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ABSTRACT

This Technical Progress Report describes progress made on the eight sub-projects awarded in the first year and the five projects awarded in the second 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 (approx. six months), the second year project TPR's 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 by Virginia Tech and West Virginia University to develop technologies that can be used by the U.S. mining industry to create new products, reduce production costs, and meet environmental regulations. This endeavor is supported through U.S. DOE Cooperative Agreement No. DE-FC26-01NT41091: Establishment of the Center for Advance Separation Technologies.

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) Chemical/Biological extraction, and
- d) Sensor and control development.

Distribution of funds has been handled via competitive solicitation of research proposals through Site Coordinators at the two universities. Two RFP's have been issued to date. The first of these, referred to as the CAST I – Round 1 RFP, was issued on August 17, 2001 and closed October 15, 2001. A total of 12 proposals were received in response to this first 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 Technical Committee made an initial selection/ranking of proposals and forwarded 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 17, 2002.

This was followed, on June 1, 2002 with the CAST I – Round 2 RFP, which closed on July 19, 2002. A total of 12 proposals were received in response to this second RFP – five were selected for funding. These were in place at the constituent universities (2 at Virginia Tech and 3 at West Virginia University) by March 1, 2003.

All thirteen of 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

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

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project).

The recovery of coarse particles by flotation is a common problem in the coal and minerals processing industry. 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 flotation reagents that will help increase the attachment force between air bubbles and coarse particles, and the other is to develop new flotation machines specifically designed to promote coarse particle flotation.

2. Separation of Small Particles due to Density Differences in a CFB Riser System

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

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project).

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

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

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project).

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

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

Period of Performance: May 17, 2002-May 31, 2004 (3-Year Project).

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

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

Period of Performance: May 17, 2002-May 31, 2005 (2-Year Project, Extended).

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.

6. Novel Surfactants as Collectors for Froth Flotation

Researcher: Richard D. Gandour (Virginia Tech)

Period of Performance: March 1, 2003-May 31, 2004 (1-Year Project).

Our goals are to synthesize novel, inexpensive surfactants that outperform current collectors in mineral flotation. These surfactants will selectively bind to particles and create a hydrophobic coating on a particle to enable selective separation by froth flotation. We plan to synthesize surfactants that have very hydrophobic, long chains, yet have sufficient water solubility for mineral processing and coal-fines processing. These amphiphiles, which we call "hydra surfactants," will have one tail and three identical functional groups on the head. These novel molecules will be useful for many different separations in mineral processing, but initially will be tested on separation of discoloring impurities (i.e., anatase (TiO₂) and iron oxides) from clay. A strategy to make these surfactants from environmentally friendly vegetable oils is outlined.

7. Column Flotation of Fine Dolomitic Phosphate by Selective Fatty Acids

Researcher: F. F. Peng (West Virginia University)

Period of Performance: March 1, 2003-May 31, 2004 (1-Year Project).

Among the detrimental impurities in phosphate ores, dolomite is considered the most troublesome for down stream operations. Dolomite may cause higher consumption of sulfuric acid, reduce filtration rates and lower P₂O₅ content in fertilizer manufacturing processes. Difficulties in separating dolomite from phosphate arise from the fact that most of the dolomite is disseminated in the phosphate mineral. Both are oxide type minerals and have the same calcium cationic component. They exhibit similar

electrokinetics, adsorption and desorption behavior in physical separation process such as flotation. Several processing schemes have been developed to handle this problem, but none are satisfactory due to high MgO content and/or low overall P_2O_5 recovery in the final phosphate concentrate. In this proposed research project, samples from Florida dolomitic phosphate minerals will be tested in an open flotation column. New selective fatty acid collectors for dolomite particles and appropriate mixtures of phosphoric acid/sulfuric acid depressant for phosphate particles will be selected and used. The aim is to achieve a phosphate concentrate containing as high as 30% P_2O_5 and less than 1.0% MgO contents at high P_2O_5 recovery. Liberation analysis of dolomitic phosphate pebble will be conducted. The selectivity and frothability of the new selective fatty acid collectors will also be characterized by determining dolomitic phosphate flotation. Success in this research project will enable the mineral industry to increase its phosphate reserve base, by recovering phosphate from formerly unusable phosphatic minerals and low grade phosphate reserves.

b) Solid-Liquid Separations

8. Development of a Novel Fine Particle Centrifuge

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

Period of Performance: March 1, 2003-May 31, 2005 (2-Year Project).

The solid-solid separation processes employed by modern coal preparation plants require large amounts of process water. After cleaning, the unwanted water must be removed from the surfaces of the particles using mechanical dewatering equipment. Coarse particles can be readily dewatered using simple screening systems, while finer particles require more complicated unit operations such as centrifuges and filters. Unfortunately, the processes used to dewater fine particles are inherently inefficient and expensive to operate and maintain. To overcome these problems, a novel centrifugal filter has been developed by researchers at Virginia Tech. Preliminary test data suggest that this new technology can reduce the moisture content of fine coal products by approximately 30-50% compared to existing dewatering processes. The objective of this project will be to construct a continuous prototype unit and to conduct a detailed experimental investigation of this new technology.

9. New Strategies for Dewatering of Coals

Researchers: M. Seehra, A. Manivannan & M. Bachlechner (West Virginia University)

Period of Performance: March 1, 2003-May 31, 2005 (2-Year Project).

A two-year innovative research program on the combined experimental-modeling studies of coal-water interactions and coal dewatering is proposed. The experimental program will first focus on determining the relative amounts of "free" and "bound" water in wet coals using analytical techniques of thermogravimetric analysis, heat capacity measurements and 1H nuclear magnetic resonance. Laboratory scale dewatering experiments will then be carried out by vacuum filtration and centrifugation, combined with pulsed heating at microwave or IR (3300 cm^{-1}) frequencies to liberate the "bound" water. These investigations will be complimented with modeling studies of the coal-water

interactions and the effect of centrifugation on dewatering from surface-bound water and coal pores. This integrated experimental-modeling approach is an important component of the proposed research since the results from the molecular-dynamics simulations could provide unique technological insights that will increase the efficiency of dewatering processes. Finally, scale-up of the resulting successful approaches for coal dewatering will be proposed at the conclusion of the two-year program.

c) Chemical/Biological Extraction

10. Novel Bioleaching Technology Assisted by Electrolytic Processes

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

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project).

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.

11. Coal Desulfurization Using Hypochlorite and Cupric Ion as a Catalyst – Feasibility Study

Researchers: E. H. Cho & R. Y. K. Yang (West Virginia University)

Period of Performance: March 1, 2003-May 31, 2004 (1-Year Project).

The utilization of coal as a feedstock to produce carbon materials is very much hampered by the presence of its organic sulfur content. However, the organic sulfur is very difficult to remove. It is generally accepted that only two methods have capability to remove the organic sulfur rather effectively; one is with a melt of sodium hydroxide/potassium hydroxide at high temperatures (Gravimelt Process) and the other is with chlorine chemicals. However, the Gravimelt Process contaminates the coal structure, and its decontamination and the regeneration of the reagents may be insurmountable problems in terms of economic feasibility. Chlorine chemicals also chlorinate the coal structure and the removal of organic sulfur is not high enough to produce a premium coal or feedstock. It is proposed that organic sulfur be leached with hypochlorite using cupric amine as a catalyst. Hypochlorite is the predominant chlorine derivative at high pH's. The catalysis of cupric amine was found during 1990s in leaching of gold with hypochlorite and other oxidants. We will conduct two kinds of consecutive experiments. In the first, coal will be leached in a reactor with a solution containing hypochlorite and cupric amine. In the second, the leached coal will be hydrolyzed in hot sodium carbonate solution, which is believed to cleave the organic sulfur bond from coal and thus further reduce the sulfur content. Leached coal and hydrolyzed coal samples will be analyzed particularly for organic sulfur and chloride content. The data will be analyzed to

determine the desulfurization potential through the two consecutive experiments and also the chlorination/dechlorination of the coal matrix through each of the two experiments.

d) Sensor and Control Development

12. Development of Electrochemical Sensor for On-Site Monitoring of Heavy Metal Ions in Coal Processing And Utilization

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

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project).

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.

13. Evaluation of Coal Cleaning Efficiency Using Transponder-Based Density Tracers

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

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project).

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

This aggregated Technical Progress Report covers the second year of operation of Cooperative Agreement DE-FC26-01NT41091: Establishment of the Center for Advanced Separation Technologies. A total of thirteen (13) sub-projects are currently funded: twelve-monthly Progress Reports (covering the period October 1, 2002-September, 2003) have been generated for the eight (8) first year sub-projects; six-monthly Progress Reports (covering the period April 1, 2003-September, 2003) for the five (5) second year sub-projects. These are attached to this document as Appendices. A brief summary of progress during the year, along with plans for the future, is given below for each of the sub-projects.

a) Solid-Solid Separation

1. Improving Coarse Particle Flotation (Appendix A)

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

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project)

Direct measurements of the bubble-particle detachment force were made during this reporting period. These tests showed that both the particle hydrophobicity and solution pH can have a dramatic impact on the detachment during flotation. In addition, several laboratory flotation tests were conducted using samples of phosphate ore. The data show that it is possible to obtain a high concentrate recovery and grade with lower insol content using reagent W. The test results were found to be superior to those obtained using a traditional reagent package consisting of fatty acid and fuel oil.

During the next reporting period, additional experiments will be conducted using the detachment force measurement apparatus. However, the device will be modified by replacing the spherical bubble with a large flat bubble to reduce the number of experimental variables. Future tests will also be performed with amine surfactants to eliminate the hydroxylation and hydration silane layers on the silica particle surfaces. This condition will better represent the effect pH may have on conventional surfactants in a flotation circuit. In addition, the test work conducted with the batch laboratory flotation machine using novel reagents will be continued using reagent W with different types of phosphate ores. Operating parameters, such as the solids content, agitation speed, pH levels, and conditioning time, will also be evaluated in greater detail.

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)

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project)

An experimental system has been designed and built for the investigation of particle separation, based on density differences, in a CFB riser. The riser flow characterization tests indicated that there is a potential flow regime in the riser for separation. This regime is frequently referred to as the transition region between fast fluidization and entrained

flow. This flow regime appears to be of no interest to combustion or chemical engineers and consequently there is no relevant literature on this regime. Initially, results indicate a high heavy particle removal efficiency, η_H , of the order of 90%. The mass fraction of heavy particles at these conditions, $\omega_{H,R}$, is of the order of 80%. Collection of data is continuing and an image acquisition and processing system is under development to measure and provide on-line monitoring of the particle separation in the CFB riser system. There appears to be no problem in completing this project in the allowed time.

The work planned for the future is to complete the test matrix for all variables listed as well as complete the development of the image acquisition and processing system for the CFB riser system. In the initial tests, it appears that some of the selected independent variables, while others are not. In this exploratory investigation, some variables may be discarded (with justification) and new variables may be explored. Early tests indicated that there may be two separation processes occurring in the riser. They are: the Saffman force, which is due to the variation of pressure over the surface of the particle, and the breaking up of clusters along the wall. These phenomena will be investigated in greater detail after collection and verification of additional data. Unfortunately, the experimental system was involved in an industrial accident; consequently, it was delivered to WVU several months late. However, it is anticipated that we will complete the project on schedule.

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

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

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project)

During the past reporting period, the flotation model has become more theoretically based. A more robust collision frequency model has been proposed which will include a large range of particle responses to turbulence. Data has been obtained in the DPIV measurements. Analysis of this data is ongoing. Model validation is currently ongoing, with data acquisition in the initial stages.

Further refinement of the flotation model will continue during the next reporting period. This will include a more in-depth theoretical analysis of the effects of turbulence on particle and bubble movements. Experimental work will include the flotation tests to validate the model as well as DPIV data analysis. Further DPIV measurements have been delayed due to the loss of the CCD camera. More experimental data may be taken as soon as repairs are completed.

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

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

Period of Performance: May 17, 2002-May 31, 2005 (3-Year Project)

Electrolytes can significantly decrease hydrophobic interactions in foam films even when their concentrations are low. They also decrease the double-layer repulsive force due to the well known "screening effect". Dilute electrolyte will inhibit bubble coalescence; which in turn is expected to increase the stability of froths and foams.

Much of the work conducted during the next reporting period will focus on the measurement of emulsion film thicknesses and disjoining pressure isotherms on foam films from common frothers, such as short-chain alcohols.

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

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

Period of Performance: May 17, 2002-May 31, 2005 (2-Year Project, Extended)

There is no ubiquitous layer of air on hydrophobic surfaces. Degassing of surfactant solutions does change the forces, but does not remove the long-range attractive force.

Plans for the next 6-months include: completion of the fabrication of the force-measuring device; the measurement of the force between air and solids in aqueous solutions; the measurement of the surface potential of surfactant coated surfaces; and the adsorption of surfactant onto hydrophobic surfaces.

6. Novel Surfactants as Collectors for Froth Flotation (Appendix F)

Researcher: Richard D. Gandour (Virginia Tech)

Period of Performance: March 1, 2003-May 31, 2004 (1-Year Project)

We have developed a procedure for making tricarboxylate surfactants and have begun a promising method to synthesize a trihydroxamate surfactant.

Over the next six months, we shall scale up the syntheses of the tricarboxylate surfactants to provide samples for flotation testing. Additionally, in the next three months, we shall complete the synthesis of the trihydroxamate surfactant and provide a sample for flotation testing as soon as we make it.

7. Column Flotation of Fine Dolomitic Phosphate by Selective Fatty Acids (Appendix G)

Researcher: F. F. Peng (West Virginia University)

Period of Performance: March 1, 2003-May 31, 2004 (1-Year Project)

Much of the effort this reporting period was directed towards the characterization of the dolomitic phosphate pebble sample A. The different size fractions have been analyzed in order to provide information on grinding/liberation requirements and to establish sizing and separation procedures. We have had problems obtaining satisfactory dolomitic phosphate sample analyses and the NRCCE Analytical Laboratory has contacted FIPR for assistance in resolving the problems. We are waiting for the resolution of these problems before making further plans.

In the next reporting period, the analysis of phosphate content in the dolomitic phosphate pebble samples will be established. A grinding/chemical analysis and optical particle liberation measurements will be carried out and an appropriate sample will be

prepared for dolomite flotation tests in a semi-batch flotation cell to determine the amounts of reagent needed for column flotation testing.

e) Solid-Liquid Separations

8. Development of a Novel Fine Particle Centrifuge (Appendix H)

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

Period of Performance: March 1, 2003-May 31, 2005 (2-Year Project)

In order to improve the removal of moisture from fine coal streams, a project has been initiated to construct and test a hyperbaric filter centrifuge. Previous tests conducted with a batch laboratory unit suggest that this new technology can reduce the moisture content of fine coal products by up to 50% compared to existing mechanical systems. During this reporting period, work focused on the design of a pilot-scale continuous prototype of this technology. The system consists of a two-stage process capable of achieving low product moistures while maintaining nearly complete recoveries of fine coal. Several laboratory tests were also conducted using a batch fed unit to verify the extent of moisture removal that can be achieved using this process.

Work will be initiated during the next reporting period to procure and fabricate components needed to construct the prototype unit. Shakedown tests will then be initiated to evaluate the pilot-scale unit. Parameters to be investigated will include air pressure, rotation speed, feed solids loading, and drying cycle time.

9. New Strategies for Dewatering of Coals (Appendix I)

Researchers: M. Seehra, A. Manivannan & M. Bachlechner (West Virginia University)

Period of Performance: March 1, 2003-May 31, 2005 (2-Year Project)

Results of initial experiments on determining the amount of water present in a coal sample 'sent to settling ponds' and dewatering of this coal by resonant heating by microwaves of 2.45 GHz frequency are described. It is shown that effective dewatering occurs rapidly by microwave heating without heating the coal or ash. The process is shown to be superior to dewatering by thermal heating. Similar experiments are planned for dewatering by resonant heating at the IR frequency of 10^{14} Hz.

Atomistic modeling of ice and water using molecular-dynamics simulations is presented. Initial simulations have established the time-step to be used and customized visualization of simulation runs is introduced.

During the next six months, reasonable estimates (cost/ton) for dewatering of coals by microwave heating will be determined. Next we propose to carry out similar experiments of dewatering by resonant absorption of IR radiation at $f = 10^{14}$ Hz as noted earlier. A source for this radiation has been acquired and these experiments are now being planned. Results from these experiments will be compared with those from the microwave heating experiments presented here.

As a next step in the atomistic modeling of the coal-water system, the computational model for carbon systems by Brenner et al. [5] will be implemented on the Beowolf-like PC cluster in the Physics Department. Investigating known properties of carbon systems will test the correctness of the implementation. Modeling the water-coal interactions will be based upon experimental investigations in this project.

b) Chemical/Biological Extraction

10. Novel Bioleaching Technology Assisted by Electrolytic Processes (Appendix J)

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

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project)

It has been found that the reduction of ferric ion to ferrous ion in an electrochemical cell largely depends on solution chemistry including ferric ion concentration and sulfate ion concentration. The sphalerite leaches well in the presence of bacteria. The leaching is particularly enhanced when this mineral is mixed with pyrite, confirming the galvanic effect by the nobler mineral of pyrite. The sphalerite in the mixture leached close to 20% in 22 days. It has been found from the same leaching experiments that the ferric concentration increases as time goes on. This means that the ferrous ion concentration decreases with increasing reaction time, suggesting that the bacteria activity is reduced as time proceeds.

Future experimental work will be focused on the leaching of minerals in the solution-circulating system. Each system with each mineral will be optimized particularly in terms of solution circulation rate and potential applied.

11. Coal Desulfurization Using Hypochlorite and Cupric Ion as a Catalyst – Feasibility Study (Appendix K)

Researchers: E. H. Cho & R. Y. K. Yang (West Virginia University)

Period of Performance: March 1, 2003-May 31, 2004 (1-Year Project)

It has been found that a series of treatments for cupric ammine leaching, hypochlorite leaching and hydrolysis give the best results of coal desulfurization in terms of coal sulfur reduction while minimizing chlorine content. The total sulfur was reduced from 2.81% to 2.12% when coal was leached with cupric ammine and then with hypochlorite both at room temperature and the leach coal was hydrolyzed 80°C. Through the hypochlorite leach, the coal attained chlorine content of 1.04%; however, through the hydrolysis, the chlorine content was reduced to 0.11% which is well below the threshold limit. The coal desulfurization with only hypochlorite at 50 and 90°C reduced the total sulfur from 2.81% to 2.14% and 1.78%, respectively. These results suggest that the temperature effect on the desulfurization is minimal.

Future experimental work will be focused on the coal desulfurization with a series of experiments of cupric ammine leaching, hypochlorite leaching and leach coal hydrolysis

on the same coal by multiple times. Also, experiments will be conducted using Co(III) ammine instead of cupric ammine. The advantage with Co(III) ammine will be such that the spent cobalt (Co(II) ammine) can be readily regenerated to Co(III) by bubbling air through the solution.

c) Sensor and Control Development

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

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

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project)

BDD sensor films have been developed in collaboration with Prof. Fujishima of the University of Tokyo. These BDD sensor films are grown using Microwave plasma chemical vapor deposition (MPCVD) techniques. Currently, we are obtaining free standing diamond films commercially produced by Element Six Inc. We have demonstrated ppb detection of mercury in laboratory-made standard solutions as well as in real samples obtained from the flue gas of a coal burning power plant. A standard addition method has been successfully used to determine the mercury concentration. In addition, preliminary results from a portable unit have been demonstrated. The interference due to copper during the detection of lead and cadmium and the approach of 3D-calibration plots were also carried out.

In future, we will use our portable on-line sensor Palm Sens in combination with RDE for the analysis of real samples. We are involved in making different sizes and shapes of diamond for the application in rotating disk electrodes to achieve hydrodynamic flow of the electrolyte so that on-line monitors can be designed for optimal sensitivity. In the case of mercury, more calibration curves and analysis will be made using thiocyanate electrolyte since there is no calomel formation in this case. Impinger solution will also be made using thiocyanate electrolyte for testing.

13. Evaluation of Coal Cleaning Efficiency Using Transponder-Based Density Tracers (Appendix M)

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

Period of Performance: May 17, 2002-May 31, 2004 (2-Year Project)

During the past reporting period, a prototype system was assembled for detecting transponder-based density tracers using components supplied by Texas Instruments. A prototype set of tracer blocks with embedded tags were also manufactured and evaluated. This prototype system was used to evaluate the capabilities of the transponders in terms of tag type, signal clarity, and detection distance (read range). Data collected to date show that tags can be successfully placed within the density blocks and detected at ranges adequate for a commercial system. However, the data indicate that two antenna will be required for

accurate detection due to orientation factors that influence the strength of the signal from the embedded tag.

