CROSSCUTTING TECHNOLOGY DEVELOPMENT AT THE CENTER FOR ADVANCED SEPARATION TECHNOLOGIES

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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. Due to the time taken up by the solicitation/selection process, these cover the initial 6-month period of project activity only.

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

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INTRODUCTION

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

- a) Solid-solid separation
- b) Solid-liquid separation
- c) Chemical/Biological Extraction
- d) Modeling and Control, and
- e) 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.

a) Solid-Solid Separation

1. 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)

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.

2. 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.

3. 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.

4. 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.

We will take a more rigorous approach to the analysis and modeling of the flotation process. 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. We will employ a Digital Particle Image Velocimeter (DPIV) that can record velocity vectors of all three phases. We will measure three-phase flow interactions of bubbles and model particles of different hydrophobicity with a turbulent flow field. We will deliver global, time-resolved velocity distributions and turbulence characteristics for each phase. 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. 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.

5. 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.

b) Solid-Liquid Separation

6. 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.

7. 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.

c) Chemical/Biological Extraction

1. 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.

2. 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.

3. 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.

4. 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 be 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.

5. 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.

6. 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.

d) Modeling and Control

1. 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.

2. 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.

e) Environmental Control

1. 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.

2. 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 April 1, 2003-September 30, 2003) was generated for each of these sub-projects and has been attached to this Document as an Appendix. A brief summary of progress during the initial 6 months, along with plans for the future on each of the sub-projects is given below.

a) Solid-Solid Separation

1. 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)

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. This effort included (i) an experimental study of the effects of surfactant addition on classifying cyclone performance and (ii) the development of a mathematical simulation program for evaluating the performance of multistage cyclone circuits. Preliminary test work indicates that the addition of surfactants into the feed of a classifying cyclone significantly reduces the particle cut size while providing improved efficiencies. A reduction of about 15-20 microns in the cut size was possible by adding fuel oil at concentrations that are typical in froth flotation. Mathematical simulations indicate that the only circuit capable of maintaining cut size while reducing bypass was a multi-stage rougher-cleaner-scavenger arrangement with recycles. However, this circuit may not be cost effective due to the large number of hydrocyclones, pumps and sumps required.

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.

2. 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 IMC Potash Carlsbad operations. Brine preparation, slimes dispersion and decantation, grinding, and flotation test procedures were established. Analytical procedures for ore samples and brines, as

well as IR determinations were also established and a certain level of competence was achieved. Currently, dispersion and flotation tests are being conducted; however, the results so far have been inconclusive. Most of the discrepancies are believed to be due to experimental and analytical errors. Therefore, a number of tests are being repeated and efforts are being made to improve the accuracy of analytical procedures.

Once the slime dispersion experiments with inorganic dispersants are completed and the sylvite flotation optimized, clay flotation will be studied with high clay ores using rod-mill ground ore samples. The effects of organic and inorganic slime dispersants, and clay flotation reagents on the flocculation and settling behavior of clays and tailings in the downstream thickeners will also be investigated. Clay flotation will then be introduced into the overall process scheme.

3. 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)

The effects of different particle size and different insoluble content of the feed material have been evaluated by bench scale flotation. Even with an insoluble content as high as 30.19%, the flotation separation is still excellent. A trona concentrate with a 99% purity can be produced using the new U of U flotation technology. The effect of fine particles, especially the slimes, on flotation is significant and causes a reduction in separation efficiency. The results indicate the use of recycled brine does not affect the efficiency of the flotation separation.

More detailed research is planned to establish a reagent schedule for pilot testing. This will include evaluation of collector composition; the use of different methods of collector preparation and application; reductions in reagent dosage rates; and changes in conditioning times and intensities. Efforts will also be made to secure a flotation pilot plant for testing at General Chemical plant site in the Summer of 2004. In addition to these activities, possible applications of the U of U flotation technology need to be considered so that a more complete economic analysis can be made.

4. 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)

In the four months since the initiation of this project, we have captured instantaneous fields of the three phases. For each case, we have about 2000 sets of instantaneous data. These are all being processed to return the velocity fluctuations and subsequently their RMS for each of the three phases.

The proposed future 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.

5. 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)

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 to resolve these problems. The mechanisms of phosphate depression and the behavior of carbonates in acid solution have also been examined.

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.

b) Solid-Liquid Separation

1. 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)

The fine coal slurry from the James River Coal Services Leatherwood Preparation plant was characterized for particle size distribution, percent solids, ash content and mineralogy. A new reagent scheme, which is a combination of lime and an anionic flocculent, was developed for effective flocculation of the slurry. Flocculation and settling studies results showed that the settling flux of the sediment can be enhanced using lime and slurry dilution.

Future settling tests will be conducted in a cylinder fitted with motorized picketed rakes to minimize the wall effect. A series of experiments varying percent solids will be conducted to determine the settling flux, reagent dosages, settled percent solids and rheology of the flocculated solids. Semi-continuous flocculation/settling tests to simulate Deep Cone thickener will be conducted using the proprietary equipment supplied by Dorr-Oliver Eimco. The characterization and other studies of the flocculated coal slurry obtained from the Arch Coal of West Virginia will also be carried out.

2. 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)

During this reporting period, work was performed to complete the basic design of a prototype horizontal belt pressure filter. The continuous test unit has been designed with a 2 inch (5 cm) wide by 6 ft (1.8 m) long carrying belt. This width provides a dry cake capacity of 100 lb/hr (45 kg/hr) when operated at a belt speed of 5.5 ft/min (1.5 cm/sec) with a 1.0 inch (25 cm) cake thickness. Other important design features described in this report include a floating carriage for the effluent collection box, a water injected Teflon pressure seal, an independent pressure chamber, and a pneumatic cake discharge system.

Work during the next reporting period will focus primarily on the procurement of parts and materials for the construction of the prototype unit. The fabrication and machine work is expected to require approximately 3 months of dedicated shop time to complete. Shakedown tests will begin immediately after the construction work is finished.

c) Chemical/Biological Extraction

1. 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 project is still in its initial stages and no substantial findings have been obtained. However, protocols have been developed to achieve such findings in the future and scoping tests are currently underway to help fine-tune the required experimental program.

Over the next 6 months, microorganisms will be cultured from the ore samples. "Natural" fungi on the ore can be cultured by growth in a malt-extract medium and on a malt extract/corn-steep agar. The resulting microorganisms will be screened for their ability to produce acid by pH measures in the culture media and using phenol-red containing agar media (K. Bosecker, 1985). 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. 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. Upon completion of these shake flask studies, the column leaching portion of the project will be initiated as the appropriate conditions will be contingent on the results. Both the direct and indirect methods will be investigated with the column studies, as well as leaching parameters.

2. 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 delayed hiring of personal, technical work on this project did not begin until September 1, 2003 and is currently five months behind schedule. However, a research team has now been assembled to develop a non-cyanide alkaline sulfide leaching process for gold extraction. Analytical methods for determining sulfide ion, hydroxide ion, and carbonate ion concentrations in an alkaline sulfide leach solution were established. Work was also initiated on developing methods for quantifying sulfate, sulfite, total sulfur and thiosulfate concentrations in the alkaline sulfide leaching solution. Preliminary thermodynamic modeling of the sulfur and gold-sulfur system was initiated. The initial review of thermodynamic data suggested very little data are available for soluble gold-sulfur complexes other than gold bisulfide complexes. Preliminary gold leaching experiments with alkaline sulfide solutions demonstrated gold extractions up to 30% were possible when metallic gold and the sulfide leaching solution were contacted for 72 hours.

Research work during the next reporting period will focus on establishing analytical methods for determining total sulfur, sulfate, sulfite, and thiosulfate in the alkaline sulfide leaching solutions. Additionally, the literature survey initiated in this reporting period will continue with an emphasis on finding gold-sulfur thermodynamic data. Gold leaching experiments utilizing both metallic gold and gold ore will also be performed to delineate the optimum conditions for leaching gold. The construction of gold-sulfur stability diagrams using both experimental and literature values will be initiated.

In the next reporting period, an agreement between the Center for Advanced Mineral and Metallurgical Processing (Dr. Corby Anderson) and Profile Resources U.S., INC. will be initiated for development of a pilot scale plant for leaching gold using the alkaline sulfide leaching process.

3. 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)

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

Leaching experiments will be conducted 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 made to establish impedance, conductivity and electrochemical parameters and compared with leaching data to determine the nature of silica catalyzed leaching of chalcopyrite.

4. 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)

In this reporting period, a research team consisting of Dr. Courtney Young, Dr. Hsin-Hsuing Huang, Dr. Eric Dahlgren, and Mr. David Douglas, was assembled to develop a rotating drum/cylinder membrane electrolytic cell to simultaneously produce copper cathode and regenerate ferric sulfate. A literature search focusing on the current “state of the art” membrane electrolytic cells was initiated and will continue to progress into the next reporting period. Analytical methods for measuring copper, iron, sulfate, and free acid concentrations are also underdevelopment.

Research work during the next reporting period will continue to focus on the literature search started on September 1, 2003. As a result of a delay in hiring of personnel, technical work on the project did not begin until September 1, 2003, and is currently five months behind schedule. It is anticipated that during the next reporting period, analytical procedures will be established and the analytical equipment will be setup to perform the analyses. Work is also planned to procure several different types of anion exchange membranes and to begin testing them in a parallel plate electrolytic cell.

5. 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)

In search of new resins to recover copper and cobalt from highly acidic, dilute solutions, a small quantity of a low-crosslinked, gel-type chelating resin was successfully synthesized. Small-scale equilibration tests were made with CuSO_4 in acidic (H_2SO_4) solutions. Comparison tests were also made with commercially available, low-crosslinked, gel type iminoacetic acid, and highly crosslinked macro-porous bis-pycolyl amine resin. The results indicate that the new thio-succinate resin coordinates less readily with Cu^{2+} than does the nitrogen in imino groups. Both the thiosuccinate and iminodiacetic acid resins were considerably less effective in absorbing Cu^{2+} from acidic solutions than the bis-pycolylamine resin.

Future work is planned in accordance with the outline of the project proposal as follows: 1) Prepare and evaluate a macro-porous version of the thiosuccinate resin, both

for Cu^{2+} and Co^{2+} absorption from acidic solutions, possibly using small-scale columns as well as batch equilibration screening procedures; 2) Prepare and evaluate, as above, a thioglycolate chelating resin; 3) Prepare and evaluate, as above, carboxymethylated diethylene triamine chelating resins; 4) Explore other possible chelating resin structures that might have potential for meeting the goals of this project; 5) Explore alternate means of utilizing available commercial resins to recover cobalt from industrial copper leach solutions.

6. 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)

Methods used to grow crystals have been determined from published literature, and the best method, as far as use for industrial applications, has been chosen for this research. Equipment for crystal growth has been assembled and is currently being tested.

Activities planned for the next report include results of the initial growth experiment and subsequent experiments using the surfactants. Induction times and relative growth rates will be determined by turbidimetry, changes in solution supersaturation, and SEM. Initial measurements of CSD by SEM will be determined. Further characterization of crystal structure by TEM, FTIR, and AFM will follow in the second phase of the project.

d) Modeling and Control

1. 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)

Initial LIBS testing has been performed on a carbon-water aqueous solution at NETL. LIBS testing for elemental composition is in progress. Signal analysis has been performed on selected samples. These samples indicate the detection of heavy metals in a water-coal mixture. Optical optimization for signal analysis and probe design are in progress. Signal analysis of the LIBS spark is in progress. Spectra will be analyzed to find average signals and prominent intensity lines in the LIBS spark, as well as calibration, which will eventually lead to a quantitative analysis of the elemental composition of the particles in the CFB.

Investigation of the LIBS process will continue at NETL until equipment is purchased and set up at WVU. Items expected on the purchase list include the USB 2000 spectrometer from Ocean Optics, an Nd:YAG laser, and specific fiber optics designed for optimization of the LIBS spark. Design of a probe to go into the CFB to monitor the efficiency of separation is in progress, and a model of the design is expected to be in development by mid-October. The probe will be inserted down into the CFB, next to a point designated for a laser spark. When the laser ignites a coal particle, the light emitted will be collected by the probe and sent to the spectrometer to be analyzed.

2. 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)

Elliptically scattered light by bubbles from a 2-phase gas-liquid medium was investigated for possible characterization of bubbles in floatation columns. Both experimental and theoretical analyses were initiated. The experimental results show that it is possible to monitor bubble size change in column by using scattering matrix elements of the bubbles. The best scattering angle should be around $\theta = 120$ deg. where change in bubble size caused significant change in S_{11} , S_{44}/S_{11} , and S_{34}/S_{11} . However, the optimum angle to conduct the light scattering measurements depends on gas pressure, frit pore size range, and as well as column diameter. Monte-Carlo model 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. It was also shown that it is possible to divide the flow characteristic to two zones, and carry out the experiments and correlations separately in each of these regimes.

EPLS for three-phase (GLS) medium experiments will be conducted and optimum sensor orientations for forth flotation will be obtained for lab-size froth flotation columns; results for 2-phase medium light scattering experiments will be compared with Monte-Carlo code developed recently; optimum sensor (PMT) angles will be obtained for three-phase flow; and a simple EPLS system will be developed for industrial-size columns.

e) Environmental Control

1. 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. This method is useful for the recovery of metals from toxic waste streams in an efficient manner. This method has demonstrated utility in removing both lead and copper from aqueous medium, and should be useful in removing additional ions as well.

In addition to the completion of the project tasks, ongoing research is currently concentrated on the improvement of the accuracy and reproducibility of the results from the electrodeposition processes. Improvement in the measurement of low amounts of metal ions in solutions is necessary to improve the accuracy of the tests, and numerous methods for measuring small ion concentrations are being investigated, such as use of different ion selective electrodes, inductively coupled plasma spectroscopy, and possibly additional electrochemical techniques. Future investigations will center around optimization of the pulse parameters for the deposition of various metal ions. Also for investigation will be the selective deposition of specific metal ions from a mixture of

multiple metal ions. The overall long-term goal of the project is the development of a scheme for removing multiple metal ions sequentially from an aqueous solution with the best possible efficiency and optimal metal recovery in purified form.

