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TECHNICAL PROGRESS REPORT

APPALACHIAN CLEAN COAL TECHNOLOGY CONSORTIUM

Cooperative Agreement No.: DE-FC22-94PC94152

Project Report for the period

January 1 - March 31, 1996

Performing Organizations:

Virginia Polytechnic Institute & State University
Blacksburg, VA

University of Kentucky
Lexington, KY

West Virginia University
Morgantown, WV

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SECTION I

INTRODUCTION

The Appalachian Clean Coal Technology Consortium (ACCTC) has been established to help U.S. Coal producers, particularly those in the Appalachian region, increase the production of lower-sulfur coal. The cooperative research conducted as part of the consortium activities will help utilities meet the emissions standards established by the 1990 Clean Air Act Amendments, enhance the competitiveness of U.S. coals in the world market, create jobs in economically-depressed coal producing regions, and reduce U.S. dependence on foreign energy supplies.

The consortium has three charter members, including Virginia Polytechnic Institute and State University, West Virginia University, and the University of Kentucky. The Consortium also includes industry affiliate members that form an Advisory Committee. Affiliate members currently include AMVEST Minerals; Arch Minerals Corp.; A.T. Massey Coal Co.; Carpco, Inc.; CONSOL Inc.; Cyprus Amax Coal Co.; Pittston Coal Management Co.; and Roberts & Schaefer Company.

OBJECTIVES

In keeping with the recommendations of the Advisory Committee, first-year R&D activities are focused on two areas of research: fine coal dewatering and modeling of spirals. The industry representatives to the Consortium identified fine coal dewatering as the most needed area of technology development. Dewatering studies will be conducted by Virginia Tech's Center for Coal and Minerals Processing. A spiral model will be developed by West Virginia University. The research to be performed by the University of Kentucky has recently been defined as: A Study of Novel Approaches for Destabilization of Flotation Froth. Project management and administration will be provided by Virginia Tech, for the first year.

SECTION II

Virginia Tech: Innovative Approach To Fine Coal Dewatering

Introduction

There are no practical solutions to the problems associated with the dewatering of fine coals at the moment. The mechanical dewatering technologies used today are inefficient while thermal drying is capital-intensive and costly to operate. Therefore, there is an impending need for innovative approaches to solving problems in fine coal dewatering.

In this project, two different approaches are taken. One approach involves displacing the water on the surface of coal by liquid butane that can be readily recovered and recycled. The other approach is to use disposable dewatering chemicals (aids) in mechanical dewatering.

The objectives of the proposed work are i) to test the liquid butane process on a variety of coals from the Appalachian coal fields, and ii) to identify suitable dewatering aids that would enable mechanical dewatering to reduce the moisture to the levels satisfactory to electrical utilities and other coal users.

Results for the Current Quarter

Task A1 Coal Sample Acquisition and Characterization

Completed in previous quarter.

Task A2 *Batch Dewatering Unit Design and Set-Up*

For the liquid butane process, a batch process unit was designed and constructed last year. Since butane has a high vapor pressure, a high-pressure vessel made by Parr Instruments was used. For the process using the dewatering aids, a buchner funnel was used as a vacuum filter.

Task A3 *Bench-Scale Batch Dewatering Tests*

During the current reporting period, dewatering tests were conducted on the Microcel™ flotation products obtained at the Middlefork Preparation Plant near Lebanon, Virginia. Parametric testing of the butane process was conducted at 5, 15, and 30% solids and at the liquid butane-to-dry coal ratios in the range of 0.5 to 2.0 by weight. The results show that lower moisture products were obtained at higher % solids. At a given % solids, the moisture content also decreased with increasing butane-to-dry coal ratios. At a butane-to-dry coal ratio of 1.0, the butane process gave product moistures in the range of 1 to 12%, depending on the percent solids of the feed. Stirring time and stirring rate (rpm) was found to have little effect on the final moisture content. Settling time also has little effect on the final moisture content, especially at higher solids feed. Settling times from 1 to 60 minutes produced a constant final product moisture content.

Task A5 *Use of Disposable Dewatering Substances in Mechanical Dewatering*

During this quarter, several more chemicals were tested over a wide range of dosages. In nearly all cases, the optimum was reached at a reagent dosage of 2 lbs or less per ton of coal. Figure 1 represents the results obtained with a Microcel™ flotation product (>50% finer than 325 mesh) at the Middlefork coal preparation plant.

