CROSSCUTTING TECHNOLOGY DEVELOPMENT AT THE CENTER FOR ADVANCED SEPARATION TECHNOLOGIES

SEMI-ANNUAL TECHNICAL PROGRESS REPORT

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ABSTRACT

This Technical Progress Report describes progress made on the seventeen sub-projects awarded in the first year of Cooperative Agreement DE-FC26-02NT41607: Crosscutting Technology Development at 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.

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INTRODUCTION

Background

The U.S. is the largest producer of mining products in the world. In 1999, U.S. mining operations produced \$66.7 billion worth of raw materials that contributed a total of \$533 billion to the nation's wealth. Despite these contributions, the mining industry has not been well supported with research and development funds as compared to mining industries in other countries. To overcome this problem, the Center for Advanced Separation Technologies (CAST) was established to develop technologies that can be used by the U.S. mining industry to create new products, reduce production costs, and meet environmental regulations. Originally set up by Virginia Tech and West Virginia University, this endeavor has been expanded into a seven-university consortium – Virginia Tech, West Virginia University, University of Kentucky, University of Utah, Montana Tech, New Mexico Tech and University of Nevada, Reno - that is supported through U.S. DOE Cooperative Agreement No. DE-FC26-02NT41607: Crosscutting Technology Development at the Center for Advanced Separation Technologies.

Much of the research to be conducted with Cooperative Agreement funds will be longer-term, high-risk, basic research and will be carried out in five broad areas:

- Solid-solid separation
- Solid-liquid separation
- Chemical/Biological Extraction
- Modeling and Control, and
- Environmental Control.

Distribution of funds is handled via competitive solicitation of research proposals through Site Coordinators at the seven member universities. The first of these solicitations, referred to as the CAST II-Round 1 RFP, was issued on October 28, 2002. Thirty-eight proposals were received by the December 10, 2002 deadline for this RFP - eleven (11) Solid-Solid Separation, seven (7) Solid-Liquid Separation, ten (10) Chemical/Biological Extraction, six (6) Modeling & Control and four (4) Environmental Control. 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 to the DOE/NETL Project Officer for final review and approval. This process took some 7 months to complete but 17 projects (one joint) were in place at the constituent universities (three at Virginia Tech, two at West Virginia University, three at University of Kentucky, three at University of Utah, three at Montana Tech, three at New Mexico Tech, and one at the University of Nevada, Reno) by May 17, 2003. These projects are listed below by category, along with brief abstracts of their aims and objectives.

Solid-Solid Separation

Development of Novel Ultrafine Sizing Methods (Joint UK/VT Project)

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

Principal Investigators: R.Q. Honaker and BK. Parekh, University of Kentucky

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

The conventional techniques employed for sizing ultrafine particles in the coal and mineral processing industries have inherent inefficiencies that negatively impact on separation performance and production costs. In light of this problem, a broad based R&D program is proposed to investigate several innovative techniques for fine particle sizing. The processes to be evaluated will include a wide array of mechanical, hydraulic, and novel approaches for fine particle sizing. For each process, detailed tests programs will be conducted to optimize operating parameters so that maximum efficiency and capacity can be achieved while maintaining particle size cuts in the 25-50 μm size range. The resultant test data will be used to mathematically simulate different circuit arrangements for the most promising technologies. A detailed economic study will be performed for those circuits that have the greatest potential for commercialization and industrial implementation. Due to the large scope of this project, the proposed work will be conducted as a joint effort between researchers at the University of Kentucky and Virginia Tech.

Dispersion and Flotation of Clays from New Mexico Potash Ores

Principal Investigators: I. Gundiler, S. Titkov, and M. Yekeler, New Mexico Tech

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

New Mexico is the largest potash producer in the United States, supplying 70% of the domestic consumption of agricultural fertilizers. Potash mining began in the Carlsbad potash district in the early 1940s and while there are still vast reserves of potash minerals, producers are now dealing with low grade ores contaminated with clays and water-soluble magnesium minerals, which adversely affect the flotation of sylvite (KCl). Sylvite is floated from saturated brines with cationic collectors. The clays present in these brines absorb flotation reagents (thus increasing reagent costs), decrease recoveries of sylvite, contaminate the product and increase energy consumption for dewatering and drying. These clays are dispersed during grinding and/or attrition scrubbing and are then removed by hydrocyclones ahead of flotation. However, significant amounts of clay are carried over into flotation, where they are further dispersed by the mechanical action of impellers, thus hindering flotation. Furthermore, elevated brine temperatures during the summer affect collector adsorption on clays, depressing sylvite flotation. The presence of high concentrations of magnesium ions in the brine, which is peculiar to this district, also affects recoveries. These technological problems must be solved for the state potash industry to remain viable and competitive. This study will investigate means of improving clay dispersion using organic and inorganic dispersants to increase the efficiency of slimes removal in existing facilities, and will study the effects of elevated magnesium ion concentrations and elevated temperatures on the flotation of sylvite. Clay flotation, which has been shown to be superior to hydroseparators for clay removal in foreign operations, will also be investigated.

Flotation Technology for the Trona Industry

Principal Investigator: Jan D. Miller, University of Utah

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

Soda ash (Na_2CO_3) produced from the trona deposits of the Green River Basin in Wyoming by chemical treatment is valued at approximately \$800 million per annum. Existing process technologies for the production of soda ash from trona involve dissolution in hot brine, drying, sedimentation and filtration for the removal of impurities, and subsequent crystallization and calcination for the recovery of soda ash. In this regard, mining and operating costs, particularly energy costs, are higher than desired. A preferred processing strategy might be to remove gangue mineral contaminants from the plant feed prior to dissolution in hot brine. It is expected that in this way improved productivity can be achieved in addition to significant savings in energy. Such a preprocessing strategy at ambient temperature and pressure has been limited by the lack of satisfactory process technology. Now based on recent results from laboratory research at the University of Utah it seems that the run-of-mine trona ore can be treated at ambient temperature and pressure using a special flotation procedure to separate the gangue minerals and make a trona concentrate with a purity of almost 99% trona at a recovery of more than 97%. Development and utilization of this new technology will allow for energy conservation, improved resource utilization, increased productivity and the development of a new product for the marketplace. In this regard a two-year research program involving industrial participation is proposed to develop the technology and demonstrate its effectiveness at a plant site.

Flotation Processes/Experiments and Analysis

Principal Investigators: D. Telionis and P. Vlachos, Virginia Tech

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

Flotation processes involve complex, three-phase flow interactions between a liquid, air bubbles and solid particles. For decades, engineers and researchers based their calculations on algebraic formulas that model these interactions. These formulas were derived from simple models, experimental data and/or arbitrary assumptions. Considerable progress has been made but this approach is still far from providing a reliable tool for the design of flotation machines. In this project, a more rigorous approach to the analysis and modeling of the flotation process will be employed. The proposed effort will combine detailed theoretical analysis and modeling with state-of-the-art, global, multi-phase flow measurements to quantify the effects of the various hydrodynamic parameters on the flotation process. The study will employ a Digital Particle Image Velocimeter (DPIV) that can record velocity vectors of all three phases. Experiments will include the measurement of three-phase flow interactions of bubbles and model particles of different hydrophobicity with a turbulent flow field. This study will deliver global, time-resolved velocity distributions and turbulence characteristics for each phase. The modeling approach will incorporate all physical parameters that affect the collision efficiency of coal particles and flotation bubbles and the probabilities of attachment and detachment. An advanced model for predicting and quantifying the efficiency of the flotation process will be the final deliverable of this two-

year effort. Such a tool will improve the design of flotation equipment and/or enhance the performance of existing systems.

Column Flotation of Relative Coarse and Fine Dolomitic Phosphate Pebbles

Principal Investigator: Felicia F. Peng, West Virginia University

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

Dolomite in phosphate flotation concentrates is troublesome for down-stream operations. High dolomite contents cause higher consumption of sulfuric acid, reduce filtration rates and lower P_2O_5 content in the fertilizer manufacturing process. However, the separation of dolomite particles from phosphate minerals is difficult because the dolomite is finely disseminated throughout the phosphatic pebbles and both are oxide type minerals with the same cationic component. Thus, they show similar electrokinetic, adsorptive and desorptive behavior in physical separation process such as flotation. Various flotation processes have been developed in the past four decades, but none is satisfactory due to high MgO content and/or low overall P_2O_5 recovery in the final phosphate concentrate. In this research project, dolomitic phosphate pebbles from Florida will be treated by column flotation. A liberation analysis of the dolomite-phosphate matrix will be conducted to determine optimum grinding conditions; new selective mixtures of fatty acid collectors and non-ionic surfactants will be evaluated on relatively coarse (minus 300 microns) and fine (minus 150 microns) dolomite particles; appropriate mixtures of phosphoric acid/sulfuric acid will be used to depress phosphate particles; and the effect of addition of non-ionic surfactants on the separation performance will be determined. The goal is to produce a phosphate concentrate containing 30% P_2O_5 and less than 1.0% MgO contents at high P_2O_5 recoveries from low grade phosphatic pebbles stockpiled at plant sites and from pebbles generated from mining lower grade reserves.

Solid-Liquid Separation

Improving Densification of Fine Coal Refuse Slurries to Eliminate Slurry Ponds

Principal Investigators: B.K. Parekh and R.Q. Honaker, University of Kentucky

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

Increased mechanization in underground coal mining has increased the volume of refuse generated by coal preparation plants. The fine refuse slurry, composed of coal and mineral matter, is usually disposed of in a holding pond (impoundment), but incidents of impoundment breakthrough have forced the industry to look for alternative methods for fine refuse storage in the future. The main objective of the proposed program is to evaluate a new technique known as "Paste Thickening Technology," which utilizes a Dorr-Oliver EIMCO Deep Cone Thickener to discharge the waste slurry as a paste. The paste material should be stackable at low repose angles and would dry over a period of time, thus avoiding the storage of slurries in ponds. The proposed study will be conducted on coal waste slurries obtained from two different preparation plants. Laboratory studies will involve the characterization of the slurries, bench-scale flocculation studies and rheological analysis of the flocculated

materials to identify yield stresses at various solid concentrations. This information will be used to establish optimum conditions for the production of a thickened paste product. A pilot-scale study will then be conducted at one of the coal preparation sites to obtain technical and economic data for a commercial installation and operation. It is anticipated that the outcome of the study will be an effective and economical process for the safe disposal of fine coal refuse.

Development and Testing of a Horizontal Pressure Belt Filter

Principal Investigators: R.-H. Yoon & G.H. Luttrell, Virginia Tech

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

A variety of mechanical processes are available for dewatering fine particles in the coal and mineral processing industries. Unfortunately, many of these processes suffer from major shortcomings such as poor dewatering performance, low throughput capacity, and high capital and operating costs. This project seeks to overcome these problems by developing a new type of dewatering process that combines the operational flexibility of a continuous belt filter with the dewatering efficiency of a batch pressure filter. The proposed project involves the design, construction, testing, and evaluation of a prototype unit and pilot-scale test circuit having a production capacity of approximately 100 lb/hr. Test data obtained from the project will be used to promote the engineering development of a full-scale commercial unit.

Chemical/Biological Extraction

Bio-Assisted Heap Leaching of Nickel Laterites for the Development of a Domestic Nickel Industry

Principal Investigator: S. Duyvesteyn, University of Utah

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

The U.S. currently imports all of its nickel, which is a strategic material used in stainless steels and other corrosion-resistant materials. Existing U.S. resources are worth around \$10 billion at current metal prices, but occur mostly in low-grade laterite deposits, for which conventional hydrometallurgical processes are not economically feasible production routes. These processes typically utilize mineral acids that cannot be recycled economically and can cause significant environmental problems. The solubilization of metal ions from ores by organic acids produced by microorganisms has been demonstrated to be a viable alternative for metal production with reduced environmental and remediation issues, as organic acids are readily biodegradable. The fact that many of these organic acids and other metabolites form strong chelating complexes with the base metal ions also results in a reduction in the acid requirements to achieve complete solubilization. This research proposal involves a biotechnological approach, called bio-assisted heap leaching (BAHL), for the production of nickel metal from low-grade ore synergistically with the co-production of citric acid. The BAHL process can be described as follows: laterite nickel ore is combined with an organic nutrient and put on heaps where fungi, such as *Aspergillus niger*, produce organic acids during their natural metabolic cycle. Recycle solution is sprayed over the heaps and its

percolation through the heaps results in the dissolution of nickel. The resulting nickel-containing leach solution is collected and the nickel and citrate values are recovered.

The Development and Utilization of Alkaline Sulfide Leaching and Recovery of Gold

Principal Investigator: C. Anderson and L.G. Twidwell, Montana Tech

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

Due to the increasing concerns over the emission of sulfur dioxide from roasting and smelting, there has been an increased interest in pressure oxidation as a means of treating gold bearing ores and concentrates. One of the problems with the partial oxidation of the sulfide host matrix to form elemental sulfur is that sulfur containing streams are difficult to treat using cyanidation. In the present study, the alkaline sulfide system will be studied as an alternative to cyanide for recovering gold from elemental sulfur. A complete thermodynamic model of the alkaline sulfide gold leaching system will be developed using Stab-Cal software and the leaching system and its kinetics will be optimized.

Hydrometallurgical Processing of Chalcopyrite Concentrates

Principal Investigator: M. Misra and M. Fuerstenau, University of Nevada, Reno

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

Hydrometallurgical processing of chalcopyrite at moderate temperature and pressure has been a goal of the copper industry for decades. Research has shown that a protective sulfur layer forms on chalcopyrite when leached with ferric salts in acidic medium. This layer limits the transport of electrons from the mineral surface to the oxidant and precludes the use of this technology for chalcopyrite processing. Research at the University of Nevada, Reno has shown that the introduction of finely-divided silica improves the kinetics of leaching dramatically. Silica adsorbs on the surface of chalcopyrite, and since it is an n-type conductor, conduction of electrons from the mineral surface to the oxidant occurs by photocatalysis of the sulfur product layer. Dissolution amounts of as much as 80% have been achieved under the limited conditions examined, namely at atmospheric pressure and 50°C.

Simultaneous Electrolysis of Copper and Ferrous Ions to Produce Copper Cathode and to Regenerate Ferric Sulfate - The Lixiviant to Dissolve Copper Sulfide Minerals

Principal Investigator: C. Young, H.-H. Huang and C. Fabian, Montana Tech

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

Copper leaching is primarily conducted on oxidized ore bodies at low pH by using sulfuric acid (H_2SO_4). The sulfate acts as the lixiviant to solubilize the copper as copper sulfate (CuSO_4). An oxidant is also needed to enhance reaction rates – typically this is dissolved oxygen (O_2) and/or ferric (Fe^{3+}) ion. The dissolved copper must then be extracted from the water to separate it from other dissolved constituents including iron. Traditional solvent extraction and electrowinning (SX/EW) procedures do this and ultimately yield quality copper cathode as product. After SX/EW, leach solution is recycled to the leaching

process and replenished with oxidant as needed. For example, biological activity can regenerate ferric ions or mechanical agitation can produce dissolved oxygen (which in turn can regenerate ferric ions). Ferric ions can also be regenerated electrolytically and simultaneously to copper cathode production. This is the basis of the proposed research. To accomplish this, a porous membrane will be used to keep the anode and cathode compartments separated and modern rotating cylinder electrodes will be used to stir solutions, obtain high current densities and ultimately produce superior grade copper cathode. Although it is possible to avoid the SX step, it will be used to produce two streams: raffinate, which will go to the anode compartment where ferric is regenerated, and pregnant or advance solution, which will go to the cathode compartment where copper metal is produced. Various chemicals and additives may have to be added to control copper cathode formation and thereby avoid, for example, dendritic growth. Preliminary cost analyses show that copper can be produced for approximately \$0.30/lb with this new, more energy efficient, technique.

Ion Exchange Recovery of Cobalt from Copper Leach Solutions

Principal Investigator: I. Gundiler and M. Hatch, New Mexico Tech

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

Cobalt is a strategic and critical metal which is used in production of super alloys for use in jet engine turbines, wear and corrosion resistant alloys, cutting tools, magnets and various other alloys and chemicals. It is not mined or refined in the United States; therefore, 80% of the cobalt consumed in the U.S. is imported. The remaining balance is met with recycled alloys and supplies from stockpiles. Although there is historical production and known reserves, these are not economical to exploit at the present. However, there is a readily available source of cobalt in the leach solutions generated in large copper mining operations in the Southwestern U.S. If only a fraction of this cobalt could be recovered, New Mexico and Eastern Arizona copper leach operations could potentially supply 20% of U.S. imports. Currently, the technology to recover the metal from these solutions economically is not available. Ion exchange processes could recover this cobalt. However, commercially available resins are either too expensive, or do not function in acidic solutions. Absorption kinetics of these resins are also fairly slow. Three new resins will be synthesized at New Mexico Tech for copper and cobalt recovery from acidic solutions. The resins will be characterized and tested in the laboratory using pure chemicals, as well as process solutions to be obtained from the Phelps Dodge Mining Company, New Mexico operations. The performance of the synthesized resins will also be compared with that of commercially available resins.

The Effect of Diphenyl Oxide Surfactants on Nucleation and Growth of Potassium Sulfate Crystals: Development of Enhanced Surfactants for the Potash Industry

Principal Investigator: G. Bond and C. Hockensmith, New Mexico Tech

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

Surfactant-controlled crystallization leads to an increase in the efficiency of potassium sulfate production, particularly when alkyl diphenyl oxide-type (ADO) surfactants are employed in synthesis. Improved control of crystallization in both the initiation and termination phases can increase the ratio of granular particles to fines, decreasing costs associated with production and facilitating the utilization of lower-grade ores. Mother liquors in potash extraction contain high percentages of magnesium as well as other ions including chloride and impurities such as clay and silica. Potassium sulfate crystals will be produced in the presence of different ADO surfactants, and evaluated by SEM, TEM, XRD, FTIR and AFM. Crystallization processes, particularly those that affect crystal morphology, size, initiation and termination, will be studied in relation to the surfactant effect. This information will be used to improve control of potassium sulfate precipitation and develop the next generation of surfactants to facilitate extraction of granular potassium sulfate.

Modeling and Control

Online Monitoring and Diagnosing of Coal Fines During Separation Process

Principal Investigator: B.S. Kang and E.K. Johnson, West Virginia University

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

The goal of this research program is to develop an on-line, non-contact, elemental analysis of coal fines during solid-solid separation process through the use of Laser-Induced Breakdown Spectroscopy (LIBS). Of particular interest is the detection and quantitative measurement of the amount of carbon, sulfur, mercury, and other trace elements in the separated coal fines. The proposed experimental technique will be applied to a circulating fluidized bed (CFB) riser system for determination of coal fines separation efficiency as well as optimization of the separation process variables using a fuzzy logic control approach.

Development of a Novel Optical Radiation Depolarization Technique for On-Line Measurements of Particle and Bubble Sizes

Principal Investigators: D. Tao, M.P. Menguc and C. Crofcheck, University of Kentucky

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

Grinding and froth flotation are the two most important processes for mineral beneficiation. The importance of grinding is well reflected in the fact that approximately 80% of beneficiation costs are for grinding, mainly due to high energy consumption. To reduce energy consumed by grinding, fines should be removed quickly from the grinding circuit. This requires a reliable on-line particle size analysis technique. Similarly, froth flotation is the most widely used solid-solid separation process for coal and minerals beneficiation and about 90% of mineral concentrates are produced by froth flotation. Air bubble size distribution plays an important role in flotation separation performance but optimization of bubble size distributions will only be possible if bubble size can be monitored on-line. The proposed project is aimed at developing an optical radiation depolarization technique for on-line size measurement of particle sizes in grinding and bubble sizes in flotation. The technique is based on the analysis of angular and radial profiles of reflection and

transmittance of an object subjected to a collimated, polarized light beam. A hybrid Monte Carlo/Ray Tracing method will be used to simulate the depolarization of radiation by particles or air bubbles and size distributions will be determined by best fitting experimentally determined vertical and horizontal polarization components of the radial and angular profiles of reflection and transmission. The proposed technique should also be able to determine water film thicknesses and bubble separation distance distributions in foams.

Environmental Control

Electrolytic Solution Purification and Metal Recovery from Metal-Bearing Toxic Waste Streams

Principal Investigator: Michael L. Free, University of Utah

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

Industry creates numerous waste streams, many of which contain dissolved metal ions that must be removed to preserve the environment. Many of these waste streams can be created by natural processes that are accelerated by industry such as acid mine drainage, made as byproducts of chemical processing such as metal extraction, or as the result of manufacturing processes such as electronic component manufacturing. Often such wastes are complex and involve multiple metal ions. Regardless of the waste origin, toxic metal ions must be removed. In the proposed project a novel method of removing multiple toxic metals from aqueous media by selective pulse-plating with high surface area electrodes will be evaluated and developed in a manner that will allow the metals to be recovered individually as purified metals in an environmentally sound way. The direct production of metal as a byproduct, rather than as a toxic waste, will contribute to better resource utilization as well as a reduction in toxic waste generation.

Determining the Effectiveness of Gold Filters for Removing Mercury from Coal Fired Power Plants

Principal Investigator: K. Ganesan, Montana Tech

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

Because the US EPA is planning to regulate mercury emissions from power plants, there is a clear need to develop devices that can cost effectively remove mercury from power plant flue gases. Most current research has focused on transferring mercury from the air stream to fly ash or converting elemental mercury to divalent mercury to absorb it in wet scrubbers. However, when low chlorine content coal is combusted most of the mercury in the flue gas exists as elemental mercury, which is very hard to remove. Thus, to comply with the potential 90% mercury reduction proposed by EPA, one must oxidize the elemental mercury to either mercuric chloride or oxide as a way to collect particulates. In either case, mercury is merely converted to a form that is also difficult and expensive to recover. Therefore, it appears that directly removing mercury from the flue gas will be the most cost effective and environmentally friendly approach. This proposal is focused on removing elemental mercury from flue gas using gold filters. The main objective of this research is to evaluate the

effectiveness of gold wire mesh in removing mercury vapor from flue gas. A wire mesh made of thin (<0.1 mm diameter) gold wires will be tested in the laboratory, initially with a synthetic gas stream containing mercury vapor in the range of $1\text{--}300\text{ }\mu\text{g}/\text{m}^3$. Similar tests will be conducted in combustion gases by burning six types of western and eastern coals. The study will be conducted for six concentration levels of mercury; 5, 10, 25, 50, 100 and $300\text{ }\mu\text{g}/\text{m}^3$.

EXPERIMENTAL

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

RESULTS AND DISCUSSION

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

CONCLUSIONS

The initial RFP for this project resulted in seventeen (17) sub-projects being funded in early May, 2003. A six-month Progress Report (covering the period October 1, 2003-March 31, 2004) was generated for each of these sub-projects and has been attached to this Document as an Appendix. A brief summary of progress during the second 6 months, along with plans for the future on each of the sub-projects is given below.

Solid-Solid Separation

Development of Novel Ultrafine Sizing Methods (Joint UK/VT Project)

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

Principal Investigators: R.Q. Honaker and B.K. Parekh, University of Kentucky

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

Project work was initiated during the past reporting period to investigate a variety of new techniques for high efficiency sizing of ultrafine particles. Much of the work conducted to date focused on improving the performance of classifying cyclone circuits by modifying slurry rheology. The test work indicates that the addition of viscosity modifiers into the hydrocyclone feed reduces the particle cut size and improves classification efficiency. Construction work was also performed to complete the fabrication and assembly of a full-scale test circuit for evaluating a new water injection apex system. If successful, this technology will reduce the bypass of ultrafines to the hydrocyclone underflow while maintaining a very fine particle cut size.

Dispersion and Flotation of Clays from New Mexico Potash Ores

Principal Investigators: I. Gundiler, S. Titkov, and M. Yekeler, New Mexico Tech

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

Potash ore samples and flotation reagents were collected from the operating plants in the Carlsbad potash district. Brine preparation, slimes dispersion and decantation, rod mill grinding, and flotation test procedures were established. Procedures for K₂O analysis in ore samples, concentrates, tailings, and brines, as well as IR determinations were also established. A high level of competence in analytical methods was achieved by the use of reference material and cross checking results with plant operations. Slimes dispersion tests with or without added dispersants, and slimes flotation tests were carried out with low, medium, and high clay ores samples, in duplicates or triplicates when necessary. The efficacy of slimes removal tests were verified by IR analyses of the products, as well as ensuing potash flotation test results. The positive effects of added dispersants in the hydro-mechanical desliming and potash flotation, and flotation desliming of medium and high clay ores have also been demonstrated at the IMC plant laboratories in collaboration with the plant personnel. These results will be presented in the final report.

Flotation Technology for the Trona Industry

Principal Investigator: Jan D. Miller, University of Utah

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

In the second budget period, the development of the new process technology for the separation of the gangue minerals and for production of a trona concentrate with very high purity and recovery rate continued in three directions. Fundamental surface chemistry studies by contact angle measurements and sum frequency spectroscopy confirmed our previous conclusions that sodium carbonate is a water structure maker while sodium bicarbonate is a water structure breaker. New bench scale flotation experiments with four different brines (trona saturated solution, mine water, synthetic sodium carbonate solution, and sodium carbonate solution from the plant) demonstrated that trona saturated solution is most effective for the trona flotation process. The saturated mine water may also be used for flotation instead of trona brine since it gives a good recovery of trona. Preparation for the evaluation of flotation parameters and optimum conditions for testing at the General Chemical plant site in the summer of 2004 was accomplished. Working with industrial partners Roberts & Schaefer Inc., EIMCO, and General Chemical, a flowsheet outlining the process technology has been developed and includes all major items of equipment and all relevant flows.

Flotation Processes/Experiments and Analysis

Principal Investigators: D. Telionis and P. Vlachos, Virginia Tech

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

Homogeneous Isotropic turbulence was created in the model flotation cell through grid turbulence. The turbulent dissipation rate was measured using a cross correlation based Particle Image Velocimeter. Particle Tracking Velocimetry was used to determine the velocity fluctuations of the solid particles relative to the fluid phase. RMS velocities of the particles were calculated and compared to experimental and theoretical models that are based on the dissipation rate. The particle RMS was in good agreement Shubert's model, having an average RMS velocity of about 13% of the free stream velocity in the fully developed region. A theoretical model, derived first by Levins and Glastonbury was found to underpredict the particle RMS. The bubble RMS was about 26% of the free stream in the homogeneous isotropic region, 100% greater than the particle RMS and not consistent with the model predictions. Good progress has been made on completing Task 1. However, it may be necessary to repeat some of the measurements, focusing the work towards more data for Task 2. In a few months, work will begin on Task 3, which will require devising an experimental method to estimate collision rates. A model flotation machine that will be required to carry out work on Task 4 has already been designed. Parts for the construction of the machine have been ordered.

