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Fuel Contaminants: Volume 4. Application of Oil Agglomeration to Coal Wastes

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Fuel Contaminants: Volume 4. Application of Oil Agglomeration to Coal Wastes

by

E.J. Mezey, Seongwoo Min, and Dale Folsom

Battelle-Columbus Laboratories
505 King Avenue
Columbus, Ohio 43201

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EPA Project Officer: Lewis D. Tamny

Industrial Environmental Research Laboratory
Office of Energy, Minerals, and Industry
Research Triangle Park, NC 27711

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ABSTRACTS

In the first phase of this program, the utility and limitations of the oil agglomeration technique for removing sulfur and trace element contaminants in coal were identified from the literature. Although the technique was found to be effective for the separation of much of the ash forming mineral matter from finely ground fresh coal, it was found to be almost ineffective for the separation of the liberated pyrite. No report could be found of the use of this technique for the recovery of coal values from coal cleaning plant wastes or for the control of effluents from such cleaning plants.

This program was undertaken to investigate the feasibility of the oil agglomeration technique for the recovery of coal values from preparation plant wastes and thereby possibly reducing the environmental consequences of coal cleaning plant effluents. The program also found several approaches for the enhancement of pyrite removal during oil agglomeration of freshly ground coal.

The following environmentally significant accomplishments and extension of the state of the art resulted from this study:

- Coal recoveries of 90 percent or greater were realized from sediments from fresh, aged and weathered cleaning plant (i.e., slurry pond) wastes.
- The total sulfur and ash concentrations of the coal recovered from wastes were lower than the coal being shipped from the cleaning plant.
- The rejected mineral matter was essentially free of coal, exhibits improved settling characteristics and appears to be suitable for land disposal and may have potential as a raw material.

- Recovered coal costs based on hypothetical flow diagram based on results from the study were estimated at $14 per ton.
- Various oils were found to be effective including coal derived liquids.
- For the first time using the oil agglomeration technique, pyrite removal from freshly ground coal was enhanced by mild chemical treatment and the use of a dispersing agent to levels attainable by float sink analysis.

Benefits that might be realized by the adaptation of the oil agglomeration technique by the coal industry include the following:

- Reduces the hazards and environmental impact of existing coal slurry ponds.
- Recovers valuable resources from wastes.
- Allows environmental control of effluents from coal preparation plants faced with increased throughput to meet energy needs and environmental constraints.
- Applicable to coal preparation plants used to prepare feed for coal conversion plants.
- Dewaters wet coal fines.
- Permits direct application of technology developed for clay stabilization to residues.
- In principle, may reduce risks of catastrophic dam failure when used as a replacement for raw wastes.

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SECTION 1

INTRODUCTION

In the first phase of the program on fuel contaminants a review was made of the utility and limitations of several technologies reported in the literature for the removal, before combustion, of contaminants in coal that produce pollutants when coal is utilized as a fuel.[1] The oil agglomeration technique was one of those that appeared to have the potential for the removal of trace elements and under special conditions the physical removal of pyritic sulfur liberated from coal during grinding. The results of the review also suggested that the technique might be used to clean up coal slurry pond sediments accumulated during coal cleaning plant operations by removing the coal values they contain. The two areas are related in that pyrite removal from old coal slurry pond sediments is enhanced by the autotrophic bacterial actions on the surface of pyrite that are supported in these sediments.[1] Understanding the cause of these effects could be useful for developing a technique for removing pyrites from freshly ground fine coal slurries by oil agglomeration. Conversely, any technique developed to enhance pyrite removal from fresh coal could in effect be used to speed up natures process and the recovery of low pyrite coal from coal waste streams, both fresh and aged.

This report presents the experimental results which extend the state of the art of oil agglomeration to the recovery of coal from coal cleaning plant wastes and the removal of pyrite from freshly ground coal to the extent that they can be removed during float-sink analysis. In this program, both an Illinois No. 6 coal and an Ohio Pittsburgh Seam Number 8 coal were investigated.

OBJECTIVE

The objectives of this study were to determine the feasibility of coal recovery from coal cleaning plant wastes by immiscible fluid agglomeration technique and to evaluate the effects of physical and chemical treatments on enhancement of pyrite removal during agglomeration of these wastes and fresh coal.

BACKGROUND

Water immiscible liquids, usually hydrocarbons, have been used to separate coal from its impurities.[1] In principle it is an extension of principles of froth flotation where the hydrocarbons wet the hydrophobic surface of coal and the mineral impurities which are mostly hydrophilic remain in aqueous suspension. Separation of the two phases takes place after agglomeration or coalescence occurs and produces agglomerates of clean coal containing the oil and an aqueous suspension of the mineral matter nearly free of combustible material. Effective separation can be made with coal with a size of minus 28 mesh (0.590 mm) and often with sizes too small for any other recovery scheme. Hydrocarbon fluids such as kerosens and fuel oils have been found very effective for the separation of the mineral matter from finely divided coal suspended in an aqueous slurry (i.e., reduce ash). The selective agglomeration process is attractive because the coal does not have to be dried after wet face mining, wet size reduction and conventional coal preparation operations. In addition the agglomerated coal can be readily dewatered by mechanical action providing energy trade-offs between oil use and drying.

The major limitation of the process as it was used in the past is that removal of pyrite is poor due to the similarity of its surfacial properties to those of coal and the fact that in some coals pyritic sulfur is uniformly disseminated in the coal and is present in the size range of 0.5 to 20 micrometers. Extensive size reduction, use of known pyrite depressants, bacterial action etc. have found only limited success in reducing the pyritic sulfur content. Nonetheless the process has the potential of removing the trace elements commonly associated with the mineral

matter in coal in a form that they exist in nature and rendering these species amenable for safe disposal.

The amount of mineral matter removed can be increased with size reduction. In general, pyrites are also released from the coal during size reduction but they are not readily removed by the agglomeration process.[3] To reject them from the oil phase into the aqueous phase, their surface properties or composition must be altered to make them hydrophilic. The common pyrite depressant reagents developed for metallurgical froth flotation separations were found to be only partially successful for enhancing pyrite removal during agglomeration.[1,2] Recent studies on Iowa coals by Min[3] suggested approaches that might be used to alter the pyrite in other coals. He found that chemically pretreating pulverized coal in a manner designed to oxidize the surface of the pyrite (to render it hydrophilic) was more effective than the application of pyrite depressants. The pretreatment involved sparging a slightly alkaline aqueous slurry of a coal with air at 80 C. (The best pretreatment was the use of 0.5 g each of Na_2CO_3 and $Ca(OH)_2$ with 100 g of coal in 500 ml H_2O for 30 minutes which resulted in about a 42 percent reduction in total sulfur.) Min also reported on other physical treatment sequences for the desulfurization of coal.[3] The most effective treatment sequence involved chemical comminution, float and sink separations at a specific gravity of 1.6, pulverizing and grinding the float fraction and recovery of the fine-size coal by agglomeration. Coal recovery was 82-84 weight percent with a reduction in pyritic sulfur of 85 to 86 percent. Optimum conditions identified for Iowa coals in the study might not be applicable to coals from other regions such as Appalachian coals.

Other studies on the theoretical aspects of coal cleaning by oil agglomeration and laboratory, bench and pilot scale studies on ash removal and dewatering have been recently reported.[4-6] Capes, et al.[4] pointed out that the utility of oil agglomeration of coal fines will increase as more mechanized mining of progressively poorer grades of coal develop. Increased percentages of fines will end up in the waste streams from the coal preparation plants (black water). Usually these wastes are impounded for long term settling before the water is discharged.

Several research organizations have become involved in developing

oil agglomeration methods. The U.S. Bureau of Mines, Pittsburgh Energy Research Center (PERC) concluded that excellent recoveries of low ash coal were possible both in a laboratory unit and a 500 pound-per-hour pilot plant but that sulfur reduction was negligible.[7] PERC is presently not active in the further demonstration of the use of agglomeration although a joint effort with Jones and Laughlin Steel Co. had been attempted in 1977.[8] Bergbau-Forshung, GMBH, of West Germany, has developed the OLIFLOC process for recovery of ultra-fine coal (minus 230 mesh) in a 3 ton-per-hour pilot plant.[9] Two, 30 ton-per-hour plants were installed during 1977. The Central Fuel Research Institute of India has also investigated oil agglomeration of a 25 percent ash coal in order to optimize processing conditions.[5] This fine coal, which was not amenable to economical cyclone washing or froth flotation, could be upgraded by oil agglomeration. A 2 ton-per-hour agglomeration unit has been installed for upgrading a coal slurry from the Lodna washery of the Bharat Coking Coal, Ltd. in India.[10] In Australia, the Broken Hill Proprietary Company, Ltd. have published the results of their studies on the process parameters controlling selective agglomeration of raw coal slurry in their pilot facility.[6] They found that agglomerates produced in a continuous process are considerably larger than those obtained from batch experiments.

Of these reports only a small amount of work was reported on improving pyrite removal during agglomeration and only one suggested the potential of the process to recover coal from fresh, aged or weathered sediments from coal slurry ponds.

COAL SLURRY PONDS

On February 26, 1972 a coal waste embankment failed near Saunders, West Virginia. The resulting flooding of the Buffalo Creek Valley took the lives of 125 people and destroyed over 500 homes in addition to extensive damage to other properties in the valley. Immediately after this disaster a special U.S. Department of Interior Task force began investigations into the coal waste hazards problem. Its objectives were to determine modes of failure of such embankments and to develop means for safe disposal of coal waste materials. The coal waste materials originated from preparation plants

at the mine sites. In early findings published by the Bureau of Mines, Busch reported that the preparation plants that fed the refuse piles studied ranged from being relatively simple to extremely complex.[11]

Since the early 1960's, the coal industry has been under constant pressure by environmental legislation to clean up liquid discharges into streams. Consequently, rather large sludge (slurry) ponds have been developed which consist of fine coal, fine soil and water. These ponds are usually formed behind large piles of coarse coal waste which together make up the often criticized coal waste impoundments. The Bureau of Mines has reported on the physical and chemical properties of fine coal wastes in two of these ponds.[12] The ponds selected for their study were inactive and partially drained. Core samples were taken from regions in the slurry ponds where saturated fine sludge accumulated at the points farthest from the discharge lines. The analysis of the sediments from the different areas in West Virginia Are given in Table 1.

The amount of coal in the slurry pond sediments varies depending on the effectivenss of the coal cleaning operation. The Bureau of Mines study concluded that the extremely fine size (50 percent by weight less than 2-10 micrometers) plus rather well graded grain sizes make permeability low and the sediments extremely difficult to drain. They suggested that the ash and Btu per pound of the dried sediment make it equivalent to the sub-bituminous coal range (9,000 Btu/lb) and the hazards of waste embankments may be resolved by utilization of the waste as a fuel. Direct recovery of the sludge without beneficiation is currently being practiced. Certainly recovery of the material becomes more attractive as coal costs rise. The high ash content is not attractive to most users, however, upgrading the waste could open new markets. If the beneficiation removes pyritic sulfur as well, the product would be even more attractive. The immiscible fluid agglomeration technique has the potential of removing most of the ash values. If pretreatment is used to enhance pyrite separation during agglomeration, a fuel with reduced sulfur (and ash) might be realized.

Other physical separation techniques (e.g., Humphreys Spiral) have been investigated as a means reducing the ash content at the Mine Resources Institute and Experiment Station at the University of Alabama.[13] In waste streams from the simpler coal preparation plants employing

TABLE 1. ANALYSIS OF SLUDGES FROM DRILL HOLES TAKEN BY BUREAU OF MINES[12] AT INACTIVE COAL SLURRY PONDS IN WEST VIRGINIA

Analysis, percent	BDH-1	WDH-1
Moisture	35.0	55.4
Moisture Free:		
Ash	25.5	32.3
Moisture and Ash Free:		
Hydrogen	4.9	4.8
Carbon	83.6	82.8
Nitrogen	1.3	1.2
Oxygen	9.2	10.5
Sulfur	1.0	0.7
Heat content, moisture free Btu/lb	10,690	9,600

screening, jigging and tabling (no flotation) the undersize fraction, often finer than 0.25 inch, is rejected resulting in 10 to 15 percent loss of the coal processed. The author of the report estimated that an aggregate of 1 million tons of coal is wasted annually in fines impounded near coal washing plants located at strip mines in Alabama. Typically the ash values for the samples of the waste which ranged between 9 and 50 percent were reduced to 5 to 12 percent ash product with about a 90 percent coal recovery. In this process, however, only the plus 200 mesh material was treated and the minus 200 mesh was discarded.

In an assessment of the feasibility of returning underground coal mine wastes to mined-out areas, a National Science Foundation report estimates "the total number and volume of sizable active and abandoned waste piles and impoundments in the eastern coal fields alone is at 3000-5000 cummulatively containing 3 billion tons of refuse" (not all of which are coal slurry pond sediments).[14] In effect the impoundments containing coal fines are a ready reserve of mined fuel wherein the mining costs have already been factored in, which can be utilized in times of shortages. In addition the reduction of the size and number of the slurry ponds would reduce the hazards and the potential for environment encroachments bv these slurry ponds. As energy goals of the Nation are met by increased mining, and greater volumes of coal passing through preparation plants to meet established emission standards, methodology to recover the coal values preparation plant tailings and slimes would appear to be an essential part of the overall program to increase the availability of the Nation's coal.

Most approaches to clean fuels from coal appear to be directed toward conversion processes (gasification and liquefaction), which requires the preparation of a finely ground coal feed stock (-200 mesh). It appears that oil agglomeration processes could contribute significantly to the removal of contaminants before the conversion process is undertaken. In addition to this, the ability of agglomeration technique to dewater finely ground wet coal suggests further incorporation of this process in any environmentally sound preparation plant supplying these conversion plants.

SECTION 2

CONCLUSIONS

This study has demonstrated that coal recoveries of 90 percent or greater are attainable from fine coal slurry wastes using the oil agglomeration technique. These high levels of recovery are attainable from fresh black water sediments generated during coal cleaning, aged sediments accumulated in slurry ponds and excavated, weathered, and partially dried slurry pond sediments. The quality of the coal was good and had lower ash and sulfur content than the coal shipped from the mine.

The residue from the agglomeration process contained between 2 to 5 percent of the oil used in agglomeration and very little coal, i.e., 90 percent ash or greater. The residue suspension obtained after agglomeration settled more rapidly than the original slurry. The residue material appears to be well suited for land disposal.

The experimental results suggest the following environmental and conservation advantages of the agglomeration process based on these current results and on understanding of the relationships between various contaminants, mineral matter and organic matter.

- Recovered coal contains lower ash and reduced sulfur (and trace heavy metals) than the parent coal.
- Recovered coal is easily dewatered and the product remains dust free.
- Volumes of waste from coal cleaning facilities can be significantly reduced resulting in less impoundment and thus less land utilization.
- Waste characteristics are improved since they are faster settling, more compatible with soil since they are not altered, and less prone to support bacterial activity that cause acid drainage.

- Rather than disposal of the concentrated mineral matter it may be amenable as a raw material for ceramics, cement and other construction purposes or for the recovery of useful mineral values such as alumina.

Coal derived liquids such as the distillate recovered from SRC dissolver product is able to yield 90 percent or greater coal recoveries. Its behavior is not any different than that of the petroleum derived liquids such as No. 2 fuel oil, No. 6 fuel oil-kerosene mixture and kerosene alone.

With regard to the enhancement of pyrite removal during agglomeration, use of sodium metaphosphate will remove 42 percent of the pyritic sulfur from freshly ground minus 48 mesh coal. This is the same as that obtained by float-sink analysis suggesting removal of all the liberated pyrite in the ground coal. Equally good results were obtained when a coal slurry was treated with oxygen in the presence of sodium carbonate at 25 C. These same treatments could be applied to black water and slurry pond sediments to enhance pyrite removal during coal recovery.

An estimation of the product cost recovered from agglomeration step as an add-on to an existing coal cleaning plant or as a portable facility is about $14/ton.

SECTION 3

RECOMMENDATIONS

Based on results of this study, it is recommended that the oil agglomeration technique be further developed as a method to control effluents from coal cleaning plants in order to reduce the hazards and environmental impact of increased quantities of wastes that would result as the Nation shifts its energy dependence to coal and strives for the production of clean fuels in an environmentally sound manner. Further work is needed to demonstrate the applicability of the process to various origins of coal wastes and the effluents from coal cleaning plants with varying degrees of complexity. The development of a bench scale process suitable for the treatment of both sediments and black water effluent should also be undertaken.

SECTION 4

EXPERIMENTAL PROCEDURES

SAMPLE ACQUISITION, HANDLING AND CHARACTERIZATION

For Studies on Enhancement of Pyrite Removal

Two samples of a drift mined Illinois No. 6 coal (Seam No. 6, Mine No. 10) and on Ohio deep mined Pittsburgh Seam No. 8 coal were used in the study. The Pittsburgh Seam No. 8 coal is characterized later.

The samples of Illinois coal had been jig washed at the mine and part was ground to pass through a 14 mesh (1.19 mm) screen (Tyler). The other part was used to prepare a minus 48 mesh (0.297 mm) coal. The sieve analysis of both sized coals are given in Table 2. The analysis for the two coal sizes and the analysis of a second sample of Illinois No. 6 coal also used in this study are given in Table 3. Included in the table are the analyses of the products from the float-sink analysis at 1.9 specific gravity. The values are given on a moisture free (MF) and moisture and ash free (MAF) basis.

For Studies on Coal Recovery from Slurry Pond Sediments

The coal and coal slurry pond sediments were obtained from the North American Coal Company preparation plants in Belmont County, Ohio. The coal being processed at the site is deep mined from Pittsburgh Seam No. 8 using room and pillar techniques. The plant is rated at 600 TPH and cleans run-of-the-mine coal (minus 8 inch) using primarily jig washing, classifying cyclones, spiral classifiers and filters. A block diagram of the operation is given in Figure 1. Waste process water is settled in a large, static thickener and the underflow is discharged into a slurry pond. A new pond was started in 1976 and the old one was used from 1972 to 1976.

TABLE 2. SIEVE ANALYSIS OF ILLINOIS NO. 6 COAL SAMPLES AFTER GRINDING

Sieve Mesh Range (Tyler)	Percent	Cumulative Percent
Minus 14 Mesh Coal (~67 percent minus 28 mesh [0.595mm])		
+14	0.05	0.05
-14 +28	33.55	33.60
-28 +48	26.43	60.03
-48 +65	8.94	68.97
-65 +80	3.39	72.36
-80 +100	3.49	75.85
-100	24.15	100.00
Minus 48 Mesh Coal (~60 percent minus 100 mesh [0.149 mm])		
+48	0.24	0.24
-48 +65	8.71	8.95
-65 +80	8.48	17.43
-80 +100	9.26	26.69
-100 +150	14.29	40.97
-150 +200	11.38	52.35
-200	47.65	100.00

TABLE 3. ANALYSIS OF ILLINOIS NO. 6 COAL SAMPLES (Weight Percent)

Coal Sample	MAF[a]			Sulfur, MAF			MF[b]	Reduction
	C	H	N	Total	Pyritic	Sulfate	Ash	S_{pyr}, %
Minus 14 Mesh (1.19 mm)	75.7	5.7	1.4	5.93	3.12	0.25	14	
Fraction at 1.9 Sp. gr.								
Float (94.1 percent)				3.89	1.28	--	9.77	59.0
Sink (5.9 percent)				37.5	25.9	--	51.3	
Minus 48 Mesh (0.297 mm)	78.8	5.7	1.5	5.75	2.89	0.27	12.9	
Fraction at 1.9 Sp. gr.								
Float (93.3 percent)				3.87	1.09	--	9.32	62.3
Sink (6.7 percent)				40.10	34.5	--	49.7	
Minus 48 Mesh (0.297 mm)[c]	--	-	-	4.07	1.36	--	11.3	

(a) MAF = Moisture and ash free basis.

(b) MF = Moisture free basis.

