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Coal Desulfurization and Deashing by Oil Agglomeration

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ABSTRACT

Coal organic matter was separated from its associated mineral matter by reducing the material to a fine-size, suspending the particles in water, selectively agglomerating with oil the particles which were largely organic, and screening the suspension to recover the agglomerates. Since particles of iron pyrites tended to be agglomerated with the coal, various means of preventing the agglomeration of pyrite were investigated. In some cases pyrite agglomeration was prevented by suspending the particles in an alkaline solution. In other cases it was prevented by pretreating the particles with a warm alkaline suspension through which air was bubbled to oxidize the surface of the pyrite. However, when this method of pretreatment was applied to several Pennsylvania coals, a considerable part of the pyritic sulfur was extracted through dissolution. An unexpected discovery revealed by scanning electron microscopy was the unusual stability of the coal microagglomerates which remained after the oil was extracted.

INTRODUCTION

Although the oil agglomeration method of separating fine-size coal and mineral matter has been studied for many years and has even been demonstrated in a number of pilot plants and prototype industrial plants in various countries, it is far from being a fully developed or widely used commercial process (1). The method suffers an economic penalty from the relatively high cost of oil. Also the method does not discriminate well between coal and iron pyrite, the principal sulfur-bearing mineral in coal. On the other hand, the method can provide a high recovery of fine-size coal with good rejection of ash-forming mineral matter and can be used to clean a wide variety of coals, including some oxidized and hydrophilic coals which do not respond well to other methods such as froth flotation. In addition, the product can be more easily dewatered than the unagglomerated coal fines and, after drying, can be a free-flowing, nondusting material. The method seems particularly well-suited for cleaning coal which will be used in coal-oil mixtures since the cost of the oil can be fully recovered.

The oil agglomeration method of separating the various components of coal takes advantage of the difference in surface properties of these components (2). Generally the inorganic minerals except pyrite tend to be quite hydrophilic or water-avid, whereas the organic macerals are either hydrophobic or at least less hydrophilic than the inorganic materials. When a small amount of fuel oil is added to a strongly agitated suspension of fine-size coal particles in water, the particles which are largely organic become oil-coated and stick together forming relatively large flocs or agglomerates, whereas the inorganic particles remain unaffected. The mixture can be separated on a screen which passes the water and unagglomerated coal.

A clean pyrite surface tends to be hydrophobic (3), and early oil agglomeration experiments showed that pyrite particles were readily wetted by fuel oil and agglomerated (4). To overcome this tendency of pyrite, Capes _et al_. (5) treated coal with iron-oxidizing bacteria to make the surface of pyrite hydrophilic and thereby improve the separation of coal and pyrite by oil agglomeration. Positive results were achieved when the coal was treated for 1 to 3 days.

An alternative, rapid chemical method of oxidizing the surface of pyrite to render it hydrophilic has been under investigation at Iowa State University for several years. In this method fine-size coal suspended in a warm alkaline solution is treated with air. The method arose from work on a related process which completely converts pyrite into iron oxide and soluble sulfates by oxidation in alkaline solutions under more rigorous conditions (6). But credit must also be given to Glembotskii *et al*. (3) who noted that wet oxidation of pyrite leads to the formation of a highly hydrated film of ferric hydroxide which greatly alters the surface properties of the material.

To evaluate the proposed chemical method of altering the surface of pyrite, numerous experiments have been conducted in which fine-size coal or pyrite alone was pretreated by this method and then subjected to oil agglomeration. The study was extended subsequently to the possible effects of the alkaline solution itself and of pH on the recovery of clean coal and rejection of mineral matter by oil agglomeration. Some of the initial work with Iowa coals will be reviewed first and then the recent work with Pennsylvania coals will be described in greater detail.

INITIAL WORK WITH IOWA COAL AND PYRITE

An extensive study of the effects of oxidative pretreatment on the oil agglomeration of high volatile C bituminous coal and of iron pyrites alone, both from the Iowa State University (ISU) demonstration mine in Mahaska County, Iowa, was carried out by Patterson (7,8). Since the coal was not protected from atmospheric oxidation during storage, it was somewhat oxidized by the time it was utilized as indicated by its relatively high content of sulfatic sulfur (1-2%). The latter usually results from the oxidation of pyrites.

In one series of experiments, -230 mesh size particles of pyrite, containing 86 wt.% FeS_2 and significant amounts of other iron, sulfur and calcium minerals, were agglomerated with No. 200 LLS fuel oil (Amoco). These particles were prepared by pulverizing pyrite nodules which were extracted from the Iowa coal. For some experiments the particles were oil agglomerated directly while for other experiments the solids were pretreated first in a warm aerated solution containing dissolved air and 2.0 wt.% sodium carbonate. After pretreatment the suspension was cooled and transferred to a kitchen blender where the suspension was agitated vigorously while oil was added to agglomerate the particles. In some experiments the oil was added directly, whereas in others it was added as an oil-and-water emulsion. For all these experiments 5 ml. of oil was used to treat 50 g. of particles suspended in 250 ml. of water. Any agglomerates produced in the blender were recovered by pouring the suspension through a No. 140 U.S. Standard sieve.