Work will continue during the next reporting period to evaluate the capabilities of prototype system. This effort will include (i) the manufacture of additional tracer blocks with embedded tags, (ii) the evaluation of the prototype system for detecting tracer blocks placed on moving conveyors and buried under different materials (i.e., beds of coal or rock particles), and (ii) the development of data acquisition, analysis, and presentation software. A variety of controlled tests will be performed in a laboratory environment to resolve issues associated with detection capabilities and limitations prior to industrial field trials. This information will be important in determining the required strength of the energizing fields and optimal locations of the reader antenna.

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

Contract Title and Number:

Establishment of the Center for Advanced Separation
Technologies (DE-FC26-01NT41091)

Period of Performance:

Starting Date: 9/17/01
Ending Date: 05/31/05

Sub-Recipient Project Title:

Improving Coarse Particle Flotation

Report Information:

Type: Annual
Number: 3
Period: 10/1/02-9/30/03
Date: 11/28/03
Code: VA003

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ABSTRACT

The recovery of coarse particles by flotation is a common problem in the coal and minerals processing industry. 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 flotation reagents that will help increase the attachment force between air bubbles and coarse particles, and the other is to develop new flotation machines specifically designed to promote coarse particle flotation.

INTRODUCTION

Background

There has been a substantial advancement in the science of flotation during the last two decades. This fundamental research has shown that the probability of bubble-particle attachment can be expressed as:

$$P = P_c P_a (1 - P_d)$$

in which P_c is the probability of collision, P_a the probability of bubble-particle adhesion after collision, and P_d is the probability of detachment after adhesion. Many investigators showed that the difficulty in floating fine particles is due to the low P_c , while the difficulty in floating coarse particles is due to high P_d . Therefore, to increase the upper particle size limit for flotation, it is necessary to increase P_d , which can be predicted by the following relationship (Yoon and Mao, 1996):

$$P_d = \exp\left(-\frac{W_a + E_1}{E_k'}\right), \quad [2]$$

where W_a is the work of adhesion and E_k is the kinetic energy for detachment. W_a is a function of surface tension (γ_v) of the flotation liquor, contact angle (θ), and particle radius (R_1), as follows:

$$W_a = \gamma_v \pi R_1^2 (1 - \cos \theta)^2. \quad [3]$$

One can also derive an expression for E_k' as follows:

$$E_k' = \frac{\rho_1 g R_2^2 \theta_0}{3} \pi R_1^2 \sin^2 \theta_0, \quad [4]$$

where ρ_1 is the density of coal particle, R_2 is the bubble radius, g the gravitational acceleration, and θ_0 is the parameter representing the fraction of the surface area of air bubble covered by coal particles (French and Wilson, 1980). These expressions show that coarse particle flotation can be improved (i) by decreasing bubble size or bubble loading and (ii) by increasing surface tension or contact angle (hydrophobicity). Of the three, the last is most important.

Objective and Approach

The objective of this project will be to develop two complementary methods for improving the recovery of coarse particles during froth flotation. One method is to use novel coarse flotation reagents that increase the adhesion force between air bubbles and hydrophobic particles. The second method is to develop a flotation machine specifically designed to promote the flotation recovery of coarse particles.

PROJECT TASKS

Task 1 – Sample Acquisition

During this reporting period, two sets of phosphate samples were obtained for use in laboratory flotation experiments. The first sample (Sample A) consisted of a mixture of both coarse and fine particles, while the second sample (Sample B) consisted of only coarse pre-classified ore. Because the samples had excessive amounts of water upon arrival, it was not practical to store or to split out representative fractions of the as-received samples. Therefore,

the samples were dried prior to storage and riffing. Comparison tests showed, however, that similar floatability results were obtained using either the dried or as-received ores.

Task 2 - Contact Angle Measurements

During the past reporting period, an experimental apparatus was constructed to directly measure the bubble-particle detachment forces as a function of varying contact angles and pH values. The experiment apparatus consists of a KSV Sigma 70 tensiometer used as a hanging balance (See Figure 1). The solid particle consisted of a glass sphere fused to the end of a tungsten wire hung from the balance. The gas phase consisted of a captive bubble on the end of a very hydrophobic glass rod that was fixed to the base of a transparent cell. The end of the glass rod was fabricated with a hemispherical cup of radius matching the size of free bubbles typically found during flotation. During the experiments, the glass sphere was brought into contact with the bubble. Measurements begin as the bubble is pulled upward by the balance until detachment occurs. The data from these tests were used to provide force and distance plots that describe the detachment process. Energy can then be calculated as the integral of the force across the range defined by the distance the system must travel for detachment. The spheres were treated with various reagents to obtain different contact angles. The solution electrolyte concentrations were also varied to observe the effect of frother concentration on the bubble-particle detachment process.

The first series of detachment tests were performed using glass spheres methylated to varying degrees with different chain-length silanes. The bulk solution pH was varied with NaOH and HCl addition to nanopure water. The preliminary results indicate a dependence between the energy of detachment and both the solution pH and hydrophobicity of the particle. Particles of different hydrophobicity were each found to have independent pH ranges at which a maximum energy of detachment was observed. This may be explained by variations in the bubble surface charge, particle surface charge, and solid-liquid interfacial tension. Varying frother concentrations were also tested to better understand the source of energy of detachment. The preliminary results suggest a much stronger dependence on bubble

Figure 1. Bubble-particle detachment apparatus.

strength than particle hydrophobicity. This finding will be further examined using values available in literature for bubble and surface charge and via experimental work to determine the interfacial tensions.

Task 4 - Batch Flotation Tests

Batch Tests Conducted Using Sample A: Several series of batch flotation tests were conducted using the coarse and fine mixture of phosphate ore described previously. The following general observations can be made based on tests conducted using reagent W without the addition of fatty acid.

- The novel reagent W performed better when no extender was used. In fact, it is possible to obtain results that were very close to those obtained using a traditional reagent package consisting of both fatty acid and a fuel oil extender.
- It was possible to produce phosphate concentrates with very low amounts of gangue (insoluble particles) by changing the ratio of reagent W and fuel oil mixture in favor of fuel oil. In some tests, the product obtained as concentrate was extremely pure.
- Alkaline pH values were found to improve overall selectivity when using reagent W and fuel oil mix. Although there was a small decrease in recovery, the grade increased by more than 3 percentage points and the separation efficiency increased by more than 1 percentage point.
- Reagent W provided a higher overall selectivity compared to fatty acid. For tests conducted at alkaline pH with the same dosage of active ingredient, reagent W provided a 4 percentage point higher grade and nearly the same amount of insols and P_2O_5 recovery as fatty acid.

Several series of tests were also performed to evaluate the performance of reagent W when used in conjunction with fatty acid. The following general observations were obtained based on these tests.

- Tests conducted with different ratios of reagent W and fatty acid showed that it was not possible to get both higher grade and higher recovery at the same time when compared to other mixtures of reagents that were examined to date.
- When fuel oil was added to fatty acid as an extender, the recovery improved by over 6 percentage points with only a slight decrease in grade. However, the opposite was found to be true when fuel oil was added to reagent W. In this case, the addition of fuel oil increased the grade by slightly more than 2 percentage points and decreased the recovery by more than 4 percentage points.
- The addition of sodium silicate (Na_2SiO_3) as a depressant was investigated to evaluate how this reagent would influence the working ability of both the novel reagent and fatty

acid. The results obtained were not satisfactory and, as a result, the use of this depressant has been abandoned.

Batch Tests Conducted Using Sample B: Several series of batch flotation tests were conducted using the pre-classified coarse phosphate ore described previously. In light of the results obtained using Sample A, this work focused on using reagent W over fatty acid. This particular set of tests examined different dosages and the effect of pH. Several two-stage cleaner flotation tests were also conducted to check the performance of the two reagents in different circuit configurations. The following general observations can be made based on the test results obtained from experiments conducted with the pre-classified coarse feed ore.

- Reagent W provided a better recovery than fatty acid for the same concentrate insol content. This finding demonstrates that reagent W is a powerful collector with better selectivity than the traditional reagent package used by the phosphate industry (i.e., fatty acid).
- Tests conducted using two stages of cleaning showed that a very good concentrate grade in excess of 30% P_2O_5 could be achieved at a recovery value close to 90% when using reagent W. Thus, reagent W is capable of providing a high recovery and very clean concentrate using only conventional (mechanical) flotation equipment.
- A reduction in pH from alkaline to neutral conditions was detrimental to flotation selectivity for both reagent W and fatty acid. However, pH appeared to have a greater impact on the flotation result obtained using fatty acid.
- At natural pH, reagent W and fatty acid gave similar results when compared at high recovery values. However, the recoveries obtained with reagent W remained higher compared to fatty acid when recovery was reduced to provide a concentrate with a very high P_2O_5 grade or low insol assay.

Task 5 - Sample Analyses

All flotation samples were assayed by standard ASTM procedures for P_2O_5 grade and acid insol content.

SUMMARY

Direct measurements of the bubble-particle detachment force were made during this reporting period. These tests showed that both the particle hydrophobicity and solution pH can have a dramatic impact on the detachment during flotation.

In addition, several laboratory flotation tests were conducted using samples of phosphate ore. The data show that it is possible to obtain a high concentrate recovery and grade with lower insol content using reagent W. The test results were found to be superior to those obtained using a traditional reagent package consisting of fatty acid and fuel oil.

FUTURE WORK

During the next reporting period, additional experiments will be conducted using the detachment force measurement apparatus. However, the device will be modified by replacing the spherical bubble with a large flat bubble to reduce the number of experimental variables. Future tests will also be performed with amine surfactants to eliminate the hydroxylation and hydration silane layers on the silica particle surfaces. This condition will better represent the effect pH may have on conventional surfactants in a flotation circuit.

In addition, the test work conducted with the batch laboratory flotation machine using novel reagents will be continued using reagent W with different types of phosphate ores. Operating parameters, such as the solids content, agitation speed, pH levels, and conditioning time, will also be evaluated in greater detail.

REFERENCES

Yoon, R.H. and Mao, L., 1996. "Application of Extended DLVO Theory, IV: Derivation of Flotation Rate Equation from First Principles," J. Colloid Interface Sci., Vol. 181, pp. 613-626.

French, R. H. and Wilson, D. J., 1980. Separation Science Technology, Vol. 15, pp. 1213.

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

Contract Title and Number:

Establishment of the Center for Advanced Separation
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Sub-Recipient Project Title:

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

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ABSTRACT

An experimental system has been designed and built for the exploration of particle separation, based on density difference, in a CFB riser. The riser characterization tests indicated that there is a potential flow regime in the riser for separation. Initially, results indicate a very high heavy solids removal efficiency (90%) and the mass fraction of the heavy particles in the product stream (80%), at low mass flow rates. Work is continuing to collect all the necessary data and an image acquisition and processing system is under development to more fully understand this separation process.

BACKGROUND

The goal of this research project is to investigate the potential for the dry separation particles, according to their densities, in a vertical flow riser. The riser is essentially the same riser component found in a circulating fluidized bed, CFB. Observations of the flow of solids in a riser indicated that heavier particles tended to migrate down along the riser wall during certain operating conditions. There appears to be no mention of this phenomenon in the open literature. Usually, other processes occurring in the riser were of more importance. However, the literature dealing with forces on particles in non-uniform flow fields describe a mechanism for creating a motion perpendicular to the general flow direction. Under ideal

conditions, this force is referred to as the Saffman force, (Saffman,1965). Therefore, an investigation was undertaken to evaluate this separation process to determine if it had any practical significance.

OBJECTIVE AND APPROACH

The objective of this research effort is to experimentally determine the effectiveness of the flow in a riser system to separate particles based on their density differences. An experimental system was constructed, Figure 1. A mixture of sand and iron particles flow into the riser, just above the distributor plate. This mixture then flows up the riser, but a tendency develops for the particles to separate. The lighter particles tend to continue with the gas flow and exit the riser. Heavier particles tend to move towards the wall and eventually down the wall. In a CFB, these heavier particles would be re-entrained and again move upward in the riser. Eventually the heavier particles would exit the riser. This up and down motion of the particles in the riser is referred to as internal recirculation. In the chemical industry, there are particles leaving the riser that have not been fully reacted, consequently, the particles leaving the riser are frequently recycled back into the riser. This is referred to as external recirculation. The mode of external recycling employed to date is batch recycling. The particles leaving the riser are first collected in the product hopper. When the flow from the feed hopper stops, the flow from the product hopper then flows into the riser and out to the feed hopper. For a third cycle, the flow from the feed hopper flows into the riser for the final separation process.

In order to capture the heavier particles moving down along the riser wall, the basic riser geometry was modified just above the distributor plate, as shown in Figure 1. The annular space, referred to as the separation ring or just ring, is in a location where there is no through-flow of gas through the ring, but only gas flow back towards the distributor plate. The inertia of heavier particles moving down along the wall drive the particles through the ring while the lighter particles will tend to follow the gas flow and miss the open ring. The heavier particles entering the riser may either be captured immediately by the ring, recirculate internally and eventually be captured, or exit the riser with the lighter particles. It should be noted that there will be light particles flowing with the heavy particles; subsequently, light particles will also flow through the ring passage way. If an external recirculation mode of operation is employed, the heavier particles may be captured during a later residence time in the riser. External batch recirculation is employed in this research.

Selecting the heavier particles as the particles to be removed, then the effectiveness is directed towards evaluating their removal. Let $\dot{m}_{H,O}$ represent the amount of heavy material entering the riser and $\dot{m}_{H,R}$ represents amount of heavy particles removed through the ring. The efficiency for the heavy particle removal process may now be written as:

$$\eta_H = \frac{\dot{m}_{H,R}}{\dot{m}_{H,O}}$$

Now let $\dot{m}_{L,O}$ be the mass of light particles entering the riser, and $\dot{m}_{L,R}$ the amount of light particles leaving with the heavy particles through the ring. The percent loss of the light material may be written as:

$$L_L = \frac{\dot{m}_{L,R}}{\dot{m}_{L,O}}$$

The total mass flow rate into the riser is:

$$\dot{m}_O = \dot{m}_{H,O} + \dot{m}_{L,O}$$

These equations illustrate the goals of this research into the separation process; namely, a high value for the heavy particle removal efficiency, a low value for the percent loss of light material, and at a commercially viable mass flow rates.

The initial approach to evaluate each test run is to evaluate the mass fraction of heavy particles exiting the riser through the ring. This equation is:

$$\omega_{H,R} = \frac{\eta_H \dot{m}_{H,O}}{\eta_H \dot{m}_{H,O} + L_L \dot{m}_{L,O}}$$

and it is a function of the mass rate of flow into the riser, the superficial gas velocity, and the number of passes through the riser.

PROJECT TASKS

The tasks scheduled for this project are shown in Table 1. In general, the project is essentially on schedule. A discussion of each task is as follows:

Task 1. Literature Survey. A search of the literature and discussions with experts in CFB risers failed to uncover any references relating to particle separation in a riser. A review of recently received literature in the library is continuing.

Task 2. Design System. The system was designed and shown in Figure 1. No changes in the design are now contemplated. Several modifications have been made to the air lines into the system to develop more stable flow in the riser. After completion of Task 4, it became apparent that the expected instrumentation ratings were inappropriate for the test conditions selected. Therefore, several instruments were replaced with instruments with a more appropriate rating.

TABLE I: Work Schedule

Tasks	First Year	Second Year
1 Literature Review	→	
2 Preliminary Analysis	→	
3 Fabrication of the Dryer System	→	
4 Screening of Geometries	→	
5 System Testing	→	→
6 Scaling Laws		→
7 Fabrication of Second Larger Dryer System		→
8 Testing and Analysis		→
9 Overall Evaluation		→
10 Reports		→

Task 3. Build System. The system has even built and is operating satisfactorily for an exploratory investigation.

Task 4. System Characteristics. A screening of possible operating conditions indicated that a relatively lean fast fluidization produced the desired flow in the region of the ring. These conditions were established with the ring gap plugged so that the flow of particles could more readily be observed. Basically, it appears that the flow characteristics with the greatest potential for success are: 1) intermittent flow of clusters down along the wall and 2) breakup of clusters about 0.3 to 0.6 m above the ring. This task is now completed. Conditions for the clusters reaching the ring intact appears to bring an excess of light particles through the ring. Clusters breaking up too far above the ring create a low efficiency for the heavy particle removal process.

Task 5. Test Matrix. The flow characteristics in a specific riser geometry are dictated by the superficial gas velocity, the mass flow rate of solids, and the pressure variation along the axis of the riser. Because of the lean fast fluidization selected, the pressure gradient along the riser wall was difficult to detect and subsequently not initially employed in the early stages of this investigation. Based on the flow observations in Task 4, the following test matrix was selected.

Superficial velocity (3)	3.25, 3.63, and 3.80 m/sec
Mass flow in (3)	1.15, 1.75, and 2.5 kg/m ² sec
Number of cycles	1 and 2 (note, each test involves two cycles)
Mass fraction steel, in (3)	0.43, 1.00 and 2.00
Riser height (2)	2.7 and 3.7 m
Ring gap (2)	4.8 and 9.6 mm
Riser flow geometry (2).

Figure 1: A Circulating Fluidized Bed (CFB) System for Particle Separation by Density Differences

The data obtained to date is presented in Figures 2, 3, and 4. Data is still being gathered and will be compiled for the final report.

Task 6 Analysis. Data has been collected for establishing the system's characteristics and the initial set of tests in the test matrix. These data were employed in producing Figures 2, 3, and 4. These results have been very encouraging. Flows through the ring have been very rich in the heavy particles (steel shot) for one pass through the riser, for a set of conditions, Figures 2 and 3. However, this occurred at relatively low mass flow rates into the riser. For additional passes through the riser, a significant amount of light particles accompanied the remaining heavier particles through the ring. This dilution of the product stream is shown in Figure 4. Conclusions cannot be reached at this time regarding the commercial viability of this concept.

Figure 2: Heavy Particle Collection Efficiency After One Pass Through the Riser

Figure 3: Heavy Particle Mass Fraction Collected

Figure 4: Effect of Number of Passes @ 3.73 m/s

During the separation procedure, the velocity and sizes of the particles may vary along the riser wall. To help determine the magnitude in which the annulus down-flow phenomenon is occurring, a three-camera image acquisition system and an image processing program based on MATLAB™ have been developed. The particle flow images will yield the nature of particle separation and particle distribution under different operation conditions.

As also shown in the figure, a lab-scale simplified riser system is set up for preliminary particle separation studies. The same mixture of sand and iron particles is used in the experiments. For a typical simulation run, the camera will continuously capture the particle flow at different time period and send the captured digital images to the main computer via local network connection for on-line digital image processing using MATLAB™. The processed image data are then shown and updated periodically on the computer monitor with the particle sizes represented by different colors. The following figure shows a typical on-line monitoring of the particle flows. As shown in the figure, the time period between each image is 1 second and the images showed some degree of gradual particle separation of the larger iron particles (in yellow color). It should be noted that the images shown are preliminary, further programming refinement and better boundary conditions for the lab-scale riser system are continuing under development in this task.

We have also installed three windows each with electrical gate valve control on the CFB system. We plan to conduct the on-line particle flows measurement using the three-camera system. The test results will be reported in the next CAST technical report.

Task 7. Preliminary Design of a Commercial System. There is insufficient data at this time to begin this task.

SUMMARY

An experimental system has been designed and built for the investigation of particle separation, based on density differences, in a CFB riser. The riser flow characterization tests indicated that there is a potential flow regime in the riser for separation. This regime is frequently referred to as the transition region between fast fluidization and entrained flow. This flow regime appears to be of no interest to combustion or chemical engineers and consequently there is no relevant literature on this regime. Initially, results indicate a high heavy particle removal efficiency, η_H , of the order of 90%. The mass fraction of heavy

particles at these conditions, $\omega_{H,R}$, is of the order of 80%. Collection of data is continuing and an image acquisition and processing system is under development to measure and provide on-line monitoring of the particle separation in the CFB riser system. There appears to be no problem in completing this project in the allowed time.

FUTURE WORK

The work planned for the future is to complete the test matrix for all variables listed as well as complete the development of the image acquisition and processing system for the CFB riser system. In the initial tests, it appears that some of the selected independent variables, while others are not. In this exploratory investigation, some variables may be discarded (with justification) and new variables may be explored. Early tests indicated that there may be two separation processes occurring in the riser. They are: the Saffman force, which is due to the variation of pressure over the surface of the particle, and the breaking up of clusters along the wall. These phenomena will be investigated in greater detail after collection and verification of additional data. Unfortunately, the experimental system was involved in an industrial accident; consequently, it was delivered to WVU several months late. However, it is anticipated that we will complete the project on schedule.

REFERENCES

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Appendix C: Modeling of Flotation From First Principles

TECHNICAL PROGRESS REPORT

Contract Title and Number:

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ABSTRACT

Flotation is widely used throughout many industries, including the mining industry. To date, the current proposed model, developed from first principles, is the only available model that incorporates all physical variables. This model will allow users to predict flotation results using key physical variables. Flotation tests, to determine the accuracy of the model, will soon be under way. Currently the flotation apparatus and supporting equipment are being constructed. DPIV measurements have been taken and are being analyzed.