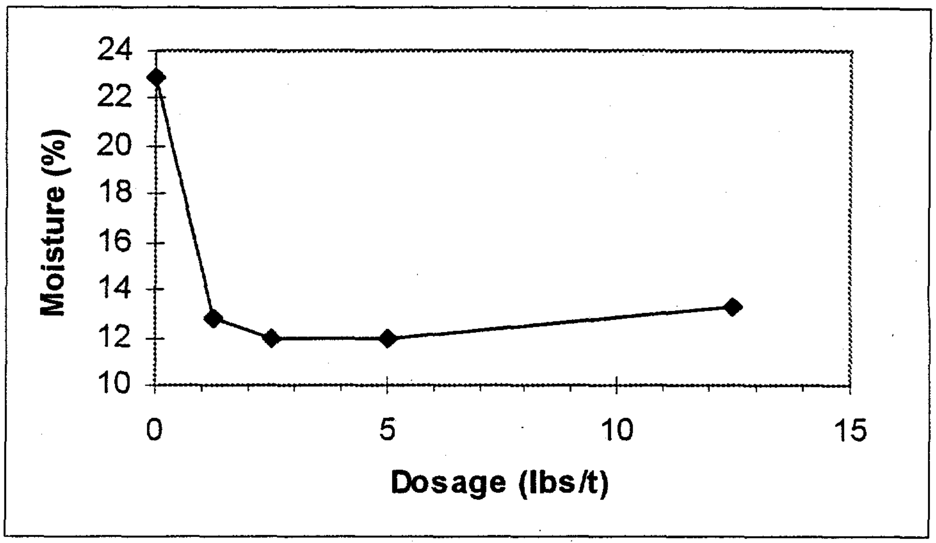

Figure 1. Results of the dewatering tests conducted on a Microcel™ flotation product obtained at the Middlefork preparation plant using reagents.

To better understand the operating range of the dewatering aids relative to pH, reagent C was tested over a pH range from 7.5 to 12. With the addition of no reagent, the moisture content went from 24% to 28% at a pH of 9 to 12. With the addition of 5 lbs/ton of reagent C, the moistures were 10 points lower than without the reagent, but there was no moisture variation with changes in pH. Reagent C is obviously insensitive to pH.

Rapid filtration is often seen with the addition of the dewatering aids. As would thus be expected, Figure 2 shows that the use of the dewatering aid results in a significant increase in porosity. Figures 1 and 2 show that the lowest moisture is achieved when the porosity of the filter bed reaches a maximum. Apparently, reagent A works as a flocculating agent. Note also that the moisture stays constant at dosages

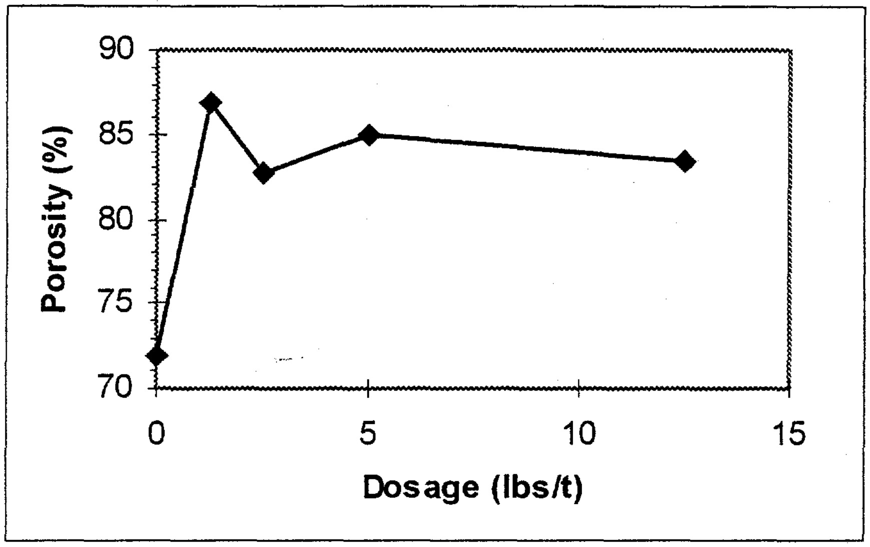

Figure 2. Change in porosity with dosage on Middlefork Column product using Reagent A.

above a certain level. This is important in actual plant usage since it is difficult to precisely control dosage with all the variations normally encountered in coal preparation plants.

One parameter of interest is the effect of vacuum pressure on product moistures. As seen in Figure 3, the higher the vacuum pressure, the lower the product moisture becomes regardless of whether the dewatering aids were used or not. At all levels of vacuum pressure, the moisture was 10 to 12% lower with the use of the dewatering aid than without.

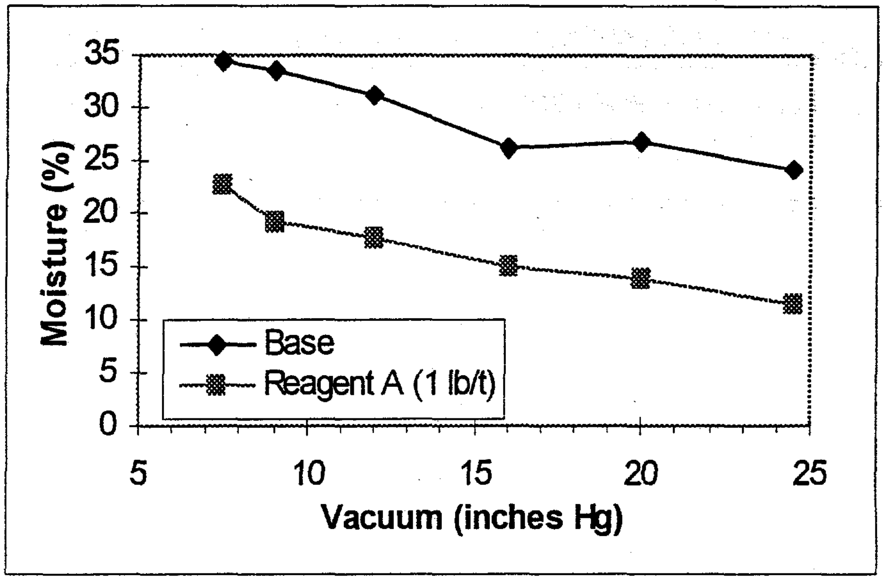

Figure 3. Change in moisture content with change in vacuum.