The percentage of the pyrite charge which was recovered as agglomerates is reported in Table 1 for different experimental conditions. When the particles were agglomerated in plain water without pretreatment, 91.7% of the material was recovered with emulsified oil and 63.8% with oil which had not been emulsified. Pretreating the solids in an alkaline solution, either with air at

TABLE 1

Agglomeration of -230 Mesh Pyrite Particles with No. 200 LLS Fuel Oil.[a]

Test	Pretreat. Conditions			Agglom. Conditions		Pyrite[b]
No.	Gas	Temp., °C	Time, min.	Na_2CO_3, %	Oil prep.	Rec., %
1	- -	- -	- -	0	none	63.8
2	- -	- -	- -	0	emulsified	91.7
3	air	23	15	2	emulsified	87.9
4	N_2	80	15	2	emulsified	84.5
5	air	50	5	2	emulsified	9.5
6	air	80	15	2	emulsified	8.8

[a] Average of duplicate runs.

[b] Weight recovered on oil- and moisture-free basis.

room temperature or with nitrogen at 80°C, was not effective in preventing agglomeration. However, when the particles were pretreated with air in a heated solution, the recovery dropped dramatically. Other experiments of a similar nature made with No. 5 light LLS fuel oil produced comparable results.

In a second series of experiments, coal from the ISU demonstration mine was ball-milled and then agglomerated with a mixture of No. 200 LLS (25 vol.%) and No. 6 LLS (75 vol.%) fuel oils (Amoco). For each agglomeration experiment, 50 g. of ground coal was suspended in 500 ml. of water. The suspension was agitated vigorously in a kitchen blender while 5 ml. of the oil mixture was added, and then for an additional 5 min. The agglomerates which formed were recovered on a No. 140 U.S. Standard sieve and returned to the blender for washing with water. The suspension was then poured onto the same screen and the agglomerates recovered. With this technique the inorganic sulfur content of the coal was reduced 40% and the ash content 35%. When the coal was pretreated first in an alkaline solution with air at various temperatures and then oil agglomerated as before at room temperature but in an alkaline solution, the results shown in Table 2 were obtained. The results achieved by pretreating the coal at room temperature (23°C) were virtually the same as those achieved without any pretreatment. On the other hand, when the coal was pretreated at 50°C or higher temperature, both the ash and inorganic sulfur contents were reduced considerably more than without the pretreatment. Although good results were achieved with a pretreatment time of only 5 min., slightly better results were achieved with a pretreatment time of 15 min., but extending the pretreatment time to 30 min. was counterproductive.

To see if pyritic sulfur was removed by leaching during the pretreatment step, further experiments were conducted in which the ball-milled Iowa coal was pretreated in a 2 wt.% sodium carbonate solution at 80°C with air and then recovered by filtration. The filter cake was washed with 10% hydrochloric acid, dried and

TABLE 2

Pretreatment and Agglomeration of -400 Mesh Iowa (ISU) Coal in 2 wt.% Na_2CO_3 Solution with Fuel Oil Mixture.[a]

Test No.	Pretreatment Temp., °C	Pretreatment Time, min.	Yield,[b] %	Composition,%[c] Ash	Composition,%[c] Inorg. S	Reduction,% Ash	Reduction,% Inorg. S
Feed	- -	- -	- -	15.66	4.96	- -	- -
1	23	15	95.1	9.50	3.00	39.3	39.5
2	50	5	91.3	6.45	1.18	58.8	76.2
3	50	15	88.6	6.20	0.90	60.4	81.9
4	80	5	92.7	6.64	1.01	57.6	79.6
5	80	15	92.9	5.76	0.62	63.2	87.5
6	80	30	90.4	6.18	1.02	60.5	79.4

[a] Average of duplicate runs.

[b] Coal yield on ash-, oil-, and moisture-free basis.

[c] Composition of oil- and moisture-free product or feed.

analyzed. While this treatment extracted most of the sulfatic sulfur, which was usually high initially (2.04%), it removed very little of the pyritic sulfur. Thus an insignificant amount of pyritic sulfur was removed when the coal was pretreated for 15 min. and only 24% when it was pretreated for 60 min. Therefore it appeared that the pretreatment step mainly affected the surface of the pyrite particles.