2. 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)

In summary, the preliminary test results indicate that gold and silver filters can remove mercury vapor up to 90% from gas streams. It seems silver may be a preferable material based on the cost. However, additional tests must be performed to confirm this. Tests are planned with silver and gold filters of three new sizes and shapes in order to determine the long-term performance of such filters. Also, regeneration of filters need be studied to evaluate the potential of these filters for use in coal-fired power plants.

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 laboratory or the filters will be taken to a coal-fired power plant and tested in the field for its performance.

REFERENCES

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

Appendix A: Development of Novel Ultrafine Sizing Methods

TECHNICAL PROGRESS REPORT

Contract Title and Number:

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

Period of Performance:

Starting Date: 10/1/02
Ending Date: 5/30/04

Sub-Recipient Project Title:

Development Of Novel Ultrafine Sizing Methods

Report Information:

Type: Semi-Annual
Number: 1
Period: 4/1/03-9/30/03
Date: 9/30/03
Code: VA008-R01

Principal Investigators:

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ABSTRACT

The objective of this project is to develop a broad base of new equipment 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, 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.

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.

PROJECT TASKS

Task 1 - Development of Mechanical Sizing Methods

One of the most successful commercial processes for efficiently sizing ultrafine particles is microsieving. Microsieving is a simple form of mechanical screening that uses a fine mesh fabric mounted on the periphery of a horizontal rotating drum. During operation, a

hydrostatic head is created across the mesh by introducing feed slurry feed through the open end of a drum. The pressure head forces ultrafines through the opening in the mesh, while solid particles that are too large to pass through the mesh are retained. The captured solids are carried by the rotating drum to the top of the unit and discharged into a collection launder. Sieve blinding is prevented by backwashing with high-pressure water sprays during every cycle. During this reporting period, the assembly of a continuous bench-scale microsieve was initiated. Because of delays associated with fabrication, the construction of the 12-inch diameter unit was not expected to be completed until the first half 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

One potential method for improving the performance of classification equipment is to modify the rheological properties of the feed slurry. Slurry viscosity is known to have a negative impact on the performance of classification processes (Laskowski, 2001). The hydrocyclone model proposed by Plitt (1976) included the effect of viscosity on cut size using a viscosity term that appeared indirectly in the form of the feed volumetric solids content. The model proposed by Lynch and Rao (1975) also used feed solids content to account for viscosity effects. Kawatra et al. (1996) demonstrated that a lower viscosity due to a lower feed solids content or higher slurry temperature results in a finer cut size. Unfortunately, a reduction in solids content often leads to a lower throughput that cannot be accepted in industrial operations. Likewise, a rise in temperature requires a large energy input that is generally not cost effective or practical for commercial circuits. A more promising approach for reducing slurry viscosity is to employ a surfactant to alter slurry rheology (Zaman et al., 2000). This approach can be particularly cost effective if the surfactant employed is already used by downstream unit operations.

During this reporting period, several test runs were conducted to evaluate the effects of chemical modifications to slurry rheology on classification performance. A hydrocyclone test rig equipped with a 2-inch diameter hydrocyclone was used for this test program. All experiments were carried out using minus 100 mesh coal particles diluted to 5% solids using fresh water. In each test, fuel oil was added directly into the feed slurry to increase particle hydrophobicity and reduce viscosity. Tests were performed at fuel oil dosages of 0.0, 0.6, 0.8, 1.0 and 1.2 kg/ton. Representative samples of the overflow and underflow streams were collected so that partition curves for the classifying cyclone could be obtained for each test. In addition, viscosity measurements were conducted in each case to evaluate the effects of fuel oil addition on slurry rheology.

Figure 1 shows the partition curves obtained at the different dosages of fuel oil. The data show a decrease in the cut size when fuel oil is added in the slurry. In this particular study, the particle cut size was reduced from about 65 microns with no reagent to about 40 microns at the highest dosage of fuel oil. This reduction represents a significant shift in the cut size by about 40%. The addition of fuel oil appears to alter the rheology of the feed slurry by enhancing the hydrophobicity of the coal particles. This suggestion is supported by the

Figure 1. Effect of fuel oil addition on the partition performance of minus 100 mesh coal slurry using a 2-inch (5 cm) diameter hydrocyclone test rig.

Table 1. Measured viscosity values of the feed and underflow streams of a classifying cyclone as a function of the surfactant concentration.

Fuel Oil (kg/t)	Feed Viscosity (cp)	UF Viscosity (cp)
0.0	1.41	1.55
0.6	1.29	1.49
0.8	1.22	1.46
1.0	1.22	1.44
1.2	1.16	1.45

viscosity measurements summarized in Table 1, which indicate a decrease in the slurry viscosity for both the feed and underflow streams after the addition of fuel oil. Since the secondary cyclone overflow often reports as waste, a reduction in cut size of this magnitude may offer significant gains in coal recovery and a corresponding reduction in waste disposal costs. The use of fuel oil is particularly attractive since it would already need to be added downstream in most industrial flotation circuits. Fuel oil is also relatively inexpensive compared to other chemicals used in preparation plants. It should be noted that the viscosity change is the result of surface modification of the coal particles, which comprise only about 50% of the total particulates in the suspension. Other chemical additives that are specifically formulated to modify the surface properties of the mineral matter particles in the slurry will be studied during the next reporting period.

Task 3 – Development of Novel Sizing Methods

Several series of selective agglomeration tests were conducted during this reporting period as a potential alternative to traditional methods for coal sizing and cleaning. In these tests, a variety of reagents were used that were specifically designed (i) to enhance the strength and size of coal particle agglomerates, (ii) to substantially decrease the consumption of the agglomerating agent, and (iii) to eliminate environmental issues associated with the use of petroleum based products. Several dozen sets of agglomeration tests were performed using these reagents at dosage levels ranging from 10 to 200 kg/t. The best overall results, which were obtained using a mixture of proprietary additives, provided a combustible recovery in excess of 63% using 22 kg/t of reagent. Additional optimization tests will be conducted during the next reporting period to further increase coal recovery and reduce reagent dosage.

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 effective method of reducing bypass is to utilize multistage cyclone circuits. To evaluate the capabilities of this approach, a spreadsheet-based program was developed during this reporting period to simulate the performance of various multistage classifying cyclone circuits. The simulator was used to evaluate both underflow retreatment (cleaning), overflow retreatment (scavenging), and recycling of byproduct streams. The results of the simulations are summarized in Figure 2. Compared to a single stage (SS) hydrocyclone circuit, the simulation data show that the bypass of ultrafines can be largely eliminated by repetitive recleaning of the coarse underflow. However, this configuration substantially increases the cut size. Likewise, cleaning circuits that retreat the cyclone overflow are capable of reducing cut size, but do not reduce the bypass of fines. The only configuration capable of maintaining cut size while reducing bypass was a three-stage rougher-cleaner-scavenger arrangement with recycle. However, this circuit may not be cost effective due to the large number of hydrocyclones, pumps and sumps that would be required.

Another method of reducing bypass is through the application of a water injection apex. This technique was made commercially available in the early 1950s by Krebs Engineers under the tradename, Cyclowash. Unfortunately, the current Cyclowash design tends to substantially increase the particle cut size, which makes it unacceptable for ultrafine sizing applications. In addition, the system requires large amounts of clarified injection water that may not be readily available in existing commercial plants. In light of these problems, technical personnel from Krebs Engineers have developed a new type of water injected cyclone that is specifically designed to overcome some of the inherent limitations associated with the Cyclowash system. A proprietary prototype has been provided to this project and a test rig is currently being fabricated. Preliminary test data obtained using this new design is expected to be available during the next reporting period.

Figure 2. Effect of fuel oil addition on the partition performance of minus 100 mesh coal slurry using a 2-inch (5 cm) diameter hydrocyclone test rig.

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. 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. Preliminary tests work indicates that the addition of surfactants into the feed of a classifying cyclone significantly reduces the particle cut size while providing improved efficiencies. A reduction of about 15-20 microns in the cut size was possible by adding fuel oil at concentrations that are typical in froth flotation. Mathematical simulations indicate that the only circuit capable of maintaining cut size while reducing bypass was a multi-stage rougher-cleaner-scavenger arrangement with recycles. However, this circuit may not be cost effective due to the large number of hydrocyclones, pumps and sumps required.

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.

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PUBLICATIONS/PRESENTATIONS

None for the current reporting period.

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

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Crosscutting Technology Development at the Center for
Advanced Separation Technologies (DE-FC26-02NT41607)

Period of Performance:

Starting Date: 10/1/02
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Sub-Recipient Project Title:

Dispersion and Flotation of Clays from New Mexico
Potash Ores

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Subcontractor Address:

"No subcontracts issued."

Report Information:

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Number: One
Period: 04/01/03-09/30/03
Date: 10/10/03
Code: NM001-R01

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ABSTRACT

Concentration of potash ores is accomplished by flotation in saturated brines with long-chain primary amine collectors. The 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. Inorganic dispersants that are added to attrition scrubbers and to the grinding section improve slimes dispersion and their removal. High-clay ores can also benefit from clay flotation ahead of sylvite flotation. This study was initiated to investigate the effect of slime dispersants and clay flotation for New Mexico ores. To date, ore samples have been acquired, and experimental and analytical procedures have been established.

INTRODUCTION

Background

New Mexico is the largest potash producer in the United States, and supplies 70% of the domestic production. 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 effects the flotation separation of sylvite (KCl) from halite (NaCl).

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

Objectives and Approach

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

- to investigate the effects of organic and inorganic clay dispersants to increase the efficiency of existing slime removal technologies for potash ores,
- to investigate flotation separation of clays from sylvinite ores using high molecular weight flocculants and amine ethers with particular emphasis on column flotation.

The effect of dispersants are being investigated by determining the free insoluble residue (IR) content of the ore samples in various size fractions, dispersing slimes in the ore by mechanical agitation, and removing IR by successive decantation from the pulp. This procedure is repeated with dispersants in the agitators, and subsequently, during the rod mill grinding stages. The effect of dispersants on flotation recovery of sylvite and the settling characteristics of the slimes are also being investigated.

Slime flotation from high-clay ores will also be investigated using amine ethers, (Lilaflot 810 and Lilaflot D 817) obtained from Akzo Nobel AB. The effect of flocculants and flotation reagents on downstream operations will also be investigated.

PROJECT TASKS

Flotation of soluble salt minerals requires rather unusual procedures. All mixing, screening, conditioning, and flotation operations have to be carried out in saturated brines. In laboratory flotation tests, the amount of salt deposited on dried products has to be accounted for and final weights 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 challenges not normally associated with common mineral separation studies. The following task were carried out:

- Ore samples were collected from IMC Potash Carlsbad operations. Four drums of ore samples were collected from the impact crusher discharge and another 4 drums of high-clay future ore samples were collected from underground workings. In addition, samples of high gray clay ore were collected near the ceiling of the ore seam, and samples of brown clay ore were collected from the working face.
- IMC's analytical procedures were adopted, reagents were prepared and two students were trained to run the chemical analyses as well as IR determinations.
- One drum of the current ore was homogenized and samples were cut for laboratory tests. Another drum of ore is being used to prepare brines. Initially, brine consumption created a bottleneck. As much as 30 liters of brine was needed for wet screening tests, just as much for dispersion and sedimentation tests. Some of the brine was recycled but if a flocculant is used during the test, that brine was discarded. Streamlining the test procedures reduced brine consumption and preparing fresh brine daily in large quantities assured ample supply of brine.
- Clay dispersion tests were 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 samples 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 is used at 1100 rpm. The agitation was carried out for 15 minutes, which is comparable to total agitation/scrubbing times at the plant. The pulp was then transferred to a 4-lt glass beaker, diluted with brine, and the minus 50- μ m (270 mesh) slimes fraction were removed through a siphon by successive decantation. The settling times were calculated using Stoke's equation, and the procedure was repeated as many as seven times. Each slime fraction was filtered, washed, dried and weighed. These tests were repeated in the presence of an inorganic slime dispersant. However, the results are not conclusive at this time and the tests are being repeated.
- The flotation tests were conducted with the rod-mill-ground and de-slimes 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 (Phillips Orfom F2) is added and frothed for 2 minutes. The concentrate and tailings were filtered with a vacuum filter, then wet weighed, dried and reweighed. The amount of salts precipitated from the brine in the products was calculated, representative samples were ground and analyzed. These tests are being repeated with different dispersant additions.

SUMMARY

Potash ore samples and flotation reagents were collected from IMC Potash Carlsbad operations. Brine preparation, slimes dispersion and decantation, grinding, and flotation test procedures were established. Analytical procedures for ore samples and brines, as well as IR determinations were also established and a certain level of competence was achieved.

Currently, dispersion and flotation tests are being conducted; however, the results so far have been inconclusive. Most of the discrepancies are believed to be due to experimental and analytical errors. Therefore, a number of tests are being repeated and efforts are being made to improve the accuracy of analytical procedures.

FUTURE WORK

Once the slime dispersion experiments with inorganic dispersants are completed and the sylvite flotation optimized, clay flotation will be studied with high clay ores using rod-mill ground ore samples. The effects of organic and inorganic slime dispersants, and clay flotation reagents on the flocculation and settling behavior of clays and tailings in the downstream thickeners will also be investigated. Clay flotation will then be introduced into the overall process scheme.

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Appendix C: Flotation Technology for the Trona Industry

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Crosscutting Technology Development at the Center for
Advanced Separation Technologies (DE-FC26-02NT41607)

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Sub-Recipient Project Title:

Flotation Technology for the Trona Industry

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No subcontracts issued.

