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ABSTRACT

This Technical Progress Report describes progress made on the eight sub-projects awarded in the first year of Cooperative Agreement DE-FC26-01NT41091: Establishment of the Center for Advanced Separation Technologies. This work is summarized in the body of the main report: the individual sub-project Technical Progress Reports are attached as Appendices. Due to the time taken up by the solicitation/selection process, these cover the initial 6-month period of activity only.

Note: SI is an abbreviation for “Le Systeme International d’Unites.”

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INTRODUCTION

The U.S. is the largest producer of mining products in the world. In 1999, U.S. mining operations produced \$66.7 billion worth of raw materials that contributed a total of \$533 billion to the nation's wealth. Despite these contributions, the mining industry has not been well supported with research and development funds as compared to mining industries in other countries. To overcome this problem, the Center for Advanced Separation Technologies (CAST) was established to develop technologies that can be used by the U.S. mining industry to create new products, reduce production costs, and meet environmental regulations.

Much of the research to be carried out at CAST will be longer-term, high-risk, basic research, and will be carried out in four broad areas:

- a) Solid-solid separation
- b) Solid-liquid separation
- c) Hydrometallurgy, and
- d) Sensor and control development.

Proposals for projects in these areas were requested from center constituents at Virginia Tech and West Virginia University for the first year of center activity. This process was handled via the issuance of a Request for Proposals that was distributed to interested researchers through Site Coordinators at the two universities. A total of 12 proposals were received in response to this RFP. These were first reviewed and ranked by a group of technical reviewers (selected primarily from industry). Based on these reviews, and an assessment of overall program requirements, the CAST Advisory Committee then forwarded the best of these proposals to the DOE/NETL Project Officer for final review and approval. This process took some 6 months to complete but 8 projects were in place at the constituent universities (5 at Virginia Tech and three at West Virginia University) by May 1, 2002. These projects are listed below by category, along with brief abstracts of their aims and objectives.

a) Solid-Solid Separation

1. Improving Coarse Particle Flotation (Appendix A)

Principal Investigators: R.-H. Yoon and G.H. Luttrell (Virginia Tech).

Heavy medium cyclones are widely used for cleaning coarse coals in the size range of approximately 50 x 1 mm, while froth flotation is used for cleaning 0.15 mm x 0 coals. The remaining material in the 1 x 0.15 mm size fraction is typically cleaned using inefficient water-based separators such as spirals, water-only cyclones, shaking tables, hydraulic classifiers, etc. The objective of this project is to develop methods of extending the upper particle size limit for flotation. The availability of such a technology will improve processing efficiency and greatly simplify the plant flowsheet. Two different complementary approaches will be used to achieve the project objective. One is to use novel coarse coal flotation reagents that will help increase the attachment force between

air bubbles and coal particles, and the other is to develop a new flotation machine specifically designed to promote coarse particle flotation.

2. Separation of Small Particles due to Density Differences in a CFB Riser System (Appendix B)

Principal Investigators: E. Johnson and B. Kang (West Virginia University).

The efficiency of separating small (less than 250 micrometers in diameter) dense particles from small light particles in the internal recirculation flow within a CFB riser is being investigated. Currently, there are many systems for separating fine particles. However, these systems lack the efficiency and/or the economics to be commercially viable in many situations. This research is directed towards removing pyrite from coal fines at a coal cleaning plant. Also, of concern will be the removal of radioactive particles from the desert sand at the Nevada Test Sites.

3. Modeling of Flotation From First Principles (Appendix C)

Principal Investigator: R.-H. Yoon (Virginia Tech).

Flotation is widely regarded as the best available technology for separating fine particles. The present form of the technology was invented nearly 100 years ago, yet there is still no reliable model for predicting flotation rate from first principles. It is the purpose of the proposed work to develop a flotation model that can predict flotation performance from both surface chemistry and hydrodynamic parameters.

4. Studies of Froth Stability and Model Development (Appendix D)

Principal Investigator: R.-H. Yoon (Virginia Tech).

Froth plays an important role in flotation. It determines the final grade of the product and the maximum carrying capacity (or throughput) of a flotation machine. Also, many operators use stronger frothers to produce smaller air bubbles and, hence, higher recovery and throughput. Despite its importance, little is known of the fundamentals of foam and froth stability. It is, therefore, proposed to study the various factors affecting the stability of flotation froth. This will be accomplished by using a thin film balance technique and by monitoring the stability of froth in a bubble column using a video camera. The results will be used for developing a froth model and also for developing effective defoamers.

5. Direct Measurement of Forces in Flotation Systems (Appendix E)

Principal Investigators: W.A. Ducker and R.-H. Yoon (Virginia Tech).

The objective of this project is to directly measure the force as a function of separation between a particle and a bubble in aqueous solution. This force controls the attachment and detachment of particles to bubbles, which is an essential step in determining the efficiency of the separation of mineral particles in a flotation cell. We are fabricating a device specially designed for these measurements. The device will use a

force-detection method from an Atomic Force Microscope and a separation-detection method from a Surface Forces Apparatus. The key advances are to explicitly measure both the separation between the particle and the bubble and the shape of the bubble at all times. Without this separation and shape data, it is not possible to compare the measured forces to theoretical estimates or to the practice of flotation. After fabrication of the device, measurements of the forces acting on hydrophilic, hydrophobic, and charged particles in aqueous solutions of surfactant molecules will be obtained.

b) Hydrometallurgy

6. Novel Bioleaching Technology Assisted by Electrolytic Processes (Appendix F)

Principal Investigators: E. Cho and R. Yang (West Virginia University).

Bioleaching of sulfide minerals using bacteria *Thiobacillus ferrooxidans* has been identified as a promising method for heap or dump leaching of low grade mixed sulfide ores containing pyrite (FeS_2), chalcopyrite (CuFeS_2), and/or sphalerite (ZnS). However, the major problem with bioleaching is that the rates are too slow for wide commercial utilization. The approach being used in this project focuses on the growth of bacteria under the influence of an applied direct potential and on the utilization of the bacteria to leach sulfide minerals. The objective is to identify the optimum conditions for the bio- and electro- leaching reactions in order to maximize overall leaching rates of the sulfide minerals.

c) Sensor and Control Development

7. Development of Electrochemical Sensor for On-Site Monitoring of Heavy Metal Ions in Coal Processing And Utilization (Appendix G)

Principal Investigators: A. Manivannan and M. Seehra (West Virginia University).

The aim of this research program is to develop a novel electrochemical sensor based on a boron-doped diamond (BDD) electrode for monitoring/controlling heavy metal ions such as Hg, Zn, Cu, Pb, As, Cd, and Fe encountered in the processing and utilization of coals. This research is based on earlier testwork in which ppb levels of Pb and Hg were detected in laboratory prepared solutions. BDD electrodes are superior to other commonly used electrodes (such as glassy carbon) in terms of their ruggedness, chemical stability, wide potential window and lower background current. These advantages are important for the simultaneous detection of a number of elements in solution.

8. Evaluation of Coal Cleaning Efficiency Using Transponder-Based Density Tracers (Appendix H)

Principal Investigators: G.H. Luttrell, R.-H. Yoon and C.J. Wood (Virginia Tech).

Density tracers are one of the most powerful diagnostic tools for evaluating the performance of heavy media circuits in coal preparation plants. The objective of this project is to develop a new generation of tracers that can be automatically tracked using recently developed transponder technology. This development also makes it possible for efficiency tests to be performed very rapidly by a single person in an extremely cost-efficient manner. The project will be carried out in two phases. In the first phase of work, the hardware and software required to develop a prototype transponder-based system will be procured and evaluated using a simulated circuit at the Virginia Tech coal laboratory. In the second phase, the monitoring system will be relocated to an industrial coal preparation plant for field-testing.

EXPERIMENTAL

The CAST initiative is comprised of a diverse group of subprojects, most of which are multistage, task-oriented developmental projects that cannot be conveniently categorized by the traditional reporting criteria required by the DOE Uniform Reporting Requirements. For example, several of the projects have required the construction of unique test equipment, others the generation of simulation models, etc., as preliminary tasks in the overall execution of the project. As such, they are more appropriately described and discussed as “Project Tasks” within the context of the individual Technical Progress Reports. These reports are attached to this document as Appendices and should be referred to for this information.

RESULTS AND DISCUSSION

The CAST initiative is comprised of a diverse group of subprojects, most of which are multistage, task-oriented developmental projects that cannot be conveniently categorized by the traditional reporting criteria required by the DOE Uniform Reporting Requirements. For example, several of the projects have required the construction of unique test equipment, others the generation of simulation models, etc., as preliminary tasks in the overall execution of the project. As such, the presentation of results is more appropriately described and discussed within the context of the individual Technical Progress Reports. These reports are attached to this document as Appendices and should be referred to for this information.

CONCLUSIONS

The initial RFP for this project resulted in eight (8) sub-projects being funded in late April, 2002. A six-month Progress Report (covering the period May 1, 2002-October 31, 2002) was generated for each of these sub-projects and has been attached to this Document as an Appendix. A brief summary of progress during the initial 6 months, along with plans for the future on each of the sub-projects is given below.

a) Solid-Solid Separation

1. Improving Coarse Particle Flotation (Appendix A)

Principal Investigators: R.-H. Yoon and G.H. Luttrell (Virginia Tech).

Preliminary contact angle measurements indicated that a novel flotation collector (Reagent A) substantially increased the hydrophobicity of coal surfaces compared to that achieved using a traditional collector (kerosene). In light of this promising result, batch flotation experiments were conducted with a novel hydrophobizing agent (Reagent E) using five different monosized fractions of Pittsburgh No. 8 coal. The experimental results showed that the flotation rate constant was increased by 103% and 66.7% for the finest (0.3 x 0.15 mm) and coarsest (2.0 x 1.7 mm) size fractions, respectively. Follow-up tests conducting with the naturally occurring 2 mm x 0 coal also showed substantial increases in flotation kinetics. Compared to kerosene, the novel flotation collector increased the flotation rate by approximately 98%, 73%, and 66% for collector dosages of 100, 300 and 500 g/t, respectively. These results demonstrate the strong collecting power of this reagent.

During the next reporting period, a variety of reagent screening tests will be conducted to evaluate several other novel collectors.

2. Separation of Small Particles due to Density Differences in a CFB Riser System (Appendix B)

Principal Investigators: E. Johnson and B. Kang (West Virginia University).

Since the start of the project in April 2002, the following have been completed: the preliminary design and construction of the system; a Chemical Hygiene Plan for approval of lab space in the NRCCE High Bay has been prepared (and is awaiting final approval by the committee); initial testing of the system including tests for air leaks in riser and the testing of basic components of the system have been completed.

The system will shortly be moved to the NRCCE High Bay. Over the next six months, the PI's plan to generate a Knowlton Diagram for the system and will begin testing the separation capabilities of the CFB Riser.

3. Modeling of Flotation From First Principles (Appendix C)

Principal Investigator: R.-H. Yoon (Virginia Tech).

