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MICRO-AGGLOMERATE FLOTATION FOR DEEP CLEANING OF COAL

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by

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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 water/dispersed-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

Contact angle measurements were conducted in the coal/water/dodecane (C/W/D) system to determine the effect of surfactant on the wettability of coal by oil. To obtain the distribution of contact angle about 40 measurements were made for each condition and the results are presented in Figure 1 for both the coal/water/air(C/W/A) and C/W/D systems. The reagent concentration was fixed at 10^{-7} M Pluronic L-64. At this concentration the contact angle for the C/W/A system was maximum (results reported previously). The surfactant increased the average contact angle by about 10 degrees in both the systems. As one can observe, the contact angle distribution in the presence of surfactant was broader when dodecane was present. Since the surfactant adsorbs at the coal surface as well as at the water/air and oil/air interfaces, a detailed analysis was not possible at this time. To determine the adsorption of this reagent on coal a method is required to measure surfactant concentration in solution. Several methods were tested but none was successful at the low concentrations being employed in this investigation. A technique has been identified which requires a pyrolyser to be used with a gas chromatograph. Arrangements are being made as a part of another project to procure this unit. To determine the adsorption at water/air interface surface tension measurements were made but some difficulties were encountered, especially at low concentrations. The procedure is being modified to overcome the problems.

The increase in contact angle in the presence of surfactant was attributed to the coverage of the hydrophilic sites of the coal surface by these molecules. It is known that coal surfaces have hydrophobic and hydrophilic sites whose respective ratios depend on the rank of coal. All the bituminous coals contain hydroxyl and carboxyl groups (about 2% of coal). Since the HLB values of hydrophilic groups in coal are greater than the HLB value of surfactant groups, the coverage of these functional groups will make them less hydrophilic. As a result contact angle will increase depending on the molecular structure and concentration of the surfactant.

Task 2. Emulsification Studies

To determine the effect of surfactant concentration on the kinetics of emulsification, droplet size was measured as a function of time and the results are given in Figure 2, plotted on a log-log scale. In the absence of the surfactant, a straight line was observed. Based on our previous studies we consider that the droplet size is determined mainly by the dispersion sub-process when the dodecane concentration is <0.1%. In the presence of the surfactant molecules, the droplet size decreased drastically within the first 30 seconds. The drops became smaller with increase in surfactant concentration. However, the slope of the curve after this initial decrease in the droplet size was about the same as that observed with dodecane alone and seems to be independent of surfactant concentration. Based on these observations we conclude that the effect of surfactant, at the concentrations used in this study, appears to be very rapid. The decrease in the drop size might be due to two phenomena resulting from presence of surfactant molecules at the interface. One is the lowering interfacial tension at the dodecane/water interface which helps dispersion. The other is the increase in the stability of droplets by preventing coalescence.

To explain the results it is necessary to determine the number of surfactant molecules at a monolayer coverage. The area per molecule (A_m) could be calculated using Gibb's equation from the surface/interfacial tension data. Monolayer adsorption (Γ_m) at the air/water or oil/water interface may be written as:

$$\Gamma_m = -(1/RT)(d\gamma/d\log C)$$

$$A_m = 1/(\Gamma_m N_A)$$

where N_A is the Avogadro's number. Since the surface tension studies are still being conducted, literature data were used to make preliminary estimates. The total surface area for oil droplets was calculated using the mean drop size at various times and the results are given in Table 1, column 3. The number of surfactant molecules to form a monolayer was calculated by assuming an area of 10 nm^2/molecule as the area occupied by one molecule at the surface(obtained from a molecular model by Hillson (J. Photograph. Sci., 11, 225, 1963).

Table 1. The total surface area of oil droplets and number of molecules at monolayer. Surfactant concentration in the system: 1×10^{-4} M (6.02×10^{19} molecules)

Time	Droplet Size (μm)	Total surface area of droplets (cm^2)	# of surfactant molecules at monolayer coverage
0.5 min	43.5	3448	3.48×10^{20}
1 min	37.9	3958	3.99×10^{20}
2 min	33.5	4478	4.52×10^{20}
4 min	29.6	5068	5.12×10^{20}
8 min	26.4	5682	5.74×10^{20}
16 min	24.4	6148	6.21×10^{20}
32 min	22.8	6579	6.65×10^{20}

Based on the above calculations it could be seen that the condition of monolayer coverage is never reached and the beneficial effect of surfactant ceases as soon as the surfactant is depleted from solution. Since the surfactant adsorption is rapid, the decrease in drop size is almost instantaneous, especially at concentrations of 10^{-5} and 10^{-4} M. At concentrations of 10^{-7} and 10^{-6} M the slope is greater at short times, showing the benefits of surfactant on rate of emulsification.