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Code: UT001-R01

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ABSTRACT

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 involves 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 was approved by the Center for Advanced Separation Technologies to develop the technology and demonstrate its effectiveness at a plant site. General Chemical, EIMCO, and Roberts and Schaefer had agreed to participate in this research project.

A bench scale trona flotation test campaign at the General Chemical plant site in Green River, Wyoming was successfully completed in June 2003. Two researchers from the University of Utah and a Sr. Processing Engineer from General Chemical participated in the test campaign. Results from the test campaign confirmed initial results obtained in laboratory studies at the University of Utah. In addition, about 500 lb. of representative feed material was collected and shipped to laboratories at the University of Utah for further bench scale flotation experiments and flotation chemistry studies.

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 for glass production, chemicals, soap and detergents, flue gas desulfurization, pulp and paper, and water treatment. The total value of soda ash sold by the U.S. industry is about 800 million dollars per annum. Production of soda ash from trona has been limited to some extent by 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;

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

Such a preprocessing strategy has been limited by the 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 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 the two-year proposed 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. Bench Scale Flotation-Experimental Procedure

A one-liter Denver flotation cell, a high solids conditioner, a micro flotation column, and a dewatering centrifuge were organized in a laboratory at the General Chemical plant site. In addition equipment for preparation of the saturated solution was arranged. Shown in Figure 1(see APPENDICES) are photographs of the facilities for the test campaign.

The procedure for bench scale flotation experiments is presented in Figure 2 (see APPENDICES). Samples (about 200 lb) were taken from the processing line before calcination each morning. Then the sample was classified into different particle size fractions by laboratory screening. 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 centrifuge and then dried in an oven at 40 °C. The water-insoluble material in both float and sink products was determined by gravimetric analysis. The solution from centrifugation was taken for use in brine recycle flotation experiments.

2. Bench Scale Flotation-Results and Discussion

2.1 The Effect of Particle Size on Bench Scale Flotation

Shown in Figure 3 (see APPENDICES) are total mass distribution and insoluble distribution with respect to particle size for the minus 2 mm material taken from the calcination feed. The results in Figure 3 indicate that the insoluble material is mainly distributed in the + 200 mesh fraction. About 26% of the total mass is distributed in the - 200 mesh fraction with only 1-2% insoluble content. The overall grade for this feed material is about 11.3% insol.

Flotation experiments for different particle size distributions were carried out and the results are shown in Figure 4 (see APPENDICES). It can be seen that for the fine particle size distributions, especially in the presence of a large amount of slimes, flotation is not as effective. The best separation was achieved for coarse particle size material. In this regard it seems that the particle size for flotation feed material should be minus 1 mm top size with the minus 200 mesh fraction removed since the minus 200 mesh material only contains 1-2 % insoluble and can be used directly as concentrate.

2.2. Flotation of 40x60 Mesh Feed Material for Preparation of a Premium Quality Trona Product

Recrystallized soda ash (40x60) is an important commercial product. In order to evaluate the possibility that the U of U flotation technology could be used directly to produce a high quality trona product of similar size, flotation experiments with 40x60 mesh feed material were carried out. A typical result from these experiments is presented in Table 1. A trona concentrate of about 99% purity can be produced using the U of U flotation technology with more than 90% recovery.

Table 1. Results from Flotation with 40x60 Mesh Feed Material

Products	Wt.	Wt. %	Insol %	Trona Recovery %
Float	38.60	25.52	71.19	9.07
Sink	112.63	72.28	1.10	90.93
Total	151.23	100.00	18.94	100.00

2.3 Flotation with Recycle of Saturated Solution

Flotation with recycle of saturated solution is of considerable importance in order to reduce consumption of water and brine. Flotation experiments with recycled brine were conducted in order to study the effect on flotation efficiency when the saturated solution was recycled. A feed material (16x 100 mesh) containing about 18% insol was used. Shown in Table 2 (see APPENDICES) are the results for flotation with both fresh saturated solution and recycled saturated solution. The results in Table 2 indicate that when the recycled saturated solution was used, there is no significant effect on the efficiency of the flotation separation.

2.4. Effect of Insoluble Content on Bench Scale Flotation

Table 3 (see APPENDICES) presents the results from flotation experiments using feed material with different levels of insoluble content (16x 100 mesh at 17.96% insol and 16x 150 mesh at 30.19% insol). As can be seen, even with an insoluble content as high as 30.19%, the flotation separation is still excellent.

2.5. Flotation with Different Collector Type

The initial flotation experiments on 16x150 mesh feed material were carried out using reagent grade chemical as collector. In order to identify an appropriate commercial collector product three commercial collectors were tested. A comparison of the results is presented in Table 4. (see APPENDICES) These results indicate that flotation with collector 2 is effective.

3. Flotation Chemistry Considerations

Important considerations which determine the flotation response of soluble salts include thermodynamic stability of the salt, viscosity of the brine, and interfacial water structure (Hancer, Hu, Fuerstenau, and Miller, 1997). For example if the salt tends to be a water structure breaker (low viscosity brine and/or hydrated surface) then flotation is possible. On the other hand, if the salt tends to be a water structure maker then flotation will be difficult (Hancer, Celik, and Miller, 2001; Ozcan and Miller, 2002). The results from surface chemistry experiments (Fig 5 in APPENDICES) indicate that trona and Na_2CO_3 have a viscosity of 2 and 3 cp respectively in their saturated solution. NaHCO_3 has a low viscosity of 1 cp in its saturated solution. This lower viscosity of NaHCO_3 solution may account for the excellent flotation of the NaHCO_3 salt with the collectors. Recently results show that surface tension for Na_2CO_3 and trona saturated solution are higher than the water surface tension as shown in Fig 6 in APPENDICES. This is an indicator of structure making characteristics. Because structure-maker ions are more hydrated the surface tension increases. In this regard trona flotation from its saturated solution will be difficult and flotation of the gangue minerals is preferred which is the basis of the U of U flotation technology.

SUMMARY

The effect of different particle size and different insoluble content of the feed material have been evaluated by bench scale flotation. Even with an insoluble content as high as 30.19%, the flotation separation is still excellent. A trona concentrate with a 99% purity can be produced using the new U of U flotation technology

The effect of fine particles, especially the slimes, on flotation is significant and causes a reduction in separation efficiency. The results indicate the use of recycled brine does not affect the efficiency of the flotation separation.

FUTURE WORK

More detailed research is planned to establish a reagent schedule for pilot testing. Research activities at the University of Utah will include evaluation of collector composition as well as reagent dosage level. Some flotation parameters such as conditioning time and conditioning intensity will also be studied

Different conditions and methods of collector preparation/application will be studied in order to reduce reagent dosage.

Efforts will made to secure a flotation pilot plant for testing at General Chemical plant site in Summer 2004. In addition to these activities possible applications of the U of U flotation technology need to be considered so that a more complete economic analysis can be made.

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PUBLICATIONS/PRESENTATIONS

- Z.S.Nickolov, O. Ozcan and J.D. Miller, FTIR Analysis of Water Structure and its Significance in the Flotation of Sodium Carbonate and Sodium Bicarbonate Salts, *Colloids and Surfaces A: Physicochemical & Engineering Aspects*, 224 (1-3), pp. 231-239, 2003

APPENDICES

Figure 1. Facilities for the Bench Scale Flotation Test Campaign at the General Chemical Laboratory

Figure 2. Procedure for Bench Scale Flotation Experiments.

Figure 3. Total Mass Distribution and Insoluble Distribution with Respect to Particle Size. Sample Taken from Calcination Feed Material (-2 mm).

Figure 4. The Effect of Particle Size on the Bench Scale Flotation (Top Size 1 mm).

Figure 5. The viscosity of NaHCO₃, Na₂CO₃, NaCO₃ and trona solutions.

Figure 6. The surface tension of Na₂CO₃ and trona solutions.

Table 2. Comparison of Results From Flotation with Fresh Saturated Solution and Recycled Saturated Solution.

Saturated Solution	Products	Wt. g	Wt. %	Insol %	Trona Recovery %
Fresh Saturated Solution	Float	33.50	23.11	70.30	8.35
	Sink	111.44	76.89	2.24	91.65
	Total	144.94	100.00	17.80	100.00
Recycled Saturated Solution	Float	32.72	23.77	70.69	8.60
	Sink	104.96	76.23	2.98	91.40
	Total	137.68	100.00	18.98	100.00

Table 3. Results from Flotation Experiments Using Feed Material with Different Levels of Insoluble Content.

Insol. %	Products	Wt. %	Insol %	Trona Recovery %
17.96 %	Float	23.11	70.30	8.37
	Sink	76.89	2.24	91.63
	Total	100.00	17.96	100.00
30.19%	Float	36.90	75.31	13.05
	Sink	63.10	3.81	86.95
	Total	100.00	30.19	100.00

Table 4. Results From Flotation with Different Collector Types

Collector	Products	Wt. %	Insol %	Trona Recovery %
1	Float	23.10	70.30	8.35
	Sink	76.90	2.24	91.65
	Total	100.00	17.80	100.00
2	Float	23.00	57.19	11.64
	Sink	77.00	3.20	88.36
	Total	100.00	15.40	100.00
3	Float	23.48	56.30	12.51
	Sink	76.52	7.09	87.48
	Total	100.00	18.02	100.00

Appendix D: Flotation Processes/Experiments and Analysis

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Crosscutting Technology Development at the Center for
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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 advance 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.

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

$$\overline{U_i^2} = 0.33 \frac{\varepsilon^{4/9} d_i}{\nu^{1/3}} \left(\frac{\rho_i - \rho_f}{\rho_f} \right)^{2/3} \quad (5)$$

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. We propose here to start “filling this void”, generating experimental results for 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 was initiated in May 2003.. We already have a working experimental facility to generate grid turbulence and study the motions of the tree phases. We are working on the following tasks:

Task 1: Phase velocities

We are employing 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 are measuring 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 are measuring 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.

So far we were able to generate bubbles of specified and well-controlled size. We have employed our method to capture instantaneous frames of the field that include bubbles and model coal particles. We are working on the software that will identify each individual

particle and will monitor and document its motion. An example of such frames is shown in the Fig. 1. The first four frames capture a 2X2 cm frame downstream of the grid. The grid spacing is also 2 cm. The quality of the reproduction is poor. But our software can identify individually based on sizing, the tracer particle, the coal-model particles, which in this case are 100 μ spheres and the bubbles, here about 1 mm in diameter. The following four frames present data obtained with a much larger window of interrogation.

SUMMARY

In the few months since the initiation of this project, we have captured instantaneous fields of the three phases. For each case represented by single frame in the Fig. 1, we have about 2000 sets of instantaneous data. These are all being processed to return the velocity fluctuations and subsequently their RMS for each of the three phases.

Fig. 1. Instantaneous frames of the flow.

FUTURE WORK

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. 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.

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PUBLICATIONS/PRESENTATIONS

No publications or presentations have resulted from this work. Two papers were submitted for conference presentation.

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

TECHNICAL PROGRESS REPORT

Contract Title and Number:

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

Period of Performance:

Starting Date: 10/1/02
Ending Date: 5/31/04

Sub-Recipient Project Title:

Column Flotation of Relatively Coarse and Fine
Dolomitic Phosphate Pebbles

Report Information:

Type: Semi-Annual
Number: R01
Period: 4/1/03-9/30/03
Date: 4/30/04
Code: WV007

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Subcontractor Address:

Insert address of subcontractor. If none awarded, insert
No subcontracts issued.

Subcontractor Information:

Phone:
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E-Mail:

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 II – IV: 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.

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

Investigator s	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
Prasad, 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

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.

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PUBLICATIONS/PRESENTATIONS

None.

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

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Crosscutting Technology Development at the Center for
Advanced Separation Technologies (DE-FC26-02NT41607)

Period of Performance:

Starting Date: 10/1/02
Ending Date: 5/30/04

Sub-Recipient Project Title:

Improving Densification of Fine Coal Refuse to
Eliminate Slurry Ponds.

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"No subcontracts issued."

Report Information:

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Number: One
Period: 4/01/03 - 09/30/03
Date: September 29, 2003
Code: KY002-R01

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ABSTRACT

During this reporting period, characterization, flocculation and settling studies were conducted on the fine waste slurry obtained from the James River Coal Services Leatherwood preparation plant. A new reagent scheme consisting of lime and an anionic flocculent was developed for effective flocculation of the slurry. A combination of 9 kg/t lime and about 200 g/t of the anionic flocculent provided settling flux of 2 ton/hr/m². Slurry diluted to about 2% solids provided a settling flux of 14 tons/hr/m². The settling flux rates are in the region required for obtaining thickened slurry of the fine waste. In the next period semi-continuous flocculation/settling tests on the slurry will be conducted. A second slurry obtained from the Arch Coal of West Virginia will also be evaluated for the paste thickening technology.

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:

Four fifty-five gallons drums of fine waste slurry were collected from James River coal Services Leatherwood coal preparation plant located in county. A representative sample of the slurry was obtained using a Carpcro Rotary Slurry Sampler and characterized for pH, particle size distribution, solid and ash contents and mineralogy. The solids content of the slurry was 14.28%, which was unusually high. The particle size distribution as shown in Table 1 shows that about 45 weight percent of particles were in +50 mesh size, this indicated some screen problem in the plant. The pH of the slurry was 8.82 and the ash content was 31.7%. The ash fraction consisted of kaolinite, quartz and magnetite as determined from x-ray diffraction analysis.

Table 1. Particle size distribution and ash content of the 'as received' coal slurry from James River coal preparation plant.

Size Fraction (mesh)	Weight (%)	Ash (%)
+50	45.80	10.1
50 x 100	11.53	21.33
100 x 200	7.91	31.41
200 x 325	3.86	36.88
325 x 400	1.92	36.02
-400	28.98	69.09
Total	100.00	31.71

The plant personnel indicated that the fine fraction should be of -100 mesh size, so for the flocculation and settling studies the plus 100 mesh fraction was removed by screening. The particle size distribution of the -100 mesh fraction obtained using the Cilas Laser Particle Size Analyzer showed that 50% of particles are finer than 18.62 microns and 90% finer than 78.40 microns. The percent solids in -100 mesh fraction was 6.6 with an ash content of 57.71%.

