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# COAL SURFACE CONTROL FOR ADVANCED FINE COAL FLOTATION

Project No. DE-AC22-88PC88878

**QUARTERLY REPORT NO. 5**
October 1, 1989 - December 31, 1989

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## 1.0 INTRODUCTION

Historically, coal surface characterization and control had not been seen to be critical to coal cleaning because of the emphasis on keeping particle size as coarse as possible. However, the current goal of near-total removal of pyritic sulfur necessitates the fine grinding of coal to liberate the pyrite. At these fine sizes, coal surface properties play an increasingly dominant role.

In order to investigate the behavior of coal surfaces and their role in coal flotation, DOE awarded a contract to The University of California at Berkeley in October 1988. The project's main goal is to characterize the surface and control the behavior of coal during advanced flotation processing. The effect of weathering on the surface characteristics and flotation response of the coal is an important part of the program.

### 1.1 Scope of this document

The Department of Energy (DOE) awarded a contract entitled "Coal Surface Control for Advanced Fine Coal Flotation", to the University of California at Berkeley, Columbia University, the University of Utah and Praxis Engineers, Inc.

This document is the fifth quarterly report prepared in accordance with the project reporting requirements covering the performance period from October 1, 1989 to December 31, 1989. This report only provides a brief summary of the technical work undertaken during this period. A list of technical reports submitted as part of this work is provided in the Appendix.

## 1.2 Overall Project Scope

The primary goal of this research project is to develop advanced flotation methods for coal cleaning in order to achieve 90% pyritic sulfur removal at 90% Btu recovery, using coal samples procured from six major U.S. coal seams. Concomitantly, the ash content of these coals is to be reduced to 6% or less. Investigation of mechanisms for the control of coal and pyrite surfaces prior to fine coal flotation is an important aspect of the project objectives.

As a part of this contract, large quantities of coal samples were procured from six major seams identified by DOE for use in this project for advanced flotation and weathering studies. Samples of the same coals were also to be supplied to the University of Pittsburgh for selective agglomeration research.

A second major objective is to investigate factors involved in the progressive weathering and oxidation of three base coals stored in three storage modes, namely, open, covered and in an argon-inerted atmosphere, over a period of twelve months. After regular intervals of weathering, samples of these coals are to be collected and shipped to both the University of Pittsburgh and the University of California at Berkeley for characterization studies of the weathered coals.

## 1.3 Work Executed at Different Locations

The project team consists of research and engineering groups at the University of California, Columbia University, the University of Utah and Praxis Engineers, with the University of California acting as the Prime Contractor with DOE. The work proposed to be conducted at the four locations is based on their respective areas of expertise and is detailed in the Project Work Plan. This report is prepared in an integrated manner, combining work at each location by topic.

The project progress is being maintained in all the technical areas. All the DOE reporting requirements of technical, cost and labor reports were met generally on schedule.

## 2.0 COAL WASHABILITY AND WEATHERING SAMPLING

### 2.1 Overview and Scope

As a part of Coal Procurement and Weathering (Task 2) Praxis Engineers collected coal samples from 3 major seams namely Illinois No. 6, Pittsburgh No. 8 and Upper Freeport PA identified as base coals and prepared them for the following purposes:

- Research samples
  - Advanced froth flotation
  - Selective agglomeration
- Washability studies
- Weathering studies

Three additional coal samples were also collected from producing mines of Upper Freeport, West Virginia, Kentucky No. 9 and Wyodak seams for research and washability studies. During this reporting period work was completed on weathering sample collection. Also, additional washability testing on the three base coals was initiated as requested by DOE. A brief description of these activities is provided here.

### 2.2 Additional Washability Studies

In addition to the washability work done at 28 mesh and 200 mesh grinds for the three base coals, DOE decided that additional washability tests should be conducted on fine samples of these coals after comminution to 100 mesh, 200 mesh, 325 mesh and 400 mesh. This study is being performed to determine the liberation characteristics of the base coals and will supplement the original washability study conducted earlier as a part of Task 2.

Based on evaluation of work done by various laboratories for Task 2 and cost comparison this work was given to Geochemical Laboratory in Somerset PA. The work was started using one

drum (450-lb) of sample for each of the three base coals. Size reduction was carried out in stages to prepare the samples for washability tests. The work on the 100 mesh and 200 mesh sizes has been completed and results have been provided as topical reports. These reports will be updated upon receiving the results of the 325-mesh and 400-mesh grinds.

### 2.3 Coal Weathering Sampling

During this period, two weathering samples (Increments 12 and 13) were collected from all the three weathering sites. These samples were split and prepared prior to shipping to UCB and the University of Pittsburgh following the sampling procedure. As Increment 13 is the last increment, the sample quantities collected were larger than usual. Following this sampling the weathering sites were dismantled at all three locations with prior approval of UCB and DOE.