To determine the effect of the order of surfactant addition, another study was performed in which the surfactant was added to the cell after emulsifying dodecane for a known period of time. The results are presented in Figure 3 in both log-log and linear-linear scales. In these studies, surfactant was added in three different ways as follows: i) with dodecane, ii) after emulsification of dodecane for 4 minutes, and iii) after emulsification of dodecane for 84 minutes. It was observed that the time of surfactant addition did not affect the final droplet size. However, the surfactant aided emulsification as soon as it was added to the system. These results are seen more clearly in the log-log plot. The information will be useful in interpreting the results in Tasks 3 and 4.

Task 3. Agglomerate Growth and Structure

Tests are being performed to determine the agglomerate growth curves for speeds greater than 4500 RPM. In addition, procedures for evaluating the structure of agglomerates are being developed.

Task 4. Agglomerate Flotation

Agglomerate flotation was carried out at each of the times (except 20 min.) used in the agglomerate growth studies at speeds of 1500, 2500, 3500, and 4500 RPM. In each test 0.01% oil additions of the 11 mm droplet size and 10^{-6} M Pluronic L-64 were used. The frother used was 50 ml of MIBC. Flotation product samples were collected and analyzed as described before.

Figure 4 shows the percent recovery of combustible material versus the cumulative percent ash for previously completed experiments in which no frother was used. This figure shows the general trend that increasing agitator speeds decreases the ash content for the same percent recovery. Figure 5 illustrates the percent recovery of combustible material versus cumulative percent ash for the tests with frother. This figure shows once again the trend, though not so clearly, that increasing agitator speed decreases the ash content for the same percent recovery.

By comparing Figures 4 and 5, it can be seen that the combination of surfactant and frother, in most cases, reduces the ash content for the same percent recovery. In addition, a wavy pattern becomes prominent when surfactant and frother are used together. This waviness shows two minima in ash content. The first occurs at 2.5 minutes of agglomeration time. The second occurs at around 7.5 minutes. The minimum at 2.5 minutes corresponds to the downward slope of the agglomeration growth curve or the deflocculation zone. This is in agreement with findings in the literature (M. Lapidot and O. Mellgren," Conditioning and Flotation of Ilmenite Ore," Trans. IMM, Sec. C,77(1968):C149-165). For this paper ilmenite was flocculated and floated. The best grade of ilmenite was obtained during this deflocculation zone. The minimum at 7.5 minutes is still under investigation. One possible theory is that floc growth and ash rejection are still occurring, but the flocs are also going through densification. This could lead to a lower ash content at decreasing floc size.

Figures 6 and 7 show the recovery versus ash curves for different agglomeration times at agitator speeds of 2500 and 4500 RPM. These figures show that the best (furthest left) curves are the 2.5 minute agglomeration time curves. Also, in both cases the 2.5 minute agglomeration curve shows the slowest initial kinetics. This means that the first data point (0-20 second flotation sample) had the lowest recovery while also having the lowest ash.

The effects of surfactant addition have been evaluated in flotation tests performed at each of the times (except 20 min.) used in the agglomerate growth studies, speeds of 2500 and 4500 RPM. In each case, 0.01% oil additions and 50 ml of frother were used. A comparison of the results obtained in the absence of surfactant and with 10^{-6} M Pluronic L-64 is given in Figure 8. It appears that surfactant addition aids in ash rejection for relative low agitation speeds in the agglomeration stage. The effect seems to disappear at higher speeds, suggesting that the surfactant may be assisting in oil dispersion. This, is consistent with the emulsification results described under Task 2 of this report.

