ADVANCED PHYSICAL COAL CLEANING SESSION

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PRODUCTION OF ILLINOIS BASIN COMPLIANCE COAL USING ENHANCED GRAVITY SEPARATION

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SPONTANEOUS COMBUSTION OF LOW RANK COAL

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ENGINEERING DEVELOPMENT OF ADVANCED PHYSICAL FINE COAL CLEANING FOR PREMIUM FUEL APPLICATIONS

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CONTRACT NO. DE-AC22-92PC92208

INTRODUCTION

Under this cost-shared contract, an Amax-led team has been working since fall 1992 on engineering development of advanced column flotation and selective agglomeration processes for cleaning of fine coal. Basic project details were presented at the annual contractors meeting last year [1]. The first public presentation on this major coal preparation R&D program was made at the 19th International Technical Conference on Coal Utilization and Fuel Systems [2]. This paper discusses the project accomplishments made since the last annual contractors meeting.

PROJECT OBJECTIVES

There are two main objectives to be accomplished by the project:

1. The first objective is to develop the engineering design base for prototype fine coal cleaning plants based on advanced column flotation and selective agglomeration processes to produce ultra-clean coal water slurry fuels (CWF). Such fuels, with less than 0.6 pound sulfur and 1 to 2 pound ash per million Btu and produced at a total cost of under $2.50 per million Btu, can replace premium fuels (oil and gas) in many utility and industrial boilers and advanced power systems. The capability of these processes for removal of toxic trace elements from coal will also be determined.

2. The second objective of the program is to develop the design base for near-term commercial applications of these two processes for incorporation into coal preparation plants to efficiently process minus 100 mesh coal fines (which are generally wasted) into a marketable product under current economic conditions.

PROJECT ORGANIZATION

Amax R&D (now part of Cyprus Amax Minerals Company) is the prime contractor for the project and most of the research and development work is being performed at its facilities in Golden. Amax Coal Midwest and Cannelton Coal companies (now part of Cyprus Amax Coal) are interested in the near-term commercial application and provide general direction for the project. Bechtel is performing the engineering design for the PDU which will be constructed by another subcontractor. Arcanum and Dr. Douglas Keller of Syracuse University are assisting in the development of selective agglomeration process. University of Kentucky and Virginia Tech are assisting in the column flotation area.

PROJECT TASKS AND SCHEDULE

The project is divided into following eleven tasks:

1. Project Planning
2. Coal Selection and Procurement
3. Development of Near-term Applications
4. Advanced Flotation Research/Development for Premium Fuels
5. Detailed Design of the PDU and Advanced Flotation Module
6. Selective Agglomeration Research/Development for Premium Fuels
7. Detailed Design of the Selective Agglomeration Module
8. PDU/Flotation Module Construction, Operation and Evaluation
9. PDU/Selective Agglomeration Module Construction, Operation and Evaluation
10. PDU Disposition
11. Project Final Report

The project started in October 1992 and was originally scheduled for completion in September 1996. The schedule has slipped by four to six months. Most of the laboratory and bench-scale research and development work will be completed by December 1994. The detailed design and construction of the PDU and Advanced Flotation Module should also be completed by then, and it will be operated in 1995. The Selective Agglomeration Module will be designed in 1994, constructed in 1995, and operated in 1996.

TASK 2. COAL SELECTION AND PROCUREMENT

Five bituminous and one subbituminous coals have been selected for the research and development work. The selection criteria were discussed at last year's contractor meeting [1]. A topical report describing the selection, acquisition and characterization was prepared and submitted to DOE [3].

Table 1 shows the ash and sulfur contents of the coals as mined and as sold (after conventional coal preparation). It also shows the projected ash and sulfur contents of the premium fuel that will be produced from these coals by the advanced cleaning processes being developed under the current project.

Twenty-tonne lots of these coals were procured, crushed to 12.5 mm (1/2-inch) size, and stored for laboratory and bench-scale research and development work under Tasks 4 and 6. Based on these results, three coals will be selected for PDU-scale testing of each process under Tasks 8 and 9.

TASK 3. DEVELOPMENT OF NEAR-TERM APPLICATIONS

Three Amax coal preparation plants (Ayrshire in Indiana, Wabash in Illinois, and Lady Dunn in West Virginia) were evaluated for potential near-term commercial application of column flotation and selective agglomeration processes to treat the minus 100- mesh fines. Bechtel performed the engineering analyses and a topical report was submitted to DOE [4]. The advanced cleaning section was designed to match the capacity and quality requirements for individual plants. Equipment sizing and cost estimation was therefore different for each plant. Three possible products were considered for marketing - centrifuge cake/moist agglomerate, dried powder, and briquettes. For thermal drying and briquetting steps, the cost was estimated based on the plant capacity only. Table 2 presents a summary of total estimated processing cost for each case. Since the selective agglomeration process turned out to be considerably more expensive at Ayrshire, it was not evaluated for Wabash.

The cost estimates presented in Table 2 would indicate that column flotation to produce a clean centrifuge cake should be economically very attractive. However, the high moisture content of the cake may preclude the possibility of blending this product with the coarse coal, and thermal drying to at least remove the surface moisture may be necessary. While briquetting adds to the cost, it may be economically attractive for niche markets.

Table 1. Ash and Sulfur Contents of the Selected Coals (Pounds/Million Btu)

Coal seam	Taggart	Winifrede	Elkhorn No. 3	Indiana VII	Sunnyside	Dietz
State	VA	WV	KY	IN	UT	MT
			As Mined			
Ash	30.5	25.8	59.0	45.5	12.1	4.0
Sulfur	0.40	0.78	0.81	0.95	0.45	0.27
			As Sold (Gravity Cleaning Processes)			
Ash	1.4	6.1	4.3	6.9	3.8	4.0
Sulfur	0.41	0.68	0.61	0.36	0.44	0.27
			Premium Fuel (AdvancedCleaningProcesses)			
Ash	< 1.0	1.8*	1.8	1.8*	1.9	2.0*
Sulfur	0.40	0.60	0.55	0.34	0.45	0.27

* By Selective Agglomeration.

Table 2. Estimated Total Processing Cost for Near-term Applications ($/Ton).

PRODUCT/PLANT	Ayrshire	Wabash	Lady Dunn
	COLUMN FLOTATION		
Centrifuge Cake	7.2	8.7	5.6
Dried powder	17.8	17.6	13.6
Briquettes	25.1	23.8	20.8
	SELECTIVE AGGLOMERATION		
Moist Agglomerates	21.4	N.D.	8.8
Dried Powder	28.8	N.D.	16.8
Briquettes	36.1	N.D.	24.0

TASK 4. ADVANCED FLOTATION RESEARCH/DEVELOPMENT FOR PREMIUM FUELS

The goal of the laboratory and bench-scale (100 lb/hour) research and development program is to provide the design data for the 2 ton/hour PDU. Accomplishments made to date in various areas are summarized below.

Subtask 4.1 - Grinding

While fine grinding is required to liberate the mineral matter from coal, excessive grinding may adversely affect recovery in the column flotation process and solids loading in the slurry formulation process. Both of these are economic penalties in addition to the high cost of grinding.

To determine the optimum grind, the coals were ground to various particle size distribution in laboratory and bench-scale ball mills and stirred ball mills. The ground products were subjected to granulometric and chemical analysis as well as washability and tree flotation release analysis. It was found that cleaning low-rank Dietz coal by flotation to meet premium fuel ash specification was not feasible. Therefore the study focussed on the five bituminous coals. Detailed results have been presented in a topical report [5]. Figure 1 shows the grind requirements for various coals. The grinding power requirements varied from 91 kWh/ton for Sunnyside (45 μm) to 153 kWh/ton for Indiana VII (20 μm) and 341 kWh/ton for Winifrede (11 μm).

Subtask 4.2 - Process Optimization Research

The goal of this subtask is to determine the "best" column design and operating conditions. The work is complete and a topical report is currently under preparation.

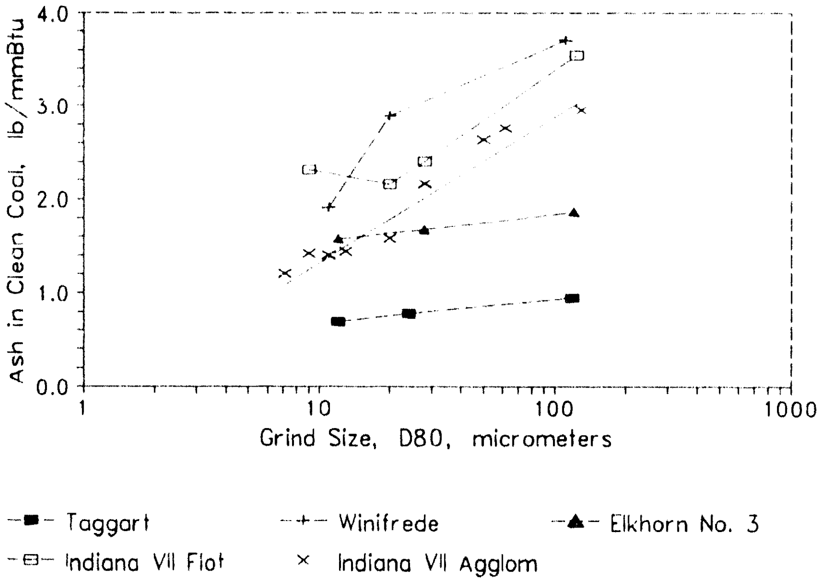

Figure 1. Effect of grind size on clean coal ash content.

Three organizations performed this work using laboratory-size columns (about 4-inch diameter, 20-ft high). Amax R&D focussed on the basic aspects of the process for all five coals such as liberation analysis and effect of flotation reagents, using a generic column as well as detailed testing on Taggart coal. The results matched the grade/recovery curve established by tree flotation release analysis.

CAER concentrated its work on evaluating the relative performance of Ken-Flote type column with both internal and external spargers using Elkhorn No. 3 and Sunnyside coals. The results were recently presented at the SME Annual Meeting [6]. Figure 2 shows that project goals of 90 percent energy recovery in a clean coal (with less than 2 lb ash/mm Btu) product can be accomplished easily with Sunnyside coal. Limited amount of work performed by CAER on packed column indicated that to achieve similar performance, much higher air and wash water flow rates had to used.

Virginia Tech evaluated the potential of Microcel™ column design for premium fuel application using Indiana VII and Winifrede coals. Preliminary results indicate that it may be possible to obtain a 2 lb ash/mm Btu product from Winifrede coal at about 85 percent energy recovery. This result is better than the result obtained in preliminary screening with smaller Microcel™ column or with other column designs.

Subtask 4.3 - Coal Water Slurry Formulation Studies

Test work is currently in progress, using clean coal concentrates produced by the bench-scale Ken-Flote column (Subtask 4.4). Preliminary results with Taggart and

Elkhorn No. 3 coals indicate that part of the cleaned coal will have to be ground and then blended to achieve desired bimodal distribution to produce a stable slurry. With small additions of Flocon stabilizer and A-23 dispersant, it should be possible to obtain high loadings (64 to 68 percent coal) at reasonable viscosity, 150 to 200 cP at 100 sec.$^{-1}$ Work is continuing on other coals.

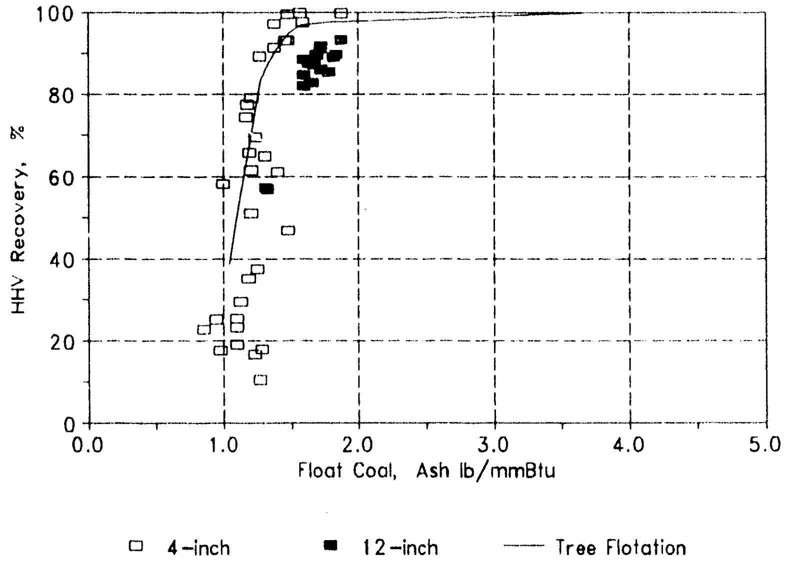

Figure 2. Flotation results obtained with Sunnyside coal.

Subtask 4.4 - Bench-scale Testing and Process Scale Up

To expedite the process of selecting "best" column design and generate design data for the 2 ton/hour PDU, it was decided to start bench-scale testing (100 lb/hour scale) at Amax R&D while the laboratory scale work was still in progress at CAER and Virginia Tech. A 12-inch diameter Ken-Flote column designed, constructed, and used by Process Technologies Inc. (PTI) at the advanced coal preparation process research facility at PETC under a prior DOE project was transferred to Golden. PTI helped in installation and start up of the column.

Scoping tests have been completed with all five bituminous coals. The grade and recovery goals have been achieved with Taggart, Elkhorn No. 3, and Sunnyside coals. As can be seen from Figure 2, the results are comparable to those obtained on laboratory scale indicating scale up should not be a problem.

Further testing is planned with Indiana VII and Winifrede coals. Since the Microcel column has produced good results with these coals on laboratory scale, it has been decided to install a 12-inch diameter bench-scale Microcel column in the Amax R&D pilot plant. The column is currently under construction.

Subtask 4.5 - Conceptual Design of the PDU and Advanced Flotation Module

The research and testing work has taken more time than originally planned. To avoid excessive slippage of project schedule and potential of project cost growth, it was decided that Bechtel should develop the conceptual design of the 2 tons/hour PDU and Advanced Flotation Module while the work described above is still in progress.

Since it has not been decided which of the three coals will be used in PDU testing, a conservative design approach was used for both grinding and flotation circuits. Provisions were also made to utilize available Amax and DOE equipment. The conceptual design package prepared by Bechtel and submitted to DOE as a topical report included process flow diagrams, preliminary P&IDs, equipment list, plant lay out and one-line electricals [7]. Bechtel has also estimated the cost of major pieces of equipment. It appears that both available space in the Amax R&D pilot plant and planned budget should be adequate for the entire PDU.

SELECTIVE AGGLOMERATION RESEARCH/DEVELOPMENT FOR PREMIUM FUELS

The goal of Task 6 is to perform laboratory and bench-scale (20 lb/hour) research and testing to provide the design data for a 2 tons/hour selective agglomeration module to be included in the PDU. Accomplishments made in performing various subtasks are summarized below.

Subtask 6.1 - Agglomerating Agent Selection

This task was completed by performing a critical review of literature. The findings were presented as a topical report [8]. It was concluded that two light hydrocarbons, heptane and pentane, are the most promising agents for premium fuel application. Two heavy hydrocarbons (kerosene and diesel) will be tested briefly to confirm that they cannot be used in this application particularly in view of the coal water slurry formulation requirements. They are more appropriate for near-term applications.

Subtask 6.2 - Grinding

This subtask has been completed and a draft copy of the topical report is currently being reviewed by DOE and project team members. Batch agglomeration tests, using heptane as the agglomerant, were performed on coals ground to different particle size. It was found that the grinding requirements were similar to those established for column flotation. Fine grinding followed by selective agglomeration was more effective in meeting the grade and recovery specifications for Indiana VII and Winifrede coals in comparison to column flotation (See Figure 1).

While column flotation was not successful in cleaning of the subbituminous coal, it appears that selective agglomeration can be used to clean the Dietz coal to less than

2 lb ash/mm Btu using either an acid treatment or special chelating agents. Further work is needed to determine if the cost goal can be met.

Subtask 6.3 - Process Optimization Research

The test plan for this subtask is currently being reviewed by DOE. It is planned to perform continuous agglomeration tests on all the six coals. Both heptane and pentane will be evaluated using (a) high and low-shear mixers in a two-stage system, and (b) a novel design single reactor.

ACKNOWLEDGMENTS

The authors would like to thank DOE and Cyprus Amax for sponsoring this project. We also gratefully acknowledge the work performed by project team members at Amax R&D, Arcanum, Bechtel, CAER, Syracuse University, and Virginia Tech.

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UPDATE OF THE LICADO COAL CLEANING PROCESS

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ABSTRACT

A novel method for fine coal cleaning, the LICADO process, is being investigated in semi-continuous and continuous test equipment. Coals tested include Upper Freeport, Pittsburgh #8 and Illinois #6 coals. A statistical study of the effects of operating parameters on the process performance with the addition of the surface modification agent was conducted in the multistage semi-continuous Research Development Unit. The Continuous Research Unit has been successfully operated at high throughput (up to 20 lb/hr) when a small amount of the surface modification agent, No.6 fuel oil, was added to the feed slurry for Pittsburgh #8 coal. Excellent results in terms of Btu recovery, ash reduction, and pyritic sulfur reduction have been achieved at a feed rate up to 14 lb/hr (the design capacity of the Continuous Research Unit is 10 lb/hr).

1.0 INTRODUCTION

The LICADO (liquid carbon dioxide) process is a novel, advanced coal cleaning method first conceived and demonstrated at the University of Pittsburgh in 1982 and developed continuously over the past ten years under the sponsorship of DOE and PEDA.(1-4) The LICADO process is based on some relatively simple principles of physical separation and uses inexpensive, readily available materials (room temperature liquid CO_2 and water) to separate mineral matter from coal. Because of the differences in the surface properties of coal and mineral matter, when the coal-water slurry makes contact with liquid CO_2, the coal particles attach to the liquid CO_2 droplet and form liquid CO_2-coal agglomerates while the mineral matter, including pyrite, remains in the water phase. Figure 1 is a schematic description of the process principles.

The current phase of the project focuses on the further improvement of process performance by applying surface modification agents in the Research Development Unit and the Continuous Research Unit.