During the past reporting period, the framework for a conceptual model of flotation has been developed that incorporates both hydrodynamic and surface chemistry parameters. Unlike previous modeling attempts, the new model will be capable of predicting flotation response under turbulent conditions that are typically encountered in industrial flotation machines. The model is currently in the preliminary stages of development. Additional effort will be required to formulate the best possible expressions for collision frequency, collision efficiency, adhesion probability, and detachment probability. Most of the experimental work conducted to date has focused on the construction of an apparatus to measure the velocities of particles and bubbles using Digital Particle Image Velocimetry (DPIV). The Engineering Science and Mechanics Department at Virginia Tech have made the DPIV system available for this project.

The development of the proposed flotation model will continue during the next reporting period. This effort will include (i) the formulation of appropriate mathematical equations that are necessary to describe the various phenomena that occur during flotation and (ii) the completion of a variety of experimental activities that are needed to refine and validate the modeling expressions. The theoretical work will be concentrated on the development of a theoretical expression for detachment energy. The experimental work will largely focus on measurements of particle and bubble velocities under controlled turbulent conditions using DPIV. These measurements are expected to continue through the next two reporting periods.

4. Studies of Froth Stability and Model Development (Appendix D)

Principal Investigator: R.-H. Yoon (Virginia Tech).

During the past reporting period, the graduate student assigned to this project visited the Max Planck Institute of Colloids and Interfaces in Golm, Germany to receive training related to the construction and operation of a Thin Film Balance (TFB). Using this technique, equilibrium film thickness values were measured at different electrolyte concentrations, pH values, and concentrations of 1-pentanol. The data were used to calculate the hydrophobicity constant.

Much of the work conducted during the next reporting period will focus on the construction of a TFB at Virginia Tech. Tasks 2 (Kinetic Studies) and 3 (Froth Model Development) will also be initiated during the next reporting period.

5. Direct Measurement of Forces in Flotation Systems (Appendix E)

Principal Investigators: W.A. Ducker and R.-H. Yoon (Virginia Tech).

During the past reporting period, the components required to construct a piezoelectric translation system were procured. In addition, steps were taken to design

and construct a vibration isolation system and to prepare model particles for the force measurement studies. Unfortunately, the project is currently running behind schedule due to difficulties in recruiting an acceptable post-doctoral researcher. Several candidates are now being considered and it is hoped that the position will be filled in the very near future.

Much of the work conducted during the next reporting period will focus on the continued construction and shakedown testing of the experimental apparatus for the direct measurement of force and separation distance between bubbles and particles. This work will resume once the project staffing problem has been resolved.

b) Hydrometallurgy

6. Novel Bioleaching Technology Assisted by Electrolytic Processes (Appendix F)

Principal Investigators: E. Cho and R. Yang (West Virginia University).

The initiation of the project was hampered by the late award date (April 2002) and subsequent difficulty in acquiring a suitable graduate student for the project. Mr. Brian Conner, a PhD student in the Chemical Engineering Department joined the project in August 2002 and the project is now progressing well. A Perkin Elmer Model 283 Potentiostat/Galvanostat was purchased in June 2002 and will be used to apply a potential to an electrical cell to help grow the bacteria; the PI's visited the University of Idaho, Moscow, Idaho on June 21 and 22, 2002 to consult with Dr. Pesic, Professor of Metallurgical Engineering about bio-leaching of sulfide minerals; a two compartment electrical cell with an anionic membrane partition has been fabricated from Plexiglas; a Plexiglas bioreactor has also been fabricated and a system to recycle the bacteria solution between the two units has been devised and installed.

A culture of *T. ferrooxidans* will be purchased shortly. The project team plans to start growing the bacteria in late October 2002 and to start a series of shakedown experiments with bacteria under the electrical field in November 2002.

c) Sensor and Control Development

7. Development of Electrochemical Sensor for On-Site Monitoring of Heavy Metal Ions in Coal Processing And Utilization (Appendix G)

Principal Investigators: A. Manivannan and M. Seehra (West Virginia University).

A Hokuto-Denko Model HZ-3000 potentiostat and an O-ring type three-electrode electrochemical cell with SCE (saturated calomel electrode) and platinum wire as the reference and counter electrodes, respectively, are being used in this study. Using cyclic voltametry techniques, the PI's work on the detection of ppb quantities of Hg has shown that the presence of chloride in solution causes the formation of a highly insoluble product, Hg_2Cl_2 (calomel), which in turn affects the reproducibility of the experiments

unless the calomel is cleaned from the electrode surface. In order to avoid this problem, they have used a new approach in which the presence of 3 ppm of gold in solution prevents the formation of Hg_2Cl_2 . This procedure will be used in future determinations of mercury. They have also been able to detect ppb quantities of lead and cadmium in solution. Observed interactions between these two elements are explained by the formation of an alloy of Pb and Cd. Below the ppb level, the interaction of these two metals is not significant, but it is important to investigate their interaction due to concentration.

Future experiments will involve the generation of ppb level calibration plots for lead and cadmium and the testing of samples from coal utilization plants.

8. Evaluation of Coal Cleaning Efficiency Using Transponder-Based Density Tracers (Appendix H)

Principal Investigators: G.H. Luttrell, R.-H. Yoon and C.J. Wood (Virginia Tech).

During the past reporting period, a detailed survey was performed to identify commercial suppliers of miniature transponders and detection antenna for this particular application. Important factors considered in the evaluation were detection range, transponder size/density, and system cost. Based on these criteria, two different systems were identified as suitable for use in controlled laboratory trials. The procurement of development kits for these two systems has been completed and controlled laboratory trials with these systems are now underway.

Work will continue during the next reporting period to evaluate the capabilities of the transponder systems purchased from Texas Instruments and Intersoft. Once completed, one of the two systems will be selected and used to develop a prototype tracking system for the density tracers. This effort will include (i) the wiring, assembly, and enclosure of the reader circuit board and power supply, (ii) the manufacture of plastic tracers that incorporate the miniature electronic tags, (iii) the fabrication of various antenna configurations and support brackets, and (iv) the development of data acquisition, analysis, and presentation software. The prototype system will then be subjected to a variety of controlled tests in a laboratory environment. These shakedown tests will be required to determine the capabilities and limitations of the transponder-based tracers prior to field testing at an industrial site.

REFERENCES

References utilized by the individual sub-projects are reported in the relevant Technical Progress Report in the attached Appendices.

Appendix A: Improving Coarse Particle Flotation

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 9/17/01 Ending Date: 12/31/03
<u>Sub-Recipient Project Title:</u> Improving Coarse Particle Flotation	<u>Report Information:</u> Type: Semi-Annual Number: 1 Period: 5/1/02-10/31/02 Date: 11/30/02 Code: VA003
<u>Principal Investigators:</u> Roe-Hoan Yoon and Gerald H. Luttrell	
<u>Contact Address:</u> 146 Holden Hall Virginia Polytechnic Institute & State University Blacksburg, VA 24061	<u>Contact Information:</u> Phone: (540) 231-4508 Fax: (540) 231-3948 E-Mail: cast@vt.edu
<u>Subcontractor Address:</u> No subcontracts issued.	<u>Subcontractor Information:</u> Phone: Fax: E-Mail:

ABSTRACT

Heavy medium cyclones are widely used for cleaning coarse coals in the size range of approximately 50 x 1 mm, while froth flotation used for cleaning 0.15 mm x 0 coals. The remaining material in the 1 x 0.15 mm size fraction is typically cleaned using inefficient water-based separators such as spirals, water-only cyclones, shaking tables, hydraulic classifiers, etc. The objective of this project is to develop methods of extending the upper particle size limit for flotation. The availability of such a technology will improve processing efficiency and greatly simplify the plant flowsheet. Two different complementary approaches will be used to achieve the project objective. One is to use novel coarse coal flotation reagents that will help increase the attachment force between air bubbles and coal particles, and the other is to develop a new flotation machine specifically designed to promote coarse particle flotation.

INTRODUCTION

Background

Heavy medium cyclones (HMCs) have been the preferred means of cleaning run-of-mine coals in the size range of 50 x 1 mm. Coarser coals are processed in heavy medium vessels or jigs, while the finer fractions are cleaned by spirals, water-only cyclones, and/or flotation. Since the mid-1980s, however, the upper-size limit for HMCs has been extended

steadily by using larger diameter units. Many coal preparation plants around the world have been built to process feed coals with 50 mm (2 inch) top size by using larger diameter cyclones. This development allowed coal preparation plants to operate with fewer cyclones to process a given tonnage of coal and to simplify the flowsheet by entirely eliminating the heavy medium vessel circuit (Robertson *et al.*, 1997). Thus, the flowsheet of a newer coal preparation plants often incorporate HMCs to clean the 50 x 1 mm fraction, spirals to clean the 1 x 0.15 mm fraction, and flotation cells to clean the 0.15 mm x 0 fines.

Unfortunately, the simplified flowsheet has its own set of problems. Recent studies showed that HMC circuits are less efficient in treating particles finer than 2 mm (Engelbrecht and Bosman, 1995). The values of Ecart Probable (Ep) become substantially larger than those for larger size fractions and the cut points shift to higher specific gravities (SGs). To correct this problem, the flowsheet can be modified to process the 2 mm x 0 fraction by spirals. It is well known, however, that spirals cannot make low SG cuts with coarser particles in the feed, which can be attributed to the fact that spirals separate particles based on both size and density (Gallagher *et al.*, 1985).

Objective and Approach

A solution to the difficulty of cleaning the troublesome 2 x 0.15 mm fraction would be to increase the upper particle size limit for flotation. In general, coal flotation is efficient in cleaning 0.15 mm x 0 coals, particularly when column cells are employed. In some plants, flotation is used to clean 0.5 mm x 0 coal, with the 0.5 x 0.15 mm fraction in one bank and the 0.15 mm x 0 in another (Firth *et al.*, 1979). It is difficult, however, to make the coarse particle flotation circuit operate efficiently using the technologies available today. Therefore, the objective of this study is to increase upper-particle size for coal flotation and to compare conventional and novel flotation collectors in terms of coarse coal recovery and flotation kinetics.

PROJECT TASKS

Task 1 – Sample Acquisition

A sample of bituminous coal was obtained from the Pittsburgh No. 8 seam for use in this investigation. The as-received sample had a particle topsize of 50 mm (2 inches) and contained 14.3% ash. Upon receipt, the sample was immediately crushed to below 2 mm using laboratory jaw and roll crushers. The crushed sample was then put into sealed plastic bags and stored in a freezer at 20°C to minimize oxidation. The coal samples were removed from the freezer immediately before use in flotation experiments. During this particular reporting period, a representative split of the crushed sample was wet screened to obtain five different monosize fractions prior to flotation testing, i.e., 2.0 x 1.7 mm, 1.7 x 1.2 mm, 1.2 x 0.6 mm, 0.6 x 0.3 mm, and 0.3 x 0.15 mm. The ash content of these fractions increased slightly from 13.0% ash for the finest (0.3 x 0.15 mm) fraction to 14.5% for the coarsest (2.0 x 1.7 mm) fraction. Chunk samples of Elkview coal were also acquired during this reporting period for use in contact angle measurements.

Task 2 - Contact Angle Measurements

Contact angle measurements were conducted to determine the effects of one of the novel flotation collectors (Reagent E) on the hydrophobicity of coal. The measurements were conducted using chunk samples of bituminous coal that were cut into small slaps using a diamond saw and polished to obtain smooth surfaces. As shown in Figure 1, the contact angles obtained after treatment with Reagent E varied from 50-70 degrees, while those obtained using kerosene were all below 40 degrees. These data demonstrate that the novel collector substantially enhances the hydrophobicity of coal compared to traditional collectors such as kerosene.