(c) Freshly ground sample.

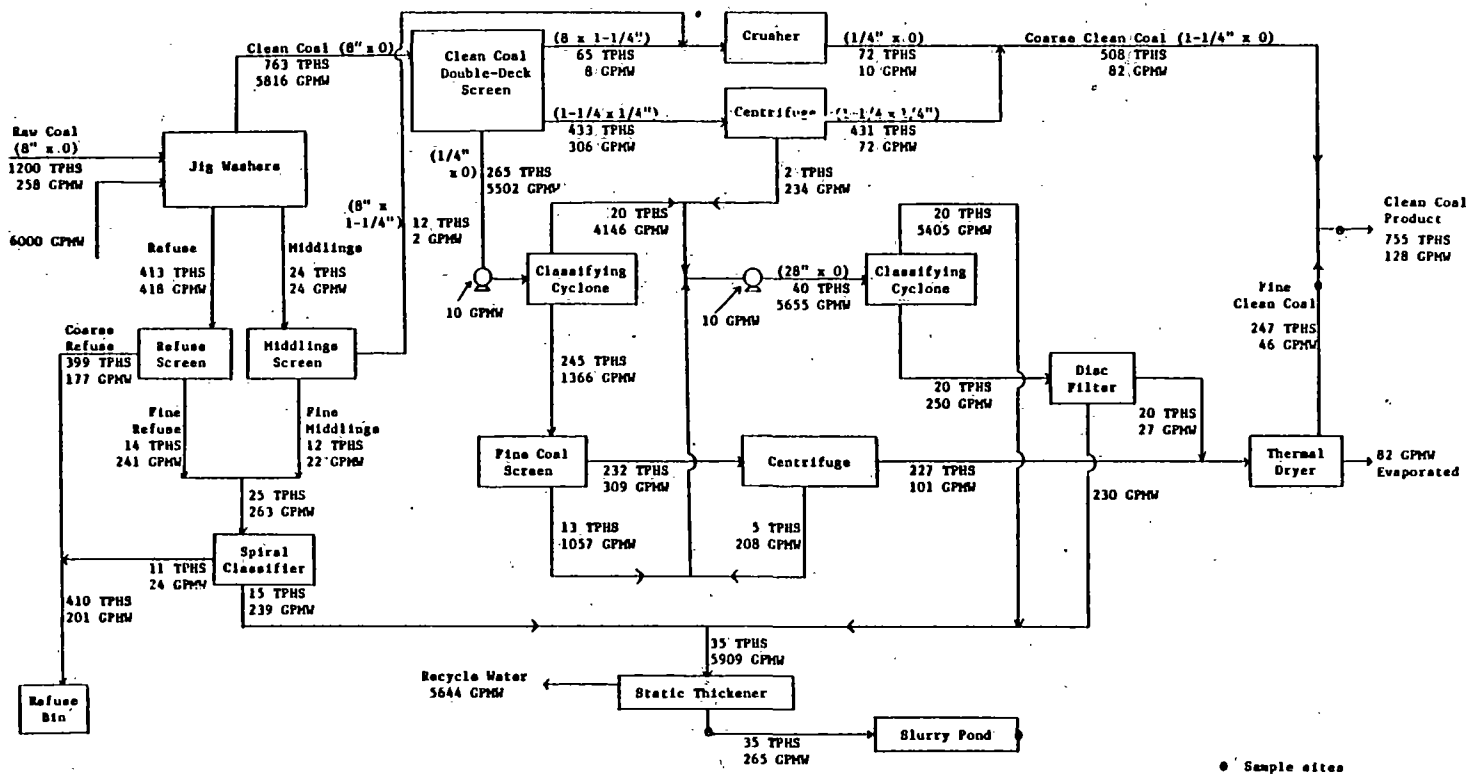

FIGURE 1. FLOW DIAGRAM OF THE NACCO MINING COMPANY COAL PREPARATION PLANT, ALLEDOMA, OHIO

Coal Slurry Sediments--

Five-gallon samples representative of the thickener underflow were taken in the plant. A sample of sediments was taken from the inactive pond in a region exposed to air near where water was draining into rivulets passing over the settled coal. The sample was taken to the depth of about 18 inches (0.5 meter) of an estimated depth of 3 feet (1 meter) using a conically shaped sludge dipper. Water from the inactive pond near the sampling point was added to the solids for bacterial culture development. A third sample of coal slurry pond sediment was obtained from a 5 year old pile from the excavation of an inactive slurry pond at the site of NACCO No. 5 mine. Samples of the cleaned coal being shipped from the No. 6 mine and the fine coal from the thermal drier before it is mixed with coarser clean coal were obtained and analyzed.

The wet slurry samples were stored in polyethylene lined 5-gallon buckets under a nitrogen atmosphere. After a 7-day period of settling, the solids and liquids levels were measured to estimate the sediment and supernatant volumes. After the supernatant water was removed the sediment was weighed to determine its specific gravity. The solids content of the slurries are given in Table 4 along with the moisture-free ash content. The results of analyses for total sulfur, pyritic sulfur and sulfate sulfur are also given on a moisture and ash free (MAF) basis. The supernatant water from the inactive pond had a pH of 7.3 while the supernatant water from the fresh sediment (black water) had a pH of 7.0.

A wet screen analysis of each of the sediments was made. The aged sediment was 77 percent minus 100 Tyler mesh (0.149 mm) while the fresh sediment was 89 percent minus 100 mesh. (NACCO attributed the difference in the size to the use of new hydroclones which have enabled the plant to improve separation of the coal fines from fresh sediments of the thickener underflow.) The consist of both sediments make it attractive for coal recovery by agglomeration techniques since the size appears to be too small for effective froth flotation recovery. Of equal significance is that the coal content of the sediments were 50 percent or greater based on the ash values.

The partially dried aged sediments from No. 5 mine were characterized in a similar manner in Table 5. It is richer in coal and total and pyritic sulfur than the sediments from No. 6 mine. The slurry of the

TABLE 4. CHARACTERISTICS OF AGED AND FRESH SEDIMENTS FROM JIG WASHING OPERATION OF OHIO PITTSBURGH SEAM NO. 8 (DEEP MINED)

Aged Sediment (Slurry Pond)

Composite:

Sediment = 91.0 volume percent
Clear Water = 9.0 volume percent (after seven days)
pH = 7.3

Sediment:

Density ∿ 1.3 g/cc
Solids = 64.1 percent
Ash = 45.2 percent (MF)

	S_{TOT}	S_{PYR}	S_{SO_4}
Percent	2.90	1.52	0.04
Percent (MAF)	5.35	2.81	0.07

Concist:

	Direct Data, %		Cumulative Data, %	
Tyler Mesh	Weight	MF Ash	Weight	MF Ash
+ 28	7.6	15.59	7.6	15.59
28 x 35	3.2	14.33	10.8	15.22
35 x 48	4.1	17.67	14.9	16.01
48 x 65	4.2	18.73	19.1	16.61
65 x 100	3.7	19.82	22.8	17.13
100 x 200	10.2	15.81	33.0	16.72
200 x 325	7.6	15.48	40.6	16.49
- 325	59.4	60.60	100.0	42.70

(77 percent minus 100 mesh)

Fresh Sediment (Black Water)

Composite:

Sediment = 64.6 volume percent
Clear Water = 35.4 volume percent
pH = 7.0

Sediment:

Density ∿ 1.2 g/cc
Solids = 41.7 percent
Ash = 50.8 percent (MF)

	S_{TOT}	S_{PYR}	S_{SO_4}
Percent	2.30	1.27	0.09
Percent (MAF)	4.73	2.61	0.18

Concist:

	Direct Data, %		Cumulative Data, %	
Tyler Mesh	Weight	MF Ash	Weight	MF Ash
+ 28	3.3	8.55	3.3	8.55
28 x 35	1.5	17.74	4.8	11.42
35 x 48	1.7	20.36	6.5	13.75
48 x 65	1.8	18.28	8.3	14.74
65 x 100	2.4	18.97	10.7	15.68
100 x 200	5.3	13.87	16.0	15.08
200 x 325	5.0	10.72	21.0	14.04
- 325	79.0	53.30	100.0	49.78

(89 percent minus 100 mesh)

TABLE 5. CHARACTERISTICS OF PARTIALLY DRIED OLD COAL SEDIMENTS FROM SOUTHWESTERN OHIO

	Percent	Percent
Moisture	17.4	
Ash	26.6	32.2 (MF)
S_{Tot}	3.76	6.71 (MAF)
S_{Pyr}	1.61	2.88 (MAF)
S_{SO_4}	1.18	2.11 (MAF)

Sieve Analysis

	Direct Data, %		Cumulative Data, %	
Tyler Mesh	Weight	MF Ash	Weight	MF Ash
+28	3.32	6.71	3.32	6.71
28x35	4.46	8.79	7.78	7.90
35x48	7.14	10.95	14.92	9.36
48x65	6.49	13.51	21.41	10.62
65x100	9.02	15.51	30.43	12.07
100x200	14.01	16.01	44.44	13.31
-200	55.56	44.09	100.00	30.41

(69 percent minus 100 mesh)

aged sediment had a pH of 2.9. The size of the material as determined by wet sieve analysis was 69 percent minus 100 mesh. The ash contained in each fraction was also determined. It was the waste from a preparation plant that used only a double cell jig operating at a water slurry specific-gravity of 1.6. The slurry was accumulated in the pond for a period of 6 to 9 months and allowed to settle for 3 months. The sediment was then excavated and stacked in piles for drainage. This sample was taken from a pile that was about 5 years old and exposed to air for the period. The concists of the sediments reflect the simpler coal cleaning operation and reduced fine coal recovery.

Coal Samples--

Samples of coal were obtained that are representative of the coarse coal shipped from the coal cleaning plant and also a sample of the thermally dried fine coal that is added back to the coarse coal before shipment (see Figure 1). A 1/64th cut of the coals were submitted for analysis and the results are given in Table 6. The 1/2 cut was ground in a hammermill to a size to pass through Tyler 48 mesh (minus 0.215 mm). The ground sample was stored under nitrogen until it was used.

TABLE 6. ANALYSIS OF COAL SAMPLES FROM COAL CLEANING PLANT PITTSBURGH SEAM NO. 8 OHIO, BELMONT COUNTY[a]

	Analysis, percent			
	Moisture	Ash	S Total	S Pyritic
As Shipped	3.91	8.88	4.26	1.78
	--	9.24 (MF)	4.88 (MAF)	2.04 (MAF)
Dried Fines	1.67	4.68	4.41	1.57
		9.84 (MF)	4.97 (MAF)	1.77 (MAF)

(a) North American Coal Co. Mine No. 6, Belmont County.

GENERAL OIL AGGLOMERATION PROCEDURE

The laboratory method for performing oil agglomeration experiments have been described by Capes et al.[4] and Min.[3] The procedures used in this study are very similar to theirs and are common to all experiments performed in this study. A single speed laboratory Waring blender operating at 15,000 RPM with water was used. The procedure consists of the following steps.

1. A weighed sample of the dry fine coal (usually 25 g) is mixed with enough water to give the selected slurry concentration and then agitated in the blender for a short interval to give a slurry. When a wet sediment was used, the water present in the sediment was considered when preparing the slurry concentration desired.
2. An amount of oil was weighed out in a syringe to give the oil concentration desired based on the dry solids present and then added to the water coal slurry.
3. The mixture was blended for a period of time, usually 2.5 minutes.
4. After blending the mixture was allowed to stand for about 15 to 30 seconds and then the mixture was poured onto a 48 mesh screen to separate the agglomerated coal from the suspended mineral matter. The separation was aided by washing the agglomerated coal with a stream of water from a wash bottle. The agglomerated coal was transferred to a weighed Buchner funnel to remove excess water. The mineral suspension passing through the screen was collected in weighed dishes.
5. The agglomerated coal was dried at 60 C in a vacuum oven and the water was evaporated from the mineral slurry in air in an oven set at 110 C. The recovered coal and mineral residue were weighed and analyzed, usually for ash and the sulfur types.

Modifications of this procedure were incorporated into the study and are identified in the discussions of the experiments where they were made. For example, when the effect of pH was examined, the pH of the coal

slurry was changed from the slurry pH by adding hydrochloric acid or sodium hydroxide. The pH measured before the addition of the oil was taken as the pH of the agglomeration. Chemical pretreatment of coal especially as it relates to pyrite removal was done with enough coal to prepare three batches for agglomeration treatment.

The experimental results that follow are divided into two major areas. The first deals with the recovery of coal from sediments and the second describes the results from experiments in which enhancement of pyrite removal from fresh coal of the same source were investigated. Techniques developed in this area could be applied to coal cleaning slurry pond sediments.

SECTION 5

RESULTS

COAL RECOVERY FROM SEDIMENTS

This part of the study was undertaken to determine the applicability of the oil agglomeration technique for the recovery of coal from fine coal cleaning or coal preparation plant wastes. Wastes of three ages were used in the study. The oldest was the sediment excavated from a slurry pond about 5 years ago and had been partially dried (drained) in a heap as part of an ongoing slurry pond reuse program. The youngest sediment investigated was the coal slurry waste stream from a thickener underflow which was being discharged to a new pond. Finally, an intermediate age sediment was typical of an inactive pond that had been in use for four years but which still had not been excavated.

The objective of the study was to determine the optimum slurry concentration, oil concentration and the oils suitable for the maximum recovery of low-ash coal from the waste streams described above. In the case of aged partially dried sediments, the study was to determine the most suitable treatment needed to recover the maximum coal values. In addition, the effect of processing variables such as the agitation speed of the blender, use of flocculating or dispersing agents and added washing stages on coal recovery were investigated. Finally the study was to characterize the residue after agglomeration including some estimation of the oil carried with the residue.

Aged Slurry Pond Sediments

The wet aged slurry pond sediments were adjusted to slurry concentrations of 5, 10 and 15 percent. The oils used in the agglomerating study were used at levels equal to 1.5, 3, 5, 10 and 20 weight percent of the dried sediment. The oils used at these levels were kerosene and

tetralin and the results of the experiments undertaken to establish mixing parameters are given in Tables 7 and 8. The mixing procedure described earlier was used. As shown in Figure 2a and 3a, a 10 percent slurry concentration when agglomerated with kerosene or tetralin at 3, 5 and 10 percent oil concentration appears to give the best recovery of agglomerated material. The recovery with kerosene was about 58 percent while with tetralin was about 53 percent. These values are not exceeded during agglomeration using an oil concentration of 20 percent. The ash in the coals recovered from 5 and 10 percent slurries (see Figure 2b) using 5, 10 and 20 percent oil concentrations were the lowest. The ash content of the coal ranged between 8.2 and 9.2 percent. The use of 1.5, 3 and 5 percent kerosene concentrations gave coals with erratic ash content. The ash contents of the coals recovered using tetralin were less erratic at the lower oil concentrations (see Figure 3b). With 1.5 percent tetralin, the ash in the coal recovered from the 5 and 10 percent slurry was between 6.5 and 7.2 percent. With 5 and 10 percent tetralin concentrations the ash content of the coal recovered was between 9.5 and 10.5 percent which is about 1 percent higher than that obtained with kerosene.

The percentage of the coal recovered from the aged sediments was estimated by the following:

$$\text{Percentage Coal Recovery} = \frac{(100 - \%\ \text{Ash})_{\text{product}} \times (\%\ \text{of Feed})_{\text{product}}}{(100 - \%\ \text{Ash})_{\text{feed}}}$$

Using this estimation, kerosene at 10 and 20 percent oil concentrations gave greater than 90 percent coal recovery for all three slurry concentrations (Figure 2c). The coal at these recovery levels contained between 8.2 and 9.2 percent ash from an aged sediment that contained about 45.6 percent ash. Tetralin at oil concentrations between 3 and 20 percent gave 80 to 96 percent recovery. The ash content of these coals recovered using tetralin from the same aged sediment as those recovered using kerosene, was between 9.5 and 10.5 percent. Coal recovery falls off for both kerosene and tetralin at oil concentrations lower than 5 percent.

The results of these experiments indicated that the experiments could be limited to the 3, 5 and 10 percent oil concentrations because of the marginal results at 1.5 percent and the small incremental gains at

TABLE 7. EXPERIMENTAL RESULTS OF COAL RECOVERY FROM AGED SEDIMENTS USING KEROSENE

Run	Agglomerating Conditions		Coal Product			Residue		
	Slurry Conc., percent	Oil Conc., percent[a]	Percentage of Feed	MF Ash, percent	Coal Recovered, percent[b]	Percentage of Feed	MF Ash, percent	Ash Removed, percent
51-1	15	20	54.1	8.57	90.9	45.9	85.40	86.0
51-2	10	20	56.2	8.97	94.0	43.8	88.18	84.7
51-3	5	20	60.1	8.64	100.9[c]	39.9	90.75	79.4
51-4	15	10	56.6	9.31	94.4	43.4	86.06	81.9
51-5	10	10	58.3	9.11	97.4	41.7	90.20	82.5
51-6	5	10	57.2	8.02	96.7	42.8	90.59	85.0
51-7	15	5	52.6	8.21	88.8	47.4	80.64	83.8
51-8	10	5	53.6	10.01	88.7	46.4	80.21	81.6
51-9	5	5	45.4	9.51	75.5	54.6	85.33	102
51-10	15	3	54.5	12.80	87.4	45.5	74.47	74.3
51-11	10	3	56.3	12.46	92.7	43.7	81.75	78.3
51-12	5	3	44.3	8.13	74.8	55.7	72.85	89.0
51-13	15	1.5	32.7	7.99	55.3	67.3	61.62	90.9
51-14	10	1.5	40.9	8.78	68.6	59.1	69.70	90.3
51-15	5	1.5	34.6	14.74	54.2	65.4	64.83	92.8

(a) Oil concentration based on weight of moisture free sediment.

(b) Coal recovered value estimated as $\frac{(100 - \% \text{ ash})_{product} \times \% \text{ of feed}}{(100 - \% \text{ ash})_{feed}}$.

(c) Value greater than 100 percent due to residual kerosene retained after drying.

TABLE 8. EXPERIMENTAL RESULTS OF COAL RECOVERY FROM AGED SEDIMENT USING TETRALIN

Run	Agglomerating Conditions		Coal Product			Residue		
	Slurry Conc., percent	Oil Conc., percent[a]	Percentage of Feed	MF Ash, percent	Coal Recovered, percent[b]	Percentage of Feed	MF Ash, percent	Ash Removed, percent
46-1	15	20	56.6	9.42	94.2	43.5	90.42	86.3
46-2	10	20	54.4	9.15	90.8	45.6	90.63	90.6
46-3	5	20	53.2	7.86	90.1	46.8	90.42	92.8
46-4	15	10	53.8	9.54	89.1	46.2	87.98	89.1
46-5	10	10	51.9	10.23	85.6	48.1	86.37	91.1
46-6	5	10	52.5	10.11	86.7	47.5	83.34	86.8
46-7	15	5	48.9	9.68	81.2	51.1	78.85	88.4
46-8	10	5	53.8	9.37	89.6	46.2	82.47	83.6
46-9	5	5	54.2	9.38	90.3	45.8	80.55	80.9
46-10	15	3	52.0	10.43	85.6	48.0	78.95	83.1
46-11	10	3	55.1	9.54	91.6	44.9	79.40	78.2
46-12	5	3	43.3	8.92	72.5	56.7	65.20	81.1
46-13	15	1.5	34.0	10.87	55.7	66.0	60.57	87.7
46-14	10	1.5	29.5	7.27	50.3	70.5	58.63	90.6
46-15	5	1.5	27.1	6.59	46.4	72.5	57.11	90.8

(a) Oil concentration based on weight of moisture free sediment used.

(b) Coal recovered value estimated as $\frac{(100 - \%\ ash)_{product} \times (\%\ of\ feed)_{product}}{(100 - \%\ ash)_{feed}}$.