2.0 EXPERIMENTAL

2.1 Sample Preparation

Three different coals were selected for the project. They are: Upper Freeport coal from Indiana County, PA; Pittsburgh #8 coal from Belmont County, OH; and Illinois #6 coal from Randolph County, IL. The coal samples received were of 2" x 0. Coal samples were reduced to a

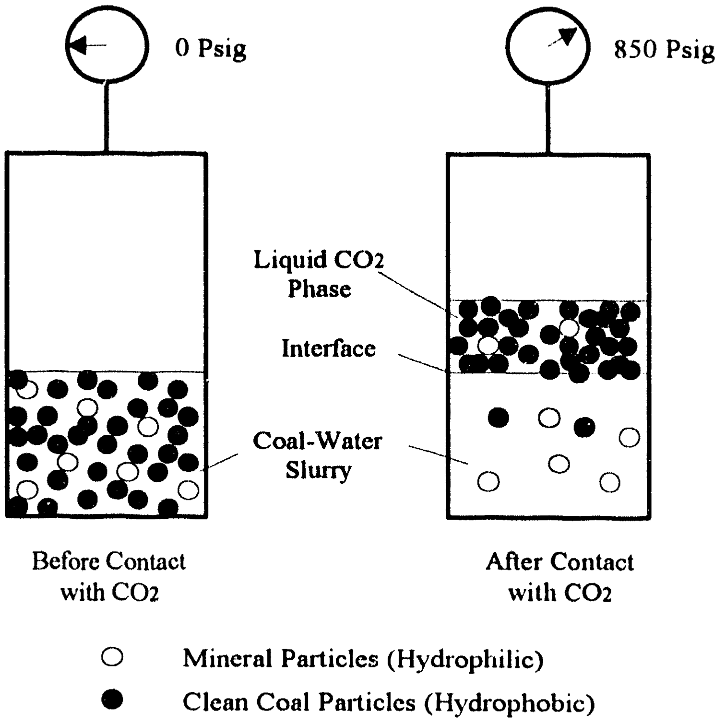

Figure 1. Principles of the LICADO Process

nominal particle size of -200 mesh by using a jar crusher and a stirred ball mill. The details of sample preparation can be found elsewhere.(5)

2.2 Experimental Procedure

The experimental study was carried out in both semi-continuous and continuous modes. For semi-continuous tests, a three-stage agitated separation column equipped with vortex-inducing contactors was used (see Figure 2).(6-7) Pittsburgh #8, Illinois #6, and Upper Freeport coals were used in these experiments. Coal-water slurry was first introduced into the agitated column. A specific amount of liquid CO_2 was then added. The coal-water slurry and liquid CO_2 were pre-mixed at high agitation speed (2,500 - 3,500 rpm) for 7 minutes. Following pre-mixing, additional liquid CO_2 was introduced through the bottom of the column, while mixing was continued at a lower agitation speed (600 - 1,700 rpm). In this case, the liquid CO_2 served as a transport fluid carrying clean coal agglomerates through the over-flow section to the product collector.

For continuous tests, a Continuous Research Unit (see Figure 3) was used. Pittsburgh #8 coal was used in these tests. A small amount of No.6 fuel oil was added to the coal-water slurry as a surface modification agent. The coal-water slurry and liquid CO_2 were introduced into the premixing tank at high mixing speed to form liquid CO_2-coal agglomerates. Then, the slurry was charged to the separation column where the clean coal agglomerates were separated from the mineral matter. The operation of the Continuous Research Unit is fully automated. A microcomputer funished with a 32 channel A/D input board, an 8 channel D/A output board, and a 16 channel relay card is interfaced with the equipment control valves, gauges, and pumps.

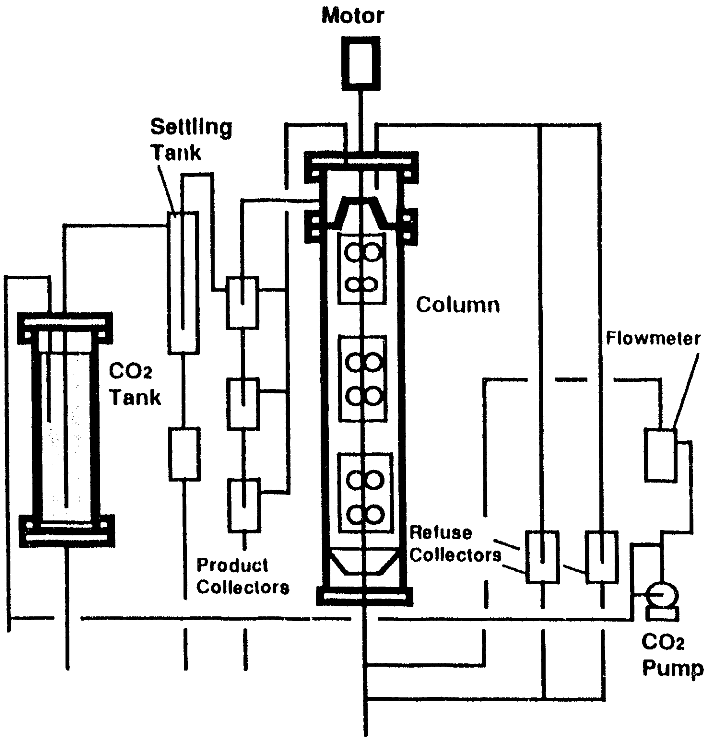

Figure 2. Schematic Diagram of the Research Development Unit

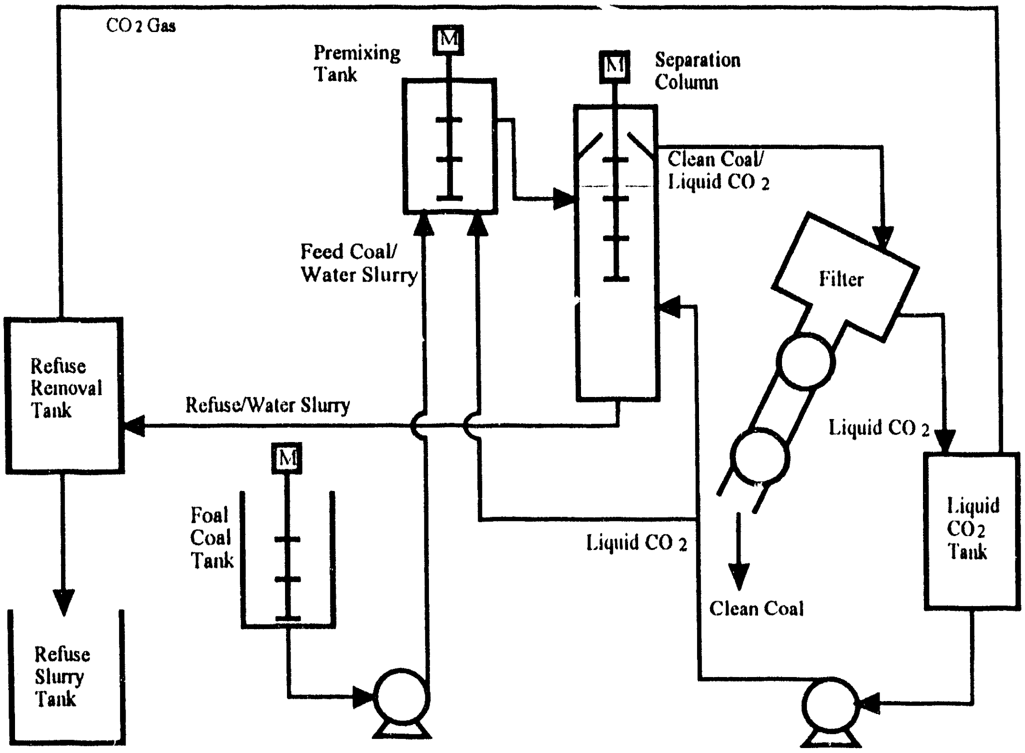

Figure 3. Schematic Diagram of the Continuous Research Unit

In both semi-continuous and continuous tests, clean coal samples were collected at the end of each experiment. These samples were dried and weighed to determine the product yield and Btu recovery. The ash and pyritic sulfur content of the samples were determined using ASTM methods. Details of the experimental procedure can be found elsewhere.(3)

3.0 RESULTS AND DISCUSSION

3.1 Semi-continuous Experiment in the Research Development Unit

Previous results obtained from the tests of a three-stage agitated column(3,6) strongly suggest that the new design concept of vortex-inducing contactors in the multi-stage arrangement and the addition of a small amount of the surface modification agent are effective in improving the process performance. To determine the effects of operating parameters on the process performance with the addition of the surface modification agent, a series of tests was performed in the three-stage agitated column under semi-continuous mode. The dosage of the surface modification agent, No.6 fuel oil, was 150 ppm for Pittsburgh #8 coal, 200 ppm for Illinois #6 coal, and 100 or 200 ppm for Upper Freeport coal. In this study, a fractional factorial design method was used to evaluate the roles of various operating parameters. The relative significance of each parameter was statistically analyzed. Liquid CO_2 flow rate (Q), the ratio of slurry level to column diameter (H/D), and mixing speed (N) were selected as three factors (see Table 1). Btu recovery and ash and pyrite contents in product coal were selected as the responses. A three-level three-factor test matrix was developed. A total of nine experimental runs were conducted in a random order.

Table 1 Three Factors and Three Levels

Level	1	2	3
Flow Rate, ml/min	800	1000	400
H/D	5.3	6.1	4.8
Mixing Speed, rpm	800	1700	1320

Pittsburgh #8 Coal

The experimental data and the analysis of variance for Pittsburgh #8 coal are presented in Tables 2. through 5. The results presented in Table 3 indicate that the Btu recovery is very strongly affected by liquid CO_2 flow rate and mixing speed in the three-stage agitated column using oil additive at the 99% confidence level. A similar effect was observed in the three-stage agitated column without oil additive. The results also reveal that the mixing speed is another important operating parameter. The analysis of variance for the slurry level (H/D) confirms that the H/D is not a significant factor affecting the performance of multi-stage agitated column. The same conclusion has also been obtained in the analysis of the variance for ash and pyrite data.

Table 2 Experimental Results for Pittsburgh #8 Coal

Factor	Q, ml/min	H/D	N, rpm	Btu recovery	Ash Content, %	Pyrite Content, %
1	800	5.3	800	0.949	3.30	1.00
2	800	6.1	1700	0.925	4.40	1.36
3	800	4.8	1350	0.933	1.70	0.81
4	1000	5.3	1700	0.928	3.60	1.29
5	1000	6.1	1350	0.947	2.10	0.90
6	1000	4.8	800	0.942	2.50	1.02
7	400	5.3	1350	0.810	1.30	0.53
8	400	6.1	800	0.838	3.00	0.84
9	400	4.8	1700	0.763	2.40	0.94

Table 3 Analysis of Variance for Btu Recovery

Sources	DF	Mean Square	F-Ratio	Note
Q	2	0.018	61.16	$F > F_{0.01}$ extremely significant
N	2	0.012	39.25	$F > F_{0.01}$ extremely significant
Error	4	0 0003		
Total	8			

The analysis related to the effects of operation parameters on ash content in product coal is presented in Table 4, which reveals that the individual effect of mixing speed on the ash content is more significant than that of CO_2 flow rate at 90% confidence level. However, both Q and N play significant roles in affecting the pyrite content in product coal (see Table 5).

Table 4 Analysis of Variance for Ash Content in Product Coal

Sources	DF	Mean Square	F-Ratio	Note
Q	2	0.61	1.68	$F < F_{0.1}$ less significant
N	2	5.89	16.22	$F_{0.01} > F > F_{0.05}$ very significant
Error	4	0.36		
Total	8			

Table 5 Analysis of Variance for Pyrite Content in Product Coal

Sources	DF	Mean Square	F-Ratio	Note
Q	2	0.086	15.1	$F_{0.01} > F > F_{0.05}$ very significant
N	2	0.422	73.8	$F > F_{0.01}$ extremely significant
Error	4	0.006		
Total	8			

Illinois #6 Coal and Upper Freeport Coal

Similar experimental results and data analysis were obtained for Illinois #6 coal and Upper Freeport coal. The detailed discussion of these results may be found elsewhere.(7,8)

3.2 High Capacity Experiments in the Continuous Research Unit

Experiments were conducted using Pittsburgh #8 coal at feed rates of 5 , 10, 15 and 20 lb/hr in the presence of a surface modification agent (No.6 fuel oil). The dosage of No.6 fuel oil was kept constant at 200 ppm. The results of high throughput tests with an oil additive are shown in Table 6.

Table 6 Effect of Feed Coal Capacity

Feed Coal: Pittsburgh #8 Coal, 5 or 10% Coal-Water Slurry
Interface Position: 9 inches below the top of the cone
Liquid CO_2 Flowrate (Separation Column): 200 gm/min
Liquid CO_2 Flowrate (Premixing Tank): 1500 gm/min
Mixing Speed (Premixing Tank): 1600 rpm
Mixing Speed (separation Column): 1000 rpm

		Product		
Feed Coal Rate, lb/hr	Slurry Concentration, %	Btu Recovery, %	Ash Content, %	Pyrite Content, %
5.2	5	93.7	5.32	1.30
10.3	5	90.1	4.98	1.20
14.1	10	89.9	5.63	1.23
18.8	10	61.7	6.61	1.49

The data in the Table indicate that high throughputs up to 14 lb/hr can be handled in the Continuous Research Unit with excellent Btu recovery. The product quality remained constant or only slightly decreased as the coal feed rate increased from about 5 lb/hr to 14 lb/hr. However, once the coal feed rate reached about 19 lb/hr (which is nearly twice the design capacity of 10 lb/hr), a decrease in both Btu recovery and clean coal product quality was observed. The possible explanation might be that at 19 lb/hr of feed coal rate the residence time of both liquid CO_2 and coal-water slurry in the premixing tank was too short and the ratio of liquid CO_2/coal-water slurry was too low to form agglomerates completely. Thus, the Btu recovery was significantly reduced. For the same reason, the incompletely formed agglomerates tended to trap refuse-laden water, resulting in a product of lower quality.

4.0 CONCLUSIONS

LICADO coal cleaning experiments were performed in three-stage semi-continuous Research Development Unit and the Continuous Research Unit. From the analysis of the experimental results, the following conclusions can be drawn:

- In the operation of three-stage separation column, liquid CO_2 flowrate and mixing speed are identified as the most important factors and the slurry level is found to be the least significant factor affecting the column performance.
- The high capacity experiments (up to 20lb/hr) have been successfully carried out in the Continuous Research Unit when a small amount of No.6 fuel oil was added to the feed slurry for Pittsburgh #8 coal..

ACKNOWLEDGMENT

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EVALUATION, ENGINEERING AND DEVELOPMENT

OF ADVANCED CYCLONE PROCESSES

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CONTRACT NUMBER: DE-AC22-90PC90177

PERIOD OF PERFORMANCE: OCTOBER 1, 1990, TO DECEMBER 31, 1994

INTRODUCTION

This research and development project is one of three seeking to develop advanced, cost-effective, coal cleaning processes to help industry comply with 1990 Clean Air Act Regulations. The specific goal for this project is to develop a cycloning technology that will beneficiate coal to a level approaching 85% pyritic sulfur rejection while retaining 85% of the parent coal's heating value. A clean coal ash content of less than 6% and a moisture content, for both clean coal and reject, of less than 30% are targeted. The process under development is a physical, gravimetric-based cleaning system that removes ash bearing mineral matter and pyritic sulfur. Since a large portion of the Nation's coal reserves contain significant amounts of pyrite, physical beneficiation is viewed as a potential near-term, cost-effective means of producing an environmentally acceptable fuel.

The project agenda consists of three phases. Phase I included a characterization of the four feedstock coals to be used throughout the project and a media evaluation consisting of a paper study and laboratory testing. The coal seams selected for use in this project are Upper Freeport, Pittsburgh No. 8, Meigs No. 9, and Illinois No. 6. Phase II involved testing several selected media and separator combinations in a closed loop circuit, conceptual cost estimates, and final medium/process selection. Phase III involves the development of a process Component Test Circuit design, equipment selection, construction and operation of a 1,000 lb/hr closed loop component test system. During the process optimization period, performance tests with each of the four test coals are planned. Finally, generation of a conceptual design and economic analyses for large scale integrated plants is planned.

Nearly 50 media candidates were considered including aqueous suspensions, aqueous solutions, organic solutions and a magnetically enhanced medium (MEM).

Separators that were considered included small diameter, high pressure cyclones, centrifuges, a hybrid separator combining flotation and cycloning in a single device, and a separator designed for MEM. In addition to gathering physical property data via a literature search, laboratory measurements and test separations were completed to eliminate the less desirable media candidates, i.e., viscosity, solubility, pH, and filter cake washing experiments.

COAL TOPSIZE, MEDIUM AND SEPARATOR SELECTION

At the conclusion of Phase I, calcium nitrate/water and the organic mixture of methylene chloride/perchloroethylene (mcl/perc) were selected as the best true heavy liquid candidates for further testing in Phase II. The MEM separator could not be readily scaled up and was dropped. The separators tested in PTI's closed loop facility during Phase II were a Krebs Cyclone, an Alfa-Laval (A-L) Model MOCL hydrocyclone (nested miniclones), and a DOE/PTI vertical centrifuge separator. Testing of decanter centrifuges and Hydro Processing & Mining's Centrifloat separator occurred off-site. All of the indicated separators were tested with both aqueous and organic media except the Centrifloat, which utilizes a water only medium, and the A-L centrifuge, which did not use the organic medium because the lab where it was tested was not equipped to handle organic liquids. HPM's Centrifloat did not achieve the targeted value for pyritic sulfur rejection and was dropped. The vertical centrifuge separator required modification beyond the budget and timing of this project and was eliminated.

Coal characterization and washability of the four test coals showed that grinding the Component Test Circuit feed coal to 100 mesh topsize would theoretically achieve the project goals. Phase II tests were conducted utilizing 100 mesh as the top size; however, 200 mesh and 500 mesh feed coals were also tested to determine separation effectiveness at smaller topsizes.

The separating performances of the calcium nitrate medium in a decanter centrifuge and the organic medium in a two-inch diameter cyclone were nearly identical, making the final separator selection a difficult task. The organic medium circuit is less costly than the salt circuit, both from a capital and operating cost standpoint. However, the calcium nitrate medium has significantly less health, safety and environmental liabilities. If a spill with the organic medium were to occur, it would shut the operation down, cause serious delays, and have the potential for very large clean-up and containment related costs. The difference in cost of the two circuits is viewed as the price paid for safety. Calcium nitrate is more commonly used for its nitrate content as fertilizer and at saturation is able to make a 1.55 sg solution. Viscosity of a 1.35 sg solution is less than 5 centipoise.

Selection of the decanter centrifuge as separator is required to meet the project goals if calcium nitrate medium is used. The high g force generated by the centrifuge is required for the calcium nitrate medium to work as a parting liquid. The Project Team achieved excellent separations with a P-660 Sharples (A-L) decanter. Comparison of the optimum separation results achieved in Phase II to the feed washability (ash vs yield relationship) is shown in Figure 1. Partition curves for the calcium nitrate/decanter centrifuge separation and others are shown in Figure 2. After considering these results and the environmental and safety elements above, the Project Team selected the calcium nitrate medium, decanter centrifuge combination. A decanter centrifuge diagram is shown in Figure 3.