Task 2. Flocculation and Rheological Studies

In this task, detailed flocculation study of the slurry was conducted to identify the optimum conditions to maximize the settling rate of the flocculated slurry. Other parameters such as the effect of mixing intensity, pH and viscosity were also conducted.

For the flocculation studies, the Nalco cationic (9850) and anionic (83949) flocculants, currently being used at the Leatherwood coal preparation plant, were utilized. The polymer stock solution of 0.2 g/l was prepared and used within three days of preparation.

Flocculation and settling tests were conducted as per the procedure developed by the Dorr-Oliver Eimco Company. A representative slurry sample was transferred to a 2L cylinder and a predetermined amount of flocculent was added to the slurry and mixed, using a plunger made with a rubber stopper mounted to a hollow tube with a syringe containing flocculent attached to the top (Figure 1). This procedure allows the uniform distribution of flocculent through out the slurry. After removing the plunger, settling rate was determined by noting the solid/solution interface as a function of time. A graph between the heights of the interface versus time was used to determine the initial settling rate from the straight line slope of the plot.

Fig. 1: Batch sedimentation apparatus

Because of water chemistry at the plant a complete flocculation was not achieved at the plant. After addition of flocculants a majority of fine particles remained suspended. We evaluated various combinations of inorganic and organic reagents to identify the best reagents combination which will provide a complete flocculation of the suspended solids. After trying different inorganic salts as coagulants, lime was selected based on its effectiveness and cost. Hence, further experiments were carried out using lime. A series of tests were conducted in a beaker using 200 ml of slurry to identify the optimum dosage of lime to induce flocculation. It was also observed that it is possible to flocculate slurry using only anionic flocculent in the presence of lime. These tests indicated that about 8 to 10 kg/t of lime and 200 to 250 g/t of anionic flocculent is required for proper flocculation of ultra fine clay. Further flocculation and settling tests were conducted at these reagent dosages.

Optimum sizing is achieved by maximizing the flux of the solids settling in the thickener. The solids settling flux rate is the free settling rate multiplied by the slurry solids concentration using the following equation:

$$\text{Settling Flux (tonnes/hr/m}^2\text{)} = \left(\frac{\text{Settling Distance (meters)} \bullet \text{Slurry Concentration (Kg/l)} \bullet 3600}{\text{Settling Time (sec)}} \right)$$

Figure 2 shows the settling flux v/s flocculent dosage at two lime concentrations using 6% solids suspension. In both cases increase in flocculent concentration increases the settling flux indicating enhanced flocculation. At a flocculent dose of 233 g/t, increase in lime concentration from 8 kg/t to 9 kg/t increases the settling flux from 1.08 to 1.53

tonnes/hr/m². In other words, a given settling flux could be achieved by reducing the flocculent dose and increasing the lime concentration.

For effective operation of the Deep Cone Thickener, a procedure developed by Dorr-Oliver Eimco Company involves settling tests to be conducted on various dilution of the slurry to determine the feed slurry concentration required for the best settling flux. Settling tests conducted at slurry concentrations of 1%, 2%, 3% and 4% are shown in Figure 3, which shows the settling flux as a function of slurry concentration at two different flocculant concentrations. An increase in percent solids from 1% to 6% at a flocculent dosage of 233 g/t decreases the settling flux from 13.65 to 1.53 tonnes/hr/m². However, it can be seen that diluting the slurry concentration from 6% to 4% increases the settling flux by 2.5 times.

Figure 2: Effect of flocculant dosage on settling flux.

Figure 3: Effect of % solids on settling flux.

Task 3: Pilot-Scale Testing and Process Optimization Studies:

For the pilot-plant studies the Dorr-Oliver Eimco will provide a Deep Cone Thickener of 1.5 m (~ 5 ft) diameter and 7.5 m (~ 25 ft) height. The overall dimensions of the unit will be 2.6 x 2.6 x 7.6 m (8.5 x 8.5 x 25 ft). A picture of the pilot-scale unit is shown in Figure 4. It is planned to conduct the pilot-scale tests at a coal preparation plant early next year.

Figure 4. Deep Cone Thickener Pilot scale unit

SUMMARY

The fine coal slurry from the James River Coal Services Leatherwood Preparation plant was characterized for particle size distribution, percent solids, ash content and mineralogy. A new reagent scheme, which is a combination of lime and an anionic flocculent, was developed for effective flocculation of the slurry. Flocculation and settling studies results showed that the settling flux of the sediment can be enhanced using lime and slurry dilution.

FUTURE WORK

Future settling tests will be conducted in a cylinder fitted with motorized picketed rakes to minimize the wall effect. A series of experiments varying percent solids will be

conducted to determine the settling flux, reagent dosages, settled percent solids and rheology of the flocculated solids. Semi-continuous flocculation/settling tests to simulate Deep Cone thickener will be conducted using the proprietary equipment supplied by the Dorr-Oliver Eimco.

The characterization and other studies of the flocculated coal slurry obtained from the Arch Coal of West Virginia will be carried out.

PUBLICATIONS/PRESENTATIONS

No presentation and publications during this reporting period.

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

TECHNICAL PROGRESS REPORT

Contract Title and Number:

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

Period of Performance:

Starting Date: 10/1/02
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Sub-Recipient Project Title:

Development and Testing of a Horizontal Pressure Belt
Filter

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No subcontracts issued.

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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 has focused primarily on the design of the prototype unit. This effort included the determination of several important design parameters including belt speed, belt width, and belt length.

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 0.7-0.8 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*. As shown in Figure 1, this new technology is very similar in design to that of a conventional horizontal belt vacuum filter. However, the new design encloses the filtering mechanism inside a pressurized chamber. During operation, feed slurry 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. The filter cloth is continuously backwashed to ensure that blinding is prevented, which is a significant advantage over a vacuum disc filter or plate-and-frame pressure filter. The external pressure can be applied using either a low-cost air compressor or a multi-stage blower. 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 bar. 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

Figure 1. Simplified schematic of a horizontal belt pressure filter.

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

The work conducted during this reporting period was associated primarily with the design of the prototype horizontal belt pressure filter and associated pilot-scale test circuit. The filter was designed based on the following target criteria:

Feed Capacity:	100 lb/hr (Variable from 25-100 lb/hr)
Cake Thickness:	1 inch (Variable from 0.25-1.00 inch)
Cycle Time:	120 sec (Variable from 60-360 sec)

Based on these values, important operating (belt speed) and design (belt length and width) variables were determined for the prototype unit.

The first series of design calculations were conducted to establish the belt length and speed required to obtain the desired cycle (cake formation plus drying) time. The cycle time (t_c) was calculated using:

$$t_c = \frac{L}{V} \quad [1]$$

in which L is the belt length and V is the belt velocity. As shown in Table 1, a belt length of 6 ft provides a total cycle time of between 60 and 360 sec for over the range of belt speeds from 1 to 6 ft/min. The target cycle time of 120 sec can be obtained using the 6 ft long belt operated at a midrange speed of 3 ft/min.

The next series of design calculations were used to identify the appropriate belt width and speed necessary to maintain the desired cake thickness. The cake thickness (H) was calculated using:

$$H = \frac{C}{\rho VW} \quad [2]$$

in which C is the production rate of dry filter cake, ρ is the dry density of the filter cake, V is the belt velocity, and W is the belt width. Using this relationship, cake thicknesses were calculated as a function of belt width and speed for production rates of 25, 50 and 100 lb/hr (dry). The results of these calculations are summarized in Table 2. As shown, a belt width of 2 inches provides the target cake thickness of approximately 1 inch (0.95 inches) for the midrange belt speed of 3 ft/min. This combination of width and speed also provides the target cycle time of 120 sec for the 6 ft long belt. Thinner cakes with thicknesses of 0.50 and 0.25 inches can be readily obtained by simply reducing the feed rate down to 50 and 25 lb/hr, respectively, while maintaining the 120 sec cycle time.

To complete the design, several other important design features were incorporated into the prototype unit. These included a floating carriage for the effluent collection box, a water injected Teflon pressure seal, an independent pressure chamber, and a pneumatic cake discharge system. These items are described in the following paragraphs.

Table 1. Calculation chart used to establish the proper belt length for the filter.

Belt Speed (ft/min)	1	2	3	4	5	6
Belt Length (ft)	Cycle Time (sec)					
4	240	120	80	60	48	40
5	300	150	100	75	60	50
6	360	180	120	90	72	60
7	420	210	140	105	84	70
8	480	240	160	120	96	80

*Cycle Time = Cake Formation Time + Drying Cycle Time

Table 2. Calculation chart used to establish the proper belt width for the filter.

Belt Speed (ft/min)	1	2	3	4	5	6
25 lb/hr Capacity:						
Belt Width (Inch)	Cake Thickness (Inch)					
1	1.43	0.71	0.48	0.36	0.29	0.24
2	0.71	0.36	0.24	0.18	0.14	0.12
3	0.48	0.24	0.16	0.12	0.10	0.08
4	0.36	0.18	0.12	0.09	0.07	0.06
5	0.29	0.14	0.10	0.07	0.06	0.05
50 lb/hr Capacity:						
Belt Width (Inch)	Cake Thickness (Inch)					
1	2.86	1.43	0.95	0.71	0.57	0.48
2	1.43	0.71	0.48	0.36	0.29	0.24
3	0.95	0.48	0.32	0.24	0.19	0.16
4	0.71	0.36	0.24	0.18	0.14	0.12
5	0.57	0.29	0.19	0.14	0.11	0.10
100 lb/hr Capacity:						
Belt Width (Inch)	Cake Thickness (Inch)					
1	5.71	2.86	1.90	1.43	1.14	0.95
2	2.86	1.43	0.95	0.71	0.57	0.48
3	1.90	0.95	0.63	0.48	0.38	0.32
4	1.43	0.71	0.48	0.36	0.29	0.24
5	1.14	0.57	0.38	0.29	0.23	0.19

*Assumes an average filter cake density of 3.5 lb/ft²/inch.

Collection Box: The effluent collection box that seals against the bottom side of the carrying belt has been designed on a floating carriage. The floating carriage is held in place using vertically slotted braces and is pushed upward against the underside of the carrying belt using pneumatic rams. This feature makes it possible to quickly adjust and accurately control the sealing pressure along the bottom side of the belt. This design also makes it possible to lower the collection box away from the carrying belt for inspection, cleaning and repairs.

Pressure Seal: A Teflon sheet has been used to provide the sealing surface between the bottom of the belt and the top of the collection box. In addition to providing a good seal, this type of material minimizes the sliding friction between the moving carrying belt and collection box. The edges of the sheet are grooved so that seal water can be injected along the entire outer rim of the collection box for additional lubrication and to improve the seal.

Pressure Chamber: The belt filter has been designed with the drive motor and filter cloth take-up placed at each end of the belt filter. Although this configuration makes the unit very long, the linear design makes it possible to minimize cross-sectional dimensions of the test

rig so that the unit can be placed length wise into a standard cylindrical pipe (with removable end caps) which serves as the pressure chamber. Since the filter mechanism is independent of the pressure chamber, this design allows the filter mechanism to be removed from the pressure chamber and operated as a standard vacuum belt filter (by simply connecting a vacuum line to the effluent collection box). This capability makes it possible to compare the performance of the unit when operating as either a pressure filter or as a vacuum filter.

Cake Discharge: A critical component in maintaining low operations costs for the horizontal belt pressure filter is the cake discharge air lock systems. To this end, the pressure chamber has been designed so that the filter cake drops directly into an air lock that sequentially opens and closes in an alternate fashion to continuously discharge the dried solids. The required gate valves and pneumatic control system for the air lock has been engineered with assistance from the Virginia Value Company.

SUMMARY

During this reporting period, work was performed to complete the basic design of a prototype horizontal belt pressure filter. The continuous test unit has been designed with a 2 inch (5 cm) wide by 6 ft (1.8 m) long carrying belt. This width provides a dry cake capacity of 100 lb/hr (45 kg/hr) when operated at a belt speed of 5.5 ft/min (1.5 cm/sec) with a 1.0 inch (25 cm) cake thickness. Other important design features described in this report include a floating carriage for the effluent collection box, a water injected Teflon pressure seal, an independent pressure chamber, and a pneumatic cake discharge system.

FUTURE WORK

Work during the next reporting period will focus primarily on the procurement of parts and materials for the construction of the prototype unit. The fabrication and machine work is expected to require approximately 3 months of dedicated shop time to complete. Shakedown tests will begin immediately after the construction work is finished.

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PUBLICATIONS/PRESENTATIONS

No 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

Contract Title and Number:

Crosscutting Technology Development at the Center for
Advanced Separation Technologies (DE-FC26-02NT41607)

Period of Performance:

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Bio-Assisted Heap Leaching of Nickel Laterites for the
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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 resulting nickel-containing leach solution is collected and then the nickel and citrate values are recovered.

The solubilization of metal ions from ores by organic acids produced by microorganisms has been demonstrated to be a viable method for metal production with reduced environmental and remediation issues, as organic acids are readily biodegradable. Because many of these organic acids and other metabolites form strong chelating complexes with the base metal ions there can be a reduction in the acid requirements to achieve complete solubilization.

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.

Since citric acid production can be carried out in aerated, solid-substrate column reactors (Y.D. Hang, 1988), this project is really proposing to study citric acid production in a "heap leach" column reactor, where the acid is consumed by the ore as it is being leached. It has been shown that the citric acid production rate is not significantly affected by the amount of inoculum used (Y.D. Hang, 1988); thus unlike for other bio-leaching applications, blending of the inoculum and ore should not be problematic.

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 to typical 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.

These objectives will be achieved by the following tasks.