## 3.0 CHARACTERIZATION STUDIES

### 3.1 pH measurements of coal-water slurries

As a matter of routine the pH of the flotation pulp is recorded. The pH values during flotation for each of the base coals has consistently been recorded in the range of 7.5 - 8.5 for Illinois No. 6 coal, 3.4 - 4.0 for Pittsburgh No. 8 coal and 3.0 - 3.5 for Upper Freeport PA coal. However, some of the pH values from the initial weathered Pittsburgh No. 8 coal samples were well above pH 6.0. This, combined with the lower pH values for the research sample of Pittsburgh No. 8, led to some concerns about the research sample. In order to resolve these concerns, a detailed study was undertaken to determine the cause of pH in the Pittsburgh No. 8 sample. Our conclusions are that the rapid oxidation of the contained pyrite is the cause of the decreased pH. A detailed report on this study was submitted to DOE.

### 3.2 Induction Time Measurements

Induction times, an innovative way of characterizing the bubble-particle attachment, were measured for the three base coals. Based on this it was concluded that the hydrophobicity of the base coals increased in the following order:

Illinois No. 6 < Pittsburgh No. 8 < Upper Freeport PA.

Similar conclusions on the hydrophobicity of the base coals were also drawn from film flotation and contact angle measurements.

## 4.0 USE OF PH AND SURFACE MODIFIERS IN FLOTATION

### 4.1 Effect of pH modifiers on flotation performance

The results of tests conducted earlier indicated that there was an increase in pyritic sulfur rejection using lime to increase the pH of the flotation pulp from 4.5 to 10 for Pittsburgh No. 8 coal. However, the yield dropped drastically at pH values greater than 10. Additional flotation tests were conducted during this period to study the effect of calcium ions from an alternate source (calcium chloride) but equivalent in concentration to the tests using lime. The pH adjustments during these tests were made using sodium hydroxide. The results indicated that the use of calcium ions from calcium chloride resulted in lower yields and combustible matter recoveries.

### 4.2 Effect of Surface Modifiers

#### 4.2.1 Effect of anionic reagents

Thus far, the effect anionic reagents 2,n-butyl thiophene and Aerosol OT have been tested by adding these reagents in the mill prior to wet grinding. During this quarter, tests were performed to investigate the effect of these reagents during dry grinding, keeping the collector and frother levels the same as for the standard test. For butyl thiophene the dosage needed for the

200-mesh dry grind using Pittsburgh No. 8 coal was 5 times the dosage for wet grinding to obtain comparable yields. Interestingly, for Aerosol OT, the dosage needed for the dry grinding tests was only 50% higher. Test work using anionic reagents was also continued in this quarter. Results of kinetic tests using 0.25 lb/T Aerosol OT were similar to those obtained with n-dodecane with an exception that the use of the former resulted in higher flotation rates. It was also observed that water carryover in the froth was lower in the case of Aerosol OT. Another kinetic test was carried out which confirmed that the water overflow from the cell is considerably lower with Aerosol OT as compared to n-dodecane flotation times of 3 minutes. Tests with dodecane (2.1 lb/T) resulted in nearly 100 ml extra water overflow as compared to test using Aerosol OT (0.32 lb/T) as collector, with all other parameters constant. Tests were also conducted using 2, n-butyl thiophene (BT). In comparison to Aerosol OT, BT resulted in lower yields even at higher dosages. The effect of both reagents on the ash and sulfur rejection will be studied once analysis of the flotation products is complete.

4.2.2 Effect of organic monomers

Work done during this period included use of monomer vinyl acetate in which polymerization inhibiter had been removed by low temperature distillation. The purpose of this research was to compare the results obtained using the monomer with and without the inhibiter to determine if the inhibiter was also preventing interaction of the vinyl acetate with reaction sites at coal surface. The improvements in flotation by using vinyl acetate without inhibiter are not significant.

Another surface modifying agent diisobutylene monomer was tested in flotation. Its use resulted in increase in yield accompanied by an increase in ash and total sulfur for Pittsburgh No. 8 coal. Tetrahydrofurfuryl butyrate when tested for its effects on flotation increased the yield of coal considerably with limited pyrite rejection capability indicating that it has a strong collecting property.

### 4.2.3 Effect of non-ionic reagents

Testwork on the use of non-ionic reagents (methanol, ethanol, glyoxal and benzaldehyde) was completed earlier on Upper Freeport PA and continued to Pittsburgh No. 8 coal. The addition of methanol gave improved pyritic sulfur rejection as compared to the standard test. The addition of ethanol at the same dosage gave even better results. Use of glyoxal and benzaldehyde showed poor performance as compared to a standard test. The tests with Illinois No. 6 coal however were very poor using both methanol or ethanol.

As the results with methanol and ethanol were encouraging with Upper Freeport PA and Pittsburgh No. 8 coal the testing of other alcohol homologs propanol and butanol were undertaken. It was interesting to note that use of alcohol homologs only without any collector and frother enhanced the combustible matter recovery significantly with the increase in the hydrocarbon chain. However, the selectivity of pyritic sulfur rejection decreased slightly.