Column Flotation of Relative Coarse and Fine Dolomitic Phosphate Pebbles

Principal Investigator: Felicia F. Peng, West Virginia University

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

Dolomitic phosphate pebble samples were obtained from IMC Phosphates. Size analyses and component analyses for each size fraction have been determined. However, efforts to establish major component concentrations in the dolomitic phosphate pebble sample were complicated by problems with the determination of phosphate content of the dolomitic phosphate pebble samples using the NRCCE Analytical Laboratory's Lachat QuickChem 8000-FIA Analyzer. Items necessary for the determination of phosphate content in dolomitic phosphate pebble samples have now been ordered. A new collector has been obtained from IMC Phosphate. Reagents will be tested in a stirred-tank batch cell. The results will be used to estimate optimum operating conditions for column flotation. The flotation column has been set-up and its bubble generation system is being modified for relatively coarser dolomitic flotation from dolomitic phosphate pebble samples. Literature on the mechanisms of phosphate flotation and the behavior of carbonates is being reviewed. The mechanisms of phosphate depression and the behavior of carbonates in acid solution have also been examined.

Solid-Liquid Separation

Improving Densification of Fine Coal Refuse Slurries to Eliminate Slurry Ponds

Principal Investigators: B.K. Parekh and R.Q. Honaker, University of Kentucky

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

During this reporting period, characterization, flocculation and settling studies were conducted on the fine waste slurry obtained from the Coal Clean Corp. preparation plant, located in Dry Branch, West Virginia. The Coal Clean Corp. plant samples of thickener underflow and the screen bowl centrifuge drain samples contained about 25% and 20% solids, respectively. The pH of both slurries was around 7. The average particle size of the thickener UF and the centrifuge samples was 9.14 and 29.54 microns, respectively. The laboratory study indicated that the thickener underflow (UF) could be thickened to 48% solids using 31 g/t of anionic and 31 g/t of the cationic flocculant. Similarly, using 15 g/t of anionic flocculant the screen bowl centrifuge drain slurry could be thickened to 58.5% solids. Settling flux of the thickener UF after adding 30 g/t of anionic and 30 g/t of cationic flocculants was 32 t/day/m², whereas for the centrifuge slurry the settling flux using only 20 g/t of anionic flocculant was 99 t/day/m². The pilot-scale study at the plant showed that the thickener UF could be thickened to about 40% solids. Additional tests are planned to utilize the slurry flocculated by the Coal Clean Corp. for dewatering using the belt filter press at the plant to obtain a comparative test result. Plans are also underway to start the characterization and laboratory flocculation and settling studies on the James River Coal and the Arch of West Virginia samples.

Development and Testing of a Horizontal Pressure Belt Filter

Principal Investigators: R.-H. Yoon & G.H. Luttrell, Virginia Tech

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

The proposed project involves the design, construction, testing, and evaluation of a horizontal belt pressure filter. The prototype unit will be evaluated in a pilot-scale test program at a design capacity of approximately 100 lb/hr of dry product. Work completed during this reporting period focused on (i) development of a spreadsheet based simulation program to assist in the design of the new filter technology and (ii) completion of engineering blueprints for the fabrication of the prototype unit. As a result of these efforts, the basic layout for the prototype horizontal belt pressure filter has been completed. The prototype has been designed with a 2 inch wide by 6 ft long carrying belt. This width provides the required throughput capacity of 100 lb/hr when operated at a belt speed of 5.5 ft/min and 0.5 inch cake thickness. Work to be completed during the next reporting period will primarily involve the procurement of materials and other components required to complete the construction of the horizontal belt pressure filter. This effort was delayed during the past reporting period due to problems associated with machine shop. The fabrication and machine work is expected to require approximately four months to successfully complete. Once the construction is completed, initial testing and evaluation of the prototype unit will begin. Test data obtained from the project will be used to promote the engineering development of a full-scale commercial unit.

Chemical/Biological Extraction

Bio-Assisted Heap Leaching of Nickel Laterites for the Development of a Domestic Nickel Industry

Principal Investigator: S. Duyvesteyn, University of Utah

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

This research proposal involves a biotechnological approach for the production of nickel metal from low-grade laterite ore in a synergistic mode with co-production of citric acid called bio-assisted heap leaching (BAHL). During this reporting period, viable microorganism colonies have been established. It has been demonstrated that they can effectively leaching nickel from two different types of laterite ores. Protocols continue to be developed for acclimating the microorganisms, chemical analyses and leaching. The scoping tests that are currently underway will help fine-tune the required experimental program. While the use of microorganisms to leach lateritic ores has been studied, the literature lacks sufficient data for comparison of the effectiveness of the different types of organic media. A critical issue will be to determine which organic media is the most effective not only in terms of citric acid production, but in terms of nickel dissolution, as different organic sources may have an influence on the types of organic acids and metabolites that are produced. Different subcultures will be allowed to ferment with different growth media. The resulting broths will be used in shake flask studies to better understand the role nutrients play in the process. Studies have shown that leaching the laterite ores with fungally-produced organic acids achieved higher dissolutions than with similar concentrations of commercial organic acids. It

has been suggested that the fungi may be producing other metabolites in small quantities that aid in the solubilization of the nickel. It may also be possible that even under the same conditions, in the presence of the nickel ore, the fungi produce more acid metabolites than when no ore is present. As a result, the shake flask studies will also be undertaken with the direct addition of the microorganisms and nutrients.

The Development and Utilization of Alkaline Sulfide Leaching and Recovery of Gold

Principal Investigator: C. Anderson and L.G. Twidwell, Montana Tech

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

The objectives of this project are (i) to develop a thermodynamic model of the alkaline sulfide leaching system, (ii) to optimize the chemistry of the alkaline sulfide gold leaching process, and (iii) to study the optimized leaching system kinetics. Significant advancements were made during this reporting period in all three of these areas. Specifically, thermodynamic modeling in the form of Eh-pH diagrams was performed. Various components and concentrations were examined to determine their potential effect on the ability of the alkaline sulfide lixiviant to leach gold. Optimization of the alkaline sulfide lixiviant chemistry was performed initially by using factorial design to determine the reagents that had a significant effect on the amount of gold leached. Based on the factorial design results, mixture models were constructed by performing statistically designed experiments to optimize the individual components in the alkaline sulfide lixiviant. Preliminary data characterizing the gold leaching kinetics of the alkaline sulfide leaching process were collected. Plots of the gold concentration plotted as function of time exhibited a linear relationship. However, it was found significant variations in the kinetics resulted from relatively small changes in the lixiviant chemistry. Thus, further characterization of the kinetics will be performed once the lixiviant chemistry has been optimized. Additional significant results were included that highlighted some of the technical achievements accomplished and demonstrated the feasibility of the process aspects that will be characterized during the next reporting period.

Hydrometallurgical Processing of Chalcopyrite Concentrates

Principal Investigator: M. Misra and M. Fuerstenau, University of Nevada, Reno

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

The effect of nanosize particles of silica in chalcopyrite leaching systems is being studied with two techniques. These are (i) leaching experiments as a function of various leaching parameters and (ii) electrochemical impedance spectroscopy (EIS). The leaching experiments are presented to show the important effect of the presence of nanosize silica. Initial electrochemical impedance spectroscopic experiments conducted during this reporting period show that the sulfur layer that forms on chalcopyrite on leaching first increases in thickness with time and then decreases in thickness in the presence of nanosilica. When chalcopyrite is leached with oxidants in acidic medium, a layer of sulfur forms on the chalcopyrite surface which inhibits dissolution, In the presence of nanosize silica, this protective layer of sulfur is not formed, and leaching can be effected at moderate temperature

and pressure. During the next reporting period, leaching experiments will be continued as a function of chalcopyrite particle size, temperature, oxidant concentration, silica concentration and degree of agitation to establish the reaction kinetics. In addition, electrochemical impedance spectroscopic measurements will be continued to establish impedance, conductivity and electrochemical parameters and compared with leaching data to determine the nature of silica catalyzed leaching of chalcopyrite.

Simultaneous Electrolysis of Copper and Ferrous Ions to Produce Copper Cathode and to Regenerate Ferric Sulfate - The Lixiviant to Dissolve Copper Sulfide Minerals

Principal Investigator: C. Young, H.-H. Huang and C. Fabian, Montana Tech

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

The objective of this project is to develop an electrolytic cell divided into two compartments with an ion exchange membrane to allow the simultaneous regeneration of ferric ions and recovery of metallic copper (Year 1) and develop an optimized leaching and electrowinning process for the recovery of copper from copper sulfide minerals (Year 2). During this reporting period, progress was made on all of the tasks detailed in the original proposal for the first seven months. The literature search began during the first reporting period was continued culminating in the gathering of several applicable papers pertinent to this project. Tafel plots were generated for several different solutions utilizing 316L stainless steel, copper, and lead electrodes to gain an understanding of the copper reduction and iron oxidation dynamics with different electrode materials. These electrode materials were chosen in order to mimic the current materials used in industry. By far the most important achievement this reporting period was the design, construction and testing of a membrane separated electrolytic cell. A current efficiency of 91% was measured in the catholyte compartment of the membrane separated electrolytic cell. Although the design proved to be effective for electrowinning copper and oxidizing ferrous ions to ferric ions, a second cell was designed and built based on data gathered from the first cell design. In addition to the research work completed, a proposal for leaching copper and demonstrating the membrane separated electrolytic cell was submitted to Montana Resources, a local copper mine. Research work for the next reporting period will include construction and testing of (i) membrane separated electrolytic cells with advanced designs and (ii) a counter current copper leaching circuit.

Ion Exchange Recovery of Cobalt from Copper Leach Solutions

Principal Investigator: I. Gundiler and M. Hatch, New Mexico Tech

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

The objectives of this project are the synthesis and evaluation of new types of chelating ion exchange resins which could potentially be lower priced than the picolyamine resins, and be effective in absorbing Cu^{2+} and Co^{2+} from pH-1.5 to pH-1.3 solvent extraction raffinate of copper leach solutions. In search of new resins to recover copper and cobalt from highly acidic, dilute solutions, small quantities of two new chelating resins (i.e., a low-crosslinked, gel-type thio-succinate resin and carboxymethylated diethylenetriamine resins)

were synthesized and evaluated. Small-scale equilibration tests were made with acidic (H_2SO_4) solutions containing Cu, Co, and Fe (III) ions. Comparison tests were also made with commercially available, low-crosslinked, gel type iminodiacetic acid, and highly crosslinked macro-porous hydroxypropyl picolylamine resin. The results indicate that both the thiosuccinate and iminodiacetic acid resins were considerably less effective in absorbing Cu^{2+} from acidic solutions than the picolylamine resin. The carboxymethylated diethylenetriamine resin, on the other hand, had copper absorption capacity comparable to, and cobalt absorption capacity, although feeble, better than that of the picolylamine resin. Ferric ion absorption on carboxymethylated diethylenetriamine, however, was much higher than the picolylamine resin in acidic solutions. Further laboratory development work will be on the synthesis of larger quantities of carboxymethylated diethylenetriamine resin for characterization of loading capacity as a function of pH, absorption and desorption kinetics, and selectivity for copper and cobalt ions in the presence of ferric, ferrous, zinc, and nickel ions.

The Effect of Diphenyl Oxide Surfactants on Nucleation and Growth of Potassium Sulfate Crystals: Development of Enhanced Surfactants for the Potash Industry

Principal Investigator: G. Bond and C. Hockensmith, New Mexico Tech

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

During this reporting period, an MSMPR crystallizer has been built and is being used to grow potassium sulfate crystals. Crystal growth rates and sizes, and crystal habits have been evaluated by atomic absorption and scanning electron microscopy. Surfactants have been added with the goal of producing a modest inhibition of nucleation, and hence shifting the crystal size distribution, in order to increase the ratio of granular particles to fines, and thus decrease the costs associated with industrial production of potassium sulfate. Five alkyl diphenyl oxide (ADO) surfactants provided by Pilot Chemical Company have been tested to date. Surfactants are either linear-chain or branched-chain disulfonates or sulfonic acids with varying active percentages of free acids. Results have shown that the linear-chain surfactants with the highest active percentage of free acid perform best, and also that sulfonic-acid surfactants perform much better than disulfonates. The focus now is on the design and selection of additional surfactants for testing in the next phase of the experiments.

Modeling and Control

Online Monitoring and Diagnosing of Coal Fines During Separation Process

Principal Investigator: B.S. Kang and E.K. Johnson, West Virginia University

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

The goal of this research program is to develop an on-line, non-contact, elemental analysis of coal fines during solid-solid separation process through the use of Laser-Induced Breakdown Spectroscopy (LIBS). Of particular interest is the detection and quantitative measurement of the amount of carbon, sulfur, mercury, and other trace elements in the separated coal fines. During this reporting period, a model that would allow for 1 ppb

sensitivity to mercury in coal was developed and an optical system is being designed that will allow optimization of light spectrum collection efficiency. In addition, several hundred LIBS sparks were taken on various samples of coal, iron, and ash. All of the spectra showed black body radiation from the spark due to the fact that there was no time delay. These spectra can be normalized if the spark temperature can be determined. This observation led to consideration of adding time-delayed resolution to the experiment. Construction of the instrument is expected to begin during the next reporting period. The laser and spectrograph are being loaned from NETL in Morgantown, WV, while the CCD detector, lenses and scanning mirror are being selected/procured. A method of controlling the timing of the laser pulse and the scanning mirror will also be developed during the equipment setup phase.

Development of a Novel Optical Radiation Depolarization Technique for On-Line Measurements of Particle and Bubble Sizes

Principal Investigators: D. Tao, M.P. Menguc and C. Crofcheck, University of Kentucky
Period of Performance: May 1, 2003-May 31, 2005 (2-Year Project)

The overall objective of the proposed research program is to develop a sensor for on-line real-time size analysis of grinding and flotation processes. To this end, a novel approach for measuring two major characteristics (bubble size and gas hold-up) of two phase column was developed using elliptically polarized light scattering (EPLS). Experiments conducted during this reporting period showed that the EPLS concept works to measure two characteristic from scattering matrix elements of GL phase medium. Experiments show that some scattering matrix elements are sensitive to bubble size distribution parameters (mean bubble size, flow rate and gas hold-up). The scattering-matrix elements can be correlated with mean-bubble diameter and gas hold-up for known surfactant concentration even at high surfactant concentrations and high gas velocities. During the next reporting period, several additional tasks will be undertaken. These will include (i) utilization of the Monte-Carlo algorithm to study the influence of various parameters on light scattering within the two-phase medium, (ii) assembly of the prototype on-line EPLS system for industrial size columns, (iii), initiation of EPLS for three-phase (GLS) medium experiments to establish optimum sensor orientations for lab-size froth flotation columns, and (iv) determination of optimum sensor angles will be obtained for three-phase flow systems.

Environmental Control

Electrolytic Solution Purification and Metal Recovery from Metal-Bearing Toxic Waste Streams

Principal Investigator: Michael L. Free, University of Utah
Period of Performance: May 1, 2003-May 31, 2004 (1-Year Project)

Pulse plating with high surface area electrodes is an effective way to remove metal ions from aqueous medium, and an effective way to recover metals individually in a more purified form. This method has demonstrated utility in removing lead, mercury, and copper from aqueous medium, and should be useful in removing additional ions as well. During the

past reporting period, research effort associated with this project concentrated on improving the efficiency of the electrode apparatus in order to decrease the amount of time and energy required to remove metal ions from aqueous medium. Future work will center on improving the ability to separate metal ions into pure products by electrolytic recovery, as well as improving the ability to reduce the residual metal concentration of the solutions to much lower levels. To accomplish these goals a further understanding of the variables at work in this process will be pursued.

Determining the Effectiveness of Gold Filters for Removing Mercury from Coal Fired Power Plants

Principal Investigator: K. Ganesan, Montana Tech

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

This overall goal of this research project is to develop a gold filter for the efficient removal of elemental mercury from coal fired flue gas. During the past reporting period, the effectiveness of gold wire mesh in removing mercury vapor from flue gas was evaluated. A copper sponge electroplated with gold was tested with a gas stream containing mercury in the laboratory. The preliminary results indicate that the mercury removal efficiency of the sponge is about 80-90%. Tests are also in progress with silver electroplated copper and stainless steel sponges. The spent gold plated sponge was then heated gently to recover the mercury. Over 99% of the mercury was recovered from the filter by heating the filter to about 100° F. Tests conducted during the next reporting period will focus on the development of a relationship between the temperature and mercury release rate from the spent filters. The mercury removal tests will be performed with three new silver and gold filters. Based on these results, tests will be performed using flue gas generated in the lab or the filters will be taken to a coal fired power plant and tested in the field for their performance.

REFERENCES

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

APPENDIX

This appendix contains copies of the Technical Progress Reports that were submitted by the participating universities in accordance with the project reporting requirements established by CAST.

Appendix A: Development of Novel Ultrafine Sizing Methods

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 4/01/03 Ending Date: 5/30/04
<u>Sub-Recipient Project Title:</u> Development Of Novel Ultrafine Sizing Methods	<u>Report Information:</u> Type: Semi- Annual Number: 2 Period: 10/1/03-3/31/04 Date: 5/9/04 Code: VA008
<u>Principal Investigators:</u> Roe-Hoan Yoon and Gerald H. Luttrell	
<u>Contact Address:</u> 146 Holden Hall Virginia Tech, Blacksburg, VA 24061	<u>Contact Information:</u> Phone: (540) 231-4508 Fax: (540) 231-3948 E-Mail: ryoona@vt.edu
<u>Subcontractor Address:</u> No subcontracts issued.	<u>Subcontractor Information:</u> Phone: Fax: E-Mail:

ABSTRACT

The objective of this project is to develop new and improved methods for fine particle sizing. The processes evaluated in this work include a wide variety of mechanical, hydraulic, and novel approaches. For each process, experimental test programs have been undertaken to optimize operating parameters so that maximum efficiency and throughput capacity can be achieved while maintaining particle size cuts in the 25-50 μm size range. The resultant test data has been used to mathematically simulate different circuit arrangements for the most promising technologies. Due to the large scope of this project, the proposed work has been carried out as a joint effort between researchers at the University of Kentucky and Virginia Tech. During this reporting period, a test program was conducted to evaluate the impact of slurry rheology on classification performance. The slurry rheology was controlled by the addition of viscosity reducing agents into the feed stream to a 4-inch diameter classifying cyclone. The test results indicate that viscosity reduction provides lower particle size cut point and improved classification efficiency. Work was also initiated to assemble a 6-inch diameter hydrocyclone test circuit that can be used to evaluate a new apex washing technology for reducing the bypass of ultrafine material to the hydrocyclone underflow.

INTRODUCTION

Background

Most mineral and coal processing plants are forced to size their particulate streams in order to maximize the efficiency of their unit operations. These sizing techniques commonly include various types of screens and classifiers. Screens exploit differences in the physical dimensions of particles by allowing fines to pass through a perforated plate or open mesh while coarser solids are retained. Unfortunately, screening systems are generally limited to particle size separations coarser than approximately 250 μm due to limitations associated with capacity and blinding. Hydraulic classifiers are generally employed for finer size separations, including both static and centrifugal devices. Hydraulic classifiers exploit differences in the settling rates of particles and are influenced by factors such as particle shape and density as well as particle size. Classifiers are generally considered to be more practical than screens for fine sizing, but the separation efficiency decreases dramatically for particles smaller than approximately 150 μm (Heiskanen, 1993). In addition, classifiers commonly suffer from bypass, which occurs when a portion of the ultrafine particles (slimes) are misplaced by hydraulic carryover into the oversize product. The unwanted misplacement can have a large adverse impact on downstream separation processes.

Objective and Approach

The development of efficient techniques for fine particle sizing is widely considered to be a high research priority by both the mineral processing and coal preparation industries. In particular, the development of new screening and classification technologies, or improvements on existing technologies, is needed to overcome the current shortcoming of existing processes for fine particle sizing. Therefore, the primary objective of this project is to develop a broad base of new sizing equipment or techniques that can be used to efficiently size ultrafine particles. Processes to be evaluated in the proposed work will include a wide array of mechanical, hydraulic, and novel approaches for fine particle sizing. Because of the inherent difficulties and large scope of work associated with this problem, the research program is being carried out as a joint research program between researchers at Virginia Tech and the University of Kentucky. During this reporting period, much of the project work focused on the evaluation of techniques for improving the performance of classifying cyclone circuits. This effort included (i) an experimental study of the effects of surfactant addition of classifying cyclone performance and (ii) the development of a mathematical simulation program for evaluating the performance of multistage cyclone circuits.

During this reporting period, much of the project work was performed to evaluate the effects of slurry rheology on the classification performance of a 4-inch diameter hydrocyclone. Data collected to date indicate that a lower particle size cut and improved classification efficiency can be achieved by lowering feed slurry viscosity. Work was also undertaken to construct a larger 6-inch diameter hydrocyclone test circuit that will be used to evaluate a new apex washing technology.

PROJECT TASKS

Task 1 - Development of Mechanical Sizing Methods

The construction of a bench-scale microsieve test circuit was temporarily delayed due to difficulties associated with the scheduling of the machine shop responsible for the equipment fabrication. The fabrication work is now expected to be completed before the end of the next reporting period. Once completed, test work will be carried to examine several process variables including feed solids content, sieve mesh size, drum rotation speed, and feed particle size distribution.

Task 2 – Development of Hydraulic Sizing Methods

During this reporting period, detailed tests were performed to evaluate the effects of changes in slurry rheology on the hydrocyclone performance. Slurry rheology was controlled by adding reagents that modify the viscosity of the feed slurry. Variables examined in this work included reagent type, reagent dosage, apex diameter, and feed solids concentration. The reagents examined in this work included sodium dodecyl sulfate (SDS) and Nalco 9762. A pilot-scale test rig equipped with a 10-cm (4-inch) diameter hydrocyclone was used in the present study. Experiments were carried out with minus 100 mesh coal slurry. An experimental program based on a three-level Box-Behnken statistical test design was performed. Separate experiments were also performed at higher solids concentrations with viscosity modifiers to achieve a greater solids recovery in the underflow stream.

The details of the parametric study on the effect of cyclone performance are given in Table 1. A detailed statistical analysis of the data was performed. Such analysis indicated that bypass is reduced significantly with an increase in the viscosity modifier concentration. Also, the modifier (SDS) improves efficiency as noted by a decrease in the imperfection value. When a smaller apex is used along with a moderate solids level in the feed, the modifier significantly reduces the cut size and increases the yield to the underflow. These observations led to the next stage of experiments with a small apex and higher solids concentration in the feed with a goal of achieving greater solids recovery in the underflow stream without the presence of the undesirable condition referred to as roping.

Results obtained with a small apex and higher solids concentrations in the feed are summarized in Table 2. Roping, which is a high solids content condition in the underflow stream that eliminates the presence of the air core, was observed in all these cases without viscosity modifiers except at a feed concentration of 10% solids. However, in the tests using the viscosity modifier, roping did not occur even at significantly higher inlet pressures. At a 10% feed solids concentration, no significant reduction in cut size was observed with the modifiers. However, with feed solid concentrations between 12.5 and 18% by weight, roping conditions were eliminated by the addition of each modifier and a substantial reduction in the particle size cut point was achieved while achieving a sharp improvement in classifying efficiency. For example, as shown in Table 2, an underflow solids concentration of around 54% solids was achieved even at a high feed solids concentration of 18% without the roping

Table 1. Experimental conditions and results for the 3-level statistical design program in which sodium dodecyl sulfate was used as the viscosity modifier.

Apex (mm)	SDS (kg/t)	%Solids in feed	Yield to UF (%)	d50 (microns)	Bypass (%)	Imperfection Value
16.6	0.0	5	68.98	36.00	12.50	0.361
16.6	1.0	5	68.99	36.00	7.50	0.278
16.6	0.5	7.5	66.78	43.80	9.90	0.457
16.6	0.5	7.5	66.36	42.80	10.50	0.491
16.6	0.5	7.5	65.96	45.00	10.00	0.433
16.6	0.5	7.5	65.51	44.00	14.50	0.398
16.6	0.5	7.5	66.04	44.00	11.00	0.455
16.6	0.0	10	67.40	43.00	11.50	0.454
16.6	1.0	10	66.83	40.50	10.00	0.386
12.7	0.0	7.5	61.27	52.00	9.80	0.490
12.7	1.0	7.5	67.61	42.50	8.50	0.277
12.7	0.5	5	69.57	37.50	8.50	0.300
12.7	0.5	10	68.51	39.00	11.00	0.324
20.5	0.0	7.5	79.66	31.10	17.50	0.389
20.5	1.0	7.5	80.22	29.20	22.70	0.428
20.5	0.5	5	79.61	29.00	22.20	0.379
20.5	0.5	10	84.14	25.50	30.00	0.422

Table 2. Viscosity modifier benefits for high solids loading in the underflow stream of a 10-cm diameter classifying cyclone using a relatively small (12.7 mm) apex: SDS=sodium dodecyl sulfate and Nalco-9762 = propriety modifier.

Type of Modifier	Dosage (kg/t)	%Solids in Feed	%Solids in Underflow	%Solids in Overflow
None	0.0	10	52.94	6.59
None	0.0	12.5	55.96	9.18
None	0.0	15	57.15	11.94
None	0.0	18	59.17	14.89
SDS	0.8	18	52.83	13.91
SDS	0.8	15	52.56	11.11
SDS	0.8	12.5	49.94	8.62
SDS	0.8	10	48.05	6.57
None	0.0	10	50.08	6.29
None	0.0	12.5	51.53	8.53
None	0.0	15	52.93	11.11
None	0.0	18	51.64	14.67
Nalco-9762	0.3	18	54.13	14.20
Nalco-9762	0.3	15	52.98	12.32
Nalco-9762	0.3	12.5	52.47	8.97
Nalco-9762	0.3	10	50.29	6.56

condition. This also indicates that water recovery to the underflow can be reduced using the modifiers while eliminating the roping condition.

Task 3 – Development of Novel Sizing Methods

No additional work was conducted under this task during this reporting period. Tests will resume during the next several months to further investigate several novel approaches have the potential to significantly improve the separation of ultrafine particles. These techniques will include free flow electrophoresis (FFE) and selective agglomerated particle elutriation. These activities will be jointly conducted by researchers at the University of Kentucky and Virginia Tech.