Modeling the equilibrium state of the organic acid-ore leaching system based on its thermodynamics can assist in understanding the organic leaching of laterites ores. Of particular importance is the type of the complexes that are formed, as many citrate complexes are polydentate in nature, which results in sequestration of metal ions. By studying the speciation of both synthetic and actual solutions and comparing the results to thermodynamic modeling studies, the influence of different parameters on the leaching can be understood.

The leaching studies will involve two types of tests. Simple diagnostic tests will be performed in shake flasks to determine ore leachability using a variety of acids and acid mixtures, including sulfuric acid, citric acid and oxalic acid, pure cultures vs. indigenous microorganisms and different types of organic media. As appropriate, speciation studies of the leachates produced will be performed and compared to the theoretical models. As the actual process will involve heap leaching, studying “typical” leaching parameters, such as temperature and solids concentration, is not applicable.

The issue of acid composition is very important. Sulfuric acid leaching is strongly pH dependent and essentially ceases above a pH of 2, while citric acid has a chelation formation mechanism occurring simultaneously with lattice destruction by hydrogen ions, making it less pH dependent. (P.G. Tzeferis and S. Agatzini-Leonardou, 1994) Sulfuric acid has also been reported to leach nickel twice as fast as citric acid, but this varies widely from study to study, indicating that leaching rates are ore specific. (K. Alibhai, et al., 1991) However, supplementing citric acid with sulfuric acid has been shown to increase the rate of leaching of nickel well beyond that of either single acid. (D.I. McKenzie, et al., 1987)

The other type of leaching test will be column tests and will be undertaken to further optimize the process once the key parameters are identified from the shake flask tests. As is common practice to simulate the leaching in heaps, the leaching studies will be performed in plexiglass columns through which the recycle water is continually pumped. Heap leach cycles can range from a few weeks to many months. Important parameters to be studied will include the 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. Throughout the cycles samples will be taken to both determine the progress of the nickel leaching and provide samples for the speciation studies. As appropriate, speciation studies of the leachates produced will be performed and compared to the theoretical models. Once analyses of the leachates have been completed, it is likely that some of the thermodynamic parameters will not be available in the literature and will need to be determined to develop the thermodynamic model.

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. Their typical chemical analyses are

shown in Table 1. To confirm these results, duplicate samples of the ores have been sent to two independent laboratories for analysis by two different techniques. Because of the chromite and other spinels present in the ore, special digestion procedures are required to ensure complete dissolution for accurate analyses. Free moisture and loss on ignition (LOI) are also being performed on the samples.

Task 2 – Establishment of microorganism cultures

Aspergillus niger has been selected as the primary fungus of interest because of its ability to produce significant quantities of citric acid, which is thought to be the primary organic acid involved in nickel leaching. *Aspergillus niger* van Tieghem, anamorph (IMI 27809 [581; Clement A-1-215; NCTC 7193; NRRL 2322; NRRL 2354; QM 6906]) was ordered from ATCC (Catalogue number 10577). The fungus has been revived using the required potato dextrose agar medium, and fermentation will be allowed to occur until an initial culture of 500 mL is achieved. All subcultures for future work will stem from this original culture.

Task 3 – Shake flask leaching studies

Initial shake flask leaching studies are underway. Figure 1 shows the results from leaching the two ore samples at a H_2SO_4 concentration of 25 g/L, a solids concentration of 20 g/L and 28 °C. While the nickel content of the Latin American ore is about twice that of the Australian, the leachability with mineral acid is about 10 times greater. Comparisons will be made between sulfuric acid and organic acid leaching, as well as the various combinations of the mineral and organic acids. Once a viable microorganism culture has been established, shake flask studies will be undertaken with the resulting broths.

Table 1: Typical analyses of ore samples used in project activities

	Ni	Co	Fe	Mg	SiO ₂
Australian sample	0.7%	0.06%	25%	8%	30%
Latin American sample	1.9%	0.04%	22%	11%	28%

Figure 1: Typical analyses of ore samples used in project activities

Task 4 – Thermodynamic modeling

Some preliminary thermodynamic modeling of the metal-organic acid systems expected to occur during leaching has been completed. These studies will help in predicting the selectivity of nickel and other metallic ions under atmospheric leaching (heap leaching or agitation leaching) and multi-ions existing conditions.

SUMMARY

As the project is still in the initial stages no substantial findings have been obtained. However, protocols have been developed to achieve such findings in the future. The scoping tests that are currently underway will help fine-tune the required experimental program.

FUTURE WORK

Microorganisms will also be cultured from the ore samples. “Natural” fungi on the ore can be cultured by growth in a malt-extract medium and on a malt extract/corn-steep agar. The resulting microorganisms will be screen for their ability to produce acid by pH measures in the culture media and using phenol-red containing agar media (K. Bosecker, 1985).

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.

Upon completion of these shake flask studies, the column leaching portion of the project will be initiated as the appropriate conditions will be contingent on the results. Both the direct and indirect methods will be investigated with the column studies, as well as leaching parameters.

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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

Contract Title and Number:

Crosscutting Technology Development at the Center for
Advanced Separation Technologies (DE-FC26-02NT41607)

Period of Performance:

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Sub-Recipient Project Title:

Development of Alkaline Sulfide Leaching and
Recovery of Gold

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ABSTRACT

Several important aspects of the CAST project titled "Development of Alkaline Sulfide Leaching and Recovery of Gold" for the current reporting period were accomplished. A research team was formed and began work on September 1, 2003. It should be noted that due to delayed hiring of personal, technical work on the project did not begin until September 1, 2003 and is currently five months behind schedule. A no-cost extension to continue the project five months longer than originally planned will be filed. Analytical procedures for quantifying the amount of free hydroxide, sulfide, and carbonate ions in the leaching solution were established and experimentally verified. Methods for analyzing total sulfur, sulfate ion, thiosulfate ion, sulfite ion, and polysulfide ion concentrations were also established. Reagents and basic lab equipment were also acquired for performing gold leaching experiments. Additionally, preliminary thermodynamic modeling of the sulfur system and preliminary gold leaching experiments were completed.

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 leaching through the use of an environmentally benign leaching process.

The technological issues which 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 establish the basic thermodynamic values, i.e., Gibbs Free Energy of Formation of the aqueous gold species formed, to enable modeling of the alkaline sulfide leaching process with STABCAL.

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 for accomplishing Task 1 and Task 2 involves determination of the sulfur and gold speciation in the alkaline sulfide system based on both literature values and experimentally determined values. Leaching experiments will be performed to determine optimized gold leaching conditions. The resulting pregnant leach solutions will be analyzed specifically for free OH^- , CO_3^{2-} , S^{2-} , total sulfur, sulfate, sulfite, and thiosulfate. Additional species will be analyzed as appropriate. The gold concentration in both the pregnant leach solution and gold concentrate/metallic gold sample will be analyzed for calculation of the amount of gold extracted. The kinetic aspects (Task 3) of the optimized leaching conditions will also be studied.

PROJECT TASKS

Project tasks accomplished during this reporting period include assembly of a research team, development and determination of analytical procedures to quantify sulfur speciation, preliminary thermodynamic modeling of the sulfur system, and completion of preliminary gold leaching experiments. These subtasks are part of Task 1: Development of a Complete Thermodynamic Model of the Alkaline Sulfide Gold Leaching System and Task 2: Optimization of the Alkaline Gold Leaching System as covered by Phase I in the proposal.

Sub-Task 1: Research Team

A research team headed by Dr. Corby Anderson (PI) and Dr. Larry Twidwell (PI) was assembled. Other team members include Dr. Eric Dahlgren, a postdoctoral researcher from the University of Missouri-Rolla who was hired one-half time for work on this project and Mr. Darby Stacey, a Master of Science graduate student. Dr. Dahlgren was also hired to work part time on CAST Project MT002 “Simultaneous Copper Cathode Production and Ferric Sulfate Regeneration”.

Sub-Task 2: Analytical Procedures

Analytical procedures using a MCI Model GT-05 Automatic Titrator were established and verified for determining the amount of free hydroxide, sulfide, and carbonate in the alkaline sulfide leaching solution. Test runs of solutions containing known amounts of hydroxide, sulfide, and carbonate were titrated. Results of five different titration runs are shown in Table I; the titrating method resulted in values within 5 % of the known value.

Table I. Determination of Sulfide, Hydroxide, and Carbonate Concentrations

Sample	Components (Actual)			Contents (Measured)			% Difference		
	S^{2-} (g/L)	OH^- (g/L)	CO_3^{2-} (g/L)	S^{2-} (g/L)	OH^- (g/L)	CO_3^{2-} (g/L)	S^{2-} (%)	OH^- (%)	CO_3^{2-} (%)
1	15.0	17.0	25.0	15.6	16.2	24.2	3.8	4.8	3.1
2	15.0	17.0	25.0	15.7	16.3	24.0	4.5	4.2	4.0
3	15.0	17.0	25.0	15.5	16.1	24.3	3.1	5.1	2.7
4	15.0	17.0	0.0	14.9	16.4	N/A	0.7	3.8	N/A
5	15.0	17.0	0.0	15.2	16.2	N/A	1.2	4.9	N/A

A method for measuring total sulfur in the alkaline sulfide leaching solutions using a LECO SC-144D2 sulfur analyzer is currently being developed. Procedures for measuring sulfate, thiosulfate, and sulfite in the leaching solutions are being evaluated. The methods under consideration include titration and measurement with a Dionex DX-100 Ion Chromatograph.

Sub-Task 3: Thermodynamic Modeling

Modeling of the sulfur system at various temperatures has been performed using STABCAL and a literature review of sulfur and gold-sulfur complexes was initiated. The initial review of the gold-sulfur thermodynamic data showed thermodynamic data was available for gold bisulfide species, but no gold sulfide complexes were found.

Sub-Task 4: Preliminary Leaching Experiments

Gold leaching experiments were performed using design of experiment methodologies. Specifically, Design Expert 5 was used to design a series of experiments and model the results. For the initial set of experiments, metallic gold was placed in a stirred leaching solution and for 72 hours. The gold leaching factors examined included temperature, sulfur content, sulfide content, thiosulfate, and sodium hydroxide to sulfur ratio. The amount of gold leached was measured gravimetrically. In some instances, approximately 30% of the gold was leached. Based on the results, it was found that temperature had the largest effect on the extractability under equilibrium conditions. Further leaching studies are currently planned.

SUMMARY

Due to delayed hiring of personal, technical work on this project did not begin until September 1, 2003 and is currently five months behind schedule. However, a research team consisting of Dr. Corby Anderson, Dr. Larry Twidwell, Dr. Eric Dahlgren, and Mr. Darby Stacey was assembled to develop a non-cyanide alkaline sulfide leaching process for gold extraction. Analytical methods for determining sulfide ion, hydroxide ion, and carbonate ion concentrations in an alkaline sulfide leach solution were established. Work was also initiated on developing methods for quantifying sulfate, sulfite, total sulfur and thiosulfate concentrations in the alkaline sulfide leaching solution. Preliminary thermodynamic modeling of the sulfur and gold-sulfur system was initiated. The initial review of thermodynamic data suggested very little data are available for soluble gold-sulfur complexes other than gold bisulfide complexes. Preliminary gold leaching experiments with alkaline sulfide solutions demonstrated gold extractions up to 30% were possible when metallic gold and the sulfide leaching solution were contacted for 72 hours.

FUTURE WORK

Research work during the next reporting period will focus on establishing analytical methods for determining total sulfur, sulfate, sulfite, and thiosulfate in the alkaline sulfide leaching solutions. Additionally, the literature survey initiated in this reporting period will continue with an emphasis on finding gold-sulfur thermodynamic data. Gold leaching experiments utilizing both metallic gold and gold ore will also be performed to delineate the optimum conditions for leaching gold. The construction of gold-sulfur stability diagrams using both experimental and literature values will be initiated.

In the next reporting period, an agreement between the Center for Advanced Mineral and Metallurgical Processing (Dr. Corby Anderson) and Profile Resources U.S., INC. will be initiated for development of a pilot scale plant for leaching gold using the alkaline sulfide leaching process.

Appendix J: Hydrometallurgical Processing of Chalcopyrite Concentrates

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Crosscutting Technology Development at the Center for
Advanced Separation Technologies (DE-FC26-02NT41607)

Period of Performance:

Starting Date: 10/1/02
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Sub-Recipient Project Title:

Hydrometallurgical Processing of Chalcopyrite
Concentrates

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"No subcontracts issued."

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Code: NV001-R01

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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). Electron micrographs and EDX spectra are presented showing what the chalcopyrite surface looks like after leaching in the absence and presence of nanosize silica. Initial leaching experiments are presented showing the important effect of the presence of nanosize silica. The equipment for the electrochemical impedance spectroscopic experiments has been set up. A photograph of the set-up is presented.

INTRODUCTION

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 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 developed at the University of Nevada, Reno, 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: Three particle size ranges will be used. Oxidants that will be used are ferric chloride, ferric sulfate, hydrogen peroxide, sodium hypochlorite and potassium permanganate. Temperature will be varied from 25° to 90°C. Leaching will also be studied as a function of time to establish reaction kinetics. Various quantities of nanosize silica will be added to the leaching systems.

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, will be used to study the electrochemical reaction of silica-catalyzed chalcopyrite leaching. Polished chalcopyrite samples will be attached to a platinum wire using conductivity silver epoxy. The specimen will be epoxy-mounted. When the resin is semi-solid, a glass tube will be inserted to prevent the platinum wire from being exposed to the solution. After curing, electrochemical experiments will be conducted with various lixivants, oxidants, silica concentration and values of pH. A photograph of the experimental set-up is given in Figure 1.