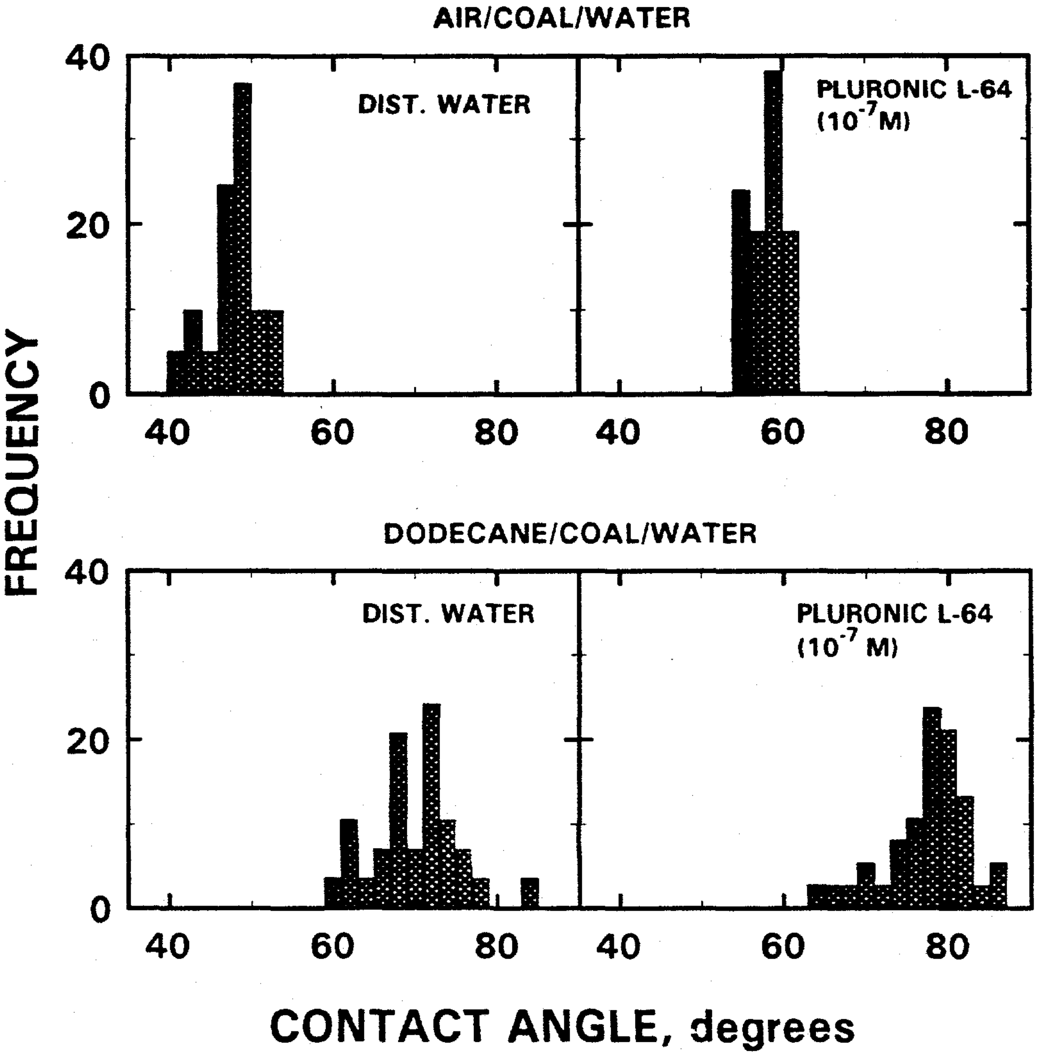

Figure 1. Contact angle distribution for the coal/water/air and coal/water/dodecane systems for the Pittsburgh Seam Coal.