Task 3 - Testing Novel Flotation Reagents on Monosized Samples

A series of flotation tests were conducted on monosized samples of Pittsburgh No. 8 coal using novel (Reagent A) and conventional (kerosene) reagents as collectors. These tests were used to establish the flotation kinetics and maximum recoverable particle size for each reagent package. Flotation tests were conducted with a 4-liter Denver laboratory flotation cell using 500 g of coal sample in each test. The tests were conducted at natural pH using tap water. The impeller speed of the flotation machine was kept at 1400 rpm for all tests. Before each flotation experiment, the pulp was agitated for 3 minutes to fully suspend the solids before adding collector and conditioning for 3 additional minutes. After the conditioning was complete, a small amount of flotation frother (MIBC) was then added to the slurry in the amount of 100 g/t. The frother was conditioned for one additional minute before introducing air to commence flotation. The froth product was collected for appropriate time intervals (i.e., $\frac{1}{4}$, $\frac{1}{2}$, 1, 2 and 3 minutes) so that the flotation rates could be calculated. Make-up water was added to maintain an appropriate pulp level. Each flotation product was filtered, dried, weighed, and subjected to ash analysis.

Figure 1. Effect of using kerosene and Reagent A on the contact angle of bituminous coal.

Table 1 compares the first-order flotation rate constants (k) obtained using Reagent E and kerosene for each size fraction. For the coarsest size fraction (2 x 1.7 mm), the flotation rate constant increased from 0.81 to 1.35 min⁻¹ when using Reagent E in place of kerosene. This improvement corresponds to an increase in flotation kinetics of nearly 67%. This improvement was even more pronounced when treating the finer size fractions. In fact, the rate constant for the finest size fraction (0.3 x 0.15 mm) increased by more than 100%. The higher flotation rate constants are very beneficial since faster kinetics makes it possible to (i) increase coal recovery in existing flotation cells or (ii) reduce the capital investment required to construct a new flotation plant.

Task 4 - Batch Flotation Tests

In order to validate the results obtained using the monosized samples, an additional series of flotation kinetics tests were conducted using the naturally occurring 2 mm x 0 Pittsburgh coal. The tests were conducted at reagent dosages of 100, 300 and 500 g/t for both Reagent E and kerosene. The test results are summarized in Table 2. At the highest dosage of 500 g/t, the use of Reagent E increased the overall rate constant by approximately 66% compared to that obtained using kerosene. The improvement was even more substantial at lower dosage levels. At the lowest dosage of 100 g/t, the use of Reagent E increased the rate

Table 1. Comparison of rate constants for the flotation of monosized coal with 300 g/t collector addition.

Particle Size (mm)	Rate Constant (k) min ⁻¹		% Increase in k
	Kerosene	Reagent E	
0.3 x 0.15	1.71	3.47	103.0
0.6 x 0.3	1.53	3.02	97.4
1.2 x 0.6	1.32	2.27	72.0
1.7 x 1.2	0.89	1.49	67.4
2.0 x 1.7	0.81	1.35	66.7

Table 2. The effect of reagent dosage on the rate constants for the batch flotation of 2 mm x 0 coal.

Reagent Addition (g/ton)	Rate Constant (k) min ⁻¹		% Increase in k
	Kerosene	Reagent E	
100	0.79	1.56	97.5
300	1.17	2.02	72.6
500	1.58	2.62	65.8

constant by nearly 98% compared to kerosene. In fact, the lowest dosage (100 g/t) of Reagent E produced essentially the same rate constant as the highest dosage (500 g/t) of kerosene. The five-fold difference in reagent dosage demonstrates the tremendous power of the novel collectors that are being developed in this project.

Task 5 - Sample Analyses

All flotation samples were assayed using a LECO TGA-500 Proximate Analyzer. In each case, representative 1 gm lots of the oven-dried samples were pulverized to a fine powder and analyzed for moisture, volatile matter, ash, and fixed carbon content. All values provided in this document are reported on a dry basis.

SUMMARY

Contact angle measurements conducted using a novel flotation collector (Reagent A) substantially increased the hydrophobicity of coal surfaces compared to that achieved using a traditional collector (kerosene). In light of this promising result, batch flotation experiments were conducted with a novel hydrophobizing agent (Reagent E) using five different monosized fractions of Pittsburgh No. 8 coal. The experimental results showed that the flotation rate constant was increased by 103% and 66.7% for the finest (0.3 x 0.15 mm) and coarsest (2.0 x 1.7 mm) size fractions, respectively. Follow-up tests conducting with the naturally occurring 2 mm x 0 coal also showed substantial increases in flotation kinetics. Compared to kerosene, the novel flotation collector increased the flotation rate by approximately 98%, 73%, and 66% for collector dosages of 100, 300 and 500 g/t, respectively. These results demonstrate the strong collecting power of this novel reagent.

FUTURE WORK

During the next reporting period, an variety of reagent screening tests will be conducted to evaluate several other novel collectors.

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PUBLICATIONS/PRESENTATIONS

To date, no major publications have resulted from this project.

APPENDICES

No appendices are included in this report.

Appendix B: Separation of Small Particles Due to Density Differences in a CFB Riser System

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 9/17/01 Ending Date: 12/31/03
<u>Sub-Recipient Project Title:</u> Separation of Small Particles Due to Density Differences in a CFB Riser System	<u>Report Information:</u> Type: Semi-Annual Number: 1 Period: 5/1/02-10/31/02 Date: 11/30/02 Code: WVA002
<u>Principal Investigators:</u> Eric K. Johnson and Bruce S. Kang	
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ABSTRACT

The efficiency of separating small dense particles from small light particles in the internal recirculation flow will be investigated. Small particles considered in this study are particles less than 250 micrometers in diameter. This research is directed towards the removal of pyrite from coal fines at a coal cleaning plant. Also, of concern will be the use of such technology to remove radioactive particles from the desert sand at the Nevada Test Sites.

INTRODUCTION

Separation in a CFB Riser:

A set of gas and solids flow conditions may be established so that a core-annulus flow condition is established in the CFB riser. The core-annulus flow in a CFB riser is characterized by flow of solids downward along the riser wall. An example of the expected vertical flow of solids across the flow area of the riser during core-annulus flow can be seen in Figure 1.

Figure 1: Core-Annulus Velocity Profile in a CFB Riser

It is known that the heavy particles will tend to flow down along the wall in a greater concentration than the lighter particles. The extent the concentration of heavier particles will increase along the riser wall is not known. In order to determine the concentration of heavier particles, the solids moving down along the wall will be removed from the riser. The riser will have a variable gap between the airflow distributor and the riser wall, which will allow the solids to flow past the distributor and into the closed heavy particle bin below the riser. The low density particles are expected to flow with the air, missing the gap, and eventually out of the top of the riser. These lighter particles will be removed from the gas stream by a cyclone, and the particles will be collected in a product hopper below the cyclone. The particles in the light product hopper can either be re-circulated through the riser for further separation or it may be the final separation product. The distributor has a drain in the center that exits into an excess particle bin that will catch any excess particles that remain in the riser at the end of a test sequence. Refer to Figure 2 for the layout of the system and storage bins.

The solid mixture will consist of sand with a density of 140 lb/ft^3 and iron with a density of 445 lb/ft^3 . The difference in density between the two particle types is significant enough to observe the ability of the system to successfully separate particles based on density alone.

System Description:

The experimental system is shown in Figure 2. The air is supplied by a 100 psi service line and is used to pneumatically transport the solid mixture into the riser from both the feed hopper and the low density product hopper, and to create the core-annulus flow through the riser.

Instrumentation:

The instrumentation that will be used for the experiment will consist of three flow meters for the air service lines, a maximum of 9 pressure transducers along the variable height of the riser that will be connected to a computer, and two load cells for the feed hopper and product hopper that will also be connected to a computer. The load cells can be used to monitor the approximate amount of solids in the riser at any given moment as well as the solid flow rates in and out of the hoppers. The pressure transducers will be used to monitor the pressure distribution along the height of the riser.

EXPERIMENTAL PROGRAM

Determination of Particle Separation Efficiency

The heavy particle bin will have both sand and iron particles in it. In order to determine the weight of collected iron in the container, a magnet will be used to collect all the iron and will then be weighed. The weight of iron particles in the heavy particle bin will be compared to the weight of the iron in the initial solid mixture to determine the collection efficiency.

Figure 2: System Outline

Determination of Particle Size and Velocity Along Riser Wall

The velocity and sizes of the particles along the riser wall will be observed using a high speed image acquisition system to determine the magnitude in which the annulus down-flow phenomenon is occurring during the test procedure. Laser spectroscopy technology will be used to observe the particle compositions through the transparent wall of the riser.

The variables in the experiment that will determine the collection efficiency of the system will include the mass flow rate of air through the riser, the mass flow rate of the particles to the riser, the number of cycles through the riser, the heavy particle gap size along the riser wall, and the system geometry (riser height, internals, etc).

Performance Map

The core-annulus flow regime must be established in order for the downward flow of solids to occur along the wall as desired for separation. The heavy particle gap shown in Figure 2 will be closed during the first tests in order to determine the conditions for the desired flow regime in the riser. These preliminary results will be presented in the form of the Knowlton chart shown in Figure 3. The chart shows the region of the solid mass flow rate and riser gas velocity combination that will create the desired annular flow. This chart will then establish the test conditions for separation. This first series of tests will use only sand particles. The sand will be added from the feed hopper and the mass flow rate into the system will be monitored using the load cells and integrating the change in weight over time using the computer. Once all the solid is dispensed from the feed hopper, the solid in the product hopper will be recirculated through the riser and the mass flow rate from the product hopper will be monitored. The mass flow rate and superficial riser velocity will be varied in order to generate the Knowlton chart. Once a preliminary chart is obtained, the system will be tested at various mass flow rates using the chart as a guide for the superficial velocity into the system in order to verify the accuracy of the chart obtained. The development of a desirable core-annulus flow regime will be investigated by changing the riser geometry such as the riser height and installing internals in the riser.

Figure 3: Knowlton Chart

Once the Knowlton chart has been successfully established for the CFB riser, the heavy particle gap can be re-opened. The system can now be tested using sand only with the gap opened. The tests will again be performed according to the chart found previously and will be ran for a given time. The flow regime will again be monitored to assure that opening the gap does not affect the Knowlton chart. The amount of solid left in the heavy particle bin at the end of the tests will be observed. The size of the gap can be adjusted if the amount of solid retrieved in the heavy particle bin is too significant. If any significant change in the Knowlton chart is noted during this test sequence, re-establishment of the Knowlton chart will be made.

The testing sequence can now begin for separation of the particle mixture. The testing will start with the mixture of sand and iron in the feed hopper. The mixture will be fed to the riser in accordance to the chart previously determined until the feed hopper is emptied. The tests will then be varied according to the length of time or amount of solid that is re-circulated from the product hopper and through the riser. Observation of the percent recovery of iron in the heavy particle bin and amounts of sand mixed in with the iron in the heavy particle bin should be used to determine what adjustment, if any, should be made to the heavy particle gap. Tests should then follow, experimenting with various gap sizes in an attempt to maximize the efficiency of the heavy particle collection. Variations in riser height should also be considered in an attempt to increase collection efficiency.