PROJECT TASKS

Electron Micrographs

An electron micrograph of chalcopyrite prior to leaching is shown in Figure 2. A micrograph of chalcopyrite that has been leached with sulfuric acid at pH 1.5, 50°C and 24 hours is shown in Figure 3. The passivating layer of sulfur formed under these conditions is readily apparent. The EDX spectrum of this surface shows a major sulfur peak (Figure 4). When nanosize silica is added to the leaching system, crystals of SiO₂ can be seen to cover the chalcopyrite surface. See Figure 5. The EDX spectrum of this surface shows a major silicon peak and a very small sulfur peak (Figure 6).

Leaching Experiments

Leaching of chalcopyrite was conducted in the absence and presence of nanosize silica particles. The results of this series of experiments are given in Table 1.

Table 1. Effect of Nanosize Silica on Dissolution of Copper from Chalcopyrite:

Conditions: 10 g/L chalcopyrite; 0.5 N H ₂ SO ₄ ; 10 ml/L H ₂ O ₂ ; 10 ml/L ethylene glycol; 75°C; 24 hr leaching.	
<u>Amount of Silica (g/L)</u>	<u>Copper Dissolution (%)</u>
10	62
3.5	50
0	12

When silica is not present, only nominal dissolution is effected. In the presence of nanosize silica, recovery is increased dramatically.

Leaching temperature has a major effect on copper dissolution from chalcopyrite. As can be seen in Table 2, increasing temperature from 25°C to 75°C increases recovery from 2 % to 50 %.

Table 2. Effect of Temperature.

Conditions: 10 g/L chalcopyrite; 0.5 N H ₂ SO ₄ ; 10 ml/L H ₂ O ₂ ; 10 ml/L ethylene glycol; 3.5 g/L silica; 4 hr leaching.	
<u>Leaching Temperature (°C)</u>	<u>Copper Dissolution (%)</u>
25	2
45	36
75	50

SUMMARY

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

FUTURE WORK

Leaching experiments will be conducted 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 made 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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Fig. 1. Electrochemical impedance spectroscopic set up

Fig. 2. Electron micrograph of chalcopyrite particle prior to leaching

Fig. 3. Chalcopyrite surface after leaching. No nanosize silica present

Fig. 4. EDX spectrum of chalcopyrite. No nanosize silica present.

Fig. 5. Chalcopyrite after leaching in presence of nanosize silica

Fig. 6. EDX spectrum of chalcopyrite after leaching in presence of nanosize silica.

**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

Contract Title and Number:

Crosscutting Technology Development at the Center for
Advanced Separation Technologies (DE-FC26-02NT41607)

Period of Performance:

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Sub-Recipient Project Title:

Simultaneous Copper Cathode Production and Ferric
Sulfate Regeneration

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Period: 4/01/03-9/30/03
Date: Sept. 30, 2003
Code: MT002

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ABSTRACT

A research team was formed and began work on the project "Simultaneous Copper Cathode Production and Ferric Sulfate Regeneration" on September 1, 2003. A literature survey was initiated and is currently ongoing according to the timeline outlined in the initial proposal. In addition to the literature search, laboratory equipment is currently being acquired and analytical procedures established for measuring the copper, iron, sulfate and free acid concentrations in the electrolytes.

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 rotating drum/cylinder electrolytic cell divided into an anolyte and catholyte compartment with an ion exchange membrane.

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 a rotating drum/cylinder 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 and consists of a literature review to identify potential membranes, design and construction of an electrolytic cell, and characterization of the electrolytic cell. Specific issues that will be addressed are the selectivity and the ionic conductivity of the ion exchange membrane. Additionally, the current efficiency of the electrolytic cell, copper cathode quality, and the influence of additives on the membrane and copper cathode will be considered.

PROJECT TASKS

Project tasks accomplished during this reporting period include assembly of a research team, setup of analytical equipment, and initiation of a literature survey focusing on

the current electrolytic membrane cell technology. Completion of these tasks is in line with the larger goal of building a rotating drum/cylinder electrolytic cell separated by an ion exchange membrane into anolyte and catholyte compartments.

Task 1 – Research Team

A research team headed by Dr. Courtney Young (PI) and Dr. Hsin-Hsuing Huang (PI) was assembled. Other team members include Dr. Eric Dahlgren, a postdoctoral researcher from the University of Missouri-Rolla who was hired one-half time for work on this project and Mr. Dave Douglas, a Master of Science graduate student. Dr. Dahlgren was also hired to work part time on CAST Project MT001 “Development of Alkaline Sulfide Leaching and Recovery of Gold”. Additionally, an agreement between Montana Tech and James Cook University is currently being initiated for inclusion of a Ph. D candidate, Ces Fabian, into the research team as a third principle investigator.

Task 2 – Analytical Equipment

Analytical procedures for quantifying copper, iron, free acid, and sulfate concentrations are currently being developed. A MCI Model GT-05 automatic titrator was acquired and a method for analyzing the amount of free acid and copper is currently being developed. Additionally, a Dionex DX-100 is being equipped for performing sulfate ion analyses.

Task 3 – Literature Search

A literature search, detailed on the original proposal as the first task, was begun on September 1, 2003. The initial search indicated two major types of electrolytic cells separated into anolyte and catholyte compartments have been developed. The first type utilizes a diaphragm (diaphragm electrolytic cells) that has a limited specificity for the type of ions that pass through while the second type utilizes an ion exchange membrane (membrane electrolytic cells) that limits the type of ion, e.g., an anion or cation, that can pass between compartments.

Several examples of diaphragm electrolytic cells were found in the literature. Two processes that utilize this type of electrolytic cell for simultaneously producing copper cathode and regenerating the leaching oxidant/lixiviant were described. Intec (2002) has developed a process whereby a sodium chloride/bromide electrolyte is used to leach copper. In this process, a BrCl_2^- (HalexTM) species is used as an oxidant for leaching with a lixiviant that contains primarily chloride ions. After leaching, copper is recovered in the cathode compartment of an electrolytic cell divided by a diaphragm and the oxidant (BrCl_2^-) is regenerated in the anode compartment. Zoppi (2000) developed a patented process for the treatment of chalcopyrite, chalcocite, and covellite utilizing a fluoroboric lixiviant containing ferric fluoroborate ions as an oxidant. This process is similar to the proposed acidic ferric/ferrous sulfate leaching system whereby copper is recovered in a catholyte compartment and ferrous fluoroborate ions are oxidized to ferric fluoroborate ions in the anolyte compartment.

Literature was found pertaining to membrane electrolytic cells constructed from anion exchange or cation exchange membranes for the electrolytic recovery of copper. Cation exchange membranes were used primarily for protecting chelating agents from oxidation at the anode. Specific examples of this application include the use of cation exchange membrane electrolytic cells for recovering copper from dilute cyanide solutions ((Lu et al., 2002) and the recovery of metals from plating waste solutions (Juang and Lin, 2001).

Anion exchange membranes have also been examined for use in membrane electrolytic cells. This type of membrane was used in a patented process (Murray, 2001) similar to the proposed project whereby metallic copper was leached with an acidic ferric sulfate solution. The copper was recovered in the cathode compartment of an anion exchange membrane electrolytic cell and ferrous sulfate ions were oxidized in the anode compartment to ferric sulfate ions for use as an oxidant in the lixiviant. Although this process is similar to the proposed research, the proposed research utilizes a rotating drum/cylinder electrode for recovering copper and is believed to offer several advantages over the patented process. Kang-gen et al. (2000) developed an anion membrane electrolytic cell for recovering copper from sulfate solutions. However, that project focused on using consumable iron anodes for lowering the energy required to recover copper.

SUMMARY

In this reporting period, a research team consisting of Dr. Courtney Young, Dr. Hsin-Hsuing Huang, Dr. Eric Dahlgren, and Mr. David Douglas, was assembled to develop a rotating drum/cylinder membrane electrolytic cell to simultaneously produce copper cathode and regenerate ferric sulfate. A literature search focusing on the current “state of the art” membrane electrolytic cells was initiated and will continue to progress into the next reporting period. Analytical methods for measuring copper, iron, sulfate, and free acid concentrations are also underdevelopment.

FUTURE WORK

Research work during the next reporting period will continue to focus on the literature search started on September 1, 2003. As a result of a delay in hiring of personnel, technical work on the project did not begin until September 1, 2003, and is currently five months behind schedule. It is anticipated that during the next reporting period, analytical procedures will be established and the analytical equipment will be setup to perform the analyses. Work is also planned to procure several different types of anion exchange membranes and to begin testing them in a parallel plate electrolytic cell.

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

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Crosscutting Technology Development at the Center for
Advanced Separation Technologies (DE-FC26-02NT41607)

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Code: NM002-R01

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"No subcontracts issued."

ABSTRACT

A new chelating ion exchange resin has been prepared. It is a low-crosslinked gel type resin with the following thiosuccinate chelating structure:

p= polymeric structure

This chelating resin absorbs Cu^{2+} from dilute very weakly acidic solutions, but not as strongly as does commercially available iminodiacetic acid resin. The laboratory scale preparation of other new resins is also underway. This includes preparation of the new resin with a strongly chelating structure, which is rather analogous to that of the well-known chelating agent, ethylenediamine tetraacetic acid.

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 at low concentrations from large volumes of copper leach solutions, however, commercially available resins are either too expensive, or may not function in acidic solutions.

Objective and Approach

The present research project aims at the laboratory synthesis and evaluation of new types ion exchange resins which 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 raffinates of copper leach solutions.

Three new resins will 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 will be made and the samples of resins will be equilibrated with dilute CuSO₄ solutions, acidified with H₂SO₄. Initial tests will be conducted using CuSO₄ solutions, rather than CoSO₄, because Cu²⁺ will be more strongly absorbed, and it will be cheaper and easier to analyze for Cu²⁺. Effective resins will then be evaluated more extensively.

PROJECT TASKS

There are two initial tasks for this project. They are: 1) make a small sample of the proposed chelating resin, 2) run screening tests on this resin with CuSO₄ solution. These initial tasks now have largely accomplished for the first chelating resin, which has the succinate structure, p-C₆H₄CH₂SCH(CO₂Na)CO₂Na. Standard laboratory ware, heating and stirring equipment were used in the small-scale preparation of this resin under a chemical hood, as needed.

The thiosuccinate resin was prepared from 50/100 mesh, 2 per cent crosslinked chloride form of quaternary ammonium ion exchange resin (Dowex1, 2X). This low-crosslinked dry resin was added stepwise to a stirred solution made from hot ethylene glycol,

mercaptosuccinic acid, and sodium hydroxide under a fume hood. The mixture was heated to 150-170°C and stirred for 20 hours. Water-washed product resin, in the di-sodium form in water, had wet-settled volume of about 30 ml. Its color was light brown, and its density was somewhat greater than that of water. It settled readily in water to form the resin bed.

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 resin color became brownish green, which indicated that, the resin indeed absorbed Cu^{2+} and was coordinating (chelating) with the thioether, as well as the carboxylate groups of the resin. 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. A measured amount of resin was equilibrated with 20.0 bed volumes of 0.046 molar CuSO_4 solution to which 4.0 bed volumes of 0.52 molar H_2SO_4 had been added. The remaining copper concentration was again determined by iodometric titration. Identical tests were made with gel type, low- crosslinked iminodiacetic chelating resin (Chelex-100) and macro-porous, highly crosslinked and very expensive bis-picolylamine resin (Dowex-M4195).

The results of the absorption test from acidic solutions indicated that the new thio-succinate 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.

SUMMARY

In search of new resins to recover copper and cobalt from highly acidic, dilute solutions, a small quantity of a low-crosslinked, gel-type chelating resin was successfully synthesized. Small-scale equilibration tests were made with CuSO_4 in acidic (H_2SO_4) solutions. Comparison tests were also made with commercially available, low-crosslinked, gel type iminoacetic acid, and highly crosslinked macro-porous bis-picolyl amine resin. The results indicate that the new thio-succinate resin coordinates less readily with Cu^{2+} than does the nitrogen in imino groups. Both the thiosuccinate and iminodiacetic acid resins were considerably less effective in absorbing Cu^{2+} from acidic solutions than the bis-picolylamine resin.

FUTURE WORK

Future work is planned in accordance with the outline of the project proposal as follows:

- 1) Prepare and evaluate a macro-porous version of the thiosuccinate resin, both for Cu^{2+} and Co^{2+} absorption from acidic solutions, possibly using small-scale columns as well as batch equilibration screening procedures.
- 2) Prepare and evaluate, as above, a thioglycolate chelating resin.
- 3) Prepare and evaluate, as above, carboxymethylated diethylene triamine chelating resins.
- 4) Explore other possible chelating resin structures that might have potential for meeting the goals of this project.
- 5) Explore alternate means of utilizing available commercial resins to recover cobalt from industrial copper leach solutions.

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**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

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Development of Enhanced Surfactants for the Potash
Industry

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ABSTRACT

The most commonly used crystallizer for research on potassium chloride is a mixed-suspension mixed-product removal (MSMPR) crystallizer. Evaluations of nucleation and crystal growth kinetics are performed with this apparatus. The nucleation process in this method is dominated by secondary nucleation, thus primary nucleation cannot be studied separately. However, for the practical (industrial) applications to which this project pertains, secondary nucleation and agglomeration are the principal means of crystal growth. The MSMPR crystallizer has been completed and is being tested. Crystal growth experiments are commencing on crystallization of K_2SO_4 with $MgSO_4$ as a second solute. $MgSO_4$ has been chosen because of its particularly good growth characteristics with KCl, and hopefully with K_2SO_4 as well. Turbidity tests will be run on the crystal slurries to identify the initiation of nucleation. Growth rates will be monitored *via* changes in solution concentration, and SEM examination of crystal sizes. Various surfactants will then be added to separate slurries to enhance the growth rates, sizes, and morphology of the crystals.