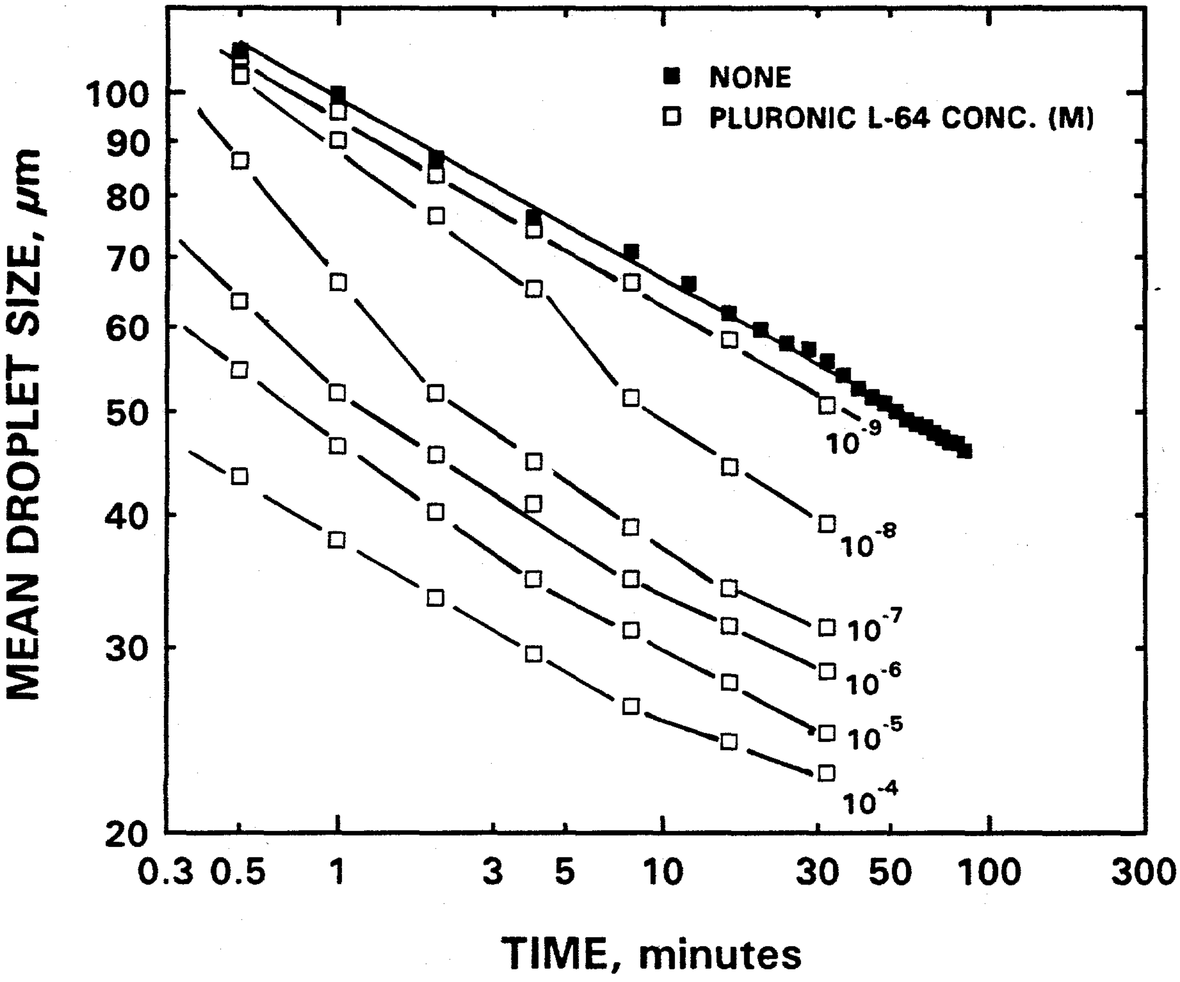

Figure 2. Kinetics of emulsification of dodecane at various surfactant concentrations. Dodecane concentration: 0.1% by volume.

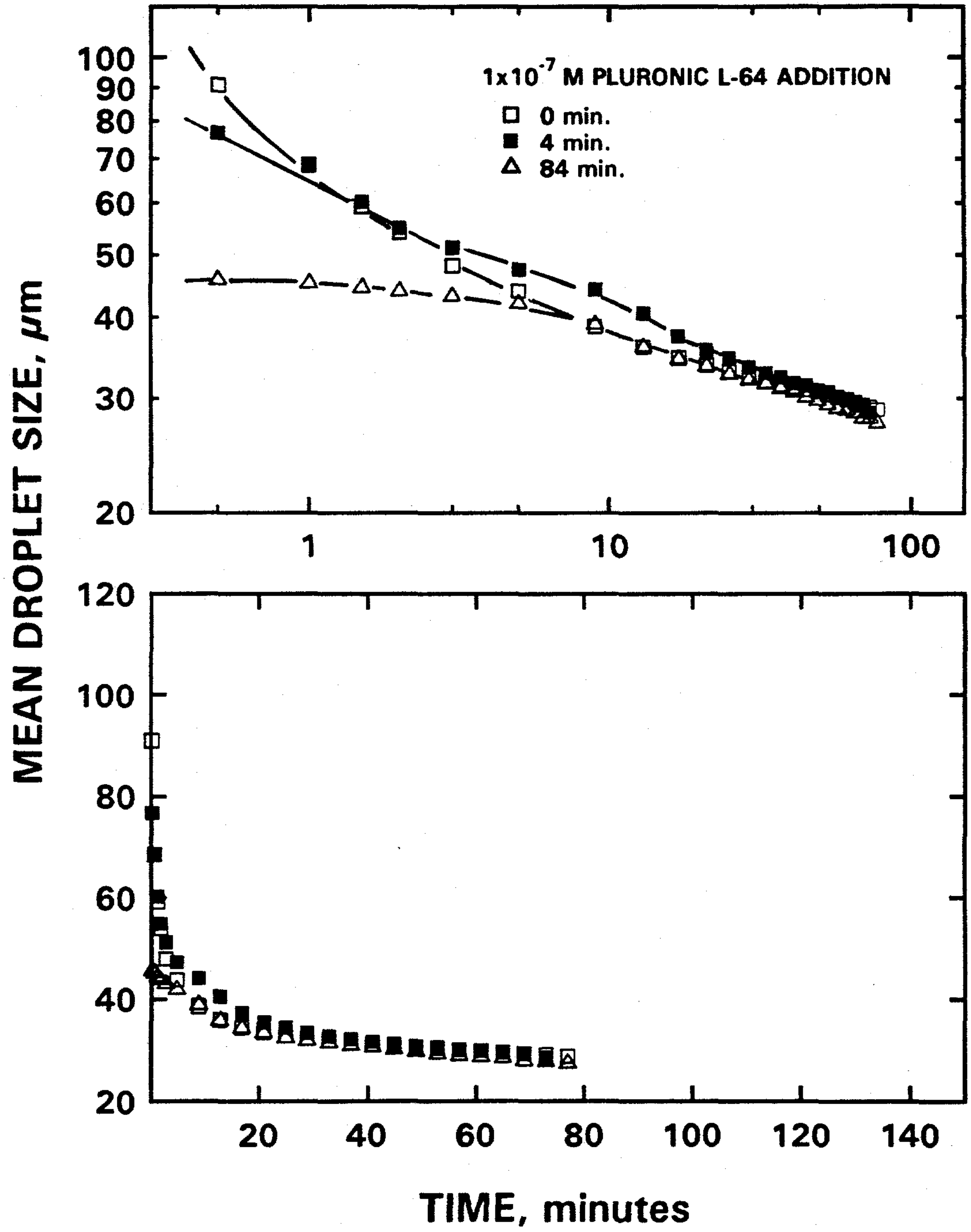

Figure 3. Kinetics of emulsification of dodecane in the presence of 10^{-7} mole/liter of Pluronic L-64. The dodecane was pre-emulsified for various times before surfactant addition. Dodecane concentration: 0.1% by volume. (A) log d_{50} vs log t, and (b) d_{50} vs t plots.