INTRODUCTION

Background

In 1905, Schulman and Picard patented a method of pumping air into oiled pulp through a perforated submersed pipe to produce small air bubbles for flotation (U.S. Patent 793,808). Before this patent was issued, air bubbles were produced by vacuum, electrolysis, and reaction of limestone with acids. Thus, the modern froth flotation is considered to begun

nearly a century ago. Despite this fact, a reliable theoretical model for predicting flotation performance is still not available.

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 flotation variables 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.

Yoon and Mao (1996) are widely credited with developing the first flotation model based purely on theoretical considerations. The model was the first of its kind to incorporate both hydrodynamic and surface chemistry parameters. However, the modeling equations were applicable only for flotation under quiescent conditions. Since industrial flotation machines operate under turbulent conditions, the flotation model developed by Yoon and Mao (1996) has not yet been widely applied in the commercial sector.

Objective and Approach

The objective of this project is to develop a universal model for the froth flotation process. The model will be constructed using the framework originally proposed by Yoon and Mao (1996). In particular, new hydrodynamic expressions will be derived so that the model can be useful for turbulent conditions. Since the modeling expressions will be developed from first principles, the flotation model will have both predictive and diagnostic capabilities. The proposed effort will involve four individual tasks, ie.: Task 1 – Model Development, Task 2 – DPIV Measurements, Task 3 – Model Validation, and Task 4 – Simulator Development.

PROJECT TASKS

Task 1 – Model Development

Current progress on this task includes research into collision frequencies. Collision in turbulent environments occurs by two mechanisms. Shear mechanism occurs by a differential velocity within a vortex, or along curved streamlines. This occurs between fluid particles and therefore does not need a differential velocity between a particle or bubble and the fluid. The accelerative mechanism occurs due to the inertia of the particles. Because of this, there is a slip velocity between the particle or bubble and the fluid. Currently accepted models used in the flotation industry use either the shear mechanism (Saffman and Turner,) or the accelerative mechanism (Abrahamson,). There are a few models that combine these two mechanisms which are currently being looked into (Kruis and Kuster, 1997; Zaichik, et al, 2003), although none of these models assume air bubbles within water (low density within a higher density) which react differently than higher density particles. Research into these mechanisms within a flotation environment is currently ongoing. The model is currently in the following form.

Current Model: Due to the turbulent environment experienced inside a flotation cell, particle-bubble collisions are modeled far differently than in a laminar environment. For laminar flows, the collision frequency may be modeled using the volume that the bubble travels through and the percent solids of the slurry (Mao, 1997). A collision efficiency would then be applied that would account for streamline and inertial effects. On the other hand, particles and bubbles in turbulent flows do not follow the path of the fluid and are modeled based upon their deviation from the fluid path. The Stokes number, a ratio of the particle relaxation (response) time to the smallest fluid relaxation time (Kolmogorov timescale), represents how well a particle follows the fluid flow and is a way to measure this deviation. If a particle's relaxation time is equal to or less than the Kolmogorov timescale then the lag time between the fluid movement and the particle movement will be zero and the particle will follow the fluid completely. Any particles with relaxation times above the kolmogorov timescale will have some departure from the fluid path.

$$St = \frac{\tau_i}{\tau_\eta} = \tau_i \left/ \left(\frac{\nu}{\varepsilon} \right)^{1/2} \right. \quad [2]$$

There are two mechanisms involved in turbulent collisions. The shear mechanism will account for relative motions of particles (fluid, solid, or gas) in a shear field. These collisions always occur in a turbulent field, even among fluid particles. Collisions between particles with Stokes numbers less than 1 occur by shear only. The accelerative mechanism accounts for inertial effects due to large and/or heavy particles. Collisions due to the accelerative mechanism occur above a Stokes number of 1 where there is some lag between the particle and fluid.

Saffman and Turner (1956) proposed a collision model based entirely upon the shear mechanism, where the Stokes number is assumed to always be zero, while Abrahamson (1975) proposed a model based entirely on the accelerative mechanism, where the Stokes number is assumed to always be infinity. Research is ongoing into combining these two mechanisms into a single collision model that is applicable for bubble-particle collisions. Since most particles in flotation have Stokes numbers greater than 1, where there is some deviation from the fluid flow, Abrahamson's model is currently being used.

Abrahamson's model,

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

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 turbulent root-mean-squared velocities of the particles and bubbles, $\sqrt{\overline{U_i^2}}$.

The turbulent root-mean-squared velocity is given by Liepe and Moeckel (1976) as

$$\sqrt{U_i^2} = 0.33 \frac{\varepsilon_d^{4/9} d_i^{7/9}}{\nu^{1/3}} \left(\frac{\rho_i - \rho_3}{\rho_3} \right)^{2/3} \quad [4]$$

Rate Constant: Knowing the collision frequency and the corresponding probability of collection, the change in particle concentration within the entire flotation cell can be calculated as the number of collisions between particles and bubbles that occur (Z_{12}) that lead to attachment (P_a) and, once attached, do not detach, either in the slurry ($1-P_d$) or the froth (R_f).

$$\frac{dN_1}{dt} = -Z_{12} P_a (1 - P_d) R_f \quad [5]$$

Comparing equation [5] with a first order rate equation [6], that most researchers believe model flotation (Arbiter and Harris, 1962; Kelsall, 1961),

$$\frac{dN_1}{dt} = -kN_1 \quad [6]$$

results in an equation for the rate constant that is dependent on hydrodynamics of the flotation cell as well as surface forces of the particles and bubbles.

$$k = \frac{Z_{12} P_a (1 - P_d) R_f}{N_1} \quad [7]$$

Particle Collection: The probability of collection is dependent on the attachment and detachment processes and is a combination of their probabilities. These are both influenced by surface properties of the particles and bubbles as well as hydrodynamics of the system. Surface energies are modeled based upon the Extended DLVO theory. This incorporates the electrostatic, V_E , van der Waals (dispersion), V_D , and hydrophobic, V_H , surface forces. These surface forces are additive and combine to form the total energy of interaction, V_T , as shown in Figure 1.

Figure 1. Surface energy vs. distance diagram for Extended DLVO theory.

For attachment there exists a maximum repulsive (positive) energy, E_1 , that must be overcome. This maximum energy occurs at the critical rupture thickness, H_c . For separations less than this distance, the free energy continuously drops. Therefore, nothing will prevent the particle and bubble from coming together once H_c is overcome.

The probability of attachment is dependent on the energy barrier that must be overcome and the kinetic energy of attachment, E_k .

$$P_a = \exp\left(-\frac{E_1}{E_k}\right) \quad [8]$$

The kinetic energy of attachment comes from the individual kinetic energies of the particles and bubbles themselves.

The probability of detachment is dependent on the kinetic energy of detachment, E'_k , and the work of adhesion, W_a , that must be overcome for detachment to occur (Figure 1).

$$P_d = \exp\left(-\frac{W_a}{E'_k}\right) \quad [9]$$

The work of adhesion is the energy needed to return the free energy of interaction to a zero value. It is assumed, that when detachment occurs, the equilibrium edge of the bubble will be past the critical rupture thickness. This is due to the small critical rupture thickness (100 nm) as

compared to the deformation that a bubble goes through, as has been seen through a high speed digital camera. Since the bubble edge will already be past the critical rupture thickness, E_I does not need to be overcome and therefore is not used in detachment. The work of adhesion is the energy required to take apart a bubble-particle aggregate into a separate bubble and particle. This energy is obtained by surface tensions (gas-solid, gas-liquid, solid-liquid) and their respective areas. A well known model used by Mao (1997)

$$W_a = \gamma_{lv} \pi R_1^2 (1 - \cos \theta)^2 \quad [10]$$

assumes that the bubble surface is completely flat. This is not that accurate in flotation, where the bubble and particle sizes are within three orders of magnitude of each other. A more accurate way to calculate W_a would be to assume a spherical bubble attached to a spherical particle. With simple geometry, this can be easily worked out and the current model uses this approach. An even more accurate method would be to account for the deformation of the bubble during detachment (which might even leave a tiny bubble attached). Differential equations can account for this but must be solved numerically to give volume and surface area values (Wark, 1933; O'Brien, 1991). This is not being used currently due to the high computational resources needed for these numerical calculations.

Energies: There are two sources of energy within a flotation cell; gravity and the impeller motion. Gravity allows particles to settle and bubbles to rise, which in turn give them a certain kinetic energy. The settling velocity of a particle is given by Dobby and Finch (1990), which was obtained from the general particle slip velocity equation proposed by Masliyah (1979). The rise velocity of a bubble is also given by Dobby and Finch (1990) and was obtained from the multi-species hindered settling equation proposed by Masliyah (1979). These rising and settling energies, along with the turbulent energies, can be directly input into the probability of attachment and detachment equations. It should be noted that attachment velocities are reduced due to a lubrication resistance force felt upon impact. Luttrell and Yoon (1992) give this collision velocity, U_{col} , as

$$U_{col} = \frac{U_{sl}}{\beta} \quad [11]$$

where U_{sl} is the velocity within the slurry and β is a dimensionless ratio, usually given by the radius of the particle over the distance of separation. A more appropriate β is given by Barnocky and Davis (1989) in which a solid particle is interacting with an air surface. U_{col} should be calculated at the critical rupture thickness, where the attachment occurs.

The other source of energy, the impeller motion, results in a turbulent environment within the flotation cell. Energy input into the flotation cell is used to provide turbulent motion of the particles, bubbles, and liquid as well as create air bubbles. Small air bubble formation requires a certain amount of energy (creating free surfaces and increasing pressure inside bubbles) which reduces the amount of energy available within the flotation cell. This leftover energy that is input into the flotation cell is transferred from the largest turbulent scale (corresponding to the impeller size) to the smallest turbulent scale (Kolmogorov microscale). A certain range of these eddy sizes will have an effect on the particles and give them their turbulent velocities. Eddies corresponding

to the particle/bubble size through the kolmogorov microscale will be able to transfer their energy to the particle/bubble turbulent velocities. Small particles can not “feel” large eddy movements while eddies smaller than the microscale do not affect fluid movement and therefore particle movement.

The energy input into the flotation cell, at steady state, will equal the energy lost from the system, but does not directly correspond to the kinetic energy of the particle and bubble. Total energy input relates to the impeller speed and the turbulent kinetic energy of the largest eddy. The turbulent kinetic energy will drop (on a log-log scale) at a rate of 8/3 corresponding to the wave number of the eddies, within the range of the particle and bubble wave numbers. The energy between the bubble wavenumber (or particle wavenumber; whichever is smallest) and the kolmogorov microscale is the maximum amount of energy available that will move the particle and bubble out of phase with the fluid. This out of phase motion allows the particles and bubbles to move independent of each other and will produce collisions. It is assumed that the average amount of this energy over the associated wavenumbers directly corresponds to the particle and bubble energy. This energy is input into the probability of attachment equation, once the particle and bubble masses are taken into account.

Detachments occur mainly due to bubble oscillations (Kondrat’ev and Izotov, 1998) and particle motions along the bubble surface (Cheng and Holtham, 1995). Since the bubble-particle aggregate can be thought of as a system unto itself, the particle has relative kinetic energy to the bubble that may be considered independent of the cascading energy of the eddies, as described in the previous paragraph. A good way to model this energy is to know the bubble surface oscillations and the particle oscillations along that surface. A way to relate these oscillations to the turbulence in the system is currently being studied.

Vortices may also destroy aggregates, which come about in three general forms (Schulze, 1984). If an attached particle and bubble are each caught in different vortices the tensile stress owing to the relative motion of the vortices themselves may pull the aggregate apart. If an attached particle and bubble are caught in different vortices that are rotating in opposite directions, the shear stress due to this may destroy the aggregate. Lastly, bubbles and particles travel in opposite directions within these vortices, with bubbles traveling towards the center and particles toward the outside, due to their different relative densities with the liquid phase (Crowe et al., 1995; Chahine, 1995). This opposite pull and high centrifugal force, will lead to high detachment energies.

To account for all of these detachment energies, which are not currently quantified, the current model considers only the particle and bubble kinetic energies (turbulent and rise/settle). The greatest energy that can be input into the bubble-particle aggregate, for detachment, is the combined energies of each individual particle

$$E'_k = \frac{1}{2}(m_1 + m_2)U_{Detach12}^2 \quad [12]$$

which results in the above equation. The energy directly after detachment is assumed to be the total energy available for detachment (at the moment of separation), from the surrounding environment, and is, therefore, used for detachment. The relative velocity is calculated with

particle and bubble velocities in opposite directions due to the respective motions of the particles and bubbles inside vortices. With respect to the turbulent particle/bubble velocity, an average energy dissipation would account for turbulent fluctuating velocity but not for bubble/particle oscillations or vortex effects. Since these are, in part, due to the turbulent nature of the system, an increase in the energy dissipation (a measurement of turbulence) would account for the average effect of these differing forms of detachment.

Froth Recovery: Froth behavior can be very complex. The coalescence of bubbles and the subsequent loss of surface area, and the drainage of liquid between bubbles can both affect the recovery of particles attached to bubble surfaces and particles entrained within the froth liquid. A simple approach to modeling this is to consider only the particles attached to the bubble surface. The only factor affecting the bubble surface would then be the coalescence of bubbles and loss of surface area. Once bubbles coalesce, a portion of their carrying capacity, for that volume of air, is lost. Once that carrying capacity is lost, it is assumed that those particles that were attached will drain back into the slurry.

This loss of surface area must be calculated with respect to the volume flow rate of air through the cell, which is assumed to be uniform throughout the slurry and froth section. A way to account for this is to calculate the surface area rates at both the initial (S_0) and final (S_f) stages of the froth. The fraction of surface area that is still useful for particle recovery would then be the ratio of these two surface area rates.

$$R_f = \frac{S_f}{S_0} = \left(\frac{3V_g}{R_{2-f}} \right) \bigg/ \left(\frac{3V_g}{R_{2-0}} \right) = \frac{R_{2-0}}{R_{2-f}} \quad [13]$$

V_g is the volumetric air flow rate normalized by the cross-sectional area of the flotation cell, and is usually referred to as the superficial air flow rate. The froth recovery then becomes a ratio of the initial to final bubble sizes. Experiments have been performed relating bubble size distribution with froth height in a two-phase froth (Yianatos, et al. 1986). A model has been proposed by Yianatos to predict the bubble size as a function of local gas holdup within the froth, although no means have been given to determine the local gas holdup, except by measurement. Three-phase froths, on the other hand, are highly complex. Aside from liquid and gas effects, particle size, shape, smoothness, hydrophobicity, contact angle, and concentration can affect froth behavior (Harris, 1982; Knapp, 1990; Johansson and Pugh, 1992; Aveyard et al., 1999).

With the limitation of Yianatos' model, which leads to an assumption of local gas holdup at froth height, and the fact that no complete, non-empirical models have been proposed for three-phase froths, a model proposed by Gorain et al. (1998), which is empirical in nature, is thought to give the best results for froth recovery, to date.

$$R_f = \exp(-\alpha \tau_f) \quad [14]$$

This model formulates the froth recovery, R_f , as a function of the froth retention time, τ_f , and a parameter, α , that incorporates both physical and chemical properties of the froth (Mathe et

al. 1998). Froth retention time is usually defined as the ratio of the froth height to superficial air flow rate, V_g . α is an empirical parameter that must be determined by experiments, for each system. α usually ranges, in industrial flotation cells, between 0.1 and 0.5 (Gorain et al., 1998).

Results: Simulations were run to show the effect of different variables on the flotation rate constant. These variables include the particle diameter, bubble diameter, surface tension, contact angle, particle zeta potential, and specific energy input. The power available for attachment is assumed to be 1% of the input power to the system. The local energy dissipation for detachment is 200 times that of the average, which is near the extreme for industrial machinery (Schulze, 1984), but related values have been found, experimentally, for local energy values around the impeller (Pyke et al., 2003). All subsequent discussions pertain to the modified energies since they are thought to better portray a flotation system and produce results similar to those found in industrial practices.

Unless specifically stated in Figures 2-6, the variables used in the simulations are those stated below. All of these variables can be found in actual flotation circuits. Specific energy input is 2 kW/m^3 . Bubble diameter is 1 mm. Particle density is 2650 kg/m^3 , which corresponds to silica. Inverse Debye length is 96 nm. Zeta potential for the particle and bubble are -20 mV and -30 mV , respectively. Liquid-vapor surface tension is 68.0 mN/m . Contact angle is 60 degrees, which corresponds to a K_{131} value of $3.27 \times 10^{-20}\text{ J}$. K_{232} is $5.25 \times 10^{-18}\text{ J}$. A_{11} is $5.04 \times 10^{-20}\text{ J}$, A_{22} is 0.0 J , and A_{33} is $4.38 \times 10^{-20}\text{ J}$. Superficial air flow rate is $1.0\text{ m}^3/\text{s/m}^2$. Froth height is 0.4 m and α is 0.03.

Figures 2 & 3 show the effect of physical variables on the rate constant. The outcome from varying the bubble diameter, along with the particle diameter, can be found in Figure 2. As the bubble diameter decreases, the rate constant increases. In addition, when the bubble diameter is decreased, the particle diameter, where the maximum rate constant occurs, is decreased. This affirms the phenomenon found in column flotation, where smaller bubbles are more beneficial to the overall rate constant but specifically to smaller particle flotation. The first phenomenon (increased rate constant overall) is mainly due to the fact that bigger bubbles have lower specific surface area (surface area per unit volume of air flow). This results in a lower amount of sites for potential particles to adhere to. The smaller the bubble, the greater the specific surface area, and therefore the greater potential for particles to become attached, no matter what their size. For the same volume of air, smaller bubbles have the potential to float more particles. The second phenomenon (shift where maximum rate constant occurs) is due, mainly, to kinetic energies, as well as surface forces. As a bubble becomes smaller, its kinetic energy becomes smaller. The energy difference between smaller and larger bubbles is more greatly felt, in interactions, by smaller particles, because of the small particles' already low kinetic energies. Surface forces are also affected by the smaller bubbles but only in the energy barrier and not in the work of adhesion. The energy barrier will decrease, like kinetic energy, when the bubble size is reduced. Since both main variables (energy barrier and kinetic energy) are reduced for the probability of attachment, it is not thought that the attachment process is affecting this movement.

Figure 2. Effect of bubble size on the rate constant. Smaller bubbles are more beneficial to the overall rate constant as well as smaller particle flotation. This is due to a combination of specific surface area, kinetic energies, and surface forces.

Probability of detachment, on the other hand, has only one variable affected by bubble size. It is thought that the detachment process of smaller bubbles will lower the maximum rate constant particle size.

The outcome from varying the specific energy input, along with the particle diameter, is shown in Figure 3. Although not much difference is seen in the particle size where the maximum rate constant occurs, there is a meaningful difference in the magnitude of the rate constant. As the specific energy input increases, the rate constant decreases. At first, this seems counter-intuitive, and the opposite effect is seen in industrial machines. It was thought that as the energy input into the system increases the rate constant would also increase. This is true up to a point after which the potential for detachment increases substantially more than the potential for attachment. Lower energy input values, which reverse the effect on the rate constant, are not shown, since most industrial flotation machines are run in the given range of energy input (2-4 kW/m³). Actual industrial flotation machines see an opposite effect because of the production of bubbles. As the energy input into a system is increased, the bubble size is decreased. The lower bubble size is what causes the increase in the rate constant. There is no relationship between bubble size and energy input in the present flotation model. The bubble size is constant throughout this simulation. A model given by Johansen et al. (1997) shows the opposite effect, where a higher energy input produces a higher rate constant.

Figure 3. Effect of specific energy input on the rate constant. Higher energy inputs decrease rate constant due to higher probabilities of detachment from higher kinetic energies of detachment.

The following figures (4-6) show the effects of surface chemistry parameters. The outcome of varying the contact angle, along with the particle diameter, can be found in Figure 4. As the angle increases, the rate constant increases. This is due, mostly, to the work of adhesion. A higher contact angle increases the work of adhesion, which in turn makes a greater “energy barrier” for detachment. This greater “energy barrier” decreases the probability of detachment and increases the rate constant. It should also be noted that the contact angle and hydrophobic force constant are related (Yoon and Ravishankar, 1994; Yoon and Ravishankar, 1996; Rabinovich and Yoon, 1994; Vivek, 1998; Pazhianur, 1999). The contact angle and hydrophobic force constant, which are directly proportional, will both increase or decrease the rate constant in tandem.