INTRODUCTION

Background

In New Mexico the production of potassium sulfate fertilizers comes from langbeinite ores. Potassium sulfate, which is sold as a fertilizer for chloride-sensitive fruits and vegetables, accounts for 4-6% of potassium sales. Langbeinite, $K_2Mg_2(SO_4)_3$, is a sulfate of potassium and magnesium with sodium chloride as the principal impurity. Beneficiation of potash ores involves a number of processes including flotation, magnetic separation, crystallization and recrystallization. Processing begins with separation of the langbeinite from the chlorides by selective dissolution of the chlorides. Potassium chloride is recovered from the solution by evaporation and crystallization, after prior removal of the sodium chloride. The langbeinite product is dewatered and dried. KCl brine may be applied to the langbeinite product in order to produce K_2SO_4 . The eventual removal of other chlorides and magnetic separation of ferrous materials delivers product K_2SO_4 filter cake that is dried and stored.

The successful and efficient production of K_2SO_4 fertilizers in the potash industry requires crystals of a sufficiently large size that they will not pass through the screening process and be reintroduced to the mother liquor. Alkyl diphenyl oxide (ADO) disulfonate surfactants, which are typical of the surfactants used to slow the dissolution of langbeinite, are 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 in this project is first to measure the growth rate, CSD, and crystal morphology of K_2SO_4 crystals grown with $MgSO_4$ 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 will then be used to enhance the growth rates, sizes, and morphology of K_2SO_4 crystals. First Calfax surfactants, supplied by Pilot Chemical Company, with linear side chains (10LA-75) and with branched side chains (DBA-70) will be used. Then three additional Calfax surfactants (10L-45, DB-45, and 16L-35) will be studied in order to examine the effects of surfactant branching and chain length. The particles produced in the absence or presence of surfactants will be characterized with the following analytical techniques: morphology and determination of CSD will be done by scanning electron microscopy (SEM) and transmission electron microscopy (TEM), structure will be examined by X-ray diffraction and FTIR, and topographic characterization of growing crystals will be completed by atomic force microscopy (AFM). 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 model improved surfactants by computer simulations.

PROJECT TASKS

CSD will be influenced by crystal nucleation and growth, and also by agglomeration. The following are chemical and crystallizer variables that affect crystal growth and habit.

Chemical Variables: 1) Increased pH increases growth rates for potassium sulfate (Kubota, 2001); 2) Impurities change the growth form of crystals as habit modifiers (Kubota, 2001); 3) MgCl and MgSO₄ as impurities in solution increase both crystal size and growth rate of KCl (Dash and Rohani, 1993); 4) Trivalent metallic ions, such as Cr(III), Fe(III), etc., are well known to be effective impurities for the retardation of crystal growth of K₂SO₄, and chromium nitrate decreases size and yield (Rohani and Ng, 1992; Kubota, 2001); 5) Lead ions increase nucleation rates and decrease growth rates in KCl due to poisoning of active sites (Rohani and Ng, 1992); 6) NaCl decreases both nucleation and growth kinetics at high concentrations (Rohani and Ng, 1992), but is nonetheless routinely added (Rohani, 1993); 7) CaSO₄ promotes formation of irregular faces and polycrystals leading to larger mean crystal size; 8) Second solvents, such as acetone in KCl, decrease solubility and induce crystallization; 9) Brownian motion is important in the dynamics of agglomeration (Dickinson, 1986).

Crystallizer Variables: 1) Mechanical agitation produces secondary nucleation resulting in smaller crystals, and also increases abrasion and breakage of larger crystals; 2) Separation of nuclei through use of surfactants in a liquid medium increases crystal size; 3) Nucleation rate is the major variable that controls the CSD; 4) All crystallizers generate supersaturation by either cooling of the solvent, evaporation of part of the solvent, addition of some substance that reduces the solubility of the solute in the primary solvent (known as salting out or drowning out precipitation), or chemical reaction. Mean crystal sizes are generally larger from cooling and evaporation (Mydlarz and Jones, 1989); 5) Analysis of CSD yields both growth and nucleation rates simultaneously; 6) Crystal agglomeration increases crystal size dramatically and is especially prevalent in systems with high levels of supersaturation (Jones, 2002); 7) If local supersaturation is high where there is a deficiency of crystal surface for growth, spontaneous nucleation will begin and lead to small grain size and broad CSD; 8) Higher crystallizer operating temperatures give larger mean crystal size; 9) Decreasing crystallizer pressure increases production, but decreases crystal size (Tadayyon and Rohani, 1999); 10) Increasing crystallizer overflow rate increases crystal size (Tadayyon and Rohani, 1999).

The nature of surface charges can be manipulated by chemical additives that encourage agglomeration. Coagulation is a process in which particles are driven together by the addition of an electrolyte to a dispersion, which reduces the potential of the electrical double layer on the particles, thereby allowing close approach and agglomeration. Polymers may also be added to adsorb on to vacant sites on the particle surfaces, resulting in agglomeration either by charge neutralization or polymer bridge formation (Simons, 1996). Two types of agglomeration thus can be distinguished: primary (as a result of 'mal-growth'), and secondary (as a result of crystal/crystal collisions) (Jones, 2002).

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. 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 feed line is wrapped with a heating coil to prevent crystallization of the feed in the tube. 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 will be removed at a time. 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. A sampling port is stationed between the reactor and intermediate dissolution tank. Samples will be gathered at regular intervals and measured with a turbidimeter to establish nucleation times. Growth rates will be monitored *via* changes in solution concentration, and SEM examination of crystal sizes.

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 the initial test run will contain an excess 10% solids, resulting in 190.3g K_2SO_4 /L H_2O and 9.9g $MgSO_4$ /L H_2O . Once dissolved by heating to 80°C in de-ionized water, the solution will be 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. At the start of an experiment, the reactor jacket is heated to 80°C to prevent early crystallization, and the reactor is filled from the feed tank. The reactor is cooled to 60°C and

the solution is circulated to the redissolution tank and feed tank. Sampling commences, to determine the start of nucleation. The jacket temperature is lowered 10°C, then 20°C, and finally 30°C between steady states. This should allow a range of supersaturation and liquor density. Samples will be taken both before and after steady state has been achieved and nucleation has occurred. Crystal samples will be washed with acetone and air dried. CSD will be determined by SEM.

SUMMARY

Methods used to grow crystals have been determined from published literature, and the best method, as far as use for industrial applications, has been chosen for this research. Equipment for crystal growth has been assembled and is currently being tested.

FUTURE WORK

Activities planned for the next report include results of the initial growth experiment and subsequent experiments using the surfactants. Induction times and relative growth rates will be determined by turbidimetry, changes in solution supersaturation, and SEM. Initial measurements of CSD by SEM will be determined. Further characterization of crystal structure by TEM, FTIR, and AFM will be follow in the second phase of the project.

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

TECHNICAL PROGRESS REPORT

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Crosscutting Technology Development at the Center for
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On-Line Monitoring and Diagnosing of Coal Fines
During Separation Process

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ABSTRACT

Coal fines, as defined in this study, are coal particles less than 250 micrometers in diameter. This research is directed towards the development of an on-line, non-contact elemental analysis of coal fines during solid-solid separation process by 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.

INTRODUCTION

Background

Laser-Induced Breakdown Spectroscopy (LIBS) is a form of atomic emission spectroscopy in which a pulsed laser, such as a Q-switched Nd:YAG laser is used to instantaneously vaporize the sample target and initiate an avalanche ionization of the sample. The excited ions and atoms emit characteristic optical radiation as they revert to lower energy states, spectroscopic sensors are used to obtain information on the elemental composition of the specimen. No sample preparation is necessary for the LIBS method, which is able to perform high-speed, non-contact elemental analysis of any material regardless of its physical

phase (i.e. solid, liquid or gas). The atomic and ionic lines, once assigned to specific transitions, allow for a qualitative determination of the corresponding elements.

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. A probe containing fiber optic cable will be inserted into the CFB riser system and collect light emitted from the LIBS spark. This will replace collection lenses and allow the signal to reach the spectrograph with minimal loss. A schematic of the system is shown in the figure below.

PROJECT TASKS

Task 1: Initial LIBS trials

An initial trial of LIBS was set up at National Energy Technology Laboratory (NETL), Morgantown, WV where a carbon sample was placed in water, which was then fired upon by an Nd:YAG laser to induce a laser spark. After observing that a spark could be formed in the carbon-water sample, a LIBS experiment was set up. The experiment was performed by using an Nd:YAG laser from Laser Photonics, an EG&G PARC 1211 pulse generator, 1460 Optical Multi-channel Analyzer, a 1421 intensified diode array, and an ISA spectrometer. The spectrometer was calibrated using a mercury lamp. The results varied from having almost no spectral data to strong spectra, depending upon integration time. Best results were obtained with a 100 μ s time delay and a 100 μ s pulse width. The spectral data results showed very clear spikes in the spectral data. This research work is being conducted at NETL by WVU graduate student Andrew Aurelio under in-kind technical supervision of NETL research scientist Dr. Steven Woodruff.

Task 2: LIBS trials to determine elemental composition

An Ocean Optics spectrometer will be used to replace the optical multi-channel analyzer and its components. The new experimental procedure was done with the same Nd:YAG laser from Laser Photonics, the Ocean Optics USB 2000 Spectrometer, a laptop computer, fiber optics to the spectrometer, a dielectric mirror, and tilt and translation tables to optimize the results shown on the spectrometer. The samples were switched over to spent coal, “raw” coal and zinc sulfide. Used coal (ash) and raw coal were used to detect carbon, and zinc sulfide was used to detect sulfur. Over 400 spectra were taken with this instrument, most being very clear and consistent. In the process of detecting mercury in the sample particulate, the spectral data shows the presence of heavy metals in the raw coal. A mercury lamp was later used for signal averaging, and a tungsten lamp was used to obtain a pseudo black body for later calibration. Below are the signals obtained from a LIBS spark in raw coal contained in water and water without any particulate. The sample coal spectrum has an unidentified elemental emission line around 395 nm and a smaller peak near 400. The area under the broad intensity curve is assumed to be the detector response to the dielectric mirror. The coal signal was relatively weak, having an emission line of 75 counts because the transmission of light into the spectrometer was not optimized. The water sample below is an average of the spectral data collected for water. There is the same detector response between 400 and 600 nm, but no defined elemental emission lines.

Task 3: Probe Design

Probe design is already in development. Optical configurations for signal optimization are included in the probe design. The probe will be placed in the CFB and will be used to monitor particle distribution by density, assuming that particles of different densities have a different elemental composition.

SUMMARY

Initial LIBS testing has been performed on a carbon-water aqueous solution at NETL. LIBS testing for elemental composition is in progress. Signal analysis has been performed on selected samples. These samples indicate the detection of heavy metals in a water-coal mixture. Optical optimization for signal analysis and probe design are in progress.

FUTURE WORK

Signal analysis of the LIBS spark is in progress. Spectra will be analyzed to find average signals and prominent intensity lines in the LIBS spark, as well as calibration, which will eventually lead to a quantitative analysis of the elemental composition of the particles in the CFB.

Investigation of the LIBS process will continue at NETL until equipment is purchased and set up at WVU. Items expected on the purchase list include the USB 2000 spectrometer from Ocean Optics, an Nd:YAG laser, and specific fiber optics designed for optimization of the LIBS spark.

Design of a probe to go into the CFB to monitor the efficiency of separation is in progress, and a model of the design is expected to be in development by mid-October. The probe will be inserted down into the CFB, next to a point designated for a laser spark. When the laser ignites a coal particle, the light emitted will be collected by the probe and sent to the spectrometer to be analyzed.

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

TECHNICAL PROGRESS REPORT

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Development of A Novel Optical Radiation
Depolarization Technique for On-Line Measurements of
Particle And Bubble Sizes

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ABSTRACT

An experimental study to characterize two-phase flows (air bubbles in water) using light scattering at different scattering angles was conducted during the last six months. An elliptically polarized light scattering (EPLS) method was employed. Scattering matrix elements (S_{ij} 's) provide information about scattered light intensity as well as the polarization of the scattered light. Scattering matrix elements were obtained experimentally at flow rates between 0.04 cm/s and 0.20 cm/s for a 45 mm diameter column and related to average bubble size and average bubble velocity. Based on the results, we conclude that it is feasible to determine size as well as bubble velocity at a scattering angle, $\theta = 120$ degrees.

The potential use of polarized light for characterization of mono-dispersed air bubbles is currently being investigated using a vector Monte Carlo approach, which accounts for the multiple scattering phenomena in the bubble column. The Monte Carlo results show that if circularly polarized light is used, bubble size, bubble separation and the thickness of the carbonaceous layer around bubbles can be determined.

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.

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 usually 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

Experimental setup: The bubble column setup employed for this study is shown in Figure 1. The column was located on a tilting stage and two translation stages in order to align accurately in vertical direction. Nitrogen gas tank was used to provide constant pressure gas to generate bubble column in the water. Bel-Art Riteflow flowmeter model # 40407-0075 was attached between gas tank and the column to control the flow-rate accurately between 3.5 ml/min and 522 ml/min.

Elliptically polarized light scattering (EPLS) method was applied to measure two-phase flow (gas-liquid) in situ. Figure 1 shows optical arrangement used in the experiments to modulate incident and scattered light to measure polarized light and scattered light by the bubbles. Polarization angle and type of incident light was modulated by retarder-1 while the first polarizer (P-1) is fixed at 45 degrees in the incident beam path. Scattered light from bubbles in the water was filtered by retarder-2 (R2) and polarizer-2 (P2). The setup was capable of taking measurements at different scattering angles (θ). A 20 mW HeNe laser ($\lambda = 632$ nm) is employed as a light source. Scattered light that passes through R-2 and P-2 was detected by a photomultiplier tube (PMT; Hamamatsu R446) as a function of scattering angle, θ .

Figure 1. Gas-Liquid (GL) phase column and Optics used in the experimental system to obtain intensity and polarization information of the medium bubbles in the water.