MEDIUM RECOVERY/REGENERATION (FILTERING, WASHING, EVAPORATION)

Development of a medium recovery system is a technical and economic requirement. The filtering system serves two functions: to recover medium and to deliver a relatively salt-free product. This operation is critical to the success of the project. The cost of the medium requires that it be recovered for reuse. Water is used to rinse the filter cake, and the dilute filtrate is recovered for restoration to the original medium gravity. The operating cost of the aqueous process is dominated by the medium regeneration, i.e., water evaporation and calcium nitrate replacement costs.

Test work was performed with two filter vendors to determine filtering efficiencies, capacities, etc. A capillary-effect filtration system utilizing ceramic disks manufactured by Outokumpu of Finland was selected. A diagram of the Outomec filter is shown in Figure 4.

By utilizing a porous sintered alumina material to create a capillary effect, the separation of liquid and solids can take place. Capillary effect causes liquids in small tubes to stand at a greater height than the corresponding static head. Capillary rise is described by:

$$H = \frac{4t \cos \theta}{g\,D\,(\rho_1 - \rho_2)}$$

where H is in cm, t is the surface tension of the liquid in dynes/cm, D is the diameter in cm, θ is the contact angle, $g = 981$ cm/sec^2, and ρ_1 and ρ_2 are the densities of the liquid and surrounding gas in g/cc.

If the height of the column H is multiplied by the difference in density and the acceleration due to gravity, the differential in pressure is obtained.

$$\Delta P = \frac{4t \cos \theta}{D}$$

The above expression indicates that the smaller the pore diameter, the greater the pressure. Capillary force in pores can be greater than that applied by vacuum. Due to the surface tension between the liquid and the hydrophilic porous material, the pores fill with liquid. The pores in the ceramic filter are of such a diameter that they are not emptied of the liquid contained in them and no air is allowed to pass. A small pump is used to convey the collected liquid away. Energy consumption is extremely low.

With the use of ceramic filter media, filter cloths and associated problems are eliminated. The ceramic media is non-blinding, non-tearing and provides an uncontaminated filtrate.

Preliminary process investigation indicates the optimum water evaporation system is a seven-effect evaporator utilizing falling-film and forced circulation units. The device removes water from the diluted medium, restoring the working medium to its proper density. A diagram of the evaporator components is shown in Figure 5.

Since the medium regeneration system utilizes well understood technologies involving thermal evaporation of water, an evaporator manufacturer will be selected to perform the studies necessary for selection of the optimum medium regeneration evaporator configuration.

DESCRIPTION OF PROCESS CIRCUIT

Detailed engineering design of a Bench Scale Circuit (BSC) capable of processing coals at a feed rate of 1,000 lb/hr was completed in late 1993 but cost constraints and limited available funds dictated a change in project scope. A flowsheet of the BSC is shown in Figure 6. After study of project goals vs. available funds, it was decided that rather than construct the complete integrated circuit, portions of the detailed engineering and the primary circuit components will be utilized to construct a Component Test System (CTS), which will test, in closed loop at 1,000 lb/hr, first the capillary-effect filtration system with a standard preparation plant flotation product and tailings, then the separator circuit with aqueous medium and preground project coals, then the deliquoring circuit with separator products, and finally the grinding circuit. In the first phase of testing, the Outomec capillary-effect filter will be tested to determine its potential effectiveness as a dewatering device in existing coal preparation plants. Next, preground samples (100 mesh topsize) of the project coals will be slurried in a sump with calcium nitrate/water medium and beneficiated through the Alfa-Laval P-3000 decanter separator where a gravimetric separation of high and low ash material will be made. The decanter products are either directed back to the feed sump and recirculated or stored/segregated in separate sumps. With the completion of processing/sampling of the project feed coal through the high g separator, the decanter test loop is shut down. The tube and ceramic disc filter circuit, is then started. The stored/segregated low ash (product) solids are pumped to the clean coal side of the deliquoring circuit, comprised of the tube filter and three discs of the ceramic disc filter. Simultaneously, the high ash (refuse) solids are pumped to the refuse side of the filter, comprised of a single disc. The solids are deliquored/sampled and directed either back to the feed sumps for recirculation or to final disposal. With the completion of the two test phases for the first coal, the second through the fourth coals are then similarly tested. Finally, 1-1/2" x 0 samples of the precleaned project coals will be reduced to 100, 150, and 200 mesh topsizes through the grinding circuit to determine circuit grinding efficiencies and energy costs.

CURRENT STATUS AND PLANS

Though this process has great potential, additional work is needed to lower processing costs. This need and cost constraints of the project led to the decision to adopt a simple component test circuit strategy. Construction of the component test facility is expected to be complete in the Summer of 1994, and the test program and final report completed in September, 1995.

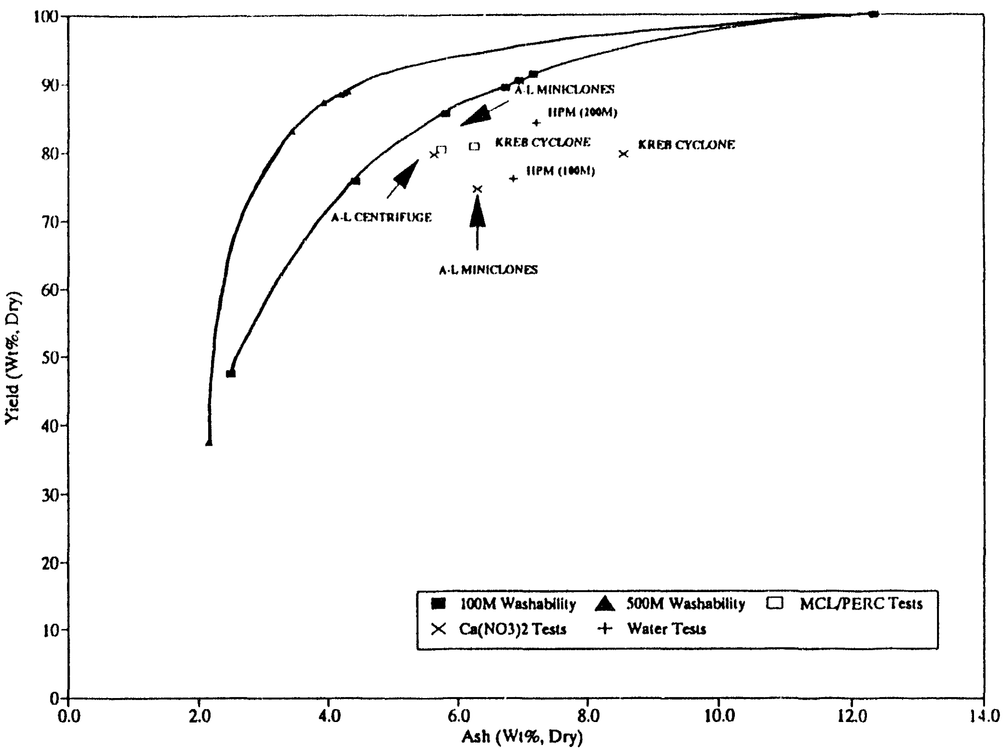
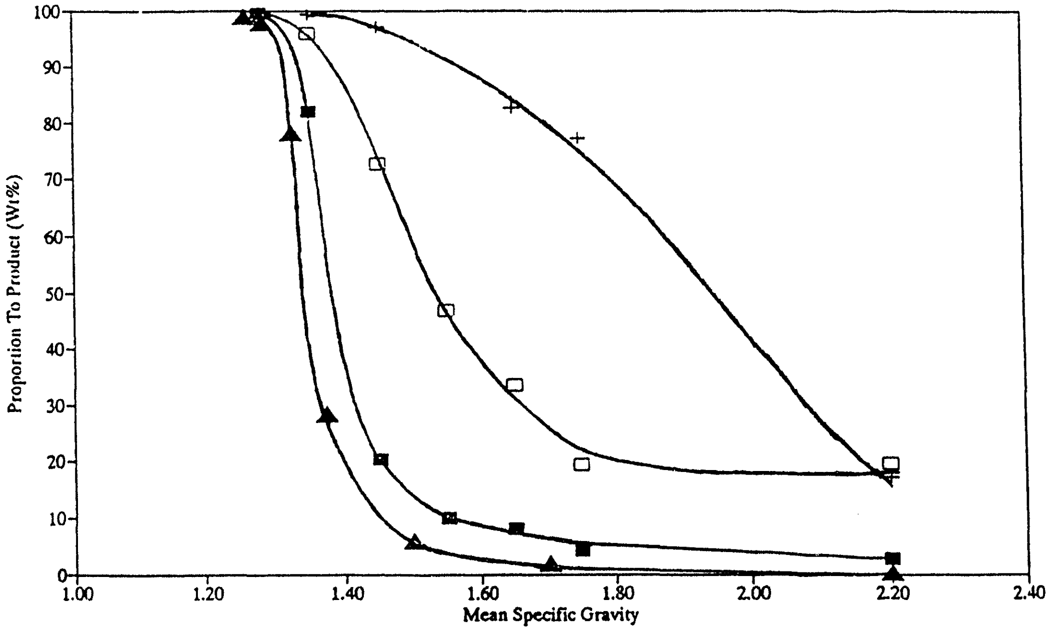


Figure 1. Comparison of Optimum Separation Results



Legend	Media	Separator	Size	Media SG	Sep'n SG	Ep
▲	Micromag	3" Cyclone	28M x 400M	1.30	1.35	0.025
☐	MCL/PERC	2" Cyclone	100M x 0	1.45	1.53	0.135
■	Ca(NO3)2	A-L Centrifuge	100M x 0	1.35	1.39	0.035
+	Ca(NO3)2	A-L Centrifuge	500M x 0	1.40	1.92	0.195

Figure 2. Partition Curves of Media/Separators

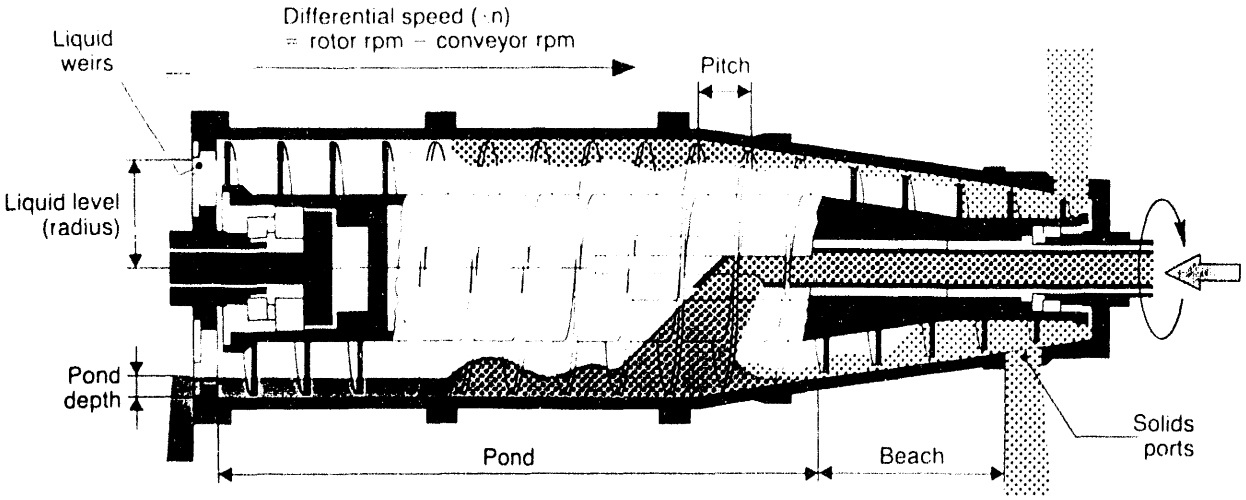


Figure 3. Decanter Centrifuge

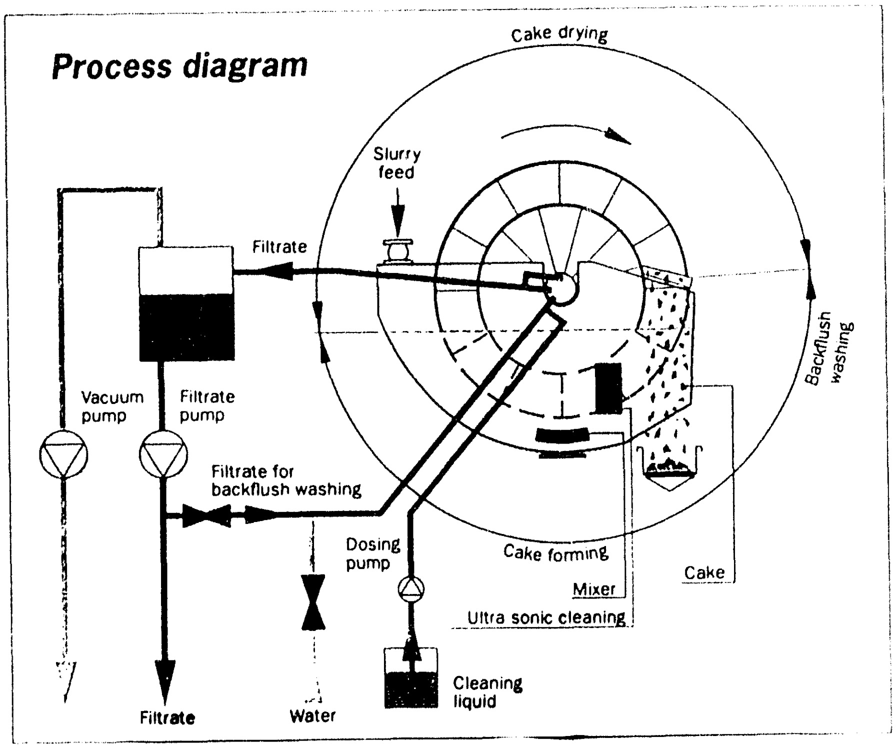
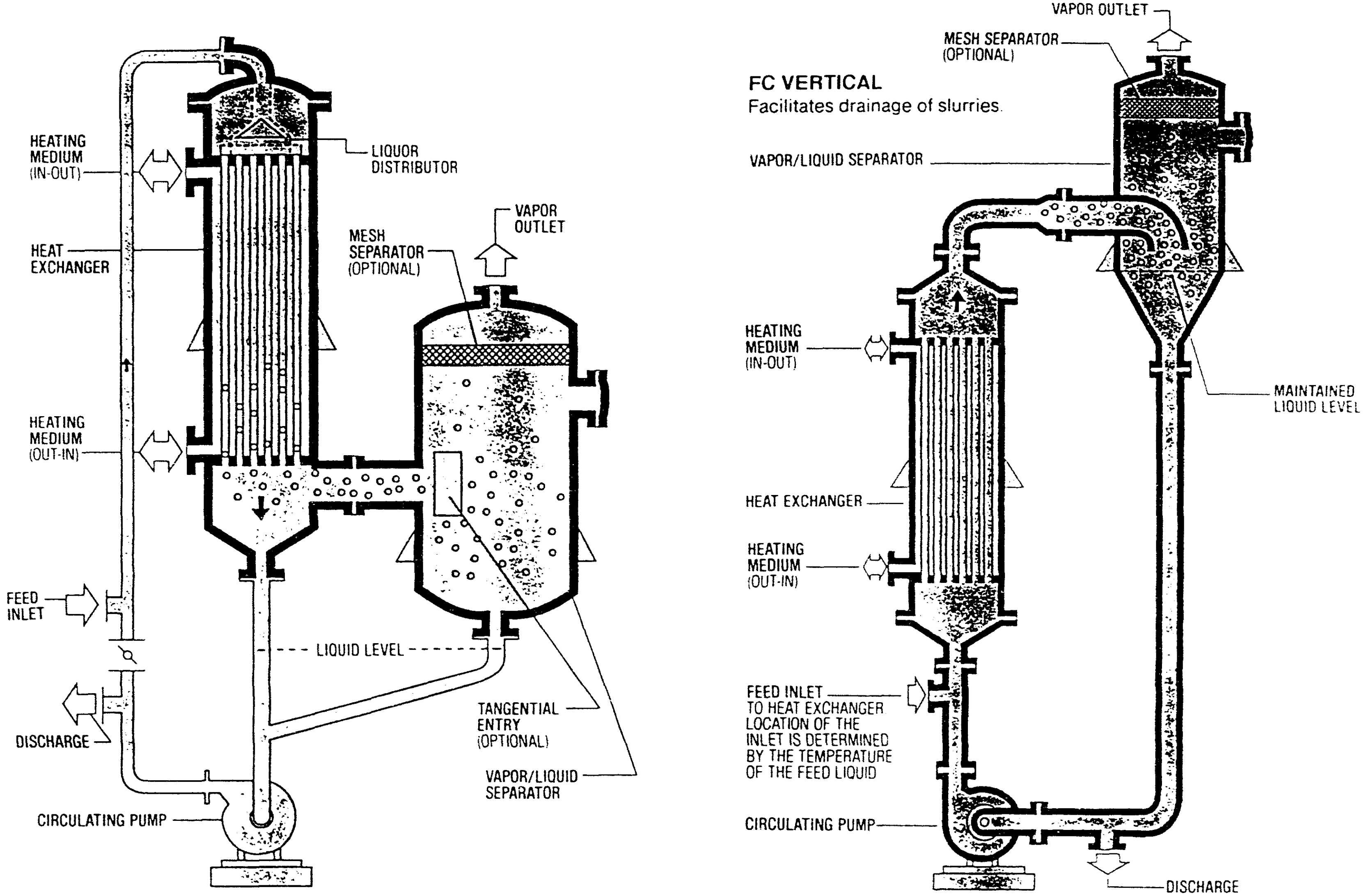


