur) but did not affect the ash reduction or product yield. A further comparison of these results with those obtained with oil agglomeration of pulverized ICO coal in Treatment-1 or 9 indicates that oil agglomeration was less effective in reducing the ash and sulfur content than the other methods. On the other hand, with Jude coal the results obtained by oil agglomeration in Treatments 1 or 9 were similar to those obtained by froth flotation in corresponding Treatments 3 or 11 but not as good as those obtained by gravity separation in Treatments 5 and 13. On the basis of these results, it appears that when the separation methods are applied individually in the manner described to Iowa or similar coal, gravity separation is more effective than oil agglomeration for reducing the ash and sulfur content of the coal and at least as effective, if not more effective, than froth flotation.

A comparison of the results of the froth flotation step of Treatment 3 with those of the oil agglomeration step of Treatment 1 and of Treatment 7 with 5, 11 with 9, and 15 with 13 indicates that the yield of product was generally a little larger with froth flotation than with oil agglomeration for both ICO and Jude coal. Also froth flotation reducted the sulfur content more than oil agglomeration did. In addition froth flotation reduced the ash content of ICO coal more than oil agglomeration did but that was not so for Jude coal. In the case of Jude coal, oil agglomeration was more effective than froth flotation at reducing the ash content.

Better results were obtained with oil agglomeration when it was preceded by fine grinding. This can be seen by comparing the overall results of Treatment 2 with 1, 4 with 3, 6 with 5, and so on for either ICO or Jude coal. In most instances, fine grinding resulted in a slightly greater yield and larger reduction in ash and sulfur. Consequently a combination of fine grinding and oil agglomeration as in Treatments 2, 6, 10 and 14 produced results more nearly comparable to the froth flotation step of Treatments 3, 7, 11 and 15.

Chemical comminution seemed to improve the subsequent separation of coal and mineral matter by any of the various methods tested. This can be seen by comparing the overall results of Treatment 9 with 1, 10 with 2, 11 with 3 and so on for either ICO or Jude coal. In most instances, the treatments which included chemical comminution resulted in greater reduction in ash and sulfur than the corresponding treatments which did not. Also in the case of Jude coal the treatments which included chemical comminution provided a larger overall yield than the corresponding treatments which did not. But in the case of ICO coal, chemical comminution provided a lower overall yield.

The addition of pulverization and froth flotation steps to gravity separation at 1.613 produced the marginal improvement indicated by the results of the froth flotation step in either Treatment 7 or 15. Thus for Treatment 7 of ICO coal, the froth flotation step reduced the ash content of the product from the gravity separation step by 26% and the pyritic sulfur content by 44% and for Treatment 15 it reduced the ash content by 14% and pyritic sulfur content by 36%. For Jude coal the marginal reduction in ash content produced by froth flotation was 19% for Treatment 7 and 8% for Treatment 15 while the marginal reduction in pyritic sulfur content was about 25% for either treatment. Apparently the marginal improvement was less in Treatment 15 than in 7 because the gravity separation step was more effective in Treatment 15 than 7 due to the inclusion of chemical comminution in Treatment 15. The recovery of coal by froth flotation following gravity separation was uniformly high being 95% or more.

The addition of pulverization and oil agglomeration steps to gravity separation at 1.613 produced only a small marginal improvement as indicated by the results for the oil agglomeration step in either Treatments 5 or 13. Thus for ICO coal the ash content of the product from the gravity separation step was reduced about 16% and the pyritic sulfur content about 6% with little difference in the results between Treatment 13 which included chemical comminution and Treatment 5 which did not. For Jude coal the ash content of the product from the gravity separation step was reduced 28% by oil agglomeration in Treatment 5 and 18% in Treatment 13. This difference appears to reflect the larger reduction in ash content produced by gravity separation in Treatment 13 (69%) compared to Treatment 5 (52%) which seems attributable to chemical comminution. On the other hand, the gravity separation step reduced the pyritic sulfur content about the same amount (61 and 65%) in both Treatments 5 and 13 and the subsequent oil agglomeration step reduced the pyritic sulfur content 9% in both treatments.

The marginal improvement provided by oil agglomeration was much larger when this method of separation was preceded by fine grinding as in Treatments 6 and 14. For ICO coal the ash content of the product from the gravity separation step was reduced 37% in Treatment 6 and 50% in Treatment 14 by oil agglomeration. Also the pyritic sulfur content was reduced 26% in Treatment 6 and 57% in Treatment 14 by oil agglomeration. For Jude coal the ash content was reduced 38% and the pyritic sulfur content 27% in Treatment 6 and ash content 49% and the pyritic sulfur content 62% in Treatment 14 by oil agglomeration. Apparently fine grinding produced another interesting effect because in this series of treatments the marginal improvement attributable to oil agglomeration was greater in Treatment 14 which involved chemical comminution than in Treatment 6 which did not. This result was just the opposite of that noted in Treatments 5 and 13 which did not include fine grinding.