The preceding study was followed by another series of experiments conducted by a different worker (9). The coal was similar being from the Childers site adjacent to the ISU demonstration mine. The coal was ball-milled and oil agglomerated as before except that No. 200 LLS fuel oil (Amoco) alone was used instead of the mixture of oils. When the ground coal was oil agglomerated in plain water, the inorganic sulfur and ash contents were reduced 25.7% and 33.5%

TABLE 3

Agglomeration of -400 Mesh Iowa (Childers) Coal with No. 200 LLS Fuel Oil.[a]

Test No.	Na_2CO_3, wt.%	Pretreatment Temp., °C	Pretreatment Time, Min.	Yield,[b] %	Composition,%[c] Ash	Composition,%[c] Inorg. S	Reduction,% Ash	Reduction,% Inorg. S
Feed	- -	- -	- -	- -	12.26	3.93	- -	- -
1	0	- -	- -	84.3	8.15	2.92	33.5	25.7
2	2	- -	- -	82.4	6.15	1.10	49.8	72.0
Feed	- -	- -	- -	- -	13.16	4.23	- -	- -
3	0	80	15	81.8	8.74	3.75	33.6	11.3
4	2	80	15	80.7	7.11	1.37	46.0	67.6

[a] Average of duplicate runs.

[b] Coal yield on ash-, oil-, and moisture-free basis.

[c] Composition of oil- and moisture-free product or feed.

respectively (Table 3). Better results were achieved when the coal was oil agglomerated in an alkaline solution which lowered the inorganic sulfur and ash contents by 72% and 49.8% respectively. But no further improvement was achieved when the coal was pretreated with air in a hot alkaline solution and then oil agglomerated.

Additional experiments were conducted in which the ground coal was oil agglomerated in various solutions having different pH levels (Figure 1). The rejection of inorganic sulfur was a maximum over a pH range from 7 to 11. Over this pH range both pyritic sulfur and sulfatic sulfur seemed to be rejected whereas at low pH only the sulfate form appeared to be removed. The removal of other ash-forming minerals seemed only slightly affected by pH except at high pH where less mineral matter was rejected. The recovery of coal organic matter by oil agglomeration was also not affected greatly by pH except at high pH where the recovery dropped. The use of calcium hydroxide solutions reduced coal recovery and also reduced sulfur rejection.

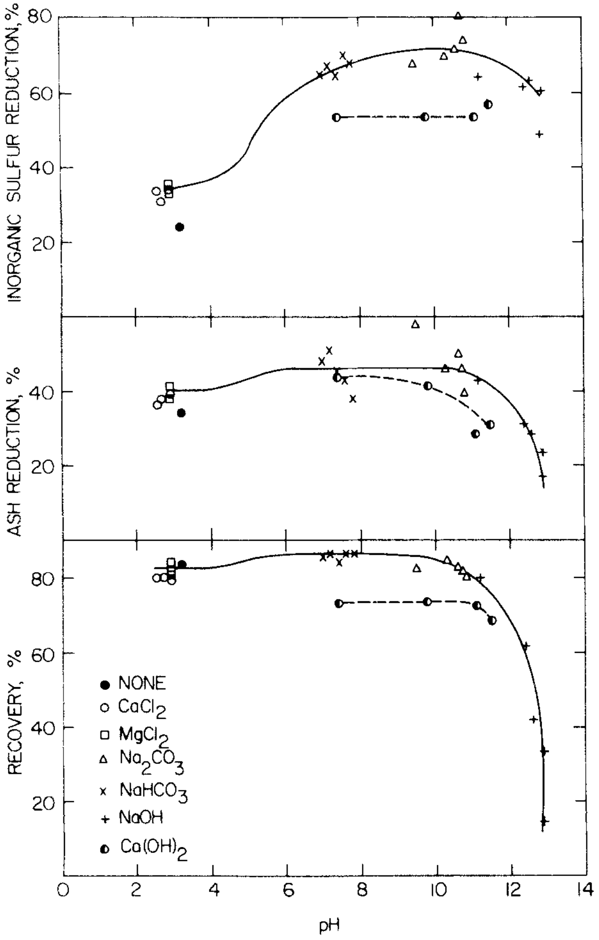

FIGURE 1. Results of agglomerating -400 mesh Iowa (Childers) coal with No. 200 LLS fuel oil in solutions having different pH levels.

These results contrasted with those of Patterson (7,8) which indicated that the oxidative pretreatment step was necessary for good pyrite rejection.

RECENT WORK WITH PENNSYLVANIA COALS

Upper Freeport coal and Pittsburgh No. 8 coal from Pennsylvania were utilized for recent work on oil agglomeration because these coals differ significantly from the Iowa coals. Both coals are higher in rank than the Iowa coals. The Upper Freeport coal is extremely hydrophobic and the Pittsburgh No. 8 coal moderately hydrophobic, whereas the Iowa coals are hydrophilic. Fresh run-of-mine samples of the Pennsylvania coals were obtained and stored under nitrogen to prevent oxidation.