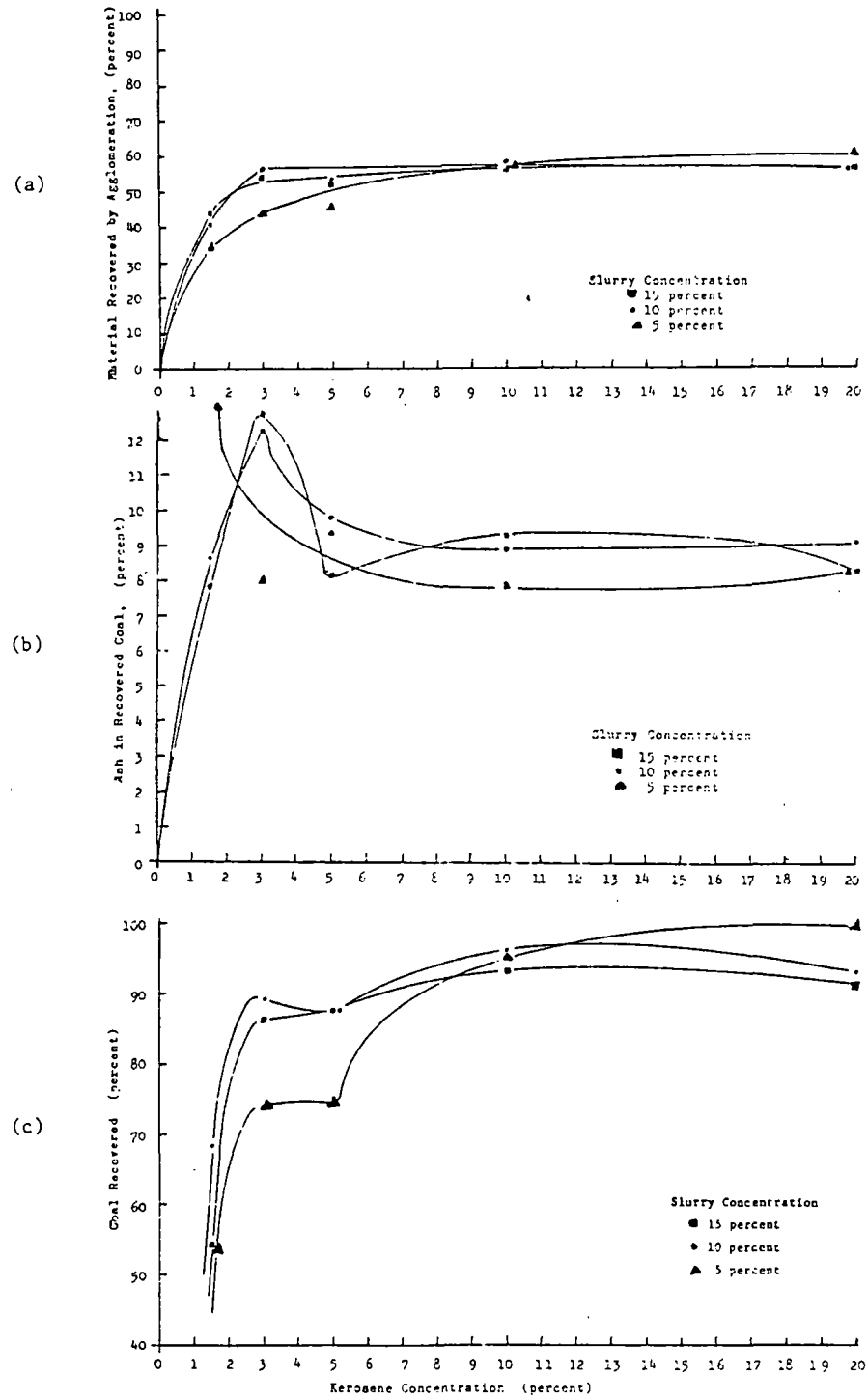

FIGURE 2. INFLUENCE OF AGED SLURRY SEDIMENT CONCENTRATION AND KEROSENE CONCENTRATION ON (a) MATERIAL RECOVERY, (b) ASH IN RECOVERED COAL AND (c) PERCENTAGE OF COAL RECOVERED

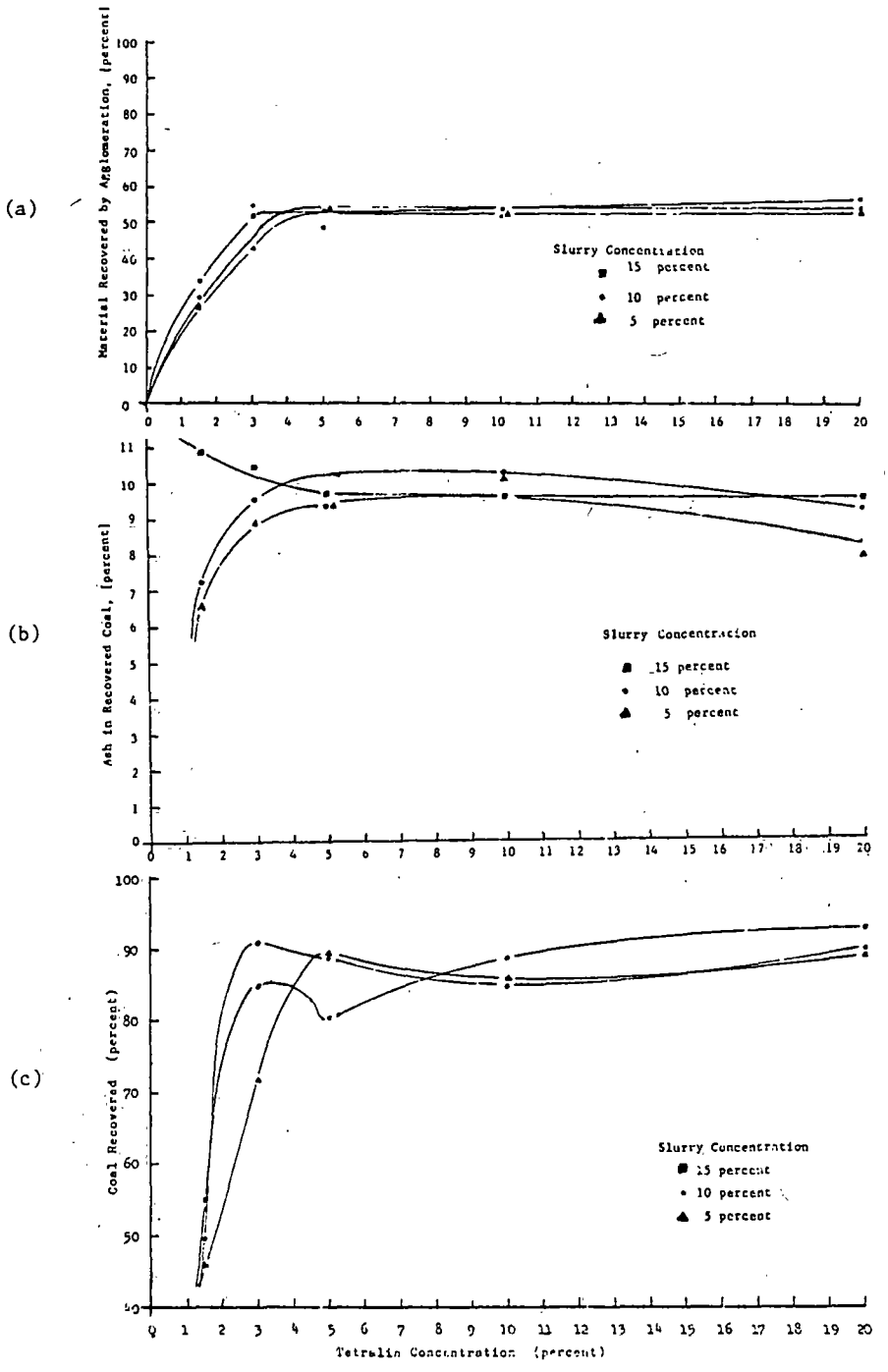

FIGURE 3. INFLUENCE OF AGED SEDIMENT SLURRY CONCENTRATION AND TETRALIN CONCENTRATION ON (a) MATERIAL RECOVERY, (b) ASH IN RECOVERED COAL AND (c) PERCENTAGE COAL RECOVERED

20 percent over that attainable at 10 percent.

The amount of coal recovered from aged slurry pond sediments and its ash content using a mixture of 12 volume percent No. 6 fuel oil and 88 percent kerosene, and No. 2 fuel oil at 3, 5 and 10 percent oil concentration are given in Tables 9 and 10 respectively. The results given graphically in Figure 4 suggests less scatter exists in the data for the material recovered, its ash content, and coal recovery than were observed with kerosene alone and tetralin.

The 45 to 55 percent material recovered from aged sediments with the No. 6 fuel oil-kerosene mixture is about the equal to the recoveries obtained with No. 2 fuel oil although there is slightly greater scatter in the latter data. The performance of the two oils differs in their ability to reduce the ash in the coal recovered from 10 and 15 percent slurries using a 3 percent oil concentration. For the coal recovered from the 15 percent slurry, an ash value of 9.2 percent was produced using No. 2 fuel oil while with the No. 6 fuel oil-kerosene mixture the ash content was about 7.5 percent. At all other oil and slurry concentrations the ash values are comparable with the No. 6 fuel oil-kerosene mixture producing a product with a slightly lower overall ash content. Highest apparent coal recovery, 98 percent, occurred using a No. 2 fuel oil concentration of 5 percent and a 10 percent sediment slurry. However this coal had about an 8.4 percent ash. The fuel oil-kerosene mixture appears to yield higher coal recoveries for all three slurry concentrations at the 5 and 10 percent oil concentrations while the No. 2 fuel oil gives a greater scatter of coal recoveries. At the 5 and 10 percent oil concentrations both give coal recoveries greater than 90 percent.

Sulfur Values of Coals Recovered from Aged Sediments--

Coal recovered from 10 percent slurries using the 1.5 to 20 percent range of oil concentrations were analyzed for pyritic and total sulfur and the results are shown on Table 11. There is a reasonable correlation of the sulfur values with ash values, i.e., the lower the ash values the lower sulfur values for the coal recovered using tetralin. Although coal recovery is lowest for the 1.5 percent oil for both tetralin and kerosene the coal still

TABLE 9. EXPERIMENTAL RESULTS OF COAL RECOVERY FROM AGED SLURRY POND SEDIMENT USING A MIXTURE OF NO. 6 FUEL OIL AND KEROSENE (12:88 VOLUME RATIO)

	Agglomerating Conditions		Coal Product			Residue		
Run	Slurry Conc.	Oil Conc.	% of Feed	MF Ash, %	Coal Recovered, %	% of Feed	MF Ash, %	Ash Removed, %
62-1	15	10	54.9	7.76	93.1	45.1	89.51	88.5
62-2	10	10	55.4	7.18	94.5	44.6	89.89	87.9
62-3	5	10	56.0	8.12	94.6	44.0	88.01	84.9
62-4	15	5	57.0	8.42	95.9	43.0	87.61	82.6
62-5	10	5	56.4	8.27	95.1	43.6	88.91	85.0
62-6	5	5	56.2	8.12	94.9	43.8	87.95	84.5
62-7	15	3	50.0	7.71	84.8	50.0	79.85	87.6
62-8	10	3	52.3	7.42	89.0	47.7	82.86	86.7
62-9	5	3	54.3	7.16	92.7	45.7	86.74	86.9

TABLE 10. EXPERIMENTAL RESULTS OF COAL RECOVERY FROM AGED SLURRY POND SEDIMENT USING NO. 2 FUEL OIL

	Agglomerating Conditions		Coal Product			Residue		
Run	Slurry Conc.	Oil Conc.	% of Feed	MF Ash, %	Coal Recovered, %	% of Feed	MF Ash, %	Ash Removed, %
59-1	15	10	54.8	7.85	92.8	45.2	85.53	84.8
59-2	10	10	57.0	8.17	96.2	43.0	89.94	84.8
59-3	5	10	57.8	7.31	98.5	42.2	90.82	84.0
59-4	15	5	53.0	8.26	89.4	47.0	81.67	84.2
59-5	10	5	58.1	8.38	97.9	41.9	87.59	80.5
59-6	5	5	53.5	8.36	90.1	46.5	83.48	85.1
59-7	15	3	49.6	9.13	82.8	50.4	76.86	85.0
59-8	10	3	52.2	8.17	88.1	47.8	76.54	80.2
59-9	5	3	43.8	7.17	74.7	56.2	75.57	93.1

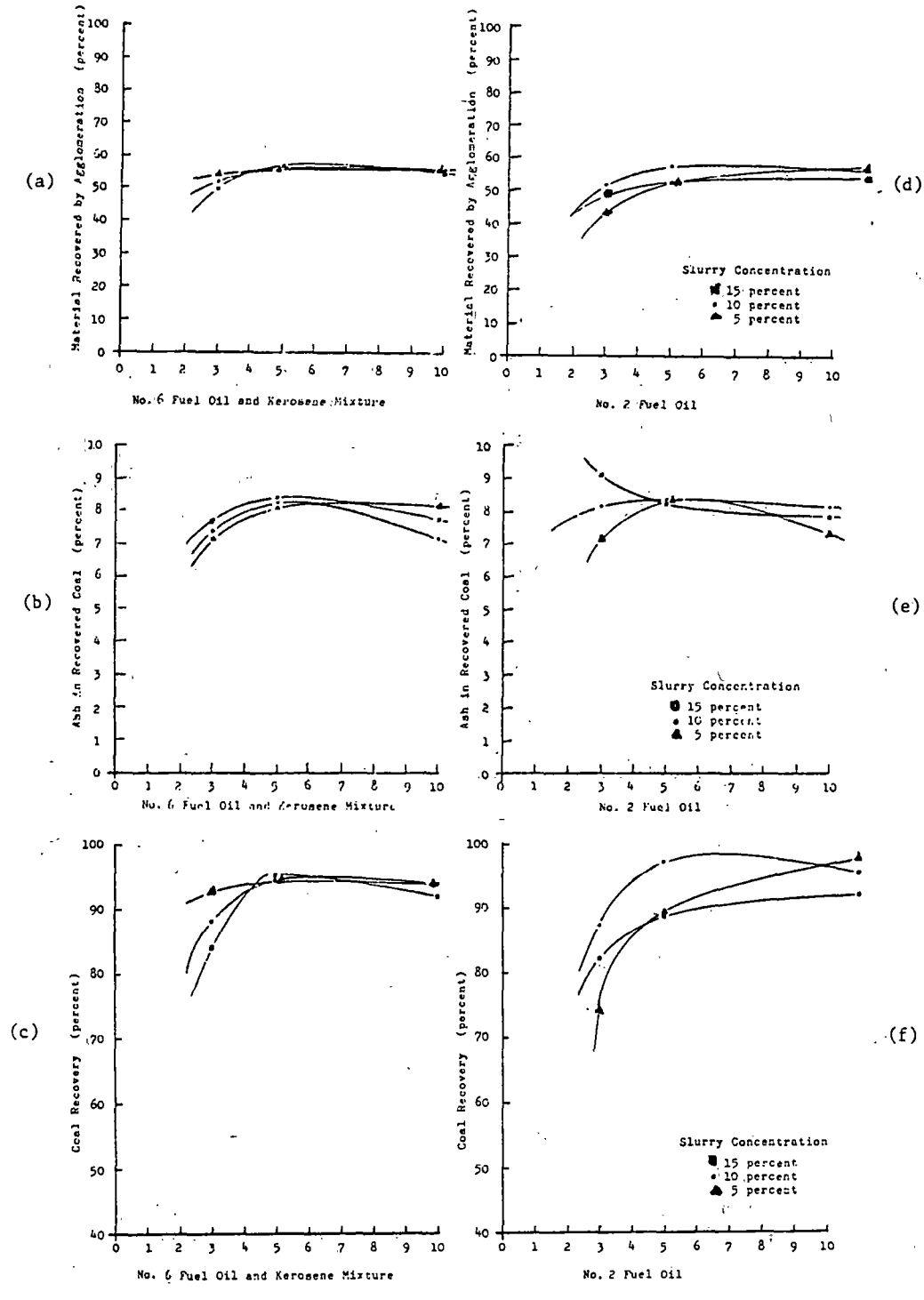

FIGURE 4. INFLUENCE OF AGED COAL SEDIMENT SLURRY CONCENTRATION AND OIL CONCENTRATION ON (a,d) MATERIAL RECOVERED, (b,e) ASH IN RECVOERED COAL AND, (c,f) PERCENTAGE COAL RECOVERED

TABLE 11. EFFECT OF OIL CONCENTRATION ON ASH AND SULFUR CONTENT OF COAL RECOVERED FROM AGED SEDIMENT (ALL 10 PERCENT SLURRY CONCENTRATIONS)

Oil Concentration, %	Coal Recovered, %	MF Ash, %	MAF Sulfur, %	
			Pyr	Total
	Tetralin			
20	90.8	9.15	1.86	3.97
10	85.6	10.23	1.96	4.14
5	89.6	9.37	1.84	3.87
3	91.6	9.54	1.89	3.86
1.5	50.3	7.27	1.48	3.27
	Kerosene			
20	94.0	8.97	2.28	3.99
10	97.4	9.11	1.98	4.10
5	88.7	10.01	1.79	3.70
3	92.7	12.46	1.65	3.57
1.5	68.6	8.78	1.56	3.23

contains a significant quantity of ash especially with kerosene. There is however a drop in the amount of pyritic (and total) sulfur contained in the coal recovered at 1.5 percent oil concentration.

Samples of coal recovered using kerosene and tetralin which had the following characteristics were selected for sulfur analysis:

- High coal recovery and low ash
- High coal recovery and high ash
- Low coal recovery and low ash
- Low coal recovery and high ash.

The results of the analyses of these samples for pyritic and total sulfur given in Table 12 suggest that only low coal recoveries produce the coal with the lowest sulfur. Of these coals the ones with the lowest ash content had the lowest percentage of sulfur. Conversely excellent coal recovery seems to keep sulfur values high and appears to be independent of ash content. This behavior suggests that the pyrites and coal are moving together either as separate particles or as finely disseminated material held in the coal. Again the tendency of tetralin to recover a lower-ash and sulfur coal than kerosene is observed.

Other Processing Variables--

The effect of the use of slower agitating speeds (as rpm of impeller) and residence times less than 2.5 minutes during agglomeration are summarized in Table 13. In these experiments the kerosene was emulsified before use to provide uniform dispersion of the agglomerating oil regardless of blender speed. At the slow rpm and short residence times it appears that the ash and the coal do not have enough time to separate into the two phases necessary for good ash removal. Although the amount of material recovered is usually about 60 percent of the feed, it has an ash content about one-half that of the feed material (45.6 percent ash).

In any attempt at reducing the oil concentrations to levels less than 10 percent (for economic and environmental reasons), one of the difficult steps in the recovery of coal by agglomeration will be the dewatering of the agglomerated coal. At oil levels less than 10 percent dewatering becomes slow and separation of the agglomerated coal from the residue slurry is incomplete. In order to improve the dewatering

TABLE 12. ASH AND SULFUR CONTENT OF COAL RECOVERED FROM AGED SLURRY POND SEDIMENT

Coal Recovered, %		MF Ash, %	MAF Sulfur, % Pyr	MAF Sulfur, % Total
		With Tetralin		
90.1 (H)[a]		7.86 (L)[b]	1.88	3.80
89.1 (H)		9.54 (H)	1.87	3.82
50.3 (L)		7.27 (L)	1.48	3.28
55.7 (L)		10.87 (H)	1.55	3.68
	AVG	8.89	1.70	3.40
		With Kerosene		
100.9 (H)		8.64 (L)	2.28	3.99
97.4 (H)		9.11 (H)	1.98	4.10
55.3 (L)		7.99 (L)	1.35	3.56
54.2 (L)		14.74 (H)	1.89	3.81
	AVG	10.12	1.88	3.87

(a) H = relative high value.

(b) L = relative low value.