Task 4 – Circuit Development and Evaluation

The performance of classifying cyclones can also be substantially improved by developing techniques that minimize the bypass of ultrafine particles into the coarse underflow stream. One promising method of reducing bypass is to modify the apex of the cyclone with a water injection system to displace the entrained ultrafines from the cyclone underflow. Unfortunately, attempts to incorporate this feature into current cyclone designs have not been successful due to (i) excessively high water consumption and (ii) an increase in the particle cut size. To overcome these problems, a new type of water injection apex has

Figure 1. Test circuit used to evaluate the water injection apex technology.

been specifically developed by Krebs Engineers for evaluation in this project. A test circuit incorporating a full-scale 6-inch diameter cyclone, proportional sampling system, and variable speed slurry pump is currently under construction for this investigation (Figure 1). The cyclone and slurry pump equipment were donated by Krebs Engineers and Morris Coker Equipment, respectively, as a cost-sharing contribution to the project. The construction work is expected to be completed during the next month and experimental testing will begin shortly thereafter.

SUMMARY

Project work was initiated during the past reporting period to investigate a variety of new techniques for high efficiency sizing of ultrafine particles. Much of the work conducted to date focused on improving the performance of classifying cyclone circuits by modifying slurry rheology. The test work indicates that the addition of viscosity modifiers into the hydrocyclone feed reduces the particle cut size and improves classification efficiency. Construction work was also performed to complete the fabrication and assembly of a full-scale test circuit for evaluating a new water injection apex system. If successful, this technology will reduce the bypass of ultrafines to the hydrocyclone underflow while maintaining a very fine particle cut size.

FUTURE WORK

Studies of the effects of surfactant addition on classification performance will continue during the next reporting period using different size hydrocyclones and different additives. In addition, fundamental studies will be undertaken to develop a better understanding of the underlying mechanisms associated with this approach. Tests will also be conducted to evaluate the impacts of a new water-injected apex on cyclone performance. It is also expected that experimental tests will be initiated using a centrifugal elutriator (Knelson concentrator) to determine whether this technology can be used to improve classification efficiency.

REFERENCES

Heiskanen K, Particle Classification, Chapman & Hall, 1993.

PUBLICATIONS/PRESENTATIONS

None for the current reporting period.

Appendix B: Dispersion and Flotation of Clays from New Mexico Potash Ores

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 10/1/03 Ending Date: 4/30/04
<u>Sub-Recipient Project Title:</u> Dispersion and Flotation of Clays from New Mexico Potash Ores	<u>Report Information:</u> Type: Semi-Annual Number: 001 Period: 04/01/03-09/30/03 Date: 10/10/03 Code: NM001
<u>Principal Investigators:</u> I. Gundiler, S. Titkov, M. Yekeler	
<u>Contact Address:</u> New Mexico Tech Bureau of Geology & Mineral Resources 801 Leroy Place Socorro, NM 87801	<u>Contact Information:</u> Phone: (505) 835-5730 Fax: (505) 835-6333 E-Mail: gundiler@gis.nmt.edu
<u>Subcontractor Address:</u> No subcontracts issued.	

ABSTRACT

Concentration potash ores is achieved by flotation in saturated brines with long-chain primary amine collectors. Presence of clay-carbonate slimes is highly detrimental to flotation recovery of sylvite (KCl) and the slimes have to be removed ahead of potash flotation. Mechanical separators however, are generally inefficient and an organic binder is used to inhibit amine absorptions on slimes remaining in the potash flotation feed. This study was initiated to investigate the effect of slime dispersants and clay flotation for processing New Mexico potash ores. It has been shown that inorganic and organic dispersants added to attrition scrubbers and to grinding section could improve slimes dispersion and their removal in the existing plants. Introducing clay flotation ahead of sylvite flotation could allow beneficiation of high-clay ores by flotation.

INTRODUCTION

Background

Potash is the common term that denotes water-soluble potassium compounds in a variety of chemical combinations. Potassium is an essential element vital for plant and animal life. New Mexico is the largest potash producer in the United States, which supplies 70% of the

domestic production. Over 90% of the potash produced is used as fertilizer combination with ammonium and phosphorus salts.

Potash mining in the state began in early 1940s. Although, there are still vast reserves of potash minerals, clean, high-grade ores are virtually exhausted. Producers have to deal with low-grade ores with high clay content, which adversely effect the flotation separation of sylvite (KCl) from halite (NaCl). New Mexico flotation plants can handle up to 4% clays in the ore; higher clay ores (6-7%) is leached in hot water, solution is clarified and KCl is re-crystallized. The latter process is water and energy intensive.

The flotation process is carried out from saturated brines with cationic collectors. Clay minerals also adsorb flotation reagents, thus increase reagent costs, decrease recovery of sylvite, contaminate the product, and increase energy consumption for drying. Therefore, clays are dispersed during grinding and in attrition scrubbers, and removed by classifiers and hydroseparators. Not all clays, however, can be dispersed and removed in the scrubbers. They are carried into the flotation cells and disperse due to the mechanical action, hindering flotation of sylvite. For medium to high-clay ores, flotation of clays ahead of the sylvite has proven to improve the efficacy of clay removal, thus increase the efficiency of sylvite flotation in foreign operations.

Objectives and Approach

This study was initiated to address problems the facing NM potash industry and provide solutions that can easily be implemented in the existing plants. Therefore, principal objectives of this study are:

- To investigate the effects of organic and inorganic clay dispersants to increase the efficiency of the existing slime removal technologies from potash ores,
- To investigate flotation separation of clays from sylvinite ores using high molecular weight flocculants and slime flotation reagents.

Flotation of soluble salt minerals requires special procedures. All grinding, screening, conditioning, and flotation operations have to be carried out in saturated brines. In laboratory flotation tests the amount of salts deposited on dried products from the brines have to be accounted for, and final weights of solids have to be adjusted accordingly. For IR determinations soluble salts have to be washed away with hot water until the effluents are free of chloride ions. Therefore, this project has presented some challenges, which is normally not associated with common mineral separation studies.

PROJECT TASKS

Materials and Methods

Four drums of ore samples (2.5% clay) were collected from the impact crusher discharge and another four drums of medium-clay (3.5-3.7%) samples were collected from underground workings from IMC Potash Carlsbad operations. In addition samples of future

high (7-8%) gray and brown clay ore samples were collected near the ceiling and the footwall of the ore seams. Similarly, present (2.3% clay) ore samples were obtained from flotation (West) plant and high-clay (6-7%) ore from leach-crystallization (East) plant from Mississippi Chemicals Corp. operations.

One drum of present ore sample another drum of medium-clay ore were homogenized and split samples were cut for laboratory tests. Remainder is used to prepare brines. As many as 30 liters of brine was needed for each wet-screening tests, just as much for multiple dispersion and sedimentation tests. Some brine was recycled; however, if a flocculant was used during the test, that brine was discarded.

Slimes Dispersion Tests

Slimes dispersion tests are conducted on as received ore (minus 9.5 mm (-3/8") impact crusher product) and on minus 1.6 mm (-10 mesh) laboratory rod mill product. The dispersion tests were conducted with 730g ore sample and 700 ml saturated brine (SG 1.258-1.260) at 45% solids, in a Denver flotation machine in agitator mode. A 50-mm diameter impeller was used at 1100 rpm. The agitation was carried out for 15 minutes, which is comparable to total agitation / scrubbing time at the plants. The pulp was then transferred to a 4-lt glass beaker, diluted with brine to 16% solids, and minus 50- μ m (270#) slimes fraction were removed through a siphon by successive mixing and decantation. These tests were repeated in the presence of inorganic dispersant, and with a mixture of organic and inorganic dispersant. Results of the desliming tests by decantation are shown in Fig.1

Figure 1- Insoluble residue removal from crushed ore by successive decantation.

Potash Flotation Tests

The flotation tests are conducted with the rod-mill-ground and de-slimed ore samples. The ore is conditioned for 2 minutes in saturated brine with guar gum (Rantec KP-4000),

primary amine (Witco Arosurf MG-140), and extender oil (Philflo Flotation oil), transferred to the Denver flotation cell; frother (Phillips Orfom F2) is added and frothed for 2 minutes. The concentrate and tailings were filtered with a vacuum filter, wet weight recorded, dried and weighed. The amount of salts precipitated from the brine on products was calculated from the moisture loss; representative samples were ground and analyzed. These tests were repeated with different dispersant additions. Results of the decantation desliming and potash flotation tests are shown in Table 1.

Table 1- Results of potash flotation tests from deslimed ore using dispersants.

Regime	Products	Weight recovery, %		Content, %		% Recovery		Difference in recoveries in comparison with test without dispersant	
		Based on flotation feed	Based on desliming feed	In solid phase		Based on flotation feed			
				K ₂ O	I.R.	K ₂ O	I.R.	K ₂ O	I.R.
Dispersant addition in the mixer									
Without Dispersant	Concentrate	22.08	18.18	56.88	1.73	77.73	53.57		
	Tails	77.92	64.13	4.62	0.43	22.27	46.43		
	Flotation feed	100.00		15.20	0.71	100.0	100.0		
With Inorganic Dispersant	Concentrate	26.26	21.68	56.29	1.08	82.87	42.30	+ 5.14	- 11.20
	Tails	73.74	60.86	4.14	0.53	17.13	57.70		
	Flotation feed	100.00		17.84	0.67	100.0	100.0		
With Inorganic And Organic Dispersants	Concentrate	28.78	23.73	58.76	0.59	85.34	28.89	+ 7.61	- 24.68
	Tails	71.22	58.73	4.08	0.58	14.66	71.11		
	Flotation feed	100.00		19.81	0.59	100.0	100.0		

The above results show that using a mixture of mixed organic and inorganic dispersants K₂O recovery in the concentrate increased by 7.6%, and IR recovery into the concentrate decreased by almost 25%, as compared to ore desliming by decantation. It should also be pointed out that not all K₂O in the ore is contained in sylvite (KCl). Because of the presence of other potassium minerals that do not respond to amine flotation, the K₂O content of the tailings remain relatively high. Nevertheless, by using dispersants K₂O content in the tailings decrease by 12%.

Slime Flotation Tests

Slime flotation tests were carried out on low and medium clay ores following the scheme shown in Figure 2. It is well established that fine slime particles have to be treated with a polymeric flocculant before flotation. Best results were obtained by using a mixture of anionic flocculant (Hyperfloc AF 304) and a non-ionic flocculant (Hyperfloc NF 301) in equal proportions. Etheramines and diamines, oxyethylated fatty acids (OEFAc), and

oxyethylated fatty amines (OEFAM) obtained from different suppliers were used as slime collectors. It has been shown that slimes recovery is strongly dependent on the flocculant concentrations; slimes recovery reaches a maxima and then decreases with increasing flocculant concentrations. Best slime recoveries were obtained using OEFAM whereas OEFAC concentrations were three times as much for comparable recoveries for medium clay ores. Etheramines, which are used as slime collectors in Canadian and Russian operations, did not give satisfactory results with New Mexico ores.

Figure 2 - Laboratory slime flotation flow diagram.

Slime Flotation and Potash Flotation

For the present low clay ores (2.3-2.5% IR), the use of dispersants in the desliming stage yielded improved K₂O recoveries decreased IR recovery in the concentrate. By using slime flotation, better K₂O recoveries can be achieved since K₂O losses to slimes are reduced. However, slime flotation would require changes in the existing plant operations and additional capital investment. For medium and high clay ores, however, desliming by slime flotation only was not sufficient to achieve satisfactory potash flotation recoveries. Preliminary results show that coarse-ore desliming by decantation (2-stage for high clay ores) followed by slime flotation yielded satisfactory recoveries by weight. Complete assessment of these results will be achieved when the chemical analyses of the flotation products are completed.

SUMMARY

Potash ore samples and flotation reagents were collected from the operating plants in the Carlsbad potash district. Brine preparation, slimes dispersion and decantation, rod mill grinding, and flotation test procedures were established. Procedures for K₂O analysis in ore samples, concentrates, tailings, and brines, as well as IR determinations were also

established. A high level of competence in analytical methods was achieved by the use of reference material and cross checking results with plant operations. Slimes dispersion tests with or without added dispersants, and slimes flotation tests were carried out with low, medium, and high clay ores samples, in duplicates or triplicates when necessary. The efficacy of slimes removal tests were verified by IR analyses of the products, as well as ensuing potash flotation test results. The positive effects of added dispersants in the hydro-mechanical desliming and potash flotation, and flotation desliming of medium and high clay ores have also been demonstrated at the IMC plant laboratories in collaboration with the plant personnel. These results will be presented in the final report.

Appendix C: Flotation Technology for the Trona Industry

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 10/1/03 Ending Date: 3/30/04
<u>Sub-Recipient Project Title:</u> Flotation Technology for the Trona Industry	<u>Report Information:</u> Type: Semi-Annual Number: 2 Period: 04/01/03-09/30/03 Date: 10/10/03 Code: UT001
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ABSTRACT

In the second budget period, the development of the new process technology for the separation of the gangue minerals and for production of a trona concentrate with very high purity and recovery rate continued in three directions. Fundamental surface chemistry studies by contact angle measurements and sum frequency spectroscopy confirmed our previous conclusions that sodium carbonate is a water structure maker while sodium bicarbonate is a water structure breaker. New bench scale flotation experiments with four different brines (trona saturated solution, mine water, synthetic sodium carbonate solution, and sodium carbonate solution from the plant) demonstrated that trona saturated solution is most effective for the trona flotation process. The saturated mine water may also be used for flotation instead of trona brine since it gives a good recovery of trona. Preparation for the evaluation of flotation parameters and optimum conditions for testing at the General Chemical plant site in the summer of 2004 was accomplished. Working with industrial partners Roberts & Schaefer Inc., EIMCO, and General Chemical, a flowsheet outlining the process technology has been developed and includes all major items of equipment and all relevant flows.

INTRODUCTION

Background

Almost all (90%) of the soda ash (Na_2CO_3) production in the U.S. comes from the trona deposits of the Green River Basin in Wyoming. This U.S. trona production of 17.1 million tons per annum is shared by 4 companies

- FMC Corporation
- General Chemical
- OCI
- Solvay

Soda ash is used in the production of glass, chemicals, soap and detergents, flue gas desulfurization, pulp and paper, and in water treatment. The total value of soda ash sold by the U.S. industry amounts to about 800 million dollars per annum. Production of soda ash from trona has been limited to some extent by the existing process technology, which involves dissolution of the ore in boiling brine, sedimentation, and filtration for the removal of impurities, crystallization, and subsequent calcination for the recovery of soda ash. A preferred processing strategy would be to remove gangue mineral contaminants from the plant feed prior to dissolution in hot brine. Such preprocessing at ambient temperature and pressure would:

- Reduce costs substantially by allowing for the use of less selective high capacity mining techniques such as long wall mining,
- Offer the possibility of obtaining a new product (trona concentrate),
- Make available additional trona resources which currently are of marginal value, and
- Result in improved operation of the chemical plant by providing high quality feed to more readily achieve refined product specifications.

This preprocessing strategy has not been realized because of lack of satisfactory process technology. For example, it has been well known that processing by flotation could not achieve the desired separation. Now, based on our recent results from laboratory research, it seems that the run-of-mine trona ore can be treated at ambient temperature and pressure using a special flotation procedure to separate the gangue minerals and make a trona concentrate (Wang, X. et al., 2002). Preliminary estimates indicate that more than 97% of the trona can be recovered in the trona concentrate and that this product will have a purity of almost 99% trona.

Objective and Approach

The objective of our two-year research program is the development of a flotation procedure for the preprocessing of trona ore to remove insoluble mineral contaminants prior to chemical treatment and production of soda ash. The scope of the work includes:

- Collector chemistry study including surface chemistry, collector composition/stability and characterization.
- Bench scale flotation experiments to provide the preferred conditions and operating variables for plant-site testing.
- Plant-site testing.
- Economic Analysis

PROJECT TASKS

1. Fundamental Surface Chemistry

We have shown in our previous report that soluble carbonate salts can be floated or not according to their structure breaking or structure making properties (as referred to their effect on the structure of liquid water) (Nickolov, Z. S. et al, 2003). The structure breaking sodium bicarbonate (NaHCO_3) salt can be floated with both anionic and cationic collectors, but the structure making sodium carbonate (Na_2CO_3) does not float due to the inability of the collector to break the organized water structure and adsorb at the surface of the carbonate particles. Trona is a complex salt of sodium carbonate and sodium bicarbonate. In the trona brine the structure making character of sodium carbonate dominates and direct floatation of trona is difficult. These facts support our proposed trona processing technology to separate the gangue minerals by flotation and prepare a trona concentrate.

In this budget period, we have extended our studies on the flotation fundamentals of carbonate salts employing contact angle measurements at the salt/brine interface and analysis of water structure of carbonate salt aqueous solutions at the liquid/air interface by sum frequency generation. Contact angle measurements are often used to evaluate the hydrophobicity of solid surfaces. In this respect contact angles at Na_2CO_3 , NaHCO_3 and trona surfaces were measured using saturated brines of the corresponding salt in order to examine the hydration state of each salt surface. The surfaces of Na_2CO_3 and trona are hydrated to the greatest extent and a contact angle could not be detected, whereas the surface of NaHCO_3 appears to be less hydrated, and a finite contact angle of 23° could be measured. These results are in agreement with previous experiments, which showed that flotation of NaHCO_3 is possible with both anionic and cationic collectors. On the other hand, as expected from bench scale experiments, flotation of Na_2CO_3 and trona is generally difficult (Ozcan, O. and Miller, J.D., 2002).

Initial studies by the interface specific method of sum frequency generation (SFG) indicate a difference in the structure making/breaking properties of NaHCO_3 and Na_2CO_3 at the salt solution / air interface.

2. Bench-Scale Flotation Experiments

2.1 *Evaluation of Brines*

Four different brines were prepared for the bench scale flotation experiments in our laboratory using a high intensity mixer. These four brines were trona saturated solution, mine

water, synthetic sodium carbonate solution, and sodium carbonate solution from the plant. For the preparation of saturated solutions, a special hot bath and a filtration device were employed to maintain constant temperature (40 °C) throughout the experiment, since sodium carbonate has the tendency to crystallize at room temperature.

The results from flotation with different saturated solutions are shown in Figure 1. They indicate that trona saturated solution is most effective for the trona flotation process. It can also be seen from the results that saturated mine water may be used for flotation instead of trona brine since it gives a good recovery of trona.

Figure 1. Flotation results with different brines.

2.2 Flotation of 60x200 Mesh Feed Material for Preparation of Premium Quality Trona Product

A bench scale flotation experiment was carried out using a sample, which was prepared at a facility in Provo, UT. The size analysis of this sample is shown in Table 1. This feed contains 17% insolubles. About 150 grams of the sample was pulped by adding saturated trona solution followed by addition of the reagent (flotation collector). The suspension was conditioned for about 2 minutes. After conditioning, the pulp was transferred to the flotation cell, and floated for about 3-5 minutes. Flotation products, sink (trona concentrate) and float (tailing), were dewatered by using a filter press and then dried. The water-insoluble material in both float and sink products was determined by gravimetric analysis.

Table 1. Screen analysis, Provo sample.

Size(Mesh)	Retained Sample (%)	Cumulative (%)
+60	45	45
-60+100	40	85
-100+200	14	99
-200	1	1

Flotation experiments with this Provo feed sample were carried out to evaluate the possibility that the U of U flotation technology could be used directly to produce high quality trona product. A typical result from this experiment is presented in Table 2. A trona concentrate of about 98.5% purity can be produced using U of U flotation technology with about 82.5% recovery.

Table 2. Results from flotation with 60x200 mesh feed material.

Products	Trona Wt (%)	Insol. (%)	Trona Recovery (%)
Concentrate	68.87	1.5	82.57
Tailing	31.13	54.0	17.43
Feed	100.00	17.84	100.00

3. Progress in Preparation for Pilot Plant Testing

Pilot plant testing is of considerable importance for the evaluation of flotation parameters and optimum conditions for testing at the General Chemical plant site in the summer of 2004. The objectives of designing, constructing and operating the alternative pilot plant as defined with our industrial partners Roberts & Schaefer Inc., EIMCO, and General Chemical have been to:

- Evaluate the efficiency and practical applicability of the proposed technology in an industrial setting.
- Ascertain that the flotation parameters and conditions are reliable to apply in the tests at the plant site.
- Determine performance limitations of existing technologies and components.
- Obtain comparative and performance data for the flotation processes.

The design of the pilot plant involved:

- Preparation of a flowsheet

The flowsheet has been developed in AutoCad software based on experimental data and discussion with industrial partners. This flowsheet contains major items of equipment, all relevant flows in and out of each piece of equipment. The detailed flowsheet, which will be used for pilot plant testing in the summer of 2004, is shown in the APPENDICES

- Equipment list

The equipment list has been derived from the flowsheet, and gives us the basic input information for preliminary capital cost estimates and identifies the available units.

- Design Criteria

The information, which will be used for pilot plant testing is shown in Table 3:

Table 3. Plot Plant Design Parameters for Trona Flotation Circuit

Stream	Parameters
Feed	Crushed material 40x200 mesh, feed rate is about 1 t/h
Conditioning	Conditioning time 2-3 min, conditioning solids 70-75 %
Flotation	5 cells in series flotation machine, flotation time 3-10 min at 15 % solids

FUTURE WORK

More bench scale flotation experiments need to be done to determine the optimum conditions for the proposed flotation technology. A detailed study of the reagent preparation is needed for the pilot plant tests including evaluation of the optimum condition for the ratio of amine to oil and the reagent dosage level. Equipment selection and installation at the plant site has to be done. Pilot plant testing will allow for the evaluation of the technical and economic feasibility of the new technology.

REFERENCES

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Appendix D: Flotation Processes/Experiments and Analysis

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Crosscutting Technology Development at the Center for Advanced Separation Technologies (DE-FC26-02NT41607)		<u>Period of Performance:</u> Starting Date: 10/1/02 Ending Date: 5/30/04	
<u>Sub-Recipient Project Title:</u> Flotation Processes/ Experiments and Analysis		<u>Report Information:</u> Type: Semi-Annual Number: 2 Period: 10/1/03 to 3/30/04 Date: 4/10/04 Code: VA009	
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ABSTRACT

Flotation processes involve complex, three-phase flow interactions between a liquid, bubbles and solid particles. For decades engineers and researchers based their calculations on algebraic formulas that model these interactions. These formulas were derived from simple models, from experimental data or just from arbitrary assumptions. Considerable progress has been made so far but this approach is far from providing a reliable tool for the design of flotation machines. Most of the experimental data were obtained decades ago with literally primitive methods. Modern experimental tools are employed in this effort to measure with great accuracy the basic features of the motion of all three phases in homogenous isotropic turbulent flow and in a model flotation cell. We will employ a unique in the US Digital Particle Image Velocimeter (DPIV) that can record with great accuracy and kHz temporal resolution velocity vectors of all three phases, namely the fluid, the solid particles and the air bubbles. We will measure three-phase flow interactions of bubbles and model particles of different hydrophobicity with a turbulent flow field. An advanced model for predicting and quantifying the efficiency of the flotation process will be the final deliverable of this two-year effort. Such a tool will improve the design of flotation systems and/or enhance the performance of existing systems.

Nomenclature

Subscript p	particle
Subscript b	bubble
Subscript l	liquid
Superscript *	nondimensional quantity
$\langle \rangle$	time average
C_{12}	collision frequency coefficient [$\text{m}^3 \cdot \text{s}^{-1}$]
d_i	diameter of i [m]
d_{12}	sum of diameters of particle and bubble
N_i	number density of i [m^{-3}]
R_{12}	radius of collision [m] = $(d_1 + d_2)/2 = R_1 + R_2$
u_i	i^{th} component of fluctuating velocity
$\sqrt{\overline{U_i^2}}$	root-mean-squared velocity of i with respect to flow [$\text{m} \cdot \text{s}^{-1}$]
$\overline{U_i^2}$	variance of i with respect to flow [$\text{m}^2 \cdot \text{s}^{-2}$]
U^2	variance of flow velocity
Z_{12}	collision frequency between particle and bubble [$\text{m}^{-3} \cdot \text{s}^{-1}$]
ε	Kinetic Energy Dissipation rate [$\text{m}^2 \cdot \text{s}^{-3}$]
ν	kinematic viscosity [$\text{m}^2 \cdot \text{s}^{-1}$]
ρ_i	density of i [$\text{kg} \cdot \text{m}^{-3}$]
τ_i	relaxation time of i [s]
L	Characteristic length
U_0	Free stream velocity
Re	Reynolds number
T	flow time scale

INTRODUCTION

Background

A well-documented approach of the performance of flotation cells is based on analytical or numerical determination of the rate constant, k (Moon, et al. (2002)). An accepted estimate of the collision rate is given by the Abrahamson (1975) equation, which requires the root-mean square of the velocities of phase 1 and 2, here the coal particles and the bubbles relative to the fluid, respectively. Abrahamson's analysis is valid only if the phase density is much larger than the fluid density. This is the case for coal particles but not for bubbles. Schubert (1999) proposes instead:

$$\overline{U_i^2} = 0.33 \frac{e^{4/9} d_i}{u^{1/3}} \left(\frac{\mathbf{r}_i - \mathbf{r}_f}{\mathbf{r}_f} \right)^{2/3}$$

This formulation is an empirical, curve-fitting procedure carried out by Liepe and Moeckel (1976), based on experimental data collected by many authors. All these data were obtained

decades ago, with almost primitive tools. Levins and Glastonbury (1972) for example record visual data in a flotation machine, along two planes and then proceed to measure manually thousands of particle-path segments. From such data they then generate the RMS of flow and particle velocity fluctuations.

These analytical tools may have served the workers in the field well so far, but this modeling represents a drastic simplification of the physics of the problem. For decades, calculations of flotation performance were based on the experimental data obtained in the 1960s and early 1970s. Luttrell and Yoon (1992) have later designed an experiment to measure the rate of particle attachment on single bubbles that were made to “hover” for a short period of time in a test tube. Pyke et al. (2002) carried out point velocity measurements in a model flotation cell. Clearly all these experimental data are very limited in spatial and temporal extend. Moreover, no effort has been made at all to monitor and document the individual motions of each phase in two-phase flows or in three-phase flows, namely a fluid-bubble-particle motion. In this project our aim is to explore in greater detail the mechanics of three-phase flotation processes.