Figure 4. Capillary Effect Filter



Falling Film Evaporator

Forced Circulation Evaporator

Figure 5

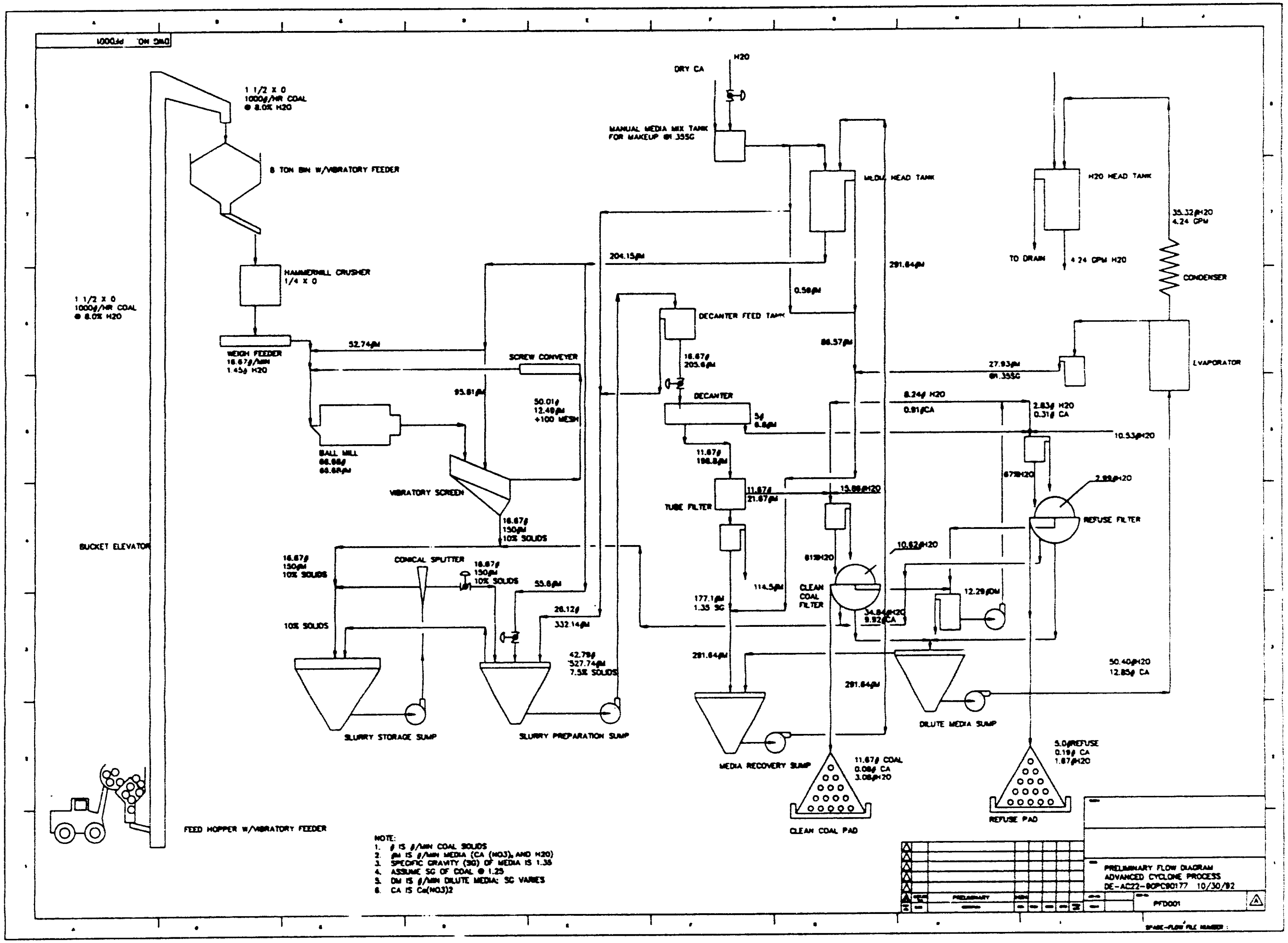


Figure 6. Bench Scale Circuit Flowsheet

Preliminary process investigation indicates the optimum water evaporation system is a seven-effect evaporator utilizing falling-film and forced circulation units. The device removes water from the diluted medium, restoring the working medium to its proper density. A diagram of the evaporator components is shown in Figure 5.

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CURRENT STATUS AND PLANS

Though this process has great potential, additional work is needed to lower processing costs. This need and cost constraints of the project led to the decision to adopt a simple component test circuit strategy. Constructing of the component test facility is expected to be complete in the Summer of 1994, and the test program and final report completed in September, 1995.

ENGINEERING DEVELOPMENT OF ADVANCED PHYSICAL FINE COAL CLEANING TECHNOLOGIES - FROTH FLOTATION

PRINCIPAL INVESTIGATORS:

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PROJECT ENGINEER
ICF KAISER ENGINEERS, INC.

Contract Number: DE-AC22-88PC88881
Period of Performance: April 1993 - March 1994

Objectives:

ICF Kaiser Engineers (ICF KE) was contracted by United States Department of Energy, Pittsburgh Energy Technology Center, to perform a project entitled "Engineering Development of Advanced Physical Fine Coal Cleaning Technologies - Advanced Froth Flotation." The objective of the project is to develop advanced froth flotation coal beneficiation technology to achieve at least 85% inorganic pyritic sulfur rejection while simultaneously maintaining at least 85% Btu recovery. A two ton per hour Proof-of-Concept (POC) test unit was designed and operated to demonstrate that the removal of inorganic sulfur by physical cleaning prior to combustion as an economical means of controlling acid rain emissions.

The contract is comprised of seventeen tasks. The first eleven tasks were completed and reported previously. During this report period, Task 12, Task 13, and Task 17 were completed. The results of these tasks are summarized in this report.

Accomplishments:

The project was begun in September 1988 with completion date of August 1994. The project participants are ICF Kaiser Engineers as the prime contractor, with team members including Babcock & Wilcox, Consolidation Coal Research, Eimco Process Equipment Company, Virginia Polytechnic Institute and State University, Illinois Sate Geologic Survey, the Ohio Coal Development Office, and the Center for Innovative Technology. The total contract price was for $8,871,500.00, and funds expended to February 1994 are $7,520,000.00. The Project Data is shown on Table 1.

The objectives of the project are to develop an advanced flotation technology that was capable of rejecting 85% of the pyritic sulfur while recovering 85% of the Btu value of the raw coal. The final product was to be 6% ash and 30% surface moisture. The reject from the process was to be no more than 35% surface moisture.

In addition to the above objectives, the team members developed several other objectives that would benefit the overall economics of the project, as well as enable commercialization of the project by 1995. These additional objectives shown in Table 2 included precleaning the raw coal to remove pure reject material and recover any coal that is naturally low in pyritic sulfur. The team members determined a conceptual flow logic as shown in Figure 1.

Task 12 was completed during this reporting period. Task 12 was the Proof of Concept Test Plan. This plan was discussed in some detail in last year's presentation. It should be noted that the plan as originally prepared was closely followed, but during the operational stage,the plan was modified as required. The modifications were made basically for two reasons - (1) to ensure that the results from testing met the project objectives, and (2) to change the operating conditions required to continue operation.

This report will consider the results obtained for the Task 13 Proof of Concept operation on the three test coals. These test coals were the Pittsburgh No. 8, donated by Ohio Power Company; Upper Freeport supplied by Camelot Coal Company; and Illinois No. 6 supplied by Kerr-McGee Coal Corporation.

During the preliminary operation, several unit operations were altered and/or deleted from the circuit. The process instrumentation was evaluated and modifications and/or deletions resulted. The changes are shown on Tables 3 and 4 respectively.

The Pittsburgh No. 8 coal was designated as the shakedown coal and subjected to extensive testing to ensure that the circuitry was performing according to the design specifications.

The precleaning circuit was initially to be tested with a goal of achieving 95-97% Btu recovery, while eliminating as much liberated free pyrite as possible as refuse. The precleaning circuit consisted of heavy-media cyclone on the plus 48 mesh size range, water-only cyclone on the crushed heavy-media cyclone clean coal and natural minus 48 mesh.

The results of the 24-hour demonstration run of the precleaning circuit are shown on Table 5. The objective of 95-97% Btu recovery was not quite reached, but an acceptable 92.2% Btu recovery was attained. The pyritic sulfur rejection was dramatic as demonstrated by rejection of 60.9% of the pyritic sulfur in the feed.

The WOC product became the feed to the advanced flotation column after the grinding circuit which was used to liberate more pyrite from the coal. Early in the testing program, results indicated that the WOC product and the feed to the advanced flotation column were not the same, even though they should have been. A testing program was instituted to determine if the precleaning and grinding circuits were at steady state conditions. The results of this test program indicated several things. The unit operations in the precleaning circuit, i.e. the HMC and WOC achieved steady state rapidly and maintained this steady state for the duration of the testing. The grinding mill circuit is a reversed closed circuit that took up to forty-five minutes to reach steady state as far as size distribution measurements. The pyritic sulfur measurements did not reach steady state in the same forty-five minutes.

The classification device for the grinding circuit was a cyclone. The cyclone orifice arrangements were installed to make a nominal 74 micron classification of coal particles. The specific gravity of pyrite is around 4.0 versus coal specific gravity of 1.4. This specific gravity differential caused the liberated pyrite to classify at less than 26 microns. In order to remedy the condition, a Vari-Sieve was installed on a portion of the cyclone underflow. The results of the classification by cyclone and Vari-Sieve resulted in steady state operation of the grinding circuit in approximately forty-five minutes with regard to size distribution and pyritic sulfur into and out of the circuit.

After the steady state test procedure and verification of results, a factorial test matrix was conducted to determine the range of values for a definitive Box-Behnken test matrix for the advanced column flotation machine. The factorial test matrix determined that the feed, frother, air rate and wash water rate were the governing variables. These were then tested in a Box-Behnken test matrix. The conclusion reached from the results of the Box-Behnken test program established the operating parameters for the advanced column flotation machine during the 24-hour demonstration run. The results of the advanced column are shown on Table 6, and the total plant results are shown on Table 7.

The same procedures used for the Pittsburgh No. 8 were employed in testing the Upper Freeport and Illinois No. 6. The steady state testing and the factorial testing were not conducted for the other test coals. The results for the Upper Freeport are shown on Tables 8, 9, and 10. The results for the Illinois No. 6 are shown on Tables 11, 12, and 13.

The conclusions for the project are shown on Table 14. The results indicate 85-89% Btu recovery and 73-78% pyritic sulfur rejection. The final ash in the product was 7-10% with a surface moisture of around 35%. All of these values are not quite the objectives of the project. The ash could be reduced at the sacrifice of Btu recovery which would then increase the pyritic sulfur rejection. Therefore the objectives of the project could be attainable. The final product surface moisture is higher than the objective because the unit operation originally installed could not be operated continuously. It was not the machine, but the mechanism used to discharge the filter cake that failed. The product moisture from the hyperbaric filter, when it operated, was less than 25% surface moisture. The project was successful in demonstrating the continuous operation of the advanced column flotation machine with an overall availability of greater than 95%. There were never problems associated with the POC circuitry during operation demonstrating that this circuit could be retrofitted to an existing preparation plant to produce a final product that, after reconstitution, could be shipped to a power plant.

The objectives were approachable and, based on testing conducted at PETC using a gravity-based unit operation in series with advanced flotation, it was determined to attempt to test this hypothesis at the POC installed for this project. Task 17 was established to test the feasibility of the series operation. Two gravity-based devices were tested, the Carpco Multi-Gravity Separator (MGS) and the Kelsey jig. Both units are fine size gravity-based devices. The preliminary results indicated some improvement of pyrite rejection with minimal Btu loss for the Kelsey jig. The MGS unit did not perform as well. The operating conditions were out of range for the MGS unit and were more ideal for the Kelsey jig. Thus the difference in results. The data is still being evaluated and not available at the time of this writing.

The remaining work for this project is Task 14 and Task 15. Both of these tasks are reports. Task 14 is the POC Operation Analysis, and Task 15 is the Final Semi-Works Conceptual Design.

TABLE 1 - PROJECT DATA

Contract Start Date	September, 1988
Expected Contract Completion Date	August, 1994
Contract Value	$8,871,500.00
Funds Expended through February 1993	$7,520,000.00

TABLE 2 - PROJECT OBJECTIVES

- Develop an advanced froth flotation technology
- Remove at least 85.0% of raw coal's pyritic sulfur
- Produce a conceptual cost estimate @ 20 TPH
- Limit energy losses to 15% of raw coal value
- Limit product ash content to 6%
- Limit reject surface moisture to 35%
- Crush no pure reject material
- Maximize product particle size
- Demonstrate technology @ 2 - 3 TPH
- Complete development by 1994

TABLE 3 - UNIT OPERATIONS CHANGES

1. **Clean Coal Thickener** - Added spray water systems to eliminate froth.

2. **Refuse Belt Press** - The addition of flocculant to this machine to make it operational poisoned the recirculated water. As a result, this unit was shut down.

3. **Conventional Flotation** - Testing of the conventional flotation resulted in overdosing the cells to ensure maximum Btu recovery. The overdosing caused a buildup of frother in the recirculated water that poisoned the system. These units were shut down.

4. **Clean Coal Filter** - The hyperbaric filter was an operating problem because of the discharge system. When operational, the filter produced a product in the 22-25% surface moisture, but could not be continuously operated. The unit was shut down.

5. **Grinding System** - Numerous changes made to the classifying cyclones configurations resulted in an acceptable classification point. However, the ball mill was undersized for the feed rate required to operate, resulting in a coarser grind.

6. **Vari-Sieve Addition** - An additional sizing device was added to the classification circuit for the ball mill to eliminate recycling of minus 200 mesh pyrite.

TABLE 4 - INSTRUMENT CHANGES

1. **Automatic Floc Control** - Numerous attempts were made to make operational an automated floc control system. They were never completely successful. The turbidity meter worked, but the settling rate device did not.

2. **Ash Analyzer** - Despite our efforts, the ash analyzer never operated properly. Efforts to obtain results for the pyrite meter were unsuccessful. The samples to the analyzer were too dilute to register.

3. **Particle Size Analyzer** - We were unable to make the particle size analyzer operate properly. Over time, the unit would lose calibration.

4. **Thermal Air Flow Meter** - For whatever reason, the air lines on which the meters were mounted contained water, even though there was an air dryer in the compressed air system. These units were removed.

5. **Orifice Plate Air Flow Meter** - These instruments were installed to replace the above and were successful.

TABLE 5
PITTSBURGH NO. 8 PRECLEANING RESULTS

AVERAGE OF 24 TESTS - PRECLEANING

	Ash %	Total Sul %	Pyritic Sul %	Btu
Feed	46.05	2.90	2.04	7329
Product	26.75	2.34	1.24	10499

Precleaning Yield Percent	64.38
Precleaning Btu Recovery Percent	92.20
Precleaning Ash Rejection Percent	62.60
Precleaning Sulfur Rejection	48.10
Precleaning Pyritic Sulfur Rejection	60.90
Feed Pounds of SO_2 Per Million Btu	7.91
Product Pounds of SO_2 Per million Btu	4.46

TABLE 6
PITTSBURGH NO. 8 COLUMN RESULTS

AVERAGE OF 24 TESTS - COLUMN

	Ash %	**Total Sul %**	**Pyritic Sul %**	**Btu**
Feed	26.75	2.34	1.24	10499
Product	7.65	2.11	1.12	13618

Column Yield Percent	75.06
Column Btu Recovery Percent	97.31
Column Ash Rejection Percent	78.08
Column Sulfur Rejection	19.94
Column Pyritic Sulfur Rejection	33.40
Feed Pounds of SO_2 Per Million Btu	4.46
Product Pounds of SO_2 Per Million Btu	3.10

TABLE 7
PITTSBURGH NO. 8 PLANT RESULTS

AVERAGE OF 24 TESTS - TOTAL PLANT

	Ash %	**Total Sul %**	**Pyritic Sul %**	**Btu**
Feed	46.05	2.90	2.04	7329
Product	7.65	2.11	1.12	13618

Plant Yield Percent	48.19
Plant Btu Recovery Percent	89.51
Plant Ash Rejection Percent	91.90
Plant Sulfur Rejection	58.57
Plant Pyritic Sulfur Rejection	73.69
Feed Pounds of SO_2 Per Million Btu	7.91
Product Pounds of SO_2 Per Million Btu	3.10

TABLE 8
UPPER FREEPORT PRECLEANING RESULTS

AVERAGE OF 30 TESTS - TOTAL PLANT

	Ash %	**Total Sul %**	**Pyritic Sul %**	**Btu**
Feed	24.09	4.41	3.20	11048
Product	19.23	2.67	1.93	11921

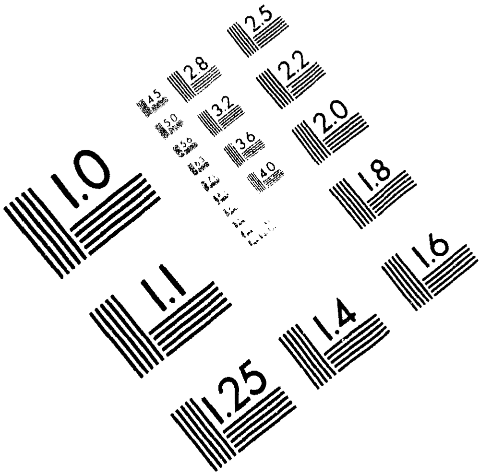
Plant Yield Percent	89.33
Plant Btu Recovery Percent	96.40
Plant Ash Rejection Percent	28.70
Plant Sulfur Rejection	45.90
Plant Pyritic Sulfur Rejection	57.30
Feed Pounds of SO_2 Per Million Btu	7.98
Product Pounds of SO_2 Per Million Btu	4.48

TABLE 9
UPPER FREEPORT COLUMN RESULTS

AVERAGE OF 30 TESTS - COLUMN

	Ash %	**Total Sul %**	**Pyritic Sul %**	**Btu**
Feed	19.23	2.67	1.53	11921
Product	10.29	2.30	1.06	13456

Column Yield Percent	80.44
Column Btu Recovery Percent	90.78
Column Ash Rejection Percent	56.83
Column Sulfur Rejection	31.45
Column Pyritic Sulfur Rejection	44.53
Feed Pounds of SO_2 Per Million Btu	4.48
Product Pounds of SO_2 Per Million Btu	3.42



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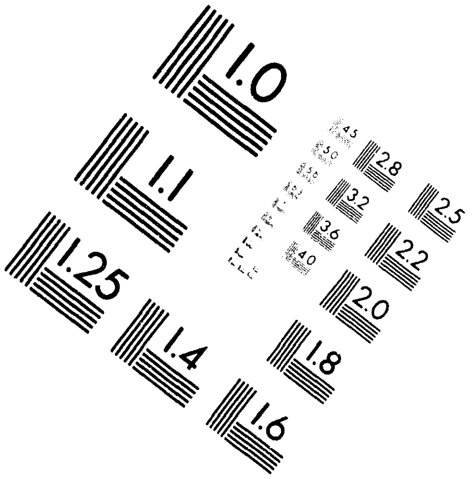