## 5.0 GRINDING WITH COLLECTOR AND FLOTATION KINETICS

The rationale of adding collector to the mill during grinding was to ensure its adsorption as soon as the new surface is created during comminution. In addition, it was expected that since the coal surface is susceptible to oxidation, the addition of dodecane to the mill would help minimize the oxidation. Earlier results of grinding with standard collector dosage indicated that the recovery as well as the initial flotation kinetics of Illinois No. 6 coal was enhanced, while the effect was detrimental on both Pittsburgh No. 8 and Upper Freeport PA coals. In order to explain the differential behavior of the coals, a more detailed kinetic study was undertaken.

The flotation response of the three base coals at higher collector dosages added to the mill was studied. The flotation response of Illinois No. 6 coal suggested that the enhanced flotation recovery and kinetics were linked to the hydrophilicity and the oxidation characteristics of the coal.

The oxidation characteristic and its effect on flotation kinetics were studied by allowing the ground coal to weather under water for various lengths of time before performing the flotation tests. The results of the tests are being analyzed. A detailed analysis of the flotation results for Pittsburgh No. 8 and Upper Freeport PA coals will be completed shortly.

## 6.0 WEATHERING STUDIES OF BASE COALS

### 6.1 Characterization of weathered coal samples

As a part of our work characterization, the pH of the flotation pulp was also measured for various increments tested for flotation using screened 28-mesh weathered coal. The Illinois No. 6 coal pulp showed a minor drop for all three modes of storage up to Increment 6. Tests on open and covered Increment 9 samples indicated that the pulp pH dropped to 5 as compared to the first increment, (pH value of over 8.0). The drop in the inerted samples was comparatively minor for this coal.

For the Pittsburgh No. 8 coal (28-mesh x 0), the drop in the pulp pH occurred in the beginning of the weathering study. Also, the pH of covered and open samples followed the same trend as the inert sample which exhibited a slightly smaller drop in pH. For the 28-mesh x 0 screened fraction of Upper Freeport PA samples the pH dropped gradually in the increasing order from inert to covered to open samples. Although the flotation of the other two coals was affected significantly, no drastic effect of summer temperatures was observed for the Upper Freeport PA increments.

### 6.2 Flotation behavior of weathered coals

The flotation response of weathered coal samples up to Increment 9 (6 months of weathering) of Illinois No. 6 and Pittsburgh No. 8 coals and Increment 10 (7 months of

weathering) of Upper Freeport PA were reported in previous reports. The flotation testing on all three coals up to the final sample, Increment, 13, is now completed.

The flotation yield of the screened 28-mesh x 0 fines from Increment 11 open sample (9 months of weathering) indicated a further drop thus maintaining the trend exhibited by earlier increments. A similar trend was also observed for the Pittsburgh No. 8 coal, except that the drop was rather severe for Increment 9. By that month, corresponding to August 1989, the coals had been exposed to relatively high temperatures and humidity.

The effect of weathering on the Upper Freeport PA coal Increment 9 was also tested. The trend of dropping yield continued but not as drastically as that of the Pittsburgh No. 8 coal. The other interesting feature is that for Upper Freeport PA coal the three storage modes (inert, covered and open) were affected in an identical manner whereas the effect of weathering was most severe for the open mode in case of Pittsburgh No. 8 coal.

## 7.0 PROJECT MANAGEMENT AND REVIEW MEETING

During this period, the following meetings and presentations were held.

- Executive committee meeting was held at Berkeley where detailed plan on the work to be included under Task 7 Exploratory Research and Development were discussed.
- Fifth Project Review meeting was held at Berkeley on December 14, 1989 by DOE TPO.

## APPENDIX

List of Publications on this report

(1) "Coal Surface Control for Advanced Fine Coal Flotation" Quarterly Report No. 1 (Oct. 31, 1988 - Dec. 31, 1988) by University of California, Berkeley, Columbia University, University of Utah and Praxis Engineers, Inc.

(2) "Coal Surface Control for Advanced Fine Coal Flotation" Quarterly Report No. 2 (Jan. 1, 1989 - March 31, 1989) by University of California, Berkeley, Columbia University, University of Utah and Praxis Engineers, Inc. June 1, 1989

(3) "Coal Surface Control for Advanced Fine Coal Flotation" Quarterly Report No. 3 (April 1, 1989 - June 30, 1989) by University of California, Berkeley, Columbia University, University of Utah and Praxis Engineers, Inc. August 15, 1989

(4) "Coal Surface Control for Advanced Fine Coal Flotation" First Annual Report (Oct. 31, 1988 - Dec. 31, 1989) by University of California, Berkeley, Columbia University, University of Utah and Praxis Engineers, Inc. (In preparation)

(5) Topical Report No. 7, Additional Coal Washability Data Analysis for Pittsburgh No. 8 seam coal, January 19, 1990. (Partial Report)

(6) Topical Report No. 8, Additional Coal Washability Data Analysis for Upper Freeport PA coal, January 19, 1990 (Partial Report)

(7) Topical Report No. 9, Additional Coal Washability Data Analysis for Illinois No. 6 coal, January 19, 1990 (Partial Report)

(8) Topical Report No. 11, Pulp pH studies of Pittsburgh No. 8 coal (In preparation)