Figure 4 shows the effect of drying cycle time on the final product moisture. The tests were conducted using Reagent A at 1 lb/ton. The moisture was reduced by 10 percentage points after only 1 minute drying cycle time, and the maximum moisture reduction was achieved at 3 minutes of drying cycle time.

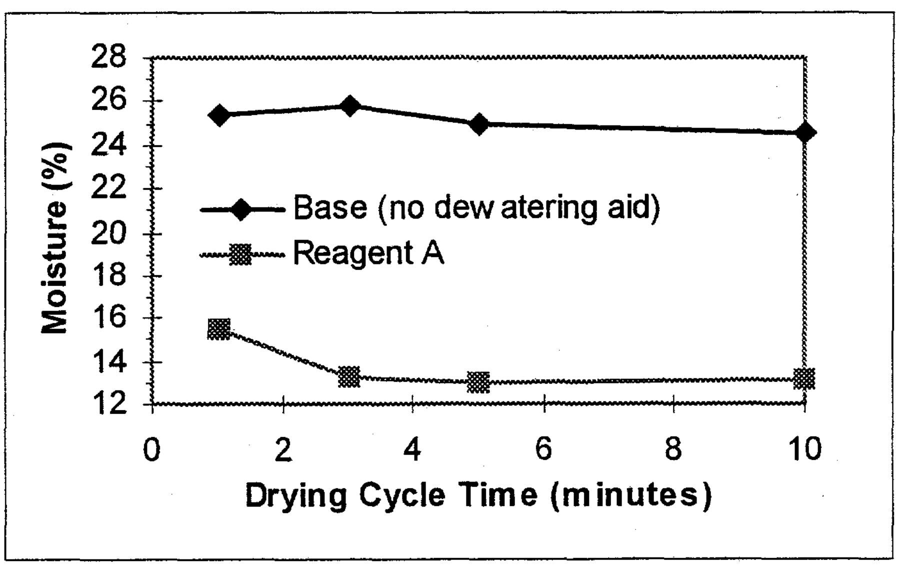

Figure 4. Moisture as a function of drying time with and without dewatering aid.

Most of the tests conducted show that acceptable levels of dewatering can be achieved at reagent dosage levels of less than 2 lbs/ton. However, reagent dosages vary from one reagent to another. It is possible to synthesize better reagents in the future.

SECTION III

University of Kentucky: Study Of Novel Approaches For Destabilization Of Flotation Froth

Abstract

Fine coal recovery from fine waste stream using froth flotation technique is becoming an important and integral part of coal preparation plans. Column flotation technique has proven to be the most effective and cost-efficient in recovery of fine coal. However, in some columns use of glycol-based frother produces a stable froth, which is not destroyed easily. The main objective of this program is to develop novel approaches for destabilization of stable froth. The approaches involve addition of either chemically treated coarse coal or addition of chemically treated magnetite-limestone suspended in an oil medium to the froth to break it down. Mechanical approaches to be tested involve utilization of ultrasonic energy or cyclone or vacuum. This report discusses technical progress made during the quarter from January to March 1996.

Introduction

In froth flotation process, frothers are utilized to produce stable small bubbles which carry the floatable particle. In case of an ideal froth flotation, the froth should have good fluidity and optimal rigidity. The froth should be just stable enough to carry the floated particles out of the flotation cell. Once the froth is scraped out the cell, it should collapse to free and concentrate the volume of floated particles. Such a froth will minimize the entrainment of undesired mineral particles into the concentrate and can provide additional selectivity for the flotation process. Too stable or too unstable froths penalize the separation efficiency and operation smoothness. If the froths are too stable, they will not break up after being scraped out of the flotation cell. Usually, such overly stable froths have low fluidity. The unwanted excessive stability can cause serious problems for downstream processes, such as dewatering of flotation concentrate, tailings handling, and re-use of processing water.

Generally, alcohol-based frothers provide froth which collapses as soon as froth is removed from the flotation cell and sprayed with water. Glycol-based frothers on the other hand produce a much stronger froth which is difficult to break by simple physical techniques and requires a large amount of chemicals to break the froth, which adds to the processing cost.

Objectives And Scope

The main objective of the proposed project is to develop new defoaming techniques for destruction of overly stable froths produced in fine coal froth flotation. It is also the objective of the project to study chemical dynamics of the three phrase froth.