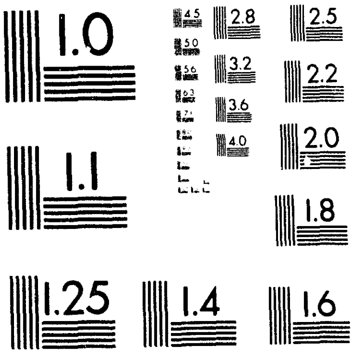

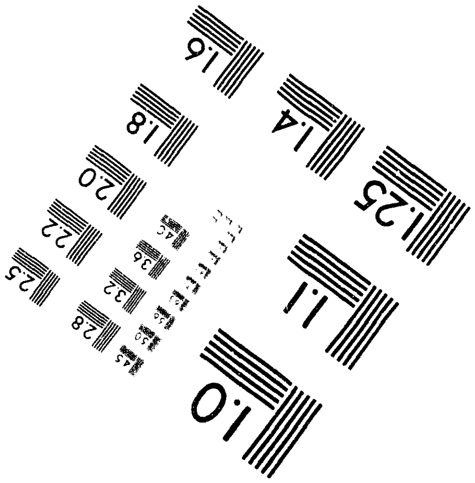

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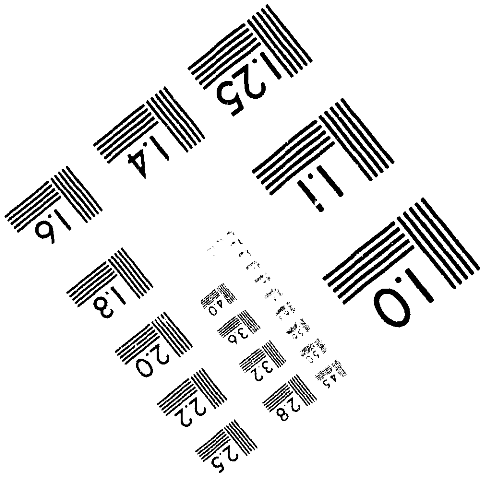

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TABLE 10
UPPER FREEPORT PLANT RESULTS

AVERAGE OF 30 TESTS - TOTAL PLANT

	Ash %	Total Sul %	Pyritic Sul %	Btu
Feed	24.09	4.41	3.20	11048
Product	10.29	2.30	1.06	13456

Plant Yield Percent	71.85
Plant Btu Recovery Percent	87.49
Plant Ash Rejection Percent	69.19
Plant Sulfur Rejection	62.27
Plant Pyritic Sulfur Rejection	75.81
Feed Pounds of SO_2 Per Million Btu	7.98
Product Pounds of SO_2 Per Million Btu	3.42

TABLE 11
ILLINOIS NO. 6 PRECLEANING RESULTS

AVERAGE OF 21 TESTS - PRECLEANING

	Ash %	Total Sul %	Pyritic Sul %	Btu
Feed	35.69	4.27	2.41	9162
Product	22.02	2.86	1.08	11191

Plant Yield Percent	76.41
Plant Btu Recovery Percent	93.30
Plant Ash Rejection Percent	52.80
Plant Sulfur Rejection	48.80
Plant Pyritic Sulfur Rejection	65.80
Feed Pounds of SO_2 Per Million Btu	9.32
Product Pounds of SO_2 Per Million Btu	5.11

TABLE 12
ILLINOIS NO. 6 COLUMN RESULTS

AVERAGE OF 21 TESTS - COLUMN

	Ash %	Total Sul %	Pyritic Sul %	Btu
Feed	22.02	2.86	1.08	11191
Product	7.20	3.00	0.86	13574

Column Yield Percent	75.86
Column Btu Recovery Percent	91.99
Column Ash Rejection Percent	75.04
Column Sulfur Rejection	20.65
Column Pyritic Sulfur Rejection	39.62
Feed Pounds of SO_2 Per Million Btu	9.32
Product Pounds of SO_2 Per Million Btu	4.42

TABLE 13
ILLINOIS NO. 6 PLANT RESULTS

AVERAGE OF 21 TESTS - TOTAL PLANT

	Ash %	Total Sul %	Pyritic Sul %	Btu
Feed	35.69	4.27	2.41	9162
Product	7.20	3.00	0.86	13574

Plant Yield Percent	57.94
Column Btu Recovery Percent	85.80
Plant Ash Rejection Percent	88.21
Plant Sulfur Rejection	59.02
Plant Pyritic Sulfur Rejection	78.65
Feed Pounds of SO_2 Per Million Btu	9.32
Product Pounds of SO_2 Per Million Btu	4.42

TABLE 14
OBJECTIVE SUMMATION

Objectv.	Value	Pgh. No. 8	Upper Free	Ill. No. 6
BTU REC %	85.0	89.51	87.49	85.8
PYR REJ %	85.0	73.69	75.81	78.65
PRO ASH %	6.0	7.65	10.29	7.2
PRO MST %	30.0	35.0	35.0	35.0
REJ MST %	35.0	10.0*	10.0*	10.0*

*Does not include fine reject material.

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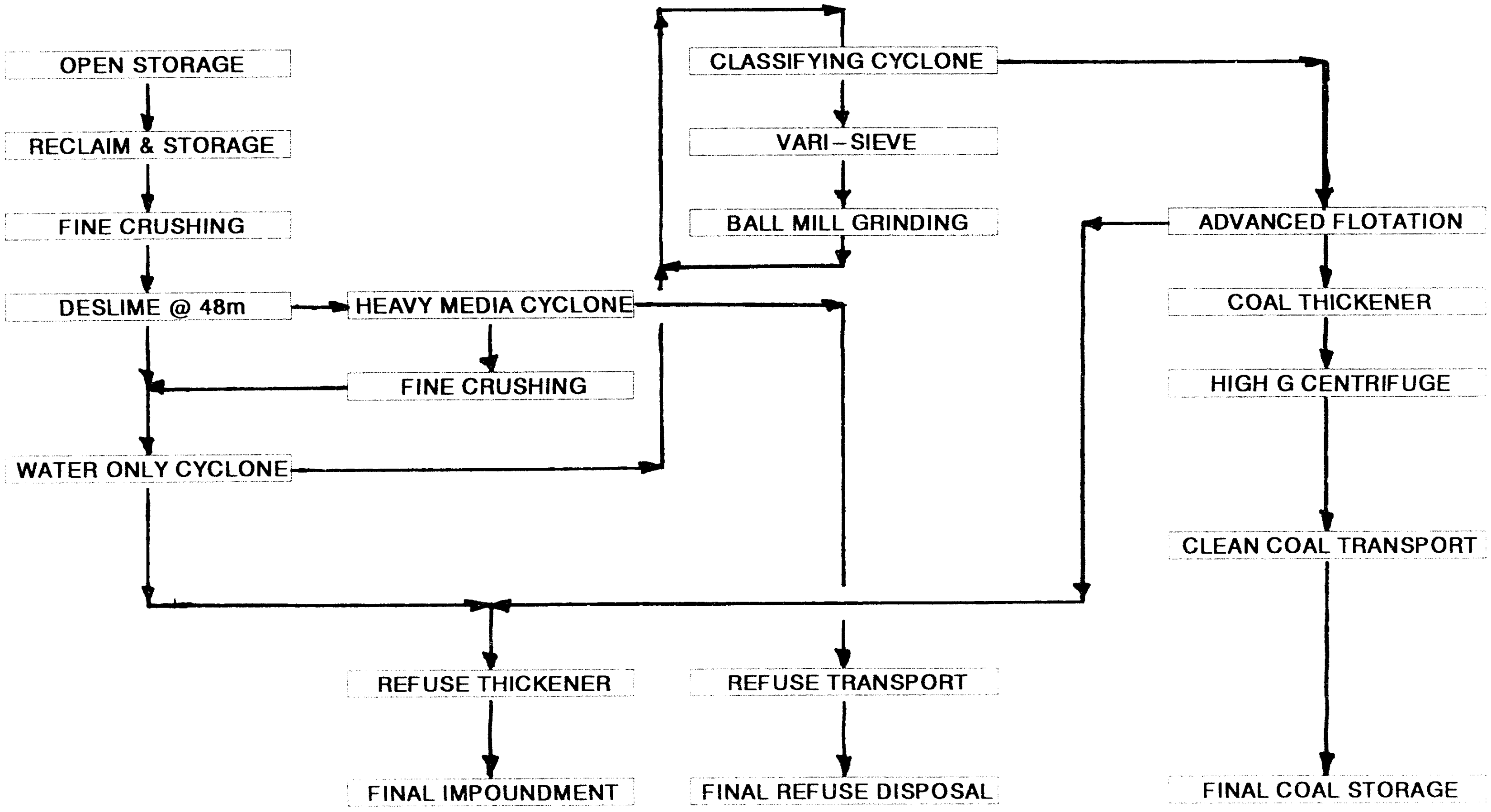
FIGURE NUMBER 1
CONCEPTUAL FLOW LOGIC



New Flotation Schemes for Enhanced Pyrite Rejection

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ABSTRACT

There are two major reasons for incomplete rejection of pyrite from coal. One is the superficial oxidation of pyrite as an inadvertent corrosion-type process, which results in surface hydrophobicity and, hence, self-induced flotation; the other is incomplete liberation, which causes a large fraction of the pyrite to remain locked with the coal as middlings that show considerable floatability. Two complementary concepts have been developed to address these problems. They are referred to as Electrochemically-Enhanced Sulfur Rejection (EESR) and Polymer-Enhanced Sulfur Rejection (PESR) processes. In the EESR process, electrochemical techniques are used to prevent the formation of hydrophobic oxidation products. Active metals and alloys are used as sacrificial anodes to cathodically-protect pyrite from oxidation and, hence, improve pyrite depression. The PESR process uses hydrophilic polymers to depress coal-pyrite middlings. Four water-soluble polymers have been studied in microflotation tests.

INTRODUCTION

The increasingly stringent restrictions on sulfur dioxide emissions from coal-fired power plants have stimulated the search for advanced coal cleaning technologies for removing sulfur from coal. Although flotation is recognized as the best available coal cleaning technique, it is not effective in rejecting pyritic sulfur from coal because 1) superficial oxidation of pyrite occurs during mining, transportation and preparation and results in self-induced flotation of pyrite, and 2) incomplete liberation of pyrite from coal causes a large fraction of the locked pyrite to float with the coal as middlings.

The self-induced flotation of pyrite is generally considered to be related to excess sulfur at the surface and has been investigated by numerous electrochemical studies. Hamilton and Woods (1981) and Buckley and Woods (1987) suggested that pyrite oxidizes to elemental sulfur, sulfate, and possibly metal-deficient sulfides, the first and the last representing the excess sulfur phase. Yoon et al. (1991) and Zhu et al. (1991) concluded that at the initial stages of oxidation, the sulfur on the surface becomes oxidized to polysulfides which represent the excess sulfur phase. Pyrite oxidation can be prevented by adding various reducing agents. Unfortunately, the required amount of reducing agents is high and the reagents themselves can be toxic.

An alternative method to prevent pyrite oxidation is to take advantage of galvanic interactions between pyrite and reactive metals. Pyrite is a semiconducting mineral and is expected to undergo galvanic interactions with other conducting materials upon contact. Since pyrite is more noble than other sulfides or metals, it will act as the cathode and its oxidation will be inhibited. Adam et al. (1984) observed the galvanic coupling between pyrrhotite and metal electrodes including mild steel, stainless steels, zinc and magnesium, which reduced the floatability of pyrrhotite. Pozzo et al. (1990) reported remarkable reduction in flotation recovery of pyrite and pyrrhotite by xanthate when they were ground in nitrogen atmosphere. These studies suggest that galvanic coupling of pyrite with active metals can be used to control the oxidation of pyrite and, hence, its floatability. This method is referred to as the Electrochemically-Enhanced Sulfur Rejection (EESR) process.

The incomplete liberation of pyrite from coal creates coal-pyrite composites, which behave more like coal during flotation. The solution to the problem may seem obvious: comminution of coal to a size at which the pyrite is fully liberated; however, grinding is energy-intensive and entails high dewatering costs. It is, therefore, necessary to develop a process that can remove pyrite when it exists in locked form at a relatively coarse size. The loss of coal in the form of coal-pyrite middlings is minimal because the population of the middlings is not high as compared to that of pure coal particles. One solution may be to use polymeric depressants that can selectively depress the middlings. This method is referred to as the Polymer Enhanced Sulfur Rejection (PESR) process.

This report describes the recent progress made in the EESR and PESR processes developed at CCMP.

EXPERIMENTAL

Samples Mineral-pyrite specimens, originally from Peru, were supplied by Ward's Scientific Co. The Illinois No. 6 coal-pyrite and the Pittsburgh No. 8 coal-pyrite were in the form of chunks and contained only small amounts of coal. The coal pyrite was crushed to -6 mm using a laboratory jaw crusher and dry pulverized in a laboratory hammer mill. They were pre-cleaned on a small-scale separation table before being used for flotation tests. Synthetic pyrite middlings were made by mixing known amounts of mineral pyrite (-16+28 mesh) with a hydrophobic resin, Serifix-SQ, manufactured by Struers, which is a cold-setting polyester resin containing methylethylketoneperoxide.

Microflotation Tests Flotation tests were conducted in a 140 ml microflotation cell containing a glass frit for dispersing gas. Buffer solutions were used in all the tests and nitrogen used as the purging and flotation carrier gas (35 ml/min). A 1.0 g sample was conditioned with kerosene (60 ppm, emulsified) and with MIBC (50 ppm) for 2 minutes prior to flotation. The recovery was determined after three minutes.

Electrochemical Measurements Pyrite electrodes for galvanic coupling studies were cut into 10×10×5 mm rectangles. A copper wire was attached to one of the 10×10 mm faces using a conducting silver epoxy. Metal electrodes were fabricated the same way. Electrodes for the measurement of potential during flotation were of smaller dimensions and mounted at the end of a 7-mm diameter glass tube. Electrochemical experiments were carried out at ambient temperature using a conventional three-electrode system. Solutions were bubbled with N_2 for at least 30 minutes before experiments and N_2 was kept flowing over the solution surface during experiments to prevent the diffusion of air into the cell. A Pine RDE-4 potentiostat was used to control the potential. Potentials were measured against a saturated calomel reference electrode and converted to the standard hydrogen electrode (SHE) by adding 0.245 V. Galvanic interactions between pyrite and active metals as a sacrificial anode were studied using two independent electrochemical cells connected by a salt bridge. Galvanic coupling between pyrite and metal electrodes was accomplished by connecting them with a copper wire.

Electrochemical-microflotation cell A detailed description of the electrochemical-microflotation cell has been provided by Walker et al. (1984). The main advantage of this cell, as Tao et al. (1993) emphasized, is that electrochemical studies and flotation tests can be done on the same system. The bed used in the present study consisted of a 1.0 g mineral-pyrite sample of -65+100 mesh particles. The bed potential was controlled with a PAR 273 potentiostat.

RESULTS AND DISCUSSION

Effect of E_h and pH on Floatability of Pyrite A series of microflotation tests were conducted to evaluate the effect of electrochemical potential (E_h) on pyrite floatability at various solution pH's. The potentials were controlled by the addition of hydrazine and sodium sulfide as reducing agents and potassium permanganate as an oxidizing agent. Because of the strong alkalinity of hydrazine and sodium sulfide, acid had to be used to adjust the pH. Platinum- and pyrite-electrodes were used to measure the redox potentials of the solutions and the potentials assumed by the mineral, respectively.

Figure 1 shows the flotation recovery of mineral pyrite as a function of potential at several pH's. Illinois No. 6 coal-pyrite exhibited similar behavior, although flotation recoveries were lower. It is clear that the floatability of pyrite is dependent on potential and solution pH. Pyrite exhibits maximum flotation recovery over a narrow potential range. Figure 2 shows similar results obtained in the electrochemical-microflotation cell in which the bed potential was controlled by a potentiostat. The lower and higher flotation edges are, respectively, -0.3 V and 0.4 V at pH 9.2, 0.1 V and 0.8 V at pH 4.6. The flotation results appear to be in agreement with the known electrochemistry of pyrite oxidation. Buckley and Woods (1984), Ahlberg et al. (1990), Yoon et al. (1991) and Zhu et al. (1991) have suggested that elemental sulfur (S^o), metal-deficient sulfide ($Fe_{1-x}S_2$, $x < 1$) or polysulfide (FeS_n, $n > 2$) are produced *via* reactions such as:

$$FeS_2 + 3OH^- = 2S^o + Fe(OH)_3 + 3e^-, \tag{1}$$

$$nFeS_2 + 3(n-2)OH^- = 2FeS_n + (n-2)Fe(OH)_3 + 3(n-2)e^-, \tag{2}$$

$$FeS_2 + 3xOH^- = Fe_{1-x}S_2 + xFe(OH)_3 + 3xe^-. \tag{3}$$

These sulfur-rich surface species are naturally hydrophobic and can render the mineral floatable. The lower flotation edge corresponds to the potential at which incipient oxidation of pyrite occurs (Tao et al., 1994). The upper flotation edge is determined by reaction (4), which represents the aggressive oxidation of pyrite to ferric hydroxide and sulfate,

$$FeS_2 + 11H_2O = Fe(OH)_3 + 2SO_4^{2-} + 19H^+ + 15e^-. \tag{4}$$

Figures 1 and 2 also reveal that the flotation recovery is generally lower at pH 9.2 and 6.8 than at pH 4.6. As the solution pH increases, more ferric hydroxide is formed on the surface of pyrite, which suppresses its hydrophobicity. Ahlberg et al. (1990) and Pang and Chander (1993) reported a substantial increase in pyrite floatability at pH 9.2 and 11 when an iron chelating agent, EDTA, was used to remove ferric hydroxide from the surface of pyrite. This is in agreement with the electrochemical-microflotation tests shown in Figure 2, which shows that EDTA dramatically increased the floatability of mineral-pyrite in pH 9.2 solution. Figure 2 also indicates that the use of kerosene in coal flotation will lead to a pronounced increase in unwanted pyrite recovery. Olson and Aplan (1987) reported that an oil dosage of 0.35 kg/ton promoted the flotation of clean coal by a factor of 3 and that of pure pyrite by a factor of 30. It is believed that moderate hydrophobicity of coal-pyrite induces a hydrophobic interaction (Xu and Yoon, 1989) between pyrite and kerosene which, in turn, considerably increases the hydrophobicity of pyrite.

Mineral-pyrite exhibits stronger floatability than Illinois No. 6 coal-pyrite. Mineral-pyrite showed almost 100% recovery at pH 4.6 and 6.8 while recovery of coal-pyrite was less than 25% (not shown). The lower floatability of coal-pyrite indicates that there are more hydroxides on its surface due to oxidation. Tao et al. (1993) observed that Pittsburgh No. 8 coal-pyrite produced lower amounts of soluble iron-hydroxyl species compared to mineral-pyrite. Coal-pyrite is poorly crystallized and possesses more defects on the surface. Consequently, it oxidizes faster than mineral-pyrite and metastable hydrophobic sulfur species may be more readily transformed to soluble sulfate, increasing the net hydrophilicity of the surface (Tao et al., 1993, Zhu et al., 1991).