Objective and Approach

We are investigating three-phase flow, namely particle-bubble-turbulence interaction via time-resolved digital particle image velocimetry (DPIV). This study is conducted downstream of a grid that generates turbulence. This design provides an approximate but controlled simulation of the motion in a flotation machine, where next to the impeller we find large vortical structures, which again break down, populating the field with smaller vortices and ultimately lead to fully-developed turbulence. We are measuring the spatial and temporal evolution of turbulence properties like length scales, time scales, Reynolds stresses and finally turbulent dissipation, which appears in both the Schubert and the Abrahamson formulations.

PROJECT TASKS

Work on this project has been progressing for almost one year. The following tasks have been defined at the beginning of this project.

Task 1: Phase velocities: We employ DPIV to study experimentally the direct interaction of bubbles and particles. The stream will be seeded with two types of particles. The first type will consist of particle sizes the order of $100\ \mu$ and will simulate coal particles. Different levels of hydrophobicity will be tested. The second type of particles will be sized down to the order of $1\ \mu$ and their purpose is to allow accurate measurements of the instantaneous velocity field around the bubbles. We will document the individual velocities and turbulence fluctuations of each individual phase.

Task 2: Particle/bubble interaction: We will measure the trajectories and velocities of solid particles traveling around bubbles. These trajectories will be compared with trajectories computed by BBO equation. From the experimental results we will compute the energy

dissipation rate, which we will be incorporated into Schubert's formulation for the efficiency estimation of flotation processes.

Task 3: Measurement of collision rates: By employing quantitative flow visualizations and advanced image processing techniques, we will measure the number of collisions between particles and bubbles. By varying parameters like sizes of particles and bubbles, as well as the density and hydrophobicity of particles, we will generate detailed statistical distributions for the probabilities of attachment and detachment. We will thus be able to evaluate the effect of different parameters on flotation efficiency.

Task 4: Tests in a model flotation machine: We will continue our experimental measurements in a model flotation machine.

PROGRESS

1. Analytical Considerations

Knowledge of particle and bubble velocities within a turbulent environment is a basis for understanding what occurs within a flotation cell. This knowledge, along with other relevant parameters, allows the prediction of a rate constant which in turn allows the prediction of recovery and grade of minerals. The flotation process occurs within a highly turbulent three-phase flow, where a detailed understanding of these flows is limited. These velocities are used to model collision frequencies which are in the form:

$$Z_{12} = C_{12} N_1 N_2 R_{12}^2 \quad (1)$$

where Z_{12} is a collision frequency coefficient and contains the relevant velocities.

Saffman and Turner (ref) proposed two collision models both assuming Stokes numbers below 1. The first took into account only the shear mechanism for collision and assumes a Stokes Number of zero:

$$Z_{12} = \sqrt{\frac{8p}{15}} R_{12}^3 N_1 N_2 \sqrt{\frac{e}{n}} \quad (2)$$

The second accounted for inertial differences due to gravity and turbulent accelerations:

$$Z_{12} = \sqrt{8p} R_{12}^2 N_1 N_2 \left(\left(1 - \frac{r_{12}}{r_1} \right)^2 (t_1 - t_2)^2 \left(1.3 \sqrt{\frac{e^3}{n}} + \frac{1}{3} g^2 \right) + \frac{1}{9} R_{12}^2 \frac{e}{n} \right)$$

Abrahamson (1975) then came up with a collision frequency where the Stokes number of the colliding particles is infinite, essentially assuming the motion of the bubbles and particles is completely uncorrelated with the flow. This frequency only accounted for the accelerative mechanism for collisions.

$$\mathbf{Z}_{12} = 2^{3/2} \mathbf{p}^{1/2} \mathbf{N}_1 \mathbf{N}_2 \mathbf{d}_{12}^2 \sqrt{\left(\overline{\mathbf{U}_1^2} + \overline{\mathbf{U}_2^2} \right)} \quad (3)$$

There are various methods to calculate the RMS of the particle and bubble velocities, $\overline{\mathbf{U}_i^2}$. One such method is a derivation from the BBO equation by Levins and Glastonbury (1972) that assumed single frequency oscillations:

$$\frac{\overline{\mathbf{U}_i^2}}{\overline{\mathbf{U}^2}} = \frac{(1-b)^2}{aT+1} \quad (4)$$

$$a = \frac{36\pi}{(2\mathbf{p}_i + \mathbf{p}_f)\mathbf{d}_p^2} \quad b = \frac{3\mathbf{p}_f}{2\mathbf{p}_i + \mathbf{p}_f}.$$

Abrahamson also included a simplification to Equation 4 by assuming solid particles in a gas ($b=0, a=1/\tau_p$) and calculating the time scale, $\mathbf{T}_L = 0.7\overline{\mathbf{U}^2}/e$, therefore reducing to equation 5, which is a common formula used in the flotation industry,

$$\overline{(\mathbf{U}_i^2)}_{\text{abs}} = \frac{\overline{\mathbf{U}^2}}{1 + 1.5t_i e / \overline{\mathbf{U}^2}}. \quad (5)$$

The most common form used in the flotation industry is a combination of the collision frequency given by Abrahamson and the particle root-mean-squared velocity with respect to the flow given by Liepe and Mockel (1976).

$$\sqrt{\overline{\mathbf{U}_i^2}} = 0.33 \frac{e^{4/9} \mathbf{d}_i^{7/9}}{n^{1/3}} \left(\frac{\mathbf{r}_i - \mathbf{r}_1}{r_1} \right)^{2/3} \quad (6)$$

This velocity was experimentally developed and is valid at intermediate Stokes numbers where the flotation process occurs.

There are limitations to all of these models for flotation. The velocity components of Saffman and Turner's models assume Stokes numbers of 1 or less while Abrahamson assumes Stokes numbers of infinity. Neither of these conditions are valid within the flotation environment over the particle sizes that are significant. Liepe and Mockel's model should be valid for particles at intermediate Stokes numbers. The limitation on this is the assumption that the density of the particle is greater than that of the fluid, which is not the case with air bubbles. To determine how greatly these limitations affect their collision frequencies, fluid velocity measurements have been recorded in grid turbulence. The velocity at the kolmogorov scale, $U=(\nu\varepsilon)^{1/4}$, has been determined from these and compared

against the RMS velocities predicted by the three models described above. The nondimensionalized forms of the Levins and Glastonbury, and Schubert models, respectively are shown in Equations 6 and 7. These comparisons will show how well each predicts small particle flow.

$$\frac{\overline{U^{*2}}}{U^{*2}} = \frac{(1-b)^2}{aT^*L/U_0 + 1} \quad (6)$$

$$\sqrt{\overline{U_i^{*2}}} = 0.33 Re^{1/3} e^{*4/9} d_i^{*7/9} \left(\frac{r_i - r_f}{r_f} \right)^{2/3} \quad (7)$$

The main objective of this project 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 Schubert equation given in Equation 7, where $\overline{U_i^2}$ is the RMS of the velocity fluctuation of species i, with respect to the flow. In addition, the measured particle velocity fluctuations will be compared to those presented by Levins and Glastonbury (Equation 6).

Each of these models are dependent upon the kinetic energy dissipation rate, which has been shown to determine the degree of droplet and bubble break up and rates of chemical reactions. Direct approximation of the dissipation rate from the definition,

$$e = \frac{u}{2} \left\langle \left(\frac{\partial u_i'}{\partial x_j} + \frac{\partial u_j'}{\partial x_i} \right)^2 \right\rangle \quad (8)$$

requires the evaluation of the strain rate fields at a spatial resolution less than the Kolmogorov length scale. So far, there are no experimental methods available that can fully resolve the dissipation rate directly. However, implementing Taylor's frozen turbulence hypothesis allows the spatial derivatives to be represented by time derivatives (Sheng et. al. 2000),

$$\left\langle \left(\frac{\partial u_i'}{\partial x_i} \right)^2 \right\rangle = \frac{1}{U_1^2} \left\langle \left(\frac{\partial u_i'}{\partial t} \right)^2 \right\rangle \quad (9)$$

This relationship can be used to determine the dissipation rate (Hinze 1994),

$$e = \frac{15u}{U^2} \left\langle \left(\frac{\partial u_1'}{\partial t} \right)^2 \right\rangle \quad (10)$$

which will be the evaluated form used in this study through means of Particle Image Velocimetry.

2. Facilities and Instrumentation

Non invasive optical flow diagnostics measurements were performed in order to characterize the particle and/or bubble interactions within homogeneous isotropic turbulence. 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 have also employed this method to record two-phase flows, namely spray flows or bubbly flows.

Digital Particle Image Velocimetry (DPIV) is the most established global flow-field measurement technique, however, time-resolved measurements with simultaneous velocity, shape and size characterization of multiple phases remains a great challenge. In the current effort, we integrate the appropriate hardware and software components necessary to perform such measurements. A Vision Research Phantom-IV camera with frame rate up to 1000 frames per second (fps) and spatial resolution of 512x512 is employed using single laser exposure per frame for the recording of the DPIV images. The camera is synchronized with a high repetition rate Copper-Vapor pulsing laser with emission wavelengths at 511nm and 578nm. The pulse duration is in the order of 25nsecs is sufficient for performing measurements for low and moderate speeds.

For multi-phase flows, saturation of the image from overexposure of bubbles or droplets is a detrimental parameter for carrying out accurate quantitative measurements. Conventional DPIV systems employ CCD cameras, which suffer from leakage effects, namely, the excessive charge from overexposed pixels, leaks to the neighboring ones saturating the whole area. In contrast, CMOS sensors isolate the individual pixels behaving as a cut-off filter without leaking the energy. Therefore, by employing CMOS technology we eliminate the blooming effect, allowing resolution of a multi-phase flow with direct imaging within a laser sheet. This feature is of great importance since it simplifies the experimental setup, enhances the signal-to-noise ratio, and more importantly allows accurate shape and size quantification of particles or bubbles present in the flow. In addition, it improves the performance of the centroid gaussian estimator, which is essential for the performance of the particle tracking methodology. Details on the performance characteristics and accuracy of the system can be found in Abiven and Vlachos (2002)

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 1). 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. 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.

Figure 1: Schematic representation of the isotropic turbulence water tunnel

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 Schubert's equation.

Time-Resolved DPIV measurements were performed in flotation cell illustrated in Figure 1. Homogeneous isotropic turbulence was generated using grid with 1 cm diameter and 1 cm spacing which also serves as the characteristic length.. The Reynolds number based on the grid spacing was on the order of $Re=1000$. The Kolmogorov length scale is on the order of $56\mu m$ and the corresponding time scale was 100ms. The experiments were performed with sampling frequency of 1000Hz ($dt=1ms$) and a spatial resolution of $37\mu m/pixels$. 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 $90\mu m$ which is on the order of the Kolmogorov length scale of $56\mu m$.

Traditional, cross-correlation based PIV measurements were used to determine the flow velocities. However, the particle and bubble velocities were measured using Particle Tracking Velocimetry (PTV). PTV tracks individual particle locations, from which velocities can be determined with any order accuracy desired.

3. Results

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 Urms

corresponding to the particle motion will be the one defined by the velocity at the level of the Kolmogorov micro scale for homogeneous isotropic turbulence, $U = (\epsilon n)^{\frac{1}{4}}$. Figure 2 shows time averaged results from the experiment. The color contours correspond to vorticity distribution (left) and turbulent dissipation rate (center). The region where the experimentation took place corresponds to a region of about 2 cm wide, centered over one of the gaps between two of the turbulence rods. The time averaged vorticity contours clearly show two regions of intense vorticity on either side of the jet. The dissipation rate computed was computed using *Taylor's hypothesis of frozen-turbulence*, Equation 10. Figure 3 (right) clearly illustrates that beyond 3 grid lengths we have fully developed homogenous isotropic turbulence. This observation serves as the basis for performing the validation of Schubert's equation which was developed on the basis of fully developed turbulent flow.

4. Evaluation of Particle RMS

Particle Tracking Velocimetry (PTV) was utilized to track the positions of the 80 μm glass particles. Figure 3 shows a brief picture of particle trajectories for different regions above the turbulence grid. The region just above the turbulence grid, $y=0-2$ shows a clear region of unsteady flow, especially on the extreme left and right of the image where the turbulence rods exist and flow reversal can be seen. Further up the grid at $y=4-6$, the particle accelerations are not as severe, however large scale fluid motion is clearly seen. Finally, in

Figure 2: Time averaged results (nondimensional) downstream of the turbulence generation grid over a length of approximately 12 grid spacing. (left) vorticity contours, (center) dissipation rate contours, and (right) dissipation rate averaged over time and x.

the region 10-12 units above the grid, homogeneous isotropic turbulence is observed in the particle motion.

Using the dissipation rate estimates, the predicted RMS velocities of the 80 μm particles were calculated and compared to the measured RMS velocities of the particles from the Particle Tracking algorithm, shown in Figure 4. Figure 4 reveals that the RMS slip velocity measurements agree well with those predicted by Shubert, Equation 8, based on the measured dissipation rate of the flow. The predicted RMS does not deviate from the experimental by more than 12% over the entire height of the experimental region. The model predicted by Levins and Glastonbury, Equation 6, underestimated the particle RMS by about 50% in the fully developed region ($y > 8$).

The bubble RMS, shown in Figure 5 is significantly higher than the particle RMS by about 100% in the homogeneous isotropic region. Shubert's equation, although not developed for the case of bubbles, is used in the flotation industry and is shown along with the levins and Glastonbury model. Both models overpredict the bubble RMS with the Levins and Glastonbury model providing a better prediction with an average percent error of 22%.

SUMMARY

Homogeneous Isotropic turbulence was created in the model flotation cell through grid turbulence. The turbulent dissipation rate was measured using a cross correlation based Particle Image Velocimeter. Particle Tracking Velocimetry was used to determine the velocity fluctuations of the solid particles relative to the fluid phase. RMS velocities of the particles were calculated and compared to experimental and theoretical models that are based on the dissipation rate. The particle RMS was in good agreement Shubert's model, having an average RMS velocity of about 13% of the free stream velocity in the fully developed region. A theoretical model, derived first by Levins and Glastonbury was found to underpredict the particle RMS. The bubble RMS was

**Figure 3 – Trajectories of 80 mm particles:
bottom $y=0-2$, middle $y=4-6$, top $y=10-12$**

about 26% of the free stream in the homogeneous isotropic region, 100% greater than the particle RMS and not consistent with the model predictions.

FUTURE WORK

We have made great progress on Task 1, as described above. We may have to repeat some of the measurements, focusing the work towards more data for Task 2. In a few months will start work on Task 3, which will require devising an experimental method to estimate collision rates. We have already designed a model flotation machine that will be required to carry out work on Task 4. Parts for the construction of the machine have been ordered.

Work on this effort will combine detailed theoretical analysis and modeling with state-of-the-art, global, multi-phase flow measurements to quantify the effects of the various hydrodynamic parameters on the flotation process. Our modeling approach will incorporate all physical parameters that affect the collision efficiency of coal particles and flotation bubbles and the probabilities of attachment and detachment. We will deliver global, time-resolved velocity distributions and turbulence characteristics for each phase. In addition, the number of collisions and detachments will be measured directly. All the experimental results will be compared with their modeled counterparts.

Figure 4 – RMS of slip velocity versus height above turbulence grid for 80 mm particles and corresponding predictions from models

Figure 5– RMS of slip velocity versus height above turbulence grid for 1.2 mm bubbles and corresponding predictions from models

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PUBLICATIONS/PRESENTATIONS

“Turbulent Particle Bubble Interactions Measured by Particle Image Velocimetry”. By Mike Brady, Demetri Telionis, Pavlos Vlachos, Ian Sherrell and Roe-Hoan Yoon. Presented at the SME Conference. Denver Colorado, February 2004.

Appendix E: Column Flotation of Relative Coarse and Fine Dolomitic Phosphate Pebbles

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-02NT41607)	<u>Period of Performance:</u> Starting Date: 10/1/02 Ending Date: 5/31/04
<u>Sub-Recipient Project Title:</u> Column Flotation of Relatively Coarse and Fine Dolomitic Phosphate Pebbles	<u>Report Information:</u> Type: Semi-Annual Number: 2 Period: 10/1/03-3/31/04 Date: 4/30/04 Code: WV007
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ABSTRACT

During this period, dolomitic phosphate pebble samples were obtained from IMC Phosphates. Size analyses and component analyses for each size fraction have been determined. Items necessary for the determination of phosphate content in dolomitic phosphate pebble samples - including a phosphate module for an existing Lachat QuickChem 8000-FIA in the NRCCE (WVU) analytical laboratory; an AFPC manual of analytical procedures of phosphate content; and phosphate rock standards - have been ordered. An ICP-OEP instrument is being used to determine the other chemical components of the samples. A new collector has been obtained from IMC Phosphate. Reagents will be tested in a stirred-tank batch cell, Results will be used to estimate optimum operating conditions for column flotation. The flotation column has been set-up and its bubble generation system is being modified for relatively coarser dolomitic flotation from dolomitic phosphate pebble samples. Literature on the mechanisms of phosphate flotation and the behavior of carbonates is being reviewed.

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 typical concentrates is detrimental to the down stream filtration steps in the phosphoric acid manufacturing process, and as a result, large quantities of high-dolomite phosphate pebbles are stockpiled or discarded in impoundments, which are wasteful of resources and can create environmental problems. Additionally as mining in Florida moves towards 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 dolomitic phosphate pebbles using a newly developed selective fatty acid soap collector, USPA-31 (or its equivalent). USPA-31 has been tested in dolomite flotation at IMC Phosphate, using conventional mechanical flotation cells (Hwang, et al., 2003), where it was shown that USPA-31 gave better separations than did PA-31. The goal here is to generate a high quality phosphate concentrate by using USPA-31 to float relatively coarse dolomite particles in acid medium while depressing phosphate particles with a mixture of phosphoric acid and/or sulfuric acid. This process will be conducted in flotation columns in order to achieve high P_2O_5 recoveries and to reduce MgO contents to less than 1%.

PROJECT TASKS

Task 1 - Material Characterization and Analytical Procedure Establishment.

A dolomitic phosphate pebble sample was obtained from IMC Phosphate Company, FL. This sample has been sized, and samples of each size fraction are being analyzed to determine phosphate, CaO , MgO , Fe_2O_3 , Al_2O_3 , and acid insol contents. The component analyses will be used to establish grinding/liberation parameters and separation procedures. The National Research Center for Coal and Energy (NRCCE) analytical laboratory at West Virginia University will analyze the dolomitic phosphate pebble samples. A phosphate module has been purchased for an existing Lachat Quicken 8000 Flow Injection Analyzer (FIA); an Association of Fertilizer and Phosphate Chemists (AFPC) manual of analytical procedures for phosphate determination and phosphate rock standards have also been obtained and the laboratory is in the process of setting up appropriate procedures for phosphate analysis. Simultaneous ICP-OES with a radial torch configuration (Varian Vista-Pro) is being used to determine CaO , MgO , Fe_2O_3 and Al_2O_3 contents and a FIPR wet chemical procedure is being used to determine acid insoluble material content. The necessary reagents for the batch flotation and column flotation phases of this study have been received from IMC Phosphate and ARR-MAZ Products, Division of Process Chemicals.

The separation of carbonates from phosphate ores by flotation is a very complex process, due to similarities in the surface chemical properties of the constituent minerals and

to the complicated solution chemistry generated by dissolved forms of the salt-type minerals present in the system. Since the 1970's, much research has been done on separation of dolomite from phosphate ores. Among the many different processes developed, froth flotation is widely recognized as the most efficient approach for the treatment of finely disseminated dolomitic phosphate ores. The flotation process can be either dolomite flotation with depression of phosphate or phosphate flotation with depression of dolomite. For the beneficiation of sedimentary dolomitic phosphate ores, floating dolomite while depressing phosphate is both technically and economically feasible because dolomite is usually much less prevalent than phosphate in these ores. The optimum pH value for dolomite flotation in acid media is one of the key parameters for maximizing dolomite flotation. Improved selectivity in dolomite flotation also depends on the effectiveness of phosphate depression. Therefore the mechanisms of phosphate depression and the surface characteristics of calcite and dolomite (Ca- and Mg-carbonates) have been examined and are summarized in Table 1. The summarized knowledge is being used to determine optimum pH's and to develop dolomite flotation strategies for dolomitic phosphate pebble flotation.

Task 2-4: Equipment Set-up

Batch flotation cells and a Denver automatic flotation machine has been set-up for reagent studies. A flotation column has also been set-up and is ready for additional modifications to prepare it for coarse size flotation column tests.

SUMMARY

Efforts to establish major component concentrations in the dolomitic phosphate pebble sample were complicated by problems with the determination of phosphate content of the dolomitic phosphate pebble samples using the NRCCE Analytical Laboratory's Lachat QuickChem 8000-FIA Analyzer. The lab is working with FIPR resolve these problems. The mechanisms of phosphate depression and the behavior of carbonates in acid solution have also been examined.

FUTURE WORK

Questions related to the analysis of phosphate content in dolomitic phosphate pebble samples should be resolved during the next reporting period. Once these problems have been resolved, the liberation of dolomite and phosphate in the different size fractions will be determined and used to establish optimum grind conditions. Samples also will be prepared for semi-batch flotation tests to determine reagent requirements and optimum operating conditions for column flotation.

Table 1. Mechanisms of phosphate depression by phosphoric acid and/or sulfuric acid for dolomite flotation in dolomitic phosphate flotation systems.

Investigators	Sample source and test scale	Flotation pH and pH modifier	Results	Explanation
Abramov, et al. (1993)	16.72% P ₂ O ₅ , calcareous phosphate ore (Turkey) Lab test	pH 5.5-6.3 H ₃ PO ₄	28% P ₂ O ₅ , 77% recovery	Formation of hydrophilic compound on calcite; thermal dynamic explanation of zero charge potential of minerals for selectivity of calcite and apatite
Anazia & Hanna (1987)	23.1% P ₂ O ₅ , 7.9% MgO phosphate ore (China), 18.5% P ₂ O ₅ , 10.3% MgO phosphate ore (India) lab tests	pH 4-5 HCl, HNO ₃ , H ₂ SO ₄ , H ₃ PO ₄	36.2% P ₂ O ₅ , 1% MgO, 79.8% recovery 38.2% P ₂ O ₅ , 0.8% MgO 82.1% recovery	Selectivity of carbonate/ phosphate separation due to higher surface dissolution and generation of micro-bubbles on carbonate particle surface
Elgillani & Abouzeid (1993)	Carbonate phosphate, phosphate ore (Egypt), Lab test	pH 5.5-6 H ₂ SO ₄ , H ₂ C ₂ O ₄ , H ₃ PO ₄ , KH ₂ PO ₄	NA	Phosphate depression follows the order of H ₃ PO ₄ > H ₂ C ₂ O ₄ > H ₂ SO ₄ due to adsorption or formation of CaHPO ₄ on apatite surface
Johnson & Leja (1978)	Dolomite and apatite Lab test	PH 6 H ₃ PO ₄	NA	Depression action of orthophosphate ion is due to formation of strong hydrogen bonding between orthophosphate ions adsorbed on apatite surface and water molecules surrounding apatite, making mineral more hydrophilic. Hydrogen bonds on dolomite are weak. Because carbon dioxide is generated from dolomite in acid media, it interferes with the formation of strong hydrogen bonds.
Moudgil, & Chanchani (1985)	Pure apatite and dolomite	PH 5-6 Apatite flotation at pH 10, dolomite flotation at pH ≤ 5	NA	Presence of excess calcium and magnesium ions dissolved from dolomite and depletion of collector by precipitation as calcium and magnesium oleate to depress apatite. More oleic acid molecules are adsorbed onto the surface of dolomite due to higher density of surface hydroxyl groups on the surface of dolomite
Rao, & Mohanty (2002)	19% P ₂ O ₅ , 9.2% MgO phosphate ore (India) Lab test	pH 4 1:1 mixture of H ₂ SO ₄ and H ₃ PO ₄	36% P ₂ O ₅ , 95% recovery	NA
Prasad, M. et al. (1995)	12% P ₂ O ₅ , 32% CaO phosphate ore (India) Lab test	PH 5.5 Carbonate flotation	27.8% P ₂ O ₅ , 66% recovery	NA
Prassad, M, et al. (2000)	13% P ₂ O ₅ , 27.1% SiO ₂ , phosphate ore (India) Lab test	PH 5-5.5 Carbonate flotation	29.5% % P ₂ O ₅ , 7.9% SiO ₂ , 60% recovery	NA

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PUBLICATIONS/PRESENTATIONS

None.

Appendix F: Improving Densification of Fine Coal Refuse Slurries to Eliminate Slurry Ponds

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 10/1/03 Ending Date: 3/30/04
<u>Sub-Recipient Project Title:</u> Improving Densification of Fine Coal Refuse to Eliminate Slurry Ponds.	<u>Report Information:</u> Type: Semi-Annual Number: 2 Period: 10/1/03-3/31/04 Date: 4/30/04 Code: KY002
<u>Principal Investigators:</u> B.K.Parekh	
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ABSTRACT

During this reporting period, characterization, flocculation and settling studies were conducted on the fine waste slurry obtained from the Coal Clean Corp. preparation plant, located in Dr Branch, W.Va. Laboratory study indicated that the thickener underflow (UF) could be thickened to 48% solids using 31 g/t of anionic and 31 g/t of the cationic flocculant. Similarly, using 15 g/t of anionic flocculant the screen bowl centrifuge drain slurry could be thickened to 58.5% solids. Pilot-scale study at the plant showed that the thickener UF could be thickened to about 40% solids. Additional test are planned to utilize the slurry flocculated by the Coal Clean Corp. for dewatering using the belt filter press at the plant to obtain a comparative test result.

INTRODUCTION

Background

Increased mechanization in the underground coal mining industry has decreased selectivity and increased the volume of refuse. Coal preparation separates non-combustibles material from coal. Thus, a coal preparation plant separates the material it receives into a product stream and a reject stream, which may be further divided into coarse and fine refuse streams. Depending on the source, 20 to 50 percent of the run-of-mine material ends up in reject stream. One of the reject streams is fine waste slurry, which is a blend of water, coal fines, silt, sand, and clay particles, and is commonly disposed of in an impoundment. As of August 2001, MSHA oversees 713 active fresh-water and slurry impoundments in the United States. The coal industry is required to monitor the impoundment constantly and maintain the dikes holding the slurry. There have been several incidents of impoundment breakthrough, of these, the Buffalo Creek in W.V in 1972 and the Martin County Coal in Kentucky in the year 2000 have drawn attention of Federal and State Governments and local people due to heavy loses of life and property. A recent study conducted by the National Research Council defined the problem in detail and provided several recommendations to avoid the slurry impoundment breakage. One of the recommendations referred to utilizing advanced dewatering technology, which would reduce the amount of water being stored in the slurry.