For the oil agglomeration experiments with the Pennsylvania coals, more comprehensive measurements and observations were made to evaluate better the oxidative pretreatment step and medium in which the oil agglomeration step was conducted. Therefore, it was possible to make more detailed material balances for sulfur and ash.

Materials and Methods

The source, composition and heating value of the Pennsylvania coals are indicated in Table 4. Detailed examination of the coals by scanning electron microscopy, energy-dispersive x-ray analysis, reflected light microscopy, and x-ray diffraction revealed much information about the chemical and physical nature of the mineral matter embedded in the coal matrix. The major inorganic phases present in these coals are pyrite, quartz, and clays (kaolinite and mixed layer illites). Some calcite is also present. The clays and much of the pyrite are present as very small particles which are finely disseminated throughout the coal matrix. Typical finely dispersed clusters of pyrite crystals in Pittsburgh No. 8 coal can be seen in Figure 2. Other photomicrographs showed that pyrite microcrystallites were not completely liberated even when the

TABLE 4

Composition and Heating Value of Pennsylvania Coals as Received.

	Upper Freeport	Pittsburgh No. 8
Source	E-Seam Helen Mine, Central PA	Ireland Mine, Moundsville, PA
Moisture, %	0.77	1.65
Ash, %	23.93	37.53
Pyrite S, %	2.57	2.53
Sulfate S, %	0.05	0.10
Organic S, %	0.63	1.32
Total S, %	3.25	3.95
Heating Value, BTU/lb.	11,830	8,810

Pennsylvania coals were ground to pass a 325 mesh screen. The fine degree of dispersion of clays within Upper Freeport coal can be seen in Figure 3.

To prepare coal for oil agglomeration, it was ground for 12 hr. in a jar mill containing 800 g. of crushed coal, 1000 ml. of water and 2000 g. of flint pebbles. Over 99% of the material would then pass a 400 mesh screen. The coal was dried in a vacuum oven and stored under nitrogen in sealed jars to prevent oxidation.

For each oil agglomeration experiment 50 g. of ground coal was suspended in 500 ml. of plain water or a 2 wt. % solution of sodium carbonate. The suspension was agitated for 1 min. with a high-speed kitchen blender whereupon the pH was measured. For the plain water suspensions, the pH ranged from 7.0 to 7.7, whereas for the alkaline suspensions it ranged from 10 to 11. After this measurement, agitation was resumed and 5 ml. of No. 200 LLS fuel oil (Amoco) was added. Agitation was continued for 5 min. to agglomerate the coal after which the agglomerates were collected on a No. 140 U.S. Standard sieve. The agglomerates were allowed to drain and were returned to the blender with 400 ml. of water or

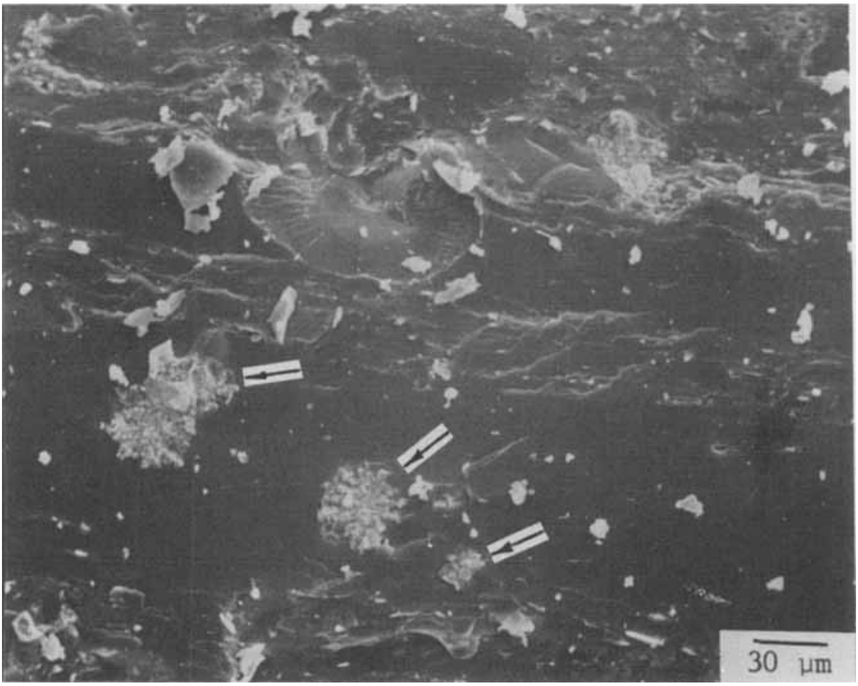

FIGURE 2. SEM image of fracture surface of Pittsburgh No. 8 coal. Pyrite clusters indicated by arrows.

sodium carbonate solution depending on which was used initially. The suspension was then agitated for another 5 min. The agglomerates were recovered by screening and then dried, extracted with hexane to remove the oil, and analyzed. The rejected material which passed through the sieve was filtered to recover the solids which were washed, dried and analyzed. The filtrate was analyzed for its total sulfur content.