The focus of this project will be to investigate new defoaming techniques. The existing commercial defoamers, such as surfactants, copolymers, hydrophobic silica, amide particle, are expensive and thus economically unfavorable for breaking up fine coal froths. In this project, new techniques for defoaming coal froth with less expensive chemical will be developed. Two approaches will be studied. One will involve use of coarse coal particles. To ensure that the surfaces of coal particles are sufficiently hydrophobic, the coal particles will be pretreated with cationic surfactant. The second approach will be to use magnetite and limestone particles. Since both magnetite and limestone particles are naturally hydrophilic, it is necessary to coat the particles with specific chemicals to make the surface highly hydrophobic (contact angle >120°). The hydrophobic particles are then dispersed in oil. It is anticipated that these new defoamers will be advantageous over existing defoamers. Besides their low cost, the use of hydrophobic limestone particles can also help to capture the sulfur dioxide during combustion and thus reduce the mission.

Approach

The project consists of four (4) tasks. Progress made in each task during the period of January- March, 1996 is described below.

Task 1. *Sample Acquisition and Characterization*

Flotation froth studies will be conducted with both flotation feed and froth product. Both samples have been obtained from the Pittston Coal Company which was recommended by the ACCTC. The flotation feed contains 32.93% ash and column froth product 8.54% ash. Exploratory defoaming tests will be performed primarily with flotation feed samples. Froth product samples will be used to determine optimum defoaming conditions.

The results of size analysis of the feed and product samples are shown in Figures 1 and 2. It can be seen that D_{50} is 40 and 80 μm for the feed and product, respectively. The froth product contains significantly less fine particles (<75 μm) than the feed (48 vs. 63%), possibly due to the removal of fine particles of minerals such as clay.

Task 2. Dynamic Stability Studies of Fine Coal Froth

Experimental system improvement

Dynamic stability studies of fine coal flotation froth will be studied using the principles of a "Foam Stabo System" developed at UKCAER, which was shown in the first quarterly report. However, preliminary tests with the original design of the system, as shown in Figure 3, indicated some serious problems such as poor reproducibility of experimental results, difficulty in cleaning bubble generator, and difficulty in data recording. Improvements were made with the system to obtain reliable data on froth stability, such as:

- *Replacing easy-action-plug stopcock with straight-bore-plug stopcock to reduce disturbance to the system*

The easy-action-plug stopcock shows significant impacts on the pressure inside the cell when it was screwed in to seal the cell, because it reduces the volume of the cell. The straight-bore-plug stopcock, on the other hand, showed essentially no disturbance to the system because it has no influence on the cell volume, and thus, is more suitable to the system.

- *Separating both reference and foam cells into two portions for easy cleaning of porous frit used as bubble generator*

It is necessary to frequently clean the porous frit to ensure good reproducibility of experimental results. However, it is very difficult to clean the frit in the original design of the apparatus because of the depth of the cells (55 cm). The new apparatus utilizes cells consisting of long top section and short bottom one. After each test, the bottom section can be readily removed for ultrasonic cleaning.

- *Connecting the pressure transducer to a computer to establish a data acquisition system*

Froth destabilization involves processes including bubble contact and coalescence; film thinning and rupture, etc. Some of these processes take place in a very short period of time. The pressure variation monitored by the pressure transducer is extremely difficult to record manually. Therefore, it is necessary to connect the system to a computer for accurate data acquisition. This is particularly important for dynamic studies of defoaming.

- *Attaching a small cup to the foam cell to add chemical reagents, coarse coal, magnetite and limestone particles during experiment without disturbance to the system*

This attachment is intended to prevent addition of defoamers to the system from introducing or discharging air during a test.

The modified apparatus is shown in Figure 4. Preliminary tests have shown that this system performed much better than the original design.

<u>Fundamentals of froth stability measurement</u>

The decay of froth stability with time can be fundamentally described by the rate of decrease of the total area of extended liquid surface. The equation of state of froth [Ross, 1969] relates the total area of liquid surface within a froth to the pressure of its contained gas, and so makes it possible to quantify froth decay in fundamental terms, by determining the rate of the build-up of gas pressure at constant volume and temperature in the head space above the froth.

The equation of state for froth in the present experimental system can be described as follows:

$$n_f RT = P_e V_f + 2\sigma A/3 \qquad (1)$$

where

n_f: number of moles of gas contained in the froth

P_e: pressure external to the froth

V_f: volume of gas in the froth

σ: surface tension

A: area of liquid surface in the froth.

Ross [1969] and Nishioka and Rose [1981] have derived that for a closed system, such as the one shown in Figure 4, at constant volume containing a froth, the equation of state can be simplified to:

$$A(t) = (3V/2\sigma)(\Delta P_\infty - \Delta P(t)) \qquad (2)$$

Where

A(t): area of liquid surface in the foam at time t

$\Delta P(t)$: change in pressure external to a froth at time t

ΔP_∞: change in pressure when the foam completely collapses.

The value of ΔP_∞ can be determined by letting the froth decay for a sufficiently long time or by adding a small amount of antifoamer to the system. Interfacial area of a foam can be measured, therefore, by monitoring the change in pressure external to a froth in a container of constant volume and temperature, if the total volume of the system is kept constant and the surface tension of the liquid can be determined.