SCHEDULE

Since the start of the project in April 2002, the following have been completed:

- 1) The preliminary design of the system

- 2) Construction of the system
- 3) The Chemical Hygiene Plan for approval of lab space in the NRCCE High Bay Test Area (awaiting final approval by the committee)
- 4) Initial testing of the system including tests for air leaks in riser and testing of basic components of the system

The following is a preliminary schedule of the project:

<i>Dec-Jan:</i>	Continue acceptance testing and address any problem areas
<i>February:</i>	Install system in NRCCE High Bay Testing Area Development of Knowlton diagram.
<i>March:</i>	Continue development of core-annulus flow field in riser Begin testing separation in system
<i>April-May:</i>	Test system separation capabilities Begin making modifications to system to improve results Establish test matrix
<i>June-Oct:</i>	Continue adjusting system to obtain highest collection efficiency possible
<i>July-Nov:</i>	End testing. Begin data analysis.
<i>December:</i>	Finalize report and present findings

ACCOMPLISHMENTS

The system is undergoing final assembly. The frame supporting the system has been completed. The feed hopper and product bin are fully assembled and have been hung from the frame using the load cells. The solid delivery systems have been connected to the bottom of the feed hopper and product bin using plastic valves. The solid delivery systems have been piped to the distributor of the riser using PVC pipe and clear, flexible tubing. Air inlet pipes and valves have been attached to the solid delivery systems and are awaiting flow meters. The riser and cyclone are fully assembled and are mounted to the frame. The top of the riser has been piped to the tangential inlet of the cyclone using clear, flexible tubing.

The pressure transducers have been ordered and will be attached to the riser shortly after delivery. The flow meters have also been ordered and will be connected to the piping of the system shortly after delivery.

Appendix C: Modeling of Flotation From First Principles

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 9/17/01 Ending Date: 12/31/03
<u>Sub-Recipient Project Title:</u> Modeling of Flotation From First Principles	<u>Report Information:</u> Type: Semi-Annual Number: 1 Period: 5/1/02-10/31/02 Date: 11/30/02 Code: VA001
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<u>Subcontractor Address:</u> No subcontracts issued.	<u>Subcontractor Information:</u> Phone: Fax: E-Mail:

ABSTRACT

Flotation is widely regarded as the best available technology for separating fine particles. The present form of the technology was invented nearly 100 years ago, yet there is not a reliable model for predicting flotation rate from first principles. It is the purpose of the proposed work to develop a flotation model that can predict flotation performance from both surface chemistry and hydrodynamic parameters. During the past reporting period, the framework for a model has been developed that incorporates collision frequency, collision efficiency, probability of attachment, probability of detachment, and froth recovery. The model is in the preliminary stages of development and more work is required to accurately determine the collision efficiency, turbulent velocity (used to calculate collision frequency and probabilities of attachment and detachment), and detachment energy.

INTRODUCTION

Background

Flotation is a three-phase phenomenon in which solid, liquid, and gas phases are interacting with each other. Therefore, there are a large number of process variables, which are difficult to put into a single mathematical model. The various parameters can be grouped into (i) hydrodynamic and (ii) surface chemistry parameters. Particle size, bubble size, and

energy dissipation, for example, belong to the first group, while hydrophobicity, surface tension, and surface potential belong to the other. Most of the flotation models developed to date focused on the prediction of hydrodynamic parameters. Furthermore, most of the models are empirical; therefore, they do not have predictive capabilities. In addition, none of the models currently available can accurately predict flotation response in turbulent conditions that are typically encountered in industrial flotation machines.

Objective and Approach

Yoon and Mao (1996) developed the first flotation model that was based purely on theoretical considerations. The model was the first of its kind to incorporate both hydrodynamic and surface chemistry parameters. Unfortunately, the modeling equations were applicable only for flotation under quiescent conditions. It is, therefore, the objective of this project to further develop this theoretical model so that it can be useful for turbulent conditions. Since the model will be developed from first principles, it will have predictive and diagnostic capabilities. The proposed effort will involve four individual tasks, i.e.: Task 1 – Model Development, Task 2 – DPIV Measurements, Task 3 – Model Validation, and Task 4 – Simulator Development.

PROJECT TASKS

Task 1 – Model Development

A universal turbulent flotation model based upon first principles includes the physical and chemical parameters of the flotation environment as well as the particles being subjected to the flotation process. The model calculates the flotation rate constant, which can then be used to find the recovery of particle classes. Most researchers believe that flotation can be modeled using a first order rate equation (Arbiter and Harris, 1962; Kelsall, 1961) given by:

$$\frac{dN_1}{dt} = -kN_1 \quad [1]$$

This states that the change in particle concentration with time is a function of a rate constant, k , and particle concentration, N_1 . The loss of particle concentration with time can also be written as the number of collisions that occur between a particle and bubble ($Z_{12}\eta_c$) combined with the probability of attaching once the collision occurs (P_a) staying attached in the slurry ($1-P_d$) and continuing to stay attached in the froth (R_f), i.e.:

$$\frac{dN_1}{dt} = -Z_{12}\eta_c P_a (1 - P_d) R_f \quad [2]$$

Combining Equation 1 and 2, the rate constant can be determined for a select particle size and characteristics using:

$$k = \frac{Z_{12} \eta_c P_a (1 - P_d) R_f}{N_1} \quad [3]$$

There are five main components of this rate equation; collision frequency, collision efficiency, probability of attachment, probability of detachment, and froth recovery.

Currently, the collision frequency is calculated using Abrahamson's model (1975):

$$Z_{12} = 2^{3/2} \pi^{1/2} N_1 N_2 d_{12}^2 \sqrt{U_1^2 + U_2^2} \quad [4]$$

which incorporates the number densities, N_i , of both the particles (1) and bubbles (2), the average diameter of the collision, d_{12} ($= R_1 + R_2$) and the root-mean-squared velocities of the particles and bubbles, $\sqrt{U_i^2}$.

There are three velocities that must be accounted for in this model. All are slip velocities, where a relative velocity with respect to the fluid is needed for collisions, attachments, and detachments to occur. The first two are the settling velocity of a particle and the rise velocity of a bubble. Both were given by Finch and Dobby (1990) and were obtained from equations proposed by Masliyah (1979). The last slip velocity is the root-mean-squared turbulent velocity. This accounts for the turbulent fluctuations of the fluid flow. According to Schulze (1984), the turbulent velocity can be estimated using:

$$\sqrt{U_i^2} \approx 0.4 \frac{\varepsilon_d^{1/2} d_i}{\nu^{1/2} j^{2/9}} \left(\frac{\rho_i - \rho_3}{\rho_3} \right)^{2/3} \quad [5]$$

where ρ is the density of the particle or fluid (3), ν is the kinematic viscosity, j is a constant between 3 and 4, and ε_d is the local energy dissipation (ratio of power input to total mass).

There are usually three forms of collision efficiency: interception, sedimentation, and diffusion. Diffusion is thought to occur in particles smaller than 1 micron and is negligible in flotation (Yao et al, 1971). Interception (where fluid flow deviation may still cause one particle to encounter another) and sedimentation/inertial effects (where particles may not travel with the fluid due to their different densities) are not well understood in turbulent flows. Due to this, the current collision efficiency is one, and the model is considered a hard-core collision model.

The probability of attachment is calculated by comparing the surface energy barrier, E_1 , that needs to be overcome by the available kinetic energy, E_k , i.e.:

$$P_a = \exp\left(-\frac{E_1}{E_k}\right) \quad [6]$$

The energy barrier is calculated using the extended DLVO theory (Yoon and Mao, 1996) at the critical rupture thickness, after which the bubble and particle will spontaneously adhere. The kinetic energy of attachment is calculated as a combined energy of the particle and bubble. The velocity used is a relative velocity of interaction assuming that the turbulent and rising/settling velocities are perpendicular to each other. The turbulent relative velocities are assumed to be additive.

The probability of detachment is in the same form as the probability of attachment and is given by:

$$P_d = \exp\left(\frac{-(W_a + E_1)}{E'_k}\right) \quad [7]$$

Equation 7 compares the work of adhesion, W_a , and the energy barrier, with the kinetic energy of detachment, E'_k . The work of adhesion is the energy needed to bring the surface energy of detachment to a zero value. This combined with the energy barrier will be the entire surface energy that will need to be overcome. The work of adhesion is given by Yoon and Mao (1996). The kinetic energy of detachment is determined from the individual energies of the particle and bubble after detachment. The available energy from the system after detachment is assumed to be the energy available at detachment. The amount of energy available for detachment is the kinetic energy of the individual particles after detachment.

The current version of the froth recovery factor is an empirical model given by Gorain et al. (1998) which states:

$$R_f = \exp(-\alpha\tau_f) \quad [8]$$

This model relates the froth recovery, R_f , to the froth retention time, τ_f , and a parameter, α , which incorporates both physical and chemical properties of the froth (Mathe et al. 1998). A more robust model produced from first principles is currently being developed under another CAST project (Studies of Froth Stability and Model Development) at Virginia Tech.

At present, there are three areas of the present model that could benefit from a more thorough understanding. These include (i) collision efficiency, (ii) turbulent velocity, and (iii) detachment energy. Work is currently ongoing to develop improved versions of the turbulent velocity and detachment energy models.

Task 2 – DPIV Measurements

Since the turbulent velocity is one of the three slip velocities encountered in a flotation environment and it is used in all aspects of the flotation model, it was given a high priority to verify the original equation for particles and bubbles and, if need be, to create new equations. To achieve this objective, the velocities of particles and bubbles will be measured using a Digital Particle Image Velocimetry (DPIV). Technical staff from the Virginia Tech

Fig. 1. Turbulent flow apparatus. Chamber 1 and 2 are identical 6"x6"x4' Lexan boxes that allow viewing of flow downward (1) and upward (2). Overflows of each chamber allow constant head while a ball valve allows varied flow rate. Grids can be replaced to alter the scope of turbulence. Particles can be introduced into the reservoir while air bubbles can be introduced into either chamber. The DPIV laser-camera setup can view any plane within either chamber.

Department of Engineering Science and Mechanics has been assisting in this effort (i.e., Dr. Demetri Telionis, Dr. Pavlos Vlachos, and Mike Brady).

During this reporting period, a device has been constructed (Figure 1) in which homogeneous, isotropic turbulence can be created. To create turbulence, liquid is passed through flow straighteners and a grid pattern. The grid pattern creates the turbulence in the fluid that eventually becomes homogeneous and isotropic a number of lengths down the cell. Flow tracers (1 micron fluorescent particles) are then added to the fluid to track the fluid flow. Glass particles of various sizes (40 to 100 micron) can also be added to study the effect of turbulence on larger particles. Air bubble of known diameter can also be injected into the cell. The turbulence data are obtained by the use of the DPIV laser-camera setup. The test data are fed directly into a computer where velocity fluctuations can be extracted.

Shakedown testing of the equipment is underway and tests to collect the required experimental information are expected to begin shortly. It is anticipated that the turbulent velocity equation experiments should be completed by the next reporting period. A new equation, or a verification of the current equation, should be available at that time. However, since the detachment energy is not calculated at the time of detachment, a true model of detachment must be developed. Currently, a literature review is ongoing into the fluid

detachment forces encountered by the particle-bubble aggregate. This will eventually lead to a model of detachment based on first principles. An update of the progress will be available within the next progress report.