TABLE 13. EFFECT OF AGITATING SPEED AND RETENTION TIME ON AGGLOMERATION OF AGED SLURRY POND SEDIMENT WITH EMULSIFIED KEROSENE[a]

Run No.	Agitating Speed rpm	Retention Time sec	Product, percent	
			Of Feed	MF Ash
84-1	3,500	10	50.2	20.5
84-2	3,500	30	63.7	23.2
84-3	3500	60	59.3	22.6
84-4	5,300	10	54.9	22.5
84-5	5,300	30	60.7	21.6
84-6	5,300	60	59.9	20.2
84-7	10,000	10	64.2	23.6
84-8	10,000	30	61.1	16.4

(a) Slurry concentration, 10 percent; kerosene concentration, 10 percent and emulsified in water ultrasonically before agglomeration.

characteristics, the addition of a flocculating agent was added before, during and after adding the oil and agglomerating was studied. The flocculating agent used was Percol 728 cationic flocculant manufactured by Allied Colloids Inc. A concentration of 10 ppm was used. A 10 percent slurry concentration was treated using kerosene at the 10 and 5 percent levels and the results of these experiments are given in Table 14. The results show that the addition of flocculant before, during and after the oil addition at the 10 percent level improved the quality of the coal (lower ash) from that obtained with out the flocculant with some loss in the coal recovery (84 to 90 percent versus 97 percent coal recovery). At the 5 percent oil leve, the quality of the coal was also improved (due to the low ash values in the coal) but only at the cost of sacrificing significant amounts of coal loss (48 to 58 percent versus 89 percent coal recovery).

Fresh Black Water Sediments

The consist of fresh black water sediments in effluents from modern coal cleaning plants suggest that this material would be more amenable to the agglomeration techniques for coal recovery than are the aged sediments. The fact that 89 percent of the material is finer than 100 mesh (0.11 mm) and that there has been little or no weathering of the coal support this hypothesis. The results of the experiments in which 5, 10 and 15 percent slurries were treated with No. 6 fuel oil-kerosene mixture (12:88 volume ratio to give a specific gravity of 0.83 at 27 C) are given in Table 15. These results are summarized in Figure 5 where the material recovered, ash in the recovered coal and the percentage coal recovery are presented as a function of the slurry and oil concentration.

The results show very little dependence on slurry concentration since there is very little scatter of points. (Similar behavior was noted when the fuel oil-kerosene mixture was used on the aged sediment slurries but for only 3, 5 and 10 percent oil concentrations). In Figure 5a, it can be seen that for all oil concentrations except 1.5 percent, the material recovery was between 45 and 52 percent regardless of the slurry concentration. As shown in Figure 5b, the amount of ash in the recovered coal did not vary greatly and fell between 6 and 7.5 percent, except when a

TABLE 14. EFFECT OF FLOCCULATION AGENT[a] ON AGGLOMERATION OF AGED SLURRY SEDIMENTS (10 PERCENT SLURRY)

Run No.	Kerosene Conc., percent	Flocculant Addition	Product, percent		Coal Recovery, %
			Of Feed	MF Ash	
37-1	10	Before	48.8	6.05	84
37-2	10	During	51.2	7.28	87
37-3	10	After	51.9	6.07	90
51-5	10	None	58.3	9.11	97
37-4	5	Before	27.8	5.35	48
37-5	5	During	32.2	4.98	56
37-6	5	After	33.1	5.05	58
51-8	5	None	53.6	10.01	89

(a) Percol 728 cationic flocculant manufactured by Allied Colloids, Inc., at the concentration of 10 ppm.

TABLE 15. EXPERIMENTAL RESULTS OF COAL RECOVERY FROM FRESH BLACK WATER SEDIMENT USING NO. 6 FUEL OIL AND KEROSENE MIXTURE (12:88 VOLUME RATIO)

	Agglomerating Conditions		Coal Product			Residue		
Run	Slurry Conc.	Oil Conc.	% of Feed	MF Ash, %	Coal Recovered, %	% of Feed	MF Ash, %	Ash Removed, %
65-1	15	20	50.9	6.31	96.8	49.1	90.77	87.7
65-2	10	20	50.5	6.43	96.0	49.5	90.70	88.4
65-3	5	20	51.7	5.90	98.2	48.3	91.06	86.6
65-4	15	10	50.2	6.82	95.0	49.8	90.13	88.4
65-5	10	10	51.6	6.75	97.7	48.4	91.45	87.1
65-6	5	10	49.5	6.54	93.9	50.5	89.72	89.2
65-7	15	5	48.0	7.03	90.7	52.0	86.91	89.0
65-8	10	5	49.5	7.56	92.9	50.5	87.84	89.3
65-9	5	5	48.9	7.27	92.2	51.1	89.11	89.6
65-10	15	3	46.1	6.71	87.4	53.9	85.55	90.8
65-11	10	3	47.9	6.88	90.6	52.1	88.85	90.8
65-12	5	3	44.7	6.64	84.9	55.3	84.66	92.2
65-13	15	1.5	27.8	6.46	52.9	72.2	63.66	90.5
65-14	10	1.5	16.0	6.61	30.4	84.0	57.42	95.0
65-15	5	1.5	21.1	5.70	40.6	78.9	62.53	97.1

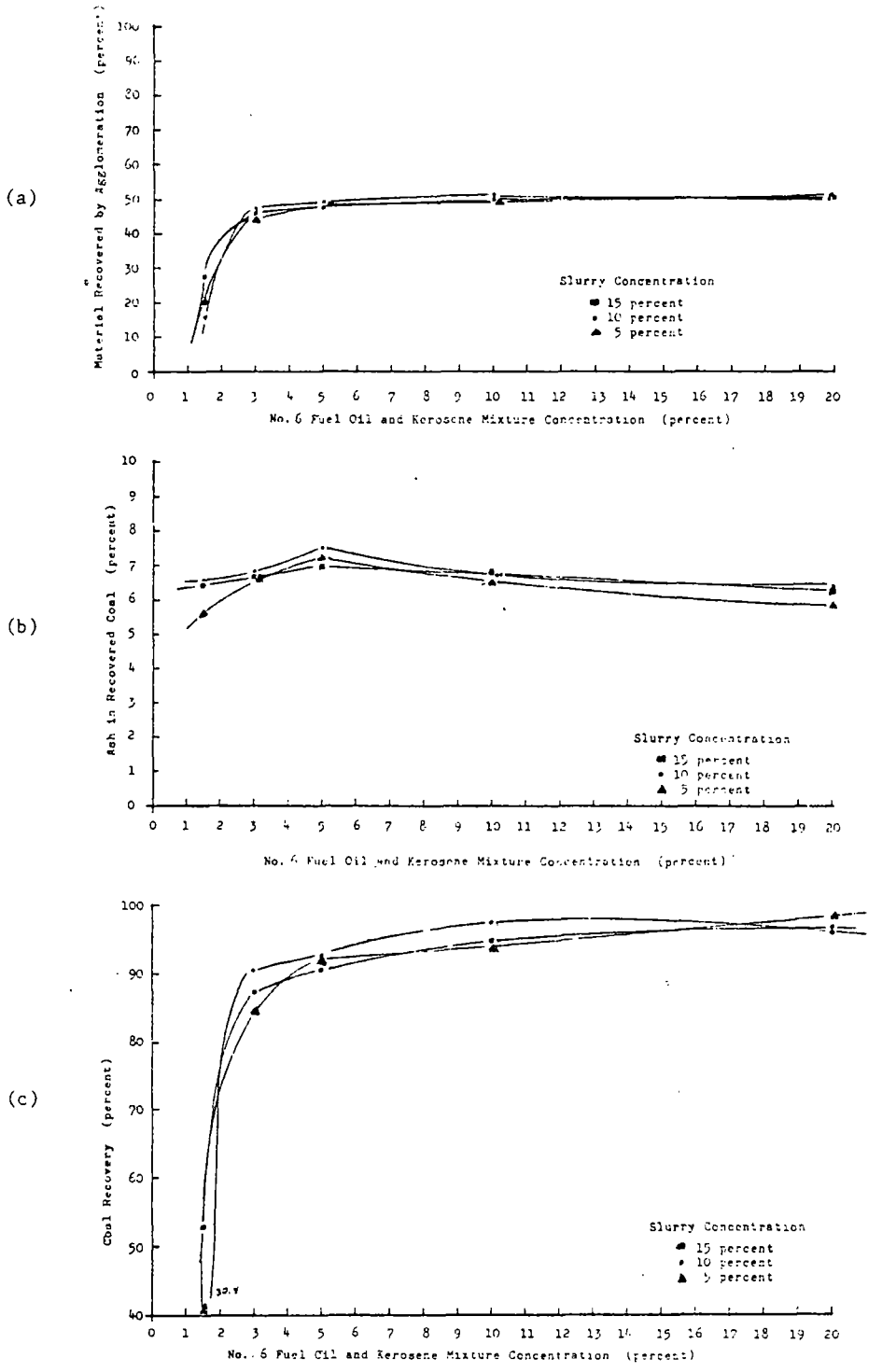

FIGURE 5. INFLUENCE OF FRESH BLACK WATER SEDIMENT SLURRY CONCENTRATION AND NO. 6 FUEL OIL-KEROSENE MIXTURE (12:88 VOLUME RATIO) ON (a) MATERIAL RECOVERY, (b) ASH RECOVERED COAL AND (c) PERCENTAGE COAL RECOVERED

1.5 percent oil level with the 5 percent slurry was used. The percentage of coal recovered was a maximum 98 percent when a 10 percent oil-kerosene level was used to agglomerate the coal in a 10 percent slurry (see Figure 5c). A 95 percent coal recovery was obtained using the same oil concentration on a 15 percent slurry.

The results of experiments in which other oils were used in the agglomerations of coal values from fresh black water sediments are given in Table 16. Tetralin, kerosene and No. 2 fuel oil were used under conditions found most effective for coal recovery from the aged sediments. At the 20 percent oil concentration levels each oil produced an apparent coal recovery of greater than 94 percent. At the 10 percent level, the amount of coal recovered from 5 percent slurries was lowest with kerosene (80.5 percent) and highest with No. 2 fuel oil (99.1 percent). Use of No. 2 fuel oil produced apparent coal recoveries near or in excess of 100 percent due to the retention of the oil after drying at 100 torr at 60 C overnight.

Since the experiments with tetralin, which is one of the hydrogen transfer agents in coal liquefaction process employing hydrogenation, were successful, the concept of using a coal derived liquid directly as an agglomerating oil were investigated and the results are given in Table 16. Unfiltered solvent refined coal (SRC) dissolver product did not give good coal recovery when used at 20, 10 and 5 percent oil concentrations. The best result was about 61 percent recovery of coal that contained 16 percent ash. Use of the distillate collected below 315 C from the SRC dissolver product gave coal recoveries of about 90 percent from 5 and 10 percent slurries using 10 and 20 percent oil concentrations. The ash in the recovered coal was between 7.5 and 8 percent which is about 1 percent higher than the coals recovered using tetralin or kerosene.

Sulfur Values of Coals Recovered from Black Water Sediments--

The sulfur content determined for the coals recovered from the black water sediments using the No. 6 fuel oil-kerosene mixture are given in Table 17. The results show the same trend as observed for the coals recovered from aged slurry pond sediment, i.e., the pyrite levels seem to follow coal

TABLE 16. EXPERIMENT RESULTS OF COAL RECOVERY FROM FRESH BLACK WATER SEDIMENT USING VARIOUS OILS

	Agglomerating Conditions			Coal Product			Residue		
Run	Slurry Conc.	Oil Type	Oil Conc.	% of Feed	MF Ash, %	Coal Recovered, %	% of Feed	MF Ash, %	Ash Removed, %
76-1	5	Tetralin	20	49.8	6.88	94.2	50.2	92.1	91.0
76-2	10	Tetralin	5	47.3	6.98	89.4	52.7	86.0	90.3
76-3	5	Kerosene	20	52.0	6.45	98.9	48.0	92.0	88.0
76-4	5	Kerosene	10	42.1	5.94	80.5	57.9	79.1	91.1
76-5	5	#2 Fuel Oil	20	55.2	6.20	105.1[a]	44.8	91.9	82.0
76-6	5	#2 Fuel Oil	10	52.2	6.51	99.1	47.8	91.3	86.9
80-1	5	SRC u[b]	20	35.5	15.66	60.9	64.5	63.2	81.2
80-2	5	SRC u	10	20.7	9.04	38.3	79.3	47.9	75.7
80-3	10	SRC u	5	17.5	7.80	32.8	82.5	57.4	94.3
80-4	5	SRC d[c]	20	48.1	8.00	89.9	51.9	85.4	88.3
80-5	10	SRC d	10	46.3	7.49	87.0	53.7	82.7	88.6
80-6	10	SRC d	5	33.2	6.89	62.8	66.8	68.4	91.02

(a) Value greater than 100 percent due to residual fuel oil retained after drying.

(b) Unfiltered solvent refined coal dissolves product.

(c) Distillate from solvent refined coal dissolver product, 315 C cut.

TABLE 17. ASH AND SULFUR CONTENT OF COAL RECOVERED FROM BLACK WATER SEDIMENTS[a]

Coal Recovered, %	MF Ash, %	MAF Sulfur, %	
		Pyr	Total
98.2	5.87	1.42	3.61
97.7	6.83	1.65	3.90
40.6	5.68	1.16	3.48
AVG	6.13	1.41	3.66

(a) Using a No. 6 fuel oil and kerosene mixture (12:88 volume ratio).

TABLE 18. EFFECT OF AGITATING SPEED AND RETENTION TIME ON AGGLOMERATION OF THE FRESH BLACK WATER SEDIMENT WITH KEROSENE[a]

Run No.	Agitating Speed, rpm	Retention Time, sec	Product, percent		Coal Recovery, percent
			Of Feed	MF Ash	
1-1	3500	10	12.5	9.07	23
1-2	3500	30	12.6	11.02	23
1-3	3500	60	23.7	9.01	44
1-4	5300	10	28.8	16.91	49
1-5	5300	30	52.6	18.24	87
1-6	5300	60	44.4	6.33	85
1-7	10000	10	42.8	11.20	77
1-8	10000	30	48.7	8.86	90
1-9	10000	60	47.3	6.32	91

(a) Slurry concentration, 10 percent; kerosene concentration, 10 percent.

recovery more closely than they do ash values. Samples of coal from a high recovery experiment containing high ash (6:83 percent) had a higher sulfur value than did those from high recovery and low ash (5.87 percent). However when the recovery is low and the ash is low (5.68 percent) the amount of pyritic sulfur in the coal is the lowest.

Other Process Variables--

Experiments were carried out with fresh black water sediments to study the effect of agitating speed (blender rpm) and retention time on agglomeration. The results of these experiments given in Table 18. The results suggest that higher agitating speeds and longer retention time gave higher coal recovery. It appears that an agitation speed of at least 5300 rpm and a retention time of 30 sec or more are necessary to achieve good recovery of a coal with the lowest ash values.

Partially Dried Old Sediments

The sample of a partially dried, old coal slurry pond sediments had a moisture free (MF) ash content value of 32.2 percent and sulfate sulfur concentration of 2.11 percent on a moisture and ash free basis (MAF). The pH of a 10 percent slurry was 2.2 and the supernatent had a yellow color. Agglomeration of this slurry with kerosene gave very poor coal recoveries even with the high oil concentrations and at high pH values (adjusted by the addition of NaOH). It appeared that during exposure to air during drying the coal particles lost their hydrophobic surfacial characteristics perhaps by adsorption of ferric ions. In an attempt to restore the hydrophobicity, the sediment was washed several times by reslurrying with fresh water after filtration of the previous wash. After each washing at approximately the same sediment to water ratio, a portion of the slurry was taken for agglomeration. Table 19 summarizes the effect of successive washing on the agglomeration characteristics of the sediment. The results indicate that repeated washings improved coal recovery and decreased the ash content of the coal recovered.

In the experiments in which chemical treatment of unwashed old slurry pond sediments was used to reduce the ferric and sulfate ions, the

TABLE 19. EFFECT OF SUCCESSIVE WASHING ON AGGLOMERATION[a] OF PARTIALLY DRIED OLD COAL SEDIMENT

No. of Washing	pH After Washing	pH[b] Before Agglomeration	Product, percent Of Feed	Product, percent MF Ash	Coal Recovery, percent
1[c]	3.1	6.6	52.3	23.00	59
2	3.6	7.6	69.0	21.00	80
3	3.9	6.9	80.9	19.66	96
4	4.0	6.9	71.5	12.57	92
7	4.0	7.7	72.1	9.98	96

(a) Agglomeration was performed with 10% No. 2 fuel at 10% slurry concentration.

(b) pH was adjusted with NaOH solution.

(c) Original slurry pH = 2.2.

TABLE 20. EFFECT OF DISPERSING AGENT ON AGGLOMERATION[a] OF UNWASHED PARTIALLY DRIED OLD COAL SEDIMENT

Run No.	Chemical Agent, g/100 g solid	pH	Product, percent Of Feed	Product, percent MF Ash
14-2	Sodium silicate (3 g)[b]	7.0	64.4	13.64
14-3	Sodium tripolyphosphate (2 g)	7.0[c]	51.0	10.74
14-4	Sodium metaphosphate (2 g)	7.0[c]	46.5	9.56

(a) Agglomeration was performed with 10 percent No. 2 fuel oil at 10 percent slurry concentration.

(b) Sodium silicate solution (containing 8.9 percent Na_2O and 29 percent SiO_2) was used to neutralize the slurry.

(c) pH was adjusted with NaOH solution before addition of agent.

slurry was adjusted to a pH greater than 7 with NaOH to precipitate iron hydroxide and then was treated with $CaCl_2$ solution to a pH of about 7 to precipitate calcium sulfate. Recovery experiments with these treated slurries using kerosene and fuel oil-kerosene mixtures indicated that the coal particles had agglomerated well. However the separation of the agglomerated coal from the residue suspension was extremely difficult due to plugging of the sieve openings by the precipitated residue. In order to control this effect, several dispersing agents were tried. The results of their use on the agglomeration of coal slurries neutralized with NaOH (no $CaCl_2$ addition) are given in Table 20. The dispersing agents improved the separation of the agglomerated coal from the residue suspension, but the coal recovery and quality were not satisfactory. Sodium metaphosphate appeared to be most promising.

The data given in Table 21 are the results of experiments in which a sequence of treatments were tried. The treatment consisted of a combination of a single stage washing with water followed by adjustment of the pH either to about 6 or 5 with sodium hydroxide which was followed by addition of sufficient sodium silicate solution to raise the pH to either about 9 or 8. The results indicate coal recovery is greater when coal is washed and sodium silicate is used. Washing the slurry before addition of sodium hydroxide and sodium silicate reduces the ash in the recovered coal. The lowest ash in the recovered coal occurred when the pH was adjusted to about 5 with sodium hydroxide alone.

This behavior was attributed to differences in the composition of the partially dried old slurry pond sediment that became segregated during use of the material. The major portion of the sediment was a loose material which had mixed with it firm lumps ranging in various sizes up to 3 inches in diameter. Towards the end of these studies, the larger lumps were used as part of the feed material.

The behavior of these two types of materials during slurry preparation and agglomeration were compared. As shown in Table 22, the aqueous slurry made from the aggregated sediment had a pH of about 6.5 while the slurry made from the loose sediment had a pH of 2.9. When the pH 2.9-slurry was adjusted to a pH of 6.5 to match that of the aggregate slurry and then agglomerated using a 10 percent concentration of No. 2 fuel

TABLE 21. EFFECT OF SINGLE WASH OF SEDIMENTS, pH ADJUSTMENT AND LOW LEVEL SODIUM SILICATE ADDITIONS BEFORE AGGLOMERATION ON COAL RECOVERY FROM PARTIALLY DRIED OLD SEDIMENTS[a]

	Slurry pH			Product, percent		Coal Recovered percent
	Initial	Adjusted NaOH	After Sodium[b] Silicate	Of Feed	MF Ash	
Unwashed	3.2	5.8	9.2	64.8	7.43	88
Washed	3.3	5.8	9.6	66.7	6.13	92
Washed	3.3	5.0	8.2	66.7	6.64	92
Unwashed	3.1	5.1	--[c]	62.3	5.40	87
Washed	3.3	5.3	--	65.0	5.36	91

(a) Slurry concentration, 10 percent; No. 2 fuel oil concentration, 10 percent.