The marginal reduction in both ash and sulfur attributable to oil agglomeration was generally greater than that attributable to froth flotation when oil agglomeration was preceded by fine grinding. This can be seen by comparing the results of the oil agglomeration step in Treatment 6 with those of the froth flotation step in Treatment 7 and the results of the oil agglomeration step in Treatment 14 with those of the froth flotation step in Treatment 15. In every instance oil agglomeration provided a larger reduction in ash and sulfur for both ICO and Jude coal except in Treatment 6 of ICO coal where the reduction in sulfur content due to oil agglomeration was less than that due to froth flotation in Treatment 7.

Addition of an oil agglomeration step to a froth flotation step as in Treatments 3 and 11 generally produced a small marginal improvement. For ICO coal the oil agglomeration step reduced the ash content of the product from the froth flotation step about 21% and the pyritic sulfur content about 15% for each of these treatments. For Jude coal the marginal reduction in ash content due to oil agglomeration was 44% in Treatment 3 and 16% in Treatment 11 and the marginal reduction in pyritic sulfur content was 40% in Treatment 3 and 22% in Treatment 11. The larger marginal reduction in ash and pyritic sulfur noted for Treatment 3 of Jude coal was an exception.

When both fine grinding and oil agglomeration were added to froth flotation as in Treatments 4 and 12, the marginal improvement was generally large. For ICO coal the oil agglomeration step reduced the ash content of the product from the froth flotation step 29% in Treatment 4 and 43% in Treatment 12 and the pyritic sulfur content 18% in Treatment 4 and 62% in Treatment 12. For Jude coal the marginal reduction in either ash or pyritic sulfur content due to oil agglomeration was about 50% for either treatment.

Addition of oil agglomeration to a sequence of gravity separation and froth flotation steps as in Treatments 7 and 15 also produced a marginal reduction in ash and sulfur contents although the reduction was not large. For ICO coal the marginal reduction in ash content due to oil agglomeration was about 21% and the marginal reduction in pyritic sulfur content about 16% for either treatment. For Jude coal the corresponding reduction in ash content was about 28% and pyritic sulfur content about 16% for either treatment.

When a combination of fine grinding and oil agglomeration was added to a sequence of gravity separation and froth flotation steps as in Treatments 8 and 16, the marginal reduction in ash and sulfur was large. For ICO coal the marginal reduction in ash content due to oil agglomeration was 32% in Treatment 8 and 46% in Treatment 16 and the marginal reduction in pyritic sulfur content 30% in Treatment 8 and 42% in Treatment 16. For Jude coal the marginal reduction in ash content due to oil agglomeration was 51% in Treatment 8 and 45% in Treatment 16 and the marginal reduction in pyritic sulfur content 60% in Treatment 8 and 47% in Treatment 16.

Conclusions

The laboratory application of sixteen different treatments involving size reduction and physical separation to high sulfur coal containing substantial amounts of finely disseminated microcrystals of iron pyrites provided several interesting and important results. Comparison of these results with a standard washability analysis showed that most of the treatments produced a cleaner product for a given yield than could be obtained by gravity separation alone of 1 1/2 in. x 0 size coal. In this regard the treatments which failed to produce a product with a lower sulfur content were generally those which involved only size reduction and oil agglomeration.

A comparison of the results of individual steps of different experimental treatments showed that gravity separation at 1.613 of crushed (1/4 in x 0) coal was more effective than oil agglomeration of pulverized (-35 mesh) coal for reducing the ash and sulfur content and it was more effective than froth flotation applied to one of the pulverized coal samples (Jude) but not the other (ICO) where it was about equal. The results of individual froth flotation and oil agglomeration steps applied to pulverized coal showed that froth flotation produced a higher yield of product with a lower sulfur content than oil agglomeration but it did not always produce a lower ash content. Whereas with one of the coal samples (ICO) froth flotation produced the lower ash content, with the other (Jude) oil agglomeration did. Moreover, oil agglomeration proved more effective when it was preceded by fine grinding. Hence, a combination of fine grinding and oil agglomeration gave results which were more like those obtained with froth flotation. When chemical comminution was included with the other size reduction methods, the subsequent separation of coal and mineral matter by any of the separation methods was facilitated.