Task 3 – Model Validation

The goal of this task will be to conduct flotation experiments that can be used to validate the flotation model predictions. At present, a plan is currently being devised to conduct such measurements using a Denver lab flotation machine. The tests will be performed with a clear plexiglass tank so that the flotation process can be easily visualized. Glass spheres of known dimensions will be floated and the rate constants for these particles will be determined. These rate constants can then be compared with those predicted by the model. These experiments should be initiated prior to the submission of the next progress report.

Task 4 – Simulator Development

This task will involve the development of a computer simulator for flotation that is capable of predicting and diagnosing plant operations. This task will begin after the completion of all other project tasks.

SUMMARY

During the past reporting period, the framework for a conceptual model of flotation has been developed that incorporates both hydrodynamic and surface chemistry parameters. Unlike previous modeling attempts, the new model will be capable of predicting flotation response under turbulent conditions that are typically encountered in industrial flotation machines. The model is currently in the preliminary stages of development. Additional effort will be required to formulate the best possible expressions for collision frequency, collision efficiency, adhesion probability, and detachment probability. Most of the experimental work conducted to date has focused on the construction of an apparatus to measure the velocities of particles and bubbles using Digital Particle Image Velocimetry (DPIV). The Engineering Science and Mechanics Department at Virginia Tech have made the DPIV system available for this project.

FUTURE WORK

The development of the proposed flotation model will continue during the next reporting period. This effort will include (i) the formulation of appropriate mathematical equations that are necessary to describe the various phenomena that occur during flotation and (ii) the completion of a variety of experimental activities that are needed to refine and validate the modeling expressions. The theoretical work will be concentrated on the development of a theoretical expression for detachment energy. The experimental work will largely focus on measurements of particle and bubble velocities under controlled turbulent conditions using Digital Particle Image Velocimetry (DPIV). These measurements are expected to continue through the next two reporting periods.

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PUBLICATIONS/PRESENTATIONS

To date, no major publications have resulted from this project.

APPENDICES

No appendices are included in this report.

Appendix D: Studies of Froth Stability and Model Development

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 9/17/01 Ending Date: 12/31/03
<u>Sub-Recipient Project Title:</u> Studies of Froth Stability and Model Development	<u>Report Information:</u> Type: Semi-Annual Number: 1 Period: 5/1/02-10/31/02 Date: 11/30/02 Code: VA002
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ABSTRACT

Froth plays an important role in flotation. It determines the final grade of the product and the maximum carrying capacity (or throughput) of a flotation machine. Also, many operators use stronger frothers to produce smaller air bubbles and, hence, higher recovery and throughput. Despite its importance, little is known of the fundamentals of foam and froth stability. It is, therefore, proposed to study the various factors affecting the stability of flotation froth. This will be accomplished by using the thin film balance (TFB) technique of Scheludko and Exerowa (1959) and by monitoring the stability of froth in a bubble column using a video camera. The results will be used for developing a froth model and also for developing effective defoamers.

INTRODUCTION

Background

In a flotation cell, particles are collected on the surface of air bubbles and rise to the surface of an ore pulp to form a froth phase. In the froth phase, bubbles laden with particles grow in size, and less strongly adhering particles drop off the bubble surface and are subsequently returned to the pulp phase. Thus, the froth phase provides a mechanism for removing the gangue minerals that are loosely held to the surface. In column flotation, wash water is added to accelerate the process of removing the entrained particles. More and more flotation

engineers recognize the importance of better understanding the physics and chemistry of froth and, thereby, improving the performance of their flotation cells. However, relatively little is known of the basic sciences involved in foam and froth and, therefore, it is difficult to model the froth behavior during flotation.

Many investigators recognize the importance of using small air bubble to increase the recovery of fine particles. To produce small air bubbles, it is often necessary to use stronger frothers, which in turn makes it difficult to control the froth at downstream. Mining companies use variety of defoamers, but most of the currently available reagents are ineffective and/or incur high costs.

Objective and Approach

The objective of this project is to study the mechanisms involved in stabilizing foams and froth. Initially, various factors affecting the stability of the thin films of water between two air bubbles will be studied. This will be achieved using the thin film balance (TFB) technique developed by Scheludko and Exerowa (1959). The technique will be useful for determining (i) the role of the various surface forces acting in the thin liquid film, (ii) the kinetics of film thinning, and (iii) the critical thickness at which the film breaks. The TFB technique will also be used for studying the effects of fine particles present in the film, that is, the technique will be used for studying the behavior of flotation froth. It is also proposed to monitor the stability of foam/froth in a specially designed bubble column. The results will be studied for developing a froth model from first principles. The result of the present work will be used for developing antifoaming reagents (or defoamers).

PROJECT TASKS

Task 1 – Foam/Froth Studies

During the past reporting period, the graduate student assigned to this project visited the Max Planck Institute of Colloids and Interfaces in Golm, Germany, to receive training in the Thin Film Balance (TFB) technique. Topics covered in this training exercise included (i) how to form an equilibrium foam film using a TFB and (ii) how to measure the film thickness using software developed by the Max Planck Institute of Colloids and Interfaces. In addition, drawings and instructions were prepared for building a TFB apparatus at Virginia Tech. The construction of this apparatus is to be completed during the next reporting period.

Effect of Surfactant Concentration

While in Germany, several experimental tests were conducted to measure the foam film thickness. In the first set of tests, the equilibrium thickness (H_e) was measured as a function of the surfactant (1-Pentanol) concentration at a constant temperature of 25°C. The tests were conducted in the presence and absence of electrolyte (NaCl). When used, the electrolyte was added to obtain a concentration of 1×10^{-4} M. A TFB ring cell of 4 mm in diameter was used in all experiments.

Fig. 1. Effect of 1-Pentanol concentration (C_s) on equilibrium film thickness (H_e).

Figure 1 shows the equilibrium film thickness values obtained at different surfactant concentrations. The upper line represents the results obtained in the absence of electrolyte, while the lower line represents the results obtained in the presence of electrolyte. The tests were repeated several times at each surfactant concentration so that statistical error bars could be established for each dosage level. When no electrolyte was added, the average equilibrium film thickness remained relatively constant at approximately 158 nm over the entire range of surfactant concentrations. Unfortunately, the amount of scatter in the data was also very considerable. Error bars with a range of up to 25 nm were obtained in some cases when no electrolyte was added. In contrast, the values of equilibrium film thickness obtained in the presence of electrolyte were significantly smaller in magnitude and increased from 91 nm to 103 nm as the surfactant concentration was increased. Exerowa (1969) also observed an increase in equilibrium film thickness with increasing surfactant concentration. In addition, the error bars were much smaller (range of <10 nm) for the tests were conducted in the presence of electrolyte. The fact that the equilibrium film thickness becomes smaller indicates that bubbles become more stable in the presence of electrolyte.

Effect of pH

Experiments were also conducted during the past reporting period to investigate the effects of pH of film stability. These tests were conducted using 1-pentanol as the surfactant and NaCl as the electrolyte. The 1-pentanol and NaCl concentrations were fixed at 1×10^{-4} M and 5×10^{-4} M, respectively. The solution pH was adjusted from pH 4 to pH 8 by adding either acid (HCl) or base (NaOH). A TFB ring cell diameter of 4 mm was used in all tests.

The test data obtained at different pH values are summarized in Table 1. As shown, the films were relatively stable at pH values 5.7 and higher. In this pH range, the equilibrium film thickness (H_e) was relatively constant at 61-64 nm. The life span of the films increased steadily from 993 sec to 1800 sec as the pH was raised from pH 5.7 to pH 10. On the other hand, a stable film could not be maintained at pH 4. The film rapidly thinned and suddenly ruptured at a film thickness of 42 nm after just 22 sec.

Several important surface chemistry parameters were determined in order to identify the phenomena responsible for the changes in the stability of the thin films with changes in pH. These included the film capillary pressure (P_c), the double layer potential (ψ_1), and the hydrophobicity constant (K_{232}). The capillary pressure was determined from the solution surface tension (γ) and ring cell radius (r) using:

$$P_c = 2\gamma/r \quad [1]$$

The double layer potential (ψ_1) was estimated from experimentally measured values of zeta potential reported by Li and Somasundaran (1991). Using these values, the hydrophobicity constant (K_{232}) was back-calculated using an expression derived by Yoon and Aksoy (1999):

$$64C_s RT \tanh^2\left(\frac{ze\psi_1}{4kT}\right) \exp(-\kappa H_e) - \frac{A_{232}}{6\pi H_e^3} - \frac{K_{232}}{6\pi H_e^3} - \frac{2\gamma}{r_c} = 0 \quad [2]$$

where C_s is the surfactant concentration, R the gas constant, T the absolute temperature, z the valence of the surfactant, e the electric charge, k the Boltzman constant, κ^{-1} the Debye length, and A_{232} is the Hamaker constant.

Table 1. Effect of pH on equilibrium film thickness and film life span.

pH	4	5.7	8	10
H_e (nm)	42.0*	61.0	64.1	62.3
τ (sec)	22.1*	993	1485	>1800
*unstable film				

Table 2. Effect of pH on various surface chemistry parameters.

pH	4	5.7	8	10
P_c	0	71	71	71
ψ_1 (mV)	-38	-58	-70	-75
K_{232} (J)	6.01×10^{-19}	6.72×10^{-19}	8.66×10^{-19}	10.9×10^{-19}

The surface chemistry data are summarized in Table 2. As shown, the capillary pressure remained relatively constant over the pH range from pH 5.7 to pH 10. This value eventually dropped to zero when the film became unstable at pH 4. On the other hand, the double layer potential decreased from -75 mV to -38 mV as the pH was reduced from pH 10 to pH 4. Over this same range of decreasing pH values, the value of K_{232} dropped from 10.9×10^{-19} J to 6.01×10^{-19} J. As such, the magnitude of the hydrophobic force is several hundred times bigger than that attributed to the van der Waals force.

SUMMARY

During the past reporting period, the graduate student assigned to this project visited the Max Planck Institute of Colloids and Interfaces in Golm, Germany to receive training related to the construction and operation of a Thin Film Balance (TFB). Using this technique, equilibrium film thickness values were measured at different electrolyte concentrations, pH values, and concentrations of 1-pentanol. The data were used to calculate the hydrophobicity constant.

FUTURE WORK

Much of the work conducted during the next reporting period will focus on the construction of a TFB at Virginia Tech. Work associated with Task 2 (Kinetic Studies) and Task 3 (Froth Model Development) of this project is also expected to be initiated during the next reporting period.

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PUBLICATIONS/PRESENTATIONS

To date, no major publications have resulted from this project.

APPENDICES

No appendices are included in this report.