For some of the experiments the ground coal was first pretreated by suspending it in a 2 wt. % sodium carbonate solution heated to 80°C in a glass reaction flask. Air was bubbled through the suspension to oxidize the surface of the pyrite particles. After the treatment, the suspension was cooled and transferred to the kitchen blender for oil agglomeration.

FIGURE 3. SEM image of fracture surface of Upper Freeport coal. White band is clay.

Experimental Results and Discussion

The results of oil agglomerating the two Pennsylvania coals in either (1) plain water, (2) a 2% sodium carbonate solution, (3) a 2% sodium carbonate solution after pretreatment for 15 min., or (4) a 2% sodium carbonate solution after pretreatment for 1 hr. are presented in Tables 5 to 7. By applying the 15 min. oxidative pretreatment step alone, coal recovery was almost quantitative, and while the pyritic sulfur content was reduced by 25 to 30%, the ash content of the coal was not affected significantly.

For the oil agglomeration experiments, the yield of coal on an ash-, oil-, and moisture-free basis ranged from 69 to 73% for the Upper Freeport coal and from 76 to 85% for the Pittsburgh No.

TABLE 5

Coal Yield, Sulfur Content, and Percent Reduction in Sulfur Content of Oil Agglomerated Penn. Coals.[a]

Process	Na_2CO_3 wt.%	Yield[b] %	H.V. Btu/lb	S Content, lb/10^6 Btu				S Redn., %	
				Pyr.	Sulf.	Org.	Tot.	Pyr.	Tot.
Upper Freeport Coal									
None[c]	- -	- -	11,180	2.52	0.07	0.57	3.16	- -	- -
Oil Agglomeration	0	68.8	12,490	1.80	0.11	0.50	2.41	38.6	23.7
Oil Agglomeration	2	73.4	12,430	1.01	0.23	0.71	1.95	59.5	38.3
Pretreat Only	2	99.7	11,150	1.90	0.21	0.42	2.53	24.6	19.9
Pretrt. & Agglom.	2	68.8	12,810	0.71	0.41	0.73	1.58	71.8	50.0
Pretrt. & Agglom.[d]	2	72.0	12,880	0.57	0.12	0.68	1.37	77.4	56.6
Pittsburgh No. 8 Coal									
None[c]	- -	- -	8,640	3.19	0.16	1.82	5.17	- -	- -
Oil Agglomeration	0	75.7	12,450	1.43	0.09	1.85	3.37	55.2	34.8
Oil Agglomeration	2	85.0	12,090	1.11	0.34	2.00	3.45	65.2	33.3
Pretrt. Only	2	100.0	8,670	2.27	0.20	1.73	4.20	28.8	18.8
Pretrt. & Agglom.	2	84.3	12,430	0.70	0.23	2.02	2.95	78.1	42.9
Pretrt. & Agglom.[d]	2	80.0	12,300	0.32	0.17	2.10	2.59	90.0	49.9

[a] Average of duplicate runs except where indicated otherwise.

[b] Coal yield on ash-, oil-, and moisture-free basis.

[c] Heating value and composition of dry, untreated coal.

[d] Pretreated for 1 hr., only one run.

TABLE 6

Distribution of Sulfur Among Product, Refuse and Suspending Liquid for Oil Agglomerated Penn. Coals.[a]

Process	Na_2CO_3 wt.%	Pyritic Sulfur, %				Total Sulfur			
		Prod.	Refuse	Liquid[b]	Lost[c]	Prod.	Refuse	Liquid[b]	Lost[c]
Upper Freeport Coal									
Oil Agglomeration	0	49.1	47.6	2.6	0.7	52.5	46.0	2.1	-0.6
Oil Agglomeration	2	29.5	59.3	4.2	7.0	45.4	52.1	3.3	-0.8
Pretreat Only	2	75.1	- -	21.4	3.5	79.7	- -	17.1	3.2
Pretrt. & Agglom.	2	19.4	49.2	22.2	9.2	34.3	46.3	17.7	1.7
Pretrt. & Agglom.[d]	2	16.4	40.9	39.8	2.9	31.3	34.1	31.8	2.8
Pittsburgh No. 8 Coal									
Oil Agglomeration	0	33.7	61.3	4.0	1.0	49.0	48.1	2.5	0.4
Oil Agglomeration	2	29.4	52.3	7.8	10.5	56.4	38.8	4.8	0
Pretreat Only	2	72.1	- -	23.2	4.7	82.2	- -	14.3	3.5
Pretrt. & Agglom.	2	18.5	47.8	22.8	10.9	47.8	36.7	14.1	1.4
Pretrt. & Agglom.[d]	2	8.2	30.0	45.8	16.0	40.3	26.8	28.3	4.6

[a] Average of duplicate runs except where indicated otherwise.