(b) pH values after adding sodium silicate solution (8.9% Na_2O + 24% SiO_2).

(c) No sodium silicate added.

TABLE 22. COMPARISON OF AGGLOMERATION BEHAVIOR OF SEGREGATED LUMPS OF LOOSE MATERIAL FOUND IN PARTIALLY DRIED OLD COAL SEDIMENT

	Slurry pH			Product, percent	
	Original Slurry	Diluted for Agglomeration	At Agglomeration[a]	Of Feed	MF Ash
Loose Sediments	2.6	2.9	6.5[b]	8.47	8.19
Aggregated Sediment	6.4	6.5	6.5[c]	60.4	5.02

(a) Slurry concentration, 10 percent; No. 2 fuel oil concentration, 10 percent.

(b) pH adjusted with NaOH.

(c) No adjustment required.

oil, only 8.5 percent of the material was separated. In contrast, agglomeration of the slurry of the aggregate yielded 60 percent of the feed and the recovered coal had lower ash content. This may have been due to the reduced exposure to weathering that these aggregates had compared to the loose materials. It could also be due to a higher coal concentration in the aggregate.

RESIDUE CHARACTERIZATION

Once coal values have been removed, the residue material is relatively free of combustible material. For example, the solids recovered from the aqueous residue suspension after agglomerating with a mixture of No. 6 fuel oil and kerosene contain about 90 percent moisture free ash while the residue solids from the aged slurry pond sediments contained about 89 percent moisture free ash. Part of the weight loss during ash determination could have been due to the loss of water so in effect the quantity of coal present is very small. As reported by Capes et al.[15] many of the trace elements in coal considered to be hazardous are removed with the mineral matter during agglomeration.

Any process designed to use the agglomeration technique for recovery of fine coal from coal slurry waste streams or to reduce the environmental threat of slurry ponds will be concerned with the disposal of the residues from the operation. To this end studies were initiated to measure the settling characteristics of the residue suspensions and the concentration of the agglomerating oil they may retain.

Settling Rates

The settling rates of the original coal slurry and of the residue suspension were obtained by preparing sufficient 10 percent slurry to make up 1700 ml and shaking the suspension thoroughly in a 2000 ml graduated cylinder for several minutes. The settling rate was measured by following the level of the clear interface with time. After completion of this cycle, the slurry was agglomerated using a 20 percent kerosene concentration in a one-gallon blender. After the usual coal recovery technique (including washing on the screen), the residue suspension was now contained in 2000 ml. The settling rate was measured again.

The settling rates for the aged slurry pond sediment and the resulting residue suspension are given in Figure 6. Settling rates for the fresh black water sediments and the resulting residue suspension are shown in Figure 7. The settling rates of both residue suspensions are faster than the parent sediment slurries containing the coal. Removal of the coal from the residues which appear to be mostly fine clays probably increases settling in part due to the decreased slurry concentration. This is a very desirable result. In addition, specific agents known to improve clay flocculation can now be applied more specifically.

The pulp density of the residues (1.09 and 1.14 g/ml) at the end of the 3-day settling period suggest that they remain pumpable. The residues recovered after settling were dried at 110 C and then analyzed (see Table 23). As expected the results for the two materials from the same mine are similar and the composition is characteristic of clays with SiO_2 to Al_2O_3 ratio of about 4 (perhaps illites since iron, calcium and potassium are present).

Oil in Residue

An estimate of the amount of agglomerating oil that is lost to the residue suspension after agglomeration was made. The procedures used for determining the oil content in the residue slurry were as follows:

1. The residue water suspension from the oil agglomeration (mostly mineral matter) was mixed well with 50 ml of carbon tetrachloride in a 1000 ml separating funnel.
2. The mixture was allowed to separate into two phases and the heavier CCl_4 phase was drained off.
3. These extraction steps were repeated five times.
4. A 24 ml aliquot of the CCl_4 extract (250 ml) was placed in a weighed dish and evaporated in a constant temperature bath at 80 C for 20 min.
5. The weight of remaining oil was measured and multiplied by 10 to calculate the total amount of oil in the residue slurry.

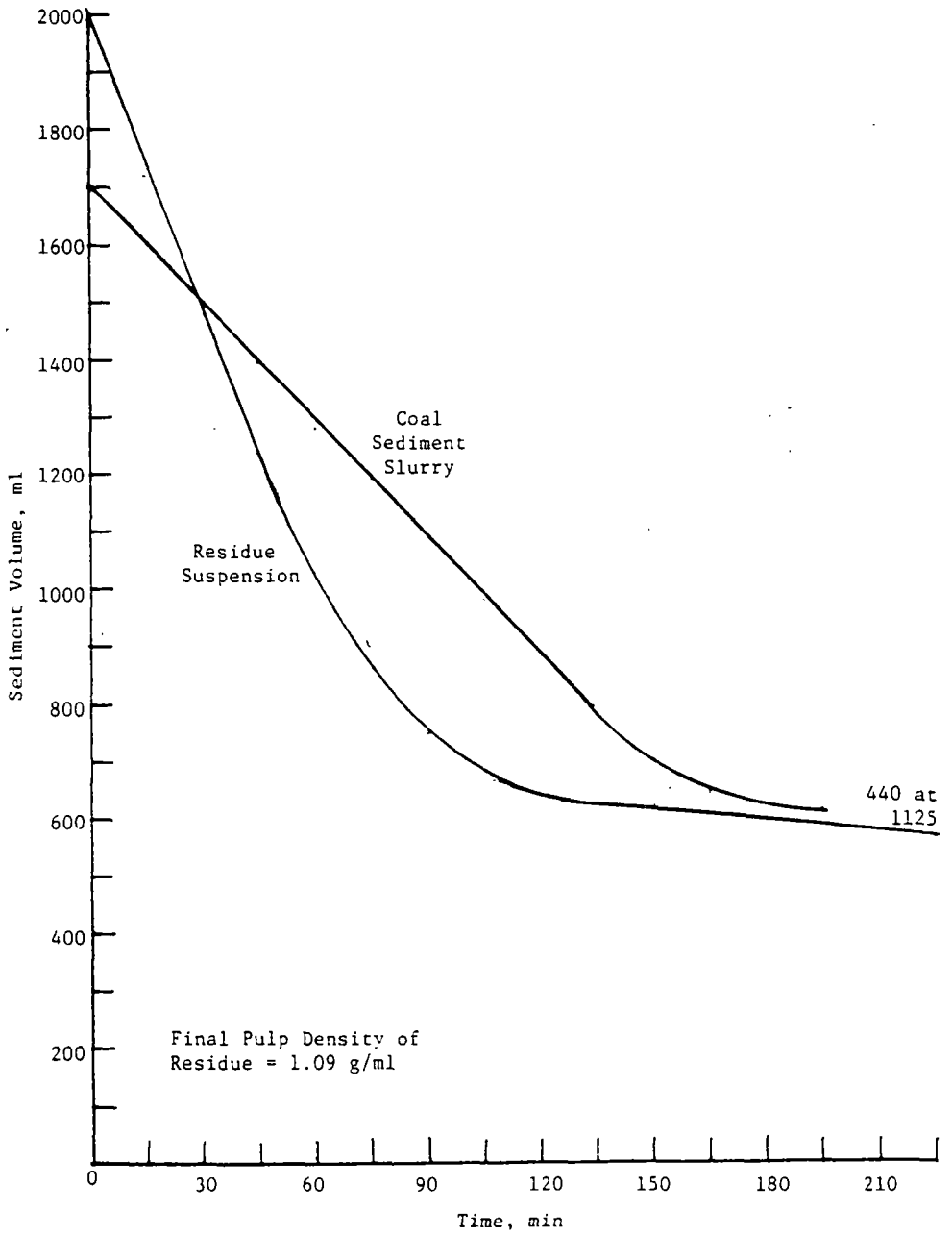

FIGURE 6. SETTLING RATES FOR 10 PERCENT SLURRY OF AGED SEDIMENTS AND THE RESIDUE AFTER REMOVAL OF COAL VALUES BY AGGLOMERATION (20 PERCENT KEROSENE CONCENTRATION)

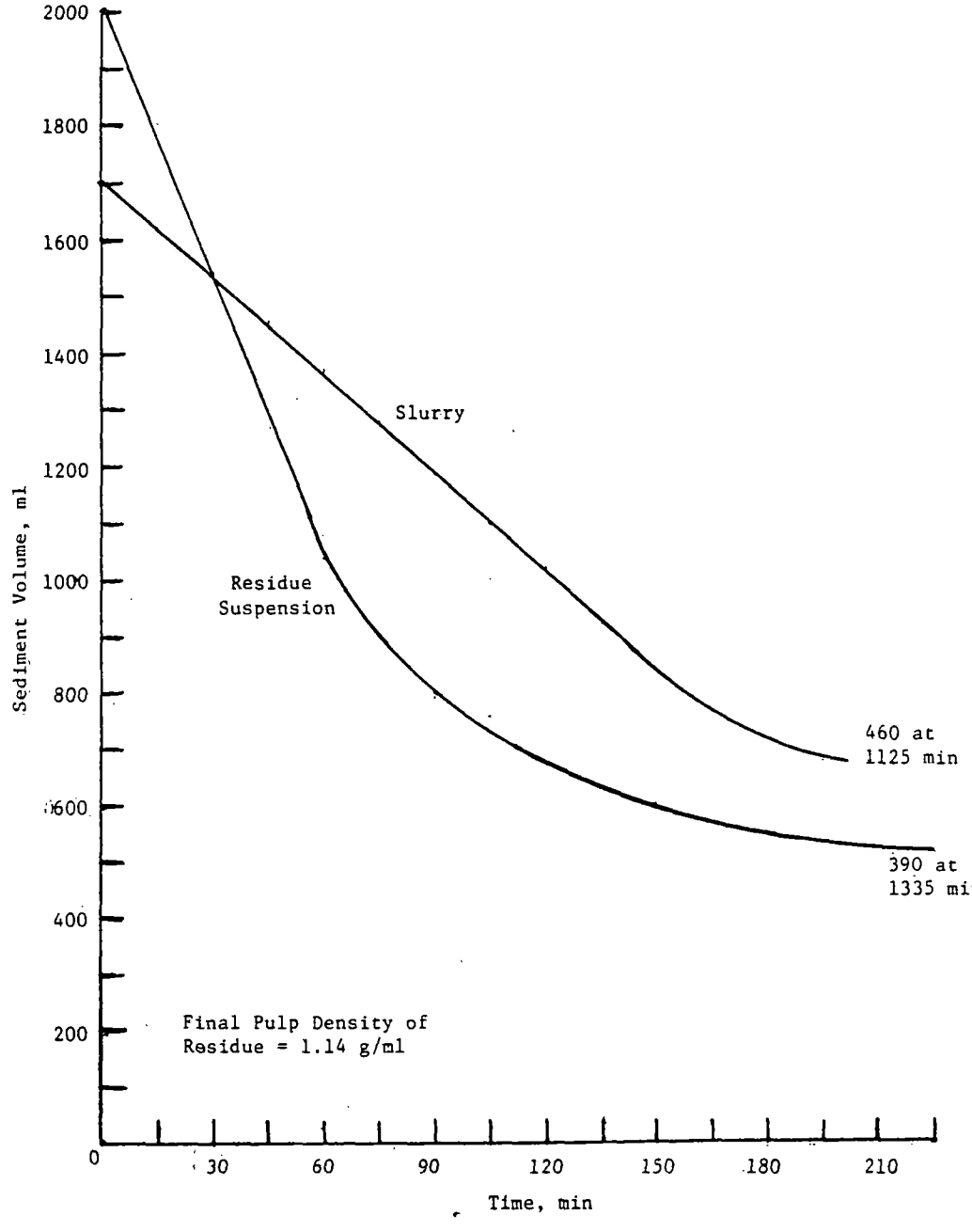

FIGURE 7. SETTLING RATES FOR 10 PERCENT SLURRY OF FRESH BLACK WATER SEDIMENT AND THE RESIDUE AFTER REMOVAL OF COAL VALUES BY AGGLOMERATION (20 PERCENT KEROSENE CONCENTRATION) BULK DENSITY AFTER 3 day = 1.14 g/cc

TABLE 23. ANALYSIS OF RESIDUES FROM AGGLOMERATION

Source of Residue	Composition, percent						
	SiO_2	Al_2O_3	Na_2O	CaO	MgO	K_2O	Fe_2O_3
Aged Sediment	54.4	21.5	0.77	6.07	0.32	1.31	3.49
Fresh Sediment	55.6	24.8	0.71	4.05	0.33	2.55	3.30

The above method, however, suffers from the following uncertainties:

- The CCl_4 does not appear to extract all of the oil present in the residue slurry.
- Some of the oil evaporates together with CCl_4.
- The original sediments may contain oily substances which can be extracted by CCl_4.

Base-line experiments were conducted to determine the amount of No. 2 fuel oil evaporated with CCl_4 at several known oil concentrations. The results indicated that the amount of oil lost during evaporation varied with the oil content. Figure 8 is the calibration curve which shows the relationship between the actual oil content and that measured by the evaporation technique.* In order to find the amount of oily substances in the original samples, the CCl_4-extraction was conducted with the aged slurry sediment. It was found that essentially no oil could be found in the sediment with this technique. Another base-line experiment was carried out to determine the amount of oil which could not be extracted by the CCl_4-extraction. The extraction experiments on the aged slurry sediment mixed with the known amount of No. 2 fuel oil indicated that about 10 percent of the oil could not be extracted by this technique.

* More precise measurements using infrared spectral analysis of the CCl_4 oil solutions are available, but were not applied to these preliminary evaluations.

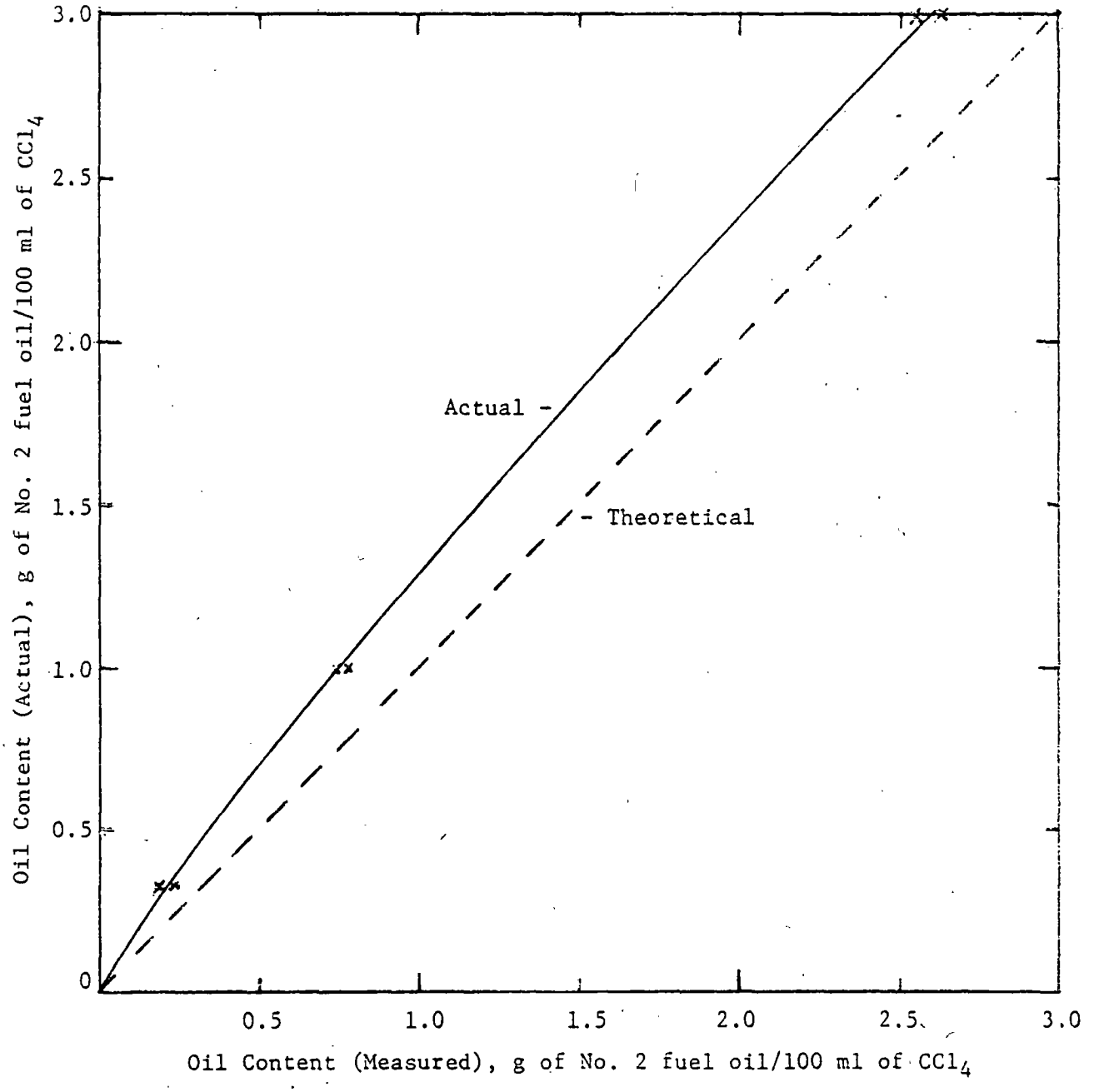

FIGURE 8. CALIBRATION CURVE FOR DETERMINATION OF OIL CONTENT BY CCl_4-EXTRACTION

This modified CCl_4-extraction technique was applied to determine the amount of oil loss to the residue suspension during agglomeration of the aged slurry sediment with No. 2 fuel oil. The results are summarized in Table 24. It is shown that the amount of oil loss in the residue varied depending upon the amount of oil used. The smallest oil loss was 2.24 percent at 10 percent oil concentration. The 20 percent oil concentration resulted in larger oil loss due to the "free" oil unattached to coal particles. At the 5 percent oil concentration, the sizes of agglomerated coal were so small that some of the coal was lost into the residue and oil was carried with it.

Staged Washing of Agglomerated Coal

Min[3] suggested that resuspension of the recovered agglomerated coals in water can be effective in further reducing the ash content of the recovered coal as well as producing large size, strong agglomerates of the coal. The washing technique consisted of performing an agglomeration of a 10 percent slurry using a 10 percent oil concentration and then placing the entire mixture into an air-float cell (60 mm ID x 300 mm tube fitted with a fritted glass disc at the bottom). A very slow flow of air bubbles lifted the agglomerated coal to the top of the cell where it was removed with a screen. Once all of the coal fraction had been collected it was either dried and analyzed or it was resuspended in clean water and air floated a second time and recovered.

The results of these air float washings are given in Table 25. The single stage washing gave only a minor improvement in the ash content (8.90 vs. 9.11 percent) of the coal recovered from the aged sediment and the 85 percent coal recovery was significantly lower than the 97 percent recovery obtained by the usual procedure. A significant improvement in ash in the recovered coal was obtained in the two stage washing (5.66 vs. 8.90 percent) at only a slightly lower coal recovery than in the single stage washing (80 vs. 85 percent). (No. 2 fuel oil and kerosene containing 1 percent palmitic acid did not offer any improvement in the two stage washings.) The pyritic sulfur in the recovered coal after the second

TABLE 24. AMOUNT OF OIL LOST TO THE RESIDUE SLURRY DURING AGGLOMERATION[a] OF THE AGED SLURRY SEDIMENT

Oil Used		Oil Content (experimental), g Oil/100 ml CO_4	Oil Content[b] (corrected), g Oil/100 ml CO_4	Oil Extracted, g	Total Oil[c] in Residue, g	Oil Loss in Residue, %
g	Conc., %					
1.25	5	0.0332	0.05	0.125	0.139	11.12
2.5	10	0.0156	0.02	0.05	0.056	2.24
5.0	20	0.0590	0.10	0.25	0.278	5.56

(a) 250 g of slurry (10% slurry concentration) was agglomerated with No. 2 fuel oil

(b) Oil content is corrected according to the calibration curve (Figure 9).

