Project Title: MICROBIAL SUPPRESSION OF PYRITE FROM ILLINOIS COALS: ENGINEERING AND SCALE UP

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ABSTRACT

This research is part of a joint effort between the ISGS and Northwestern University with an overall goal of developing microbial methods to augment coalescence/flotation physical desulfurization of Illinois coals. Objectives to achieve the goal are divided into two parts (A) examine mechanisms and enhancement of pyrite suppression in these processes and (B) provide engineering guidance and interpretation, then scale up of a total process. Six principal tasks define the approach to achieving the objectives and are divided between the two research groups. Tasks I-IVa are performed by ISGS researchers under J. B. Risatti's direction and are:

Task I. Continue chemical studies to identify the specific compounds in extracts from E. Coli filtrates that enhance suppression, and extend this work to include thiobacilli and perhaps other microorganisms.

Task II. Evaluate other bacteria for a suppressant that enhances rates of pyrite suppression.

Task III. Determine optimal conditions of activity for these suppressants and define conditions or specific compounds that inhibit suppressant activity.

Task IVa. Comparison and chemistry of microbial suppressants to commercially available suppressants.

Task IVb. Evaluation of pyrite suppression parameters for commercially available suppressants and select for comparison with microbial suppressants.

Task V. Evaluate the use of microbial suppressants on -325 mesh pyrite and coals using small scale flotation cells.

Task VI. Evaluate the feasibility of producing microbial suppressants on a commercial scale.

Suppression tests with cultures of E. Coli and known chemical suppressants showed best combination of coal derived pyrite suppression and coal BTU recovery with microbial agents. A major project milestone was met when both ISGS and NUCRL research groups independently observed pyrite suppression of 50-80% with microbial extracts. Neutral to acidic pH during flotation favors E. coli and carboxy methyl cellulose suppression of coal derived pyrite. Small scale flotation devices appears successful for pyrite suppression testing, but further intermediate (fractional liter and 8 liter) scale up corroboration is needed and scheduled in 1988-89. Using data and other (including untested) assumptions for reagent (to achieve 50% pyrite rejection at 80% BTU recovery at kg/ton doses) production, separation, and isolation, a preliminary reagent cost of a few dollars/lb. Staged separation and ofsite production of the E. coli grown on low cost substrates may further reduce costs and are foci for further scale up work in 1988-89.

Pages 5 through 19 contain proprietary information.
EXECUTIVE SUMMARY

Our overall objective this year has been twofold: 1) determine mechanisms of improved pyrite removal in interfacial cleaning processes by the employ of microbial culture byproducts and 2) examine feasibility of scale up for an engineered system utilizing these to improve pyritic sulfur rejection in Illinois coals. We have obtained substantial information to provide answers to three specific questions: 1) are microbial derived agents that exhibit pyrite suppression similar to other known chemical suppressants, 2) can ultrafine (-325 mesh) coal derived pyrite be suppressed by microbial agents and 3) can a physical coal desulfurization system using microbial derived suppressants be cost effectively engineered. Our approach has been to define and execute tasks IV, V and VI described in the abstract to achieve the overall and specific objectives.

INTRODUCTION AND BACKGROUND

Motivations are severalfold to find a microbially assisted "physical" coal cleaning process. First and foremost, many coals may be theoretically deep-cleaned by fine and ultrafine (particularly interfacial) coal cleaning processes. Secondly, current reagents employed in existing and emerging flotation or agglomeration cleaning of Illinois coals are neither sufficiently effective nor economic in increasing pyrite rejection while maintaining high BTU recovery. As with many new interfacial cleaning processes, maximum cleaning benefit may only occur with ultra grinding but biogents may make this unnecessary. Thirdly, we expect bacterially derived reagents will be cost effective, even when prepared remotely from the coal cleaning plant. Fourthly, pursuit of the former goals may lead to finding possible abiotic reagent analogs as well. The overriding goal is to find a microbial reagent system compatible with existing coal preparation plants.

EXPERIMENTAL PROCEDURES

In tasks IV and V, coal and coal derived pyrite are comminuted and used in small scale flotation cells along with various reagents. Independent variables include material type and preparation (communion), reagent doses and small flotation cell operation while dependent variables include extent of flotation and grade of products and tails. In task VI, concepts are employed. Calculations are based on measurements from tasks I - V and other works and assumptions as necessary.

A) Materials used include: a raw and cleaned coal derived pyrite. *E. coli* and culture extracts were obtained from glucose and salts medium using protocol developed at ISGS (tasks I - III). Other suppressants were commercially obtained.