The outcome from varying the particle zeta potential, and how it relates to the particle diameter, can be found in Figure 5. The rate constant decreases as the particle zeta potential decreases (increases in negativity). The particle size where the maximum rate constant occurs will also decrease. Both effects are due to the electrostatic surface force. For the first effect, as the electrostatic force decreases, with increasing zeta potential, the energy barrier decreases and the critical rupture thickness increases. The critical rupture thickness increase allows the kinetic energies of attachment to increase by decreasing the resistive lubrication force’s effect. The increase in kinetic energy and the decrease in the energy barrier both contribute to an increase in the probability of attachment, which increases the overall rate

Figure 4. Effect of contact angle on the rate constant. Higher contact angles increase the work of adhesion, which decreases the probability of detachment. This increases the rate constant. It should be noted that contact angles and hydrophobic force constants are directly related. Both increase or decrease the rate constant in tandem.

constant. For the second effect, as the zeta potential decreases, the energy barrier will increase, and the critical rupture thickness decrease, more for larger particles than smaller particles (Shaw, 1992). These larger particles will, therefore, have a higher energy barrier to overcome and less kinetic energy to overcome it. This lowers the rate constant for larger particles and moves the maximum rate constant to lower particle sizes.

The final surface force parameter that was varied is the surface tension. This is shown in Figure 6, along with the effect of particle diameter. Similar to the contact angle, the effects shown here are entirely due to the work of adhesion. A higher surface tension increases the work of adhesion, which makes it harder for particles to become detached. Therefore, the probability of detachment decreases, with increasing surface tension, and the rate constant increases.

It should be noted that all simulations that were run show a maximum, of the rate constant, around a particle diameter of 100 microns. This is seen in industrial flotation cells and is a good sign as to the validity of the model and the assumptions used to derive the model. This can be seen with or without the given attachment and detachment energy multipliers.

Figure 5. Effect of particle zeta potential on the rate constant. As particle zeta potential increases, rate constant and particle size where maximum rate constant occurs both increase. This is mainly due to the interaction between the energy barrier, critical rupture thickness and lubrication force.

Figure 6. Effect of liquid-vapor surface tension on the rate constant. Higher surface tensions increase the work of adhesion and decrease the probability of detachment. This increases the overall rate constant.

These simulations show that surface chemistry parameters play as important a role in flotation as physical parameters. An analysis of flotation cannot be conducted while only looking at the physical characteristics of the flotation machinery and the feed to that machinery. The chemical interactions between all aspects of flotation must be considered. This includes water chemistry and surface chemistry. A big determining factor in flotation is the hydrophobic force. This manifests itself in the hydrophobic force constant and contact angle. If this force is omitted, a flotation equation cannot be considered universal and will only be valid in very few situations. The current equation incorporates all current surface chemistry as well as hydrodynamic knowledge. Although further refinement of the model is needed, it still predicts trends that are seen in industry. A more precise knowledge of the hydrodynamics encountered in the flotation industry will provide a much more detailed model. Further refinement of this model is currently ongoing with hopes of attaining this goal.

Task 2 – DPIV Measurements

The main goal of this task is to record the fluctuations of particles in a homogenous turbulent flow field. The RMS of these velocity fluctuations corresponding to the Kolmogorov micro scale will then be calculated in order to confirm or modify accordingly the turbulent root-mean-squared velocity

$$\sqrt{U_i^2} = 0.33 \frac{\varepsilon_d^{4/9} d_i^{7/9}}{\nu^{1/3}} \left(\frac{\rho_i - \rho_3}{\rho_3} \right)^{2/3} \quad [4]$$

The turbulent dissipation will also have to be calculated in terms of the flow velocity field.

Facilities and Instrumentation: Experiments to characterize the particle interaction with turbulence were performed. A small-scale water tunnel has been constructed in which we generate homogenous isotropic turbulence (Figure 7). The design allows quick change of the fluid/particle mixture and flushing of the system for more tests. The facility is appropriate for mixing different sizes of particles with different densities, as well as generating air bubbles of different sizes.

Digital particle-image velocimetry (DPIV) is employed. This method records the instantaneous flow field in a plane and has been recently employed by the authors to monitor two-phase flows. DPIV requires a plane sheet of intense laser light. This sheet cuts the domain of interest along planes of interest. A CMOS digital camera is then employed to record the instantaneous position of different objects in the flow field. Recording the position of seed particles that follow the flow, allows us to calculate the instantaneous velocity field. Over the past few years, we were able to improve this method by increasing the frequency response by two orders of magnitude over commercially available systems. We

Figure 7: Schematic representation of the isotropic turbulence water tunnel

have also employed this method to record two-phase flows, namely spray flows or bubbly flows.

Homogeneous isotropic turbulence is generated by grids. This is the simplest reproducible and repeatable example of turbulence. Moreover, the multi-phase flow data thus generated can be compared with the results of other investigators. Such data are used to obtain relationships, including the RMS of the bubble/particle velocity fluctuations in terms of the fluid velocity fluctuations. This allows us to generate new and more reliable data to corroborate or to replace Equation 4.

Results: Validation of Equation 4 for particles with $St < 1$: Very small particles at the asymptotic limit of the Stokes number < 1 will behave as fluid elements responding to all the fluctuations of the flow. At that level, the U_{rms} corresponding to the particle motion will be defined by the velocity at the level of the Kolmogorov micro-scale for homogeneous isotropic turbulence.

$$U = (\varepsilon \nu)^{\frac{1}{4}} \quad [15]$$

Time-Resolved DPIV measurements were performed in the flotation cell illustrated in Figure 7. Homogeneous isotropic turbulence was generated using a grid with 0.01m diameter and 0.01m spacing. The Reynolds number based on the grid spacing was on the order of $Re=1000$. The Kolmogorov length scale is on the order of $50\mu m$ and the corresponding time scale was 100ms. The experiments were performed with sampling frequency of 1000Hz ($\Delta t=1ms$) and spatial resolution on the order of $20\mu m/pixels$. The DPIV data analysis scheme was optimized for the maximum spatial resolution, with the minimum spatial averaging effects introduced by the cross-correlation. Therefore the velocity measurements were produced by a minimum interrogation window of 8×8 pixels with 3pixels (75% overlap) spacing between consecutive vectors. This results in spatial resolution for the flow field on the order of $60\mu m$, which is practically the same as the Kolmogorov length scale. Figure 8 shows time averaged results from the experiment. The color contours correspond to vorticity distribution (right) and turbulent dissipation rate (left) computed using Taylor's hypothesis of frozen turbulence.

Figure 8: Time averaged results downstream of the turbulence generation grid over a length of approximately 6 grid spacing. (left) turbulent dissipation rate contours (right).

The results clearly illustrate that beyond 3 grid lengths, we have fully developed homogenous isotropic turbulence. This observation serves as the basis for performing the validation of Equation 4 which was developed assuming fully developed turbulent flow. Results are shown in Figure 9 clearly demonstrated that Schubert's equation underestimates the predicted fluctuation velocities by a factor of 2 (200% error) or more. Considering the fact that the semi-empirical relation appears to scale with $Re^{1/3}$ compared to $Re^{-(1/4)}$, that is the case for homogeneous isotropic turbulence, it can be conjectured that the deviation between the two will increase exponentially.

Figure 9: Comparison between the Urms predicted by Schuberts equation and the Urms estimated by the turbulent energy dissipation rate measured.

Task 3 – Model Validation

Model validation will occur with flotation experiments within a flotation setup as shown in Figure 10. This setup includes a flotation cell, a Lightnin Labmaster mixer, mixing tank, and several sampling areas. The cell will be a Rushton flotation cell, where mixing characteristics are well developed and well understood (Pyke et al, 2003; Armenante and Chang, 1998). Air will be introduced through a glass frit in the bottom of the cell. The cell will be run continuously, as industrial machines are. This produces a more reliable, reproducible result where conditions are not constantly changing and a flotation rate constant is not arbitrarily set, as in batch tests (de Bruyn and Modi, 1956; Jowett and Safvi, 1960; Mehrotra and Padmanabhan, 1990). The Labmaster mixer will allow a stable speed as well as a power input readout which is needed for the current form of the model.

Figure 10. Continuous flotation setup. Silica beads of differing sizes and hydrophobicity will be fed to the flotation cell (2 liter) at a constant rate. Automatic paddles will be used to facilitate easy and consistent removal of the froth. Froth height will be adjustable by up and down movement of a flexible tube where the tailings are being discharged. Once steady state is reached, samples may be obtained. The rate constant may then be calculated from these samples.

Variables that will be tested include the particle size, bubble size, hydrophobicity, and power input (measure of turbulence). Silica beads were purchased from Potters Industries and will be tested in 5 size ranges; 120x140 mesh, 140x170 mesh, 170x200 mesh, 200x270 mesh, and -270 mesh. Hydrophobicity will be altered by silanating the silica surfaces. This procedure is outlined by Flinn (1996). Bubble size will be altered by using frits with differing pore diameters.

Data acquisition is currently in the initial stages and will be completed by the next reporting period.

Task 4 – Simulator Development

This task is not currently being pursued. Simulator development will begin after the completion of all other tasks.

SUMMARY

During the past reporting period, the flotation model has become more theoretically based. A more robust collision frequency model has been proposed which will include a large range of particle responses to turbulence. Data has been obtained in the DPIV measurements. Analysis of this data is ongoing. Model validation is currently ongoing, with data acquisition in the initial stages.

FUTURE WORK

Further refinement of the flotation model will continue during the next reporting period. This will include a more in-depth theoretical analysis of the effects of turbulence on particle and bubble movements. Experimental work will include the flotation tests to validate the model as well as DPIV data analysis. Further DPIV measurements have been delayed due to the loss of the CCD camera. More experimental data may be taken as soon as repairs are completed.

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PUBLICATIONS/PRESENTATIONS

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

Appendix D: Studies of Froth Stability and Model Development

TECHNICAL PROGRESS REPORT

Contract Title and Number:

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Technologies (DE-FC26-01NT41091)

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ABSTRACT

Coal and sulfide minerals float well in salt water, apparently because electrolytes such as NaCl reduce the coalescence of gas bubbles when present above a critical concentration (Craig, et al., 1993). Equilibrium film thickness and disjoining pressure isotherms for foam films made from the ionic surfactant SDS show that dilute electrolytes inhibit bubble coalescence, due to a significant decrease in hydrophobic attraction.

INTRODUCTION

Background

In order to understand the physics and chemistry of the froth layer in a flotation cell, we need to study, in some detail, bubble coalescence and its overall effect on froth stability. Much work has been done on the effect of cationic and ionic surfactants on the stability of froths and foams, but the effect of electrolytes on froth stability has drawn little attention, despite their importance in many real systems.

A good review of electrolytes inhibiting bubble coalescence has been given by Weissenborn and Pugh (1995), who included electrical repulsive forces, a reduction in the

hydrophobic force, surface elasticity effects and the counter-ion hydration mechanism as possible explanations. Our current theoretical and experimental approach has enabled us to quantitatively obtain the magnitude of surface forces, including the hydrophobic force, and to qualitatively determine the stability between air bubbles.

Objective and Approach

The objective of this project is generally to study the mechanisms involved in stabilizing foams and froth. The current report shows the effect of electrolytes on foam stability. This has been achieved through the use of a thin film balance (TFB) technique developed by Scheludko and Exerowa (1959). We use traditional Scheludko cells, which are known to work at low disjoining pressures, to determine the magnitude of the hydrophobic force in foam films. Then we probe the equilibrium film thickness over a range of disjoining pressures to generate disjoining pressure isotherms, which enable us to understand the surface properties at air/water interfaces. We can also approximately determine the critical pressure under which the foam film will rupture, simulating the critical pressure for bubble coalescence.

PROJECT TASKS

Task 1: Foam/Froth Studies

During the past reporting period, construction of the Thin Film Balance was completed, with help from Dr. H.J. Mueller of the Max Planck Institute of Colloids and Interfaces in Golm, Germany. Measurement precision has been improved through the use of advanced data mining techniques and we have been kindly provided with a bike-wheel microcell (Pereira, et al., 2001) by Prof. C.J. Radke's group at UC Berkeley to measure the thin-film forces. This microcell has given us the ability to work over a much greater range of disjoining pressures than previously (because of more uniform liquid drainage inside the film holder).

Surface tension isotherms have been generated for 10^{-4} M SDS solutions for two fixed NaCl concentrations: 0, 0.4 mM and 1 mM. The surfactant adsorption isotherms were calculated from the Gibbs adsorption equation. For SDS solutions in the absence of NaCl, we use the following equation with $n=2$ (after Tajima (1970)):

$$\Gamma = -\frac{1}{nRT} \frac{d\gamma}{d \ln C} \quad [1]$$

However, for SDS solution in the presence of 0.0004 M NaCl, we chose $n=1$ for surfactant concentrations, $C_{\text{SDS}} \leq 10^{-4}$ M, since there is excess salt in the surfactant solution, and we use $n=2$ for $C_{\text{SDS}} > 10^{-4}$ M.

Using the Poisson-Boltzmann approximation, we can obtain the Gibbs potential (ψ_0), then deduce the Stern potential (ψ_s) with our recently developed counter-ion binding model

and that of Warszynski, et al (1998). The validity of the present counter-ion binding model is confirmed since we have obtained values of $\sigma_1 / \sigma_0 \approx 0.8$, which agree well with the findings of Kralchevsky, et al. (1999). The Stern potential at the air/water interface is shown in Fig. 1.

Figure1. The double-layer potentials at the air-water interface as calculated from counter-ion binding model.

From figure 1, the higher the SDS concentration, the higher the surface potential. This is due to the increased adsorption of negatively charged surfactant ions. The added electrolyte (NaCl) promotes surfactant adsorption at low surfactant concentrations, which tends to increase the surface charge density. But the double-layer potentials are inversely proportional to the ionic strength. The added salt increases the ionic strength of the solutions so greatly that it outweighs the increase in the surface charge density, thus decreasing the surface potentials. As shown in Figure 1, the surface potentials for the surfactant solution with 0.4mM NaCl or 1.0 mM NaCl are consistently lower than those in SDS solutions without salt. The decrease in the surface potential at high SDS concentrations (above 10^{-3} M) should be ascribed to the increase in the ionic strength of the solutions.

Figure 2. Equilibrium film thickness as a function of SDS concentration for three fixed NaCl concentrations: 0, 0.4mM and 1.0 mM at pH 5.7-6.0 and at $25 \pm 0.1^\circ\text{C}$.

Figure 2 shows the equilibrium film thickness values obtained at different surfactant concentrations. The filled squares represent the equilibrium film thickness obtained in the absence of electrolyte; the filled circles and triangles represent the results obtained in the presence of 0.4mM and 1.0 mM electrolyte, respectively. These measurements agree well with the experimental data obtained by Aksoy (1997) and Exerowa et al. (1979). In the low SDS concentration region, equilibrium film thickness increases with increasing SDS concentration were observed for all three lines. A general explanation for this phenomenon is that the increase of equilibrium film thickness could be connected to an increase in the surface potential (Exerowa and Kruglyakov, 1998). The residual presence of the maximum in film thickness may be due to the competition of surface charge contribution and screening effect of electrical double layer at air/water interface. Interestingly, this maximum shifts from 5×10^{-6} M SDS for the solutions without salt, to 5×10^{-5} M SDS with 0.4mM NaCl, and to 1×10^{-4} M SDS with 1mM NaCl. When the SDS concentration is above 10^{-3} M, SDS predominates and the ionic strength of the solutions at a given SDS concentration will be close to each other. It is likely that the screening effect of the electrical double layer determines the film thicknesses under these circumstances. Consequently, these three curves tend to overlap.

Figure 3. The values of K_{232} for the foam films in the presence of SDS as calculated using the Extended-DLVO theory. Only the positive values of K_{232} are plotted. The three curves represent K_{232} versus the surfactant (SDS) bulk concentration for three fixed NaCl concentrations: 0, 0.4mM and 1.0mM. The open diamonds represents the K_{232} values calculated using surface potential data predicted by the KR model (Kalinin and Radke, 1996). The open squares represents the K_{232} values calculated from experimental data by Warszyski *et al.* (1998). Clearly, these three sets of hydrophobic force data are close to each other.

From Figure 3, one can see that added salt significantly decrease the magnitude of the hydrophobic force at low surfactant concentrations. At a certain salt concentration, the hydrophobic force decreases with increase in surfactant concentration, consistent with previous work (Yoon and Aksoy, 1999; Angarska, et al., 2004).

In figure 4, for 10^{-4} M SDS, there is a big gap between the Extended-DLVO fit (solid lines) and the DLVO fit (dotted lines). The distance of this gap represents the magnitude of the hydrophobic force. For the SDS solution containing 0.4 mM NaCl, this gap is still discernible despite being much smaller, as it almost disappears for a SDS solution containing 1.0 mM NaCl. This trend clearly shows that salt significantly reduces the hydrophobic force.

Figure 4. Disjoining pressure isotherms for 0.1mM SDS in different salt solutions: ■ 0 mM NaCl; ● 0.4 mM NaCl; ▲ 1 mM NaCl. The solid lines are obtained according to the Extended-DLVO theory: $K_{232}=2.33\times 10^{-18}$ J, $\psi_s = -114.3$ mV for SDS solution without salt; $K_{232}=8.38\times 10^{-20}$ J, $\psi_s = -110.0$ mV for SDS solution with 0.4mM NaCl; $K_{232}=1.41\times 10^{-21}$ J, $\psi_s = -106.4$ mV for SDS solution with 1.0 mM NaCl. The dotted lines are obtained from the classical DLVO theory with equal surface potentials set to Extended-DLVO fits.

The curves calculated from the Extended-DLVO theory (solid lines) agree well with the experimental data: those calculated from classical DLVO fits (the dashed line and dotted line) show a larger discrepancy for pure SDS solutions. The critical pressure for film rupture is just 0.9 KPa without rupture for a 10^{-4} M SDS foam film alone, and is around 6.0 KPa for a 10^{-4} M SDS foam film with 0.04 mM NaCl, indicating that the latter is more stable. Films from the 10^{-4} M SDS solution containing 1.0 mM NaCl, shown by the filled triangles, are much stronger and there is no rupture observed up to the entry capillary pressure of the film holder (8.5 KPa).

SUMMARY

Electrolytes can significantly decrease hydrophobic interactions in foam films even when their concentrations are low. They also decrease the double-layer repulsive force due to the well known “screening effect”. Dilute electrolyte will inhibit bubble coalescence; which in turn is expected to increase the stability of froths and foams.

FUTURE WORK

Much of the work conducted during the next reporting period will focus on the measurement of emulsion film thicknesses and disjoining pressure isotherms on foam films from common frothers, such as short-chain alcohols.

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PUBLICATIONS/PRESENTATIONS

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

Appendix E: Direct Measurement of Forces in Flotation Systems

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Establishment of the Center for Advanced Separation
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Date: October 31, 2003
Code: VA004-R03

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ABSTRACT

We are nearing completion of the fabrication of a device for measuring the forces relevant to flotation systems. In the next reporting period we expect to report the first results from this apparatus. While completing this equipment development and building task, we have also completed two other tasks that are relevant to an improved understanding of the flotation process. Recent literature has suggested that air bubbles adsorb to hydrophobic surfaces, and that these bubbles drastically influence surface forces. We have shown, using ellipsometry, that if these bubbles are present, then they are very rare on surfaces. In addition, we have shown that the process of degassing solutions to remove these putative bubbles does change the surface forces in the presence of surfactant solution, but that the change is probably due to a change in pH. The change in pH is caused by a loss of CO₂ and affects the surface forces by changing the electrostatic forces.

INTRODUCTION

Background

Froth flotation is the most important solid-solid separation process for upgrading run-of-the-mine (ROM) ores and coal in the mining industry.¹ 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 the mineral ore. Purification of the ore is based on differences in the attachment and/or detachment of particles to the bubbles: particles that attach and stay attached to the bubble are carried away from the rest of the ore. It is believed that the attachment of particles to a bubble surface is caused by a 'hydrophobic' interaction.^{2,3} 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 a thermodynamic 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. In addition to thermodynamic barriers, the drainage of the water film also provides a hydrodynamic barrier to attachment of the particle.

There are many reports of measurements of attractive forces that act over a range of 10-100 nm between hydrophobic surfaces in water. If this force is real, it constitutes a critical mechanism for flotation because it would act against any activation or hydrodynamic barrier and pull the particle into contact with the bubble. An understanding of this attractive hydrophobic force is therefore central to an understanding of the flotation process.

Objective and Approach

Our objective is to discover whether or not there is a non-contact hydrophobic force between surfaces, and to discover the range, magnitude, and surface chemical conditions for this force.

PROJECT TASKS

Task 1: Development and Fabrication of the Wetting Film Balance

Fabrication of the Wetting Film Balance is almost complete. A schematic of the apparatus is shown below. The remaining tasks are to install a pressure gauge, to improve the resolution in altering the pressure, and to perform some standard experiments for calibrating the apparatus.