(c) Total amount of oil in the residue is estimated as $\frac{\text{oil extracted (g)}}{0.9}$.

TABLE 25. EFFECT OF SECONDARY WASHING OF COAL RECOVERED BY AGGLOMERATION[a]

Oil Used[a]	Single Stage Wash			Two Stage Wash		
	Product, percent		Coal Recovery, percent	Product, percent		Coal Recovery, percent
	Of Feed	MF Ash		Of Feed	MF Ash	
Aged Sediment						
Kerosene	50.8	8.90	85	46.2	5.66	80
No. 2 fuel oil[b]	--	--	--	41.0	5.22	71
Kerosene[b]	--	--	--	45.8	5.40[c]	80
Black Water Sediment						
Kerosene	50.4	8.15	94	48.1	5.78	92

(a) Slurry concentration, 10 percent; oil concentration, 10 percent.

(b) Oils contain 1 percent palmitic acid.

(c) For coal recovered S_{total} = 3.38 percent, S_{pyr} = 1.05 percent (MAF).

washing was about one-half of that obtained in coal recovered by the conventional method (1.05 vs. 1.98 percent).

The results from the experiment using fresh black water sediments were better. Coal recovery after two stage air float washing was 92 percent and the ash content of the recovered coal was 5.78 percent which is significantly lower than the 8.16 percent ash for a coal recovery of 94 percent using the usual agglomeration technique.

ENHANCEMENT OF PYRITE REMOVAL

Because of similarity in the surface characteristics of coal and pyrite (i.e., both are hydrophobic), oil agglomeration faces difficulty in removing pyritic sulfur from coal. The earlier study by Sun and McMorris[16] showed that the oil agglomeration process was very effective for recovery of low ash coal but the reduction in sulfur content was negligible. The Bureau of Mines recent study[7] also confirmed that the agglomeration process provided only limited sulfur reduction. Thus, in order to enhance pyrite removal during oil agglomeration, it is necessary to modify the surface characteristics of pyrite to become hydrophilic.

There are many chemicals which are considered to be good pyrite depressants in the flotation practice of sulfide minerals. They include lime, cyanides, permanganates, sodium sulfite or sulfide, etc. The effectiveness of these chemicals during agglomeration of coal had been tested by Cape et al.[17] and Min.[3] The results showed that these chemicals provided only limited success on depressing pyrite. The preliminary work in earlier phases of this program[2] also confirmed that the pyrite depressants tried did not improve the separation of pyrite from coal significantly. This ineffectiveness may be due to the highly porous structure of coal. The coal particles may adsorb the depressing agents rapidly before they can alter the surface property of pyrite particles. Hence, an excessive amount of depressing agents may be needed to affect the pyrite. In general, however, the use of excessive agents deteriorates coal recovery.

Instead of using the conventional pyrite depressants, other approaches have been studied to alter the surfacial characteristics of the pyrite. Capes, et al.[17] showed that the surface of the pyrite could become

hydrophilic during grinding in a slurry containing iron-oxidizing bacteria, Ferrobacillus-Thiobacillus group. More than 90 percent of the pyritic sulfur could be removed after such a treatment. It was postulated that the surface of the pyrite particles were oxidized by bacterial action rendering hydrophilic surfaces. On the other hand, Min[3] reported that the surface of the pyrite could also be altered by mild chemical treatments in an aqueous alkaline solution with air at elevated temperature. Presumably the surface oxidation of pyrite in water led to the formation of a film of hydrated ferric oxide which reduced the floatability of the pyrite.

During this screening study, the following alternative approaches were tried to find an effective method which could selectively alter the pyrite surface to become hydrophilic:

- Aqueous oxidation treatment
- Electrolytic treatment
- Microwave treatment
- Wetting-agent treatment

The approaches and results are described in the subsequent sections.

Aqueous Oxidation Treatment

Unheated Treatments--

Pretreatment of the coal with a pyrite depressant at 25 C was done before any attempt at agglomeration. Known pyrite depressants were used at concentrations of 5×10^{-4} g per g of coal (or one lb per ton of coal) or less. An attempt was also made to pretreat coal with ferric sulfate solution under conditions more mild than the TRW-Meyers process which is known to react with pyrites.[1] When this was done, the coal was separated by filtration before agglomeration was attempted. The slurry pH was adjusted to a specied value before agglomeration with dilute sodium hydroxide or sulfuric acid solutions. Studies on the use of depressants to improve pyrite removal were done using kerosene with a loading of 20 percent of the dry coal weight and a blending time of 2.5 minutes to accomplish the agglomeration. The results of the experiments on the effect of chemical treatment at 25 C on pyrite removal during agglomeration are given in Table 26.

In Table 27, the reduction of pyritic sulfur of untreated and

TABLE 26. RESULTS OF CHEMICAL PRETREATMENT AT 25 C ON PYRITE SEPARATION FROM ILLINOIS NO. 6 COAL DURING AGGLOMERATION (25 Grams Coal in 225 Grams Water)

Experiment No.	Mesh Size	Pretreatment of Coal: Agent	Pretreatment of Coal: Amount ml/25 g Coal	Pretreatment of Coal: Time, min	Pretreatment of Coal: Temp., C	Agglomeration Conditions: Oil Type[a]	Agglomeration Conditions: Oil Charge, g	Agglomeration Conditions: Time, min	Agglomeration Conditions: pH	Product, percent: Feed	Product, percent: MF Ash[b]	Product, percent: MAF[c] S_{TOT}	Product, percent: MAF[c] S_{PYR}	Residue, percent: Feed	Residue, percent: MF Ash[b]	Residue, percent: MAF[c] S_{TOT}	Residue, percent: MAF[c] S_{PYR}
Feed Coal	-14										14.0	5.93	3.12				
60	-14	NaOCl Solution	4.0	0.5	25	A	7.5	0.5	10.8	10.8	9.47	4.64	2.33	84.8	12.7	5.20	2.41
62	-14	NaOCl Solution	0.4	10.7	25	A	5.0	2.5	10.7	58.4	7.92	4.38	1.67	39.2	15.0	5.45	2.73
65	-14	2N $Fe_2(SO_4)_3$	150[d]	15	25	A	5.0	2.5	2.3	2.0	6.51	3.75	2.02	96.0	11.7	4.84	2.32
66	-14	2N $Fe_2(SO_4)_3$	150[d]	60	25	A	5.0	2.5	2.3	1.6	--	--	--	93.2	--	--	--
67	-14	2N $Fe_2(SO_4)_3$	150[d]	15	25	A	5.0	2.5	11.0	3.2[e] 33.2[f]	8.34 8.67	4.10 4.23	1.51 1.50	52.0	14.0	5.09	2.42
70	-14	.1N $Fe_2(SO_4)_3$	2.0	0.5	25	A	5.0	2.5	4.0	63.6	8.82	4.62	1.80	32.4	16.6	5.60	2.82
71	-14	.1N $Fe_2(SO_4)_3$	2.0	2.5	25	A	5.0	2.5	4.0	56.4	8.15	4.68	1.83	39.2	17.4	6.00	3.19
72	-14	.1N $Fe_2(SO_4)_3$	150[d]	15	25	A	5.0	2.5	2.3	24.8	7.42	4.21	1.62	70.4	12.6	5.07	2.49
74	-14	.1N $Fe_2(SO_4)_3$	2.0	15	25	A	5.0	2.5	4.5	44.0	8.06	4.52	1.79	53.2	14.7	5.48	2.81
75	-14	.1N $Fe_2(SO_4)_3$	2.0	15	25	A	5.0	2.5	10.9	0.4	--	--	--	101.6	--	--	--
76	-14	.1N $Fe_2(SO_4)_3$	2.0	15	25	A	5.0	2.5	7.4	23.6	7.59	3.78	1.44	72.8	13.1	4.76	2.60
77	-14	.1N $Fe_2(SO_4)_3$	2.0	15	25	A	5.0	2.5	4.4 to 8.0 8.0 to 6.2	9.2	--	--	--	87.6	--	--	--
78	-14	NaOH	150[d]	15	25	A	5.0	2.5	10.7	72.0	8.24	4.51	1.80	26.8	20.96	6.91	3.94
79	-14	0.1M $K_4Fe(CN)_6$	3.0	15	25	A	5.0	2.5	4.6	68.8	7.93	4.39	1.52	29.2	19.2	6.24	3.44
80	-14	0.1M $K_3Fe(CN)_6$	4.0	15	25	A	5.0	2.5	4.4	61.6	8.27	4.37	1.65	36.8	16.6	6.09	3.01
1	-14	.1N $Fe_2(SO_4)_3$	150[d]	15	25	A	5.0	2.5	2.1	2.0	--	--	--	97.6	--	--	--
Feed Coal	-48										12.9	5.75	2.89				
2	-48	.1N $Fe_2(SO_4)_3$	150[d]	15	25	A	5.0	2.5	2.3	0.4	--	--	--	94.8	--	--	--
3	-48	.1N $Fe_2(SO_4)_3$	2	15	25	A	5.0	2.5	5.2	85.6	7.47	4.59	1.99	9.6	40.5	11.06	8.53
4	-48	0.1M $K_4Fe(CN)_6$	3	15	25	A	5.0	2.5	5.3	83.5	8.08	4.54	1.89	12.8	33.9	9.64	7.38
5	-48	0.1M $K_3Fe(CN)_6$	4	15	25	A	5.0	2.5	5.2	94.0	7.81	4.43	1.81	7.6	53.6	20.3	17.0
6	-48	0.1M $K_4Fe(CN)_6$	3	15	25	A	5.0	2.5	5.2	94.8	7.81	4.52	1.87	7.6	53.7	19.9	17.2
8	-48	NaOH	150	15	25	C	5.0	2.5	5.4	86.4	8.62	5.01	2.11	7.6	41.3	8.93	6.39

(a) Oil types: A = Kerosene; B = No. 2 Fuel Oil; C = Tetralin

(b) MF = Moisture-Free basis

(c) MAF = Moisture- and Ash-Free basis

(d) Pretreatment of coal in separate vessel and filtered before use in agglomeration

(e) Separation on 28 mesh sieve

(f) Separation on 48 mesh sieve.

TABLE 27. EFFECTIVENESS OF DEPRESSANTS FOR REMOVAL OF PYRITE FROM ILLINOIS NO. 6 COAL DURING AGGLOMERATION COMPARED TO RESULTS FROM FLOAT-SINK ANALYSIS

	Mesh Size	Pretreatment of Coal	Product (Float)				Residue (Sink)				Pyritic Sulfur Reduction, %
			% Recovered	MF[a] Ash, %	MAF,[b] % S_{TOT}	MAF,[b] % S_{PYR}	% Recovered	MF Ash, %	MAF, % S_{TOT}	MAF, % S_{PYR}	
Feed Coal	-14	---	--	14.0	5.93	3.12	--				
Agglom. 41[c]	-14	None	43.6	9.18	4.43	1.56	49.2	13.8	5.52	2.70	50
Agglom. 61	-14	pH 10.7	64.8	7.97	4.18	1.62	32.8	21.1	6.48	3.56	48
Agglom. 70	-14	2 ml, 0.1N $Fe_2(SO_4)_3$ 30 seconds	63.6	8.82	4.62	1.80	32.4	16.6	5.60	2.82	42
Agglom. 79	-14	3 ml, 0.1M $K_4Fe(CN)_6$ 15 min	68.8	7.93	4.39	1.52	29.2	19.2	6.24	3.44	51
Float-Sink Analysis	-14	1.9 specific gravity	94.1	9.77	3.89	1.28	5.9	51.3	37.5	25.9	59
Feed Coal	-48	---	--	12.9	5.75	2.89	--				
Agglom. 50	-48	None	84.4	7.83	4.15	1.53	10.0	42.3	17.4	14.4	47
Agglom. 3	-48	2 ml, 0.1N $Fe_2(SO_4)_3$ 15 min	85.6	7.47	4.59	1.99	9.6	40.5	11.1	8.53	31
Agglom. 6	-48	3 ml, 0.1M $K_4Fe(CN)_6$ 15 min	94.8	7.81	4.53	1.87	7.6	53.7	19.9	17.2	35
Float-Sink Analysis	-48	1.9 specific gravity	93.3	9.32	3.87	1.09	6.7	49.7	40.10	34.5	62

(a) MF = Moisture Free basis

(b) MAF = Moisture and Ash Free basis

(c) All agglomerations were performed with kerosene using 20 percent of the weight of the coal feed.

pretreated coal are compared to the reduction attainable from float sink analysis for the two coal sizes studied. These data suggest that of the reagents tried with the coarser coal, only potassium ferrocyanide seemed to give good coal recovery and pyrite separation. However, it does not attain the performance of float-sink separation. The next best system appears to be the adjustment of the pH of 10 to 11. Potassium ferrocyanide exhibited similar improvements in coal recovery and pyrite removal for the minus 48 mesh coal. Although these improvements with the finer coal are significant, they do not match the separation possible at a specific gravity of 1.9. This is especially true for pyrite in the residue. It should be noted that ash remaining with coal after agglomeration treatment is less than that obtained by the float-sink separation. In all but the experiment in which potassium ferrocyanide was used, the amount of misplaced coal may account for this effect.

Solutions with concentrations typical of that used by the TRW-Meyers process (i.e., 2 Normal) were used to treat the coal for period of 15 and 60 minutes but with no heating. The intent of these experiments was to attack the surface of the pyrites through the same reaction that consumes them during the TRW-Meyers process. It was found that the hydrophobic character of the coal was destroyed, essentially no agglomeration occured under conditions known to be successful, and more than 90 percent of the coal passed through the screen (Experiments 65, 66, and 67, Table 26). Even solutions of 0.1N $Fe_2(SO_4)_3$ caused the coal to be wetted by water. By decreasing the dosage to only 2 ml of 0.1N Fe_2SO_4 per 25 g of coal (0.6 g $Fe_2(SO_4)_3$/100 g) only slight improvements were noted. Adjustment of the pH to 10.9 compounded the hydrophylic effect probably because the absorbed ferric ion on the coal surface formed the hydroxide. (The effect of acid was not investigated.)

In those experiments where agglomeration gave 80 percent coal recovery or better, the water occluded in the coal-kerosene agglomerate was about 46 percent of the wet cake. This amount was reduced to 24 by only mechanical action (kneading on the screen).

Heated Treatments--

The jib-washed coal samples from Illinois No. 6 described earlier

were ground to minus 48 mesh and pretreated in an aqueous slurry before oil agglomeration. Figure 9 shows the apparatus used for this treatment step. One hundred grams of ground coal was mixed with 400 ml of distilled water in a 500 ml gas washing bottle and a small amount of chemical was added. The slurry was agitated with a magnetic stirrer and heated by an electrical heating tape. After the temperature reached above 90 C, air bubbles were introduced through a porous glass plate at about 400 cc/min for 30 minutes. The reaction temperature was maintained about 90 C and a condenser was mounted above the reactor to prevent loss of water by evaporation.

After the pretreatment, the slurry was diluted to 10 percent slurry concentration by adding distilled water and cooled to room temperature. One-quarter of the slurry was taken and agglomerated with 5 g of kerosene. With each pretreated slurry, three agglomeration runs were made at acid, neutral and basic pH values by adjusting with either hydrochloric acid or sodium hydroxide solution. The experimental results are summarized in Table 28. The data show that the aqueous oxidation treatments significantly improved pyrite removal during agglomeration as compared with the untreated coal samples (Run #24). However, the observed differences in sulfur reduction among the different chemical conditions are too small to choose which condition is the best for treating the pyrite. It appears that the adjustment of pH after the chemical treatment did not have any marked effect on the agglomeration results.

Another series of aqueous oxidation treatments were carried out with the jig-washed coal sample from Ohio Pittsburgh Seam No. 8 coal to examine the effects of wider variety of chemical conditions. The apparatus and experimental procedures were the same as the previous runs except that the treated slurry was agglomerated with 2.5 g of No. 2 fuel oil. Table 29 summarizes the pretreatment conditions and the agglomeration results. For the sake of comparison, a float-sink analysis of the same coal (minus 48 mesh) at 1.59 specific gravity is also shown in the table. Since the specific gravity of pyrite is about 5.0, the float fraction at the specific gravity 1.59 is supposed to be free from liberated pyrite and the remaining pyrite represents that locked in the coal matrix. Hence, the pyritic sulfur reduction obtained by the 1.59 specific gravity float was set as the attainable goal by the oil agglomeration technique.