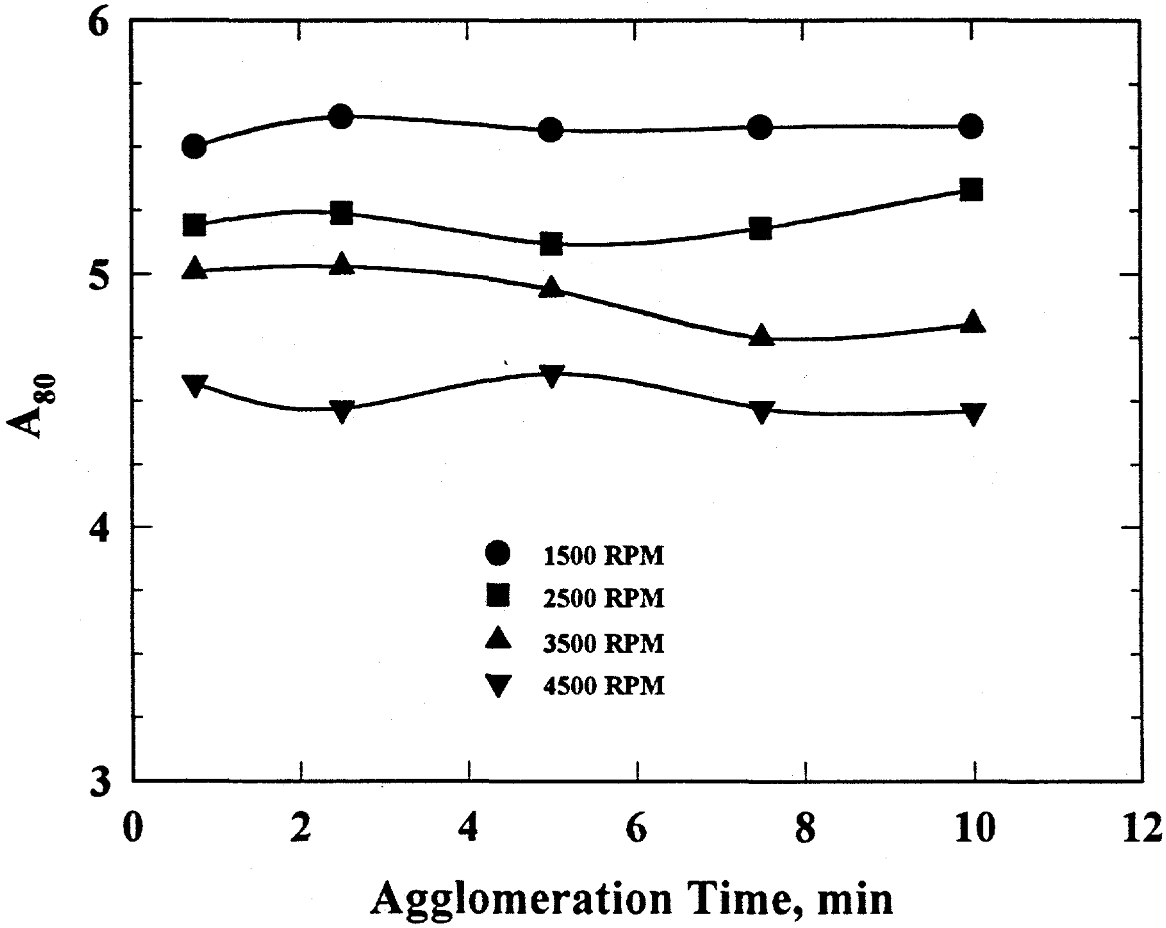

Figure 4. Effects of agglomeration time and agitation speed on cumulative ash percent A_{80}, at 80% recovery by flotation in the absence of frother.