Calibration for pressure transducer

The pressure transducer has been calibrated for the relationship between the output of voltammeter and the pressure. The calibration curve is shown in Figure 5. The best fitting equation can be described as:

$$Pressure(mm\ H_2O) = 35.92 Voltage(volts) \qquad (3)$$

Task 3. *Fine Coal Froth Destabilization Studies*

This task will consist of studies on chemical and mechanical defoaming techniques for fine coal flotation froth. The chemical process involves use of coal, magnetite, or limestone particles coated with surfactant for froth spraying. The mechanical process utilizes cyclone, ultrasonic energy, or vacuum to destabilize froth. Work in this area will be initiated in later stage of the project.

Activities For Next Quarter

Work in the next quarter will be focused on dynamic stability studies of fine coal froth with respect to:

- half-life time
- drainage time constant

- diffusion time constant

It is also planned to conduct a number of defoaming experiments with coal, magnetite or limestone particles rendered hydrophobic by coating with surfactants. The parameters to be investigated include:

- particle size
- surfactant concentration
- conditioning time

References

Ross, S., 1969. Ind. Eng. Chem. 61(10):48.

Nishioka, G., 1981. J. of Colloid and Interface Sci., 81(1):1.

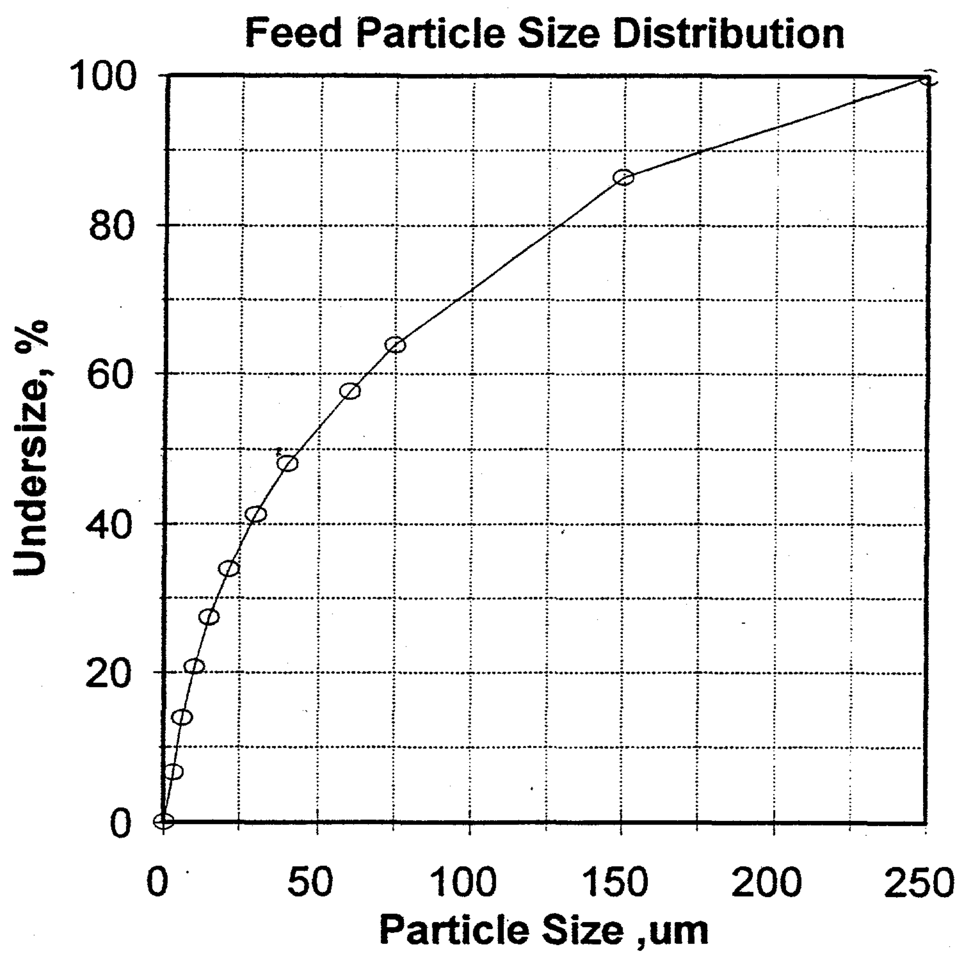

Fig. 1 Particle distribution of flotation feed

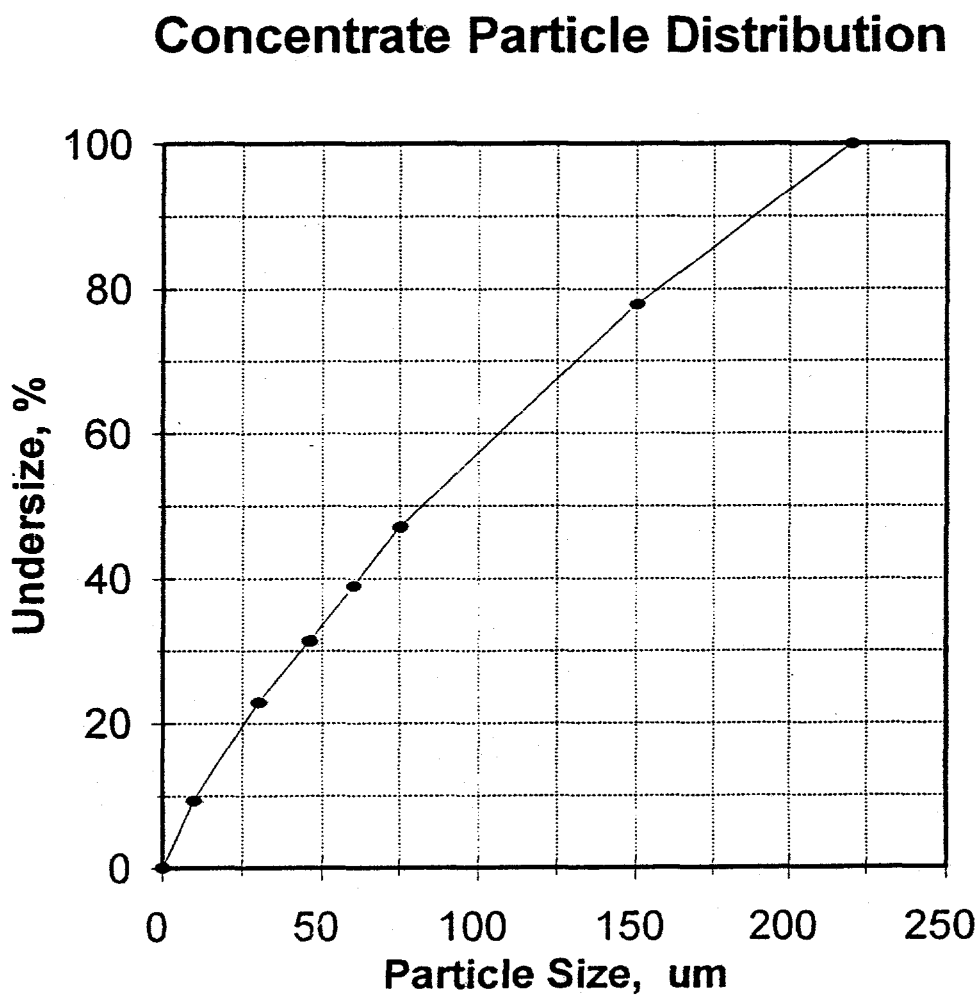

Fig. 2 Particle distribution of flotation product

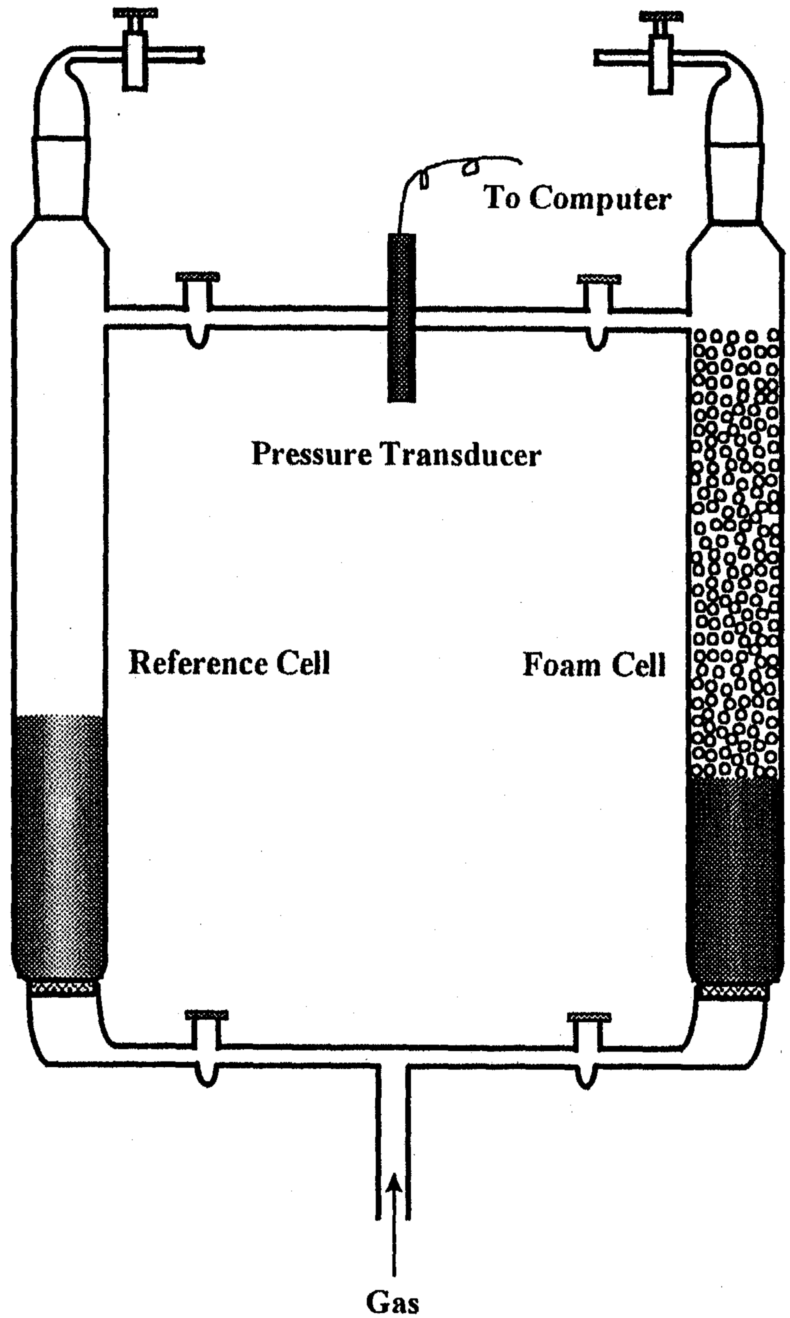

Fig. 3 Original apparatus for measuring the total surface area and the drainage rate of foam