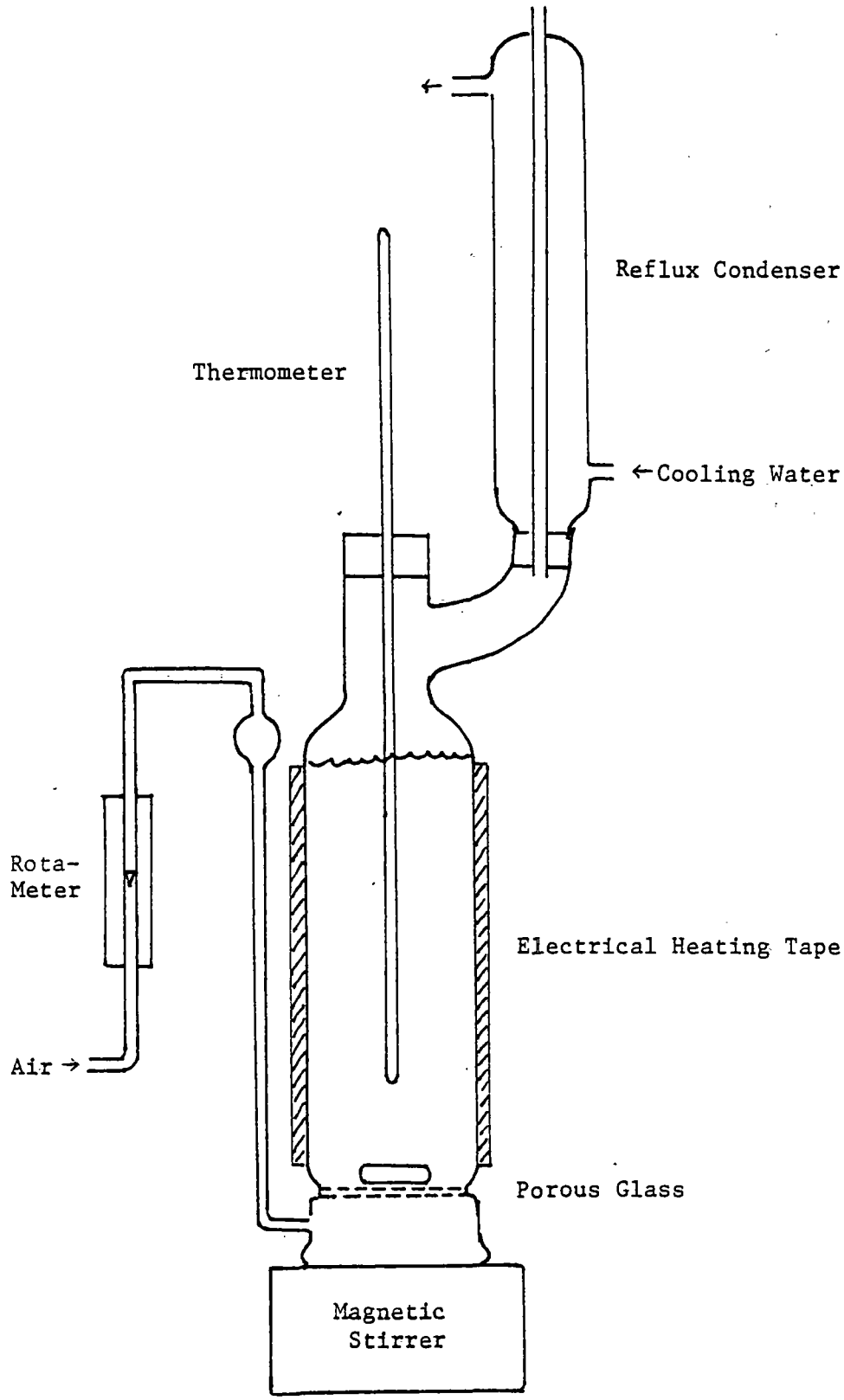

FIGURE 9. EQUIPMENT FOR CHEMICAL PRETREATMENT OF A COAL SLURRY

TABLE 28. EFFECT OF AQUEOUS OXIDATION PRETREATMENT ON PYRITE REMOVAL DURING OIL AGGLOMERATION OF ILLINOIS NO. 6 COAL (FRESH GROUND)

Run No.	Chemical Agent 0.5 g/100 g coal	pH	Product, percent: Of Feed	MF Ash	MAF S_{Tot}	MAF S_{Pyr}	Reduction, percent: Ash	S_{Tot}	S_{Pyr}
Feed coal				11.3	4.07	1.36			
24-1	None	4.3	98.0	8.70	3.79	1.27	23.0	6.9	6.6
-2	None	7.4	94.0	9.02	--	--	--	--	--
-3	None	9.0	97.7	9.15					
7-1	Air	5.3	94.0	7.64	3.53	1.00	32.4	13.3	26.5
-2	Air	7.2	90.9	7.78	3.56	1.00	31.2	12.5	26.5
-3	Air	8.9	87.8	7.82	3.61	1.15	30.8	11.3	15.4
12-1	Na_2S+Air	7.2	92.1	7.50	3.74	1.01	33.6	8.1	25.7
-2	Na_2S+Air	5.0	91.6	7.30	--	--	35.4	--	--
-3	Na_2S+Air	8.9	83.9	7.32	--	--	35.2	--	--
14-1	$Fe_2(SO_4)_3$+Air	3.1	93.7	8.05	3.58	1.08	28.8	12.0	20.6
-2	$Fe_2(SO_4)_3$+Air	5.1	91.3	8.20	--	--	27.4	--	--
-3	$Fe_2(SO_4)_3$+Air	6.9	94.3	8.41	--	--	25.6	--	--
16-1	$NaHCO_3$+Air	7.0	87.1	7.63	3.51	1.03	32.5	13.8	24.3
-2	$NaHCO_3$+Air	5.1	93.1	7.70	--	--	31.9	--	--
-3	$NaHCO_3$+Air	9.1	92.4	8.04	--	--	28.8	--	--
22-1	$(NH_3)_2CO_3$+Air	7.8	95.4	8.03	3.76	1.06	28.9	7.6	22.1
-2	$(NH_3)_2CO_3$+Air	5.2	86.6	7.62	--	--	32.6	--	--
-3	$(NH_3)_2CO_3$+Air	8.8	92.6	7.78	--	--	31.2	--	--
27-1	Na_2O_2+Air	8.3	90.5	7.72	3.70	0.98	31.7	9.1	27.9
-2	Na_2O_2+Air	5.1	92.3	7.77	--	--	31.2	--	--
-3	Na_2O_2+Air	6.9	91.2	7.78	--	--	31.2	--	--

TABLE 29. EFFECT OF AQUEOUS OXIDATION PRETREATMENT ON PYRITE REMOVAL DURING OIL AGGLOMERATION OF OHIO PITTSBURGH SEAM NO. 8 COAL

Run No.	Chemical, g/100 g coal	Temp., C	Time, min	pH	Product, percent Of Feed	MF Ash	MAF S_{Tot}	MAF S_{Pyr}	Reduction, percent Ash	S_{Tot}	S_{Pyr}
Feed Coal						10.50	5.25	2.24			
Float at 1.59 Sp. Gr.					95.4	8.69	4.22	1.30	17.2	19.6	42.0
44-1	None			6.7	97.2	7.44	4.89	2.32	29.1	6.9	(-3.6)
46-1	Air	RT	900	7.2	96.5	6.50			38.1		
41-1	Air	96	30	8.3	95.1	6.16	4.19	1.65	41.0	20.2	26.3
89-1	O_2	RT	30	3.7	96.4	6.98	4.18	1.57	33.5	20.4	29.9
91-1	O_2	92	30	2.9	96.5	6.91	4.20	1.63	34.2	20.0	27.2
97-1	Na_2S (0.1)	RT	30	4.7	96.8	6.68	4.19	1.54	36.3	20.2	31.3
7-1	Na_2S (0.1)	95	30	4.0	95.8	6.62	4.22	1.58	36.9	19.6	29.5
52-1	Air + Na_2S (1.0)	RT	900	9.7	95.6	6.03	4.15	1.51	42.5	21.0	32.6
48-1	Air + Na_2S (1.0)	96	30	10.9	94.1	5.84	4.17	1.49	44.3	20.6	33.5
93-1	O_2 + Na_2S (0.1)	RT	30	4.7	96.0	6.67	4.09	1.48	36.4	22.1	33.9
99-1	Na_2CO_3 (0.1)	RT	30	4.5	96.0	7.13	4.12	1.93	32.1	21.5	13.8
9-1	Na_2CO_3 (0.1)	99	30	3.7	95.6	6.53	3.95	1.39	37.8	24.8	37.9
95-1	O_2 + Na_2CO_3 (0.1)	RT	30	4.5	96.4	6.86	4.04	1.35	34.6	23.0	39.7
65-1	Sediment wash water[a]	RT	240	3.8	96.0	6.96	4.24	1.82	33.7	19.2	18.8
74-1	Sediment wash water[a]	RT	5280	2.7	90.5	6.54	4.17	1.57	37.7	20.6	29.9
	Na_2O_2 (1.0) + Air	96	30	11.5	79.6	6.79	4.18	1.65	26.5	20.6	29.9

(a) The sediment wash water was filtrate of the slurry containing 100 g partially dried old coal sediment and 500 ml distilled water.

With reference to Table 29, the following qualitative observations can be made:

1. As compared with the float-sink values, the oil agglomeration products were lower in ash content but higher in pyritic sulfur content. However, the total sulfur contents of the pretreated samples were as low as or lower than that of the float-sink value.
2. All of the pretreatments provided a cleaner product than could be obtained by direct oil agglomeration (Run 44-1).
3. In general, the pyritic sulfur reductions were higher with oxygen treatments than those with air treatments, while the ash reductions were reversed.
4. A comparison of Runs 89-1 and 91-1 indicates that the low temperature provided a higher pyrite reduction than the high temperature. This may be due to the lower solubility of oxygen at higher temperature.
5. In the sodium sulfide treatments (Runs 97-1 and 7-1), a higher pyritic sulfur reduction was obtained at lower temperature. This may indicate that the depressing action of sodium sulfide was caused by adsorption rather than by chemical reaction.
6. The results of Runs 89-1, 97-1 and 93-1 show that the treatment with sodium sulfide and oxygen together provided a higher pyritic sulfur reduction than could be obtained by either one alone. The results of Runs 89-1, 99-1 and 95-1 also show the similar synergetic effect.
7. In the sodium carbonate treatments (Runs 99-1 and 9-1), a higher temperature provided significantly cleaner product. This suggests that the depressing effect of sodium carbonate was apparently caused by chemical reaction.

8. The treatments with sediment wash water, which may contain some iron-oxidizing bacteria, show that prolonged reaction was needed to depress the pyrite.

Electrolytic Treatment

Another approach was the electrolytic pretreatment of a coal slurry prior to oil agglomeration. It was hoped that electrolytic reaction might offer a selective means of modifying the surface characteristics of pyrite particles. The apparatus used for the electrolysis is shown in Figure 10. A stainless steel rod (3/4 in. dia. x 4 in.) was used as a rotating cathode and a sheet of brass or steel (4 x 8-1/2 in.) rolled into a cylinder was used as an anode. The cathode chamber was kept separated from the anode chamber by a porous alundum thimble (1-3/4 in. dia. x 5 in.). A 400 ml beaker was used in all experiments. Coal slurry containing 25 g of the ground Ohio Pittsburgh Seam No. 8 (minus 48 mesh) was electrolyzed for 30 minutes at 10 volt potential and 0.5 ampere limiting current. Electrolysis was carried out in two different configurations: one with the porous thimble in place and the other without the thimble. The treated coal slurry was then agglomerated with 2.5 g of No. 2 fuel oil at 10 percent slurry concentration. Tables 30 and 31 summarize the experimental conditions and agglomeration results. In general, the electrolytic treatments were not as effective as the aqueous oxidation treatments on the pyrite removal during agglomeration. This might be due to the poor reactor configuration in which the oxygen bubbles generated from the anode surface failed to make good contact with the pyrite particles. The best pyrite removal was obtained when sodium carbonate was used as an electrolyte (Run 42-1), but the amount of coal recovery was very low.

Microwave Treatment

Another approach employed was the use of 2450 MHz microwave energy. It was hoped that pyrite particles might be preferentially heated by the microwave energy, thereby modifying their surface characteristics. The ground Ohio Pittsburgh Seam No. 8 coal (minus 48 mesh) in either dry or wet state was exposed to microwave energy under a nitrogen atmosphere in a

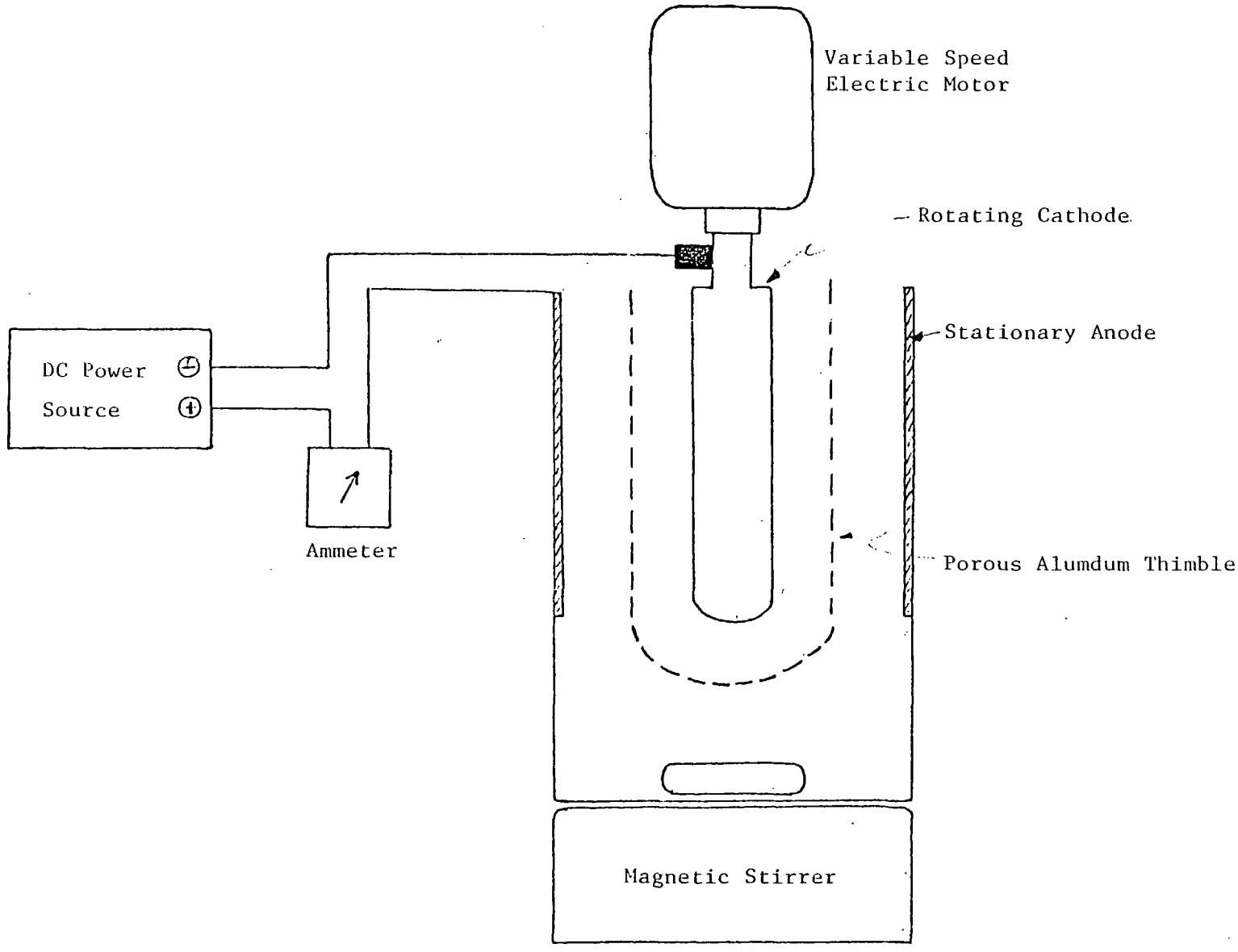

FIGURE 10. EQUIPMENT FOR ELECTROLYTIC PRETREATMENT OF COAL SLURRY

TABLE 30. EFFECT OF ELECTROLYSIS ON THE PYRITE REMOVAL DURING OIL AGGLOMERATION OF OHIO PITTSBURGH SEAM NO. 8 COAL (WITHOUT THIMBLE)

Run No.	Anode	Electrolyte	pH Before	pH After	Product, percent Of Feed	Product, percent MF Ash	Product, percent MAF S_{Tot}	Product, percent MAF S_{Pyr}	Reduction, percent Ash	Reduction, percent S_{Tot}	Reduction, percent S_{Pyr}
Feed Coal						10.50	5.25	2.24			
Float at 1.59 Sp. Gr.					95.4	8.69	4.22	1.30	17.2	19.6	42.0
44-1	No Pretreatment		6.7	6.7	97.2	7.44	4.89	2.32	29.1	6.9	(-3.6)
19-1	Brass	None	3.5	5.3	92.3	7.86	4.31	1.90	25.1	17.9	15.2
19-3	Brass	NaOH[a]	10.0	10.3	95.6	10.21	--	--	2.8	--	--
19-4	Brass	NaOH[a]	7.0	10.0	96.6	10.39	4.62	2.33	1.0	12.0	(-4.0)
34-1	Steel	0.5% NH_4OH	10.8	10.5	89.2	7.73	4.38	1.86	26.4	16.6	17.0
34-2	Steel	0.1% $Fe_2(SO_4)_3$	2.7	2.6	93.7	7.78	4.73	2.13	25.9	9.9	4.9
34-3	Steel	0.1% Na_2S	8.4	8.2	94.6	8.66	4.92	2.17	17.5	6.3	3.1
42-1	Steel	0.03% Na_2CO_3	5.4	6.5	84.3	7.99	4.25	1.48	23.9	19.0	33.9

(a) One molar sodium hydroxide solution was added to adjust the pH.

TABLE 31. EFFECT OF ELECTROLYSIS ON PYRITE REMOVAL DURING OIL AGGLOMERATION OF OHIO PITTSBURGH SEAM NO. 8 COAL (WITH THIMBLE)

Run No.		Content	pH Before	pH After	Product, percent Of Feed	MF Ash	MAF S_{Tot}	MAF S_{Pyr}	Reduction, percent Ash	S_{Tot}	S_{Pyr}
Feed Coal						10.5	5.25	2.24			
Float at 1.59 Sp. Gr.					95.4	8.69	4.22	1.30	17.2	19.6	42.0
44-1			6.7	6.7	97.2	7.44	4.89	2.32	29.1	6.9	(-3.6)
19-11	Anode (brass)	Coal slurry	3.5	5.2	95.3	7.57	4.53	2.08	27.9	13.7	7.1
	Cathode	1 wt. % $CaCl_2$	7.7	12.0							
19-10	Anode (brass)	1 wt. % $CaCl_2$	7.7	5.9							
	Cathode	Coal slurry	3.5	11.8	87.9	8.48	--	--	19.2	-	--
32-1	Anode (steel)	Coal slurry	3.3	2.6	91.7	7.44	4.26	1.94	29.1	18.9	13.4
	Cathode	1 wt. % NaOH	11.9	11.8							
32-2	Anode (steel)	Coal slurry	3.3	2.3	87.3	7.86	4.42	2.01	25.1	15.8	10.27
	Cathode	1 wt. % Na_2S	11.8	11.8							
19-7	Anode (brass)	Coal slurry	3.3	4.0	93.8	7.14	4.16	1.92	32.0	20.8	14.3
	Cathode	Old coal sediment	2.5	3.3	53.5	27.67					
19-5	Anode (brass)	Old coal sediment	2.5	3.8	60.8	20.32					
	Cathode	Coal slurry	3.5	10.8	91.9	9.23	--	--	12.1	--	--

Varian Industrial Microwave Systems Model EW3-DPM35. After treatment, 25 g of coal was taken and agglomerated with 2.5 g of No. 2 fuel oil at 10 percent slurry concentration. Table 32 summarizes the treatment conditions and agglomeration results.

Improvement in pyrite reduction could be noticed when the wet coal impregnated with sodium hydroxide (Run 29-3) was heated by the microwave. One advantage of the microwave treatment is short reaction time, i.e., seconds vs. minutes, and hence this treatment may be suited for continuous pretreatment before oil agglomeration

Wetting-Agent Treatment

Another approach was addition of chemical reagent from the known classes of either wetting or dispersing agents. In the pretreatment step, 100 g of ground coal (minus 48 mesh) was mixed with 400 ml of distilled water and a small amount of reagent. The slurry was agitated with a magnetic stirrer at the room temperature for a specified time. After the pretreatment, one quarter of the slurry was taken and agglomerated with 2.5 g of No. 2 fuel oil at 10 percent slurry concentration.

The specific chemical reagents were chosen for the following reasons:

- Sodium-di-octyl sulfosuccinate and sodium dodecyl sulfate are commonly known as wetting agents. In a U.S. patent by Chia,[18] these agents are claimed to be effective for desulfurizing high sulfur low grade coal.
- Phytic acid and myo-inositol-2-monophosphate are chosen because of their structural similarity with phosphatidal-inositol which is identified as the wetting agent secreted by bacteria during their oxidation of sulfide minerals.[19]
- Sodium metaphosphate, sodium carboxy methyl cellulose and sodium tripolyphosphate are dispersing agents. A U.S. Bureau of Mines study[20] shows that they are effective in dispersing mineral particles during selective flocculation of coal slimes.

TABLE 32. EFFECT OF MICROWAVE TREATMENT ON PYRITE REMOVAL DURING OIL AGGLOMERATION OF OHIO PITTSBURGH SEAM NO. 8 COAL

Run No.	Coal Sample	Microwave Energy, watt	Exposure Time, min	Temp., C	pH	Product, percent: Of Feed	MF Ash	MAF S_{Tot}	MAF S_{Pyr}	Reduction, percent: Ash	S_{Tot}	S_{Pyr}
Feed Coal							10.50	5.25	2.24			
Float at 1.59 Sp. Gr.						95.4	8.69	4.22	1.30	17.2	19.6	42.0
16-1	Dry powder	500	3					4.77	2.22			
		1000	2	238	4.7	96.6	9.10			13.3	9.1	0.9
29-1	Coal + 1% NaOH	500	3	120	10.4	96.8	8.18	4.27	2.14	22.2	18.7	4.5
	Overdried				5.9[a]	96.9	8.12	--	--	22.7	--	-
29-3	Coal + 1% NaOH	500	3	98	11.4	84.5	7.31	4.14	1.69	30.4	21.1	24.6
	Wet paste				6.9[a]	92.5	8.21	--	--	21.8	--	--

(a) pH was adjusted with HCl solution before agglomeration.