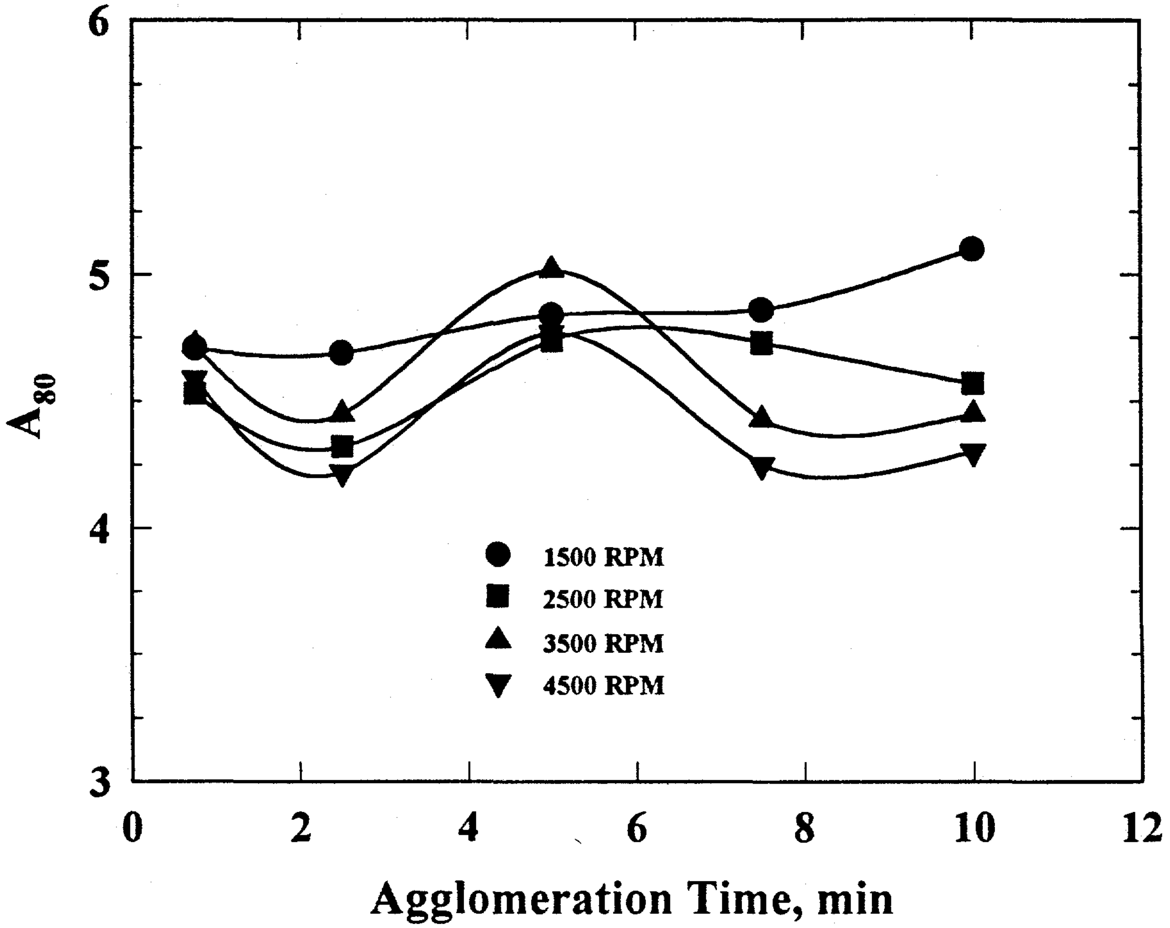

Figure 5. Effects of agglomeration time and agitation speed on cumulative ash percent A_{80}, at 80% recovery by flotation with 50 µl MIBD as frother.