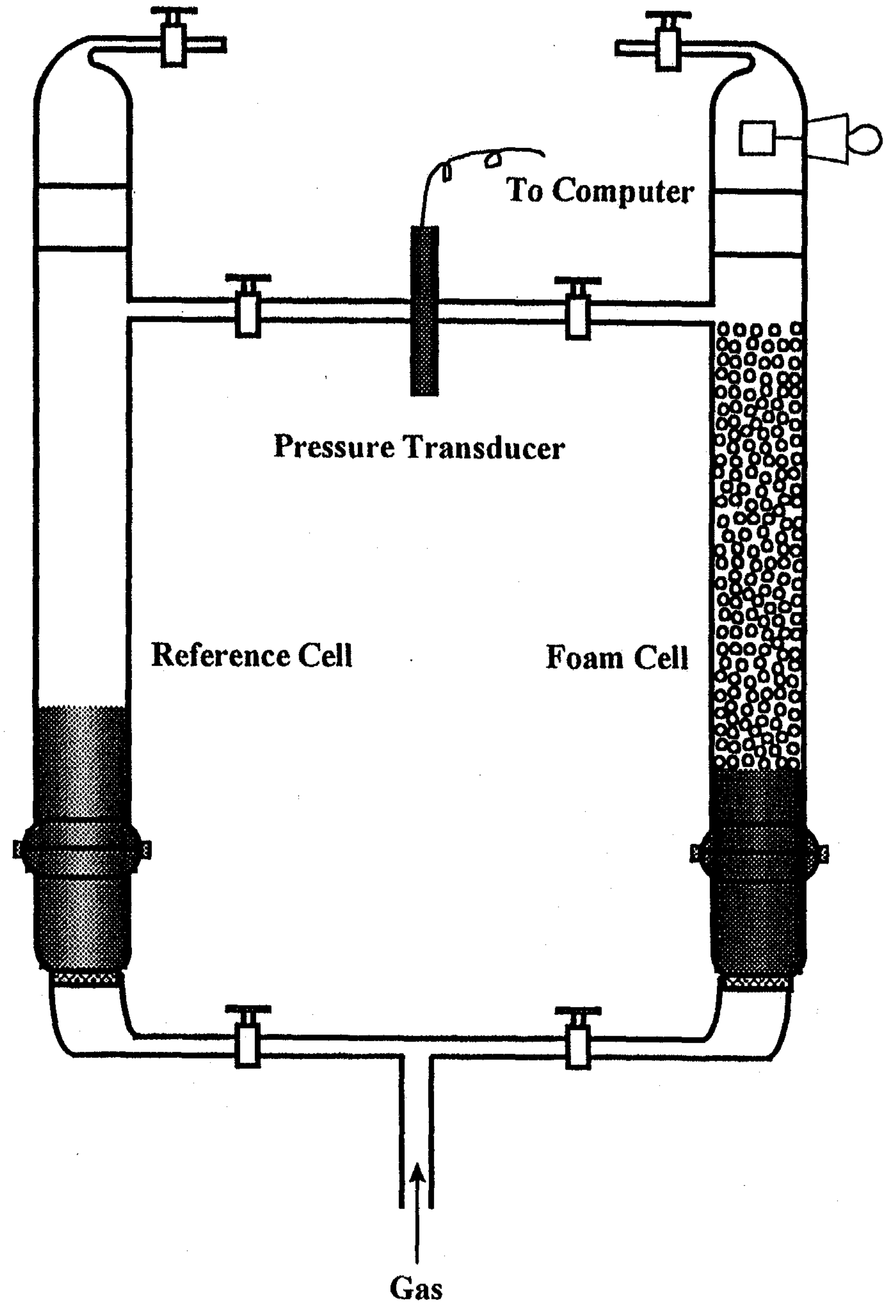

Fig. 4 Improved apparatus for measuring the total surface area and the drainage rate of foam