The use of two and even three different separation methods in series proved more effective than any single method by itself. When the float product recovered by gravity separation at 1.613 was pulverized and subjected to either froth flotation or oil agglomeration, the ash and sulfur content of the material was reduced noticeably by the second separation step and the recovery of product was generally high. Although froth flotation provided a greater marginal reduction in pyritic sulfur content than oil agglomeration, the latter generally resulted in a larger marginal reduction in ash content. Also if the float product was finely ground before applying oil agglomeration, the marginal reduction in both ash and sulfur content given by oil agglomeration was generally greater than that given by froth flotation of pulverized but not ground material.

When oil agglomeration was used to treat material which had been cleaned first by froth flotation or by a combination of gravity separation and froth flotation, a further reduction in the ash and sulfur content was produced by the oil agglomeration step. When the oil agglomeration step was applied without further size reduction, the decrease in ash and sulfur content which it provided was small but when it was preceded by fine grinding the reduction in ash and sulfur content was large. Consequently the treatments which included all three separation steps in series with size reduction between each separation step generally produced the cleanest coal.

These results indicate not only that froth flotation and oil agglomeration compliment gravity separation as a means for beneficiating coal but that oil agglomeration also compliments froth flotation expecially if the oil agglomeration step is preceded by fine grinding. Moreover oil agglomeration can produce spherical agglomerates which are dust-free and large enough for easy dewatering and handling.

Of course, these results should be considered prelimary in nature and not necessarily indicative of what might result from applying the same treatments to high sulfur coal from other regions. Obviously similar experiments should be carried out on many different samples of coal from a number of regions. Furthermore, the oil agglomeration and froth flotation methods themselves should be optimized because it was unlikely that they were applied in an optimum manner in this investigation. Finally an experimental investigation such as this needs to be supported by a careful economic evaluation to see if the improvement resulting from additional size reduction and separation steps can be justified economically.

VII. LITERATURE CITED

1. Leonard, J. W., and Mitchell, D. R., (editors), Coal Preparation, Am. Inst. of Mining, Metallurgical, and Petroleum Engineers, New York, 1968.

2. Leonard, J. W., and Cockrell, C. F., Basic Methods of Removing Sulfur from Coal, Mining Congress Journal 56 (no. 12), 65 (1970).

3. 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.

4. Gaudin, A. M., Flotation, 2nd ed. McGraw-Hill, New York, 1957.

5. Sirianni, A. F., Capes, C. E., and Puddington, I. E., Recent Experience with the Spherical Agglomeration Process, Can. J. Chem. Eng. 47, 166 (1969).

6. Capes, C. E., McIlhinney, A. E., Sirianni, A. F., and Puddington, I. E., Bacterial Oxidation in Upgrading Pyritic Coals, Canadian Mining and Metallurgical (CIM) Bulletin 66, 88 (1973).

7. Capes, C. E., Smith, A. E., and Puddington, I. E., Economic Assessment of the Application of Oil Agglomeration to Coal Preparation, CIM Bulletin <u>67</u>, 115 (1974).

8. Aldrich, R. G., Keller, D. V., and Sawyer, R. G., Chemical Comminution and Mining of Coal, U.S. Patent 3,815,826 (June 11, 1974).

9. Howard, P., Hanchett, A., and Aldrich, R. G., Chemical Comminution for Cleaning Bituminous Coal, Symposium II Clean Fuels from Coal, Institute of Gas Technology, Chicago, June 23-27, 1975.

10. 1974 Annual Book of ASTM Standards, Part 26, Gaseous Fuels; Coal and Coke; Atmospheric Analysis, American Society for Testing Materials, Philadelphia, 1974.

11. Malik, A. M., Air and Water Backwashing of Granular Filters, M.S. thesis, Iowa State University, Ames, Iowa, 1972.

12. Greer, R. T., Nature and Distribution of Pyrite in Iowa Coal, Joint Meeting of the Electron Microscopy Society of American and Microbeam Analysis Society, Miami, Florida, August 9-13, 1976.

13. Zimmerman, R. E., Froth Flotation in Modern Coal Preparation Plants, Mining Congress Journal <u>50</u> (no. 5), 26 (1964).

14. Yancey, H. F., and Taylor, J. A., Froth Flotation of Coal; Sulphur and Ash Reduction, Report of Investigations 3263, U.S. Bureau of Mines, 1935.

15. Baker, A. F., and Miller, K J., Hydrolyzed Metal Ions as Pyrite Depressants in Coal Flotation: A Laboratory Study, Report of Investigations 7518, U.S. Bureau of Mines, 1971.

16. Miller, K. J., Flotation of Pyrite from Coal: Pilot Plant Study, Report of Investigations 7822, U.S. Bureau of Mines, 1973.

17. Methods of Analyzing and Testing Coal and Coke, Bulletin No. 638, U.S. Bureau of Mines, 1967.