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**NOVEL MICROORGANISM FOR SELECTIVE SEPARATION
OF COAL FROM ASH AND PYRITE**

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SUMMARY

This report summarizes the progress made during the sixth quarter of the research project entitled "A Novel Microorganism for Selective Separation of Coal from Ash and Pyrite", DOE Grant No. DE-FG22-93PC93215.

The objective of this research project is to study the effectiveness of a novel hydrophobic microorganism, *Mycobacterium phlei* (*M. phlei*), for the selective flocculation of coal from pyrite and ash forming minerals. During the reporting period, the effect of pH on the column flotation of flocs was investigated in detail for both, IL No.6 and KY No.9 coal samples. The effect of pH on the combustible recovery, pyritic sulfur rejection and ash rejection were studied. Results showed that maximum combustible recovery and pyritic sulfur and ash rejection could be obtained in the pH range of 3-6 with the extracellular surfactant derived from *M. phlei*.

The role of hydrophobic interactions in the selective flocculation of coal was studied. Calculations showed that the hydrophobic interaction energy is approximately 3 orders of magnitude higher than the interaction energy due to columbic forces indicating that hydrophobic interactions between coal and *M. phlei* is the major cause for flocculation.

INTRODUCTION

The selective separation of pyrite and ash-forming minerals from coal can be accomplished by flotation, agglomeration and selective flocculation. The methods currently used for selective flocculation of coals include addition of natural or synthetic polymeric flocculants along with precise pH control. In some cases, these flocculants are nonselective or work imperfectly. It is known that many highly charged planktonic algae and bacteria will adhere to certain solid surfaces if the charge or hydrophobic interaction between the organism and the solids are favorable for adhesion. The resultant microorganism-mineral entities, if formed, can flocculate and can be separated. In addition, many living organisms produce extracellular biopolymers that can also cause flocculation. The microorganism, *M. phlei*, has the properties of being both highly charged and highly hydrophobic. The aim of the present investigation is to study the effectiveness of *M. phlei* and biopolymers derived from the organism for selective flocculation and separation of fine coal from pyrite and ash.

EXPERIMENTAL PROCEDURES

1. Cultivation of *Mycobacterium phlei*

The freeze dried culture of microorganism, *M. phlei*, was first transferred

to a rehydration medium (supplied by Carolina Biological Supply Company) and incubated at 35°C for 48 hours. *M. phlei* was grown in a culture medium consisting of the following : 10 g/l D-(+)-glucose, 1 g/l beef extract, 1 g/l yeast extract, and 2 g/l enzymatic hydrolysate casein. The above materials were supplied by Sigma Chemical Company, St. Louis, MO. The culture medium was sterilized at 121°C for 25 minutes in a Spectroline Model 750 autoclave. The sterilized culture medium was cooled and the incubated bacteria was inoculated into the medium. Culturing was carried out in 250 ml flasks continuously shaken at 150 rpm at 35°C in a G24 Environmental incubator shaker (New Brunswick Scientific Co. Inc., NJ). After about 30 hours of culturing, *M. phlei* suspension was filtered using a 0.45 mm Millipore filter paper, washed twice and then resuspended in distilled water. Sterilized glassware and distilled water were used throughout the investigation.

2. Floc Separation

Floc separation studies were performed using a laboratory scale column flotation cell. The setup consisted of a column with a working volume of 320 ml. Nitrogen gas was passed at the bottom at the required flow rate. Flow rate of gas was controlled using a Gilmont No.13 flow meter. After flocculation, the entire slurry was transferred to the flotation cell. No pH adjustments were done at this stage. Required amount of frother (MIBC) was added and flotation was carried

out for 5 minutes at the required flow rate. The float and tail were filtered, dried, weighed and analyzed.

Baseline flotation experiments were performed with coal using kerosene as collector and MIBC as frother. In this case, pH adjustments were carried out before the addition of frother and promoter. After 4 minutes of conditioning, the coal slurry was transferred to the column and flotation was carried out for 5 minutes. These experiments were performed for comparison with the floc flotation results.

RESULTS AND DISCUSSION

1. Floc Separation

The effect of pH on flotation recovery in the presence of different flocculants was investigated for both coal samples. Only whole cells and extracellular surfactant were used for studying the effect of pH on the flotation of flocs. Kerosene was used for comparison purposes.

The effect of pH on the combustible recovery, pyritic sulfur rejection and ash rejection for IL No.6 coal are shown in Figures 1 to 3 respectively. In the case

of kerosene, combustible recovery varied with pH exhibiting a maximum in the neutral pH range. This is consistent with values reported in literature (Groppo, 1986). A maximum combustible recovery of about 72% was obtained at pH 6.1. In the presence of whole cells, combustible recovery increased in the acidic pH range and a maximum of 80% recovery was observed at pH 4. Further increase in pH decreased the recovery to values comparable with those obtained with kerosene. However, in the case of extracellular surfactant, the combustible recovery increased over the entire pH range. Recoveries on the order of 85-92% were obtained in the pH range of 2-6. At pH values greater than 6, a slight decrease in recovery was obtained. One of the reasons for the higher recoveries in the presence of extracellular surfactant over the entire pH range might be due to increased hydrophobicity. Also, better flotation kinetics in the presence of extracellular surfactant could be partially responsible for the greater recoveries.