Relationship between Flow Rate and Scattered Light Intensity: In order to understand scattering light intensity behavior for different flow rates, scattering light intensity measurements were made at $\theta = 90$ degree. For each experiment at different flow rate, 2400 intensity measurements were taken during 120 seconds. The experiment was repeated for 7 different flow-rates. The average scattering light intensity is shown in Figure 2 as a function of flow rate and gas velocity. There are two regions in terms of the intensity of scattering light: in Region 1 while flow rate increases, volume fraction of bubble increases as bubble diameter

Figure 2. Flow-rate regions based on scattered light intensity

increases slowly. However, in Region 2, while flow rate increases, small bubbles start coalescing with each other to form larger bubbles. This means that in Region 2, we have smaller number of bubbles than Region 1, but they are, on the average, larger.

Determination of Size Distribution of the Bubbles: The digital images of bubbles were taken before and after each experiment for different flow rates. These images were taken with a Nikon D100 digital camera and image processed with Adobe PhotoShop and SIAMS-600 image processing software. The bubble size distribution was calculated based on total surface area method by SIAMS-600. As an example, the size distribution plot and corresponding processed image for $Q = 35.26$ ml/min are shown in Figure 3. Depending on the flow rate, location of the peak on size distribution curve changes. When the flow rate increases the major peak shifts to the right and the smaller peak disappears. The reasons for having a bimodal size distribution can be explained by noting that increasing aeration pressure increases the gas flow rate, which yields higher probability of bubble coalescence and presence of larger bubbles [Lain-1999].

Figure 3. Bubble size distribution for flow rate $Q = 35.26$ ml/min for the image shown.

Relationship between flow rate, volume fraction of bubbles and average bubble diameter: The frit pore sizes of the glass column were between 25 μ m and 50 μ m. Pressure of N_2 gas was kept at 5 psi. The experiments were conducted for five different flow rates: 35.26, 52.25, 74.28, 100.77, and 133.12 ml/min. Close pictures of bubbles were taken before and after the measurement for each flow rate. Adobe Photoshop and SIAMS-600 image processing software were used to process the bubble pictures in order to find average bubble sizes for each flow rate. After image processing steps are given in [Aslan et al-2003], diameter of each bubble based on equivalent surface area of the bubble was calculated and for each picture, maximum, minimum, average bubble sizes were calculated by the software automatically. Figure 4 shows the relationship between

Figure 4. The relationship between flow rate, volume fraction of bubbles and average bubble diameter.

flow rate, volume fraction of bubbles and average bubble diameter. Note that when the flow rate increases, average bubble diameter increases logarithmically, but volume fraction of bubbles increases linearly.

Task 2. Customization of Algorithm

A detailed numerical study has been carried out [Wong and Mengüç-2002] 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.

SUMMARY

Elliptically scattered light by bubbles from a 2-phase gas-liquid medium was investigated for possible characterization of bubbles in floatation columns. Both experimental and theoretical analyses were initiated.

The experimental results show that it is possible to monitor bubble size change in column by using scattering matrix elements of the bubbles. The best scattering angle should be around $\theta = 120$ deg. where change in bubble size caused significant change in S_{11} , S_{44}/S_{11} , and S_{34}/S_{11} . However, the optimum angle to conduct the light scattering measurements depends on gas pressure, frit pore size range, and as well as column diameter.

Monte-Carlo model 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. It was also shown that it is possible to divide the flow characteristic to two zones, and carry out the experiments and correlations separately in each of these regimes.

FUTURE WORK

1. 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.
2. Results for 2-phase medium light scattering experiments will be compared with Monte-Carlo code developed recently.
3. Optimum sensor (PMT) angles will be obtained for three-phase flow.
4. A simple EPLS system will be developed for industrial size columns.

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

TECHNICAL PROGRESS REPORT

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Electrolytic solution purification and metal recovery
from metal-bearing toxic waste streams

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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. The investigation so far has shown that both copper and lead can be reduced to less than 1 ppm concentration using pulse plating schemes. The application of these 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 with multiple applied potentials and resistances for recovering purified metal products 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 these techniques require additional steps afterward 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 reduced toxic waste production. The use of pulsed electrodeposition maximizes mass transport and current efficiency, and the sequential application of different electrical potentials allows for the recovery of high purity metal products. Because each metal has a unique electrochemical potential below which it will begin depositing, metals can 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, pulse magnitude, pulse on and off times, and aqueous medium flow rate will be 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 1cm² screens separated by inert polymeric screens. These screens are mounted in a filter 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 them in a cyclic manner. Pulsing is accomplished using a computer-controlled potentiostat that is connected to lead wires from the screens or felts.

The metal ions are monitored using ion-selective electrodes set in the fluid being cycled through the system. A computer is used to record the potential output by the ion selective electrode over the course of the pulse plating. The ion-selective electrode is calibrated using a set of three standard solutions with a known copper concentration, so that a mathematical relationship between the copper concentration and the ion-selective electrode can be determined in accordance with established electrochemical principles.

Experimental Procedure

Fluid is cycled through the system using a pump for multiple passes while a potential is pulsed on each of the electrodes. Various pulse potentials, pulse on-times, and pulse-off times are applied to the electrodes (Fig. 1 shows an example of the potential vs. time for a 2 ms on, 10 ms off pulse), and the level of metal ions present in the aqueous fluid is monitored using an ion selective electrode and the results are recorded.

Fig. 1: A sample pulse segment of a 2ms on, 10ms off pulse having a -2V amplitude and a -1V offset.

Task 1 (electrode evaluation/screening)

Tests have been conducted with both copper and lead ions separately in aqueous solution, and the results obtained shows a reduction in the amount of both metals in the solution. Initial tests with 100 ppm copper solutions using the platinum mesh electrode apparatus resulted in a reduction of 50 cm³ of solution from 100 ppm to 1 ppm in 6 minutes at -0.4V, with a 2 ms on time and 20 ms off time in the pulse. Figure 2 shows results for another test using a 10 ms on time, 10 ms off time and starting with a 50 ppm copper solution

that is reduced to approximately 8 ppm in approximately 10 minutes. The potential of the copper ion selective electrode decreases approximately 27 ± 2 mV for each decade of copper concentration (in other words, the content of copper decreases logarithmically, and a reduction of the copper concentration to 10% of the original concentration results in a decrease of approximately 27 mV in the potential shown by the ion selective electrode).

Fig. 2: Copper Selective Ion Electrode Potential vs. Time

Thus, it appears that the 2 ms on time and 20 ms off time is the most effective setting evaluated thus far.

Similar results are obtainable using both the platinum mesh and graphite felt electrodes to remove lead from aqueous solutions. Solutions containing 50 ppm lead show a rapid response to the various pulsing schemes, although at these low levels of lead concentration the ion selective electrode has shown questionable response and accuracy. Visual inspection of the electrodes following the tests confirms the presence of the desired metal product plated on the electrode surface due to electrodeposition. Improvements in quantifying the results of both lead and copper ion removal from the aqueous medium are of primary concern in further investigating this system, as it is desirable to know both the rate at which the metal ions can be recovered from medium and the amount of residual ions remaining in the medium as the number of cycles of the aqueous medium through the system become very large.

Task 2 (pulse on/off time evaluation)

The evaluation of graphite felt and platinum mesh (100 Mesh) electrodes indicates that both electrode types work reasonably well under the conditions evaluated. Both effectively remove metal from solution during the pulse-plating process. However, because the graphite felt is approximately 10 mm thick and contains significantly greater surface area than the 100 mesh platinum screen, it is likely that the solution flow rate will have a very significant effect upon the efficiencies of the two electrodes. Because the effect of solution flow rate is not scheduled for evaluation until early next year, additional evaluation of these electrodes has been deferred.

SUMMARY

Pulse plating with high surface area electrodes is an effective way to remove metal ions from aqueous medium. This method is useful for the recovery of metals from toxic waste streams in an efficient manner. This method has demonstrated utility in removing both lead and copper from aqueous medium, and should be useful in removing additional ions as well.

FUTURE WORK

In addition to the completion of the project tasks, ongoing research is currently concentrated on the improvement of the accuracy and reproducibility of the results from the electrodeposition processes. Improvement in the measurement of low amounts of metal ions in solutions is necessary to improve the accuracy of the tests, and numerous methods for measuring small ion concentrations are being investigated, such as use of different ion selective electrodes, inductively coupled plasma spectroscopy, and possibly additional electrochemical techniques. Future investigations will center around optimization of the pulse parameters for the deposition of various metal ions. Also for investigation will be the selective deposition of specific metal ions from a mixture of multiple metal ions. The overall long-term goal of the project is the development of a scheme for removing multiple metal ions sequentially from an aqueous solution with the best possible efficiency and optimal metal recovery in purified form.

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

TECHNICAL PROGRESS REPORT

Contract Title and Number:

Crosscutting Technology Development at the Center for
Advanced Separation Technologies (DE-FC26-02NT41607)

Period of Performance:

Starting Date: 10/1/02
Ending Date: 5/30/04

Sub-Recipient Project Title:

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

Principal Investigators:

Dr. Kumar Ganesan

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Subcontractor Address:

“No subcontracts issued.”

Report Information:

Type: Semi-Annual
Number: 1
Period: 4/1/03-9/30/03
Date: 9/30/03
Code: MT003

Contact Information:

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ABSTRACT

This research project is aimed at the removal of 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 wire mesh made of thin (<1 mm diameter) gold wire was tested in the laboratory initially with a synthetic gas stream. In addition, silver wires were also tested for its ability to remove mercury vapor from the air stream. Initial tests with silver showed the removal efficiency of 63 to 89% for the inlet concentration of 34-1172 $\mu\text{g}/\text{m}^3$ of mercury vapor. Based on this additional tests were performed with gold and silver filters. The results are reported in this semi-annual report. These are preliminary results and detailed tests are planned to further evaluate the effectiveness of gold and silver filters.

INTRODUCTION

This research project is focused on the removal of mercury vapor from the flue gases from coal-fired power plants. The results of this research will help to determine the potential of the proposed technology and its viability to use in reducing mercury emissions from power

plants. This is a semi annual progress report. It highlights the work completed up to date and the proposed work plan for the next six months. The results also will be presented at the upcoming CAST conference in Charleston, West Virginia, during the month of November 2003.

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 relatively low cost. The preliminary tests were completed with two filters and wire in gold as well as in silver. The mercury vapor concentration in the air stream varied from 34-1172 $\mu\text{g}/\text{m}^3$. Similar tests will be conducted in combustion gases by burning both western coal and eastern coal. The study will be conducted for six concentration levels of 5, 10, 25, 50, 100 and 300 $\mu\text{g}/\text{m}^3$ of mercury to reflect the typical range of mercury concentrations observed in power plant flue gas.

PROJECT TASKS

This research involves six tasks. Task 1 involves the production/purchase of gold wire mesh. In Task 2, a synthetic mixing chamber will be set up. Task 3 involves the test with synthetic gas. In Task 4, the combustion chamber will be set up to burn six different coal types to represent coal from different regions in the US. In Task 5, the test results will be analyzed and the effectiveness of the filter will be determined. Task 6 will present data in report form and will publish this summary on 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.

The preliminary test results are given in Tables 1 through 5.

TABLE 1. (Preliminary Test)		
Control of Mercury Vapor: Silver Wire @ 5 lpm flow		
HG Vapor $\mu\text{g}/\text{m}^3$		
Inlet	Outlet	Removal
		%
34.4	12.7	63.1
66.8	18.8	71.9
75	19.5	74.0
117.2	132	88.7

*Weight of silver used: wire – 8.35 g

TABLE 2		
Control of Mercury Vapor: Silver Wire* and Filter** @ 5 lpm flow		
HG Vapor $\mu\text{g}/\text{m}^3$		
Inlet	Outlet	Removal
		%
215	47	78.1
198	43	78.3
192	45	76.6

*Weight of silver used: wire – 8.35 g

**Filters – 3.05 g

TABLE 3		
Control of Mercury Vapor: Silver Wire* and Filter** @ 3 lpm flow		
HG Vapor $\mu\text{g}/\text{m}^3$		
Inlet	Outlet	Removal
		%
252	36	85.7
263	27	89.7
263	34	87.1

*Weight of silver used: wire – 8.35 g.

**Filter: 5.05 g

TABLE 4		
Control of Mercury Vapor: Silver Wire* @ 3 lpm flow		
HG Vapor $\mu\text{g}/\text{m}^3$		
Inlet	Outlet	Removal
		%
354	38	89.3
360	42	88.3
298	32	89.3

*Amount of gold in wire: 8.05 g.

**Filter: 7.28 g.

TABLE 5		
Control of Mercury Vapor: Silver Wire and Filter** @ 5 lpm flow		
HG Vapor $\mu\text{g}/\text{m}^3$		
Inlet	Outlet	Removal
		%
196	55	71.9
184	54	70.7
186	52	72.0

*Amount of gold in wire: 8.05 g.

**Amount of gold in filter: 7.28 g.

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: This task will be performed in the spring semester at six temperature conditions and at six mercury concentrations. The concentration levels chosen are 1, 5, 25, 50, and 100 $\mu\text{g}/\text{m}^3$ and these reflect the range of mercury concentrations observed in coal fired power plant flue gas. Similarly, the temperature range of 50-150° C is selected to reflect the temperature of flue gas in a typical stack.

Task 4: Six different regional coal types based on mercury and chloride content will be combusted in a chamber to simulate the furnace and to produce the flue gas. The flue gas then will be cooled to the required temperature to perform the tests.

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 ($\mu\text{g}/\text{g}$), 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 test results indicate that gold and silver filters can remove mercury vapor up to 90% from gas streams. It seems silver may be a preferable material based on the cost. However, additional tests must be performed to confirm this. Tests are planned with silver and gold filters of three new sizes and shapes in order to determine the long-term performance of such filters. Also regeneration of filters need be studied to evaluate the potential of these filters for use in coal-fired power plants.

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 laboratory or the filters will be taken to a coal-fired power plant and tested in the field for its performance.

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PUBLICATIONS/PRESENTATIONS

By November there will be enough data from tests to give a presentation in the upcoming CAST conference in Charleston, West Virginia.