Figure 1 Schematic diagram for Wetting Film

Task 2: Detection of Bubbles on Hydrophobic Surfaces

There are many accounts of long-range attractive forces between hydrophobic surfaces. In 1994 it was first suggested that these forces were caused by bubbles attached to hydrophobic surfaces. Recently this hypothesis has become very popular; there are a large number of reports of measurements that show that the attractive force decreases or is removed when the solution is degassed, and also reports of direct observation of air-bubbles on surfaces. This hypothesis is important for flotation because flotation necessarily occurs in aerated water.

If air-bubbles are present on hydrophobic surfaces, then they should be easily detected by instruments that are sensitive to the refractive index of media because the refractive index of water is ~ 1.33 and the refractive index of air is ~ 1.00 . We performed a series of ellipsometric measurements to discover the extent of any air layers on a variety of hydrophobic surfaces that were immersed in water. The water was highly purified, but no attempt was made to remove the dissolved air. Table 1 summarizes our results for four hydrophobic surfaces. Ellipsometry does not tell us the shape of the adsorbed layer, it yields optical data that can be fitted to various models. In model one, we assume that the air layer

is uniform. Under this assumption, the air layer is so thin as to have no physical meaning. In models two and three, we assume that the bubble is spherical. Under this assumption, we find that even small bubbles are quite rare (at least one micrometer apart). In model 4 we assume that the water has a slightly lower density near the hydrophobic surface as compared to in bulk. Only a slightly lower density is required to fit the data.

In summary, our data is consistent with only a very small amount of air on hydrophobic surfaces. Therefore, it seems to be unwise to invoke the universal existence of a large amount of air on hydrophobic surfaces.

Table 1: Amount of Air on Hydrophobic Surfaces

Model	1	2	3	4
Surface	homogeneous air layer thickness	spherical end cap (macroscopic contact angle) area / bubble	spherical end cap ($r=80$ nm, $h=15$ nm) area / bubble	1 nm film depletion %
OTS A	0.01 nm	$(10\mu\text{m})^2$ *	$(2.3\mu\text{m})^2$	1%
OTS B	0.04 nm	$(5\mu\text{m})^2$ *	$(1.2\mu\text{m})^2$	5%
OTS C	0 nm	(infinite) *	(infinite)	0%
TMCS	0.01 nm	$(14\mu\text{m})^2$ †	$(2.3\mu\text{m})^2$	1%

* assuming $\theta = 100^\circ$, then for $r = 80$ nm, $h = 66$ nm

† assuming $\theta = 80^\circ$, then for $r = 80$ nm, $h = 94$ nm

Task 3: Measurement of Forces between Hydrophobic Surfaces

There are widespread reports that degassing of solutions reduces or removes the attractive force between hydrophobic surfaces.⁴ The proposed mechanism is that equilibrated water contains dissolved air. This air produces air-bubbles attached to hydrophobic surface. The long-range attractive forces between hydrophobic surfaces are not really long-ranged forces, they are due to the bridging of bubbles between the surfaces. Support for this hypothesis comes from the fact that the measured forces change when the water is degassed, thereby removing the source of air for the bubbles. Particularly dramatic results were reported by the group of Higashitani⁵ on surfaces that were rendered hydrophobic through the adsorption of the surfactant, octadecyltrimethylammonium bromide. We performed a more detailed set of experiments to determine whether this mechanism is correct. Our results are shown in Figures 1 and 2.

Figure 1 shows the results before degassing and Figure 2 shows the results after degassing. The overall form of the forces is similar before and after degassing. *In particular, the long-range attraction remains after degassing.* Closer inspection shows that the force–concentration dependence has changed after degassing. This is consistent with Higashistani’s work: if only a single concentration is examined, the force changes on degassing. However, Higashistani’s conclusion is incorrect, degassing does not remove the long-range attraction, degassing merely changes the concentration dependence of the force. Our hypothesis is as follows. Degassing the solution changes the pH by removing dissolved CO_2 . We have confirmed this by experiment. This alters the charge on the solid surface and therefore alters the adsorbed amount of surfactant. The change in the adsorbed amount causes a change in the force. We now need to verify whether degassing actually changes the adsorbed amount. We also need to determine the mechanism of the change in force- is it electrostatic or does it correspond to a long-range hydrophobic force?

Figure 1

Figure 2

SUMMARY

1. There is no ubiquitous layer of air on hydrophobic surfaces.
2. Degassing of surfactant solutions does change the forces, but it does not remove the long-range attractive force.

FUTURE WORK

1. Complete fabrication of force-measuring device and measure the force between air and solids in aqueous solutions.
2. Measure the surface potential of surfactant coated surfaces, and the adsorption of surfactant to hydrophobic surfaces

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Appendix F: Novel Surfactants as Collectors for Froth Flotation

TECHNICAL PROGRESS REPORT

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ABSTRACT

The first hydra surfactants have been synthesized and characterized.

INTRODUCTION

Background

Froth flotation involves separating finely divided solid particulates suspended in water.(Fuerstenau and Herrera-Urbina, 1989) Many mining companies worldwide employ froth flotation to enhance the concentration of desired mineral and coal fines. Processing occurs on the scale of billions of tons of ore annually and consumes millions of kilograms of reagents—collectors, depressants, activators, modifiers, and frothers. The proposed hydra surfactants will function as collectors.

Objective and Approach

Our goals are to synthesize novel, inexpensive surfactants that outperform current collectors in mineral flotation. These surfactants will selectively bind to mineral particles and create a hydrophobic coating on a particle to enable selective separation by froth

flotation. We plan to synthesize surfactants that have very hydrophobic, long chains, yet have sufficient water solubility for mineral processing. These amphiphiles, which we call 'hydra surfactants', will have one tail and three identical functional groups on the head. These novel molecules will be useful for many different separations in mineral processing.

We expect the hydra surfactants to enhance collector properties in two critical areas: (1) stronger binding to the particle through multi-valent attachment and (2) increasing the solubility for longer chains. First, they should improve binding of the surfactant to the particle because multiple functional groups increase the chances for attachment. After the initial attachment, it is easier for the remaining functional groups to attach. Second, the increased polarity of the head group will increase the water solubility of very long hydrophobic chains. Consequently, fewer bound molecules will be needed to produce the desired hydrophobicity. Improvement in both critical areas will ultimately produce a method that uses a smaller amount of collector while achieving a better separation

PROJECT TASKS

Task 1. Description of Synthesis. During the past 7 months, we have spent all of our efforts on the synthesis of hydra surfactants. We have assembled a research team of four graduate students and three undergraduates to facilitate rapid progress. One graduate student is supported full-time by the grant.

Scheme 1. i. BnN⁺Me₃OH, DME, 70–80 °C, 1 h (73%); ii. H₂, Raney Ni, EtOH, 38–40 °C, 18 h (90%); iii. (*t*-BuOCO)₂O; iv. R₁CH₂COCl, PhH, Et₃N, 42 h (80%) or R₁CH₂COOH, DCC, HOBT, THF, 48–72 h (33–60 %); v. R₁-NH₂; vi. HCOOH, 48 h (55–80 %).

3CAm(#): R₁ = *n*-C_nH_{2n+1}, *n* = 12, 14, 16, 18, 20 and # = 13, 15, 17, 19, 21; For **3CUr(#):** R₁ = *n*-C_nH_{2n+1}, *n* and # = 14, 16, 18, 20, 22

Scheme 1 describes our progress on the synthesis of tricarboxylate surfactants. We have succeeded in preparing and characterizing seven new surfactants. We have begun studying the

physical properties of the **3CAm**(#) series. We are studying the solubility at different pH's. We find that solubility increases with pH, which we suspect reflects the degrees of ionization of the three carboxyl groups in the head. Our preliminary results show that **3CAm**(**21**), the longest chain in the series, is soluble at 5×10^{-2} M at pH. We have given a sample of **3CAm**(**13**) to researchers in Professor Yoon's laboratory for flotation tests and will provide more samples as needed.

The synthesis of trihydroxamate surfactants is progressing. We are pursuing couple of strategies. Scheme 2 shows the initial strategy, where we start with the long chain attached, and modify the head group. We have not yet optimized these reactions; they appear to produce mixtures of where only one or two of the head groups has been modified.

Scheme 2. i. SOCl_2 ; ii. $\text{H}_2\text{N-OBn}$, Et_3N , THF, 20 h Broken arrow means that the products are not fully or satisfactorily characterized.

Scheme 3 shows the strategy, where we construct the head group first and attach the long chain second. Starting with acryloyl chloride, we have made the known *N*-(benzyloxy)acrylamide in quantitative yield. Condensation of three equivalents of this amide with nitromethane gives **2** in high yield. Reduction of the nitro group to the amine **3** appears to work well, but the compound has not been fully characterized. Attachment of the long chain, debenzoylation, and neutralization with KOH will give **3HUr**(**16**).

Scheme 3. i. $\text{H}_2\text{N-OBn}$, Et_3N , THF (100%); ii. $\text{BnN}^+\text{Me}_3\text{OH}$, DME, 70–80 °C, 1 h (73%); iii. Zn/HCl , EtOH, 38–40 °C, 18 h; iv. R1-NCO ; v. H_2 ; Pd/C, then KOH.

Task 2. Experimental Details.

General Comments. Melting point data were obtained with an Isothermal 9200 Digital Melting Point Apparatus. ^1H and ^{13}C NMR spectra were obtained on a JEOL Eclipse 500MHz. IR spectra were obtained on neat samples with a Midac FT-IR with a

DuraSampLIR attachment. Mass spectrometry data were obtained on a JEOL HX110 Duel Focusing MS. Elemental Analysis was performed by Atlantic Microlab, Inc. in Norcross, GA.

Synthesis of Di-tert-butyl 4-Nitro-4-[2-(tert-butoxycabonyl)ethyl]-heptanedioate (nitrotriester). A solution of nitromethane, Triton-B (benyltrimethylammonium hydroxide), and DME (dimethoxyethane) was heated to 65 °C. Approximately half of the *tert*-butyl acrylate was added dropwise to the solution, maintaining the temperature between 77-80 °C. Additional Triton-B was added dropwise to the solution. The remaining *tert*-butyl acrylate was then added dropwise. Triton-B was added dropwise to the solution. The reaction mixture was stirred at 70-80°C for an hour. The reaction mixture was concentrated in vacuo, resulting in an orange solid. The solid was dissolved in CHCl₃, washed with 10% aqueous HCl, brine, and dried with MgSO₄. Concentration in vacuo resulted in a yellow solid, which was crystallized in 95% ethanol yielding white needles (69%); ¹H NMR (CDCl₃) δ 1.42(s, CH₃, 27H), 2.18 (m, CH₂, 12H); ¹³C NMR δ 28.10 (CH₃), 29.87 (CH₂CO), 30.41 (CCH₂), 81.24 (CCH₃), 92.27 (O₂NC), 171.16 (CO); IR 2974, 1719, 1534.

Synthesis of Di-tert-butyl 4-Amino-4-[2-(tert-butoxycabonyl)ethyl]-heptanedioate, 1, (Behera's Amine). A mixture of nitro triester, Raney Ni, and ethanol (95% or absolute) was hydrogenated for 20h. The mixture was filtered through Celite. The solvent was removed in vacuo, resulting in a viscous liquid. The liquid was placed under vacuum which yielded a white solid. The product was used without further purification. ¹H NMR (CDCl₃) δ 1.41(s, CH₃, 27H), 1.58(t, CH₂, 6H), 2.21 (t, CH₂, 6H); ¹³C NMR δ 28.14 (CH₃), 30.05 (CH₂CO), 34.46 (CCH₂), 52.40 (O₂NC), 80.41 (CCH₃), 173.15 (CO).

General procedure A for long chain tri tert-butylesters, 3CAm(#): Procedure A. Behera's amine was dissolved in dry Benzene. Triethylamine and the appropriate acid halide were added to the flask. Addition of the acid halide resulted in an immediate cloudy solution. The solution was stirred for 48h. The reaction mixture was washed with sat. NaHCO₃, water, cold 10% aqueous HCl, and brine. The solution was dried with Na₂SO₄. The solvent was concentration yielding an off-white solid which was crystallized with EtOH/H₂O which yielded a white needles or white solid (61-83%).

Procedure B. A mixture of the appropriate carboxylic acid, DCC, and 1-hydroxybenzotriazole was dissolved in dry THF and stirred at room temperature. A white precipitate crashed out of solution after approximately 1 h. The solution is stirred for 3 d. The precipitate was filtered and the filtrate was concentrated in vacuo. The slightly yellow solid was dissolved in CH₂Cl₂. The solution was placed in the freezer overnight. The resulting precipitate was again removed by filtration. The filtrate was washed with cold 10% aqueous HCl, water, sat. NaHCO₃, and brine. The solution was dried with Na₂SO₄. The solvent was concentration yielding an off-white solid which was crystallized with EtOH/H₂O which yielded a white solid (30-49%).

4-(2-(tert-butoxycabonyl)ethyl)-4-(1-oxotetradecylamino)heptanedioic acid di-tert-butyl ester, 3EAm(13) The general procedure (B) described above afforded a white solid; mp 72.8-73.7 °C; ¹H NMR (CDCl₃) δ 0.87 (t, CH₃, 3H), 1.20-1.30 (bm, CH₂, 20H), 1.42 (s, CH₃,

27H), 1.57 (t, CH₂, 2H), 1.95 (t, CH₂, 6H), 2.08 (t, CH₂, 2H), 2.21 (t, CH₂, 6H), 5.7, (s, NH, 1H); FAB HRMS: 626.4981 (M⁺, calcd for C₃₈H₇₁NO₇), 626.4996.

4-(2-(tert-butoxycarbonyl)ethyl)-4-(1-oxohexadecylamino)heptanedioic acid di-tert-butyl ester, 3EAm(15): The general procedure (A) described above afforded a white solid; mp 66.6-67.2 °C ¹H NMR (CDCl₃) δ 0.87 (t, CH₃, 3H), 1.31-1.1.30 (bm, CH₂, 28H), 1.42 (s, CH₃, 27H), 1.95 (t, CH₂, 6H), 2.08 (t, CH₂, 2H), 2.21 (t, CH₂, 6H). ¹³C NMR δ 14.18, 22.76, 25.89, 28.14, 29.40, 29.43, 29.59, 29.72, 29.72, 29.76, 29.90, 30.08, 31.99, 37.71, 57.33, 80.03, 173.01, 172.68; FAB HRMS: 654.5309 (M⁺, calcd for C₃₈H₇₁NO₇, 654.5269. IR 3395, 2914, 1730, 1725, 1713, 1669, 1526; Anal. Calcd for C₃₈H₇₁NO₇: C, 69.79; H, 10.94; N, 2.14; O, 17.12. Found: C, 69.76; H, 10.96; N, 2.21; O, 17.14.

4-(2-(tert-butoxycarbonyl)ethyl)-4-(1-oxooctadecylamino)heptanedioic acid di-tert-butyl ester, 3EAm(17): The general procedure (A) described above afforded a white solid; mp 66.6-67.2°C; ¹H NMR (CDCl₃) δ 0.87 (t, CH₃, 3H), 1.21-1.30 (bm, CH₂, 32H), 1.42 (s, CH₃, 27H), 1.57, (t, CH₂, 2H), 1.95 (t, CH₂, 6H), 2.08 (t, CH₂, 2H), 2.21 (t, CH₂, 6H); ¹³C NMR CH₃ 28.14, 29.40, 29.43, 29.59, 29.73, 29.78, 29.90, 30.07, 32.00, 57.33, 80.70, 172.68, 173.01; IR 3397, 2915, 1730, 1725, 1714, 1670, 1528, 1148

4-(2-(tert-butoxycarbonyl)ethyl)-4-(1-oxoicosylamino)heptanedioic acid di-tert-butyl ester, 3EAm(19): The general procedure (B) described above afforded a white solid; mp 70.6-71.3°C; ¹H NMR (CDCl₃) δ 0.87 (t, CH₃, 3H), 1.21-1.31(bm, CH₂, 32H), 1.42 (s, CH₃, 27H), 1.57, (t, CH₂, 2H), 1.95 (t, CH₂, 6H), 2.08 (t, CH₂, 2H), 2.21 (t, CH₂, 6H), 5.77 (s, NH, 1H); IR 3336, 2914, 1731, 1724, 1713, 1669, 1526, 1147

4-(2-(tert-butoxycarbonyl)ethyl)-4-(1-oxodocosylamino)heptanedioic acid di-tert-butyl ester, 3EAm(21):: The general procedure (B) described above afforded a white solid; mp 74.7-75.0°C; ¹H NMR (CDCl₃) δ 0.87 (t, CH₃, 3H), 1.21-1.30 (bm, CH₂, 36H), 1.42 (s, CH₃, 27H), 1.57, (t, CH₂, 2H), 1.95 (t, CH₂, 6H), 2.08 (t, CH₂, 2H), 2.21 (t, CH₂, 6H); FAB HRMS: 738.6212 (M⁺, calcd for C₃₈H₇₁NO₇), 738.6248.

General synthesis of long chain triacid: Triester was dissolved in 96% formic acid and stirred overnight. The milky white solution was concentrated in vacuo. The white solid was crystallized in either ethyl acetate or glacial acetic acid/hexane which yielded a white solid (55-80%).

4-(2-carboxyethyl)-4-(1-oxotetradecylamino)heptanedioic acid, 3CAm(13): The general procedure described above afforded a white solid; mp 162.7-163.1°C; ¹H NMR (CD₃OD) δ 0.89 (t, CH₃, 3H), 1.20-1.35 (bm, CH₂, 20H), 1.58 (t, CH₂, 2H), 2.00 (t, CH₂, 6H), 2.16 (t, CH₂, 2H), 2.26 (t, CH₂, 6H); ¹³C NMR δ 13.12, 22.41, 25.89, 27.91, 29.11, 29.34, 29.45, 31.75, 36.36, 57.19, 174.68, 175.80, 186.68

4-(2-carboxyethyl)-4-(1-oxohexadecylamino)heptanedioic acid, 3CAm(15): The general procedure described above afforded a white solid; mp 164.5-165.1°C; ¹H NMR (CD₃OD) δ 0.89 (t, CH₃, 3H), 1.26-1.26 (bm, CH₂, 24H), 1.58 (t, CH₂, 2H), 2.00 (t, CH₂, 2H), 2.16 (t, CH₂, 6H), 2.26 (t, CH₂, 2H); IR 3417, 3100, 2915, 1723, 1694, 1636, 1520.

4-(2-carboxyethyl)-4-(1-oxooctadecylamino)heptanedioic acid, 3CAm(17): The general procedure described above afforded a white solid; mp 165.9-166.9°C; ¹H NMR (CD₃OD) δ 0.89(t, CH₃, 3H), 1.21-1.37 (bm, CH₂, 28H), 1.58 (t, CH₂, 2H), 2.00 (t, CH₂, 6H), 2.16 (t, CH₂, 2H), 2.26 (t, CH₂, 6H). IR 3358, 2918, 1721, 1707, 1677, 1150 IR 3417, 3100, 2916, 1722, 1694, 1636, 1521, 1175

4-(2-carboxyethyl)-4-(1-oxoicosylamino)heptanedioic acid, 3CAm(19): The general procedure described above afforded a white solid; mp 162.5-163.8°C; ¹H NMR (CD₃OD) δ 0.89(t, CH₃, 3H), 1.25-1.35 (bm, CH₂, 32H), 1.58 (t, CH₂, 2H), 2.00 (t, CH₂, 6H), 2.16 (t, CH₂, 2H), 2.26 (t, CH₂, 6H). FAB HRMS: 738.6212 (M⁺, calcd for C₄₄H₈₄NO₇) 738.6248. IR 3418, 3100, 2916, 1720, 1694, 1652, 1521, 1175

4-(2-carboxyethyl)-4-(1-oxodocosanylamino)heptanedioic acid, 3CAm(21): The general procedure described above afforded a white solid; mp 165.0-165.9°C; ¹H NMR (CD₃OD) δ 0.89 (t, CH₃, 3H), 1.24-1.35 (bm, CH₂, 36H), 1.58 (t, CH₂, 2H), 2.00 (t, CH₂, 6H), 2.16 (t, CH₂, 2H), 2.26 (t, CH₂, 6H).

SUMMARY

We have developed a procedure for making tricarboxylate surfactants. We have begun a promising method to synthesize a trihydroxamate surfactant.

FUTURE WORK

We shall scale up the syntheses of the tricarboxylate surfactants to provide samples for flotation testing. In the next three months, we shall complete the synthesis of the trihydroxamate surfactant and provide a sample for testing as soon as we make it.

REFERENCES

Fuerstenau, D.W. and Herrera-Urbina, R., 1989. "Flotation Reagents." In: S. Chander and R.R. Klimpel (Editors), *Advances in Coal and Mineral Processing Using Flotation*. Society for Mining, Metallurgy, and Exploration, Inc., Littleton, Colorado, pp. 3-18.

