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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

To determine the adsorption of surfactant molecules at water/air and water/oil interfaces, surface tension measurements were continued. Substantial dynamic effects were observed at concentrations less than the CMC (critical micelle concentration) for Pluronic L-64. This reagent has been found to be most effective in enhancing agglomeration and flotation of several coals. Therefore, a more detailed study of the effect of time on surface tension has been initiated.

Measurements have been completed for two homologous series of PEO/PPO/PEO block co-polymers. The contact angle was found to be a complex function of reagent concentration and molecular weight. A model to explain the effect of the hydrophylic and hydrophobic groups in the surfactant and on the coal surface is being developed.

Task 2. Emulsification Studies

Analysis of the emulsification kinetics results was continued and a model has been developed for the dispersion sub-process. The effect of coalescence will be incorporated at a later date. For this purpose the results for the droplet size distributions for the emulsification of 0.1% of dodecane by volume in water are given in Figure 1 as a function of time. It can be seen that the size distributions are self-preserving. Thus, a representative droplet size, for example, the median droplet size, X_{50}, can be utilized to represent the changes in the drop size as a function of time (Figure 2).

The emulsification model was developed following Hinze [1955], who suggested that breakage of an isolated droplet is determined mainly by the ratio of external and internal stresses acting on the droplet. The external stress, τ, is the force per unit surface area and acts in such a way as to cause deformation of the droplet. However, the interfacial tension, γ, will give rise to a surface force that will counteract the deformation. If X is the diameter of the droplet, the internal stress due to the surface tension force will be in the order of magnitude of γ/X. Hinze defined the ratio of external and internal stresses as a generalized Weber number, $N_{We} = \tau X/\gamma$ and suggested that the break-up occurs at a critical value $(N_{We})_{crt}$.

This approach was used by Shinnar, 1961 to develop a dispersion model to predict the maximum stable droplet diameter X_{max} at steady state conditions. According to this model,

$X_{max} = D_a C We^{-0.6}$ where D_a is the impeller diameter, N is the impeller speed, ρ is the fluid density, C is a constant between 0.126 and 0.15 and We is the Weber number ($=\rho N^2 D_a^3 / \gamma$).

In the present investigation, Hinze's approach was used to develop a kinetics model for the emulsification process. In a standard vessel with 4 baffles the flow regime is turbulent, which means that there is a distribution of eddies of various sizes which induce the external stresses that lead to deformation of droplets. The efficiency of breakage is a function of both the size of the eddies and the droplets. Glasgow et al., (1985) state that:

> " clearly, large eddies can not break small drops and small eddies can not break large drops. Further, so little energy is contained at comparable entity sizes. Thus, a practical limit for particle size reduction in a given system is the length scale on the order of Kolmogorov(s) microscale (of turbulence).....".

If the energy input into the dispersion vessel is constant it is reasonable to assume that the distribution of eddy sizes will be relatively stable, resulting in a time-invariant microscale of turbulence. Nevertheless, the average droplet size will gradually decrease with time. If the microscale of turbulence is comparable to the droplet size, a significant and increasing fraction of droplets with sizes less than the microscale of turbulence will be generated during the dispersion process. In other words, the effectiveness of the eddies, hence the breakage rate, will decrease as a function of time.

On the basis of the above hypothesis one might suggest that the rate of change in the droplet size is inversely proportional to the dispersion time. The functional form, which is not known *a priori*, could be estimated from actual emulsification experiments. One could calculate the Kolmogorov microscale of turbulence, λ_0, for the system being tested. Then, the fraction $F(\lambda_0,t)$, of droplets that is finer than λ_0, could be determined experimentally as a function of time. The functional relationship between breakage rate and the dispersion time could be estimated from a plot of $F(\lambda_0,t)$ versus t. This exercise has been carried out for our system as follows:

By dimensional analysis, Kolmogorov (1949) suggested that the energy dissipation rate, ε, and kinematic viscosity, ν, can be arranged to give a length-scale for the turbulence, λ_0, in the system.

$$\lambda_0 = \left(\frac{\nu^3}{\varepsilon}\right)^{\frac{1}{4}}, \varepsilon = \frac{P}{m}$$

where P is the power input into the system and m is the mass of the medium in the tank. Power input is given by:

$$P = N_p D_a^5 N^3 \rho$$

where N_p is the power number which is a function of the Reynolds number, D_a is the impeller diameter, N is the impeller speed and ρ is the density of the medium. For the standard four-baffled vessel with a turbine type stirrer (its speed maintained constant to within 1% of the nominal value of 1000 rpm) the Reynolds number is around 10^4. In this region N_p is constant and equal to 4 [Tatterson, 1991]. This results in a power input of about 1.025 watts, which in turn gives a λ_0 value of about 30 µm.