[b] Solubilized and transferred to the liquid.

[c] Lost and unaccounted for.

[d] Pretreated for 1 hr., only one run.

TABLE 7

Ash Content of Oil Agglomerated Penn. Coals and Distribution of Ash Between Product and Refuse.[a]

Process	Na_2CO_3 wt.%	Product Ash, %		Ash Distribution, %			Corrected Dist.[b] %	
		Content	Redn.	Product	Refuse	Sum	Product	Refuse
Upper Freeport Coal								
None	- -	24.8[c]	- -	- -	- -	- -	- -	- -
Oil Agglomeration	0	15.8	36.2	39.4	58.1	97.5	39.4	58.1
Oil Agglomeration	2	16.2	34.7	43.3	66.8	110.1	33.2	66.8
Pretreat Only	2	24.8	0	100.3	- -	100.3	100.0	- -
Pretrt. & Agglom.	2	13.7	44.9	33.4	73.4	106.8	26.6	73.4
Pretrt. & Agglom.[d]	2	13.2	46.7	33.5	71.7	105.2	28.3	71.7
Pittsburgh No. 8 Coal								
None	- -	37.4[c]	- -	- -	- -	- -	- -	- -
Oil Agglomeration	0	9.2	75.4	12.9	84.5	97.4	12.9	84.5
Oil Agglomeration	2	11.9	68.3	19.2	88.3	107.5	11.7	88.3
Pretreat Only	2	36.8	1.7	99.6	- -	99.6	99.6	- -
Pretrt. & Agglom.	2	9.4	74.9	14.7	89.3	104.0	10.7	89.3
Pretrt. & Agglom.[d]	2	10.1	72.9	15.3	89.8	105.1	10.2	89.8

[a] Average of duplicate runs except where indicated otherwise.

[b] Corrected ash distribution on an alkali-free basis.

[c] Ash content of dry, untreated coal.

[d] Pretreated for 1 hr., only one run.

8 coal (Table 5). The yield appeared slightly greater for oil agglomeration in an alkaline solution than for oil agglomeration in plain water and slightly lower for the pretreated coal than for the untreated coal in the alkaline solution. The pyritic sulfur content of both coals was reduced more by oil agglomeration in an alkaline solution than in plain water, and even further by pretreatment and agglomeration in such a solution. Maximum sulfur removal was achieved with a pretreatment time of 60 min. followed by oil agglomeration. This combination reduced the pyritic sulfur content of Upper Freeport coal 77% and Pittsburgh No. 8 coal 90%.

A detailed sulfur balance was made for each experiment based on the sulfur content of the product, refuse and liquid in which the coal was suspended (Table 6). Since the amount of sulfur found in the liquid in which the coal was agglomerated corresponded rather closely to the amount of pyritic sulfur which disappeared from the solids, it seemed that some pyrite was oxidized to soluble sulfur compounds. The pyritic sulfur which was not accounted for ranged from 1 to 16% but was less than 10% for the majority of experiments. Considering all forms of sulfur together, less than 5% was unaccounted for in every case. For both coals the 15 min. pretreatment step dissolved from 21 to 23% of the pyritic sulfur and the 1 hr. pretreatment step from 40 to 46% of the pyritic sulfur. Although a substantial amount of pyritic sulfur was dissolved, a large amount was also discarded in the solid refuse during the oil agglomeration step following pretreatment. However, it is not possible to ascertain whether the pretreatment step actually improved pyrite rejection by the oil agglomeration step or only served to dissolve some of the pyritic sulfur.

The percent reduction in ash content achieved by oil agglomeration and the distribution of ash between product and refuse are shown in Table 7. For oil agglomeration in an alkaline solution, the total amount of ash in the product and refuse was 4 to 10% larger than that in the feed because some alkali was retained by the agglomerated product. Since most of the alkali could have been removed by washing the product, the ash distribution was corrected to reflect this possibility. Because the refuse was washed before analysis, it was assumed that little or no alkali was retained by the refuse. From 58 to 73% of the ash was rejected in the refuse produced by oil agglomerating Upper Freeport coal and from 85 to 90% by oil agglomerating Pittsburgh No. 8 coal. The amount of ash rejected was slightly larger when oil agglomeration was conducted in an alkaline solution than when it was conducted in plain water. Also slightly more ash was rejected when oil agglomeration was preceded by the pretreatment step. On the other hand, the pretreatment step alone followed by washing had virtually no effect on the ash content of the coal.

