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OBJECTIVES

The goals of this research program are to demonstrate the technical and economic feasibility of a micro-agglomerate flotation process and to establish the essential criteria for reagent selection and system design and operation.

1. Introduction

The development of practical technologies for the deep cleaning of coal has been seriously hampered by the problems of carrying out efficient coal/mineral separations at the very fine sizes (often finer than 10 mm) needed to achieve adequate liberation of the mineral matter from the coal matrix. It is generally recognized that surface-based separation processes such as froth flotation or selective agglomeration offer considerable potential for such applications but there remain many problems in obtaining the required selectivity with acceptable recovery of combustible matter. In froth flotation, selectivity is substantially reduced at fine sizes due, primarily, to overloading of the froth phase which leads to excessive carryover of water and entrained mineral matter. Oil agglomeration, on the other hand, can provide good selectivity at low levels of oil addition but the agglomerates tend to be too fragile for separation by the screening methods normally used. The addition of larger amounts of oil can yield large, strong agglomerates which are easily separated but the selectivity is reduced and reagent costs can become excessive.

We are investigating the use of a hybrid process - Micro-agglomerate flotation - which is a combination of oil-agglomeration and froth flotation. The basic concept is to use small quantities of oil to promote the formation of dense micro-agglomerates with
minimal entrapment of water and mineral particles, and to use froth flotation to extract these micro-agglomerates from the waterdispersed-mineral phase. Since the floating units are agglomerates (about 30-50 mm in size) rather than individual coal particles (1-10 mm) the problems of froth overload and water/mineral carryover should be significantly alleviated.

Micro-agglomerate flotation has considerable potential for the practical deep cleaning of coal on a commercial scale. In principle, it should be possible to achieve both high selectivity and high yield at reasonable cost. The process requires only conventional, off-the-shelf equipment and reagent usage (oil, surfactants, etc.) should be small. There are, however, complications. The process involves at least five phases: two or more solids (coal and mineral), two liquids (oil and water) and one gas (air). It is necessary to maintain precise control over the chemistry of the liquid phases in order to promote the interfacial reactions and interactions between phases necessary to ensure selectivity. Kinetics as well as thermodynamic factors may be critical in determining overall system response.

The research program has been organized into several specific tasks as indicated below.

**Task 1. Interfacial Studies**

In order to provide a rational basis for reagent selection, fundamental studies of the various interfaces involved in Micro-Agglomerate Flotation are being conducted. In particular, data are being obtained on:
- liquid/air and liquid/liquid interfacial tensions for aqueous solution/hydrocarbon systems.
- solid/liquid/air and solid/liquid/liquid contact angles for coals and important minerals (quartz, pyrite, etc.).

**Task 2. Emulsification**

The emulsification of oil in the presence of fine particles plays a critical role in the development of micro-agglomerate properties and in the rejection of pyritic sulfur and ash during agglomerate formation. The process is being investigated by measurement of emulsion droplet size distributions in agitated vessels of standard design. The effects of:

- coal type (especially hydrophobicity)
- surfactant type and concentration
- hydrodynamics

are of particular concern.

**Task 3. Agglomerate Growth and Structure**

In order to achieve the degree of selectivity required for effective deep cleaning of fine coal it is desirable to produce agglomerates which are large enough to be separated from the dispersed, refuse material and have sufficiently high density to minimize the inclusion of water and dispersed mineral particles. Studies of size/density relationships for oil-agglomerated fine coal are an important part of the research program. The role of hydrodynamics in agglomerate densification is of particular interest.
Task 4 - Agglomerate Flotation

The final separation of selectively aggregated fine coal particles from mineral matter is to be achieved using froth flotation. Standard procedures for flotation testing are being used to evaluate the floatability of micro-agglomerates formed under various conditions. Specific studies being carried out include determination of the effects of micro-agglomerate size and structure on the kinetics of flotation and evaluation of the potential for further cleaning of the floated material in multi-stage flotation circuits.

PROJECT STATUS

Task 1. Interfacial Studies

Adsorption of PEO/PPO/PEO type triblock copolymers at the air/water interface has been investigated using surface tension measurements. This phase of the work is essentially complete and has led to the following conclusions:

- Surface tension is a function of time at concentrations below about $10^{-6}$. This is attributed to slow diffusion of the surfactant molecules to the surface.

- The surface tension versus concentration profiles for these surfactants can be divided into three distinct regions:
  
  1. Region I, which extends to a surfactant concentration of about $10^{-6}$ M, mainly involves the adsorption of monomers. Surface tension decreases rapidly with concentration.
2. Region III corresponds mainly to the adsorption of fully developed micelles. Surface tension is essentially independent of concentration.

3. Region II represents the transition between Regions I and III and is postulated to reflect adsorption of dimers, trimers, etc. which arise as a result of the polydispersibility of the PO groups. This region can be divided into three sub-regions: A, B and C which are distinguished by an increasing slope with increasing concentration. Since dimers, trimers etc., would occupy a larger surface area than individual molecules, the slope of surface tension versus concentration curve would be expected to be smaller in general in the transition region. The increase in the slope of the curve from sub-region A to sub-region C could be attributed to re-configuration of the aggregates at the surface with increasing concentration. In this case, more dimers and trimers would fit at the interface, leading to a steeper slope in sub-regions B and C.

- The slope of the surface tension curve is not a function of molecular weight in Region I. The surface excess concentration, hence, the parking area per molecule, was found to be the same for three surfactants with different molecular weights. However, the time to reach the equilibrium surface tension increased with an increase in the molecular weight of the block co-polymer, indicating differences in mass-transport behavior.

- The transition concentration between Region I and Region II was found not to be a strong function of molecular weight. However, sub-region B in the transition region disappeared with increasing molecular weight most probably due to a more
rapid reconfiguration of larger molecules compared to smaller ones. The concentration where fully developed micelles begin to form (transition concentration between Regions II and III) decreased significantly with increasing molecular weight.

- Surfactants with different fractions of EO groups seem to give virtually the same surface tension profile.

**Task 2. Emulsification**

To investigate the effects of block co-polymeric surfactants on the kinetics of emulsification of oil, a set-up was designed to carry out *in-situ* size distribution measurements as a function of time using light scattering. Based on the results of studies:

- A phenomenological model has been proposed to describe drop breakup in an agitated dodecane/water system. The emulsification behavior of oil can be described by two empirical parameters, namely, the mean droplet size at one minute dispersion, \([X_{50}(t=1)]\), and a breakage rate constant, \([k]\).

- The model fitted the data quite well for dispersed phase concentrations less than 0.1% by volume. At higher oil concentrations (1.0% by volume and higher) the contribution of coalescence became large. At 1% by volume of the dispersed phase, dispersion was dominant at short times, but coalescence became significant at times longer than about 2 minutes, after the number of droplets had increased substantially.

- Addition of block co-polymers enhanced the dispersion of dodecane at all the concentrations tested. This effect was a function of surfactant type and
concentration. At a fixed concentration, the drop size obtained was smaller for the more surface active molecules.

- The presence of the block co-polymers resulted in two distinct regions in the $X_{50}$ vs. time plots. The placement of these regions along the time axis was a function of surfactant type and concentration. A high breakage rate was observed in the first region and is associated with adsorption at oil/water interface. A lower breakage rate was observed in the second region as the increase in surface area led to an effective depletion of the reagent at the surface.

**Task 3/Task 4**

The complex role of surfactants in micro-agglomerate flotation is illustrated in Figure 1. A detailed quantitative analysis of these processes, based on the data obtained in this study, is currently in progress.
Figure 1. A schematic representation of the role of surfactant in micro-agglomerate flotation.