Table 33 summarizes the experimental results. The data show that the reagents generally provided cleaner product than could be obtained without the reagent. In particular, the results obtained with sodium metaphosphate are surprisingly good and the product was cleaner than that of 1.59 Sp. Gr. float. Although more work is needed to verify this exceptionally good result, it appears that sodium metaphosphate disperses the liberated pyritic particles to prevent them from being entrapped in the agglomerated coal.

Combined Treatment

An exploratory experiment was conducted to examine the added effectiveness of successive pretreatment steps. One hundred grams of the ground Ohio Pittsburgh Seam No. 8 coal was mixed with 0.1 g sodium carbonate in 300 ml distilled water and electrolyzed without the thimble as described previously. After the electrolysis, the treated slurry was divided into four parts and each part was agglomerated with 2.5 g of No. 2 fuel oil at the following conditions:

1. Agglomeration without further treatment.
2. Agglomeration after mixing with 0.25 ml of 5 percent sodium metaphosphate solution.
3. Same as (2) except after agglomeration, 0.25 ml of 0.1 percent Percol 728 cationic flocculant was added before screening.
4. Same as (3) except sodium metaphosphate solution was added.

The experimental results are shown in Table 34. Except Run 42-4, the data indicate that the agglomerated product became cleaner as more steps were added. The product of Run 42-3 was much cleaner than that of 1.59 Sp. Gr. float.

TABLE 33. EFFECT OF CHEMICAL REAGENT ON PYRITE REMOVAL DURING OIL AGGLOMERATION OF OHIO PITTSBURGH SEAM NO. 8 COAL

Run No.	Reagent, g/100 g coal	Time, min	pH	Product, percent Of Feed	MF Ash	MAF S_{Tot}	MAF S_{Pyr}	Reduction, percent Ash	S_{Tot}	S_{Pyr}
Feed Coal					10.50	5.25	2.24			
Float 1.59 Sp. Gr.				95.41	8.69	4.22	1.30	17.2	19.6	42.0
44-1	None		6.7	97.2	7.44	4.89	2.32	19.5	6.9	(-3.6)
56-1	Sodium-dioctyl sulfosuccinate (0.2)	100	7.3	96.6	6.98	4.20	1.61	24.5	20.0	28.1
58-1	Sodium dodecyl sulfate (0.2)	100	7.3	96.0	8.05	4.37	1.77	12.9	16.8	22.0
62-1	Phytic acid calcium salt (0.2)	100	6.8	96.2	6.37	4.37	1.73	31.1	16.8	22.8
60-1	Myo-inositol-2-monophosphate (0.0004)	3900	4.8	92.5	6.61	4.44	1.77	28.5	15.4	22.0
1-1	Sodium metaphosphate (0.5)	30	4.2	94.0	6.39	4.10	1.29	30.8	21.9	42.4
3-1	Sodium carboxy methyl cellulose (0.1)	30	4.1	95.2	7.85	4.23	1.60	15.0	19.4	28.6
5-1	Sodium tripolyphosphate (0.5)	30	5.1	97	6.96	4.31	1.68	24.7	17.9	25.0

TABLE 34. EFFECT OF COMBINED TREATMENT ON OIL AGGLOMERATION OF OHIO PITTSBURGH SEAM NO. 8 COAL

Run No.	Treatment	Product, percent				Reduction, percent		
		Of Feed	MF Ash	MAF S_{Tot}	MAF S_{Pyr}	Ash	S_{Tot}	S_{Pyr}
Feed			10.50	5.25	2.24			
Float at 1.59 Sp. Gr.		95.4	8.69	4.22	1.30	17.2	19.6	42.0
42-1	Electrolysis	84.3	7.99	4.25	1.48	23.9	19.0	33.9
42-2	Electrolysis + sodium metaphosphate	86.1	7.21	4.12	1.38	31.3	21.5	38.4
42-3	Electrolysis + sodium metaphosphate + Percol 728	85.0	6.55	3.99	1.26	37.6	24.0	43.8
42-4	Electrolysis + Percol 728	86.5	10.19	--	--	3.0	--	--

SECTION 6

DISCUSSION

COAL RECOVERY FROM WASTE STREAMS

The coal mining industry is under constant pressure to limit the effluents from coal mining and preparation operations and coal refuse handling and water management are two areas of immediate concern for the industry. Laws regulating pollution control and tailing water runoff exist. The ultimate goal is to produce clear water for reuse in the preparation plant, while the undesirable solids end up as a dry manageable solid that can be disposed of as a landfill or as mine backfill to reduce acid mine drainage. The less coal present in this solid, the more attractive it is with respect to minimizing environmental impact and land requirements for disposal while maximizing the recovery of a valuable fuel from what usually is considered a waste.

As mentioned at the beginning of this report the present strategy is to impound fine coal cleaning wastes in slurry ponds to permit sufficient residence time for settling to occur before the water is discharged to natural waterways or reused. This approach has resulted the accumulation of billions of tons of refuse in active and abandoned waste piles and impoundments. A greater accumulation is anticipated as mining and coal cleaning activity increase to meet the Nation's increasing dependence on coal.

The results from this study on the recovery of coal from fine (minus 28 to 0 mesh) coal cleaning wastes suggest that good coal recovery from sediments by the oil agglomeration technique is technically feasible. The technique can be applied to black water and aged slurry pond sediments directly, but partially dried and weathered sediments excavated from slurry ponds require modest treatment before coal recovery is attempted. This study has identified what appears to be the conditions to recover 90 percent

or more of the coal value from wastes containing about 50 percent coal for one small region in southeastern Ohio. Even within this region it was found that conditions for recovery of coal values from black water sediments are slightly different from those used for recovery of aged sediments. This was due in part to recent changes in the coal cleaning plant unit operations which produced a much finer suspension making the waste stream more responsive to coal recovery by the oil agglomeration technique. What is even more significant is that the technique can be modified slightly and applied to aged sediments as well for recovery of a quality fuel without the associated mining costs.

The quality of the coal recovered* from aged slurry pond sediments and black water sediments compared to that presently being shipped from the mine (after jig washing) is given in Table 35. The quality of the dryer product is also included to give a comparison to fine coal. It can be seen that the recovered coals are lower in ash and sulfur and generally of better quality than the coal shipped from the mine. In addition the recovered coal can be dewatered easily. The residues from the operations retain only about 2 to 5 percent of the agglomerating oil used and consist of about 92 percent ash. Their mineral composition probably consists of the unaltered major minerals normally associated with coal (i.e., illites, kaolinite, montmorillonite, quartz, gypsum, pyrite, calcite, dolomite, siderite) and possibly many of the minor minerals (and the trace elements commonly associated with them). Indications are that some of the pyrites liberated from the coal in the wastes are removed in the process. Chemical treatment of the slurry by techniques developed for reducing the pyrites in the coal (discussed later) could be used to further reduce the pyritic sulfur in the recovered coal.

Since the residues from the coal recovery operation consist mostly of unaltered mineral matter taken from the earth, they would be compatible with any landfill disposal method. The residue slurry settles rapidly and can be concentrated by settling. Since it now consists mostly of clays, technology developed to improve settling of such materials could be applied

* Using agglomeration technique without chemical treatment for enhanced pyrite removal.

TABLE 35. COMPARISON OF QUALITY OF COAL RECOVERED FROM SEDIMENTS TO CLEANED COAL

Coal Product	MF Ash, %	MAF Sulfur, %	
		Pyr	Total
Shipped Clean Coal[a]	9.24	2.04	4.88
Dryer Product[b]	9.84	1.71	4.97
Recovered from Sediment from Slurry Pond (Avg)[c]	8.89	1.70	3.40
Recovered from Sediment from Black Water (Avg)[c]	6.13	1.41	3.66

(a) Jig cleaned.

(b) Fines before mixing for shipping.

(c) Average of values for high coal recovery-high ash, high recovery-low ash, and low recovery-low ash.

more specifically through the use of flocculants and/or coagulants. The material also may be used as raw material directly (e.g., for ceramic products) or as a source of mineral for metal recovery (e.g., alumina).

In addition to the coal recovery from the slurry wastes, the oil agglomeration technique can be utilized for cleaning and dewatering of fine coal. For example, oil agglomeration can provide more effective means of cleaning ultrafine coal than the froth flotation. It was demonstrated in Germany that the use of the oil agglomeration process for the minus 250 mesh coal improved the capacity and selectivity of fine coal cleaning circuit, and the product was easy to filter, rendering low moisture content.[9] If the coal cleaning industry adopts new desulfurization techniques such as high-gradient magnetic separation, chemical treatments and bacterial treatments in which the coal sizes are required to be very small for effective treatment, the oil agglomeration technique will be a viable means of isolating and dewatering of the desulfurized product. Furthermore, if the use of coal-oil mixture becomes widely accepted in commercial boilers, the oil agglomeration technique will be an ideal method of coal cleaning because the oil used for agglomeration will not represent any additional cost and the agglomerated product can be readily dispersed in the oil.

PREPARATION OF COAL FEED TO LIQUEFACTION PLANTS

Reports about facilities proposed to prepare clean fuels by liquefaction of coal often skim over the critical aspects of the coal preparation plant operation that prepares the fine coal to be fed into the oil slurry preparation prior to entering the liquefaction process. The coal must be ground to a fine size usually 70 percent minus 200 mesh (0.05 mm) and then mixed with recycle oil to prepare a slurry. Grinding the coal to this size is an extremely dusty operation when done dry but wet grinding is usually ruled out because of the energy required for drying before the coal can be utilized. However, wet grinding would be advantageous for environmental and health reasons.

This study demonstrated that coal can be recovered from fine coal slurries with coal liquid distillates as well as with hydrocarbons derived from petroleum. These agglomerates could be dewatered to levels of

∿ 15 percent. In addition when a coal is ground to minus 200 mesh, significant amount of mineral matter is liberated and can be removed during agglomeration. Thus a process is envisioned where wet grinding can be utilized to remove significant ash from the coal feed before entering the liquefaction step. The feed would be agglomerated with an oil used to prepare the oil slurry feed to the liquefaction process preheater or dissolver. The reduced ash loading would significantly reduce filtration and/or catalyst life problems and reduce trace element emissions in the subsequent gasification of the char or liquefaction residues.

ENHANCEMENT OF PYRITE REMOVAL

These studies have shown that chemical treatment specifically directed at making the surface of pyrite hydrophylic have improved the removal of pyrite liberated from the coal. Pyrite removal of 42 percent has been reached and is equal to that obtained by float-sink separation at a specific gravity of 1.59. This is especially significant for the fine size of the fresh coal evaluated (minus 48 mesh Tyler). The two chemical treatments capable of producing this level of removal are (1) the treatment with oxygen at room temperature of a slurry of coal containing 0.1 g of Na_2CO_3/100 g of coal and (2) the treatment of a coal slurry with 0.5 g of sodium metaphosphate/100 g of coal. In Treatment 1, it is believed that the pyrite surface was oxidized to produce a hydrated ferric oxide layer which renders the surface hydrophylic. When Treatment 2 is used, it is believed that the pyrite surface adsorbed phosphate ion to make them wettable. When the treatment with sodium metaphosphate was preceeded by electrolysis and then followed by the addition of a flocculant, further reductions in pyritic sulfur were realized but in general did not exceed that attainable in laboratory float-sink separations.

ESTIMATION OF PRODUCT COST

The experimental data have shown that the oil agglomeration technique can recover low ash coal from the coal preparation plant wastes. Furthermore, the sulfur content of the agglomerated product can be

significantly reduced through suitable treatments. For the purpose of preliminary estimation of product cost, a conceptual design of an oil agglomeration plant was made. Figure 11 shows a hypothetical flowsheet of the oil agglomeration unit which can be either an add-on unit to an existing coal cleaning plant for the purpose of recovering coal fines from the thickener underflow or a portable plant for reclaiming coal values from the coal waste pond sediments.

The thickener underflow or waste pond sediment containing 35 wt. percent solids is fed to the pretreatment tank where sodium carbonate and air bubbles are introduced to oxidize the slurry. The pretreated slurry is then sent to the conditioning tank where the slurry is diluted to 10 wt. percent solid and sodium metaphosphate is added to provide good dispersion.

The conditioned slurry is pumped to the oil agglomeration tank where oil is added and agglomeration is carried out with a high-shear agitation. After agglomeration is completed, the slurry is transferred to the flocculation tank where flocculating agent is added to facilitate settling of reject materials. The slurry is then sent to a vibrating screen where agglomerated coal is separated from residue slurry. The recovered coal is fed into a dewatering centrifuge to reduce the moisture content. The residue slurry is pumped to a static thickener where reject materials are settled, and water and some oil are recovered for recycling.

The material balances shown in Figure 11 are chosen based on the information obtained from this experimental work. From an economic point of view, one of the most important variables in the process is the amount of oil used. The experimental data have shown that a 5 percent oil concentration will give adequate recovery of coal when the No. 6 fuel oil-kerosene mixture was used (Figure 5). With these values, material costs for the agglomeration process are estimated and summarized in Table 36.

The results show that the total material cost is $11.48/ton of product, of which about 97 percent represents the cost of oil. In addition, cost of power requirement will range from 20 to 30¢/ton of product (@ 2.5¢/kWh). The total capital and fixed costs are approximately $2.00/ton of product.[21] With these economic estimates, the product cost will be about $14/ton. Considering the current market price of coal at $20/ton, it appears that the oil agglomeration process is economically viable in the

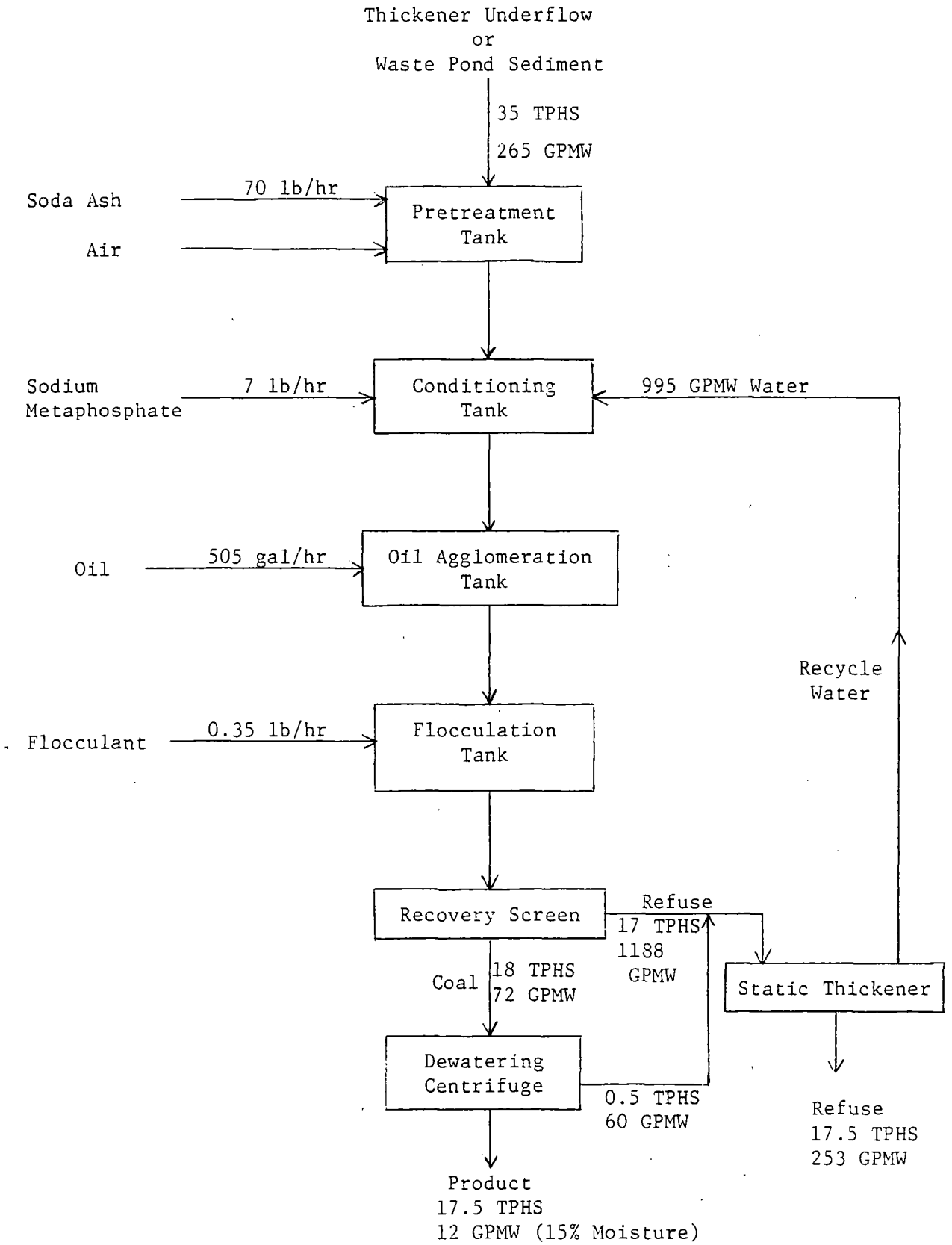

FIGURE 11. FLOW DIAGRAM OF OIL AGGLOMERATION PROCESS

TABLE 36. MATERIAL COSTS FOR OIL AGGLOMERATION PROCESS

Item	Feed Rate	Unit Price	Costs $/Ton of Clean Coal
Soda ash	70 lb/hr	$91/ton	0.18
Sodium metaphosphate	7 lb/hr	$33/100 lb	0.13
Flocculant	0.35 lb/hr	$1.77/lb	0.04
Kerosene	444 gal/hr	$0.40/gal	10.15
No. 6 fuel oil	61 gal/hr	$0.28/gal	0.98
Total			11.48

case of coal recovery from wastes that have essentially no value.

As discussed above, the major cost determinant of the oil agglomeration product is the cost of the oil used. The oil used, however, will contribute to the overall heating value of the product. The heating value of agglomerated product using 5 percent oil can be estimated as:

Heating value of marketed coal	-	11,000 Btu/lb
Heating value of oil	-	140,000 Btu/gal
Heating value of agglomerated coal	-	11,484 Btu/lb

Hence, the product cost based on the heating value will be 61¢/MM Btu compared to the market price of coal at 91¢/MM Btu.

In addition to the profitability, oil agglomeration provides a number of additional possible advantages. In particular, the oil agglomeration process will significantly reduce the waste volume which will not only save handling and disposal costs but also reduce environmental problems from its disposal.

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16. ABSTRACT The report gives results of a study of the application of oil agglomeration to coal wastes. There are an estimated 3000-5000 sizeable active and abandoned coal waste piles and impoundments in the eastern U.S. coal fields alone, containing 3 billion tons of refuse, part of which are slurry ponds. The impoundments, containing coal fines from coal preparation/cleaning plants, are a ready reserve of mined fuel for use in times of shortages. It appears that oil agglomeration could contribute significantly to the removal of contaminants before the conversion process is undertaken. The ability of agglomeration to dewater finely ground wet coal also suggests further incorporation of the process in any environmentally sound preparation plant supplying these conversion plants. Early studies indicated that, although agglomeration can effectively remove much of the ash forming minerals, it was unable to separate the liberated pyrite from coal. This program was undertaken to investigate several approaches, identified during the first phase, to enhance pyrite removal during agglomeration and to demonstrate the utility of the technology to reduce the environmental impact of increased quantities of coal cleaning refuse. Study results show that the coal recovered is of better quality than the coal now being shipped from the mine, in that sulfur and ash values are lower. Coal value recoveries were >90%.

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a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Liquefaction	Pollution Control	13B	07D
Coal	Tailings	Stationary Sources	21D,08G	
Wastes	Slime	Coal Waste Piles		08H
Agglomeration	Pyrite	Oil Agglomeration		
Dewatering	Desulfurization		13H,07A	
Coal Preparation			08I	

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