B) Methods are defined for comminution, micro flotation tests, interfacial separation test development, interfacial measures, feedstock preparation development. Comminution equipment included rod and ball mill in an attempt to obtain maximum liberation. Flotation tests used a modified Hallimond tube and a combination of frother, suppressants and modifying reagents with approximately one gram of mineral solids. Bio-surfactants were extracted and concentrated, then used in the flotation/suppression tests. Results were analyzed by examining the recovery of both pyrite and coal gravimetrically and chemically, then calculating suppression as that fraction not recovered. Several problems with the Hallimond tube method motivated a program to extend the size and capabilities of an improved batch mini flotation cell. These principally include the analytical accuracy with small sample size and accounting for frothing phenomena, and scale - up factors. Interfacial charge measurements via electrophoresis and surface tension may more quickly identify and correlate the nature of the active bio-suppressant. The effect of pH, pulp density and known suppressant [Fe(III)] on pyrite and coal electrophoretic mobility was analyzed for a Herrin seam (high chlorine) preparation plant sample. Interfacial tension was used to interpret adsorption in surfactant and coal mixtures at various pulp densities and initial surfactant concentration. To examine ultra liberation of pyrites and prepare reproducible small samples of unoxidized materials 100 gm quantities were comminuted at NUCRL using various mills and products analyzed for size at NUCRL by Coulter counter.
C) Scale up activities for flotation, bioreactor/separater and total system are separately considered. Commercialization and scale up potential is assessed from microflotation test results surpassing 50% pyrite suppression. Scale up sequence is 1:5:80 by volume and 1:100:1000 by mass. Data are obtained from lab (batch or continuous) bioreactors and separation devices to obtain the parameters for process scale-up. We estimate kinetic and yield constants, operational factors for bioreactor sizing and bioagent filtration/separation. Calculations then determine the critical path for development and scale-up. A bioprocessing facility is assumed to produce necessary bacterial agent for a 100 ton/hour coal cleaning operation. Flotation plant operating conditions assume an Illinois No. 6 coal processed at 10% solids to achieve 80% BTU recovery while rejecting an additional 50% pyrite.

RESULTS AND DISCUSSION

TASK IV

Results from this task largely identify if microbial derived agents exhibit pyrite suppression similar to known chemical and other abiotic suppressants. Several series of Hallimond tube tests with both commercial and microbial derived suppressants examined effects of solution pH, aeration and suppressant dose. Decreasing the pH of flotation from 9 to 5 showed maximum suppression at intermediate frother (kg/ton) and CMC suppressant (fractional kg/ton) dose. Between 20 - 42 percent coal derived pyrite suppression was observed for the ranges of variables, pH = 5 to 9 CMC = 0 - 200 g/ton and MIBC = 0 - 4 kg/ton. At pH = 5 rcdp shows greater suppression at intermediate CMC concentration than ccdp and overall greatest variation in response.

We continue to find advantages of using coal derived pyrite outweighing drawbacks and opted to continue major focus on cdp (in terms of cleaning response) and thus obtained a new two kilogram sample for use in suppression flotation tests. A new mini-flotation device, similar but several times larger than the PETC DOE cell, with optional assisted froth removal was designed, constructed and tested and baseline operation established.

Collateral interfacial measures (electrophoretic mobility and surface tension) show trends that appears to mimic and correlate both the bioderived suppression and the abiotic response. Electrophoretic mobility of natural whole coal and coal derived pyrite samples in the presence of dilute ferric iron suggest a suppressant adsorption/desorption specific to both coal and pyrite. The adsorption is clearly a function of the added ferric ion and pH. The pH response suggests that selective flotation with optimal pyrite depression of this Illinois coal is possible. Microbial by-product adsorption on pyrite may work by a similar mechanism, but this must be further examined. Surface tension of whole coal slurries in the presence of known adsorbing surfactants shows the effect of pulp density and surfactant dose on air water surface tension and surfactant adsorption. Surface tension lowering appears to increase with increasing pulp density and decreases with increasing dose of surfactant and decreasing charge on the surfactant.

TASK V

Answers to whether ultrafine (-325 mesh) coal derived pyrite be suppressed by microbial agents is obtained by ultracommunication of coal and pyrite and small scale flotation tests. Grade and recovery is measured in -325 mesh sizes using techniques pioneered by NUCRL. We tested several commercial mills and found them capable of producing a 10 m mean size for various coal and pyrite samples. We ordered a device will able to quickly produce up to 25 gm quantities of various coal or pyrite fractions with a predetermined surface condition. Using E-coli K-12 cultures, several flotation/suppression tests were completed with whole cultures and cell free extract. Suppression response of the cell cultures as a function of frother dose were very dramatic and more extensive in the presence of extract than whole cells. Maximum suppression of 80 percent was noted at 4 kg/ton MIBC.
TASK VI

This task aims to determine if a physical coal desulfurization system using microbial derived suppressants can cost effectively be engineered. Conditions were found to grow \textit{E. coli} with bench scale shake flasks at ISGS and a continuous small scale bioreactor at NUCRL. We have defined initial, but not optimal bioreactor and extraction parameters to scaleup the overall pyrite biosuppression process. In fact, our estimate of bioreactor size/configuration and ultimately cost is still high. Nevertheless, a preliminary flowsheet using a feasible production as high as 0.05 gm/gm synthesized cell mass and other data and assumptions for reagent production, separation, and isolation could yield costs as low as $1.00/lb of agent while obtaining 50% pyrite rejection and 80% BTU recovery. Efforts at improving on this with multiple conditioning steps was stymied by serious illness of one of our team members for most of the fourth quarter. This effort will continue in 1988 -89. As results from tasks I - V come in we will redo our process system design for commercial scale flotation coal desulfurization. Continued work on task III - V may yield an active chemical analog suppressant or at least analogous structures. Finally, plans for continuous testing will follow success at larger batch scale.

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