Appendix E: Direct Measurement of Forces in Flotation Systems

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 9/17/01 Ending Date: 12/31/03
<u>Sub-Recipient Project Title:</u> Direct Measurement of Forces in Flotation Systems	<u>Report Information:</u> Type: Semi-Annual Number: 1 Period: 5/1/02-10/31/02 Date: 11/30/02 Code: VA004
<u>Principal Investigators:</u> William Ducker and Roe-Hoan Yoon	
<u>Contact Address:</u> 304 Davidson Hall and 146 Holden Hall Virginia Tech Blacksburg VA	<u>Contact Information:</u> Phone: 540-231-2249 Fax: E-Mail: cast@vt.edu
<u>Subcontractor Address:</u> No subcontracts issued.	<u>Subcontractor Information:</u> Phone: Fax:

ABSTRACT

The objective of this project is to directly measure the force as a function of separation between a particle and a bubble in aqueous solution. This force controls the attachment and detachment of particles to bubbles, which is an essential step in determining the efficiency of the separation of mineral particles in a flotation cell. We are fabricating a device specially designed for these measurements. The device will use a force-detection method from an Atomic Force Microscope and a separation-detection method from a Surface Forces Apparatus. The key advances are to explicitly measure both the separation between the particle and the bubble and the shape of the bubble at all times. Without this separation and shape data, it is not possible to compare the measured forces to theoretical estimates or to the practice of flotation. After fabrication of the device, measurements of the forces acting on hydrophilic, hydrophobic, and charged particles in aqueous solutions of surfactant molecules will be obtained.

INTRODUCTION

Background

Froth flotation is the most important solid-solid separation process for upgrading run-of-the-mine (ROM) ores and coal (Leja, 1982). In froth flotation, a stream of small air bubbles is introduced to the bottom of a tank (or flotation cell) in which a finely ground ore is suspended in

water. The air bubbles rise to the top of the tank under a buoyancy force, and in doing so, they collide with suspended particles. Purification of the ore is based on differences in the attachment and/or detachment of particles to the bubbles. It is believed that the attachment of particles to a bubble surface is caused by a “hydrophobic” interaction. A hydrophobic particle is a particle that can form only relatively low-energy bonds (or other interactions) with water. During a collision with a bubble, a portion of the particle surface can leave the water and enter the air phase inside the bubble, and therefore achieve a lower energy state. In contrast, hydrophilic particles form relatively high-energy bonds with water, so the energy is not decreased when part of the surface enters encounters the gaseous interior. Therefore, the particle does not attach to the bubble. Flotation thus separates mixtures of ore, based on differences in the hydrophobic/hydrophilic nature of the individual particle surfaces. An additional complication arises because there is often an energetic barrier (an activation barrier) before the particle can actually penetrate the bubble. This can, in principle, prevent the flotation of a hydrophobic material, or allow selectivity among ores based on forces that operate over a finite distance.

Several investigators have attempted to directly measure the forces between air bubbles and particles, but the results are not consistent with experience from flotation practice. The main difficulty lies in the fact that bubbles deform during in the interaction. This deformation leads to confusion as to the real separation between a particle and a bubble. Knowledge of the separation is vital to elucidate the range of the force, and thus the mechanism of the interaction. The range of the force is a required input for calculation of the kinetics of flotation.

Objective and Approach

The overall objective of this project is to perform direct measurements of forces acting on different types of particles when they collide with bubbles. Data from these measurements make it possible to determine the relative importance of long-range and short-range forces in flotation and to examine the role of collectors (surfactants) in controlling these forces. In particular, the data make it possible to develop a better understanding of the nature of the “hydrophobic” interaction that is thought to be responsible for the capture of particles by bubbles. The project is divided into three tasks. In the first task, a device that can measure the forces interacting between an air bubble and a particle will be constructed. The device will be designed to simultaneously measure both the bubble shape and the separation distance. In the second task, the device will be used to obtain force-separation data for the bubble-particle interaction under a wide variety of experimental conditions. Finally, in the third task, the force-separation measurements will be used to develop a better understanding of the kinetics of the attachment of particles to bubbles.

PROJECT TASKS

Task 1 – Design and Fabrication

This task involves the design and construction of a device capable of simultaneously measuring the force between a bubble and particle as well as the shape and thickness of the thin film between the bubble and particle surfaces. A simplified process schematic for the device is shown in Figure 1. The apparatus will use the force detection method commonly employed by an Atomic Force Microscope (AFM). In this method, a small particle will be attached to a micro-fabricated cantilever spring. The deflection of the spring will be used to determine the interaction force. The apparatus will also make use of the separation detection method commonly employed by a Surface Forces Apparatus (SFA). In this technique, the separation distance will be indirectly measured using an interferometer.

The construction of the apparatus has been delayed due to staffing problems. The principle investigators are currently seeking a post-doctoral researcher who is qualified to perform the research. The candidate must have experience in optics because the project requires development of an advanced optical technique. Several candidates are now being considered and it is hoped that the position will be in the very near future. Because of this staffing problem, the only progress made to date is (i) the procurement of components for the piezoelectric translation system, (ii) design and fabrication of a vibration isolation system, and (iii) preparation of model particles that will interact with the bubbles. The design of the vibration isolation system is critical to the success of the project. It is absolutely necessary to minimize the magnitude of vibrations from the environment that are transmitted to particles in order to measure the force as a function of distance between two small objects (e.g. particle and bubble). Otherwise, the particles will not occupy a unique position. To achieve this vibration isolation, a pulley system has been designed to suspend on bungee cords the AFM unit and various optical components. The preparation of model particles is also very critical to the success of the project. The use of an interferometer to measure the distance to a particle requires a clean reflective particle and

Fig. 1. Experimental apparatus designed to simultaneously measure interaction force and separation distance for a bubble-particle system.

analysis requires spherical particles. The principal investigators have now developed the art of reproducibly making small (20–50 μm) spherical gold particles by melting gold wire in a hydrogen flame. The production of these particles was an essential step in enabling the project to proceed.

Task 2 – Experimental Measurements

In this task, the experimental apparatus constructed in Task 1 will be used to obtain force-separation data for bubble-particle interactions under a wide variety of experimental conditions. Direct measurements will be conducted to determine the forces required to attach and detach hydrophobic and hydrophilic particles to bubbles. To date, no activity has been reported under this task.

Task 3 – Data Analysis

In this task, the force-separation measurements conducted in Task 2 will be used to develop a better understanding of the kinetics of the attachment of particles to bubbles. The experimental data will be analyzed and used to advance scientific knowledge related to the surface, solution, and shape parameters that affect the bubble-particle interaction. This information will also provide improved inputs for developing predictive models of flotation behavior. To date, no activity has been reported under this task.

SUMMARY

During the past reporting period, the components required to construct the piezoelectric translation system were procured. In addition, steps were taken to design and construct a vibration isolation system and to prepare model particles for the force measurement studies. Unfortunately, the project activities are currently running behind schedule because of problems associated with identifying a post-doctoral researcher who is qualified and willing to perform the proposed research. Several candidates are now being considered and it is hoped that the position will be in the very near future.

FUTURE WORK

Much of the work conducted during the next reporting period will focus on the continued construction and shakedown testing of the experimental apparatus for the direct measurement of force and separation distance between bubbles and particles. This work is expected to be resumed once the project staffing problems have been resolved.

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PUBLICATIONS/PRESENTATIONS

To date, no major publications have resulted from this project.

APPENDICES

No appendices are included in this report.

Appendix F: Novel Bioleaching Technology Assisted by Electrolytic Processes

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 9/17/01 Ending Date: 12/31/03
<u>Sub-Recipient Project Title:</u> Bioleaching Technology Assisted by Electrolytic Processes <u>Principal Investigators:</u> Eung Ha Cho and Ray Y. K. Yang <u>Contact Address:</u> Dept. Of Chemical Engineering West Virginia University P. O. Box 6102 Morgantown, WV <u>Subcontractor Address:</u> No subcontracts issued.	<u>Report Information:</u> Type: Semi-Annual Number: 1 Period: 5/1/02-10/31/02 Date: 11/30/02 Code: WVU001 <u>Contact Information:</u> Phone: (304) 293-2111 ext 2433 Fax: E-Mail: eung.cho@mail.wvu.edu <u>Subcontractor Information:</u> Phone: Fax: E-Mail:

ABSTRACT

Bioleaching of sulfide minerals using bacteria *Thiobacillus ferrooxidans* has been identified as a promising method as it applies to leaching low grade mixed sulfide ore in a heap leaching or dump leaching method. The mixed sulfide ore commonly contains sulfide minerals of iron, copper and zinc. However, the major problem with the bioleaching system is that the rate is so low that it takes a long time (e.g., 1-2 years) to complete the heap or dump leaching. Thus, the slow rate of the bioleaching reaction renders limitations and restrictions for wider commercial utilization of this biotechnology. The rate can be enhanced, however, by applying direct current potentials to the bioleaching system. This proposal is based on this electrobioleaching of sulfide minerals of pyrite (FeS₂), chalcopyrite (CuFeS₂), and sphalerite (ZnS). The approaches are focused on the growth of the bacteria under the influence of applied direct potential. The objectives of this project are to identify the optimum mode of application for the bio- and to optimize the conditions of the mode. Also, the objective is to determine the technical and economic feasibility of this technology as applied to a commercial process in which low grade mixed sulfide ore is leached.

INTRODUCTION

An approach will be tested in an effort to search for the optimum conditions of application for growing bacteria *Thiobacillus ferrooxidans* under the influence of direct potential and thus for accelerating leaching rate of sulfide minerals of pyrite, chalcopyrite and sphalerite. In the approach, the apparatus will consist of an electrical cell and a bioleaching reactor. A solution will be circulated from the cathode compartment of the electrical cell to the bioleaching reactor. In this circulation, the solution containing mostly ferrous iron will be pumped from the cathode compartment of the electrical cell to the bioleaching reactor. The idea of this setup is that the ferrous iron will be fed to the bioleaching reactor, and will grow the population of *T. ferrooxidans* which will catalyze the leaching of sulfide mineral. At the same time, the catalysis of the leaching reaction converts the ferrous iron to ferric iron in the bioleaching reactor which will be reduced back to ferrous iron at the cathode compartment of the electrical cell later.

In this approach, the concentration of dissolved metal values will be determined as a function of time under various parametric conditions including applied potential and solution circulation rate. The results will be analyzed as to which combination of parametric conditions yields the highest leaching rate of each sulfide mineral. Also, the results will be analyzed for the feasibility of this leaching mode as applied to the dump or heap leaching method of the low grade mixed sulfide ore.

PROGRESS TO DATE

The initiation of the project was hampered by a late award date which impacted the acquisition of a suitable graduate student for the project. Mr. Brian Conner, a PhD student at the Chemical Engineering Department joined the project in August 2002 and is progressing with many of the technical aspects of the project. The particular accomplishments that have been achieved since April 2002 are listed as follows:

- 1) Perkin Elmer Model 283 Potentiostat/Galvanostat was purchased during June 2002. This instrument will be used to apply a potential to an electrical cell to help grow bacteria, *T. ferrooxidans*.
- 2) PI's, Drs. Eung Ha Cho and Ray R.K. Yang visited the University of Idaho, Moscow, Idaho on June 21 and 22, 2002 to consult with Dr. Pesic about bio- and electro-leaching of sulfide minerals. Dr. Pesic, is a Professor at Metallurgical Engineering Department at the Moscow, Idaho campus.
- 3) An electrical cell was fabricated with Plexiglas sheets. The cathode and anode compartments were designed to hold 1.5 and 0.75 liters plus some surge volumes, respectively. The two compartments are partitioned using an anionic membrane (Ionics, Inc. AR204SZRA).