In the case of pyritic sulfur rejection, the best results were obtained with the extracellular surfactant. A maximum rejection of about 75% was observed at pH 4. At higher pH values, the pyritic sulfur rejection dropped in all the three cases. However, ash rejection remained constant with change in pH. In the case of extracellular surfactant, ash rejection remained essentially constant at around 56%. With whole cells and kerosene, ash rejection varied in the range of 40 - 50%.

The effect of pH on the combustible recovery and rejection of pyrite and

ash were conducted with KY No.9 coal and the results are presented in Figures 4-6. The results showed a similar trend as in the case of IL No.6 coal although the magnitudes were different. The recoveries in the case of KY No.9 coal were slightly less compared to IL No.6 coal and this could be due to the lower hydrophobicity of the coal. Also, it was shown in the adhesion experiments that less bacteria adheres to the surface of KY No.9 coal than onto IL No.6 coal which could lead to lower recoveries. The pyritic sulfur and ash rejection were also similar in comparison with IL No.6 coal.

2. Hydrophobic Interaction Energy Calculations

According to the DLVO calculations (Sixth Quarterly Report), it is clear that if columbic interactions were the determining factor, then the same interactions would not distinguish between the coal and pyrite samples in terms of adhesion and their flocculation efficiency. But adhesion tests showed that *M. phlei* attaches preferentially to coal in comparison to coal-pyrite. Also, the amount of *M. phlei* adhering to IL No.6 coal is much greater than that onto KY No.9 coal. Therefore, the results of adhesion and flocculation tests cannot be explained adequately by DLVO theory. However, a more reasonable explanation can be offered from the consideration of hydrophobic interactions.

The importance of hydrophobic interactions becomes apparent from the

examination of contact angle data of the two coal samples. Contact angle measurements clearly indicate that IL No.6 coal is relatively more hydrophobic than KY No.9 coal. Hydrophobic interactions between IL No.6 coal and *M. phlei*, are probably responsible for the differential adhesion of bacteria. At this time, there is no convincing theory or method which can be used to estimate the energy due to hydrophobic interactions. Only one method exists which can be used to obtain an approximation for the hydrophobic interaction energy. The theory of this method and the results obtained are discussed below.

Hydrophobic interaction between hydrophobic surfaces immersed in water, which is largely entropic, arises mainly from the configurational rearrangement of water molecules around the surfaces, and forces the hydrophobic particles to come together. It is believed that hydrophobic interaction energies cannot be accounted for by conventional theories of van der Waals forces. Despite several recent attempts (Eriksson et al., 1989; Attard, 1989; and Ruckenstein and Churaev, 1991) to provide a theoretical model or explanation for hydrophobic interaction, such as the phenomenological theory on the basis of experiments and the hydrodynamic theory, the origin of hydrophobic interaction remains unknown.

In the early 1980s, Israelachvili and his colleagues (1984) directly measured the hydrophobic interaction force acting between two mica surfaces

rendered hydrophobic by the cationic surfactant hexadecyltrimethylammonium bromide in aqueous solution and presented an empirical expression of the force,

$$F_{HI} = -0.14 \alpha \exp(-h/1.0) \quad (1)$$

where α is the radius of the spherical particle (in m), h is the shortest distance between the particles (nm), and F_{HI} is the hydrophobic interaction force (N).

In recent years, many researchers have studied the direct measurement of hydrophobic force (Claesson and Christenson, 1988; Rabinovich and Derjaguin, 1988; and Christenson et al., 1992) and all of them have shown that the hydrophobic force obeys an exponential relationship to separation distance, and can be expressed as

$$F_{HI} = \alpha C \exp(-h/h_0) \quad (2)$$

where

$$C = 2.51 \times 10^{-3} \text{ Nm}^{-1}$$

$$h_0 = 12.2 \pm 1.0 \text{ nm}$$

They also pointed out that the interaction force and decay length depend on the degree of hydrophobicity. After direct measurement of attractive force between the hydrophobic silica filaments (0-100) and silica filaments immersed in water, Rabionvich and Derjaguin (1988) modified equation 2 by introducing a coefficient

of incomplete surface hydrophobicity k_1 . Hence, equation 2 becomes

$$F_{HI} = -2.51 \times 10^{-3} \alpha k_1 \exp(-h / h_0) \quad (3)$$

$$h_0 = k_1 (12.2 \pm 1.0) \text{ nm} \quad (4)$$

where $0 \leq k_1 \leq 1$.