An advanced thickening technique known as “Paste Thickening Technology” marketed by EIMCO, has been successfully applied in alumina processing industry, for dewatering ‘red mud’ a most difficult material to dewater. The technique utilizes DEEP CONE Thickener specially designed, holds a bright prospect of dewatering the fine coal refuse tailings to a high percent solids so it could discharge as a paste. The thickened material could be stacked at a low angle of repose rather than stored in a pond. Thus, the fine refuse slurry ponds could be completely eliminated. Even though the “Paste Thickening Technology” is being used in the alumina industry, no basic rheological or other data exists on fine coal tailings. There is an urgent need to develop a process alternate to conventional ponding of the waste slurry industry.

Objective and Approach

The main objective of the proposed program is to evaluate the application of DEEP CONE technology for the disposal of fine coal refuse. The program includes study of the basic rheological properties of the flocculated fine refuse solids for producing highly thickened solids capable of disposing as a paste. It is also the objective of the proposed research to utilize the rheological data obtained in pilot-scale testing of the “DEEP CONE thickener to obtain technical and economic data for a commercial operation. The technique will be evaluated on the thickener feed slurry (pre-flocculated) as well as flocculated slurry obtained from a thickener underflow.

PROJECT TASKS

Task 1. Acquisition and Characterization of Samples

Two five gallons buckets of fine waste slurry from the thickener underflow, and one five gallon bucket of screen bowl centrifuge main drain, were collected from the Coal Clean Corp. preparation plant located at Dry Branch, West Virginia. A representative sample of the slurry was obtained using the Carpcro Rotary Slurry Sampler and characterized for pH, particle size distribution, solid and ash contents and mineralogy. The solids content of the thickener underflow slurry was 24.28% and that of centrifuge main drain was 18.7%. The +325 mesh in the thickener UF and the centrifuge main drain was 27.9% and 75%, respectively. The particle size distribution of both the samples is shown in Table 1. The pH and ash content of the thickener UF were 6.68 and 62.55%, respectively. Similarly, the pH and the ash content of the centrifuge drain slurries was 7.00 and 10.7%, respectively. The ash fraction consisted of kaolinite, quartz and magnetite as determined from x-ray diffraction analysis.

Table 1. The particle size distribution of the thickener UF and the centrifuge main drain of the Coal Clean Corporation preparation plant.

Sample Name	D10% microns	D50% microns	D90% microns
Thickener Underflow	1.42	9.14	40.74
Screen Bowl Main Drain	3.21	29.54	98.03

Task 2. Flocculation and Rheological Studies

Flocculation Studies

In this task, a detailed flocculation study of both the slurries was conducted to identify the optimum solids concentration at which flocculation is most effective, resulting in the highest settling rate in addition to minimizing the amount of flocculants. The Coal Clean Corp. currently uses 90 g/t of cationic and 24 g/t of cationic in their thickener. The following flocculants were used for the study to simulate the current flocculation practice at the plant.

Cationic: Percol 368
Anionic: Magnafloc 358

Flocculation and settling tests were conducted as per the procedure developed by the Dorr-Oliver Eimco Company and were described in earlier report. The product of the initial settling velocity (maximum settling rate, m/hr) and the diluted slurry solids concentration (tones dry solids/m³) gives the solids settling flux (tones/hr/m²). Testing of the refuse thickener underflow showed that addition of 75% of anionic dosage and then 100% of the cationic, and then 25% of the anionic flocculants dosage gave the best results. Table 2 lists experimental data on both the slurries.

Table 2. Settling Flux data of the Thickener UF and the Screen bowl centrifuge samples.

Sample	Feed solids Wt. %	Diluted solids, Wt. %	Cationic floc. dosage g/t	Aninic floc.dosage g/t	Settling flux, t/day/m ²
Thickener UF	25	4-5	30-35	30-35	32
Screen bowl drain	20	10-12	None	15-20	99

A series of 2-liter standard settling tests were conducted on each sample to reconfirm the flocculation conditions and initial settling velocity determined in the flux tests. The settled solids concentration was determined to obtain data on compaction of solids which are listed in Table 3.

Table 3. Compaction data of Thickener UF and the Screen bowl centrifuge slurry samples.

Sample	Initial Solids Concentration. wt%	Initial settling velocity, m/day	Magana floc 358 ppm	Percol 368 ppm	Ultimate solids Concentration, wt%
Thickener UF	4.97	628	31	31	48.8
Centrifuge screen bowl drain	12.0	861	15	0	58.5

Rheological Studies

Yield stress measurements were made on the thickener underflow settled solids to determine the possible underflow density operating range that is representative of a 'paste' or 'high density' Paste Thickener Underflow. Figure 1 shows the solids concentration vs. the yield stress of the thickener UF. A practical operating point for a paste thickener will be at yield stress of 150 Pa. giving about 63% solids in the paste.

Task 3: Pilot-Scale Testing and Process Optimization Studies

The pilot-plant studies were conducted at the Coal Clean Corp. plant using the Dorr-Oliver Eimco a Deep Cone Thickener of 1.5 m (~ 5 ft) diameter and 7.5 m (~ 25 ft) height (Figure 2). Initially tests were conducted on the thickener UF feed containing about 25% solids. The flocculation of the slurry was conducted by adding the anionic flocculant using the duct system of the Deep Cone thickener. The results showed that about 40% thickened solids could be obtained from the slurry. However, it was noticed that the thickener UF flocculated by the preparation plant for dewatering the fine refuse using the belt filter press was of different in consistency and appeared to be better flocculated. Thus, it was decided to use the pre-flocculated slurry from the plant for further testing.

Figure 1. Solids Concentration vs. Yield Stress of Thickener Underflow from Coal Clean Corporation.

SUMMARY

The Coal Clean Corp. plant samples of thickener underflow and the screen bowl centrifuge drain samples contained about 25% and 20% solids, respectively. The pH of both slurries was around 7. The average (D_{50}) particle size of the thickener UF and the centrifuge samples was 9.14 and 29.54 microns, respectively. Settling flux of the thickener UF after adding 30 g/t of anionic and 30 g/t of cationic flocculants was 32 t/day/m², whereas for the centrifuge slurry the settling flux using only 20 g/t of anionic flocculant was 99 t/day/m². Laboratory studies provided compact solids of 48.8% for the thickener UF and 58.5% for the centrifuge drain samples. The pilot-scale study of the centrifuge slurry provided 58.5% thickened solids.

FUTURE WORK

Future pilot-scale will be conducted using the flocculated thickener UF slurry provided by the Coal Clean Corp. In these tests, the feed rate, and bed height of the settled solids in the Deep Cone Thickener will be varied. We also plan to start the characterization and laboratory flocculation and settling studies on the James River Coal and the Arch of West Virginia samples.

PUBLICATIONS/PRESENTATIONS

One presentation made at the Annual Cast program review meeting in Charleston. Four presentations and two publications have been scheduled in the next couple of months.

Figure 2. Deep Cone Thickener Pilot-Scale Unit.

Appendix G: Development and Testing of a Horizontal Pressure Belt Filter

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 4/01/03 Ending Date: 5/30/04
<u>Sub-Recipient Project Title:</u> Development and Testing of a Horizontal Pressure Belt Filter	<u>Report Information:</u> Type: Semi-Annual Number: 2 Period: 10/1/03-3/31/04 Date: 5/9/04 Code: VA010
<u>Principal Investigators:</u> Gerald H. Luttrell and Roe-Hoan Yoon	
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ABSTRACT

A variety of mechanical processes are available for dewatering fine particles in the coal and mineral processing industries. Unfortunately, many of these processes suffer from major shortcomings such as poor dewatering performance, low throughput capacity, and high capital and operating costs. This project seeks to overcome these problems by developing a new type of dewatering process that combines the operational flexibility of a continuous belt filter with the dewatering efficiency of a batch pressure filter. The proposed project involves the design, construction, testing, and evaluation of a prototype unit and pilot-scale test circuit having a production capacity of approximately 100 lb/hr. Test data obtained from the project will be used to promote the engineering development of a full-scale commercial unit. Work completed during this reporting period focused on (i) development of a spreadsheet based simulation program to assist in the design of the new filter technology and (ii) completion of engineering blueprints for the fabrication of the prototype unit.

INTRODUCTION

Background

Filtration processes are commonly used in the coal and minerals processing industry to remove excess moisture from the surfaces of fine particles. In the U.S., fine coal filtration has traditionally been carried out using vacuum disc filters. These units are capable of maintaining high coal recoveries (>97%) while generating product moisture contents in the 25-30% range (which is strongly dependent on particle size). Disc filters consume very little floor space for a given production rate, but suffer from problems associated with poor cake discharge and blinding of the filter medium. Disc filters also have the tendency to produce somewhat higher moistures than other filter designs because of the blow back of water that occurs during cake discharge. Because of these problems, vacuum belt filters have become more popular method for dewatering fine coal in Australia and South Africa. Advantages of this design include the ability to clean the filter cloth on the return side using high-pressure sprays, the ability to control the cake thickness (by varying belt speed), and the independent control of cake formation and drying cycle times. In addition, maintenance requirements are generally very low due to the slow belt speed (i.e., low rates of wear and very low failure rates). Unfortunately, the performance of vacuum filters is limited by the vacuum level that can be effectively maintained across the filter cake. The vacuum cannot theoretically exceed 1 atm and is typically limited to 0.8 atm or less in industrial practice. To overcome this limitation, several different designs of pressure filters have been developed including tube presses and plate-and-frame filters. These units, which can operate at pressures up to 6 atm, provide higher filtration rates and lower product moistures compared to vacuum filters. Unfortunately, industrial applications have been relatively limited due to the high capital cost of the equipment and long production cycle created by the batch mode of operation.

A tremendous incentive exists to develop a filtration process that (i) makes use of a high differential pressure, (ii) operates in a continuous mode, (iii) minimizes filter cloth blinding while avoiding blow back of moisture, and (iv) offers operational flexibility in terms of independent control of cake thickness and drying cycle time. A process that is capable of meeting all of these criteria is a horizontal belt pressure filter. This new technology is very similar in design to that of a conventional horizontal belt vacuum filter, except the filtering mechanism is enclosed inside a pressurized chamber. During operation, feed is injected into the pressured chamber at the head of the filter belt. The high pressure drives the water through the filter cloth/belt where it is discharged into an effluent collection chamber maintained at atmospheric conditions. The filter cake is dropped into an air lock that sequentially opens and closes to continuously discharge the dried solids. Because of the high pressure differential, the filter cake produced by the new filter would be significantly drier than that obtained using disc or belt vacuum filters that are limited to a practical maximum differential pressure of approximately 0.8 atm. The elimination of the blow back of moisture during cake removal ensures that the driest possible cake is produced. Also, the capital cost of the compressor or staged blower can be less than 20% of the cost of a vacuum pump with an equivalent volumetric capacity. This difference would significantly reduce the cost of the proposed belt filtration system in comparison to vacuum based filters.

Objective and Approach

The primary objective of this project is to develop and test a horizontal belt pressure filter that is capable of efficiently dewatering fine coal in a cost effective manner. The new filter combines the operational benefits of a continuous belt filter with the dewatering efficiency of a batch pressure filter. The proposed project activities include project planning, equipment design/construction, shakedown testing, and detailed testing. In addition, a complete technical and economic evaluation of the new technology will be performed after the proposed experimental work has been completed.

PROJECT TASKS

Task 1 – Equipment Design/Construction

Work performed during this reporting period primarily focused on the development of design criteria for the prototype belt filter. Because of the large number of process variables involved, a mathematical simulation program was developed to assist in the design of the new equipment. The program was constructed based on empirical expressions developed from laboratory filtration tests. The test data were collected for a minus 1 mm clean coal sample using a 4-cm diameter batch filter. The batch tests were conducted as a function of solids loading (cake thickness), applied pressure, and drying time. In addition, several dewatering aids were used to improve filter performance. During each experiment, measurements were taken to determine the cake formation time and equilibrium cake moisture.

Statistical analyses were conducted in order to relate the experimental test data to the various process parameters. The analyses suggest that cake formation time is related to a normalization parameter “A” given by:

$$A = H/P \quad [1]$$

in which H is the cake thickness (inches) and P is the applied pressure (inches Hg). This relationship is plotted in Figure 1 for filtration tests conducted using two different dewatering aids. These plots indicate that the cake formation time (t_f) can be determined using the following power relationship:

$$t_f = 48100 (H/P)^{1.74} \quad \{\text{No reagent added}\} \quad [2]$$

$$t_f = 43.6 (H/P)^{2.46} \quad \{\text{With filter aid}\} \quad [3]$$

According to these relationships, the cake formation time is improved by decreasing cake thickness or increasing the filtration pressure. In addition, the addition of a dewatering aid greatly increased the cake formation time. In fact, the formation time was reduced by nearly three orders of magnitude via the addition of the filter aid reagent.

Figure 1. Statistical correlation between cake formation time and normalization factor “A” with and without the addition of a dewatering aid.

The statistical analyses also suggest that the final equilibrium cake moisture (M) can be related to a normalization factor “B” given by:

$$B = P (t_d) / H^2 \quad [4]$$

in which t_d is the cake drying time (min), P is the applied pressure (inches Hg), and H is the cake thickness (inches). As shown in Figure 2, this parameter makes it possible to

$$M = 31.4 - 2.28 \ln [P (t_d) / H^2] \quad \{ \text{No reagent added} \} \quad [5]$$

$$M = 27.9 - 2.46 \ln [P (t_d) / H^2] \quad \{ \text{With filter aid} \} \quad [6]$$

These expressions show that the final filter cake moisture can be reduced by increasing pressure, increasing drying time, and reducing cake thickness. Of these, cake thickness has the greatest overall impact on moisture due to the squared power for this term. In addition, the addition of the filter aid reduced the overall moisture by approximately 4 absolute percentage points when compared at the same value of the normalization factor.

The empirical expressions from the laboratory tests were used to develop a mathematical simulation program for the horizontal belt pressure filter. Input variables for the simulation program included:

Figure 2. Statistical correlation between equilibrium cake moisture and normalization factor “B” with and without the addition of a dewatering aid.

- applied pressure (P),
- dry solids feed rate (F),
- belt length (L),
- belt width (W)
- belt velocity (V),
- dry cake density (ρ), and
- filter aid type.

From these parameters, the cake thickness (H) and total filtration time (t_t) was calculated using the following analytical relationships:

$$H = F/(\rho V W) \quad [7]$$

$$t_t = L/V \quad [8]$$

Once the thickness was known, Equation [2] or [3] was used to determine the required cake formation time (t_f). For a given belt geometry and speeded, the drying time that remained was then determined by noting that:

$$t_d = t_t - t_f \quad [9]$$

Depending on whether or not a filter aid was employed, Equation [5] or [6] was then used to calculate the expected cake moisture (M). For convenience, these expressions were incorporated into a spreadsheet for simulating the performance of the belt filter. An example of the output from the simulation routines is presented in Figure 3. Design information obtained from the simulation program has been used to design the 100 lb/hr prototype filter. Procurement of the construction materials and preliminary fabrication of the prototype unit is now underway.

SUMMARY

The basic design of a prototype horizontal belt pressure filter has been completed. The prototype has been designed with a 2 inch wide by 6 ft long carrying belt. This width provides the required throughput capacity of 100 lb/hr when operated at a belt speed of 5.5 ft/min with a 0.5 inch cake thickness. Work is now underway to procure the necessary construction materials and components required to complete the fabrication of the unit.

Figure 3. Simulation program for the horizontal belt pressure filter.

FUTURE WORK

Work to be completed during the next reporting period will primarily involve the procurement of materials and other components required to complete the construction of the horizontal belt pressure filter. The fabrication and machine work is expected to require approximately four months to successfully complete. This effort has been delayed due to problems associated with departmental machine shop personnel and is expected to be correctly very shortly. Once the construction is completed, initial testing and evaluation of the prototype unit will begin.

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PUBLICATIONS/PRESENTATIONS

None publications or presentations have been given during the current reporting period.

Appendix H: Bio-Assisted Heap Leaching of Nickel Laterites for the Development of a Domestic Nickel Industry

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)		<u>Period of Performance:</u> Starting Date: 10/01/03 Ending Date: 03/31/04	
<u>Sub-Recipient Project Title:</u> Bio-Assisted Heap Leaching of Nickel Laterites for the Development of a Domestic Nickel Industry		<u>Report Information:</u> Type: Semi-Annual Number: 2 Period: 10/01/03-03/31/04 Date: 03/31/04 Code: UT002	
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ABSTRACT

This research proposal involves a biotechnological approach for the production of nickel metal from low-grade laterite ore in a synergistic mode with co-production of citric acid called bio-assisted heap leaching (BAHL). There are two possible modes of operation of BAHL processes. The direct route involves combining the nickel laterite ore with an organic nutrient and placing it on heaps where fungi, such as *Aspergillus niger*, produce organic acids during their natural metabolic cycle. Recycle solution is sprayed over the heaps, and its percolation through the heaps results in the dissolution of nickel. The indirect route involves the separate production of a citric acid fermentation broth for leaching by fungi with the addition of growth medium. This organic acid broth is sprayed over the heaps and dissolves the nickel. In both cases the The resulting nickel-containing leach solution is collected and then the nickel and citrate values are recovered.

INTRODUCTION

Background

The fungi typically used in bioleaching do not directly degrade the mineral, but rather degradation is achieved via the production of organic acid metabolites. The metal extraction by microbially-produced acids can occur through two possible mechanisms, which can take place separately or simultaneously. (O.H. Tuovinen and D.P. Kelly, 1974) First, metal cations may be directly displaced from the ore by hydrogen ions produced by the microorganisms resulting in a common acid leaching mechanism. (P.G. Tzeferis, 1994B) Second, compounds produced by the microorganism can bind metals into soluble complexes by chelation. (D.I. McKenzie, et al., 1987)

While leaching laterite ores with sulfuric acid releases substantial amounts of nickel, organic acids, especially hydroxy-carboxylic acids, can achieve similar or better nickel dissolution. (K.A.K. Alibhai, et al., 1993; P.G. Tzeferis, 1994A) While a variety of organic acids have given good results, citric acid, a well-established product of fungal metabolism, has been found to be the most effective mobilizer of nickel from laterites. When leaching is performed by combining organic acids with small amounts of sulfuric acid to maintain low pH's, there has shown to be a synergistic effect on leaching, such that the Ni dissolution is actually higher than simply a sum of the individual dissolutions.

Objective and Approach

The specific objectives of the proposed research are to:

- demonstrate the feasibility of the bio-assisted heap leaching process for the selective dissolution of nickel from low-grade laterite ores;
- establish viable fungi cultures that have been acclimated for heap leaching conditions;
- determine the important process parameters, such as inoculum addition, acid addition composition(s), flowrate of recycle water, size distribution of agglomerated ore particles, effect of ions in recycle water, and initial and interim additions of the carbon source.
- develop methods for metal/citrate species analyses;
- determine the most effect process method: the *direct* approach, where the ore is contacted directly with nutrients and fungi in the heap, or the *indirect* approach, where the citric acid is fermented separately to produce a broth for leaching in a stirred reactor or a heap.

PROJECT TASKS

Task 1 – Acquisition and characterization of ore samples

Because of the very heterogeneous nature of laterite deposits, two ore samples have been acquired for use in the project activities. One ore is from an Australian laterite deposit,

while the other is from a Latin American laterite deposit. The initial analysis of the two ore samples has been completed. The results are shown in Table 1.

Task 2 – Establishment of microorganism cultures

Aspergillus niger was selected as the fungus of interest because of its ability to produce significant quantities of citric acid, which is thought to be the main organic acid involved in nickel leaching. *Aspergillus niger* van Tieghem, anamorph was revived using the prescribed potato dextrose agar medium. All subcultures have stemmed from this initial culture.

Two types of cultures methods have been used. As the culture media for the leaching test will be molasses based, the microorganisms have been acclimated to this media, which consists of molasses with essentials salts such as copper sulfate, zinc sulfate and ammonium phosphate. To acclimate the microorganisms to the ore, ore was added to the potato dextrose agar medium recipe. The viable organisms have been established by alternating these methods. After the initial culture was established, a 1 inch by 1 inch square of the colony was removed and added to the molasses-based medium. Once this colony was established, a 1 inch by 1 inch square of it was removed and added to a potato-based medium that contained ore. Again once this colony was established, a 1 inch by 1 inch square of it was removed and added to a molasses-based medium and so on. Figure 1 shows various images of a colony established on a molasses-based medium. Figures 2 – 4 show various images of colonies established on potato-based media that contain varying amounts of ore. Figure 4 clearly shows the spores and accompanying structures that are typical of fungi.

Attempts are being made to culture the “naturally-occurring” fungi that are present on the ores. While some colonies have been established, the organisms still need to be identified.

Table 1: Chemical analyses of laterite ore samples.

Analyte (%)	Latin American ore	Australian ore	Composite sample	
			Laboratory results	Calculated results*
Co	0.037±0.003	0.042±0.004	0.030±0.009	0.039
Cr	0.278±0.009	0.589±0.06	0.262±0.06	0.427
Fe	16.1±0.9	21.8±1	14.6±1	18.8
Mg	8.42±0.1	3.73±0.03	7.74±0.6	6.17
Mn	0.246±0.02	0.334±0.05	0.215±0.05	0.288
Ni	1.41±0.04	0.564±0.03	0.96±0.04	1.00
Si solids	52.8±0.4	52.9±1	57.1±1	52.8
LOI	1.11±0.06	0.81±0.06	1.12±0.3	0.963
Moisture	23.5±2	28.0±0.5	31.7±5	25.6

* A composite sample of the 2 samples was produced and analyzed. Based on the average results shown for these two samples and the weighting of the mixture, the values were calculated for the anticipated results.

Figure 1: Images of *Aspergillus niger* colonies cultured on a molasses-based medium.

Figure 2: Images of *Aspergillus niger* colonies cultured on a potato-based medium.

Figure 3: Images of *Aspergillus niger* colonies cultured on a potato-based medium.

Figure 4: Images of *Aspergillus niger* colonies cultured on a potato-based medium.

Task 3 – Shake flask leaching studies

Shake flask leaching studies have been underway. Leaching was performed on the two ore samples using the lixiviants H_2SO_4 at a concentration of 25 g/L or citric acid, oxalic acid and glycine at a concentration of 0.5 M, a solids concentration of 20 g/L and 28 °C. Figure 6 shows the leaching of iron from the ores. The results in Figure 5 show that while oxalic acid is not the most efficient lixiviant in terms of nickel leaching, it is very effective for minimizing the leaching of iron from the ore. For shorter leaching times, glycine is also an effective lixiviant; however at longer times, the nickel precipitates out resulting in the reduction of the nickel concentration in the solution.

Preliminary leaching studies are underway using the viable microorganisms. Once such an organism colony was established, an aliquot of the broth was used to inoculate a leach slurry with a solids concentration of 20 g/L. Figure 5 shows the comparison of leaching with the microorganisms and mineral and organic acids. Before the precipitation that occurred at longer leaching times, the leaching by the fungus is much more effective than citric acid.

Task 4 – Column leaching studies

Initial column leaching studies are underway. This first required developing an agglomeration procedure using sulfuric acid to create agglomerates with an approximate top size of ½ inch. Based on these preliminary studies, columns are to be set-up that will be used to leach the ore both in-situ and ex-situ with the microorganism.

Figure 5: Leaching of laterite ores at an organic acid concentration of 0.5 M, a mineral acid concentration of 25 g/L, a solids concentration of 20 g/L and 28 °C.

Figure 6: Leaching of laterite ores at an organic acid concentration of 0.5 M, a mineral acid concentration of 25 g/L, a solids concentration of 20 g/L and 28 °C.

SUMMARY

Viable microorganism colonies have been established. It has been demonstrated that they can effectively leaching nickel from two different types of laterite ores. Protocols continue to be developed for acclimating the microorganisms, chemical analyses and leaching. The scoping tests that are currently underway will help fine-tune the required experimental program.

FUTURE WORK

While the use of microorganisms to leach lateritic ores has been studied, the literature lacks sufficient data for comparison of the effectiveness of the different types of organic media. A critical issue will be to determine which organic media is the most effective not only in terms of citric acid production, but in terms of nickel dissolution, as different organic sources may have an influence on the types of organic acids and metabolites that are produced. Different subcultures will be allowed to ferment with different growth media. The resulting broths will be used in shake flask studies to better understand the role nutrients play in the process.

Studies have shown that leaching the laterite ores with fungally-produced organic acids achieved higher dissolutions than with similar concentrations of commercial organic acids. It has been suggested that the fungi may be producing other metabolites in small quantities that aid in the solubilization of the nickel. It may also be possible that even under the same conditions, in the presence of the nickel ore, the fungi produce more acid metabolites than when no ore is present. As a result, the shake flask studies will also be undertaken with the direct addition of the microorganisms and nutrients.

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PUBLICATIONS/PRESENTATIONS

To date no scholarly works have resulted from the project activities.

Appendix I: The Development and Utilization of Alkaline Sulfide Leaching and Recovery of Gold

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 10/1/03 Ending Date: 3/31/04
<u>Sub-Recipient Project Title:</u> Development of Alkaline Sulfide Leaching and Recovery of Gold	<u>Report Information:</u> Type: Semi-Annual Number: 2 Period: 10/1/03-3/31/04 Date: 3/31/04 Code: MT001
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ABSTRACT

During this reporting period, progress was made on all aspects of the proposed tasks. It should be noted that due to a delay in hiring personal, that technical work on this project began five months behind schedule. A no-cost extension to continue the project five months longer has been requested. Some of the key accomplishments that were achieved during this reporting period include: developing thermodynamic models of the alkaline sulfide leaching system; development of optimized gold leaching conditions utilizing statistically designed experiments; performed high-temperature gold leaching experiments with the alkaline sulfide leaching process; demonstrating the ability to leach gold from several industrial ores and concentrates with the alkaline sulfide leaching process; performing a small pilot-scale gold leaching test, demonstrating the feasibility of recovering gold from an alkaline sulfide solution using several different techniques; and, establishing a method for treating alkaline sulfide solutions to recover sulfur.