- 4) A bioreactor was also fabricated with Plexiglas sheets. It was designed to hold 1.5 liters plus some surge volumes.
- 5) A method was designed and constructed to allow a solution to be recycled from the cathode compartment of the electrical cell to the bioreactor. A level sensor is placed in the cathode compartment. The solution in the cathode compartment is pumped to the bottom of the bioreactor until the level sensor is deactivated. The solution level in the bioreactor rises and the solution drains through a hole which is positioned at the original solution level on the wall of the bioreactor. The drained solution flows through a tube, a valve and a tube again, and reaches the cathode compartment. This solution will activate the sensor after some time and the process will be repeated.
- 6) Other supply items such as two platinum gauze electrodes, an overhead stirrer to stir the solution of the bioreactor, a shaker with which to maintain the stock solutions of the bacteria, and two flowmeters have been ordered.
- 7) *A culture of T. ferrooxidans* will be purchased, and we will start growing the bacteria around the end of October 2002.
- 8) We will start conducting a series of shaking-down experiments with bacteria under the electrical field during November 2002.

**Appendix G: Development of Electrochemical Sensor for On-Site
Monitoring of Heavy Metal Ions in Coal Processing And Utilization**

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 9/17/01 Ending Date: 12/31/03
<u>Sub-Recipient Project Title:</u> Development of Electrochemical Sensor for On-site Monitoring of Heavy Metal Ions in Coal Processing and Utilization <u>Principal Investigators:</u> A. Manivannan and Mohindar S. Seehra	<u>Report Information:</u> Type: Semi-Annual Number: 1 Period: 5/1/02-10/31/02 Date: 11/30/02 Code: WVU003
<u>Contact Address:</u> Dept. of Physics West Virginia University P. O. Box 9160 Morgantown, WV 26506	<u>Contact Information:</u> Phone: (304) 293-3422 ext:1429 Fax: E-Mail: amanivan@wvu.edu
<u>Subcontractor Address:</u> No subcontracts issued.	<u>Subcontractor Information:</u> Phone: Fax: E-Mail:

ABSTRACT

The aim of this research program is to develop a novel electrochemical sensor based on boron-doped diamond (BDD) electrode for monitoring/controlling heavy metal ions such as Hg, Zn, Cu, Pb, As, Cd, Fe) encountered in the processing and utilization of coals. This research is based on our initial results in which ppb levels of Pb and Hg have been detected in laboratory prepared solutions. It is established that the BDD electrodes are superior to other commonly used electrodes (such as glassy carbon) in terms of their ruggedness, chemical stability, wide potential window and lower background current. These advantages are important for the simultaneous detection of a number of elements in some solution. In this report, results are reported for the detection of mercury (ppb levels) and the simultaneous detection of Pb and Cd.

INTRODUCTION

The proposed investigations will include: (i) Development of the calibration curves for different elements using laboratory prepared solutions; (ii) Testing of samples obtained from a coal preparation plant and an acid mine drainage site and validation of the method employing other analytical techniques; and (iii) Development of a portable unit for on-site detection. The project will benefit from the collaborations provided by the Consolidation Coal Co. and Prof. Fujishima of the University of Tokyo where the BDD electrodes are synthesized.

PROGRESS TO DATE

BDD films deposited on conductive silicon substrates, are shown to possess extremely low background current and higher sensitivity compared to glassy carbon electrode [1]. A Hokuto-Denko Model HZ-3000 potentiostat and an O-ring type three-electrode electrochemical cell with SCE (saturated calomel electrode) and platinum wire as the reference and counter electrodes respectively, were used. A quasi-platinum reference electrode was used along with SCE to reduce noise. The supporting electrolyte was 0.1 M KNO₃ acidified with HNO₃ (pH = 1). The standard mercury solutions were prepared from Hg(NO₃)₂. Initial results from our laboratory have been reported [1,2] for detecting ppb levels of mercury, lead and cadmium ions in solutions.

Detection of Mercury

Cyclic voltammetric scans for millimolar concentrations of Hg at a BDD electrode revealed significant anodic oxidation and cathodic reduction peaks at 0.4V vs. SCE and 0.32V vs. SCE respectively in high pure nitrate electrolyte. Figures 1a and 1b show the CVs for the high-purity mercuric nitrate as well as the effect of the addition of 0.14% chloride. It is evident that the addition of chloride significantly shifts the anodic peak to 0.18V vs. SCE and as well as the peak current.

The shift is due to the fact that chloride anion forms an insoluble mercury compound (Hg₂Cl₂) as shown by the following reaction:

It should be noted here that, because the oxidation process involves the formation of highly insoluble product Hg₂Cl₂ (calomel), the electrode must be cleaned carefully with concentrated HNO₃, followed by rinsing with high-purity water. This procedure can perhaps be avoided by use of a thiocyanate containing electrolyte (3) or gold co-deposition method which is explained later. This approach is being evaluated at present in our laboratory. In order to achieve higher detection sensitivity, we have employed the DPV technique. This technique can increase the sensitivity by isolating the Faradaic response from the associated effects of solution resistance and capacitance.

Figure 1. Cyclic voltammetry for $\text{Hg}(\text{NO}_3)_2$ solution (2×10^{-5} M) in 0.1 M KNO_3 (pH = 1) electrolyte a) without b) with the addition of 0.14% KCl. The mercury stripping peak appeared at 0.4 V vs. SCE (a) is shifted to 0.18V vs. SCE (b). This clearly explains the effect of chloride addition.

As noted above, the presence of ionic species such as chloride and nitrate also influence the sensitivity especially for mercury. Presence of chloride ions improves the sensitivity than nitrates indicating the formation of mercurous chloride which however affects the reproducibility. It should be noted that the important observation is the oxidation process that involves the formation of highly insoluble product Hg_2Cl_2 (calomel) which can affect the reproducibility of the experiment unless the calomel is cleaned from the surface. In order to avoid this problem, we followed a new approach in which 1-3 ppm of gold was co-deposited on the BDD electrode surface simultaneously.

In order to validate our method, a comparison with cold vapor atomic absorption spectrometry (CVAAS) has also been carried out using a real sample (KCl impinger solution) obtained from the flue gas coal fired power plant. Figure 2 shows the DPV analysis of the real sample using BDD. The concentration of mercury in the sample was estimated as 120 ± 7 ppb using standard addition method. A comparison of the same solution by CVAAS indicated a mercury level of 115 ± 5 ppb that agrees well with the value estimated using our diamond electrodes.

In the presence of 3 ppm of gold solution, we are able to avoid the formation of Hg_2Cl_2 and hence the sensitivity. In Fig.3, the calibration curve for the detection of mercury in the 2-10 ppb range is shown. This procedure will be used in future determinations of mercury.

Figure 2. DPV of a real sample (supplied by NETL) with three standard additions of mercury solutions of 300, 500, 700 ppb concentrations. An intercept value of 120 ppb has been obtained for the unknown mercury. Deposition time, 120 s, at -0.5 V vs. SCE; pulse width, 40 ms, pulse delay, 160 ms, pulse amplitude, 50 mV; sweep rate, 20 mV/s.

Figure 3. Calibration curve for DPV peak currents for Hg^{2+} concentrations at BDD covering a range from 0-50 ppb (a) and 1 ppb to 10 ppb (b). 3 ppm of gold standard solution was added to the electrolyte. Details of this work will be presented in future reports and publications [1,2].

Detection of Lead and Cadmium:

We have also observed similar detection levels for lead and cadmium. Since it is important to study the stripping peaks simultaneously since the interaction of these metals can play a role during the detection analysis. Presently, we describe a part of these results due to the interaction of Pb and Cd during the anodic voltametric analysis. Figure 4 shows the stripping behavior of Cd deposited from various solution concentrations of Cd in the presence of 5 μM of $\text{Pb}(\text{NO}_3)_2$. In addition to the Cd stripping peak at -0.85 V, the Pb stripping peak can be seen at -0.65 V vs. SCE. In the presence of 5 μM Pb, the peak currents for Cd (Fig. 5) were consistently ca. 55% smaller than those obtained in pure Cd^{2+} solutions (Fig. 4). The decreases in the peak currents for Cd can be explained by the formation of an alloy of Pb and Cd, as discussed later. Figure 6 depicts the calibration curves for Cd in pure solution (curve a) as well as in the presence of Pb (curve b) based on the DPV results in Figs. 4 and 5. Linear behavior was observed in both cases. For the Pb stripping peak (5 μM Pb), slight increases in the peak current were observed with increasing Cd concentration (curve c). Below ppb level detection the interaction of these metals are not significant and less important. But it is important to investigate their interaction due to concentration.

Future experiments will involve ppb level calibration plots for lead and cadmium and testing samples from coal utilization plants.

(left) Figure 4. DPASV curves for the stripping of Cd deposited from solutions containing 1-5 μM $\text{Cd}(\text{NO}_3)_2$ in 0.2 M acetate buffer (pH = 5.0); the deposition time was 2 minutes at -1.0 V vs. SCE.

(right) Figure 5. DPASV curves for the stripping of Cd and Pb from solutions containing $\text{Cd}(\text{NO}_3)_2$ in 0.2 M acetate buffer with 5 μM $\text{Pb}(\text{NO}_3)_2$; the deposition time was 2 minutes at -1.0 V vs. SCE.

Figure 6. Calibration curves for the differential stripping peak current for Cd, from solutions containing 0 mM to 5 μM Cd^{2+} in 0.2 M acetate buffer: a) in the absence of added Pb^{2+} ; b) in the presence of 5 μM Pb^{2+} . In addition, the differential peak currents for Pb stripping are shown (curve c) for the same solutions; the deposition time was 2 minutes at -1.0V vs. SCE.

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Appendix H: Evaluation of Coal Cleaning Efficiency Using Transponder- Based Density Tracers

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)		<u>Period of Performance:</u> Starting Date: 9/17/01 Ending Date: 12/31/03	
<u>Sub-Recipient Project Title:</u> Evaluation of Coal Cleaning Efficiency Using Transponder-Based Density Tracers		<u>Report Information:</u> Type: Semi-Annual Number: 1 Period: 5/1/02-10/31/02 Date: 11/30/02 Code: VA005	
<u>Principal Investigators:</u> Gerald H. Luttrell and Roe-Hoan Yoon		<u>Contact Information:</u> Phone: (540) 231-4508 Fax: (540) 231-3948 E-Mail: cast@vt.edu	
<u>Contact Address:</u> 146 Holden Hall Virginia Polytechnic Institute & State University Blacksburg, VA 24061		<u>Subcontractor Information:</u> Phone: Fax: E-Mail:	
<u>Subcontractor Address:</u> No subcontracts issued.			

ABSTRACT

Density tracers are one of the most powerful diagnostic tools for evaluating the performance of coal preparation plants. The objective of this project is to develop a new generation of tracers that can be automatically tracked using transponder technology. During the past reporting period, a detailed survey was performed to identify commercial suppliers of miniature transponders and detection antenna for this particular application. Important factors considered in the evaluation were detection range, transponder size/density, and system cost. Based on these criteria, two different systems were identified as suitable for use in controlled laboratory trials. The procurement of development kits for these two systems has been completed and controlled laboratory trails with these systems are now underway.