The fraction of droplets that is finer than λ_0=30 µm increases with time as shown in Figure 3. The figure shows that the fraction of droplets that fall below the microscale of turbulence can be approximated as a linear function of time except for very short times, when this quantity increases rapidly.

Using the two approaches presented above, Hinze's criterion and the inverse relationship between the breakage rate and the time of dispersion, a simple model is proposed. If one assumes that only breakage occurs in the system, which is mostly true for dispersed phase concentrations of 0.1% by volume or less, then, it might be stated that the change in the mean droplet size of a given system with time will be proportional to the generalized N_{We} defined by Hinze while it will be inversely proportional to dispersion time. That is :

$$\frac{d}{dt}[X_{50}(t)]=k'\left[\frac{\tau(t)\,X_{50}(t)}{\gamma t}\right]$$

where X_{50} (t) and τ(t) are the mean droplet size and the external stress per unit area at time *t*, respectively. γ is the interfacial tension and k' is a proportionality constant. Assuming that τ(t) can be replaced with a time-averaged stress per unit area, τ, [Tatterson, 1991] allows us to collect k', τ(t) and γ as a new dimensionless constant k. It follows that:

$$\frac{d}{dt}[X_{50}(t)]=k\frac{X_{50}(t)}{t}$$

Integrating the above equation yields:

$$\ln[X_{50}(t)]+\ln(C)=k\ln(t)$$

Defining $X_{50}(t=1)$ as the mean droplet size at 1 minute of dispersion, one can estimate the constant C. Hence,

$$\ln[X_{50}(t)] = \ln[X_{50}(1)] + k\ln(t)$$

A plot of $\ln[X_{50}(t)]$ versus $\ln(t)$ should result in a straight line with an intercept of $X_{50}(t=1)$ and a slope of k (See Figure 4). On the basis of this analysis, one might conclude that dispersion is the dominant process within the time frame employed for the 0.1 % dodecane concentration. At 1.0% dodecane, on the other hand, coalescence becomes significant after 3 minutes of emulsification and the slope of the curve decreases as shown in Figure 5. This model is being used to interpret the effects of various reagent types and concentrations on the emulsification process.

Task 3. Agglomerate Growth and Structure

Direct measurements of the growth of agglomerates of fine coal in the presence of oil (dodecane) at low concentration have revealed a consistent, general pattern. Typically, the median agglomerate size increases rapidly during the first few minutes after oil addition. This rapid growth stage is followed by a period of progressive decrease in size which has been attributed to agglomerate breakage and/or densification in the agitated suspension. Further examination of the agglomerate size distributions provides additional insight into the nature and complexity of the process.

An example of the evolution of the agglomerate size distribution is given in Figure 6. The pattern shown is typical of results obtained under a variety of conditions. It appears that the initial stage of agglomeration involves the formation of a multimodal distribution consisting of some dispersed fines together with a hierarchy of agglomerates of different size. As the process continues, these coalesce into a narrow distribution of relatively large agglomerates corresponding to the maximum in the median size. With further agitation, the multimodal distribution re-emerges, due to breakage of the large agglomerates. Finally, the smaller agglomerates recombine to form a stable, relatively narrow distribution of agglomerates which are somewhat smaller and probably denser than those present at the maximum in the growth curve. Qualitative confirmation of this pattern has been obtained by direct, microscopic examination of the agglomerates. We believe that the complex agglomeration/deagglomeration sequence is a consequence of simultaneous growth and breakage in combination with redistribution of the oil phase.

It is postulated that the pattern of agglomerate development described above is responsible for the variations in selectivity with agglomeration time noted previously (Quarterly Progress Report: October 1 to December 31, 1994). Agglomeration up to and including the peak in the overall growth curve is relatively non-selective. Breakdown of these agglomerates favors ash rejection and enhanced selectivity. Further breakdown, however, may reduce selectivity by increasing carryover of the aqueous phase during flotation. Recombination of the small agglomerates first improves selectivity by reducing carryover but eventually this is outweighed by reattachment of liberated and partially liberated ash particles to the stable agglomerates. The complexity of the agglomerate growth process and its effects on selectivity clearly demonstrate the importance of control of fine particle agglomeration in the use of froth flotation for deep cleaning of coal.