INTRODUCTION

Background

An alternative, non-cyanide gold leaching process based on the use of environmentally benign sulfur compounds as both the oxidant and lixiviant components of the leach solution is currently underdevelopment. The use of non-cyanide reagents has become particularly relevant in light of recent public concerns involving the use of cyanide for gold production. Furthermore, the development of an alkaline sulfide based leaching processes is particularly well suited for treatment of sulfide gold ores pretreated with low temperature pressure oxidation whereby the majority of gold tends to accumulate in the elemental sulfur produced. Additional potential advantages of this process include the production of value added byproducts and improved public perception of gold mining through the use of an environmentally benign leaching process.

The technological issues that are currently hindering the use of alkaline sulfide leaching are a lack of basic understanding of the leaching chemistry and thermodynamics associated with the process. Thus, this study was undertaken to develop an understanding of the basic reaction chemistry which occurs in the alkaline sulfide leaching process and to establish a thermodynamic model in order to predict optimum leaching conditions under various conditions.

Objectives and Approach

The objectives of this project (Phase I) are:

- Task 1 – Develop a thermodynamic model of the alkaline sulfide leaching system;
- Task 2 – Optimize the chemistry of the alkaline sulfide gold leaching process; and,
- Task 3 – Study the optimized leaching system kinetics.

The general approach taken for accomplishing Task 1 consisted of performing a literature search for relevant thermodynamic data. Once the appropriate thermodynamic data were compiled, they were modeled with STABCAL, a thermodynamic modeling program. Optimized gold leaching conditions are being developed as part of Task 2. Statistically designed experiments are being used in order to efficiently find conditions conducive to producing an alkaline sulfide lixiviant that is both stable and rapidly leaches gold. The kinetic aspects of the optimized gold leaching conditions are being evaluated by analyzing the gold concentration as a function of time while conducting the lixiviant optimizing experiments. Further kinetic studies are planned that account for increased leaching temperatures.

PROJECT TASKS

Task 1: Thermodynamic Modeling of the Alkaline Sulfide Leaching System

Thermodynamic models of the alkaline sulfide leaching system with varied components were developed utilizing STABCAL. The thermodynamic data used to generate the models were obtained from literature values from the National Bureau of Standards. A value for the free energy of formation of the soluble AuS^- specie was calculated based on data from Hiskey & Atluri (1986). An Eh-pH diagram showing the sulfur species at thermodynamic equilibrium was constructed and is illustrated in Figure 1. The diagram is based on a solution containing 75 g/L sulfur and 1 g/L gold at 30°C. A meta-stable Eh-pH diagram was constructed using identical conditions (Fig 2). It is believed that the meta-stable Eh-pH diagram is a better representation of the alkaline sulfide system. Experimentally measured potentials and gold concentrations are currently being measured to verify the applicability of the meta-stable Eh-pH diagram. Preliminary results show close agreement with the meta-stable Eh-pH diagram.

Figure 1. An Eh-pH diagram of the gold-sulfur system; 75 g/L sulfur, 1 g/L gold at 30°C

Figure 2. A meta-stable Eh-pH diagram of the gold-sulfur system; 75 g/L sulfur, 1 g/L gold at 30°C.

Task 2: Optimization of the Alkaline Sulfide Leaching Process

Optimum conditions for leaching gold with the alkaline sulfide leaching process are being developed using statistically designed experiments. Initially, a factorial design was used to identify the important components of the alkaline sulfide leaching lixiviant. A two-level four factor one-half matrix model was used to help identify the components that had a significant effect on the alkaline sulfide lixiviant's ability to leach gold. The factors included in the design were the free hydroxide concentration, sulfur concentration, sulfide concentration, and thiosulfate concentration. By utilizing factorial design, it was found that thiosulfate additions to the alkaline sulfide lixiviant had a negligible effect on the amount of gold leached. However, it was found that the sulfur, sulfide, and free hydroxide concentrations were all important. A surface response model showing the effect of sulfide and free hydroxide concentrations and the amount of gold leached is shown in Figure 3. It can be seen from the figure that more gold was leached when the lixiviant contained 0 g/L free hydroxide and 50 g/L sulfide. The surface response model in Figure 4 shows that a

Figure 3. Surface response model illustrating the percent of gold leached as a function of sulfide and free hydroxide concentrations.

Figure 4. Surface response model illustrating the percent of gold leached as a function of sulfur and free hydroxide concentrations.

solution containing 50 g/L sulfide and 25 g/L sulfur resulted in a lixiviant that leached the most gold.

Based on the results from the factorial design, statistically designed experiments were performed to develop mixture models. Results from the mixture model analyses have shown that lixiviant containing high concentrations of sulfide with low concentrations of sulfur and free hydroxide are capable of relatively high gold recoveries. Development of the mixture models will continue. However, it should be noted that a significant improvement in the amount of gold leached has resulted from the optimization of the alkaline sulfide leaching process.

In addition to optimizing the basic components of the alkaline sulfide leaching lixiviant, factorial experiments were performed to analyze the effects of potential additives. Although several additives, e.g. peroxide, atmospheric air, sodium sulfite, were tested, none had a significant effect on the amount of gold dissolved. Testing of several more additives is planned during the next reporting period.

Task 3: Characterization of the Alkaline Sulfide Process Leaching Kinetics

The gold dissolution kinetics are highly dependent on the chosen chemistry of the alkaline sulfide lixiviant. However, in several instances, plots of the gold concentration as a function of leaching time resulted in a linear relationship. Further characterization of the gold leaching kinetics is planned at low, medium, and high temperatures.

Additional Significant Results

Results that were produced during this reporting period and were deemed significant but did not fall directly within the above tasks are detailed in the following itemized list:

- A gold recovery of 82% was achieved from an industrial gold concentrate that was processed using a nitrogen species catalyzed partial oxidation process followed by leaching with an alkaline sulfide solution at high temperatures;
- An alkaline sulfide solution containing 1 g/L of dissolved gold was produced when leaching at high temperatures;
- Testing of the alkaline sulfide leaching process on a small pilot scale with a gold concentrate obtained from Profile Resources (Profile Resources is a local gold producer and has contributed a significant amount of resources towards the development of the alkaline sulfide leaching process);
- Demonstrated the feasibility of recovering gold from an alkaline leach solution using electrowinning and ion exchange; and,
- Discovered that sodium sulfate and sulfur could be produced when the alkaline sulfide solutions were treated with pressure oxidation in an autoclave.

SUMMARY

Significant advancements were made during this reporting period in all three of the proposed task areas. Specifically, thermodynamic modeling in the form of Eh-pH diagrams was performed. Various components and concentrations were examined to determine their potential effect on the ability of the alkaline sulfide lixiviant to leach gold. Optimization of the alkaline sulfide lixiviant chemistry was performed initially by using factorial design to determine the reagents that had a significant effect on the amount of gold leached. Based on the factorial design results, mixture models were constructed by performing statistically designed experiments to optimize the individual components in the alkaline sulfide lixiviant. Preliminary data characterizing the gold leaching kinetics of the alkaline sulfide leaching process were collected. Plots of the gold concentration plotted as function of time exhibited a linear relationship. However, it was found significant variations in the kinetics resulted from relatively small changes in the lixiviant chemistry. Thus, further characterization of the kinetics will be performed once the lixiviant chemistry has been optimized. Additional significant results were included that highlighted some of the technical achievements accomplished and demonstrated the feasibility of the process aspects that will be characterized during the next reporting period.

FUTURE WORK

Research work during the next reporting period (Phase II of the Development of Alkaline Sulfide Leaching and Recovery of Gold will have begun) will focus on optimizing gold recovery processes such as carbon adsorption, ion exchange, chemical reduction, and electrowinning. Additionally, the alkaline sulfide leaching process will be used to process industrial gold ores and concentrates that are not amenable to traditional gold recovery by cyanidation. Research efforts will also be directed towards treating the alkaline sulfide

leaching solution to produce value added products such as sodium sulfate and a caustic solution which can be recycled back into the alkaline sulfide lixiviant. Since Phase I of the project is currently 5 months behind schedule due to a delay in hiring research personnel, a no-cost extension has been requested. If the request is approved, it is believed that all of the objectives in Phase I can be successfully completed.

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PUBLICATIONS/PRESENTATIONS

Three scholarly works that resulted from this projects activities were accomplished this reporting period. A conference paper by Dr. Anderson titled “Alkaline Sulfide Recovery of Gold Utilizing Nitrogen Species Catalyzed Pressure Leaching” was published in the proceedings from Hydrometallurgy 2003: 5th International Symposium in Honor of Professor Ian Ritchie. Additionally, two different presentations demonstrating the features of the alkaline gold leaching process were given. The first presentation was made at the Southwest Montana Technology Network. The second presentation was made at the Society for Mining, Metallurgy, and Exploration Inc. annual meeting in Denver, Colorado.

Appendix J: Hydrometallurgical Processing of Chalcopyrite Concentrates

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 4/1/03 Ending Date: 5/30/04
<u>Sub-Recipient Project Title:</u> Hydrometallurgical Processing of Chalcopyrite Concentrates	<u>Report Information:</u> Type: Semi- Annual Number: 2 Period: 10/1/03 to 3/30/04 Date: 3/25/04 Code: NV001
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ABSTRACT

The effect of nanosize particles of silica in chalcopyrite leaching systems is being studied with two techniques: (1) leaching experiments as a function of various leaching parameters and (2) electrochemical impedance spectroscopy (EIS). Leaching experiments are presented showing the important effect of the presence of nanosize silica. Initial electrochemical impedance spectroscopic experiments have been conducted which show that the sulfur layer that forms on chalcopyrite on leaching first increases in thickness with time and then decreases in thickness in the presence of nanosilica.

INTRODUCTION

Background

Chalcopyrite (CuFeS_2) is the most abundant and important source of copper metal available in the earth's crust. Over the years considerable research has been devoted to developing hydrometallurgical processes for leaching copper sulfide concentrates, especially chalcopyrite, at moderate temperature and pressure. Impetus for this research has been the desire for an economical alternative to smelting with the attendant generation of sulfur dioxide.

Widely-used oxidants for the leaching of chalcopyrite are ferric chloride and ferric sulfate in an acidic medium. The ferric chloride leaching reaction can be written as:

In sulfuric acid solutions containing ferric sulfate, the reaction is:

In ammoniacal solution the reaction is seen to produce thiosulfate and elemental sulfur:

The sulfur layer that forms on the surface of the chalcopyrite in all of these reactions is passivating and highly protective. The limited leaching response of chalcopyrite under these conditions is due to the passive sulfur layer formation. To increase recovery investigators have tried a number of methods. Munoz et al. (1979) reduced the chalcopyrite particle size to four microns and achieved about 60 % recovery at 90°C, 1200 rpm and 1.0 M sulfuric acid. When the particle size was increased to 12 microns, leaching had to be conducted for 100 hours to achieve about the same recovery.

One of the most successful techniques was developed by Miller (1979) using silver catalysis. Recovery was almost 100 %, but the economics of using silver to extract copper precludes its use.

Ozone oxidation was tried by Halvik and Skrobjan (1990). Again, this process has poor economics and has not been commercialized. Electrochemical oxidation has been tried using chalcopyrite as an anode (Illangovan et al., 1975). This has also not been successfully applied.

Objective and Approach

The objective of this investigation is to establish conditions under which chalcopyrite can be leached effectively at moderate temperature and pressure. A technique has been developed at the University of Nevada, Reno, that shows great promise for processing at

moderate conditions. This involves the addition of nanosize silica to the leaching systems. Two approaches will be used in this investigation: leaching of sized particles of chalcopyrite and electrochemical impedance spectroscopy.

Leaching of Chalcopyrite

Leaching studies are being carried out with various oxidants, ferric chloride, ferric sulfate and hydrogen peroxide in the absence and presence of nanosilica. Temperatures have been varied from 60° to 90°C.

Electrochemical Impedance Spectroscopic Characterization

A Schlumberger Model SI 1286 electrochemical interface connected to a Schlumberger Model SI 12650 Gain Phase Analyzer, controlled by a computer, is being used to study the electrochemical reaction of silica-catalyzed chalcopyrite leaching. Polished chalcopyrite samples are attached to a platinum wire using conductivity silver epoxy. Electrochemical experiments are being conducted with various oxidants, silica concentrations and pH.

PROJECT TASKS

Leaching Experiments

Leaching of chalcopyrite was conducted in the absence and presence of nanosize silica particles. Typical results obtained with Fe^{3+} as oxidant are given in Table 1. From these data, it is apparent that ferric sulfate is not as effective as ferric chloride as an oxidant/lixiviant in this system. The improvement in dissolution of chalcopyrite with higher level of addition of nanosilica is also apparent.

Table 1. Effect of ferric as oxidant in leaching of chalcopyrite. Conditions: 2.5 g/L chalcopyrite (74 x 37 μ), 0.5 N H_2SO_4 , 75°C, 24 hr-leaching.

Amount of Silica (g/L)	Ethylene Glycol (ml/L)	Ferric Salt (g/L)	Chalcopyrite Dissolution (%)
1.0	0	15 (ferric chloride)	56.3
1.0	0	15 (ferric sulfate)	17.2
3.5	10	15 (ferric sulfate)	39.5
1.0	0	30 (ferric sulfate)	56.8
3.5	10	30 (ferric sulfate)	69.0

Electrochemical Impedance Spectroscopy

Experiments were conducted with a chalcopyrite electrode in the absence and presence of nanosilica as a function of time. As shown in Figure 1, as reaction time proceeds, the impedance or resistance of the sample increases up to 8 hours. After that time essentially the same values of impedance are observed. What these data indicate is that the sulfur layer forming on the chalcopyrite surface increases in thickness for up to about 8 hours of leaching after which time no further oxidation or dissolution of the surface occurs.

Figure 1. Electrochemical impedance spectroscopic experiments of chalcopyrite in the presence of air in the absence of nanosilica.

In the presence of nanosize silica, a number of interesting phenomena are noted. First, a maximum in impedance is noted after two hours of oxidation has occurred (Figure 2). In other words the sulfur layer increases in thickness up to that time. After that time, however, the inhibiting effect that nanosilica has on sulfur layer formation is clearly shown. These data also show that the action of nanosilica occurs over a period of time.

SUMMARY

When chalcopyrite is leached with oxidants in acidic medium, a layer of sulfur forms on the chalcopyrite surface which inhibits dissolution, In the presence of nanosize silica, this protective layer of sulfur is not formed, and leaching can be effected at moderate temperature and pressure.

Figure 2. Electroscopic impedance experiments of chalcopyrite in the presence of air, H₂O₂ and nanosilica.

FUTURE WORK

Leaching experiments will be continued as a function of chalcopyrite particle size, temperature, oxidant concentration, silica concentration and degree of agitation to establish the reaction kinetics.

Electrochemical impedance spectroscopic measurements will be continued to establish impedance, conductivity and electrochemical parameters and compared with leaching data to determine the nature of silica catalyzed leaching of chalcopyrite.

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PUBLICATIONS/PRESENTATIONS

Results and discoveries resulting from this project were presented at the 2003 CAST 2003 Annual Workshop November 19-21, 2003.

Appendix K: Simultaneous Electrolysis of Copper and Ferrous Ions to Produce Copper Cathode and to Regenerate Ferric Sulfate - The Lixiviant to Dissolve Copper Sulfide Minerals

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 10/1/02 Ending Date: 5/31/04
<u>Sub-Recipient Project Title:</u> Simultaneous Copper Cathode Production and Ferric Sulfate Regeneration	<u>Report Information:</u> Type: Semi-Annual Number: 2 Period: 10/1/03-3/31/04 Date: 3/31/04 Code: MT002
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ABSTRACT

Progress was made on all aspects of the tasks on the original time-line in the proposal for months 2-7. The project is currently behind schedule by five months as a result of a delay in hiring personal. A no-cost extension has been requested. Several elements of each task were completed and including: generation of iron and copper Tafel plots, designed several different types of membrane separated electrolytic cells, obtained two different types of ion exchange membranes, constructed two different versions of a membrane separated electrolytic cell, and tested a membrane separated electrolytic cell whereby a noticeable amount of copper was deposited on the cathode. It was found that the current efficiency for the catholyte compartment was greater than 90%.

INTRODUCTION

Background

An integrated closed-circuit process for treating copper sulfide minerals based on acidic ferric leaching and the subsequent electrolytic recovery of copper is being developed as an alternative low cost method for copper production. The process is based on the simultaneous recovery of copper and regeneration of ferric ions using a membrane separated electrolytic cell divided into an anolyte and catholyte compartment.

In a conventional copper electrowinning cell, the cathodic reaction is the electrodeposition of copper on a stainless steel or copper starting sheet and the anodic reaction is the dissociation of water into hydrogen ions and oxygen resulting in the production of acid as described by the following electrochemical half-cell reactions:

From the half-cell reactions, an overall theoretical cell voltage of 0.892V was calculated.

Alternatively, the electrochemical reactions occurring in the proposed electrolytic cell would result in the deposition of copper on a stainless steel or copper starting sheet and the oxidation of ferrous ions, produced from the reduction of ferric ions during leaching of the copper sulfide minerals, to ferric ions for recycle as a lixiviant for the dissolution of copper sulfide minerals. The following electrochemical half-cell reactions describe the reactions that would occur in an electrolytic cell separated into an anolyte and catholyte compartment with an ion exchange membrane:

A theoretical cell voltage of 0.434V was calculated when the oxidation of ferrous ions is the anodic reaction compared to 0.892V when the dissociation of water is the anodic reaction. Thus, the proposed cell would offer a net reduction in the cell potential of 0.458V.

Objective and Approach

The objective of this project is to develop an electrolytic cell divided into two compartments with an ion exchange membrane to allow the simultaneous regeneration of ferric ions and recovery of metallic copper (Year 1) and develop an optimized leaching and electrowinning process for the recovery of copper from copper sulfide minerals (Year 2). The approach that will be taken to develop the proposed electrolytic cell follows the timetable outlined in the initial proposal. Specifically, the objectives for this reporting period include: performing a literature review and performing preliminary electrode characterization studies, designing membrane separated electrolytic cells, constructing membrane separated electrolytic cells, testing of the membrane separated electrolytic cell.

PROJECT TASKS

Task 1: Literature Review and Preliminary Electrode Characterization Studies

Several papers with information pertinent to the current research effort to develop a membrane separated electrolytic cell have been collected. In particular, a recent paper was located titled "Aspects of the development of a copper electrowinning cell based on reactive electrodialysis" by Cifuentes, L., et al. (Chemical Engineering Science 59 (2004) p. 1087-1101). The paper contains many details related to recovering copper from a membrane separated electrolytic cell and contains performance data for various types of electrode materials. Data obtained in from this paper will greatly aid in the selection of electrode materials for our cell.

Figure 1. Tafel plot of the copper oxidation/reduction reaction occurring on the surface of a 316L stainless steel electrode in a stirred 4.5 g/L copper plus 18.0 g/L sulfuric acid solution.

Figure 2. Tafel plot of the copper oxidation/ reduction reaction occurring on the surface of a 316L stainless steel electrode in a non-stirred 4.4 g/L copper plus 18.1 g/L sulfuric acid solution.

Figure 3. Tafel plot of the iron oxidation/reduction reaction occurring on the surface of a lead electrode in a stirred 2.9 g/L ferrous plus 15.0 g/L sulfuric acid solution.

Figure 4. Tafel plot of the iron oxidation/reduction reaction occurring on the surface of a lead electrode in a stirred 2.9 g/L ferrous plus 14.7 g/L sulfuric acid solution.

Tafel plots were generated under a variety of experimental conditions with various types of electrodes. Specifically, 316L stainless steel electrodes, lead, and copper electrodes were characterized. A Tafel plot showing the reduction of copper from a stirred solution on a 316L stainless steel electrode is shown in Figure 1. A similar Tafel plot was constructed by reducing copper on the surface of a 316L stainless steel electrode from a non-stirred solution. Comparison of the limiting reduction current densities illustrated the importance of stirring the electrolytes. Tafel plots were also constructed to characterize the oxidation of ferrous ions to ferric ions using lead electrodes (Figures 3 and 4). The results obtained from the iron oxidation plot also illustrate the need for vigorous agitation to obtain high current densities. Based on these studies, the membrane separated electrolytic cell was designed for flow through operation.

Task 2: Designing the Membrane Separated Electrolytic Cell

Several different designs for membrane separated electrolytic cells have been devised. The parameters that were incorporated into the designs include: flow through capability, flat-plate cathodes with high surface area anodes, and a plate in frame membrane holder. Additional designs that appear to offer great promise include modification of an EMEW® electrolytic cell. This type of electrolytic cell appears to be easily modifiable to incorporate a membrane. A lab-scale EMEW® electrolytic cell is currently being sought.

Task 3: Construction

Currently, two membrane separated electrolytic cells have been constructed. The first cell is shown in Figure 5. Plexi-glass was used for cell construction as it is highly resistant to the acidic solutions used in the copper industry and allows high visibility of the cell contents.

Task 4: Testing of the Membrane Separated Electrolytic Cell

The membrane separated electrolytic cell shown in Figure 5 was tested with great success. A digital image of the copper electroplated onto the surface of a stainless steel cathode is shown in Figure 6. Additionally, a plot of the current running through the membrane electrolytic cell is shown in Figure 7. From the data used to construct the plot, the average current flow was determined. This information was subsequently used to determine the current efficiency (91%) of the cathode reactions occurring in the catholyte compartment. Based on these positive results, it is anticipated that the second generation cell which has been built but not tested will produce even better results.

Figure 5. Digital image of the 1st generation of membrane separated electrolytic cell built at Montana Tech.

Figure 6. Digital image of a stainless cathode with electrowon copper .

Figure 7. Plot of the current running through the membrane separated electrolytic cell as a function of time.

SUMMARY

During this reporting period, progress was made on all of the tasks detailed in the original proposal for the first seven months. The literature search began during the first reporting period was continued culminating in the gathering of several applicable papers pertinent to this project. Tafel plots were generated for several different solutions utilizing 316L stainless steel, copper, and lead electrodes to gain an understanding of the copper reduction and iron oxidation dynamics with different electrode materials. These electrode materials were chosen in order to mimic the current materials used in industry. By far the most important achievement this reporting period was the design, construction and testing of a membrane separated electrolytic cell. A current efficiency of 91% was measured in the catholyte compartment of the membrane separated electrolytic cell. Although the design proved to be effective for electrowinning copper and oxidizing ferrous ions to ferric ions, a second cell was designed and built based on data gathered from the first cell design. In addition to the research work completed, a proposal for leaching copper and demonstrating the membrane separated electrolytic cell was submitted to Montana Resources, a local mine.

FUTURE WORK

Research work for the next reporting period will follow the time-line submitted in the original proposal. Specifically, more membrane separated electrolytic cells with advanced designs will be constructed and tested. Additionally, a counter current copper leaching circuit will be built and operated in conjunction with the membrane separated electrolytic cell. The research effort is 5 months behind schedule as a result of a delay in hiring personal. A no-cost time extension was requested. If the time extension is granted, it is believed that all of the project objectives can be successfully completed.

PUBLICATIONS/PRESENTATIONS

Results and discoveries resulting from this project were presented at the 2003 CAST 2003 Annual Workshop November 19-21, 2003.

Appendix L: Ion Exchange Recovery of Cobalt from Copper Leach Solutions

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 04/10/03 Ending Date: 05/30/05
<u>Sub-Recipient Project Title:</u> Ion Exchange Recovery of Cobalt From Copper Leach Solutions	<u>Report Information:</u> Type: Semi-Annual Number: 2 Period: 09/30/03-03/31/04 Date: 03/31/04 Code: NM002
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ABSTRACT

Two new chelating ion exchange resins have been prepared. The first resin is a low-crosslinked gel type resin with thiosuccinate chelating structure. It absorbs Cu^{2+} from dilute, weakly acidic solutions, but not as strongly as does commercially available iminodiacetic acid resin. The second resin has a carboxymethylated diethylenetriamine structure. It absorbs Cu^{2+} well from pH 1.7 to pH 1.1 sulfuric acid solutions as affectively as commercially available hydroxypropyl picolyl amine resin, but weakly absorbs Co^{2+} from sulfuric acid solutions. However, this new resin absorbs Fe^{3+} more strongly than the picolyl amine resin. Synthesis and preliminary testing of a third resin with picolylated diethylene triamine structure is currently under way.

INTRODUCTION

Background

Cobalt is a strategic and critical metal which is used in production of super alloys for use in jet engine turbines, wear and corrosion resistant alloys, cutting tools, magnets, and various other alloys and chemicals. It is not mined or refined in the United States; therefore, 80% of the cobalt consumed in the U.S. is imported. The remaining balance is met with recycled alloys and supplies from stockpiles.

There is a readily available source of cobalt in the southwestern U.S. In the process of hydrometallurgical extraction of copper, leach solutions in large copper mining operations contain 0.03-0.10 Kg/m³ of cobalt. If only a fraction of cobalt can be recovered, New Mexico and eastern Arizona copper leach operations could potentially supply significant portion of the U.S. imports. Currently, the technology to recover the metal from these solutions economically is not available.

Ion exchange processes could recover cobalt present at low concentrations in large volumes of copper leach solutions, however, commercially available resins are either too expensive, or may not function in acidic solutions. Furthermore, solvent extraction process, which is universally used to recover copper from the leach solutions, is also under scrutiny due to large organic inventory involved in the process. Chelating ion exchange resins may also be considered as potential substitutes for the organic liquid extractants used for copper extraction to eliminate fire hazards and potential for ground water pollution.

Objective and Approach

The objectives of this project are the synthesis and evaluation of new types of chelating ion exchange resins which could potentially be lower priced than the picolylamine resins, and be effective in absorbing Cu²⁺ and Co²⁺ from pH-1.5 to pH-1.3 solvent extraction raffinate of copper leach solutions.

Initially three new resins were to be synthesized for copper and cobalt recovery from acidic solutions, a thiosuccinate resin p-C₆H₄CH₂SCH(CH₂CO₂H)CO₂H, a thioglycolate resin p-C₆H₄CH₂SCH₂CO₂H, and a carboxymethylated diethylene triamine resin, p-C₆H₄CH₂N(CH₂CO₂H)CH₂CH₂N(CH₂CO₂H)CH₂CH₂N(CH₂CO₂H)₂.