EESR process An important conclusion that can be drawn from the above study is that pyrite can be depressed under reducing or strongly oxidizing conditions; however, oxidizing conditions are not preferred for coal-pyrite depression because they also oxidize coal, thus decreasing its floatability and reducing the separation efficiency. Sadowski et al. (1988) studied the behavior of Upper Freeport coal and found that the oxidation of coal gradually increased both the carboxyl and hydroxyl concentration on the coal surface and reduced the hydrophobicity of coal. Therefore, reducing conditions may be more appropriate for enhancing pyrite rejection. Zinc, manganese and aluminum have their reduction potentials at -1.662, -1.180 and -0.763 V, which are substantially more negative than that of pyrite. The rest potential of pyrite is 0.6 V at pH 4.6 and 0.18 V at pH 9.2 (Chander and Briceno, 1987). The galvanic interaction will take place between pyrite and the metal upon contact, with pyrite acting as the cathode and the metal as the sacrificial anode.

Figure 3 illustrates the potentials of Pittsburgh No. 8 coal-pyrite and metal (aluminum, zinc and manganese) electrodes as a function of galvanic coupling time at pH 4.6. Prior to galvanic coupling, pyrite had a potential of about 0.3 V and aluminum, zinc and manganese had potentials of -0.65, -0.84 and -1.10 V, respectively. Upon galvanic coupling, the potential of pyrite was lowered to -0.24, -0.35 and -0.42 V by aluminum, zinc and manganese, respectively. The corresponding galvanic current was dependent on the metal. Manganese gave rise to the highest current and aluminum the lowest. Galvanic coupling experiments at pH 9.2 showed similar results. It is believed that the following reactions occur upon galvanic coupling in the absence of oxygen in the electrolyte,

$$\textit{Anode:}\quad M = M^+ + e^- \tag{5}$$

$$\textit{Cathode:}\quad Fe(OH)_3 + e^- = Fe(OH)_2 + OH^- \tag{6}$$

$$S^o + H_2O + 2e^- = HS^- + OH^- \tag{7}$$

where reaction (5) represents the oxidation of metal atoms M to cations M^+ and reactions (6) and (7) are the reduction of oxidation products of pyrite.

Figure 4 shows the first voltammogram of an Illinois No. 6 coal-pyrite electrode after it was galvanically coupled with a manganese anode at pH 4.6. In quiescent solution, galvanic coupling greatly reduced the anodic peak at 0 V and the cathodic peak at -0.2 V. In stirred solution, galvanic coupling eliminated these peaks. These two peaks were found by Hamilton and Woods (1981) and Tao et al. (1993) to correspond to oxidation/reduction processes involving the S^o/HS^- couple. Apparently, galvanic coupling reduced sulfur-like species to HS^-, which diffuse away from the surface. Solution stirring accelerated the diffusion process. The removal of sulfur-like species from the surface eliminates the source of the hydrophobicity of pyrite and, therefore, reduces its self-induced floatability.

Microflotation tests were conducted to determine the most effective sacrificial anode material to depress pyrite. Pyrite was conditioned with metal powders (-325 mesh) for 10 seconds prior to flotation. Figure 5 shows the effect of galvanic coupling with Mn and Zn on the potential and floatability of Illinois No. 6 coal-pyrite at pH 4.6. As shown, pyrite was remarkably depressed by galvanic contact with the metals. In the absence of metal powders, the coal-pyrite exhibited a flotation recovery of 73%. With the addition of Mn and Zn powders, the coal-pyrite showed only negligible floatability.

Of the anodes examined in this work (Zn, Mn, Fe, Al and several alloys), zinc was the most effective for depressing pyrite, although it did not lower the potential of pyrite as much as manganese. This may be due to the lower solubility of $Zn(OH)_2$ ($K_{sp}=7.18\times10^{-17}$) than $Mn(OH)_2$ ($K_{sp}=2.04\times10^{-13}$), leading to a higher degree of passivation. During galvanic interaction, metal ions released from the anode by oxidation may migrate to the cathode to combine with OH^-, forming hydroxides. Such hydrophilic coatings may aid in depressing pyrite. This is in agreement with the conclusions of Kuhn and Chan (1983). It is believed that galvanic coupling of pyrite with active metals depresses pyrite through two important mechanisms: 1) decreasing the pyrite potential to a value negative enough to prevent superficial oxidation and/or reduce hydrophobic species already present on the surface, and 2) preferentially forming metal hydroxides on the surface by the generation of hydroxyl ions, i.e., reactions (6) and (7).

PESR process One of the most important mechanisms of pyrite recovery in coal flotation is the existence of pyrite-coal composite particles resulting from incomplete liberation. It was observed by Wang et al. (1993) that composites containing small amounts of coal had flotation behavior resembling coal rather than pyrite. Oblad (1985) reported that all pyrite particles recovered in the froth product had coal on the surface and those remaining in the tailings were free of coal. It appears necessary to mask the carbonacious part on the surface before middling particles can be depressed.

Polymers are commonly used as flocculants in mineral and coal processing processes but their applications as depressants are scarce, especially for sulfide minerals. Griffith and Parkinson (1975) reported that acrylamide polymers can be employed as gangue depressants in cassiterite ore flotation. Recently, Nagaraj et al. (1992) showed that some functionalized synthetic polymers sharply decreased pyrite flotation recovery by xanthate. This is attributed to the incorporation of sulfide-specific functional groups into these hydrophilic polymers which strongly adsorb on the mineral surface and provide more hydrophilic sites. However, polymer depressants have not been studied for pyrite-coal composite particles. If functional groups in the polymer react with pyrite, the hydrophilic polymer chains may be able to stretch over the coal inclusions, rendering pyrite-coal composites hydrophilic.

Four functionalized synthetic polymers have been developed recently by CYTEC Industries (formerly American Cyanamid). They were dissolved in water and emulsified to make 3% aqueous solutions prior to use. The polymers were tested on freshly-ground -100+200 mesh mineral-pyrite and -100+200 mesh Pittsburgh No. 8 coal at pH 6.8. In each test, diluted and emulsified polymer was added directly to microflotation cell and conditioned for 1.5 minutes before the addition of kerosene. Figure 6 shows the effect of polymer dosage on the flotation of coal and pyrite. Dosages of 50 to 100 g/ton are high enough for effective depression of pyrite and higher dosages do not offer much additional benefits. With the exception of polymer S7261, these polymers also reduced the floatability of coal even at relatively low dosages. Polymer S7261 exhibited significant depression effect on pyrite and marginal adverse influence on coal floatability at dosages less than 100 g/ton and is clearly the most effective.

The results of microflotation tests on Illinois No. 6 coal-pyrite middlings and Serifix-pyrite composites using polymer S7261 at pH 6.8 are given in Figure 7. A dosage of 50 g/ton gives rise to an impressive reduction in middlings recovery from 61 to 46% and a reduction in Serifix-pyrite-composite recovery from 29 to 15%. Dosages greater than 50 g/ton have almost no further depression effect.

To further evaluate the depressing effect of S7261, SEM-Image Analysis studies were conducted on the feed, concentrate and tailing for the test in which a dosage of 50 g/ton polymer was added. Figure 8 illustrates the effect of the polymer in rejecting different middling particles. It is obvious that the polymer is more effective in depressing middlings with more pyrite. This is because the pyrite provides adsorption sites for the polymer that covers the carbonacious part of the surface. For particles with 30-70% pyrite by weight, the polymer rejected 50-60% of the pyrite-coal middlings.

CONCLUSIONS

1. Pyrite acquires hydrophobicity upon superficial oxidation, the lower and upper potential limits for flotation being a function of pH.
2. Flotation of pyrite can be depressed effectively by controlling the potential using oxidizing or reducing agents.
3. The floatability of pyrite can be significantly reduced by the metal hydroxides that precipitate on the surface in alkaline solutions. The use of EDTA, which can remove the hydroxides, can dramatically increase the floatability.
4. Galvanic coupling of pyrite with active metals and alloys can prevent its superficial oxidation and/or reduce the hydrophobic species formed as a result of oxidation.
5. Cytec Polymer S7261 gave remarkable depression of pyrite and pyrite-coal middlings without significant adverse effect on coal floatability.

ACKNOWLEDGEMENTS

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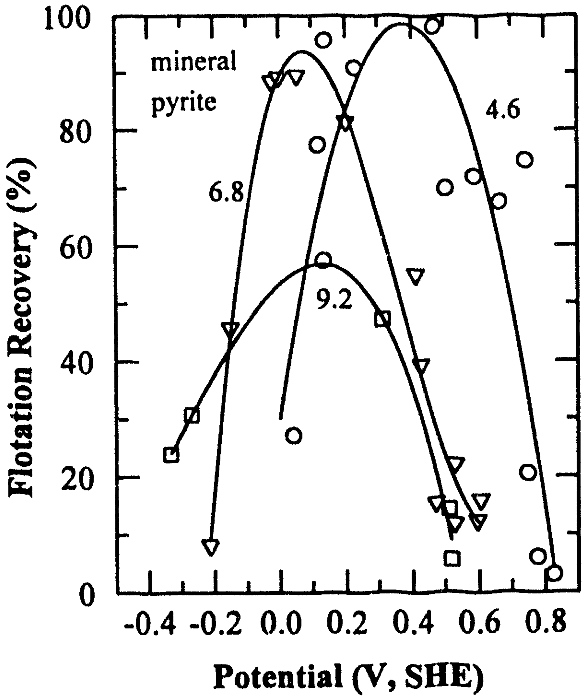

Figure 1. Flotation recovery of 100-200 mesh mineral-pyrite as a function of pyrite potential at different pH's.

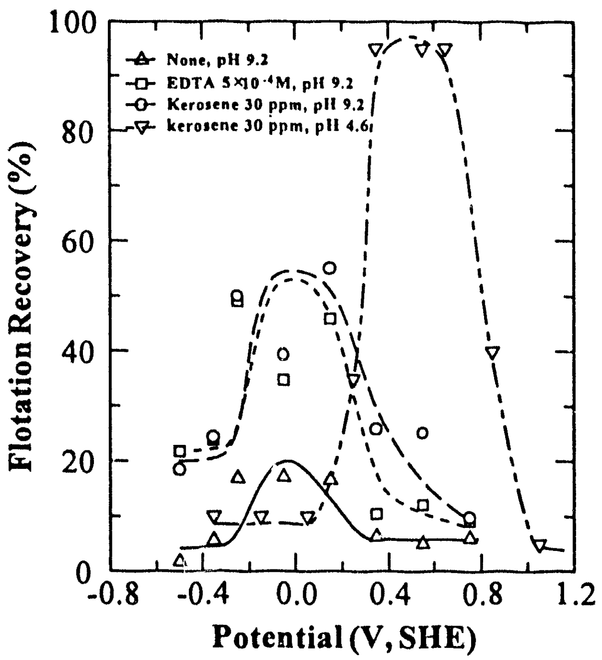

Figure 2. Flotation recovery of 65-100 mesh mineral-pyrite as a function of potential at pH 4.6 and 9.2.

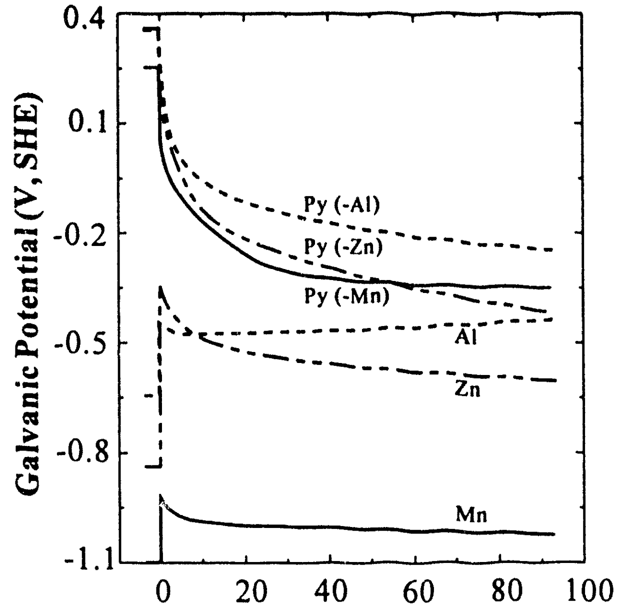

Figure 3. Potentials of Illinois No. 6 coal-pyrite and metal electrodes as a function of galvanic coupling time at pH 9.2.

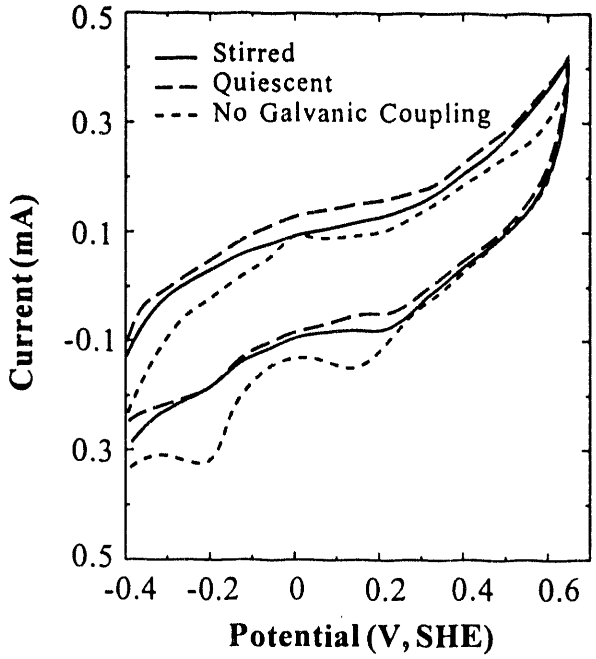

Figure 4. The effect of galvanic coupling of Illinois No. 6 coal-pyrite with a manganese anode on the first voltammograms at pH 4.6.

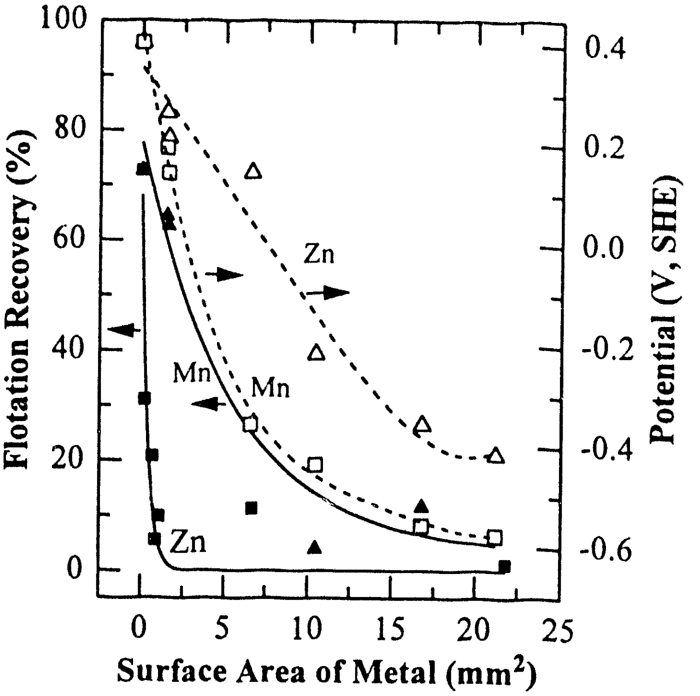

Figure 5. The effect of the surface area of manganese and zinc powders on the flotation and electrochemical potential of 100-200 mesh Illinois No. 6 coal-pyrite at pH 4.6.

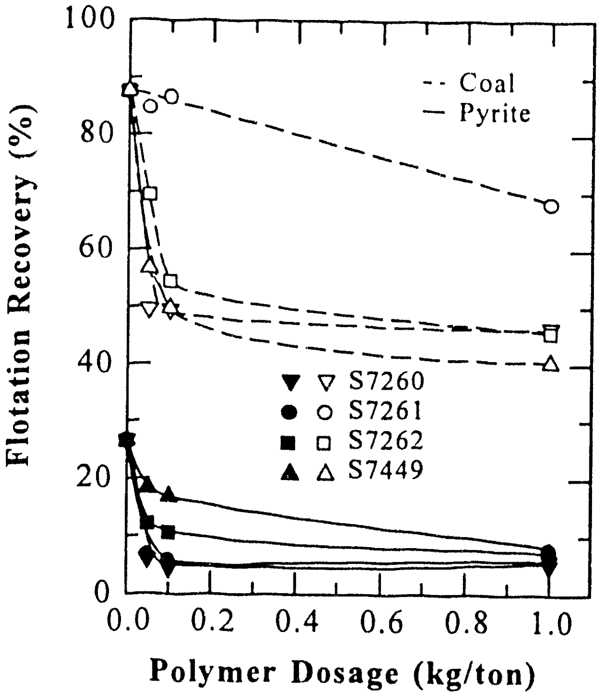

Figure 6. The effect of polymer dosage on the flotation recovery of 100-200 mesh mineral-pyrite (solid line) and Pittsburgh No. 8 coal (dashed line) at pH 6.8.

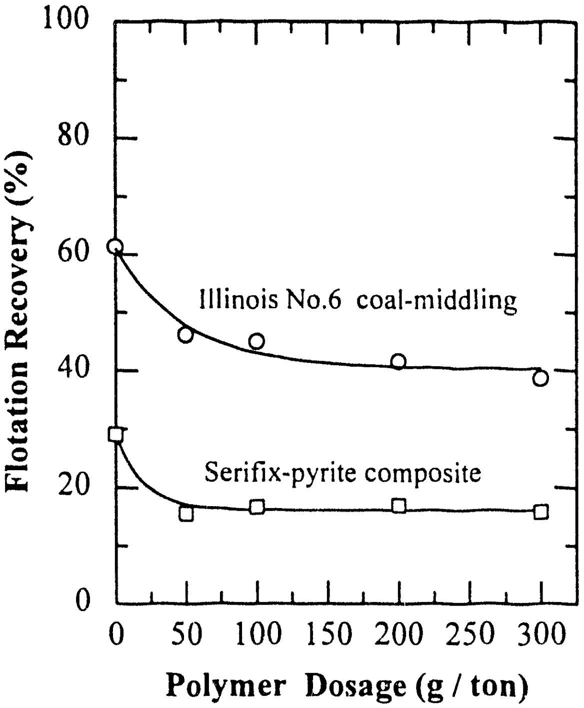

Figure 7. The effect of polymeric depressant S7261 on the recovery of Illinois No. 6 middlings and on Serifix-pyrite synthetic composite middlings at pH 6.8.