The conclusions in the previous paragraphs are based on the observations of agglomerate size alone. The selectivity of coal cleaning depends on both the structure and size of the agglomerates, however. Since agglomerates are too fragile to be handled individually, the information about agglomerate structure was inferred indirectly from agglomerate flotation results and is discussed in the following section.

Task 4. Agglomerate Flotation

Some experimental results showing the effects of surfactant on selectivity were described in a previous report (Quarterly Progress Report: October 1 to December 31, 1994). The tentative conclusion was that surfactant addition was beneficial at low agitation speed but had little effect at higher speeds. The effect was generally attributed to enhancement of the emulsification process at low agitation speeds. Further evaluation of the data, supplemented by additional experiments, has been carried out. The results, expressed as ash content at 85% recovery of coal (A_{85}), are presented in Table 1.

It is clear from Table 1 that surfactant addition affects selectivity but in a rather complicated fashion. Some clarification is offered in Figure 7 which is a direct comparison of selectivity with and without surfactant addition. If the surfactant had no effect, the points would fall on or at least close to the diagonal line marked on the figure. Points above and to the left of the line indicate detrimental effects of surfactant; points below and to the right show beneficial effects. Obviously both kinds of effects occur depending on agitation speed and agglomeration time. Somewhat different patterns emerge for different speeds. Surfactant is largely detrimental at 4500 rpm but beneficial at 2500 and 7800 rpm, depending on time. In the presence of surfactant, there are significant, though complex, effects at 2500 and 4500 rpm, but relatively little effect at 7800 rpm. On the other hand, with no added surfactant, there are only small time effects at 2500 and 4500 rpm but quite significant effects at 7800 rpm.

Based on these results, it is apparent that the role of surfactant in the selectivity of agglomerate flotation encompasses more than just facilitating emulsification. Other factors such as contact angle modification must also come into play. Evaluation of these factors in the context of our interfacial studies (Task 1) and emulsification studies (Task 2) is in progress.

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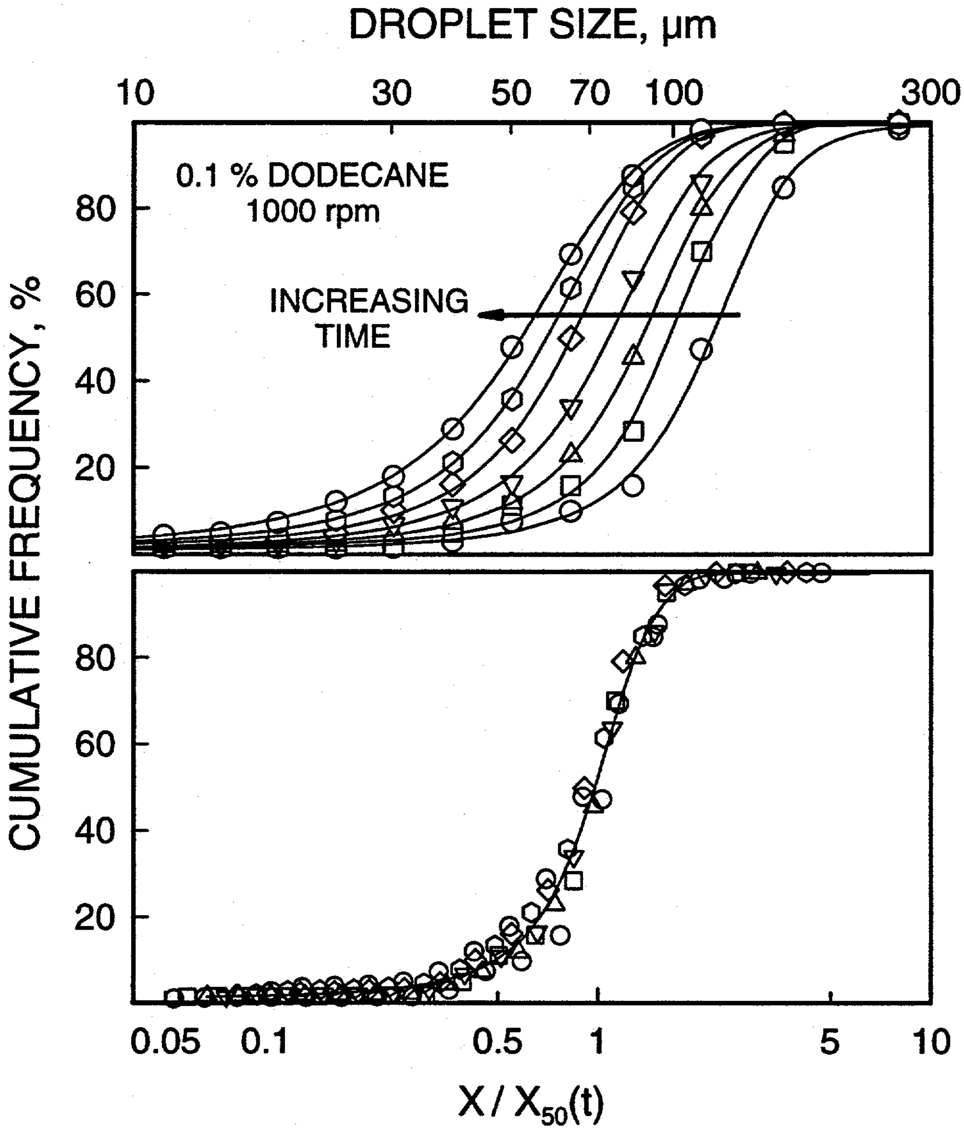