Analysis of the products of these experiments by x-ray diffraction showed that the inorganic mineral content of the Pennsylvania coals was reduced substantially by oil agglomeration. This method of analysis also verified the removal of pyrite by both the pretreatment step and the oil agglomeration step, with the greatest removal being accomplished by application of both steps in tandem.

Examination of the products by scanning electron microscopy revealed an unexpected result. The coal particles which had been recovered by oil agglomeration and then extracted with hexane to remove the oil were still agglomerated, though the agglomerates were very small (Figure 4). The particles were strongly bonded even without oil. The bonding may have been due to hydrophobic association or van der Waals attraction (10). Similar microagglomerates have been produced with other hydrophobic mineral particles suspended in water through application of large shearing forces (11).

The particles which had been pretreated but not oil agglomerated were not aggregated when examined by scanning electron microscopy (Figure 4). These particles, which must have been similar in size to the feed, had an average diameter of about 6 μm. The microagglomerates of Upper Freeport coal were about twice as large and of Pittsburgh No. 8 coal about three times as large (Table 8).

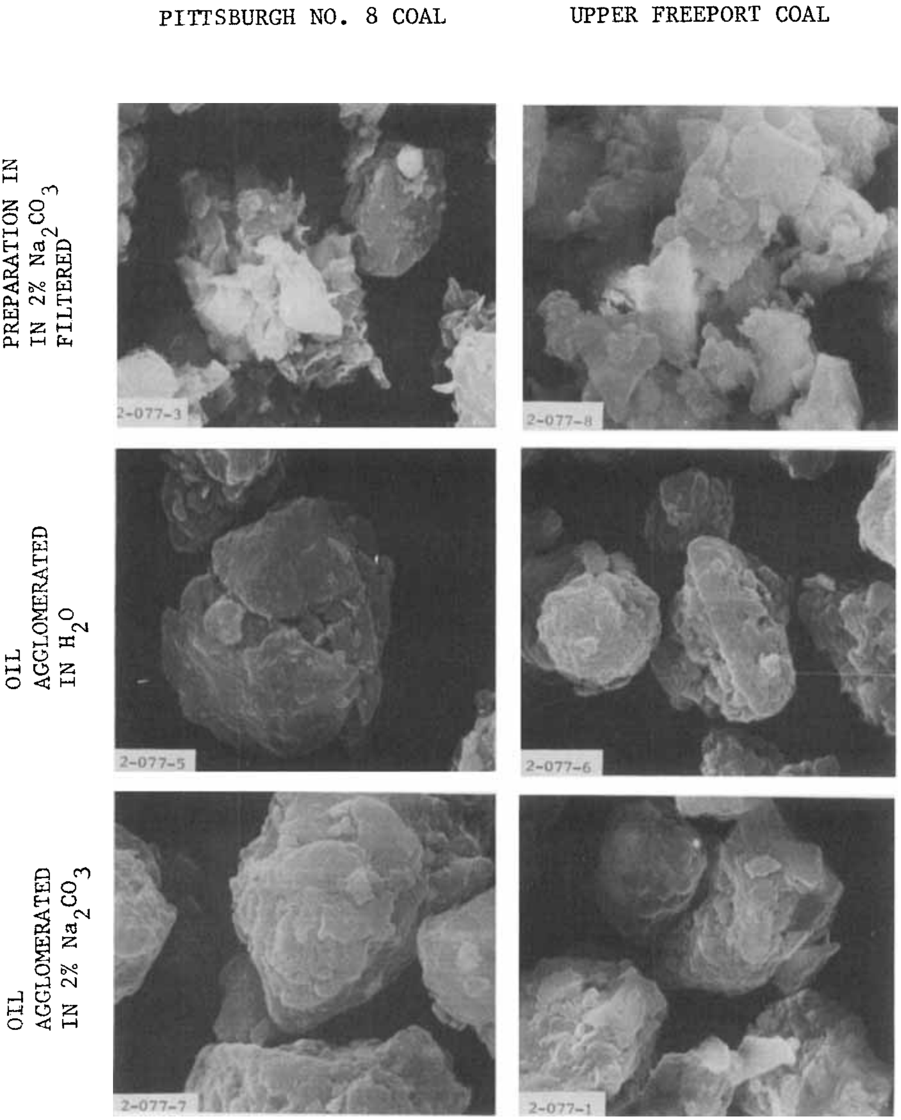

FIGURE 4. SEM images of individual coal particles (top row) and coal microagglomerates (bottom two rows) produced by oil agglomeration and extraction with hexane. Pittsburgh No. 8 coal on the left, Upper Freeport coal on the right.

TABLE 8

Size of Microagglomerates Remaining after Hexane Extraction of Oil Agglomerated Pennsylvania Coals.