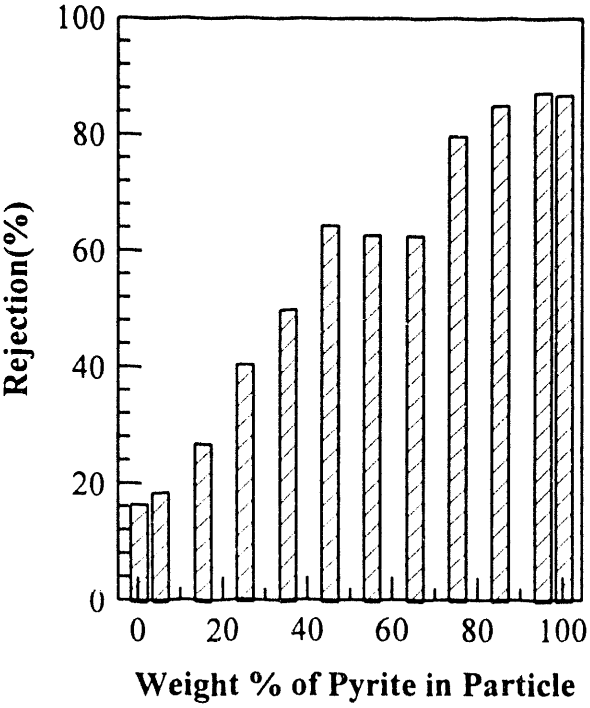

Figure 8. The effect of polymer in rejecting coal-pyrite middling particles containing different percent of weight of pyrite at pH 6.8.

DURABILITY OF VARIOUS RAW AND DRIED LOW-RANK COALS

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EXECUTIVE SUMMARY

Low-sulfur subbituminous coals have high moisture content and, consequently, low heating value, leading to boiler derating in U.S. midwestern and eastern utilities as well as switching and/or blending coals to achieve SO_2 compliance. In their drive to develop cost-effective coal-drying processes, coal developers have focused on heat content of the products and neglected the critical stability issues of friability and dusting, moisture reabsorption, and spontaneous heating. The Energy & Environmental Research Center (EERC), in an effort to establish new standards for dried products, has used various known methods as well as developed new methods to evaluate the propensity of lump western coals, raw and dried, to produce dust and absorb water. Three drying methods—air, hot water, and saturated steam—were used to generate low-moisture upgraded products. New indices for dust generation and friability were determined to assess the effects of moisture removal and upgrading methodology on coal stability. Analysis of the dried coals using various strength tests indicated that the reduction in moisture made the lump coal unstable, yielding substantially higher dust and friability indices relative to those of the raw coals.

INTRODUCTION

The low-rank coal (LRC) upgrading technologies being developed include evaporative and nonevaporative drying and mild pyrolysis/gasification. An obstacle facing their development is the stability of the product with regard to dusting, moisture reabsorption, and spontaneous combustion. Because stability phenomena are often given only minor attention, the development of improved stability-testing methods was deemed a necessary, yet complementary, component in the successful demonstration of upgrading technologies (1). Currently, four ASTM procedures are available to address the physical stability of coal or coal-derived products: D1412-86 (equilibrium moisture), D441-45 (tumbler test), D409-71 (Hardgrove index), and D440-49 (drop–shatter test) (2). This report documents the preliminary results of the development of laboratory tests to assess the stability of LRCs treated by conventional and advanced drying/pyrolysis processes.

Three drying methods (air, hot water, and saturated steam) were used to generate low-moisture, upgraded products for physical stability measurements. Standard test methods as well as methods developed at the EERC were used to evaluate the propensity of lump western LRCs (raw and dried) to produce dust or coal fines, which make them difficult to handle by conventional means. Indices for dust generation and friability were generated for raw and upgraded coals to observe the effect of moisture removal and upgrading methodology on coal stability. Spontaneous combustion testing or "self-heating" studies on LRC and dried LRCs are planned to begin in 1994.

EXPERIMENTAL PROCEDURE

Coal Preparation and Drying. Coals processed in subsequent drying tests were sized to 12.7 x 6.7 mm via stage crushing and bottom sizing. This size range was determined to be representative of upgraded coals produced by drying and pyrolysis processes currently in stages of development ranging from bench through demonstration scale (3, 4).

The three coal-drying methodologies tested included air drying, hot-water drying (HWD), and saturated steam drying (SSD). Air drying was performed to observe the effects of low-temperature, evaporative drying on coal stability. The drying period was extended, as necessary, until the desired moisture content was attained; the total coal moisture content was verified by ASTM Method D3173.

The hydrothermal drying processes (HWD and SSD) were performed to observe the effects of nonevaporative drying on coal stability. During HWD, the coal is totally immersed in the water phase, whereas during SSD, the coal is in contact with only the vapor phase (saturated steam). The systems and procedures for hydrothermal treatment have been described elsewhere (4–6).

Durability Testing. A modified ASTM tumbler test was used to determine the relative friability and abrasiveness of the sized, raw, and treated coals during simulated handling. The main internal flights were adjusted to accommodate a smaller coal size, 12.7 x 6.7 mm. A more detailed presentation of the modified tumbler test assembly and procedures can be found elsewhere (7).

Prior to tumbler testing, the weights of test coals retained on 9.5- and 6.7-mm screens were determined. These two screen fractions were recombined prior to tumbler testing. Tumbler tests were performed by varying rotational speed (40 to 80 rpm, ASTM = 40 rpm), coal charge (100 to 1000 grams, ASTM = 1000 grams), and total revolutions (600 to 14,400, ASTM = 2400). Tumbled coal samples were classified into seven size-fractions ranging from 9.5 mm to 0.60 mm. The weights of the feed and tumbled coal weight fractions were used to calculate the tumble index (T_i), defined by Equation 1, for each screen size fraction.

$$T_i = (W_T - W_F) \times (100/W_A) \qquad \text{[Eq. 1]}$$

where W_T = Weight of tumbled coal for screen size i, grams
W_F = Weight of feed coal for screen size i, grams
W_A = Weight of total feed coal for tumbler test, grams

This equation was derived to remove the effect of feed coal size and sample mass variations on tumbler results, thus allowing comparison of different coal types.

In addition to tumble indices, the screening results from durability testing were converted to friability and dust indices. Background on the ASTM tumbler tests and calculation of friability indices are presented elsewhere (2). The "s" factor was calculated using Equation 2, and the friability indices were calculated by Equation 3. The former equation represents a modified method of calculating the "s" factor, which relates the fraction of coal on individual screens to the average feed coal size rather than that of the top screen only (ASTM procedure). Reference to an estimated average particle size for the feed coal broadens the base point used for calculations, thus more accurately reflecting the variability and size of the feed coal. The sample's dust indices were determined similarly to ASTM procedures by simply measuring the weight percent of coal passing the 0.3-mm (50-mesh) screen.

$$s = \mathrm{wt\%}_{(on\ screen)} \times \mathrm{A}_{is}/\mathrm{A}_p \qquad \text{[Eq. 2]}$$

where A_{is} = Average initial screen size
A_p = Estimated average particle size of feed material

$$\mathit{Friability}\ (\%) = 100 - \Sigma s \qquad \text{[Eq. 3]}$$

A modified ASTM D440 drop–shatter test was also used to determine the relative size stability and its complement, friability, via a method similar to the tumbler test. Drop–shatter testing is used to estimate the ability of coal to withstand breakage when subjected to handling at the mine and during transit to the consumer. In this test, 50 grams (50 pounds, i.e., 2268 grams, in ASTM method) of raw or dried coal was classified to determine size distribution, recombined, and then dropped through a 1.83-m section of PVC pipe. Each coal sample was dropped 10 consecutive times, and classification was performed after the second, sixth, and tenth (final) drop.

Coal durability testing was also completed on Colstrip subbituminous samples using a modified Jameson cell, developed at the University of Newcastle (Australia) (8). The Jameson unit consists of an ASTM tumbler cell with an in-line dust collection system. This test method combines the tumbler and dust tests into one procedure. Results are determined by sieve analysis, amount of dust collected, and the moisture content of periodic samples.

RESULTS

Drying Testing. Hydrothermal drying tests were performed with three coals. Knife River lignite (North Dakota), Colstrip subbituminous (Montana), and Little Tonzona Creek subbituminous (Alaska). Saturated steam drying and hot water drying were performed at 300°C. Table 1 summarizes the proximate and ultimate analyses (equilibrium moisture basis) for the raw and dried coals. The changes in each coal caused by the drying processes included irreversible removal of moisture, enhancement of heating value, and reduction of oxygen content (via decarboxylation). The theoretical emissions of ash and SO_2 (lb/MMBtu) were 1) significantly reduced for the Colstrip subbituminous; 2) significantly increased for the Knife River lignite; and 3) relatively unchanged for the Little Tonzona Creek subbituminous.

TABLE 1

Proximate, Ultimate, and Heating Value for
Raw, HWD,[1] and SSD[2] Subbituminous and Lignite Coal (equilibrium moisture basis)

Coal:	Little Tonzona			Colstrip			Knife River		
Drying Type:	–	HWD	SSD	–	HWD	SSD	–	HWD	SSD
Equil. Moisture, wt%	31.0	11.1	9.5	25.3	9.3	8.6	35.1	15.0	12.6
Proximate, wt%									
Volatile Matter	36.1	39.4	39.1	29.9	34.4	34.2	29.7	35.1	36.2
Fixed Carbon	25.8	39.5	41.0	37.2	47.6	48.2	27.7	38.8	39.9
Ash	7.1	10.0	10.4	7.6	8.7	9.0	7.5	11.1	11.3
Ultimate, wt%									
Hydrogen	6.8	5.2	5.1	6.0	5.3	4.9	6.7	5.4	5.3
Carbon	41.2	58.3	59.1	50.4	63.8	63.8	40.3	55.7	56.9
Nitrogen	0.5	0.6	0.6	0.5	0.7	1.0	0.5	0.7	0.8
Sulfur	1.1	1.3	1.2	0.8	0.8	0.7	0.9	1.4	1.4
Oxygen	43.4	24.6	23.5	34.7	20.6	20.6	44.0	25.7	24.3
Ash	7.1	10.0	10.4	7.6	8.8	9.0	7.5	11.1	11.3
Heating Value, Btu/lb	7030	10,030	10,200	8550	10,850	10,830	6740	9400	9550

[1] HWD, hot-water-dried.
[2] SSD, saturated-steam-dried.

Durability Testing. Prior to evaluation of dried coals, tumbler tests were performed with sized, raw Colstrip subbituminous coal to determine appropriate tumbling parameters: lifting shelf dimensions, mass of coal sample, tumbler speed, and total revolutions. Tests were first performed using two different lifting shelves at an ASTM specification tumbling speed of 40 rpm and total revolutions of 2400. Friability and dust indices of raw coals tumbled with the ASTM specification lifting shelf (1.6-cm gap, 1.9-cm ledge) were 30% to 50% lower than indices obtained when tumbling the same coals with the modified lifting shelf. Tumbler testing also indicated a substantial increase in fines production as the revolutions increased, little difference in fines production as tumbler speed changed, and a proportional relationship between fines generated and the amount of coal used for the tumbler test. However, the repeatability of indices was adversely affected by a reduction in coal test quantity (100 grams versus 1000 grams) when using the ASTM specification lifting shelf. Because of the limited amount of dried coals available for subsequent testing, the modified lifting shelf was considered necessary to assure sufficient test coal agitation and achieve repeatability of indices.

Further, an evaluation of tumbling speed was performed on the raw, sized coals by comparing friability and dust indices obtained at 40 rpm and 2400 revolutions (ASTM specifications) and 80 rpm and 2400 revolutions. The indices were not substantially different; consequently, the higher tumbling speed (80 rpm) was implemented to test dried coals and to allow testing of more coal samples within the study test period. The appropriate insert dimensions and tumbling speed were established prior to performing tests on sized raw, air-dried (AD), HWD, and SSD samples of Colstrip and Little Tonzona subbituminous coals and Knife River lignite. Revolutions were varied from 1200 to

14,400 in 1200 revolution increments. As an example, Figure 1 illustrates the effects of varying the total revolutions for 100-gram samples of raw, AD, HWD, and SSD Colstrip coals. A negative tumble index reflects a net mass reduction for a particular coal size as a result of comminution; conversely, a positive tumble index reflects a net mass increase for a particular coal size due to comminution of larger particles. The moisture content of the tumbled samples and the method of drying may both have been factors affecting the level of coal comminution. The AD, HWD, and SSD Colstrip coals, with tumbler-tested moisture contents of 10.7, 9.4, and 4.4 wt%, respectively, experienced significant reduction of the +6.7-mm fractions relative to the raw coal that was tested at 30 wt% moisture. In addition to tumble index, the friability and dust indices were also calculated and are summarized in Table 2 for the three different coal samples. Results reported in Table 2 represent 100-gram tests performed at 80 rpm for 2400 revolutions. Table 3 summarizes the sieve analysis, estimated average particle size, and indices for tumbling tests completed with Colstrip coal samples.

Drop–shatter test results for two- to ten-drop tests on the raw coals indicated that the Little Tonzona friability index varied from 0.7 to 3.8, while the more friable Colstrip and Knife River coals varied from 2.0 to 10.7 and from 0.5 to 5.3 for two to ten drops, respectively. The friability indices of all dried coals were significantly higher than those of the parent coals, reemphasizing that dried samples are anticipated to be much more susceptible to excessive breakage when handled. Results for the drop–shatter test program are summarized for ten-drop data and presented in Table 2.

Table 2 also presents the test moisture of the coal samples and the Hardgrove indices in the various samples. Similarities were realized in ten-drop and tumbler friability data. However, substantially more fines were generated during tumbler tests for the same three Colstrip samples. This indicates that the tumbler test had more attrition, and drop–shatter testing presented more of an impact test to the coal product.

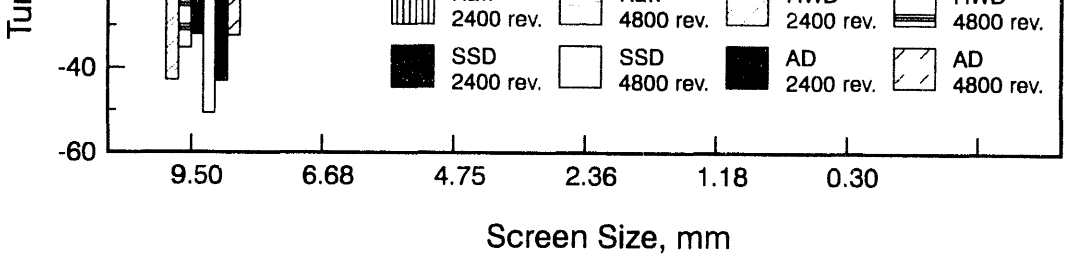

Figure 1. Tumble indices for raw, AD, HWD, and SSD Colstrip as a function of total revolutions.

TABLE 2

Hardgrove Index, Friabilities, and Dust Indices for Raw, AD,[1] HWD, and SSD Subbituminous and Lignite Coals

Coal:	Little Tonzona				Colstrip				Knife River			
Drying Type:	Raw	AD	HWD	SSD	Raw	AD	HWD	SSD	Raw	AD	HWD	SSD
Moisture, wt%	30.0	9.0	8.5	7.2	22.5	10.7	9.4	4.4	37.5	8.1	9.6	11.6
Hardgrove Index	21	ND[2]	69	64	44	ND	65	64	64	ND	74	74
Processing												
Friability, %	ND	ND	13.4	14.3	ND	ND	7.1	4.6	ND	ND	10.9	17.6
Dust Index, %	ND	ND	0.7	0.4	ND	ND	0.6	0.2	ND	ND	1.1	0.4
Tumbler Test (2400 revolutions)												
Friability, %	6.7	14.1	20.9	37.1	7.2	26.0	33.0	39.2	7.2	37.4	41.1	38.4
Dust Index, %	0.7	2.9	6.8	13.6	1.7	7.0	6.2	10.3	1.7	6.0	10.3	7.5
Drop–Shatter Test (10 drops)												
Friability, %	3.8	13.2	20.7	26.6	10.7	33.1	26.3	40.5	5.3	35.6	34.8	34.2

[1] AD, air-dried.

[2] ND, not determined.

TABLE 3

Summary Information from Tumbler Tests Conducted on Various Colstrip Samples

Drying Type:	Raw		Air-Dried		HWD		SSD	
Moisture, wt%	22.5		10.7		9.4		4.4	
Revolutions	___	2400	___	2400	___	2400	___	2400
Ave. size, mm	10.5	9.5	10.0	7.0	9.7	6.5	9.3	5.7
Size, mm	Cumulative Weight Percent Retained on Screen							
9.5	81.1	58.1	63.6	20.8	54.0	11.2	40.1	8.2
6.68	100.0	90.0	100.0	59.2	100.0	53.8	100.0	45.3
4.75	100.0	95.5	100.0	74.6	100.0	71.7	100.0	61.2
2.36	100.0	97.3	100.0	86.3	100.0	83.8	100.0	73.0
1.18	100.0	97.7	100.0	90.1	100.0	88.3	100.0	80.7
0.03	100.0	98.3	100.0	93.0	100.0	93.8	100.0	89.7
Friability Index %	9.8		26.0		33.0		39.2	
Dust Index %	1.7		7.0		6.2		10.3	

Figures 2 and 3 summarize the results from Jameson test results for raw and treated Colstrip samples when tumbled in the ASTM cell for 180 minutes. Figure 2 indicates a dramatic decrease in raw coal moisture content to 9 wt%, while only slight variances in moisture content for the treated samples. Figure 3 represents the amount of fines, classified as −0.8-mm material, versus tumbling time for the same three Colstrip samples. This figure indicates that fines amounts increase substantially for the raw coal as the coal dries, similarly to that in the treated products. These results indicate that for the three drying methods evaluated, the amounts of fines that were generated were not necessarily process-specific, but more closely relate to the moisture content of the individual fuel.

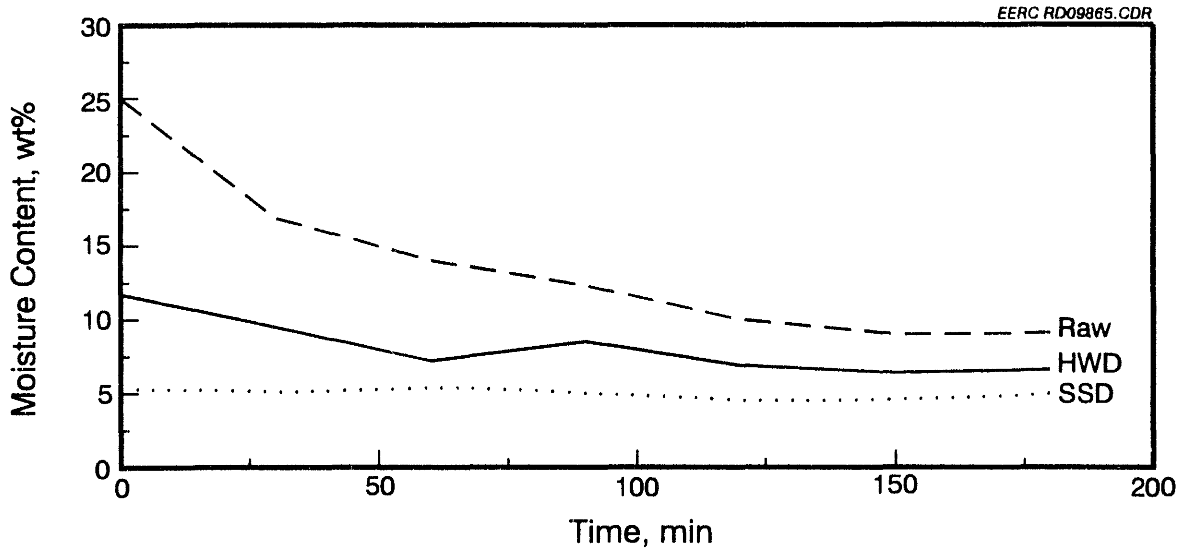

Figure 2. Jameson test results, moisture content versus tumbling time, for various Colstrip samples.