Figure 1. Size distribution of dodecane droplets in water .

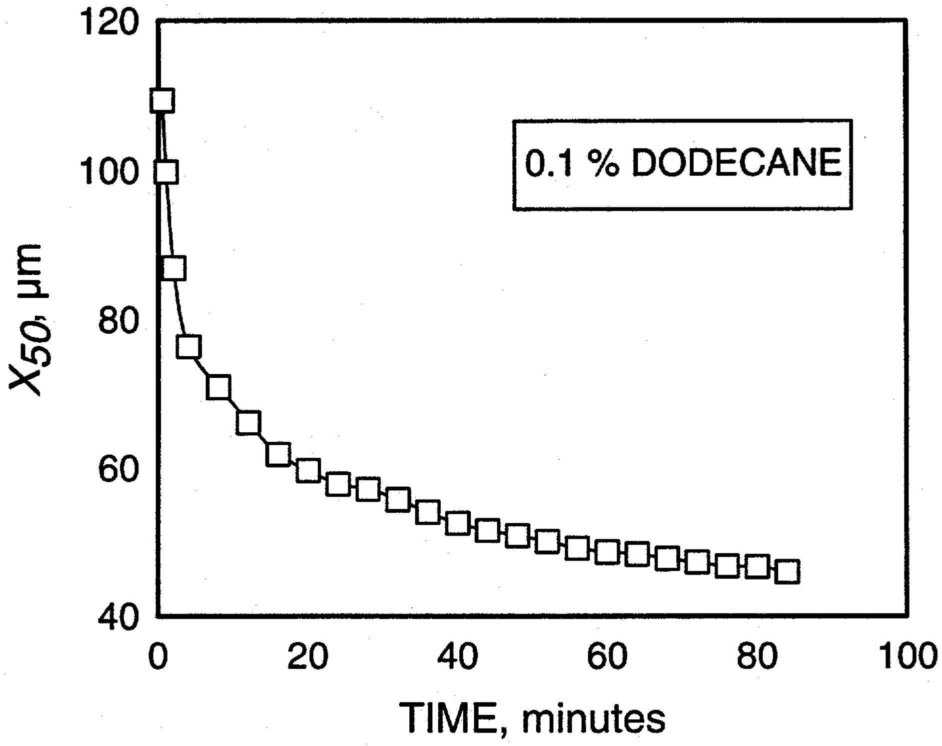

Figure 2. Change in the mean droplet size, X_{50}, as a function of time.