PUBLICATIONS/PRESENTATIONS

Williams, A. A.; Kite, B. L.; Gandour, R. D. Synthesis and properties of tri-headed surfactants. 77th ACS Colloid and Surface Science Symp., June 15–18, 2003 Abstract 386

Appendix G: Column Flotation of Fine Dolomitic Phosphate by Selective Fatty Acids

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Establishment of the Center for Advanced Separation
Technologies (DE-FC26-01NT41091)

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Sub-Recipient Project Title:

Column Flotation of Fine Dolomitic Phosphate Pebbles

Report Information:

Type: Annual
Number: 1
Period: 4/1/03-9/30/03
Date: 4/29/04
Code: WV-006

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No subcontracts issued.

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ABSTRACT

A dolomitic phosphate pebble sample (Sample A) was obtained from FIPR and IMC Phosphates for use in this study - this sample has been sized and component analyses for each of the size fractions are being generated. A phosphate module has been purchased for an existing Lachat QuickChem 8000-FIA Analyzer housed in the NRCCE, WVU analytical laboratory; a copy of the AFPC manual for the analysis of phosphate content and standard phosphate rock samples have been ordered and the laboratory is establishing standard procedures for the determination of the phosphate content of the dolomitic phosphate pebble samples. An ICP-OEP instrument is being used for the other chemical component analyses. Our flotation column is being modified for this particular study.

INTRODUCTION

Background

The recovery of phosphate from the dolomitic phosphate resources of Florida has been studied since 1970. Some encouraging results have been achieved, but most of the

processes so far developed cannot produce acceptable phosphate concentrates (more than 30% P_2O_5 and less than 1% MgO). The high MgO content of the concentrates is detrimental to the down stream filtration step in the phosphoric acid manufacturing process. Currently, large quantities of high dolomitic phosphate pebbles less than 1 mm and fine slimes minus 0.1 mm are stockpiled and discarded in impoundments, which waste resources and cause environmental problems. Additionally, as Florida mining moves toward the southeast of the state, lower quality phosphate reserves with high MgO become a major problem. In the hope of alleviating these problems, this research project proposes to study the removal of MgO from fine dolomitic phosphate pebbles, using the moderately selective acid soap collector, PA-31, for dolomite particles and a mixture of phosphoric acid/sulfuric acid as depressant for the phosphate particles in acid media. The newly developed PA-31 selective fatty acid collector has been tested in dolomite flotation at the Department of Mining Engineering, WVU (Peng and Gu, 2003), using a flotation column with structure packing. The results of that study showed that the goal of reaching a phosphate concentrate containing more than 30% P_2O_5 and less than 1.0% MgO content can be achieved with this improved process.

Objective and Approach

The objective of this research project is to use the selective fatty acid soap collector, PA-31 (or its substitute), for the flotation of dolomite particles, and the mixture of phosphoric acid/sulfuric acid for the depression of phosphate particles in a dolomite flotation stage. The removal of MgO from fine dolomitic phosphate pebble samples will be conducted in flotation columns in order to reduce MgO content below 1% and achieve high P_2O_5 recoveries. The use of selective fatty acid collectors for dolomitic flotation; surfactant effects in acid medium; and phosphoric/sulfuric acid depression of phosphate particles will also be examined in detail.

PROJECT TASKS

Task 1 - Material Characterization and Analytical Procedure Establishment: A dolomitic phosphate pebble sample (Sample A) was obtained from the Florida Institute of Phosphate Research (FIPR) and IMC Phosphate Company, FL. This sample has been sized and a sample of each size fraction has been subjected to analysis for phosphate, CaO , MgO , Fe_2O_3 , Al_2O_3 , and acid insoluble material. The component analysis results will be used to further determine grinding/liberation requirements and separation procedures. A phosphate module for an existing Lachat Quicken 8000 Flow Injection Analyzer (FIA); an AFPC (Association of Fertilizer and Phosphate Chemists) manual of analytical procedures for phosphate content determination; and standard phosphate rock samples have been purchased. These items are necessary for the National Research Center for Coal and Energy (NRCCE) Analytical Lab at West Virginia University (WVU) to establish an appropriate procedure to determine P_2O_5 content of dolomitic phosphate pebble samples for this research project. Simultaneous ICP-OES with a radial torch configuration (Varian Vista-Pro) is being used for the determination of CaO , MgO , Fe_2O_3 , and Al_2O_3 and a FIPR wet chemical procedure is being used to determine acid insoluble materials. The necessary reagents, including fatty acid

collectors and foaming agents, for the column flotation test work were obtained from ARR-MAZ Products, a Division of Process Chemicals, FL.

Task II-IV – Equipment Set-up: Batch flotation cells and a Denver automatic flotation machine have been set-up for the reagent study. Flotation columns with and without structure packings have also been set-up and are being modified in preparation for the column flotation tests.

SUMMARY

Much of the effort this reporting period was directed towards the characterization of the dolomitic phosphate pebble sample A. The different size fractions have been analyzed in order to provide information on grinding/liberation requirements and to establish sizing and separation procedures. We have had problems obtaining satisfactory dolomitic phosphate sample analyses and the NRCCE Analytical Laboratory has contacted FIPR for assistance in resolving the problems. We are waiting for the resolution of these problems before making further plans.

FUTURE WORK

In the next reporting period, procedures for the analysis of phosphate in the dolomitic phosphate pebble samples will be established. A grinding/chemical analysis and optical particle liberation measurements will be carried out and an appropriate sample will be prepared for dolomite flotation tests in a semi-batch flotation cell to determine the amounts of reagent needed for column flotation testing.

REFERENCES

Peng, F. F. and Gu, Z. X., 2003, "Processing Florida dolomitic phosphate pebble with double reverse-flotation processing," Preprint 03-153, 2003 SME Annual Meeting, Cincinnati, OH, Feb/ 24-26, 2003.

PUBLICATIONS/PRESENTATIONS

(None)

Appendix H: Development of a Novel Fine Particle Centrifuge

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Establishment of the Center for Advanced
Separation Technologies (DE-FC26-01NT41091)

Period of Performance:

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Ending Date: 5/31/05

Sub-Recipient Project Title:

Development of a Novel Fine Particle Centrifuge

Report Information:

Type: Annual
Number: 1
Period: 3/1/03-9/30/03
Date: 11/30/03
Code: VA006

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ABSTRACT

The processes used to dewater coal are inefficient in removing surface moisture from fine particles. To overcome this problem, a novel hyperbaric centrifugal filter has been developed by researchers at Virginia Tech. Preliminary test data obtained using a batch unit suggest that this new technology can reduce the moisture content of fine coal products by approximately 30-50% as compared to existing dewatering processes. The objective of this project will be to construct a continuous prototype unit and to conduct a detailed experimental study of this new technology. Work performed during this reporting period has largely focused on the design of the prototype unit.

INTRODUCTION

Background

One of the most difficult and costly steps in coal preparation is the removal of moisture from the surfaces of fine coal particles. Although thermal dryers can effectively reduce moisture, these units require large capital expenditures and stringent air quality standards make it impossible to obtain new operating permits. As a result, coal producers resort to mechanical systems for fine coal dewatering. Unfortunately, the performance of mechanical dewatering equipment diminishes sharply for particles finer than 0.1 mm. The

unacceptably high moisture content associated with this fraction forces the majority of coal producers to discard their coal fines to waste impoundments. In the U.S. alone, approximately 2 billion tons of fine coal has been discarded in abandoned ponds and 500 to 800 million tons in active ponds. On a yearly basis, U.S. coal producers discard approximately 30 to 40 million tons of fresh coal fines into ponds. This represents a loss of valuable natural resources, loss of profit for coal producers, and creation of significant environmental concerns.

Objective and Approach

The availability of a low-cost mechanical dewatering device that can efficiently remove moisture from fine coal will greatly benefit the U.S. coal industry. In light of this need, researchers at Virginia Tech have developed a novel hyperbaric filter centrifuge that can reduce the moisture contents of fine coal by 30-50% as compared to currently available dewatering methods (Yoon and Asmatulu, 2000). The new technology employs both gas pressure and centrifugal force to increase the driving force for removing water from the fine capillaries present in a filter cake. The specific objectives of this project are (i) to construct a small-scale continuous prototype unit for testing, (ii) to evaluate the effects of key operating and design variables, and (iii) to demonstrate the capabilities of the new technology using fine coals from different coal preparation plants.

PROJECT TASKS

Task 1 – Filter Centrifuge Design/Construction

The objective of this task is to design and construct a prototype of the hyperbaric filter centrifuge. The most difficult part of this task was to design a system that could accept dilute coal slurry and introduce compressed gas without disturbing the filter cake. Preliminary experiments showed that the filter cake cannot be disturbed while being dewatered without losing air pressure. In addition, the filter cloth used in the batch unit could not be used in a continuous unit because of blinding and excessive wear that would occur during cake removal. To overcome this problem, a two-stage process was designed. The first stage uses a thickening unit (i.e.,

Figure 1. Hyperbaric filter centrifuge processing circuit.

paste thickener) to efficiently separate the water from feed solids (Figure 1). This system ensures that a high coal recovery is maintained. The thickened underflow is then pumped into a rotating centrifuge unit that is a variant of the Hyperbaric/Inverting Filter Centrifuge that is widely used by the specialty chemical and pharmaceutical industries (see Figure 2 below). These centrifuges are semi-continuous sequential devices that consist of a rotating pressure chamber that is horizontally mounted and is driven by an electric motor. A second hollow shaft is located along the same axis as the drive shaft to allow feed and air to enter the pressure chamber. This second shaft is connected to two sets of end plates that serve to seal the pressure chamber on one end and to discharge the cake on the other.

Figure 2. Simplified schematic of an inverting filter centrifuge (After HEINKEL Aktiengesellschaft)

The unit is closed and sealed at the start of the operating cycle (Fig. 2a). During operation, thickened feed solids are pumped into the pressure chamber until the unit is filled. Feed to the unit is then stopped and air is introduced until the desired pressure is achieved. The chamber is held under pressure for a period of time sufficient to complete the drying cycle and obtain the target moisture content. After releasing the air pressure, a pneumatic ram is used to separate the two sections of the centrifuge and permit the product cake to exit the centrifuge (Fig 2b). The unit is then closed and the cycle is repeated.

Task 2 – Filter Centrifuge Testing

Several tests were performed using a batch version of the hyperbaric filter centrifuge to verify the findings obtained in earlier studies (Yoon and Asmatulu, 2000). Table 1 provides a summary of the test results obtained using the batch unit as a function of drying time. The tests were conducted with and without air pressure (0 and 20 psig) and with and without rotation (0 and 346 Gs). In addition, the tests were performed using two types of filter medium (i.e., a tightly woven filter cloth and a thin synthetic filter mesh). As shown, the moisture dropped by several percentage points as the drying time increased from 30 to 120 sec for both the filter cloth and filter mesh tests. However, the moistures obtained using the filter cloth were generally lower than those obtained using the filter mesh by up to 1 percentage point. The lower moisture was believed to be due to higher losses of ultrafine coal

Table 1. Comparison of batch data obtained using filter cloth and filter mesh medium.

Cycle Time (sec)	Centrifugal Force (Gs)	Filter Cloth		Filter Mesh	
		Moisture Content (%)		Moisture Content (%)	
		0 psig	20 psig	0 psig	20 psig
30	346	19.8	15.2	20.1	16.3
60	346	18.7	13.8	19.7	15.7
90	346	18.3	13.0	19.1	15.4
120	346	17.9	12.4	18.4	14.8

that passed more readily through the larger openings in the filter mesh. On the other hand, an increase in air pressure from ambient conditions (0 psig) to 20 psig substantially lowered the moisture contents of the filter cakes. For the filter cloth, the moisture was reduced from 17.9% to 12.4% after the addition of air pressure for the longest cycle time of 120 sec. For the filter mesh, the moisture content dropped from 18.4% to 14.8% under the same test conditions. Due to motor restrictions, the rotational speeds used in this program were not sufficient to produce the higher gravitation forces (e.g., 500 Gs). Therefore, the moisture reductions obtained in this test program were not as great as those shown in previous research.

SUMMARY

In order to improve the removal of moisture from fine coal streams, a project has been initiated to construct and test a hyperbaric filter centrifuge. Previous tests conducted with a batch laboratory unit suggest that this new technology can reduce the moisture content of fine coal products by up to 50% compared to existing mechanical systems. During this reporting period, work focused on the design of a pilot-scale continuous prototype of this technology. The system consists of a two stage process capable of achieving low product moistures while maintaining nearly complete recoveries of fine coal. Several laboratory tests were also conducted using a batch fed unit to verify the extent of moisture removal that can be achieved using this process.

FUTURE WORK

Work will be initiated during the next reporting period to procure and fabricate components needed to construct the prototype unit. Shakedown tests will then be initiated to evaluate the pilot-scale unit. Parameters to be investigated will include air pressure, rotation speed, feed solids loading, and drying cycle time.

REFERENCES

Yoon, R.-H. and R. Asmatulu, "Methods of Improving Centrifugal Filtration," U.S. Patent Application Serial No. 09/531,373, filed March 21, 2000.

PUBLICATIONS/PRESENTATIONS

The work associated with this project was presented at the 2003 Annual CAST Conference in Charleston, West Virginia, on November 19-21, 2003. The presentation was titled "Improving the Centrifugation of Fine Coal" was coauthored by R.T. Burchett, G.H. Luttrell, and R-H. Yoon.

APPENDICES

No appendices are included in this report.

Appendix I: New Strategies for Dewatering of Coals

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Establishment of the Center for Advanced Separation
Technologies (DE-FC26-01NT41091)

Period of Performance:

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Ending Date: 12/31/05

Sub-Recipient Project Title:

New Strategies for Dewatering of Coals

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Report Information:

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Number: 01
Period: 3/1/03 to 9/30/03
Date: 9/29/03
Code: WV004-R01

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ABSTRACT

Results of initial experiments on determining the amount of water present in a coal sample 'sent to settling ponds' and dewatering of this coal by resonant heating by microwaves of 2.45 GHz frequency are described. It is shown that effective dewatering occurs rapidly by microwave heating without heating the coal or ash. The process is shown to be superior to dewatering by thermal heating. Similar experiments are planned for dewatering by resonant heating at the IR frequency of 10^{14} Hz.

Atomistic modeling of ice and water using molecular-dynamics simulations is presented. Initial simulations have established the time-step to be used and customized visualization of simulation runs is introduced.

INTRODUCTION

Background

Since water is used extensively in coal preparation and cleaning, dewatering of coals is required prior to shipment to power plants. However, finer fractions of coals are difficult to dewater and consequently these fractions are stored in settling ponds, causing environmental problems and loss of a large fraction of coals. Thermal drying of coals is not an efficient process since hot air heats both coal and water. An objective of this project is to investigate new strategies for coal dewatering which involve selective energy absorption by water without heating coal. These new strategies include selective heating by microwaves and infrared radiation combined with modeling of the coal-water interactions.

Objective and Approach

The overall objectives of this project are to investigate coal dewatering by selective heating of water by microwave and infrared radiations, without any significant heating by coals, supplemented by modeling studies of the coal-water interactions. The power absorbed by a unit volume of a material from electromagnetic (em) radiation can be written as [1,2]:

$$P = 55.63 \times 10^{-12} |E_0|^2 f \varepsilon'', \text{ w/m}^3 \text{ ----- (1)}$$

where $|E_0|^2$ and f are respectively the intensity and frequency of the em radiation and ε'' is the loss factor (imaginary part of the dielectric constant). The approach of this program is based on the fact that ε'' for water has sharp peaks at selective frequencies, making P very high at those frequencies. At the microwave frequency $f = 2.45$ GHz (1 GHz = 10^9 Hz), ε'' for water is 12 compared to 0.1 for coals making power absorbed by water 120 times larger than that for coal. This is the frequency used for microwave cooking. Similarly at the IR frequency $f = 10^{14}$ Hz, ε'' for water is 30,000 [3]. In this report, we present experimental results of coal dewatering obtained using microwave heating at 2.45 GHz. Experiments using selective IR heating are planned for the near future.

The computational investigations of this project use molecular-dynamics simulations techniques to model coal, water, and coal-water interactions. Within this method, the atoms follow Newton's second law of motion, $\Sigma \mathbf{F}_i = m_i \mathbf{a}_i$, where m_i is the mass of atom i ($i = 1$ to N_{atoms} with N_{atoms} being the total number of atoms in the system), $\mathbf{a}_i$ is its acceleration, and $\Sigma \mathbf{F}_i$ is the net force on atom i due to neighboring atoms. The velocity-Verlet algorithm is used to integrate these $3 \times N_{\text{atoms}}$ partial differential equations numerically in order to get velocities and positions of all the atoms at subsequent time steps. The quality of the interatomic forces is essential for a realistic description of the respective material. Present simulations focus on water systems; carbon systems as well as water-carbon systems will be investigated in the near future.

PROJECT TASKS

To make this project industrially relevant, we acquired four samples of coal in kg quantities from a preparation plant owned/operated by Consol Inc. The proximate and ultimate analyses of those samples are given in Appendix I. The most relevant sample for dewatering studies is coal #1 which is the sample sent to settling ponds, and it contains 52.5% moisture, 26.6% carbon and 15.2% ash. Most of the experiments described below were carried out on this sample since the other samples contain only minute amounts of moisture. Graduate assistant A. Kalra was involved in Tasks I and II and undergraduate assistant Wm. Trevor Swan was involved in Task III.

Task I: Under this task, we measured the moisture loss using thermogravimetric analysis (TGA) on the sample ‘sent to ponds’ and also measured heat capacity of the sample using DSC (Differential Scanning Calorimetry). The results of the TGA experiments are shown in Fig. 1 for different heating rate and those of the DSC experiments in Fig. 2. The weight loss in Fig. 1 is primarily due to loss of moisture since most of this loss occurs for $T \leq 100^\circ\text{C}$, and it agrees with the % moisture given in Appendix I. These experiments were done under ‘thermal’ heating, using in-house Mettler 3000 TGA system and DSC-30 system.

Fig1. TGA spectrum of the coal

Fig2. DSC spectrum of the coal

Task II: This task involved the selective dewatering of the ‘sample sent to ponds’ (see Table 1) using microwave heating at 2.45 GHz. For these experiments, we purchased a conventional microwave oven (GE Model JES838SH001) with maximum power of 800 Watts. The oven has 10 power settings so that power level 7 means microwaves are on 70% of the time. The coal samples were placed in styrofoam coffee cups and covered with paper with numerous holes for moisture to escape. The samples were treated for 5 seconds at power level 1, taken out and weighed, and the procedure was followed for about 20 minutes when there was no further reduction in weight. The results of these experiments for four different initial weights of the coal samples (25, 50, 100 and 150 grams) are shown in Fig. 3. The rate of moisture loss, which eventually reaches 50%, is the largest for the smallest initial mass as

Fig. 3. Weight loss by microwave heating

Fig. 4. X-ray diffraction of the coal

expected. The slope of the initial mass loss probably represents the loss of “free water”, whereas the slower rates at larger times are due to the release of “bound water” contained in the pores of the coal structure.

In order to determine whether microwave heating has in any way affected the coal or ash in the sample, we used x-ray diffraction of the ‘before’ and ‘after’ sample from the experiments in Fig. 3. The x-ray diffraction patterns (Fig. 4) show absolutely no change in the lines due to ash signifying that coal and ash are not affected by microwave heating whereas moisture in coals is effectively removed by this technique. This is in contrast to thermal drying of coals where both coal and water get heated simultaneously.

Task III: The emphasis of this task is to computationally model dewatering of coals. During this period, we focused on the atomistic modeling of water. A sequential code was developed and implemented on a PC to perform molecular-dynamics simulations of single water molecules, ice, and water. The interatomic forces used in the simulation are based on the model introduced by Teleman et al. [4]. This code was tested for correctness by monitoring the positions and energies for long-time simulation runs. In a sequence of simulations, various time steps were used to find the time step that comfortably satisfies the conservation of energy over long periods of time. A time step of 0.0001 fs (1 femto second = 1 fs = 10^{-15} s) could be established for our preliminary studies of ice/water systems.

Fig. 5: H-O distance over time using different time steps from 0.1 fs to 0.001 fs.

Fig. 6: Visualization of an ice phase 1h crystal. Large spheres ... oxygen atoms; small spheres ... hydrogen atoms

We tested the code for simple cases, namely one oxygen atom and a single hydrogen atom as well as one water molecule. Different initial conditions, such as atoms displaced from equilibrium but without initial velocities (see Fig. 5) and atoms placed in their respective equilibrium positions but given initial velocities, were used to further investigate the stability of the simulation for long simulation runs.

To model bulk ice and/or water we start the simulation from a particular crystalline structure. There are about a dozen different ice phases; phase 1h is the one that shares the triple point with liquid and vapor. As a first step, the setup of a phase 1h ice lattice was implemented. During the summer, an REU (research experience for undergraduates) student, supported by the Virtual Environments Laboratory at WVU, joined our efforts on this project. He developed and implemented tools on our computing platforms customized to this project's needs of visualizing systems over a period of time (see an initial configuration of ice phase 1h in Fig. 6).