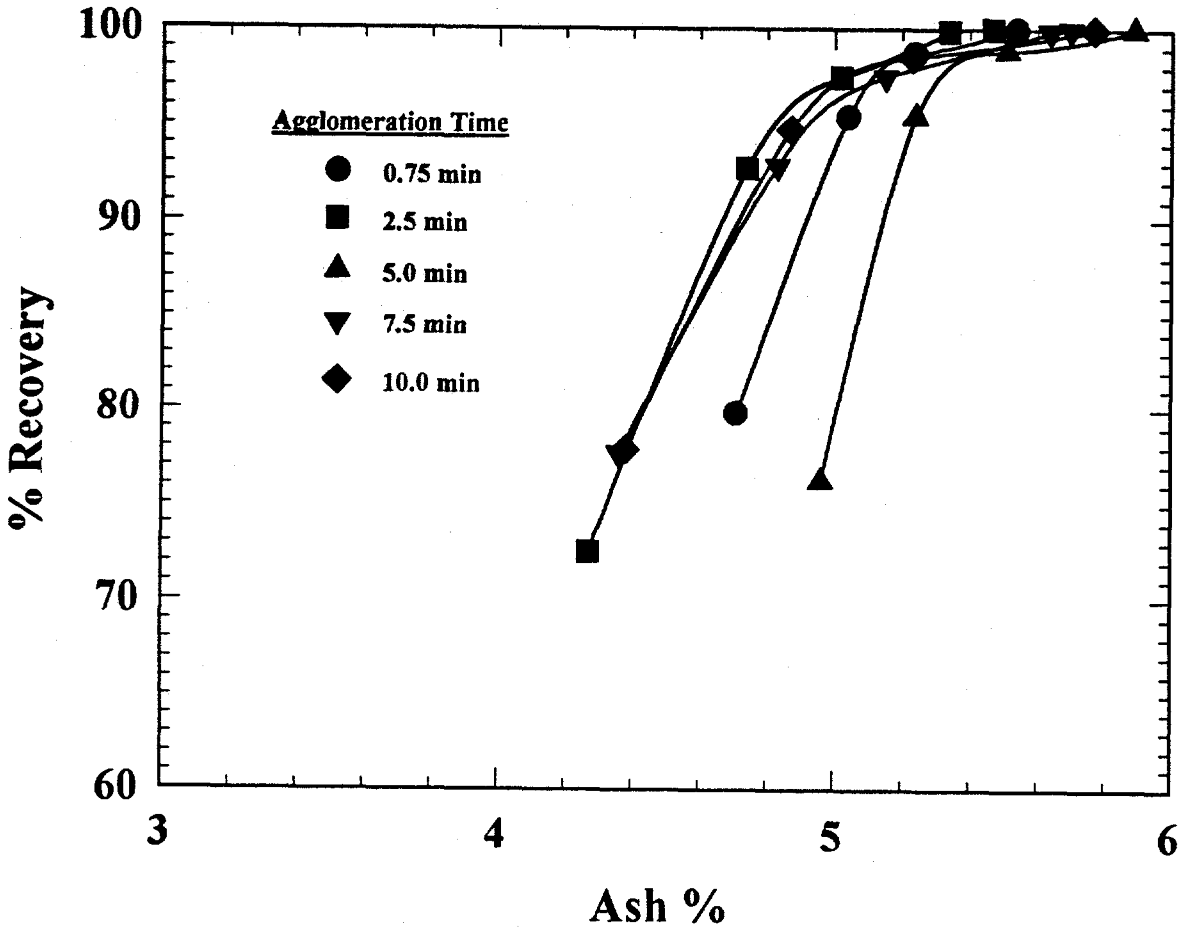

Figure 6. Recovery versus product ash content for flotation of coal pre-agglomerated with 0.01% oil and 10^{-6} M Pluronic L-64 at 2500 rpm.