Small laboratory scale synthesis of the new resins was made and the samples of resins were equilibrated with dilute CuSO₄ solutions, acidified with H₂SO₄. Initial tests were conducted using CuSO₄ solutions, rather than CoSO₄, because Cu²⁺ is more strongly absorbed, and it is cheaper and easier to analyze for Cu²⁺. Effective resins were then evaluated more extensively by small column loading and H₂SO₄ elution for copper, cobalt, and iron containing solutions.

PROJECT TASKS

There are two initial tasks for this project. They are: 1) to make a small sample of the proposed chelating resins, 2) to run screening tests on these resins with Cu, Co, and Fe containing solutions. These initial tasks now have largely been accomplished for the thiosuccinate (MH-13) and carboxymethylated diethylene triamine (CM-DER) resins. Standard laboratory ware, heating and stirring equipment were used in the small-scale preparation of these resins under a chemical hood, as needed.

Experimental Results

The thiosuccinate resin was prepared from 50/100 mesh, 2 per cent crosslinked chloride form of quaternary ammonium ion exchange resin (Dowex1, 2X). Further details of the synthesis procedure were given in the first progress report.

The absorption capabilities of this resin were first investigated qualitatively by immersing a small quantity of the resin in a very dilute aqueous solution of CuSO_4 . The total cation exchange capacity of the resin was determined next. A measured quantity of the wet-settled resin in a small glass column was washed slowly with excess aqueous ammoniacal CuSO_4 solution. It was then rinsed with dilute ammonia water, and finally, the resin was washed with 1.0 molar H_2SO_4 to eluate all of the copper (II) cations. All the eluate was collected and it was titrated for Cu (II) by standard iodometric procedures. The results indicated that the resin had a total wet capacity of 0.72 milliequivalents per milliliter of resin bed (0.36 millimoles of Cu^{2+} per ml of resin). This compares well with the absorption capacity of commercially available iminodiacetic acid resin, Chelex -100, which is found as 0.9 meq Cu^{2+} per ml of resin.

The absorption capacity of the synthesized thiosuccinate resin from strongly acidic solutions was also investigated. However, the results indicated that the new resin only absorbed about 10% of copper from the solution. The iminodiacetic acid resin absorbed about 25%, and the bis-picolylamine resin absorbed about 50%. This pattern of absorption was also found with the acid forms of the resins. This indicates, however, those thioether (sulfur) groups of the new resin coordinate less readily with Cu^{2+} than does the nitrogen in imino groups. Based on these results, the synthesis of the proposed thioglycolate resin was deferred because it deemed unlikely that this resin will absorb copper and cobalt from acidic solutions as well as the thiosuccinate resin.

The carboxymethylated diethylenetriamine (CM-DER) was prepared in two steps. In the first step quaternary ammonium ion exchange resin (Dowex 1, 2x) was reacted with diethylene triamine in ethylene glycol for about 20 hours to produce diethylene triamine resin, which was highly cross-linked. However, this resin would not chelate copper even from very mildly acidic solutions.

The diethylene triamine resin was then heated at reflux at about 100C in an aqueous solution of sodium chloroacetate, $\text{ClCH}_2\text{CO}_2\text{Na}$, buffered with sodium bicarbonate. This procedure introduced the carboxymethyl groups on the nitrogen atoms of the polyamine resin

to give carboxymethylated diethylenetriamine structure. Small column (3 ml resin) absorption tests in duplicate were conducted with this resin and compared with the thiosuccinate resin, iminodiacetic acid (IDA) resin (Chelex-100), and a hydroxypropyl picolylamine (HPPR) resin (Dow XFS-43084). The resins were then eluted with 1M H₂SO₄ solution and total absorbed copper ion concentrations were determined. These results are tabulated in Table 1.

Using the two higher capacity resins (HPPR and CM-DER), further column tests were conducted with more concentrated solutions and progressively more acidic solutions. Performance of both resins was comparable under these conditions (Table 2). The relative performance these two resins for cobalt absorption was determined from dilute sulfuric acid solutions and compared with that of iminodiacetic acid (IDA) resin CH-100. The columns were stripped with 1M H₂SO₄ solution and the eluates were analyzed for cobalt by iodometric titration. The show that the newly synthesized CM-DER resin has the highest capacity under these conditions; however, cobalt absorption is 60 times less than that of copper (Table 2) at the same pH.

Table 1. Absorption capacity of chelating IX resins for Cu(II).

Resin	[Cu ⁺²] ppm	H ₂ SO ₄ ml	H ₂ SO ₄ M	pH	Capacity, meq Cu/ml
HPPR	38	1.00	0.018	1.7	0.45
CM-DER	38	1.00	0.018	1.7	0.38
CH-100	38	1.00	0.018	1.7	0.31
MH-13	38	1.00	0.018	1.7	0.06

Table 2. Absorption of copper on HPPR and CM-DER resins at various pH levels.

Resin	[Cu ⁺²] ppm	H ₂ SO ₄ ml	H ₂ SO ₄ M	pH	Capacity, meq Cu/ml	%capacity at pH 1.9
HPPR	190	4.00	0.072	1.1	0.30	~70%
CM-DER	190	4.00	0.072	1.1	0.30	~70%
HPPR	190	8.00	0.144	0.8	0.11	~25%
CM-DER	190	8.00	0.144	0.8	0.90	~25%
HPPR	190	16.0	0.288	0.5	0.06	~15%
CM-DER	190	16.0	0.288	0.5	0.05	~15%

Table 3. Ferric ion absorption on chelating ion exchange resins.

Resin	[Fe ⁺³] mg/L	H ₂ SO ₄ ml	H ₂ SO ₄ M	pH	Capacity, meq Fe / ml
CH-100	190	1.00	0.018	1.7	0.84
CM-DER	190	1.00	0.018	1.7	0.78
HPPR	190	1.00	0.018	1.7	0.14

Ferric ion absorption on CH-100, picolylamine (HPPR), and CM-DER resins was also studied similar to copper and cobalt absorption. Analysis of the 1M H₂SO₄ stripping eluates was done by colorimetric determination of iron as thiocyanate complexes. The results of ferric ion absorption studies are tabulated in Table 3.

It is observed that the two resins, which contain cation exchanging carboxymethyl groups – the CM-DER and HPPR, have considerably higher capacity for Fe⁺³ than they do for Cu⁺² absorption. However, the picolylamine resin has considerably lower capacity for ferric ion because it has only cation complexing amino groups. The latter resin is promoted as a potential alternative for use in extraction of copper from acidic leach solutions, instead of the solvent extraction process.

SUMMARY

In search of new resins to recover copper and cobalt from highly acidic, dilute solutions, small quantities of two new chelating resins – a low-crosslinked, gel-type thio-succinate (MH-13) resin and carboxymethylated diethylenetriamine (CM-DER) resins – were synthesized and evaluated. Small-scale equilibration tests were made with acidic (H₂SO₄) solutions containing Cu, Co, and Fe (III) ions. Comparison tests were also made with commercially available, low-crosslinked, gel type iminodiacetic acid (Chelex-100), and highly crosslinked macro-porous hydroxypropyl picolylamine (HPPR) resin (Dow XFS-43084). The results indicate that both the thiosuccinate (MH-13) and iminodiacetic acid (CH-100) resins were considerably less effective in absorbing Cu²⁺ from acidic solutions than the picolylamine resin. The CM-DER resin, on the other hand, had copper absorption capacity comparable to, and cobalt absorption capacity, although feeble, better than that of the picolylamine resin. Ferric ion absorption on CM-DER, however, was much higher than the picolylamine resin in acidic solutions.

FUTURE WORK

Commensurate with the objectives of this research project, two new resins were synthesized and tested in small-scale columns. Further laboratory development work will be on the synthesis of larger quantities of carboxymethylated diethylenetriamine resin (CM-DER) for characterization of loading capacity as a function of pH, absorption and desorption kinetics, and selectivity for copper and cobalt ions in the presence of ferric, ferrous, zinc, and nickel ions. Efforts are currently underway to synthesize a third resin having picolylated diethylene triamine structure, instead of thioglycolate resin that was originally proposed. Preliminary absorption test results with this resin appear to be encouraging and further details will be provided in the next progress report.

PRESENTATIONS

Preliminary results of this project were presented at the CAST Conference in Charleston, WV, on November 20, 2003, and at the CAST Advisory Committee meeting in Denver, CO, on Feb. 22, 2004.

Appendix M: The Effect of Diphenyl Oxide Surfactants on Nucleation and Growth of Potassium Sulfate Crystals: Development of Enhanced Surfactants for the Potash Industry

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 10/1/03 Ending Date: 5/31/04
<u>Sub-Recipient Project Title:</u> Development of Enhanced Surfactants for the Potash Industry	<u>Report Information:</u> Type: Semi-Annual Number: 3 Period: 10/1/03-3/31/04 Date: 3/31/04 Code: NM003
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ABSTRACT

An MSMPR crystallizer has been built and is being used to grow potassium sulfate crystals. Crystal growth rates and sizes, and crystal habits have been evaluated by atomic absorption and scanning electron microscopy. Surfactants have been added with the goal of producing a modest inhibition of nucleation, and hence shifting the crystal size distribution, in order to increase the ratio of granular particles to fines, and thus decrease the costs associated with industrial production of potassium sulfate. Five alkyl diphenyl oxide (ADO) surfactants provided by Pilot Chemical Company have been tested to date. Surfactants are either linear-chain or branched-chain disulfonates or sulfonic acids with varying active percentages of free acids. Results have shown that the linear-chain surfactants with the highest active percentage of free acid perform best, and also that sulfonic-acid surfactants perform much better than disulfonates. Thus the direction of the research is now focused on linear-chain sulfonic-acid ADO surfactants with higher active percentage of free acid.

INTRODUCTION

Background

The successful and efficient production of K_2SO_4 fertilizers in the potash industry requires a sufficiently large sized crystal that will not pass through the screening process and be reintroduced to the mother liquor. ADO surfactants are thus added to the mother liquor in order to influence crystal nucleation and growth, and thus the crystal size distribution (CSD). Crystal shape, which is affected by mechanical abrasion, breakage, and attrition from other causes, is also an important issue.

Objective and Approach

The objective of this project is first to measure the growth rate, CSD, and crystal morphology of K_2SO_4 crystals grown in the presence of $MgSO_4$ as a second solute, which was used by Dash et al., (1996) in the growth of KCl crystals. Impurities, in this case $MgSO_4$ being the most important, are well known to affect crystal growth and size. ADO surfactants are then used to increase the growth rates and sizes, and enhance the morphology of K_2SO_4 crystals. First Calfax surfactants, supplied by Pilot Chemical Company, with linear chains (10LA-75) and with branched chains (DBA-70) were used. Then three additional Calfax surfactants (10L-45, DB-45, and 16L-35) were studied in order to examine the effects of surfactant branching and chain length. The particles produced in the absence or presence of surfactants are characterized with the following analytical techniques: crystal morphology and CSD are determined by scanning electron microscopy (SEM), growth rates are determined by atomic absorption (AA), and structure is examined by X-ray diffraction and Fourier Transform Infrared Spectroscopy (FTIR). Once the effects of surfactant chain branching and chain length on crystallization and CSD have been determined, that information will be used to design and test improved surfactants.

PROJECT TASKS

All experiments require a crystallizer for production of crystals. The mixed-suspension mixed-product removal (MSMPR) crystallizer was selected because we can monitor nucleation and crystal growth kinetics simultaneously, most closely approximating industrial applications. An MSMPR reactor has been built as specified (Dash et al., 1996; Rohani, 1993; Dash and Rohani, 1993) as shown in Figure 1 (Dash and Rohani, 1993). The MSMPR crystallizer consists of a 1L jacketed glass vessel with four vertical wall baffles and a three-bladed 2.5 in. diameter propeller, run by a 1/10 hp motor, which is inserted in the reactor vessel. Temperature control in the crystallizer is maintained by circulating cooling water through the jacket from a heating/cooling bath. A 19L Pyrex bottle, which is used as a feed tank, is placed on a magnetic heater/stirrer and maintained at constant temperature. The feed is pumped into the crystallizer by means of a peristaltic pump at a rate of 75 ml/min. The product is removed from the crystallizer with another peristaltic pump, which runs intermittently at a high flow rate of 210 ml/min. to ensure isokinetic product removal. Approximately 10% of the reactor volume is removed at a time. The return line is wrapped with a heating coil to prevent crystallization of the feed in the tube. The solution moves to

an intermediate dissolution bottle of 1L capacity also placed on a magnetic heater/stirrer. This is done to dissolve crystals returning from the reactor and to help control the feed tank temperature. A return line from the intermediate dissolution tank to the feed tank is gravity fed. Samples are gathered at regular intervals; a pipette is used to draw samples directly from the reactor vessel. Atomic absorption (AA) is used to establish nucleation times and growth rates of crystals.

Figure 1 — Experimental set-up.

The feed used is A.C.S. reagent-grade K_2SO_4 and $MgSO_4$ provided by Sigma. The feed solution for all tests contains an excess 10% solid, resulting in 190.3g K_2SO_4/L H_2O and 9.9g $MgSO_4/LH_2O$. Once dissolved by heating to 80°C in de-ionized water, the solution is vacuum filtered through 1.6 micron filter paper and poured into the feed tank. The solution is then cooled to the saturation temperature at 60 °C and stirred for one day.

Initially the reactor jacket is heated to at least 70°C to prevent early crystallization, and the reactor is filled from the feed tank. The reactor is then cooled to 60 °C as the solution is circulated to the re-dissolution tank and feed tank. A single temperature drop of 10°C from the saturation temperature to the operating temperature of 50°C is used in order to have better conformity in the results of all test runs. Samples are generally taken at 55°C and when 50 °C is reached, and every 10-15 minutes thereafter until the end of the test run, for AA and FTIR analysis. AA samples are vacuum filtered through 1.6 micron filter paper and maintained at a temperature of 70°C to prevent crystallization within the samples before they are analyzed. FTIR samples are taken from the dried samples, and also from crystals grown in the cooled mother liquor. Additional intermediate samples are taken every 10-15 minutes for SEM analysis, with a polycarbonate filter paper. No surfactants were added to the initial tests, so that primary growth characteristics could be determined. Tests without surfactants show that crystals begin to grow immediately after the temperature drops from 60°C, and volumetric growth of crystals continues at a steady rate for 1.5 to 2 hours, at which time no further growth is observed. If more than one test run is performed the same day, the reactor vessel is heated to 80°C and stirred until all crystals are dissolved, and then allowed to cool until equilibrium is achieved throughout the apparatus before another test is run. Acidity tests were done on the solution and a nearly neutral pH of 6.75 was found for samples with and without surfactant.

SEM is then used to determine crystal shapes and growth habits, and to measure size distribution. Tests without surfactants show that, immediately after nucleation, which begins as the temperature is dropping to the operating temperature, tabular six-sided crystals of roughly 10-20 micron sizes form and gradually grow out from the edges into pyramids that contain voids within the walls. These voids gradually fill in until a hexagonal di-pyramid-shaped first-order crystal results, often with truncated basal layers. Single crystals gradually agglomerate through secondary nucleation to form larger crystals, while further nucleation and growth of new crystals continue. Crystals of 1mm in size are reached within 10 minutes after the operating temperature is reached, and larger crystals of 2mm in diameter are reached after 20 minutes, after which sizes generally do not increase. Agglomerated crystals, when viewed with the SEM, are seen to be composed of nearly all growing undeveloped crystals, all fully formed crystals, or a mixture of both. Some large crystal agglomerates are seen to have less well defined crystal planes and a generally rounded appearance, likely due to abrasion with other crystals during prolonged times in solution. Agglomerated crystals are generally durable and resistant to breakage, and spherical in overall shape. A total of approximately 10% of the total potassium in solution in the mother liquor crystallizes with one 10°C temperature drop.

X-ray diffraction tests show that resultant crystals are most closely associated with the mineral Arcanite (K_2SO_4), and that most peaks can be attributed to this phase. A second phase is also present and this corresponds to the mineral Langbeinite ($K_2Mg_2(SO_4)_3$). Langbeinite is the ore commonly used in the production of potash fertilizers. This is beneficial to know so that any positive results can be directly applied to the industrial production of crystals. All peaks from X-ray diffraction of the crystal samples can thus be matched to either Arcanite or Langbeinite. FTIR is used to evaluate the crystals grown in the reactor, as well as wet and dry single crystals grown from the mother liquor at room temperature. The presence of sulfate anions has been determined from the very beginning of the crystal growth cycle.

The most beneficial ADO surfactant added to the potassium sulfate solution was a linear-chain ADO sulfonic acid surfactant, 10LA-75. Concentrations of 1 and 2ml per 1L solution were analyzed. The results are encouraging as an abundance of nuclei were formed, although fewer than without the surfactant. This would be expected, considering that the purpose of the surfactants is to poison some nucleation sites but not all, so that larger crystals may grow from the remaining solution. SEM analysis of crystals shows generally four-sided planar crystals, many of which have serrated edges. Studies as to why this occurs continue. Crystals in the size range of .5mm agglomerate within 5 minutes of reaching the operating temperature, and reach a maximum size of approximately 1mm after 50 minutes with the 10LA-75 surfactant. Overall growth rate and size ranges were lower than those in the absence of surfactants. Crystals are generally less hard and durable than those grown in solution without surfactant, and are often more elongated than spherical. Crystals grown in the mother liquor at room temperature have a fibrous “hairy” structure unlike those grown with any of the other surfactants. A total of 4.5 to 5% of the mother liquor crystallized during test runs. The differences in agglomeration between crystals grown with 10LA-75 and those grown without surfactant are also being examined with a dissecting microscope, which is more easily capable of analyzing large (1mm and above) crystals than the SEM.

The first branched-chain ADO sulfonic acid surfactant to be tested was DBA-70. Concentrations of 1.5 and 3ml surfactant per 1L of solution were prepared. The addition of DBA-70 killed most nucleation sites. A total of less than 1% of the mother liquor crystallized with one temperature drop at concentrations of 1.5ml per 1L of solution, and no growth was seen in solutions containing higher levels of surfactant. Crystals that grew were seen through SEM imaging to have an eroded appearance.

A second branched-chain ADO disulfonate surfactant, with lower active percentages of free acid, DB-45, was also added to a new solution batch with similar results to those obtained for DBA-70. Low concentrations of .5 and 1ml surfactant per 1L solution were added. The few crystals which grew at the start of the test failed to grow to an appreciable size. No statistical growth was seen according to visual and atomic absorption tests, and SEM analysis confirmed that few crystals had grown.

Two additional linear-chain ADO disulfonate surfactants with lower active percentages of free acid, 10L-45 and 16L-35, have also been tested. Very low concentrations of .25ml surfactant per 1L solution were added. Very few crystals were seen to grow with either surfactant, and these failed to grow to any appreciable size, as was confirmed by atomic absorption. SEM analysis of the few resultant crystals is continuing.

SUMMARY

An MSMR crystallizer has been built and used to grow potassium sulfate crystals. Crystal growth rates and growth characteristics have been determined by SEM, AA, xray diffraction, and FTIR. The influence of ADO surfactants on nucleation and growth of potassium sulfate has been found to be strongly dependent on the nature of the surfactant itself. The most promising results have been obtained with the 10LA-75 surfactant. This surfactant produces the modest inhibition of nucleation that we seek, without excessive inhibition of crystallization. This follows the general trend that we have observed, wherein better results are obtained with linear-chain sulfonic-acid surfactants with higher free-acid content. Additional surfactants will now be studied, on this basis.

FUTURE WORK

The project is generally running ahead of schedule. Analysis of the larger crystals is continuing with a dissecting microscope. Results show that linear-chain ADO sulfonic-acid surfactants with a higher active percentage of free acid should perform better than those used previously. The focus now is on the design and selection of additional surfactants for testing in the next phase of the experiments.

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Appendix N: Online Monitoring and Diagnosing of Coal Fines During Separation Process

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 04/01/03 Ending Date: 12/31/05
<u>Sub-Recipient Project Title:</u> On-Line Monitoring and Diagnosing of Coal Fines During Separation Process	<u>Report Information:</u> Type: Semi-Annual Number: 2 Period: 9/31/03 – 3/31/04 Date: 3/31/04 Code: WV008
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ABSTRACT

The goal of this research program is to develop an on-line, non-contact, elemental analysis of coal fines during solid-solid separation process through the use of Laser-Induced Breakdown Spectroscopy (LIBS). Of particular interest is the detection and quantitative measurement of the amount of carbon, sulfur, mercury, and other trace elements in the separated coal fines. The proposed experimental technique will be applied to a circulating fluidized bed (CFB) riser system for determination of coal fines separation efficiency as well as optimization of the separation process variables.

INTRODUCTION

Background

Laser Induced Breakdown Spectroscopy (LIBS) is a technique that uses focused laser beam to ablate a sample of a desired material. This ablation causes a plasma formation in which the material is broken down into excited ionic and atomic states. The atoms then emit characteristic optical radiation known as an emission spectrum. Collection of the emitted light spectrum can be used to provide information on the elemental composition of the material.

There are several key advantages to LIBS that are beneficial for an on-line monitoring and diagnostic. LIBS is essentially a non-contact, non destructive test; it requires nothing more than the light spectrum collected from the plasma created by the laser and ablates insignificant amount of particles. Because LIBS only requires collection of the emitted light spectrum to be able to yield sufficient data, it can be used for deployment to hostile or high temperature environments. Also, LIBS requires no sample preparation, which makes it suitable for on-site, in-situ measurement.

Objective and Approach

LIBS will be applied for on-line elemental analysis and diagnosing of coal fines during solid-solid separation process, i.e. the CFB riser system. The experiment will first be performed in a laboratory environment, away from the riser system. The experiment will be to determine quantitatively the amounts of carbon, sulfur and other trace elements.

Detection and monitoring of mercury will prove to be the most difficult task because of its trace concentrations in coal (typically less than 0.5 ppm). An optical system that will optimize light collection in the UV range, where the strongest mercury emission line occurs, has been designed and will be implemented in a laboratory environment.

PROJECT TASKS

Task 1 – Experimentation with a Spectrometer

Several samples have been taken of coal spectra. Over 400 spectra of coal were taken. Some samples were taken in a coal-water mixture, while others were taken in the open without being mixed with anything. When it was discovered that the iron lines would interfere with the detection of mercury, several spectra of iron were also taken to see which possible lines would interfere with the mercury signal. Below is an example of a LIBS spark of raw coal and a sample of steel filings.

The broad band seen here under the spectra is the black body radiation from the spark. Since there was no time delay, the spark temperature has not cooled, resulting in a broad black body under the spectra. If the spark temperature was known, the spectra that is on top of the black body could be normalized, however, a time-resolved spectrum of coal is desired to detect mercury. Since each elemental emission signal has a different rate of decay, a time-resolved system will help optimize the capture of the mercury signal. However, a time-resolved LIBS experiment could prove very costly. The traditional method of achieving time resolution in a spectroscopy experiment is to have an intensified CCD detector and a laser synchronized with a pulse delay generator. The traditional method results in the purchase of vexpensive equipment. Intensified CCD detector can run twice as much if not more than the price of a regular CCD detector, which is typically around \$20,000. An alternative approach

to the time resolved system is the polygonal scanning mirror. A scanning mirror reflects the laser beam via a spinning mirror. This allocates a different position of the reflection of the laser beam for a different time. The result of applying a scanning mirror to the LIBS experiment will be a cost-effective time resolved study of the LIBS spark of coal.

Task 2 – Finalization of Sample Experimentation Design

The detection of mercury is the primary focus because of its trace amounts in coal. A mathematical model using simplifying assumptions was developed to determine if mercury was detectable by LIBS to one part per billion. The simplifying assumptions were making a spherical coal particle of 100 micrometers in diameter, and the plasma temperature was 10,000K. With those assumptions, the coal particle was calculated to have 2.11×10^6 atoms. Going through the Boltzman distribution, it was estimated that 7200 mercury atoms emitted the light at the 253.7 nanometer line. After the Boltzman distribution, a problem occurred with the collection objects in question. With the designed collection probe, it was estimated that the best efficiency using a collection lens was one percent of the light, which made the photon count down to 72 photons before going through optical losses on the spectrograph and the CCD detector, making it impossible to achieve 1 ppb sensitivity. Because of this realization, a different design in the collection optics was made an off-axis parabolic reflector will be used to collect light emitted from the laser spark as opposed to the lens collector probe. This will allow more light to be collected, which results in a better chance at 1 ppb sensitivity to mercury.

The sensibility issue is not the only issue that makes mercury difficult to detect. Upon looking at the MIT wavelength tables for standard optical emissions of elements, it was discovered that the iron, also found in coal, had very close emission lines to that of mercury. This presents interference with the detection of the mercury lines. However, this interference can be avoided by a higher resolution spectrometer, which will enable the users to better distinguish the iron emission line from the mercury emission line.

A schematic of the final design is shown in the figure below. The equipment is currently being carefully selected according to a more detailed design. The laser and spectrograph are being loaned from NETL in Morgantown, WV, while the CCD detector is in the procurement process. The lenses and the scanning mirror motor will be selected according to the finalized design. The experimental layout will allow optimum signal collection as well as time resolution of the LIBS spark of coal. The laser will fire and ablate the coal particle. Once the laser spark occurs, the light will be collected and collimated by an off-axis parabolic reflector. The collimated light will then go through a focusing lens made from optical material that allows the transmission of UV light. The light is then focused down onto a spot on the scanning mirror. When the spot hits the scanning mirror, it reflects into a collimating lens and is once again collimated. The collimated light then goes through another focusing lens, which is focused down on the entrance slit of the spectrometer. Since the light is reflected by a spinning mirror, there will be a line entering the slit. Each segment of the line will simulate a time delay, which will be read by the CCD detector. The laser, the scanning mirror, and the CCD detector will all be remotely controlled by the end user via a PC.

SUMMARY

A model that would allow for 1 ppb sensitivity to mercury in coal was developed and an optical system is being designed that will allow optimization of light spectrum collection efficiency. The schematic has been drawn out, and the optics are currently being selected according to design constraints.

Several hundred LIBS sparks were taken on various samples of coal, iron, and ash. All of the spectra showed black body radiation from the spark due to the fact that there was no time delay. These spectra can be normalized if the spark temperature can be determined. This observation led to consideration of adding time-delayed resolution to the experiment.

FUTURE WORK

The schematic presented above will be assembled and calibrated at our Photomechanics and Materials Laboratory, West Virginia University. The distances from the laser spark to the scanning mirror and from the scanning mirror to the entrance slit of the spectrograph will be determined by the lenses used. A method of controlling the timing of the laser pulse and the scanning mirror will also be developed during the equipment setup phase. Completion of the experimental setup is projected for the summer of 2004. The experimental tasks that follow the immediate experimental setup should be completed by September or October, 2004.