SUMMARY

The initial results presented here show that selective absorption of em radiation by water at 2.45 GHz is a very effective technique for dewatering of coal, without heating the coal. The cost-effectiveness of dewatering by resonant heating by microwaves still needs to be worked out.

The implementation of an ice/water model presented here established a time-step of 0.0001 fs for molecular-dynamics simulations of these systems. Visualization supporting the analysis of simulation results has been developed. Further tests on stability of various ice phases need to be performed.

FUTURE WORK

First, reasonable estimates (cost/ton) for dewatering of coals by microwave heating will be determined. Next we propose to carry out similar experiments of dewatering by resonant absorption of IR radiation at $f = 10^{14}$ Hz as noted earlier. A source for this radiation has been acquired and these experiments are now being planned. Results from these experiments will be compared with those from the microwave heating experiments presented here.

As a next step, the model for carbon systems by Brenner et al. [5] will be implemented on the Beowolf-like PC cluster in the Physics Department. Investigating known properties of carbon systems will test the correctness of the implementation. Modeling the water-coal interactions will be based upon experimental investigations in this project.

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PUBLICATIONS/PRESENTATIONS

1. *Atomistic Modeling of Dewatering of Coals*, Swan, Bachlechner, Seehra, Manivannan, Poster presented at the Research Horizons of the Eberly College of Arts and Sciences, WVU, April 22, 2003, and at the Seminar 2003: Regional Business Opportunities in Supercomputing from the Pittsburgh Supercomputing Center, Waynesburg College, July 14, 2003
2. *Graphical Analysis of Water Molecules*, Watson, Swan, Van Scoy, Bachlechner, Seehra, and Manivannan, Poster presented at the Seminar 2003: Regional Business Opportunities in Supercomputing, Pittsburgh Supercomputing Center, Waynesburg College, July 14, 2003
3. *Atomistic Modeling and Visualization of Dewatering of Coals*, Swan, Watson, Bachlechner, Van Scoy, Seehra, Manivannan, Oral presentation at the REU conference 2003, Virtual Environments Lab, WVU, August 1, 2003.

APPENDIX-1

Table 1. Analysis of different coal samples

SAMPLE ID	ANALYSIS	AS RECEIVED		DRY BASIS	
SAMPLES SENT TO PONDS	Loss on Drying	52.53	%		
	Carbon	26.59	%	56.01	%
	Hydrogen	6.50	%	1.31	%
	Nitrogen	<0.5	%	<0.5	%
	Sulfur	1.42	%	2.99	%
	Chlorine	230	ppm	485	ppm
	Ash	15.23	%	32.08	%
	Oxygen (by diff)	50.24	%	7.56	%
SAMPLES MAGNETICALLY SEPARATED	Loss on Drying	16.88	%		
	Carbon	3.44	%	4.14	%
	Hydrogen	1.49	%	<0.5	%
	Nitrogen	<0.5	%	<0.5	%
	Sulfur	0.33	%	0.40	%
	Chlorine	160	ppm	193	ppm
	Ash	68.03	%	81.85	%
	Oxygen (by diff)	26.69	%	14.07	%
COAL AS MINED	Loss on Drying	0.71	%		
	Carbon	62.74	%	63.19	%
	Hydrogen	4.57	%	4.52	%
	Nitrogen	1.10	%	1.11	%
	Sulfur	4.46	%	4.49	%
	Chlorine	489	ppm	493	ppm
	Ash	18.29	%	18.42	%
	Oxygen (by diff)	8.79	%	8.22	%
COAL SENT TO POWER PLANT	Loss on Drying	1.12	%		
	Carbon	75.74	%	76.60	%
	Hydrogen	5.46	%	5.40	%
	Nitrogen	1.37	%	1.39	%
	Sulfur	3.17	%	3.21	%
	Chlorine	637	ppm	644	ppm
	Ash	6.21	%	6.28	%
	Oxygen (by diff)	7.99	%	7.07	%

Appendix J: Novel Bioleaching Technology Assisted by Electrolytic Processes

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Establishment of the Center for Advanced Separation
Technologies (DE-FC26-01NT41091)

Period of Performance:

Starting Date: 9/17/01
Ending Date: 5/31/05

Sub-Recipient Project Title:

Novel Bioleaching Technology Assisted by
Electrolytic Processes

Report Information:

Type: Annual
Number: 3
Period: 10/1/02-9/30/03
Date: 10/7/2003
Code: WV001-R01

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ABSTRACT

This project is based on the electrobioleaching of sulfide minerals of pyrite (FeS_2), chalcopyrite (CuFeS_2) and sphalerite (ZnS). The approach is focused on the growth of the bacteria *A. ferrooxidans* under the influence of applied direct current. The major objective is to optimize the conditions of the electrobioleaching process.

In the period for this annual report, potentiostatic experiments were conducted where potential was scanned from 0.6 to 0 Volt for the reduction of ferric ion. It was found that each polarization curve consists of well defined activation and concentration polarization regions and that 0.3 Volt is the highest potential to give a maximum current. The next series of experiments were on the potentiostat mode where a constant potential of 0.3 Volt was applied to the cathode. It was found that the reduction rate of ferric ion is not the same value as shown in the polarization curve but depends largely on its concentration and the concentration of sulfate ion added to the cathode solution.

The next study was conducted on the leaching of sphalerite and a mixture of sphalerite and pyrite in a bioreactor in the presence of the bacteria. It was found that sphalerite leached 6% in 18 days while the mineral leached almost 20% in 22 days in the presence of pyrite. These results clearly demonstrate the galvanic effect by the nobler mineral of pyrite.

INTRODUCTION

Background

It is known that the bacteria *A. ferrooxidans* catalyzes the leaching of sulfide minerals including sphalerite (ZnS), chalcopyrite (CuFeS₂) and pyrite (FeS₂). The bacteria grow in their nutrient of ferrous ion and produce ferric ion. Thus if we reduce the ferric ion produced from the growth of the bacteria to ferrous ion, the bacteria will grow continuously and leach sulfide minerals. This is the idea of this project.

An experimental system is designed with two reactors. One is a bioreactor in which sulfide minerals are leached with the bacteria *A. ferrooxidans* and the other is an electrochemical cell in which a leaching byproduct of ferric ion is reduced to ferrous ion at the cathode compartment. The solution will be recycled from the cathode compartment of the electrochemical cell to the bioreactor by a pump, and at the same time, the solution will be recycled back to the cathode compartment of the electrochemical cell from the bioreactor by gravitational force. In this way, the bacteria will grow continuously in the bioreactor and will catalyze the leaching reactions of sulfide minerals.

Objective

The major objective of this project is to optimize the conditions of the electrobioleaching process.

PROJECT TASKS

This project will be conducted in five tasks. They are:

Task 1 - Mineral Sample Preparation and Apparatus Set-Up

Lumps of sphalerite (ZnS), pyrite (FeS₂) and chalcopyrite (CuFeS₂) were purchased from Ward's located in Rochester, New York. These samples were crushed by a Jaw crusher and then a Roll crusher, and screened to a 200 x 270 mesh (75 x 53 microns) fraction which has been used in this research project. The sphalerite sample was leached in aqua regia and analyzed by atomic absorption spectrophotometry - the result showed that the purity of the mineral was 89.1%. Chemical analyses will be conducted on the pyrite and chalcopyrite samples later.

A Perkin Elmer Model 283 Potentiostat/Galvanostat was purchased and has been used in this project. Two bioreactors of 1 liter capacity each were fabricated with 0.25" thick Plexiglas. Also, an electrical cell was fabricated with the same Plexiglas; each compartment of cathode and anode was 1 liter in capacity and an anionic membrane was inserted in between the compartments.

Task 2 – Preparation of Bacteria Mass

A culture of *Acidithiobacillus ferrooxidans* (formerly *Thiobacillus*; ATCC 13598) has been successfully established and maintained since December 2002. the original culture of the bacteria, as well as Wolfe's trace mineral solution, was purchased from ATCC. Care was

taken during the initial period of culture establishment to provide more options for the bacteria's propagation. Except for minor modifications, including shorter subculture period, ATCC's procedure for the growth and maintenance of *A. ferrooxidans* has been followed closely with stringent sterilization steps enforced particularly during subculturing. Sufficient amounts of culture have since been continuously maintained and used in bioreactor experiments.

Task 3 – Electrochemical Reduction of Ferric Ion

Potentiostatic experiments were conducted to produce polarization of cathodic reaction (reduction of ferric to ferrous). The cathode solution was stirred by a magnetic spin bar while the anode solution was stirred by an overhead stirrer. Sodium sulfate was used as the electrolyte of the solutions at 0.2 molar. The potential was varied from 0.6 to 0 Volt and scan rate was 20 mV/s. The results are shown in Figure 1. It can be seen from the figure that there are two distinct regions on each curve. The upper region is activation polarization and the lower region is concentration polarization. Also, it can be seen that the lower the concentration of ferric ion, the smaller the current.

From the curves, 0.3 volt was chosen to apply in the next study where ferric ion is reduced under various conditions of concentrations of ferric ion, ferrous ion and sodium sulfate. The pH of the cathode solution was 1.9. The concentration of the electrolyte in the anode solution

was 0.2 molar. Ten-ml liquid samples were withdrawn every hour up to 5 hours and analyzed for ferric ion using an idometric titration method.⁽¹⁾ The results are provided in Table 1.

Table 1. Potentiostatic Reduction of Ferric Ion

$[\text{Fe}^{3+}]$, M	$[\text{Fe}^{2+}]$, M	$[\text{Na}_2\text{SO}_4]$, M	I_{ave} , Amp	Ferric Red, %
0.05	0	0	0.07	18.6
0.05	0	0.1	0.0043	2.0
0.05	0	0.2	0.0044	3.9
0.05	0.03	0	0.043	18
0.025	0	0	0.0043	1.9
0.025	0	0.1	0.004	2.0
0.025	0	0.2	0.019	13.5
0.025	0.55	0	0.012	14

The data in Table 1 show two aspects of electro-chemistry. One is solution conductivity and the other is formation of ferric-sulfate complex ions. When ferric ion concentration is 0.05 molar, the solution conductivity seems high enough for good reduction of ferric ion. However, when sodium sulfate was added to a level of 0.1 or 0.2 molar, the Fe^{3+} concentration goes down because the concentrations of the ferric-sulfate ions increases. This may be the reason that the reduction of ferric ion is very small as can be seen from the second and third rows in the table. When the initial ferrous concentration is 0.025 molar, the opposite phenomena occur. It can be concluded here that the reduction of ferric ion depends on the solution chemistry, particularly on its concentration and the concentration of sulfate ion.

Task 4 – Bioleaching of Sphalerite

Two experiments were conducted on the leaching of sphalerite in the bioreactor. One experiment was conducted with 20 grams of sphalerite alone and the other was conducted with a mixture of 20 g sphalerite and 20 g of pyrite. Both experiments were conducted with 1 liter solution which consisted of 250 ml of 13-day old sub-cultured bacteria solution and 750 ml of 0.0719 molar ferrous ion solution which was adjusted to pH 1.5 with sulfuric acid. Air was bubbled through the solution throughout the experiments to help grow the bacteria. The results are shown in Figure 2. The sphalerite leaches about 6% in 18 days; however, when the sphalerite is mixed with pyrite, it leaches much more than that with the conversion being close to 20% in 22 days. These leaching conversions are more than those reported in the literature.⁽²⁾ This comparison of sphalerite leaching rate for the mineral alone with that in the presence of pyrite clearly demonstrates the galvanic effect by the nobler mineral of pyrite. In this case the sphalerite acts as a sacrificial anode.

Figure 2

Figure 3 shows the variation of ferric ion concentration as time goes on from the same experiment as for Figure 2. It can be seen from the figure that the ferric ion concentration increases as time goes on. This means that the ferrous ion decreases with increasing time, which suggests that the bacteria activity is reduced as time proceeds. Close investigation of this point is required for the rest of this project. In Figure 3, some data points have more than 100% for the ratio of ferric ion concentration to the total soluble iron concentration. This is undoubtedly experimental error.

SUMMARY

It has been found that the reduction of ferric ion to ferrous ion in an electrochemical cell largely depends on solution chemistry including ferric ion concentration and sulfate ion concentration. The sphalerite leaches well in the presence of bacteria. The leaching is particularly enhanced when this mineral is mixed with pyrite, confirming the galvanic effect by the nobler mineral of pyrite. The sphalerite in the mixture leached close to 20% in 22 days. It has been found from the same leaching experiments that the ferric concentration increases as time goes on. This means that the ferrous ion concentration decreases with increasing reaction time, suggesting that the bacteria activity is reduced as time proceeds.

FUTURE WORK

Future experimental work will be focused on the leaching of minerals in the solution-circulating system. Each system with each mineral will be optimized particularly in terms of solution circulation rate and potential applied.

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PUBLICATIONS/PRESENTATIONS

No publication or presentation has been made from the work of this research project.

**Appendix K: Coal Desulfurization Using Hypochlorite and Cupric Ion as a
Catalyst – Feasibility Study**

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Establishment of the Center for Advanced
Separation Technologies (DE-FC26-01NT41091)

Period of Performance:

Starting Date: 9/17/01
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Coal Desulfurization Using Hypochlorite and
Cupric Ion as a Catalyst – Feasibility Study

Report Information:

Type: Annual
Number: 1
Period: 3/1/03-9/30/03
Date: September 30, 2003
Code: VA005-R01

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ABSTRACT

In this period, more than 20 experiments were conducted to explore the feasibility of desulfurization of Pittsburgh No. 8 coal with hypochlorite and cupric ammine. It was found that ammonia which was used to solubilize cupric ion reacts with hypochlorite ions; thus, the two leaching experiments of cupric ammine and hypochlorite should be separated. Much of the work in this reporting period was conducted by separating the two leaching experiments.

Through many combinations of cupric leaching and hypochlorite leaching, it was found that a series of treatment of cupric leaching at room temperature, hypochlorite leaching also at room temperature and hydrolysis of the leach coal at 80°C gave a promising route for effective reduction of coal sulfur while minimizing chlorine content in coal. The results of leaching experiments with only hypochlorite show that the effect of temperature on the coal desulfurization was minimal.

INTRODUCTION

Background

It is known that aqueous chlorine can leach most of the coal pyrite and a significant fraction of organic sulfur.^(1, 2) However, the most serious problem with the method is that aqueous chlorine chlorinates the coal matrix at a level of 20-30 wt %. This is the major reason that no commercial coal desulfurization process utilizing aqueous chlorine has been developed. However, it has been reported that hypochlorite, a chlorine derivative to be stable at high pHs can also leach a significant fraction of organic sulfur with only a mild chlorination of the coal matrix.⁽³⁾ This present research tries to improve the hypochlorite leaching particularly by leaching coal with cupric ammine as pretreatment.

Objective

The major objective of this project is to optimize the conditions of the coal desulfurization using hypochlorite and cupric ammine.

PROJECT TASKS

Task 1 - Sample Material Preparation

Coal samples of Pittsburgh No. 8 coal which had been crushed and screened to 65 x 150 mesh for a previous research project, were floated and used in this project. The coal samples were analyzed for total sulfur, pyretic sulfur, sulfate sulfur, and chloride content using ASTM methods. The results show that the average total sulfur was 2.81%; pyretic sulfur, 0.99%; sulfate sulfur, 0.09%; and chloride content, 0.056%. From these sulfur values, the organic sulfur was calculated to be 1.72%. The total sulfur was analyzed with a LECO Model SC-432 Total Sulfur Analyzer. This total sulfur analyzer was repaired twice and now is in good condition.

A chlorine stock solution was prepared by dissolving chlorine gas into 4 liters of 1.6 molar NaOH. Chlorine concentration was analyzed by the idometric titration method using sodium thiosulfate. It was 0.7 molar.

Task 2 – Leaching Experiments and Hydrolysis

More than 20 experiments were conducted using a various combinations among chlorine concentration, cupric ammine concentration, and temperature. The solution pHs were high, mostly above 12. It was found from the early experiments that the solution could not be prepared by mixing cupric ammine solution and hypochlorite solution because hypochlorite reacts with ammonia to produce hydrazine. Thus, the experiments using cupric ammine and hypochlorite were separated.

The results of more than 20 preliminary experiments show that a series of cupric leaching at room temperature, hypochlorite leaching also at room temperature and hydrolysis

at 80°C yielded the best results in terms of sulfur reduction while minimizing chlorine content. Twenty grams of coal was leached in 50 ml ammonia containing 0.2 molar cupric for one hour; the leach coal was again leached in 100 ml of 0.7 molar hypochlorite solution for two hours; and finally the leach coal was hydrolyzed in 100 ml of 0.3 molar sodium carbonate solution for two hours. The results showed that the total sulfur was reduced from 2.8% to 2.23% through the two leaching steps and reduced to 2.12% through the hydrolysis. The results again showed that the effect of hydrolysis was minimal; however, it reduced the chlorine content from 1.04% to 0.11% which is well below the threshold level (0.3%). The high level of chlorine content (1.04%) was made through the hypochlorite leaching. The reduction of total sulfur content was mostly due to the reduction of pyretic sulfur.

Hypochlorite leaching of 10 g coal in 500 ml of 0.49 molar hypochlorite at 50 and 90°C reduced the total sulfur from 2.81% to 2.14% and to 1.78%, respectively. These results suggest that the effect of temperature on the coal desulfurization with hypochlorite is minimal. The chlorine content increased to 1.35%. These results suggest that coal leaching with hypochlorite at high temperatures such as at 90°C is not a commendable desulfurization method.

SUMMARY

It has been found that a series of treatments for cupric ammine leaching, hypochlorite leaching and hydrolysis give the best results of coal desulfurization in terms of coal sulfur reduction while minimizing chlorine content. The total sulfur was reduced from 2.81% to 2.12% when coal was leached with cupric ammine and then with hypochlorite both at room temperature and the leach coal was hydrolyzed 80°C. Through the hypochlorite leach, the coal attained chlorine content of 1.04%; however, through the hydrolysis, the chlorine content was reduced to 0.11% which is well below the threshold limit.

The coal desulfurization with only hypochlorite at 50 and 90°C reduced the total sulfur from 2.81% to 2.14% and 1.78%, respectively. These results suggest that the temperature effect on the desulfurization is minimal.

FUTURE WORK

Future experimental work will be focused on the coal desulfurization with a series of experiments of cupric ammine leaching, hypochlorite leaching and leach coal hydrolysis on the same coal by multiple times. Also, experiments will be conducted using Co(III) ammine instead of cupric ammine. The advantage with Co(III) ammine will be such that the spent cobalt (Co(II) ammine) can be readily regenerated to Co(III) by bubbling air through the solution.

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PUBLICATIONS/PRESENTATIONS

No publication or presentation has been made from the work of this research project.

**Appendix L: 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>	<u>Period of Performance:</u>
Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	Starting Date: 9/17/01 Ending Date: 5/31/05

<u>Sub-Recipient Project Title:</u>	<u>Report Information:</u>
Development of Electrochemical Sensor for On-site Monitoring of Heavy Metal Ions in Coal Processing and Utilization	Type: Annual Number: 3 Period: 10/1/02-9/30/03
<u>Principal Investigators:</u>	Date: 9/29/03
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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, Pb, As, Cd, Zn and Cu encountered in the processing and utilization of coals. This research is based on our initial results in which ppb levels of Pb and Hg were 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 this report, calibration curves for the detection of Hg in ppb range in different electrolytes (KNO₃, KCl, KSCN) are presented using gold-modified BDD electrodes. Also presented are initial results with the use of rotating disc electrode, detection of Hg in KCl impinger samples from flue gas of a coal power plant and results on the detection and analysis of lead, cadmium and copper.

INTRODUCTION

Background:

The development of new analytical techniques for the detection (and control) of mercury emissions from coal-fired power plants is a necessity, since over 30% of the mercury emissions come from these power plants. The detection of trace levels of Hg and other elements such as As and Se in the environment is a highly important yet challenging analytical problem. Because of the growing awareness of environmental mercury pollution and its high toxicity, it is becoming more urgent to develop highly sensitive techniques for the detection of Hg [1]. Spectroscopic techniques such as cold-vapor atomic fluorescence spectrometry (CV-AFS),[2] cold-vapor atomic absorption spectrometry (CV-AAS),[3] and inductively coupled plasma-mass spectrometry (ICP-MS)[4] have been used successfully for the detection of mercury. However, all of these techniques possess certain limitations. Some of those limitations are the pretreatment of the sample before analysis, detection level, interference with other elements, requirement of relatively large sample volumes, on-line monitoring capacity and cost effective. The other commercial continuous emission monitors (UV detectors) involves pretreatment and also lack in performance due to the deterioration of the gold trap for continuous use. In this work, we have undertaken the development of a low-cost electrochemical sensor for mercury based on boron-doped diamond electrodes. Progress to date is given below.