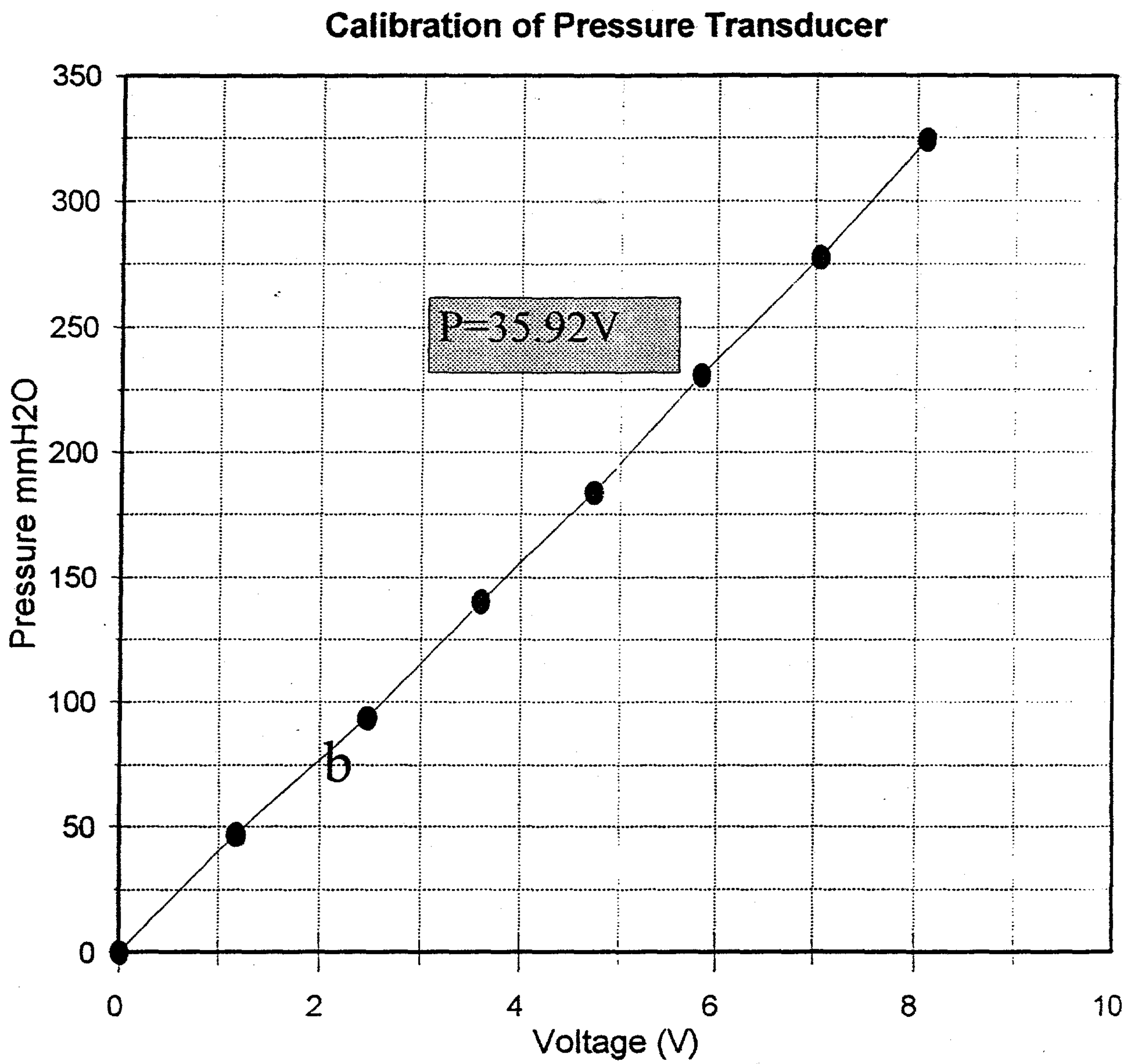

Fig. 5 Calibration of pressure transducer

SECTION IV

West Virginia University: Spiral Modeling

In the coal industry, the cleaning of coal is an increasingly important function. Raw coal containing ash minerals and particularly sulfur minerals makes the use of unclean coal environmentally unsound. Cleaning the coal removes most of these undesirable constituents.

Coal cleaning is done by many different methods. Some of these depend on dense media, others on selective surface chemistry, some on particle shape and particle density. As the particle size decreases, cleaning becomes more difficult. Smaller particle sizes limit the type of methods that may be used for coal cleaning.

As the requirements for cleaner and cleaner coal is pressed, the coal must be processed at finer and finer particle sizes. In the finer sizes below 500 microns and coarser than 150 micron, there are two methods that are effective: froth flotation and spiral separation. Because froth flotation uses environmentally toxic substances, spiral separation is preferred. Spirals use only flowing water to do the coal cleaning. Thus spirals are environmentally friendly.

Spirals, invented by the Greeks, were reinvented in the U.S. during WW-II. At that time, old tires were cut in half and concatenated together. These were used to separate phosphate sands from silica sands. Because of the unusual difficulty in modeling spirals, no fundamental analysis of spiral design was ever undertaken.

This project has undertaken a fundamental review of what physically happens to fluids and particles in the complex curvilinear flow fields of spirals. We are satisfied that we have developed the basis understanding of how a spiral behaves, are able to design spirals for specific feeds, and predict spiral design behavior for different types of particles. We feel our work to date is an excellent beginning.

Thus far we have completed the following tasks. We have: 1) developed the physical model, 2) developed the mathematical model, and 3) developed the numerical model. Using the numerical model, we have simulated: 3a) pure water flow, 3b) curvilinear flow, and 3c) slurry flow. For simulation, we are developing a software program that will accurately portray a spiral's behavior for a wide variety of spiral designs and particle designs. In this program, all spiral profiles can be assumed to be elliptical.

While there remains much work to be done, we believe that we have satisfactorily fulfilled all third quarter objectives promised in the proposal. We remain on time or ahead of schedule. While the problem was more difficult than we thought, we have made more progress than thought possible.