INTRODUCTION

Background

Density tracers offer a rapid and low-cost method for assessing the performance of heavy medium circuits in coal preparation plants (Davis *et al.*, 1985a; 1985b). Density traces are simply plastic blocks (usually cubic) that incorporate high-density fillers to create artificial particles with densities of 1.20-2.60 SG with an accuracy of ± 0.005 SG. The blocks can be introduced into a separation process (such as heavy medium cyclones) to mimic the

behavior of particles of coal or rock. During a typical test, tracers of different densities are selected based on the anticipated circuit operating conditions. The tracers are fed by hand into the process feed stream together with the run-of-mine coal. The tracers pass through the separator and report to either the high- or low-density product streams as dictated by the particular characteristics of the separator. The tracers are normally brightly colored so that they can be manually retrieved (by hand) from the drain and rinse screens in the plant. Tracers reporting to clean coal are recovered and counted separately from those that report to refuse. By arranging the blocks in order of density, a quick picture can be established as to how well the circuit is performing. A typical test requires about an hour to complete, compared to several days (or even weeks) for traditional sampling and laboratory analysis. In addition, the procedure is less costly and less hazardous to the environment compared to competitive float-sink tests that utilize toxic organic liquids. Unfortunately, the use of density tracers in industrial operations has been limited due to problems that occur during the retrieval step. The amount of labor required to manually collect the blocks can be excessive for large plants or complicated circuits. In addition, the data can sometimes be unreliable since tracers can be easily lost when buried in a thick bed of particles.

Objective and Approach

The objective of this project is to develop a new type of density tracer that can be automatically tracked using an electronic tagging system. The proposed system makes use of miniature electronic tags (transponders) that are embedded within the tracer blocks. These “passive” tags remain inactive until they become externally powered by a transmission signal from an antenna of a remote interrogator/reader. Once energized, the tags transmit a unique digital code back to the interrogator/reader that identifies the density and size of the tracer. The successful development of this technology will eliminate statistical counting errors associated with lost tracers and will make it possible for tests to be performed by a single individual.

The proposed project will be carried out in two phases. In the first phase of work, the hardware and software required to develop the transponder-based system will be procured and evaluated. This effort will include the manufacture of density tracers that incorporate electronic transponder tags and the construction of stationary readers for identifying and counting the tagged tracers. Electronic interfaces and graphical software will also be developed to convert the tracer counts into efficiency curves for use by plant personnel. The prototype system will be tested and evaluated at the Virginia Tech coal laboratory using a simulated circuit. In the second phase of work, the monitoring system will be relocated to an operating coal preparation plant for field-testing. A regional coal company will provide an industrial site for the testing of the transponder-based tracers.

PROJECT TASKS

Task 1 – Transponder Evaluation

A detailed study was conducted during the past reporting period to compare the capabilities of several commercially available transponder systems. The technical factors

considered in the evaluation included transmission mode/frequency, storage capacity, programmability, detection range, interference susceptibility, physical size/density, and mechanical durability. Smaller tags are more attractive since they are easier to incorporate within the tracer blocks and are less likely to cause variations in the absolute density of an individual tracer block. However, the initial evaluation of commercially available systems showed that detection distance decreases with transponder size (i.e., the read range is very short for a very small transponder). Therefore, as a compromise between size and read range, transponders incapable of providing a minimum read range of at least 15 cm (6 inches) and tags larger than 32 mm (1.25 inches) were not considered for this application. In addition, component cost was viewed as one of the primary considerations in the development of the prototype system. Since the tracer blocks will not be recovered, the tags must be available at a price that will allow them to be disposable.

In addition to size and cost, the choice of transmission frequency is perhaps the most important consideration in the selection of a transponder system. At present, commercial systems are available that operate in three general frequency ranges (see Table 1). The frequency must be carefully matched to the conditions of the given application. In the current application, the transponder tags will be placed within density tracers of tight density tolerances and small dimensions (e.g., 16 mm tracer cubes). The tracers will be introduced into the density separation circuit, which could include unit operations such as centrifugal pumps, dense medium concentrators, vibrating screens, and an array of sumps, pipes, chutes, or bins. The tracers will eventually report to either the clean coal or refuse conveyor belts, where they may be buried within several inches of damp coal or rock. Each step in the process introduces a different challenge to being monitored by the transponder technology.

Two types of transponder systems were considered for use in this application, i.e., induction and electromagnetic. Induction systems typically operate in the 125-134 kHz and 13.56 MHz frequency range. These devices are called “induction” transponders since the energizing field and data stream are transmitted by means of inductive coupling (much like a transformer). During operation, the antenna of the reader generates a magnetic field that supplies energy by inducing a voltage in the coil of the tag. Data transmission is accomplished by changing one parameter of the transmitting field (i.e., amplitude, frequency, or phase). The transmitted signal field strength is strongly dependent on the separation distance (d) between the tag and the antenna. The field is generally proportional to $1/d^3$ to $1/d^4$, depending on the orientation of the tag with respect to the reader transmitter loop. Therefore, the working range of these tags must be kept very short (generally within several inches).

Table 1. Transmission Frequencies for Commercial Transponder Systems.

Category	Transmission Frequency	
I	Low (LF) and High (HF)	30kHz – 300 MHz
II	Radio (RF) and Ultra High (UHF)	300 MHz – 3 GHz
III	Microwave (MF)	>3 GHz

Electromagnetic (or radio frequency) transponders operate in the 400 to 1000 MHz frequency range. These devices make use of conventional electromagnetic wave propagation to transmit data, commands, and power (for passive tags). During operation, the interrogator transmits an electromagnetic wave that passes outwards with a spherical wave front. The energy propagates through the atmosphere (or other material) by exciting electrons that, in turn, radiate energy at the same frequency. The process continues as newly excited electrons radiate other nearby electrons in an expanding progression. Tags placed within the field are immersed in the propagating wave and collect some of the energy as it passes. The amount of energy available at any particular point is related to the distance between the tag and transmitter (d). The field is proportional to $1/d^2$, which makes the working distance of these devices significantly greater than that of induction based systems.

Signal interference is an issue that must be addressed when developing a transponder-based monitoring system. Electromagnetic waves are similar to light waves and behave in a similar manner. These waves can be:

- reflected off radio conductive surfaces,
- refracted between dissimilar dielectric media, and
- diffracted around sharp edges.

These phenomena have the potential to substantially degrade the transmission signal between the tag and reader. In general, electromagnetic systems involve shorter wavelengths than induction systems and, as such, are much more prone to interference.

Reflection occurs when electromagnetic waves rebound off conductive surfaces such as metal, water, etc. When a transmitted wave meets at some point with an opposite reflected wave, a signal cancellation (or null) can occur, resulting in a no read situation. On the other hand, the signal strength may be intensified if the two waves meet at some point in phase. Unfortunately, nulls are much more prevalent than enhancements. The use of multiple antennae configured at 900 MHz can reduce, but cannot eliminate, the adverse effects of these problems associated with wave reflection.

Refraction and diffraction are also important considerations. Refraction is a measure of the ability of electromagnetic waves to penetrate (or pass through) a substance. This ability depends largely on the electrical conductivity of the materials involved. For example, the particulate solids contained in run-of-mine coals have low electrical conductivities and are expected to pass electromagnetic waves. On the other hand, water has a high electrical conductivity and will tend to reflect and absorb electromagnetic energy. Thus, the presence of moisture is a concern for electromagnetic systems. Refraction is caused by the change in velocity of an electromagnetic wave when it crosses a boundary between one propagating medium and another. If this crossing is at an angle, then one part of the wave front will change speed before the other, thereby changing the direction of the wave. Both of these phenomena may interfere with the transmission process.

Table 2. Comparison of Commercial Providers of Transponder Systems.

Manufacturer	Description of Capabilities
Balogh	Staff has considerable experience in new industrial applications, but product line appears to be too costly for density tracer applications.
BioMark	Company focuses on animal tagging/identification and offered little flexibility in terms of developing other applications.
Checkpoint Systems	Company is developing low-cost tags for electronic article surveillance (EAS), but size limitations with their products are a concern.
Intermec	High-end products do not currently appear to be cost-effective for use in disposable density tracers.
Intersoft	The company offers an inexpensive product line and can provide low-cost product development kits for new applications.
Matrics	This group deals exclusively with 900 MHz frequencies that could not function in a moist environment due to interference problems.
RFID Inc.	Company recognized that a 135 MHz frequency would be best suited for density tracers, but communication with technical staff is difficult.
Texas Instruments	This group currently offers tags with the most capabilities and a reasonable price. The density consistency of their tags is a concern.
Trolley Scan	Products from this company were found to be incapable of meeting the required size specifications for density tracer applications.

Table 2 provides an overview of some of the commercial distributors of transponder systems that were directly contacted in conjunction with this project. A description of the capabilities and limitations associated with each distributor is included for comparison. This initial review suggests that the most promising distributors appear to be Intersoft and Texas Instruments. The units provided by Texas Instruments were generally more affordable.

Task 2 – Transponder Procurement

During the past reporting period, purchase orders were issued for the procurement of two transponder development kits. Both kits have now been received. The first kit was purchased from Intersoft. The kit included a reader board, several miniature glass-encased tags (6 and 9 mm), and a 5 x 10 cm rectangular gate antenna. The system was powered by a standard 9-volt battery. The second kit was purchased from Texas Instruments. This system included a reader board, a 14 cm (5.5 inch) long rod type antenna, and an assortment of miniature tags (e.g., molded plastic and glass encased). This system required the additional purchase of an external regulated power supply to power to the reader module. Several

miscellaneous components, such as wiring, connectors, electrical boxes, etc., were purchased from local suppliers. Preliminary evaluations are now underway using the two commercial transponder systems to determine which system is best suited for the density tracer application.

SUMMARY

A detailed study was carried out during the past six months to evaluate several commercially available transponder systems. Important factors considered in the evaluation were detection range, transponder size/density, and system cost. Based on these criteria, two different systems, i.e., Intersoft and Texas Instruments, were identified as possible candidates for use in density tracer applications. The two systems were purchased and preliminary tests were initiated with the assistance of technical representative from each supplier.

FUTURE WORK

Work will continue during the next reporting period to evaluate the capabilities of the transponder systems purchased from Texas Instruments and Intersoft. Once completed, one of the two systems will be selected and used to develop a prototype tracking system for the density tracers. This effort will include (i) the wiring, assembly, and enclosure of the reader circuit board and power supply, (ii) the manufacture of plastic tracers that incorporate the miniature electronic tags, (iii) the fabrication of various antenna configurations and support brackets, and (iv) the development of data acquisition, analysis, and presentation software. The prototype system will then be subjected to a variety of controlled tests in a laboratory environment. These shakedown tests will be required to determine the capabilities and limitations of the transponder-based tracers prior to field testing at an industrial site.

REFERENCES

Davis, J.J., Wood, C.J. and Lyman, G.J., 1985a. "Density Tracers Can Improve Coal Preparation Plant Yield," *Australian Coal Miner*, July 1985, pp. 9-11.

Davis, J.J., Wood, C.J. and Lyman, G.J., 1985b. "The Use of Density Tracers for the Determination of Dense Medium Cyclone Partitioning Characteristics," *International Journal of Coal Processing*, Vol. 2, No. 2, pp. 107-126.

PUBLICATIONS/PRESENTATIONS

To date, no major publications have resulted from this project.

APPENDICES

No appendices are included in this report.