Objectives and Approach:

The broad objectives of this program are: (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 benefits from collaborations with NETL, Consolidation Coal Co. and Prof. Fujishima of the University of Tokyo where the BDD electrodes are synthesized. Graduate assistant Ms. L. Ramakrishnan is involved in these studies.

PROJECT TASKS:

Task 1: Experimental Setup:

During this period we made significant progress in the detection of mercury, lead, and cadmium and the effect of copper intermetallics formation. As we described before, 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. We also used BAS inc. potentiostat and a Palm Sens portable potentiostatic unit. The supporting electrolytes were 1M KNO₃, KCl

acidified with HNO_3 ($\text{pH} = 1$) and KSCN ($\text{pH} = 4$). The standard mercury solution was purchased from Fisher Scientific.

Task 2: Experimental

A differential pulse voltammetry (DPV) technique was used for all the experiments. In anodic stripping voltammetry (ASV) of metals, the metal species (Hg^{2+} , Pb^{2+} , Cd^{2+}) in solution is first deposited (reduced) electrolytically as Hg, Pb, and Cd onto an inert electrode at a constant applied potential. A dc-voltage ramp (mV/sec) is then applied in a direction that will cause the deposited material to be stripped (oxidized) from the electrode at a characteristic potential, E_p . Rectangular voltage pulses with adjustable pulse height and width are usually imposed on this voltage ramp. This allows the separation of the charging current from the Faradic current component, which is proportional to the concentration of the analyte. Since E_p is different for different species, simultaneous detection of several species is possible. Clearly, for the technique to work the chemical species must adhere to the electrode surface.

Task 3: Data Acquisition and Analysis:

Detection of Mercury in ppb range (nitrate and chloride electrolytes):

Additional experiments have been carried out for the mercury analysis in KCl and KNO_3 electrolytes. At this time, the calibration curve has been made for the range of 2-30 ppb using a free standing diamond film obtained from Element Six Inc. As shown in Fig. 1, excellent stripping currents are observed for mercury in 0.1M KNO_3 in the presence of 3 ppm of Au. The stripping peaks were uniform.

Figure 1. DPV peak currents for various Hg^{2+} concentrations covering a range from 2 ppb to 30 ppb in 0.1M KNO_3 ($\text{pH}=1$). 3 ppm gold standard solution was added to the electrolyte. SCE = saturated calomel electrode.

Two significant peaks have been observed at 0.25V vs. SCE possibly due to Hg to Hg^+ and 0.55V vs. SCE due to Hg to Hg^{2+} . In the case of KCl, experiments have been carried out in 0.1M KCl and 1M KCl and in different pH conditions in the presence of 3ppm of gold. Fig.2 shows the currents due to mercury stripping in 1M KCl at around 0.33V vs. SCE. The addition of 3 ppm of Au helped in obtaining steady mercury stripping peaks due to its nature of forming an amalgam with mercury metal deposited on the diamond surface before stripping. Figures 3a and 3b shows the calibration plots for mercury ranges from 2-10 ppb and 10-50 ppb respectively.

Figure 2. DPV peak currents for various Hg^{2+} concentrations covering a range from 2 ppb to 10 ppb in 1M KCl (pH=1). 3 ppm gold standard solution was added to the electrolyte.

Figure 3a. Calibration plot for Hg in the 2-10 ppb range in 1 M KCl (pH = 1) electrolyte for BDD electrode. Deposition time was 30 seconds at -0.5 V vs. SCE; pulse amplitude, 50 mV; sweep rate, 100 mV s^{-1} . Appropriate standard gold solution was added so that the concentration of gold in the solution is 3 ppm.

Figure 3b. Calibration plot for Hg in the 10-50 ppb range in 1 M KCl (pH = 1) electrolyte for BDD electrode. Deposition time was 30 seconds at -0.5 V vs. SCE; pulse amplitude, 50 mV; sweep rate, 100 mV s^{-1} . Appropriate standard gold solution was added so that the concentration of gold in the solution is 3 ppm

It was mentioned in our previous report that the presence of chloride ions in solution affects the reproducibility of results for Hg due to the formation of highly insoluble Hg_2Cl_2 . To overcome this problem, a new approach is being investigated in which ppb amount of gold is co-deposited on the BDD electrode which acts as a getter for Hg. As we show in our present results, this approach is very promising towards reproducibility, sensitivity, and short data acquisition time.

Samples from the coal utilization plants have also been tested for the presence of mercury and those results are compared with CVAAS technique. (given in RDE section).

Thiocyanate (KSCN) electrolyte:

DPV experiment was also carried out using thiocyanate electrolyte with free standing BDD electrodes. As shown in Figure 4 excellent DPV scans are observed leading to a linear calibration plot. No gold solution was added since there is no calomel formation here due to the absence of chloride. More experiments are underway using thiocyanate electrolyte. For practical applications, detection of mercury in chloride medium is a challenging topic. Therefore, we mainly focused on the calibration plots using chloride electrolyte.

Figure 4. DPV peak currents for various Hg^{2+} concentrations covering a range from 50 ppb to 250 ppb in 1M KSCN (pH=4).

Effect of rotation speed of RDE electrode:

A specially made free standing diamond electrode of 6mm diameter was custom made and attached to a stainless steel disk which can be easily mounted on a rotating disk electrode rotator made by Pine Instruments. We have carried out several experiments with this disk electrode using a normal potentiostat and a portable potentiostat made by Palm Sens. Rotating disk electrode technique is an important technique which can increase the detection level due to the hydrodynamic flow of the electrolyte at the surface of the electrode. DPV scans were recorded for various concentrations of mercury and also for various rotation

speeds of the disk electrode. Figures 5-7 shows the DPV scans for ppb levels of various concentrations of mercury at different rotation speed. Figure 5 shows two stripping peaks at 0.22 and 0.30 V vs. SCE due to surface mercury and gold-mercury alloy respectively under no rotation for mercury concentrations of 3 ppb-50 ppb. This is similar to the experiment shown in Figure 3 indicating two stripping peaks. As the rotation speed is increased from 1000 rpm to 2500 rpm the stripping currents have improved and the second peak at 0.35 V vs. SCE becomes more prominent where as the first peak at 0.26 V vs. SCE decreases and becomes almost negligible at a rotation speed of 2500 rpm (Figures 6&7). A 3 ppm gold standard solution was added for all the experiments. It is obvious from these results that the gold co-deposition with mercury becomes more uniform forming gold-mercury alloy and the one electron stripping of surface mercury is less significant. A calibration plot with the RDE is also performed using the Palm Sens unit and Figure 8 shows DPV scans for mercury concentrations in the range of 2-12 ppb.

Figure 5 (left): DPV scans for various mercury concentrations recorded without the rotation of RDE. (bottom scan: lower concentration, top scan: higher concentration)

Figure 6 (right): DPV scans for various mercury concentrations recorded at 1500 rpm rotation of RDE. (bottom scan: lower concentration, top scan: higher concentration)

Figure 7 (left): DPV scans for various mercury concentrations recorded at 2500 rpm rotation of RDE. (bottom scan: 2 ppb, top scan: 30 ppb)

Figure 8 (right): DPV scans for various mercury concentrations observed using Palm Sens unit. (scans F,H,J,L,B,D are 2,4,6,8,10,12 ppb respectively)

The detection of mercury using gold co-deposition combined with RDE is very reproducible on BDD, when compared with gold electrodes and gold coated glassy carbon electrodes. Gold is usually poisoned by mercury and the gold electrode has to be polished/cleaned and a new gold film has to be deposited each time in the case of glassy carbon electrode before each experiment. Gold deposition on glassy carbon is being used in the EPA 2420 method. Considering these factors, the present BDD with controlled gold co-deposition seems to be a better method with less background current and reproducible DPV scans. Further development on this approach is continuing.

Standard addition method for DOE samples:

Standard addition method was used for the determination of mercury in KCl impinger solution obtained in the coal fired power plants. The advantage of using standard addition method eliminates the background/matrix effects due to the presence of other impurities. In standard addition method, a known amount of the sample to be analyzed is taken and DPV scans are carried out by adding known amounts of mercury to it. The extrapolation of the stripping current on the negative side gives the amount of mercury present in the sample to be analyzed. We have carried out a series of standard addition experiments for several real samples and compared with CVAA experiments carried out using different instruments.

As an example, the standard addition methods on a KCl impinger sample made from the flue gas obtained during coal burning is shown in Figure 9. It is observed that the DPV scans shows a good linear behavior and the extrapolation of the linear plots gave the concentration of mercury present in the solutions. The same samples were also analyzed by CVAA techniques using CETAC M6000A at WVU and NETL. Similarly, several solutions

have been analyzed. It should be noted that the amount of mercury in some real samples were below 1 ppb. The concentration of mercury detected for all samples analyzed here by these two methods are quite comparable. It is clearly evident that our results using DPV method with BDD electrodes is a promising technique especially, for portable on-line monitors.

Figure 9. Standard addition method used to determine the mercury concentration in impinger solution. Mercury concentration of 0.72 ppb was determined.

A comparison of Hokuto-Denko potentiostat and Palm Sens unit has been carried out using RDE for the detection of mercury concentration in a real flue gas KCl impinger sample using standard addition method. The mercury concentration found as 0.18 ppb and 0.12 ppb using the Kokuto-Denko potentiostat and the Palm Sens unit respectively, were found to be close and also comparable to 0.24 ppb obtained by CVAA. In Figure 10 the portable Palm Sens unit with the glass cell and the data acquisition using a Palm is shown.

Figure 10. Photograph of the Palm Sens unit with the glass cell and a Palm unit for data collection.

Lead, Cadmium and Copper Results:

Though we have achieved success in detecting ppb levels of Pb, Cd, and Cu separately, it is important to address the issues related to their mutual interference. In our previous report, we presented the stripping peaks for pure cadmium with and without the addition of lead. In this report, we have carried out the lead stripping peaks for different concentrations with and without the presence of cadmium. It is very important in both cases how the stripping peaks are affected. Figure 11 shows the DPASV results for various concentrations of Pb alone. Excellent linear dependence was observed. Figure 12 shows the results for Pb stripping in acetate buffer in the presence of 5 μM $\text{Cd}(\text{NO}_3)_2$. During the first incremental addition of Pb (1 μM), the differential stripping peak current for 5 μM Cd decreased markedly, dropping from 10.8 μA to 6.3 μA . Further additions of Pb caused only slight additional decreases in the peak currents for Cd stripping. In the presence of 5 μM Cd^{2+} the peak currents for Pb were ca. 40% larger compared to those for Pb^{2+} in the absence of Cd^{2+} . Again, this is mainly due to the interaction between Pb and Cd, i.e., alloy formation. However, the linearity of the two curves is excellent, with the corresponding uncertainties in slopes and intercepts given in Table I. The slight decreases in the Cd peak currents with further additions are also evident for the interaction of Pb with Cd.

Figure 11. DPASV curves for the stripping of Pb from solutions containing $\text{Pb}(\text{NO}_3)_2$ in 0.2 M acetate buffer (pH = 5.0); the deposition time was 2 minutes at -1.0V vs. SCE.

Figure 12. DPASV curves for the stripping of Cd and Pb from solutions containing $\text{Pb}(\text{NO}_3)_2$ in 0.2 M acetate buffer with 5 μM $\text{Cd}(\text{NO}_3)_2$; the deposition time was 2 minutes at -1.0V vs. SCE.

Table I: Analytical parameters for the ASVDPV analysis of lead and cadmium, both alone and in the presence of each other

A. Cd Analysis

$[\text{Pb}^{2+}]$, μM	Slope, $\mu\text{A } \mu\text{M}^{-1}$	Intercept, μA	Detection limit, μM
0	2.206 ± 0.053	-0.114 ± 0.161	0.25
5	0.965 ± 0.038	-0.191 ± 0.191	0.45

B. Pb Analysis

$[\text{Cd}^{2+}]$, μM	Slope, $\mu\text{A } \mu\text{M}^{-1}$	Intercept, μA	Detection limit, μM
0	2.582 ± 0.035	-0.0594 ± 0.107	0.31
5	3.604 ± 0.126	$+0.348 \pm 0.382$	0.35

Note: uncertainties are given as one standard deviation. The detection limits are given in terms of two standard deviations.

With a new approach using 3D plots, it is now possible to carry out a quantitative analysis for a Pb-Cd mixed solution, even though there is a significant cross-interference. This can be done by means of successive approximations in the following manner. Taking the Cd stripping height peak for an unknown sample containing only Pb and Cd, a horizontal cut would be made on the 3D surface of the plot in Fig. 13A. This would give a range of possible Cd concentrations. This range would then be used to narrow down the possible range of Pb concentrations that would be obtained from the horizontal cut on the 3D surface of Fig. 13B, obtained from the Pb stripping peak height. The resulting range of Pb concentrations would then be used to narrow down the range of possible Cd concentrations. Working back and forth between the two 3D plots, a good approximation could be made for both concentrations. Of course, this procedure can be implemented mathematically in a straightforward manner. The interaction due to copper will be presented in future report.

Figure 13. Three-dimensional calibration curves for the differential pulse anodic stripping currents for A) Cd and B) Pb in acetate buffer solutions containing both metals.

SUMMARY:

The BDD sensor films have been developed in collaboration with Prof. Fujishima of the University of Tokyo. We travel to the University of Tokyo in order to further develop this electrode and optimize the film growth conditions. These BDD sensor films are grown using Microwave plasma chemical vapor deposition (MPCVD) technique. Currently, we are obtaining free standing diamond films commercially produced by Element Six Inc. We have demonstrated ppb detection of mercury in laboratory made standard solutions as well as in the real samples obtained from flue gas of a coal burning power plant. A standard addition method has been successfully used to determine the mercury concentration. In addition, preliminary results from a portable unit have also been demonstrated. The interference due to copper during the detection of lead and cadmium and the approach of 3D-calibration plots was also carried out.

FUTURE WORK:

In future, we will use our portable on-line sensor Palm Sens in combination with RDE for the analysis of real samples. We are involved in making different sizes and shapes of diamond for the application in rotating disk electrodes to achieve hydrodynamic flow of the electrolyte so that on-line monitors can be designed for optimal sensitivity. In the case of mercury, more calibration curves and analysis will be made using thiocyanate electrolyte since there is no calomel formation in this case. Impinger solution will also be made using thiocyanate electrolyte for testing.

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PUBLICATIONS/PRESENTATIONS:

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

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Establishment of the Center for Advanced Separation
Technologies (DE-FC26-01NT41091)

Period of Performance:

Starting Date: 9/17/01
Ending Date: 5/31/05

Sub-Recipient Project Title:

Evaluation of Coal Cleaning Efficiency Using
Transponder-Based Density Tracers

Report Information:

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Number: 3
Period: 10/1/02-9/30/03
Date: 10/31/03
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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 technical evaluation was performed using developer kits provided by two suppliers of commercial transponder systems. Based on these initial evaluations, a prototype system was assembled using components supplied by Texas Instruments. The original components provided in the developer kit were modified in an attempt to improve the detection distance and signal clarity. This was achieved by purchasing a high power module for the reader and a large rectangular gate-type antenna. Controlled laboratory experiments are currently underway to evaluate the capabilities of the prototype system.

INTRODUCTION

Background

Density tracers offer a rapid and low-cost method for assessing the performance of heavy medium circuits in coal preparation plants (Davis, 1987). Density tracers 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 as 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

As indicated in the last technical report, the first task in the development of this transponder based tracer program was to evaluate what was available in terms of transponder technology and how the current technology will be able to meet the requirements for this project. A detailed study was conducted to compare the capabilities of several commercially available transponder systems to determine how their operation will meet the challenges of this industrial environment. The primary factors to be considered in the evaluation of the tags will include storage capability, user programmability, transmission-receiver signal reliability, interference filtering, physical size, and mechanical durability. In addition, the costs associated with the procurement and construction of both the reader and tags will be considered prior to selecting an appropriate system. Based on this evaluation, a basic transponder system provided by Texas Instruments was selected for use in this project.

Task 2 - Transponder Procurement

A Texas Instruments TIRIS system was purchased for use in this project. The system included a reader board, an assortment of molded plastic and glass-encased tags, and a short (14 cm long) rod-type antenna. To improve signal strength and read range, a high power module was also purchased as a separate item to increase the input power to the reader module. Also, an additional set of glass-encased tags (ten 23 mm and ten 32 mm) and a larger gate antenna (101 x 41 cm) were also purchased from Texas Instruments for the prototype system.

Task 3 – Preparation of Density Tracers

This task involves the preparation of density tracers equipped with the transponder technology. For initial development work, a set of forty preprogrammed tags were encased within tracer blocks to uniquely identify both the size and density of the block. The 32 mm cubic blocks were manufactured by Partition Enterprises in Australia using twenty 23 mm and twenty 32 mm tags. These prototype blocks were used to conduct trial runs of the proposed counting system in a laboratory environment. Additional blocks will be manufactured using well defined SG increments between 1.55 and 1.75 SG for follow-up laboratory tests and final field trials.

Task 4 – Testing and Evaluation

Several series of laboratory trials were conducted using the prototype tracers. This work was performed (i) to develop a protocol

Figure 1. Photograph of transponder-based prototype tracers prepared for this project.

for how the transponders would be installed within the plastic blocks of different densities, (ii) to confirm that the plastic polymer used in manufacturing the tracers would not inhibit the transponder activation or return signal, and (iii) to determine whether the required tolerances on density could be maintained after embedding the transponders. Particular emphasis was placed on identifying factors that would optimize the read range, improve accuracy, and reduce interference during the detection of the tracer blocks (Sorrells, 2000). Several important components were successfully tests during this reporting period. These included:

RI-CTL-MB2A RS232	Control Module
RI-RFM-007B	Hi-Performance Reader Module
RI-ANT-G04E	Gate Antenna
RI-TRP-RRHP	23 mm Read Only Transponder
RI-TRP-RR2B	32 mm Read Only Transponder
RI-ACC-AT12	Antenna Tuning Indicator
IHC24-2.4	International Power 24VDC power supply

These components were installed on a platform that allowed the location of the transponders

Figure 2. Test platform constructed to establish the tag detection limits (read range).

Figure 3. Rectangular grid used to quantify detection limits and tag orientation.

Figure 4. Vertical and horizontal read range for tags placed in different orientations.

within the reader field to be accurately recorded. The reader, control module, and antenna were installed on the test apparatus (Figure 2). The transponders were placed on a graduated grid (Figure 3) so that the perimeter of the detection limits (read range) could be established. The detection limit tests were performed by placing the transponder tags in three different orientations (i.e., 0, 45 and 90 degrees). The results of these tests are summarized in Figure 4.

The data provided in Figure 4 indicate that the selected transponder tags could indeed be detected by the reader system. As shown, the tags have a maximum read range of approximately 62 cm (24.5 inches). However, the read range is strongly dependent on the orientation of the transponder tag. The 90 degree (standing) orientation provided the strongest signal when placed directly in front of the antenna. The signal diminished at the boundaries to each side of the transponder. In contrast, the 0 degree (flat) orientation provided good signals when the antenna was located to each side of the transponder, but was essentially invisible (no detection was possible) when placed directly ahead of the antenna. Therefore, this work shows that two antenna, oriented at right angles to each other, will be required to ensure that all possible orientations of the embedded transponder tags will be accurately identified as they pass by the detection point.

SUMMARY

During the past reporting period, a prototype system was assembled for detecting transponder-based density tracers using components supplied by Texas Instruments. A prototype set of tracer blocks with embedded tags were also manufactured and evaluated. This prototype system was used to evaluate the capabilities of the transponders in terms of tag type, signal clarity, and detection distance (read range). Data collected to date show that tags can be successfully placed within the density blocks and detected at ranges adequate for a commercial system. However, the data indicate that two antenna will be required for accurate detection due to orientation factors that influence the strength of the signal from the embedded tag.

FUTURE WORK

Work will continue during the next reporting period to evaluate the capabilities of prototype system. This effort will include (i) the manufacture of additional tracer blocks with embedded tags, (ii) the evaluation of the prototype system for detecting tracer blocks placed on moving conveyors and buried under different materials (i.e., beds of coal or rock particles), and (ii) the development of data acquisition, analysis, and presentation software. A variety of controlled tests will be performed in a laboratory environment to resolve issues associated with detection capabilities and limitations prior to industrial field trials. This information will be important in determining the required strength of the energizing fields and optimal locations of the reader antenna.

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PUBLICATIONS/PRESENTATIONS

The work associated with this project was presented at the 2003 Annual CAST Conference in Charleston, West Virginia, on November 19-21, 2003. The presentation, which was titled "Evaluation of Coal Cleaning Efficiency Using Density Tracers," was coauthored by G.H. Luttrell, C.J. Barbee, and R-H. Yoon.