Song and Lu (1994) have shown that the hydrophobic adhesion force is an exponential function of the hydrophobicity represented by the contact angle of up to $\theta = 60^\circ$. In the case of *M. phlei*/coal system, the maximum contact angle is in the range of $65\text{-}70^\circ$. Therefore, it is reasonable to assume that the exponential function is valid for the case of *M. phlei*/coal system. Consequently, k_1 can be expressed as follows:

$$k_1 = \frac{\exp(\theta/100) - 1}{e - 1} \quad (5)$$

According to equation 5, k_1 will equal 1 if $\theta = 100^\circ$, and if the particles are hydrophilic ($\theta = 0^\circ$), $k_1 = 0$ and $F_{HI} = 0$. In other words, there is no hydrophobic interaction force between hydrophilic particles. The final equation for the hydrophobic interaction potential energy (V_H) between hydrophobic particles is as follows:

$$V_H = -2.51 \times 10^{-3} a k_1 h_0 \exp(-h / h_0) \quad (6)$$

If two particles of different radii and hydrophobicities are interacting, then the values of a and k_1 can be estimated by using the harmonic mean of the two values.

From equation 6, the hydrophobic interaction energies for *M. phlei* whole cells/coal interface and *M. phlei* whole cells/coal-pyrite interface were calculated as a function of separation distance and the results are tabulated in Tables 1-3. The values for V_R and V_A have also been tabulated for comparison purposes.

Table 1. Potential energies of interaction for IL No.6 coal and
M. phlei whole cells (10^{-10} ergs)

H_0 (nm)	V_R	V_A	$V_R + V_A$	V_H
1	-0.296	-0.7112	-1.131	-571.7
6	-0.0348	-0.1185	-0.1741	-234.57
11	-0.0063	-0.06466	-0.0823	-96.25
21	-0.00023	-0.03387	-0.0400	-16.20
51	0	-0.01394	-0.01683	-0.0773
71	0	-0.01001	-0.0118	-0.00219
100	0	-0.00741	-0.0087	-0.000025

Table 2. Potential energies of interaction for KY No.9 coal and *M. phlei* whole cells (10^{-10} ergs)

H_0 (nm)	V_R	V_A	$V_R + V_A$	V_H
1	-0.1797	-0.7113	-0.891	-271.54
6	-0.0206	-0.1185	-0.139	-78.00
11	-0.0037	-0.0646	-0.068	-22.41
21	-0.00014	-0.0339	-0.034	-1.85
51	0	-0.0139	-0.0139	-0.00104
71	0	-0.01001	-0.0100	-0.00
100	0	-0.00741	-0.0074	-0.00

Table 3. Potential energies of interaction for Coal-pyrite and *M. phlei* whole cells (10^{-10} ergs)

H_0 (nm)	V_R	V_A	$V_R + V_A$	V_H
1	-0.3506	-0.6	-0.9506	-492.47
6	-0.04103	-0.1	-0.141	-189.73
11	-0.00745	-0.0545	-0.0619	-73.09
21	-0.00027	-0.0285	-0.0288	-10.85
51	0	-0.0118	-0.01176	-0.0354
71	0	-0.00845	-0.00845	-0.0078
100	0	-0.00625	-0.00625	-0.00

From the above calculations, it is clear that the hydrophobic interaction energies are much greater than the interaction energies due to van der Waals

forces. In all three cases, the hydrophobic interaction energies were found to be at least three orders of magnitude greater than the attractive energy. These results clearly point out the importance of hydrophobic interactions in determining the adhesion behavior of *M. phlei*.

When the hydrophobic interaction energies of the two coal samples are compared, the hydrophobic interaction energy of IL No.6 coal is twice that of KY No.9 coal. This can be attributed to the fact that IL No.6 coal is more hydrophobic than KY No.9 coal. This explains the fact that greater quantities of *M. phlei* adheres to IL No.6 coal than onto KY No.9 coal.

However, in the case of coal-pyrite, the hydrophobic interaction energy is close to that of IL No.6 coal which means that *M. phlei* should adhere to coal-pyrite equally well. But the experimental results obtained from adhesion tests are contradictory to these results. Therefore, hydrophobic interaction energy calculations cannot adequately explain the adhesion behavior of *M. phlei* onto coal-pyrite. The exact reason is not clear at this time. It appears that along with the surface charge and hydrophobicity, the surface chemical composition might be a determining factor in controlling the adhesion of *M. phlei* onto coal and its associated impurities. Hence more experiments will be necessary to confirm the role of surface chemical composition in controlling the adhesion behavior of *M.*

phlei.

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Figure 1. Combustible recovery for IL No.6 Coal in the presence of different reagents as a function of pH

Figure 2. Ash rejection for IL No.6 Coal in the presence of different reagents as a function of pH

Figure 3. Pyritic sulfur rejection for IL No.6 Coal in the presence of different reagents as a function of pH

Figure 4. Combustible recovery for KY No.9 Coal in the presence of different reagents as a function of pH

Figure 5. Ash rejection for KY No.9 Coal in the presence of different reagents as a function of pH

Figure 6. Pyritic sulfur rejection for KY No.9 Coal in the presence of different reagents as a function of pH