Process	Na_2CO_3 wt.%	Mean Diameter, μm	
		Upper Freeport	Pitts. No. 8
Oil Agglomeration	0	10.6	16.2
Oil Agglomeration	2	12.5	19.3
Pretreat Only	2	5.9	5.7
Pretrt. & Agglom.	2	12.8	15.8

CONCLUSIONS

Recent results achieved with Pennsylvania coals together with the earlier results obtained with Iowa coal and with pyrite isolated from Iowa coal present a complicated picture which is difficult to interpret. On the one hand, the work of Patterson (7, 8) indicated that pyrite particles were not recovered by oil agglomeration if they were first subjected to an oxidative pretreatment step which seemed to remove very little pyritic sulfur by itself. Application of this step to fine-size coal greatly enhanced sulfur rejection during subsequent agglomeration with a mixture of fuel oils. Patterson's work also indicated that without the pretreatment step similar results were obtained whether Iowa coal was oil agglomerated in plain water or an alkaline solution. On the other hand, subsequent work with Iowa coal using No. 200 LLS fuel oil showed that while an alkaline solution was effective in rejecting pyrite during oil agglomeration, oxidative pretreatment made little difference. Moreover, the recent work with Pennsylvania coals indicates that the oxidative pretreatment step by itself extracted a significant amount of pyritic sulfur from these coals by leaching. The latest work also indicates that more pyrite was rejected when the Pennsylvania coals were agglomerated with No. 200 LLS fuel oil in an alkaline solution than in plain water. But this work does not show whether the pretreatment step increases pyrite rejection by altering the surface of the particles.

Generally, slightly more ash-forming mineral matter was rejected when the coals were oil agglomerated in an alkaline solution than in plain water. While Patterson's (7, 8) results with Iowa coal seem to differ in this regard, they were obtained with a different type of oil (actually a mixture of No. 200 LLS and No. 6 LLS fuel oils) which may account for the difference. Slight variations in experimental technique may also have been a factor.

Several differences in the properties of the coals from Pennsylvania and Iowa may account for the differences in results noted above. The Iowa coals were hydrophilic and somewhat oxidized. They contained an appreciable amount of sulfatic sulfur and formed an acidic suspension when mixed with water. In contrast, the Pennsylvania coals were hydrophobic, contained very little sulfatic sulfur, and formed a slightly basic suspension when mixed with water. At least some of the pyrite in the Iowa coals was partly oxidized before the material was utilized whereas very little, if any, of the pyrite in the Pennsylvania coals was oxidized. Interaction of pyrite oxidation products with the alkaline solution may have been responsible for some of the effects noted above.

The formation of coal microagglomerates which were not destroyed by extracting the fuel oil with hexane was unexpected. The microagglomerates seemed to be held together by hydrophobic bonding or van der Waals attraction.

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REFERENCES

1. Oil Agglomeration Offers Technical and Economic Advantages, Mining Engineering 35, 1230 (1980).

2. T. D. Wheelock and R. Markuszewski, Chemistry and Physics of Coal Utilization--1980, (B. R. Cooper and L. Petrakis, eds.), AIP Conf. Proceed. No. 70, Am. Inst. Physics, New York, 1981, p. 357.

3. V. A. Glembotskii, V. I. Klassen, and I. N. Plaksin, Flotation, Primary Sources, New York, 1972.

4. G. St. J. Perrott and S. P. Kinney, Chem. and Met. Engr. 25 (5), 182 (1921).

5. C. E. Capes, A. E. McIlhinney, A. F. Sirianni and I. E. Puddington, Canadian Mining and Metallurgical Bull. 66 (739), 88 (1973).

6. K.-C. Chuang, M.-C. Chen, R. T. Greer, R. Markuszewski, Y. Sun and T. D. Wheelock, Chem. Eng. Commun. 7 (1-3), 79 (1980).

7. E. C. Patterson, The Effect of Chemical Pretreatment on the Desulfurization of Coal by Selective Oil Agglomeration, IS-ICP-64, Energy and Mineral Resources Research Institute, Iowa State University, Ames, Iowa, 1978.

8. E. C. Patterson, H. V. Le, T. K. Ho, and T. D. Wheelock, in Volume V Coal Processing Technology, Am. Inst. Chem. Engrs., New York, 1979, p. 171.

9. T. D. Wheelock and R. Markuszewski, in Fossil Energy Annual Report, IS-4714, Oct. 1, 1978-Sep. 30, 1979, Ames Laboratory, Iowa State University, Ames, Iowa, 1980, p. A-1.

10. A. W. Adamson, Physical Chemistry of Surfaces, 3rd edition, John Wiley & Sons, New York, 1976, p. 321.

11. L. J. Warren, Chemtech, 11, 180 (1981).