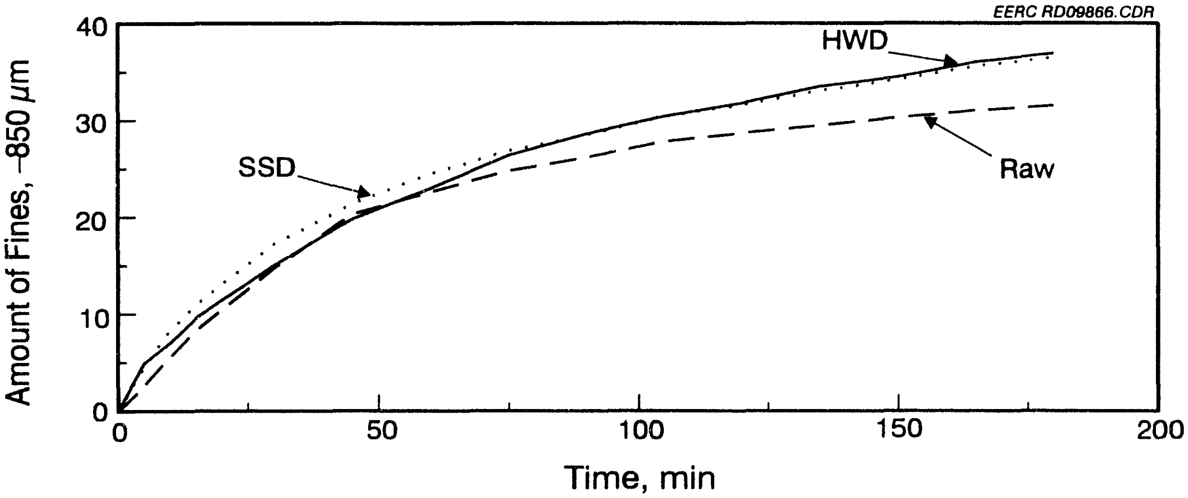

Figure 3. Jameson test results, amount of fines versus tumbling time, for various Colstrip samples.

CONCLUSIONS

This report presents data for three raw coals and dried coal products analyzed by various strength and stability test methods. The results show that as the moisture content is decreased, the amount of generated dust substantially increased to levels viewed as unacceptable by industry (i.e., fines less than 0.5 mm not to exceed 10 wt%) (9). Tests performed to evaluate the tendency for moisture reabsorption of dried LRCs indicated that coals tend to reabsorb the moisture during air drying, whereas hydrothermal treatment processes do not allow reabsorption. Through development of these laboratory techniques, better predictions on the effects that transport, handling procedures, and climate have on the stability of dried LRCs are hoped. This is extremely important when the virtues of a particular western coal type are marketed, as the coal is transported long distances to eastern or foreign markets. If commercial drying of LRCs is to be successful, efforts must continue to develop stability analysis and cost-effective, stable products.

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The following manuscript was unavailable at the time of publication.

A COMPARISON STUDY OF COLUMN FLOTATION TECHNIQUES FOR CLEANING ILLINOIS COALS

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ELECTROSTATIC BENEFICIATION OF COAL

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ABSTRACT

Dry physical beneficiation of coal has many advantages over wet cleaning methods and post combustion flue gas cleanup processes. The dry beneficiation process is economically competitive and environmentally safe and has the potential of making vast amounts of US coal reserves available for energy generation. While the potential of the electrostatic beneficiation has been studied for many years in laboratories and in pilot plants, a successful full scale electrostatic coal cleaning plant has not been commercially realized yet. In this paper we review some of the technical problems that are encountered in this method and suggest possible solutions that may lead toward its full utilization in cleaning coal.

ELECTROSTATIC BENEFICIATION OF COAL

The electrostatic beneficiation process is based on the difference between physical properties of organic coal and those of the inorganic impurities. One process uses the difference in electrical resistivities while a second uses differences in electronic surface structure. In the first process, a rotating metal drum separator is used that carries the particles through a corona charging zone where the particles acquire a charge, the magnitudes of which depend upon the size and dielectric constant of the particles. Once the charged particles leave the charging zone and are carried along the surface of the rotating electrically grounded drum, the particles loose their charge at a rate depending upon their electrical resistivity. Conducting particles loose their charge rapidly and are thrown from the drum surface by gravity, often aided by an induction field. The insulating particles retain their charge, and are held to the drum surface until they are brushed off. In this manner, highly resistive coal particles are separated from the inorganic mineral particles.

In the second method, particles are charged triboelectrically against the grounded surface of a metal, most frequently copper. Because of the differences between the electronic surface structures organic coal particles acquire a positive charge while inorganic impurities, such as pyrites and clay particles acquire a negative charge. The coal particles are then separated from the impurities by passing the particles through a separator, consisting of two parallel plate electrodes across which an electric field is applied. Positively charged coal particles move toward the negative electrodes and deposit on the electrode surface while the mineral particles, such as pyrites and silicates move toward and deposit on the positive electrodes. The design of the electrodes and the magnitude of the applied electric field are often optimized for maximum separation. The deposited particles are then removed from the electrode surfaces and collected. The process can be performed continuously.

In both corona and tribocharging processes the separation is effective only when mineral particles have been liberated from the organic coal matrix during the grinding process and have electrical resistivity or tribocharging properties that are significantly different from those of the organic coal particles. Once these two fundamental constraints are met, the electrostatic beneficiation process is simple in operation, results in less overall environmental pollution than wet cleaning or post combustion flue gas cleaning, and is energy efficient.

PREVIOUS STUDIES: FAILURES AND SUCCESSES

Work on electrostatic separation of ash from coal was reported[1] as early as 1914 by Withington and in two U.S. patents for electrostatic separation techniques granted to F.W.C. Schniewend in 1915. The first pilot plant and larger scale implementations of electrostatic cleaning were done around 1940 in Germany. The German coal could be reduced from 14-17% ash to 1.5%. Most early work was done on intermediate size material (10 - 100 mesh). Many systems required pre-separation of the ground coal by size, mainly to eliminate the 'dust' which adversely affected separation. During this period, ultrafine coal was financially insignificant. Now pulverization of coal for power plants produces powdered coal that is about 70% below 200 mesh. In addition, granule size for pyrites has been found to be less than five micrometers.[2] Therefore, without fine grinding, the pyrites may remain locked within the coal matrix and cannot be separated by physical cleaning methods.

Singewald, in a 1976 US patent, described a triboelectric separator with a feed size of 800 µm and at a feed rate of 5 tons per hour. A recovery rate of 88% was obtained in the form of concentrate containing 94.7% pure coal from a feed having only 57% purity.[3] Advanced Energy Dynamics (AED) developed electrostatic separators for both fine and ultrafine coal. Using pilot scale studies with rotating-drum separators, they designed a continuous belt system for separating pyrites from coal. However, the test results showed that the belt system worked on one type of coal while it was ineffective against another type of coal. The electrostatic drum-type separator was only marginally successful at best.

In 1983, Masuda, et al.,[4] reported a triboelectric cyclone charger and a separator system that was effective in separating coal from mineral matter, however, they observed that the material to be chosen for the cyclone wall will depend upon the type of coal used. In a 1984 patent, Ciccu reported a tribocharger where the particles are charged by impaction using a rotating disk placed inside a cylinder. The particles are fed at the center of the rotating disk and are therefore thrown off by centrifugal forces and impact against the cylindrical wall surrounding the rotating disk. Ciccu, et al.[5] examined this tribocharging process against different materials, particularly stainless steel and copper, and also at different temperatures. They also noted that various coal macerals have different tribocharging properties. He and his colleagues have been operating a pilot plant in Italy since 1990. In 1980, Inculet, et al.[6] reported their studies on the triboelectrification of ultrafinely ground and finely ground Canadian coal for separation using a closed loop system where particles can be recirculated for a more efficient separation.

The Pittsburgh Energy Technology Center (PETC) of the Department of Energy (DOE) has been investigating triboelectric coal beneficiation since 1985.[7] They have developed a static copper pipe charger in which particles are carried on a jet stream of nitrogen at a high velocity through a helix shaped copper tube. The high velocity of particles inside the charging section charges the particles triboelectrically and keeps the oppositely charged particles separate from each other before they enter into the separator. Test results using a parallel plate separator showed good separation for Pittsburgh #8, Illinois #6, and Upper Freeport coal samples. Gidaspow et al.,[8] have reported a fluidized bed particle separator in which both particle charge and the particle density are taken into account in the separation process. Their work shows excellent removal of pyrites from coal.

TECHNICAL PROBLEMS IN ELECTROSTATIC SEPARATION PROCESS

Particle Size Distribution

Definitions of "locked", "attached", and "liberated" pyritic impurities are sometimes made to correspond to particles consisting of <30%, 30-70%, and >70% pyrite, respectively. For grind levels of -28, -100, and -400 mesh, the percent of the total pyrites falling into the liberated category was found by Irdi, et al.,[2] to be 37-61, 64-84, and 76-90, respectively, depending on the origin of the coal. Therefore, adequate liberation of the pyrites from the organic coal requires that the run-of-mine (ROM) coal be ground to about -325 mesh. However, ultrafine grinding of coal is expensive and storage of such ultrafine coal creates an explosion hazard since the increased particle surface area promotes rapid oxidation.

In the corona separating process using rotating drums, the fine particles adhere to the surface of the drum and the van der Waals forces of attraction dominate over the electrostatic forces. Therefore, the fine ash and pyritic particles do not fall off from the drum surface once they loose their charge and cannot be separated efficiently using the rotating drum method.

In the tribocharging process, where the charging is performed by impaction of the particles against the wall of the charger, the ultrafine particles do not come in close contact with the metal surface because of their low inertial mass unless a very high velocity is used. However, with high velocity gas flow through the static charger, larger particles will cause rapid erosion of the charging unit so that the copper charger must be frequently replaced. In order to have effective removal of the pyritic particles from the organic coal matrix, the electrostatic separators must employ techniques where particle charging is efficient and oppositely charged particles do not agglomerate. Dust containment and safety features against possible explosion hazards must be included.

Tribocharging through a milling process similar to charging of toner particles in electrophotography, is efficient. However, since coal and mineral particles are charged with opposite polarities, there may be a significant problem due to the agglomeration of the particles of opposite polarities. The tribocharger developed at the PETC has a high velocity air passing through the charger and therefore both the impaction on the surface and the associated turbulence keeps the oppositely charged particles apart from each other.

TRIBOCHARGING OF THE PARTICLES

The basic mechanisms involved in the tribocharging of the coal and mineral particles may include: 1) electron transfer, 2) ion transfer, and 3) material transfer, but the actual process is not well understood. It is therefore necessary to characterize the surface properties of micronized coal powders by scanning electron microscopy, x-ray diffraction analysis, and x-ray photoelectron spectroscopy in order to correlate the tribocharging properties with the electrostatic surface structure and work functions which depend on 1) the type of coal, 2) surface contamination, 3) presence of dust layer, and 4) moisture content. Perhaps the most important parameter affecting the charging process is the oxide layer that covers the coal surface. Therefore the process of optimization will require an understanding of the surface activation of coal either by physisorption or chemisorption mechanisms. Experimental determination of charge-to-mass ratio distribution as a function of particle size for different types of coal maceral and mineral particles are needed.

An automated control of the electrostatic beneficiation process with in-situ measurements of the electrodynamic properties of the coal and mineral particles inside the separator is needed in order to optimize the separation and collection processes. Further, an efficient means for dislodging the coal and mineral particles deposited on the electrodes needs to be developed. An alternative design would be such that the particles do not make contact with the electrode, yet the particles can be collected efficiently in a continuous process.

For developing a self-cleaning electrode, we are designing an electrodynamic screen where the electrodes will consist of a pair of insulating parallel plates with embedded parallel wires. The wires of each plate will be connected to a DC high voltage (+ 25 kV for positive electrodes and - 25 kV for negative electrodes) with a superimposed AC field (3.5 kV p-p) of variable frequency between alternate wires in the same plate. The DC field will provide the electrical migration velocity of the charged particles toward the electrodes whereas the superimposed AC field, which extends only a few millimeters beyond the surface of the plate will provide a confinement force preventing particles from contacting the parallel plates.

EXPERIMENTS AND RESULTS

The surface energy structure of ROM coal particles are being determined with respect to coal surface chemistry, specific surface area, particle size and shape, and the status of new surface formation (with respect to the time from when the particles are freshly ground). Using an E-SPART analyzer, the electrostatic charge and particle size distribution of the coal particles have been measured after tribocharging against a copper surface. Table I shows that the particles were bipolarly charged. A bipolar charge distribution is expected for a mixture of orgnaic coal and inorganic mineral particles. The particle size distribution is shown in Figure 1. This size distribution represents particle size for both coal and mineral particles. We are also developing a real-time digital image processor to analyze the particle size, charge-to-mass ratio, and the trajectories of the particles inside the separator. Application of the E-SPART analyzer and the image processor will be presented in detail. In addition, we will present a new configuration of the separator with electrodynamic screen to be used in the laboratory scale separator unit.

CONCLUSION

A comprehensive analysis of electrostatic charging processes related to coal and mineral particles, an understanding of the particle motion under the influence of aerodynamic and electrostatic forces inside a separator, and development of self-cleaning electrodes are needed in order to achieve commercial application of electrostatic beneficiation in coal cleaning.

TABLE I

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PITT 8

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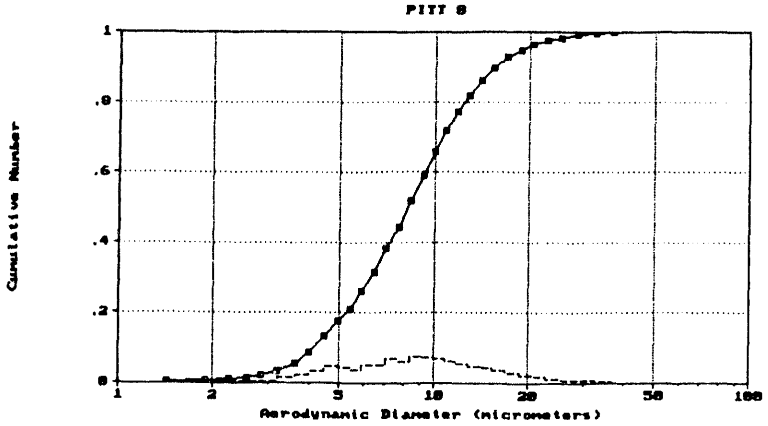
Field Voltage:   50.00 volts    Particle Density:  1.00 g/cm^3

                    ------ Negative ------      ------ Positive ------        Total
No.  Dia.(um)  Count  femto-C     uC/g      Count  femto-C     uC/g          uC/g
  1    1.43      11     -2.39  -141.15          3     0.17    36.45        -103.09
  2    1.89      12     -7.74  -182.95          2     3.83   542.39         -79.33
  3    2.25       7     -0.93   -22.41          4     3.51   147.67          39.44
  4    2.56      11     -9.51   -98.74          2     1.76   100.70         -68.06
  5    2.83      12     -4.91   -34.39          3     0.21     5.90         -26.33
  6    3.19      35    -15.83   -26.58         11    14.88    79.47          -1.22
  7    3.63      58    -24.06   -16.51         13     1.18     3.63         -12.82
  8    4.03      97    -51.87   -15.59          9    12.89    41.77         -10.72
  9    4.48     142    -52.95    -7.95         16    42.54    56.66          -1.40
 10    4.97     123    -98.30   -12.41         17    16.53    15.10          -9.07
 11    5.43     109    -45.77    -5.00         15    13.69    10.86          -3.08
 12    5.94     148    -74.79    -4.61         19    38.00    18.26          -2.01
 13    6.49     151    -43.94    -2.04         21     8.46     2.82          -1.44
 14    7.08     212   -110.92    -2.82         16     5.80     1.95          -2.49
 15    7.72     184   -103.40    -2.33         21     7.73     1.53          -1.94
 16    8.42     222   -181.79    -2.62         28    45.88     5.25          -1.74
 17    9.19     218   -171.89    -1.94         22    39.78     4.44          -1.35
 18   10.00     209   -133.84    -1.22         22     6.70     0.58          -1.05
 19   10.86     178   -223.73    -1.87         21    48.50     3.45          -1.31
 20   11.80     158   -179.90    -1.32         24    30.49     1.48          -0.96
 21   12.85     143   -159.29    -1.00         18    28.60     1.43          -0.73
 22   14.08     124   -129.85    -0.72         19    19.33     0.70          -0.53
 23   15.43     108   -140.85    -0.68         14     7.20     0.27          -0.57
 24   16.96      91   -129.03    -0.55         10    38.75     1.52          -0.35
 25   18.73      54   -102.20    -0.55         13     9.25     0.21          -0.40
 26   20.54      51   -214.14    -0.93          5     3.74     0.16          -0.83
 27   22.66      32    -67.23    -0.34          8     5.90     0.12          -0.25
 28   25.13      23    -50.38    -0.26          3     4.58     0.18          -0.21
 29   28.32      22    -57.57    -0.22          5    49.45     0.83          -0.03
 30   32.64      13    -24.68    -0.10          1     0.85     0.05          -0.09
 31   36.84      11    -25.96    -0.09          2     1.92     0.04          -0.07

                         Negative     Positive       Total
Count                        2969          387        3356
Mass (nano-gram)          3043.39       452.43     3495.83
Charge (femto-C)         -2639.63       512.10    -2127.53
Charge/Mass (uC/g)          -0.87         1.13       -0.61

Max particle charge (neg) = -61.41 femto-C
Max particle charge (pos) = 42.07 femto-C
Count Median Diameter = 8.256 micrometers
Mass Median Diameter  = 17.807 micrometers
```

FIGURE 1



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Sample Time: 2571 sec

Count Median Aerodynamic Diameter        = 8.256
Mass Median Aerodynamic Diameter         = 17.807
Count Weighted Geometric Std. Deviation = 1.679
Mass Weighted Geometric Std. Deviation  = 1.607
(Based on data in diameter range 1.00 to 100.00)
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