PUBLICATIONS/PRESENTATIONS

To date, no publications or presentations have resulted from the project.

**Appendix O: Development of a Novel Optical Radiation Depolarization Technique for
On-Line Measurements of Particle and Bubble Sizes**

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 10/1/03 Ending Date: 3/31/04
<u>Sub-Recipient Project Title:</u> Development of A Novel Optical Radiation Depolarization Technique for On-Line Measurements of Particle And Bubble Sizes	<u>Report Information:</u> Type: Semi- Annual Number: 2 Period: 10/1/2003-3/31/2004 Date: 4/1/2004 Code: KY003
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ABSTRACT

It has been shown experimentally that elliptically polarized light scattering (EPLS) approach can be used to measure both bubble size and gas-hold-up during froth flotation. During the experiments carried out, the effects of nitrogen gas flow rate on bubble size and gas hold-up were determined using a video and image processing system at four different surfactant concentrations (10, 20, 100, 200 ppm). Based on image information, bubbles were assumed to be spherical for calculation of the normalized scattering matrix elements. Scattering matrix elements were calculated from experimentally measured intensity values for different polarization modulation of incident and scattered light. With EPLS method, normalized scattering matrix elements (S_{ij} 's) at different side and back scattering angles provide the information about scattered light intensity as well as polarization stage of the scattered light. S_{ij} 's were correlated with the mean bubble size and gas hold-up rates. It is concluded that it is feasible to measure bubble size as well as bubble ascending velocity at scattering angle around $\theta = 120^\circ$ where change in bubble size caused significant changes in S_{11} , S_{44} , and S_{34} at the gas velocity between 0.04 cm/s and 0.35 cm/s. The optimum scattering angle for measurements depends on gas pressure, frit pore size, and column diameter.

INTRODUCTION

Background

Grinding and froth flotation are the two most important processes for mineral beneficiation. The importance of grinding is well reflected in the fact that approximately 80% of beneficiation costs are for grinding, mainly due to high energy consumption. To reduce energy consumed by grinding, fines should be removed quickly from the grinding circuit. This requires a reliable on-line particle size analysis technique. Froth flotation is the most widely used solid-solid separation process for coal and minerals beneficiation and about 90% of mineral concentrates are produced from froth flotation. It is now recognized that air bubble size distribution plays an important role in flotation separation performance. Optimization of bubble size distribution is possible only if bubble size can be monitored on-line. Obviously, an on-line analysis technique for particle and bubble size is critical for enhanced grinding and flotation process efficiency.

Light scattering is one of the most effective concepts for characterization of particles and bubbles. When either vertically or horizontally polarized light is incident on the medium, it goes through a number of scattering events. Bubbles are considered much larger than the wavelength of the incident light, which is a reasonable approximation even for bubble diameters as small as 5 μm . A model based on a hybrid Monte Carlo/Ray Tracing technique allows the Fresnel reflections on the bubble-medium interfaces. This algorithm has already been developed and currently it is adapted to our experimental system.

Objective and Approach

The overall objective of the proposed research program is to develop a novel sensor based on optical radiation depolarization measurement technique for on-line real-time size analysis of grinding and flotation processes to minimize energy consumption during grinding and maximize flotation efficiency. The technique is based on use of angular and radial profiles of reflection and transmission of an object subjected to a collimated, polarized light beam. The circular platform around the column will house the fiber-optic connections as well as the polarizers. The angular scattered light will be collected at several different angles and will be directed to the detectors. This approach is non-intrusive and can be designed and constructed inexpensively with the advances in diode lasers, fiber-optics, and logic boards.

PROJECT TASKS

Task1. Design and Fabrication

Development of a laboratory scale EPLS System was already discussed in previous report. We are in process of developing a prototype on-line EPLS System, as shown in Fig. 1. It is the simple version of EPLS system developed by Aslan et al. [1]. He-Ne laser is connected to light scattering measurement ring by a fiber optic with a collimator. Scattered lights at two different scattering angles are collected by two polarization-maintaining fiber-optic to the detector via polarization optics box where scattering light intensity, polarization

state and degree will be measured. The data will be collected using a data acquisition board on a PC. Scattering angles where the measurements are taken can be changed to measure bubble size depending on flow rate and surfactant ratio by two rotational disks. We expect to have more details about this system in the next report.

Figure 1. Prototype On-Line EPLS System.

Task 2. Customization of Algorithm

A detailed numerical study has been carried out [2] to understand the propagation of polarized light in a bubble-laden medium, which is similar in essence to froth flotation system. The potential use of polarized light for characterization of mono-dispersed air bubbles is investigated using a vector Monte Carlo approach. The scattering matrix for the entire medium is constructed based on the Fresnel equations. Examination of the absorbing and multiple-scattering results show that if circularly polarized light is used, the bubble size, the bubble separation, as well as the thickness of carbonaceous layer around bubbles can be determined if careful experiments are conducted. It has been shown that circularly polarized light is a better choice than the linearly. We are still improving the model to have a direct comparison with the experimental results.

Task 3. Calibration and Verification

After we finish the prototype, we will be able to make direct evaluation of the system capability. We will have direct comparisons with the laboratory scale set-up and the numerical models.

Independent Bubble Size Measurement

Fig. 2 shows typical bubble formation in GL column. The size and distribution of bubbles was determined using the photographs of the bubble column taken during experiments. An image analysis algorithm was developed using the pre-built modules available in the Image Processing Toolbox (Matlab). The results were validated by manual measurements on statistically chosen sections of the image. Fine

Figure 2. Bubbles in the GL Column.

tuning of the algorithm is needed for more accurate results, particularly for pictures taken from experiments using higher flow rates and surfactant concentrations.

Effect of Bubble Size and Number in Two Phase Flow

The gas velocity affects both bubble size and number of bubbles in the water (gas hold-up). Experiments were conducted to establish the relationship. The frit pore sizes of the glass column were between 25 μ m and 50 μ m. Pressure of N₂ gas was 5 psi. Ten different gas velocities between 0.04 cm/s and 0.35 cm/s were used. Pictures of bubbles were taken before and after the measurement at each flow rate. Adop-Photoshop and SIAMS-600 image processing software were used to process the bubble pictures to determine mean bubble sizes.

Image processing steps are as follows. 4x4 M. pixel images of the bubbles were taken by Nikon D100 digital camera with a white background. The images were converted to gray scale images in Adop-Photoshop. The bubble images were converted to binary image file in order to do image processing in SIAMS-600. Diameter of each bubble based on equivalent surface area was calculated and for each picture, maximum, minimum, mean area equivalent bubble diameters (d_{32}) were calculated by the software automatically. In addition to those calculations shape factor for each flow rate was calculated to quantify the bubble shape deviation from sphere. Gas hold-up was determined from the difference in water level (h) measured in the absence and presence of gas. The results indicate that more surfactant increases gas hold-up decreases bubble diameter. When the gas flow rate increases, mean bubble diameter decreases logarithmically, but gas hold-up increases linearly. Bubble diameter does not decrease if gas velocity is greater than 0.2 cm/sec.

Figure 3. S_{ij} 's at 120 degree as a function of mean bubble diameter.

Relationship between Bubble Sizes and S_{ij} Parameters

In order to understand the relationship between gas velocity and S_{ij} parameters, single-angle scattering measurements were conducted at $\mathbf{q} = 120^\circ$. After gas velocities were converted to mean bubble diameter and gas hold-up, measured S_{ij} values were plotted to evaluate effect of both bubble diameter and gas hold-up parameters separately. Fig.3 shows that it is possible to predict bubble diameter based on scattering measurements: S_{11} , S_{22} , S_{33} , S_{44} , and S_{34} parameters are sensitive to bubble diameter at low gas velocities with medium-low surfactant concentrations. At high flow rate ($V_g > 0.2$ cm/sec.), there is no significant change in bubble size. Depending on surfactant concentration, it is difficult to measure bubble diameter by S_{ij} values if there is multiple scattering.

Relationship between Gas Hold-up and S_{ij}

Gas hold-up is the second parameter which is correlated with the gas velocity. Even though the gas hold-up increases linearly with increasing gas velocity, effect of gas hold-up on S_{ij} on surfactant concentrations. For low-medium surfactant concentration, S_{11} , S_{33} , and S_{44} profiles increase as increasing gas hold-up. S_{12} and S_{34} increase or decrease depending on flow rate and surfactant within the gas hold up range of 0.01-0.18. S_{22} shows large differences at high surfactant concentrations unlike other scattering matrix elements because shape factor of bubbles decreases with increasing gas velocity and number of bubbles (multiple scattering regime). Monitoring gas hold-up based on S_{ij} measurements is possible at some gas velocities for known surfactant concentrations.

SUMMARY

A novel approach for measuring two major characteristics (bubble size and gas hold-up) of two phase column was developed and it was showed experimentally that elliptically polarized light scattering (EPLS) concept works to measure two characteristic from scattering matrix elements of GL phase medium. Experiments show that some scattering matrix elements are sensitive to bubble size distribution parameters (mean bubble size, flow rate and gas hold-up). The scattering-matrix elements can be correlated with mean-bubble diameter and gas hold-up for known surfactant concentration even at high surfactant concentrations and high gas velocities. S_{11} , S_{33} , and S_{44} at $\mathbf{q} = 120^\circ$ are good candidates at low-medium flow rate and surfactant concentration to monitor bubble size and gas hold-up, S_{22} at $\mathbf{q} = 120^\circ$ is only scattering matrix element that can be used to monitor gas-hold-up at high flow rate and surfactant concentration. S_{12} has two major problems not to be considered as a monitoring parameter: (1) It decreases at low surfactant concentration with increasing gas hold-up, but it increases when surfactant concentration medium-high. (2) Because of multiple scattering affect, it is a very small value and does not have a trend for different gas flow rates at medium-high flow rate and surfactant concentration.

FUTURE WORK

- We will continue to utilize the our Monte-Carlo algorithm to study the influence of various parameters on light scattering within the two-phase medium.

- The prototype on-line EPLS system will be assembled for industrial size columns.
- EPLS for three-phase (GLS) medium experiments will be conducted and optimum sensor orientations for froth flotation will be obtained for lab-size froth flotation columns.
- Optimum sensor (PMT) angles will be obtained for three-phase flow systems.

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**Appendix P: Electrolytic Solution Purification and Metal Recovery from Metal-Bearing
Toxic Waste Streams**

TECHNICAL PROGRESS REPORT

Contract Title and Number: Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	Period of Performance: Starting Date: 6/1/03 Ending Date: 5/30/04
Sub-Recipient Project Title: Electrolytic Solution Purification and Metal Recovery from Metal-Bearing Toxic Waste Streams	Report Information: Type: Semi-Annual Number: Period: 10/1/03 – 3/31/04 Date: 3/31/04 Code: UT003
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ABSTRACT

Research has shown that using high surface area electrodes, toxic metal ion concentrations in aqueous media can be drastically reduced. By careful selection of the electrode potential, recovery of the metals individually can also be accomplished. The application of pulse plating schemes with high surface area electrodes for reducing the concentration of toxic metal ions is being investigated, as is the use of such a system for recovering a purified metal product from a mixture of metal ions based on the difference in electrochemical potentials between different metals.

INTRODUCTION

Background

Various waste streams containing dissolved metal ions are created both by industry and by natural processes such as acid mine drainage. Toxic metal ions contained in these waste streams are of concern because of their impact both on the natural environment and on resources such as the drinking water supply. These waste streams can often be a complex mixture of multiple metal ions, complicating the removal of the ions from the waste streams.

Currently, ion exchange and precipitation are commonly used to remove metal ions from these waste streams. However, both of these techniques require additional steps in order to recover the metals for recycling, such as stripping or redissolution followed by electrowinning and regeneration. Precipitation often results in a hazardous sludge of toxic metals that is simply disposed of in a hazardous waste disposal site instead of recycled. Additional processing steps used for recovering metals collected in the ion exchange and precipitation processes consume additional energy and chemicals in order to produce a purified metal product. The presence of multiple metals in a waste stream further complicates these metal recovery processes.

Objective and Approach

The objective of this project is to provide a method for removing multiple metal ions from aqueous streams by selective pulse-plating with high surface area electrodes. This method can be used to recover metals individually as purified products rather than as toxic waste. This direct production of metal as a by-product contributes to better resource utilization and reduces toxic waste production. The use of pulsed electrodeposition maximizes mass transport and current efficiency, and the sequential application of different electrical potentials allows for recovery of high purity metal products. Because each metal has a unique electrochemical potential below which it will begin depositing, metals can often be separated effectively on the basis of their individual potentials. Placement of a series of electrodes, each at different potentials, can be used to successively recover individual metals in a purified form. The use of a system in which cartridge type electrodes are used can facilitate recovery and recycling of individual metals rather than disposal of the metals as waste. In this investigation, various parameters such as electrode composition and surface area, electrode pulse potential, solution composition, and pulse scheme are investigated.

PROJECT TASKS

Equipment Setup

Two different electrode types are currently used in the investigation. The first is a platinum mesh electrode consisting of cathodic and anodic 1cm^2 screens separated by thin, inert polymeric screens. These screens are mounted in a flow-through apparatus. The second electrode is constructed similarly, with graphite felt used in place of the platinum screens. These electrodes are mounted so that fluid flows through in a cyclic manner. Pulsing is

accomplished using a computer controlled potentiostat that is connected to wires from the electrode screens.

The metal concentration of the water is analyzed using differential-pulse stripping voltammetry. This process allows for the determination of multiple metal concentrations in aqueous media simultaneously. In this type of analysis, a 10 cc sample of the water being processed is taken at the desired time interval. This sample is then put into contact with a mercury thin film electrode, which then accumulates all of the metal in the solution into the mercury thin film by electrodeposition of the metals via a highly negative potential. After this accumulation time, the potential of the mercury thin film electrode is scanned from low to high voltage in a pulsed manner, with the current difference between the high and low pulse currents being plotted against the potential. When the potential of the scan reaches a point that is related to the individual element's standard potential, the current for the high potential pulse side is anodic while the low potential pulse side is cathodic, making the differential between those currents quite large. This creates a peak in the differential current at a potential that is characteristic of the element, and because the current amplitude is a function of concentration, the peak height will correspond to the concentration of the element. Figure 1 shows an example plot from this type of analysis, with the three distinct peaks visible for, from left to right, cadmium, lead, and copper. These peak heights vary with concentration, and so this type of analysis is useful for determining the concentration of dissolved metal ions.

Fig. 1: Example plot from differential pulse stripping voltammetry for 50 ppm Cd, Pb, Cu. The peaks are from left to right for Cd, Pb, and Cu.

Experimental Procedure

Fluid is repeatedly cycled through the system using a pump while a potential is pulsed on each of the electrodes. Various pulse potential schemes are applied to the electrodes (in these tests a pulsed potential with a 2 ms on, 10 ms off time was used), and the level of metal ions present in the aqueous fluid is monitored by taking samples at known time periods and finding the dissolved metal content of those samples using differential pulse stripping voltammetry.

Results

In the previous report, tests had been conducted with both copper and lead ions separately in aqueous solution, and the results obtained showed a reduction in the amount of both metals in the solution. Further tests have been conducted to investigate the use of different types of electrode materials for removing more types of metal ions from solution, particularly the use of high surface area graphite felt electrodes. Tests have also been conducted to investigate the separation of various metals as a purified product from the solution by pulse plating each metal out separately, using different potentials to recover different metals.

Carbon felt electrodes having a high surface area were used in the recovery of mercury from aqueous solution. Figure 2 shows the removal of mercury from water as a function of passes through the electrode apparatus. This was accomplished using a potential of -2.5 V. vs. the counter electrode, and it can be seen that mercury concentration can be quickly reduced from 12.5 ppm to approximately 0.6 ppm in 7 passes.

Fig. 2: Hg concentration versus number of passes through the carbon felt electrode apparatus.

Fig. 3: Metal removal rate in ppm/min versus electrode pulse plating potential.

Also investigated was the use of platinum electrodes to recover metals individually based on the potential at which the metals plate out of the solution. The electrodes were placed at different potentials and the reduction in metal content of the water was analyzed for a set time period. Fig. 3 shows a plot of the metal removal rate for various electrode potentials.

At -0.2 V, only copper is removed from the solution, as this is above the plating potential for cadmium and lead. At -0.4 V, both lead and copper are removed, and cadmium stays in solution. At -0.6 V, the rate of removal for lead and copper is higher because of there being a higher overpotential for the removal of those elements, but cadmium remains in solution because it only will be removed at potentials lower than -0.63 V. In this way, metals can be effectively separated as pure products, or purified in aqueous form.

Metal removal rates can be affected by a number of parameters, such as the species concentration, electrode surface area, overpotential, and solution ionic strength. Using a potential of -0.5 V and the presence of 0.05 M sodium nitrate to increase ionic strength (the results of Fig. 3 are for solution without added salt), it is possible to remove lead very effectively from solution, as shown in Fig. 4. Copper in this case is removed more slowly, while cadmium is not removed at a significant rate. The concentration fluctuations are most likely experimental variations in the analysis technique. This technique is highly effective for metal separations, especially that between lead and copper.

Fig. 4: Concentration in ppm vs. number of passes through pulse plating electrodes.

SUMMARY

Pulse plating with high surface area electrodes is an effective way to remove metal ions from aqueous medium, and an effective way to recover metals individually in a more purified form. This method has demonstrated utility in removing lead, mercury, and copper from aqueous medium, and should be useful in removing additional ions as well.

FUTURE WORK

Ongoing research is currently concentrated on improving the efficiency of the electrode apparatus, in order to decrease the amount of time and energy required to remove metal ions from aqueous medium. Future work will center around improving the ability to separate metal ions into pure products by electrolytic recovery, as well as improving the ability to reduce the residual metal concentration of the solutions to much lower levels. To accomplish these goals a further understanding of the variables at work in this process will be pursued.

**Appendix Q: Determining the Effectiveness of Gold Filters for Removing Mercury from
Coal Fired Power Plants**

TECHNICAL PROGRESS REPORT

<u>Contract Title and Number:</u> Establishment of the Center for Advanced Separation Technologies (DE-FC26-01NT41091)	<u>Period of Performance:</u> Starting Date: 10/1/03 Ending Date: 3/31/04
<u>Sub-Recipient Project Title:</u> Determining the Effectiveness of Gold Filters for Removing Mercury from Coal Fired Power Plants	<u>Report Information:</u> Type: Semi-Annual Number: 2 Period: 10/1/03 – 3/31/04 Date: 3/31/04 Code: MT003
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ABSTRACT

This research is to remove elemental mercury from coal fired flue gas using a gold filter. The main objective of this research is to evaluate the effectiveness of gold wire mesh in removing mercury vapor from flue gas. A copper sponge electroplated with gold was tested with a gas stream containing mercury in the laboratory. The preliminary results indicate that the mercury removal efficiency of the sponge is about 80-90%. Tests are also in progress with silver electroplated copper and stainless steel sponges. The spent gold plated sponge was then heated gently to recover the mercury. Over 99% of the mercury was recovered from the filter by heating the filter to about 100° F. Further tests will be conducted to develop the relationship between the temperature and mercury release rate from the spent filters.

INTRODUCTION

Background

Coal contains relatively low levels of mercury that range from 0.010 to 3.5 ppmw. However, the mercury emissions from coal combustion in power plants have received special attention because coal is burned in about 1700 power plants in the US. Mercury is classified as a hazardous air pollutant under the Clean Air Act Amendments (CAAA) of Title III. The EPA's 1998 Utility Air Toxics Report to the US Congress indicated that mercury posed the greatest concern of all the toxics emitted from power plants. It is reported that in 1999, 43 tons of mercury were emitted from US coal fired power plants.

The US EPA announced its intention to rulemaking in 2003 to regulate power plant mercury emissions. The final regulations are expected in 2004, and compliance is projected for 2007. If EPA has its way, the new regulations will require 90% reduction in mercury emissions from power plants. This requirement will have significant financial implications for power plants. Therefore, developing cost effective control technologies to remove mercury will become increasingly critical.

Several control technologies are being studied. They mainly focus on pre-combustion and post combustion processes. Pre-combustion involves coal-cleaning technologies to reduce mercury burden at the source. Post combustion involves adsorption by carbon-based materials and conversion of mercury vapor to oxidized form for removal by wet system or particulate filters. It is reported that 90% of mercury emitted from burning western coal is in the form of mercury vapor (elemental) but that eastern coal combustion generates 60% elemental mercury and another 40% mainly in the form of divalent mercury.

Objective and Approach

The main objective of this research is to evaluate the effectiveness of gold wire mesh in removing mercury vapor from flue gas. The objective was modified to include silver as another material to be tested along with gold for mercury vapor removal mainly due to its lower cost. The preliminary tests with gold and silver filters and with beads electroplated with silver or gold indicated over ninety percent efficiency in removing mercury from air streams. To further evaluate this, copper sponges were electroplated with nickel and then with gold and were tested during this reporting period.

The project approach is as follows. Gold plated sponges were tested for their effectiveness in removing mercury from gas streams. The tests indicated about eighty to ninety percent mercury removal. The results are given in Tables 1 and 2 and also in Figures 1 and 2. The spent sponges were then heated to less than 100° F and they released over 99 percent of the mercury. Additional tests are currently being carried out to evaluate the temperature and mercury release rates. The physico-chemical processes involved in the amalgamation of mercury with gold will also be evaluated.

Table 1 (Test 1): Gold Electroplated on Copper Sponge @ 15 lpm flow rate

Inlet HG Vapor ($\mu\text{g}/\text{m}^3$)	Outlet HG Vapor ($\mu\text{g}/\text{m}^3$)	Removal (%)
112.4	13.1	88.3
96.7	11.0	88.6
90.2	9.8	89.1
89.3	9.6	89.2

Table 2 (Test 2): Gold Electroplated on Copper Sponge @ 15 lpm flow rate

Inlet HG Vapor ($\mu\text{g}/\text{m}^3$)	Outlet HG Vapor ($\mu\text{g}/\text{m}^3$)	Removal (%)
432.15	51.28	88.1
334.30	50.40	85.4
280.25	48.83	82.6
233.15	46.28	80.2

The electroplated sponges were filled in a 2.5 cm diameter and 15 cm long plastic tube. A flow rate of 15 lpm was maintained to provide a residence time of 0.3 seconds. The flow rate for this experiment was calculated based on 0.3 second residence time. The design of the test system is based on a proposed theory as follows. The filter efficiency could be assumed to follow a simple first order equation as follows:

$$E = 1 - e^{-\frac{(17.6LD)}{md^2}}$$

E = Efficiency of mercury filter system (fraction)

L = Length of the filter, m

D = Diffusion coefficient of mercury vapor, m/s²

μ = Superficial velocity, m/s

d = Average diffusion distance

This simple equation proposed above will be used as the starting point to evaluate the engineering design of mercury filters. There is not enough information in the literature that explains the theoretical basis of amalgamation. Therefore, the data collected in this research project with different metal filters and sizes will be used to further evaluate, improve, or modify this proposed model equation.

It is also an added goal of the investigator to develop a theoretical basis for the mercury amalgamation with gold or silver surfaces. Some of the main factors involved are:

- Available surface area per volume of filter
- Diffusivity of mercury vapor
- The residence time and;
- The property of the gas stream.

This theoretical evaluation will help us understand the amalgamation of mercury vapor with metal surfaces such as gold or silver.

PROJECT TASKS

This research involves six tasks. Task – 1 involves the production of sponges electroplated with gold or silver. In Task – 2 a synthetic mixing chamber will be set up. Task – 3 involves making the sponges to conduct the efficiency test. In Task – 4 the sponges are tested in a reactor and the samples are collected using a mercury tracker instrument. In Task – 5 the test results will be analyzed and the effectiveness of the filter will be determined. Task – 6 will present data in a report form and will publish the summary in the CAST web site.

Task -1: Four gold filters were made out of thin solid gold plate of 2.5 cm in diameter. Pinholes of less than one mm diameter were made to have the plates act as filters. In addition, gold threads of less than one mm diameter were made in 30 centimeter lengths. These filters and threads were also made in silver. Since silver will be relatively cheaper than

gold it was decided that tests may be done with silver in parallel with gold to understand its effectiveness in removing mercury. The initial tests were performed at room temperature conditions. (Work completed)

Task - 2: The mercury vapor was generated by passing room air through a closed box containing mercury contaminated soil. The air was passed through the mercury contaminated soil and the mercury from the soils volatilized in to the stream. The rate of airflow was controlled to generate the desired level of mercury vapor in the air stream. This seems like a safe and easy way to generate mercury vapor. Since we have several soil samples contaminated from mine sites this worked well for us.

Task – 3: Task three has been modified to concentrate the effort on the development of the filter materials. In this regard, commercially available copper and stainless steel sponges were electroplated with gold or silver and being tested for their effectiveness in one set of temperature conditions. Once the filter test results give consistent performance then the test will be done with actual coal flue gas at different temperatures and concentration levels.

Task - 4: Task four also is modified to focus the research on evaluating the physico-chemical processes involved in amalgamation. The literature review and analyzing the spent gold filters under SEM/EDX are the two procedures that will be used to accomplish this task

Task - 5: The performance of the gold and silver filters under various temperatures and inlet concentrations will be evaluated to assess the potential for mercury vapor removal in a typical power plant flue gas. The filter efficiency and its removal capacity ($\mu\text{g/g}$), that is, the amount of mercury the filter can hold before its regeneration will be determined.

Task - 6: The PI will write the final report at the end of the project. A project summary will be posted in the CAST web site as well as in Montana Tech's web site.

SUMMARY

In summary, the preliminary tests results indicate that copper sponges electroplated with gold filters can remove over ninety percent of mercury vapor from gas streams. The preliminary results also indicate that the spent sponges may release mercury with a minimum amount of heating. Similar tests are under way with silver sponges also. The physico-chemical processes will be evaluated to better understand the amalgamation process.

FUTURE WORK

The mercury removal tests will be performed with three new silver and gold filters. Based on these results, tests will be performed using flue gas generated in the lab or the filters will be taken to a coal fired power plant and tested in the field for their performance.

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PUBLICATIONS/PRESENTATIONS

The data collected thus far will be presented in an international mercury conference during June 2004. The preliminary results were also presented in the 2003 CAST annual conference in Charleston, West Virginia. At the end of spring, 2004 a paper will be presented in another technical conference also. The final report will be ready one month after the end of the term of this contract which is May 2004.