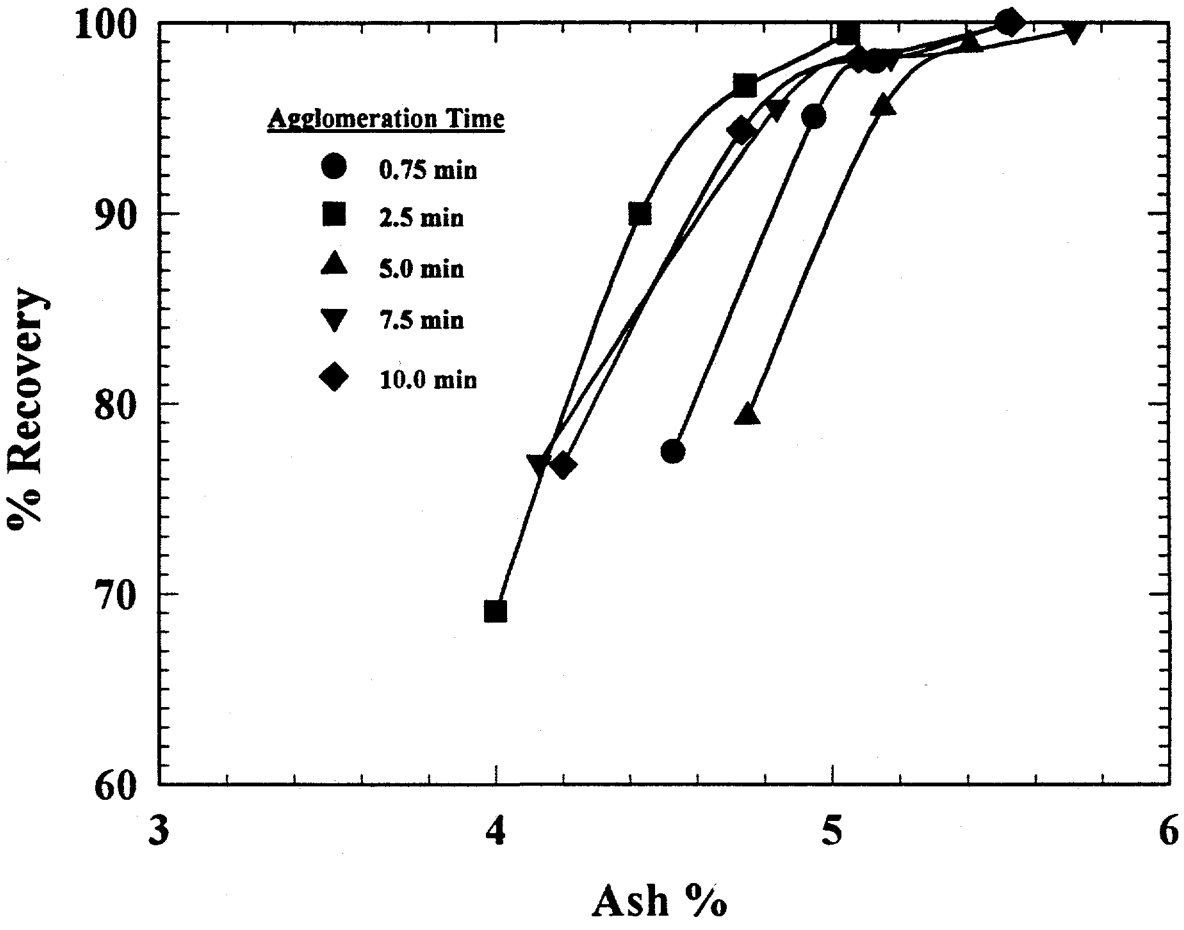

Figure 7. Recovery versus product ash content for flotation of coal pre-agglomerated with 0.01% oil and 10^{-6} M Pluronic L-64 at 4500 rpm.

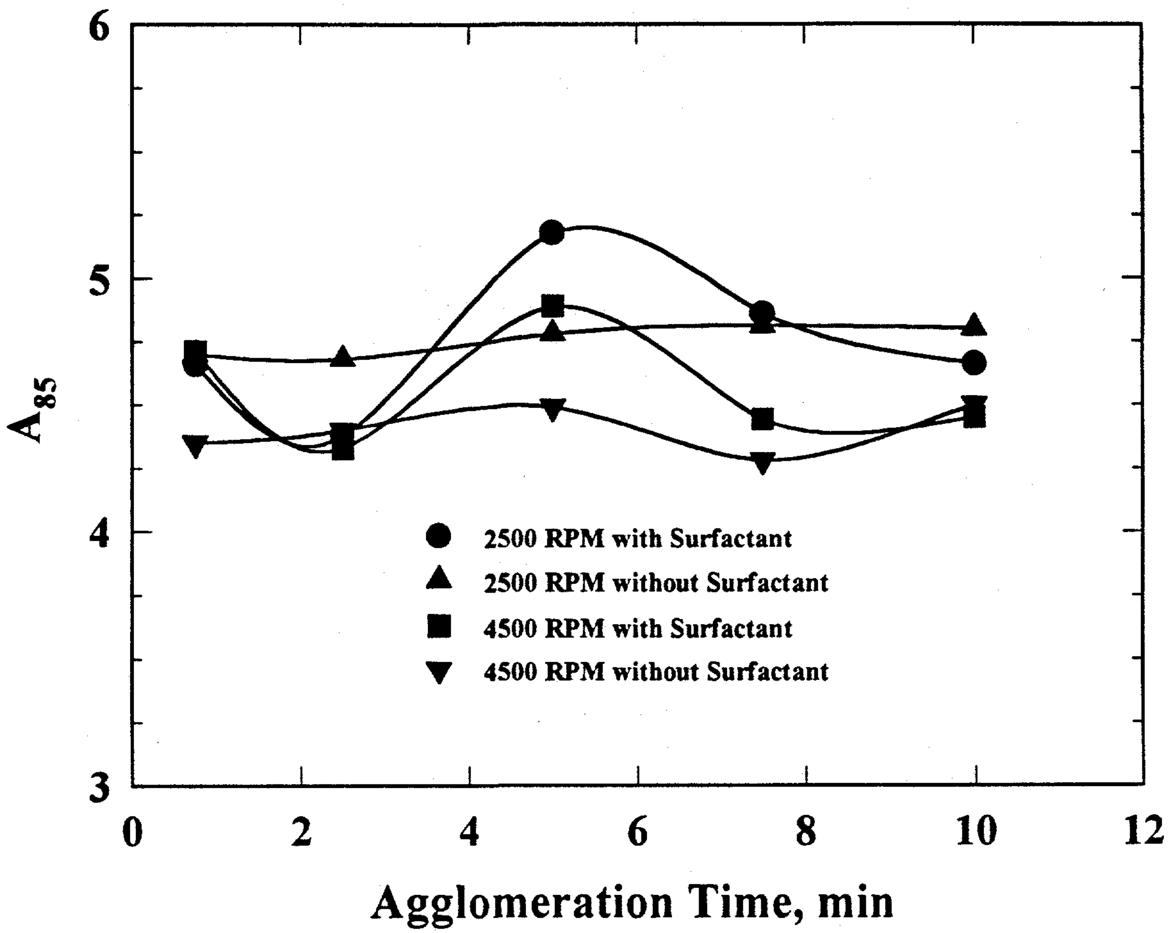

Figure 8. Effect of surfactant addition (Pluronic L-64) on ash rejection in coal flotation following pre-agglomeration for different times and agitation speeds.