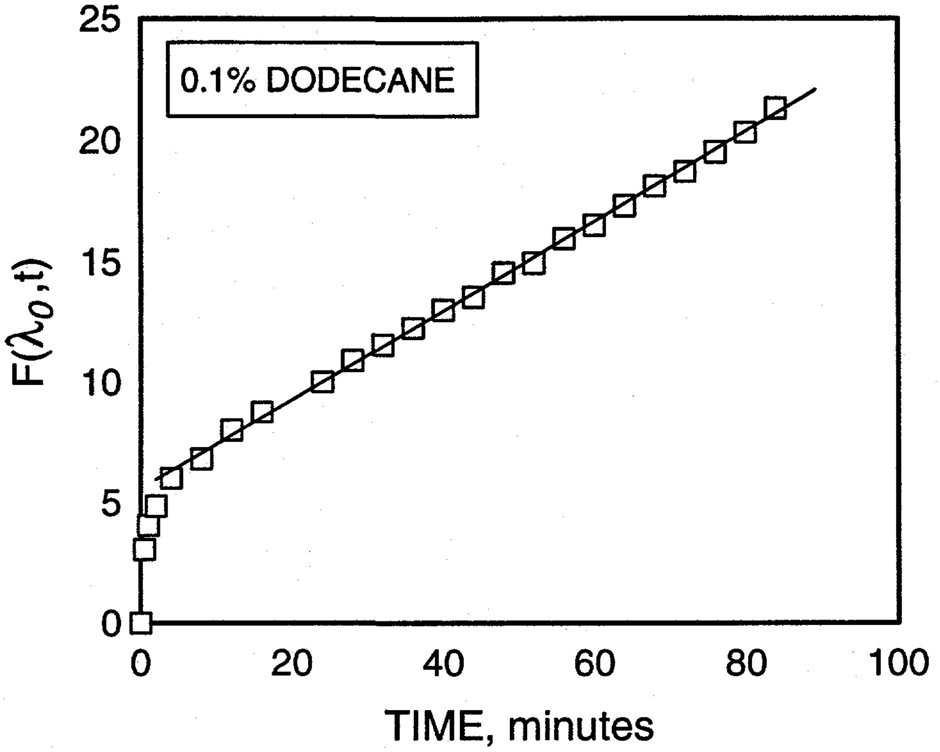

Figure 3. A plot of the fraction of droplets that are smaller than λ_0 as a function of time t.

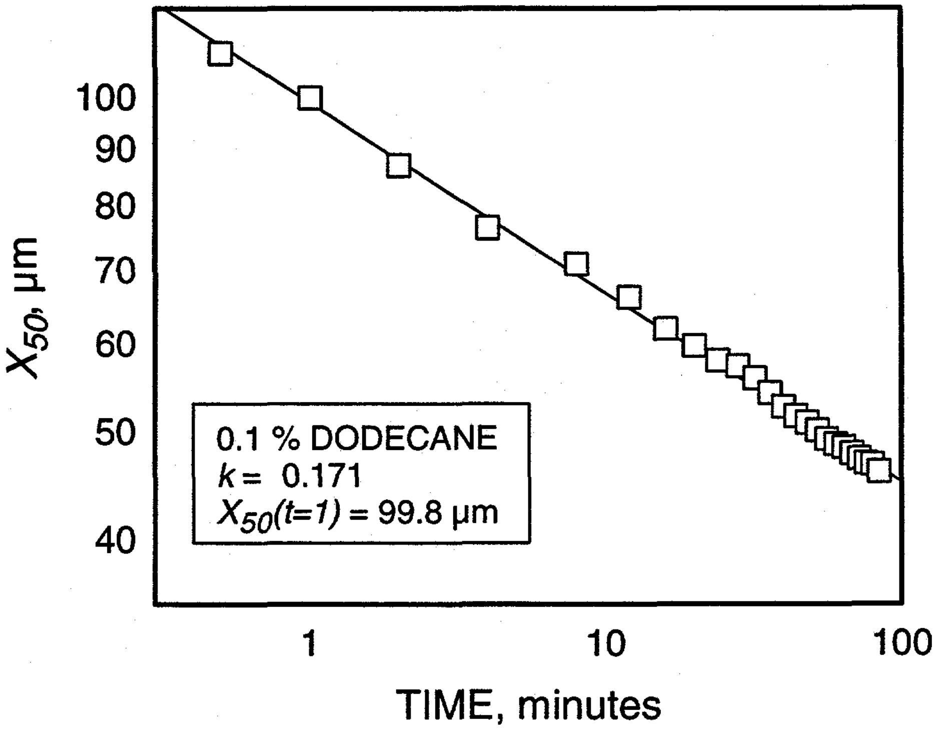

Figure 4. Change in the mean droplet size as a function of time.

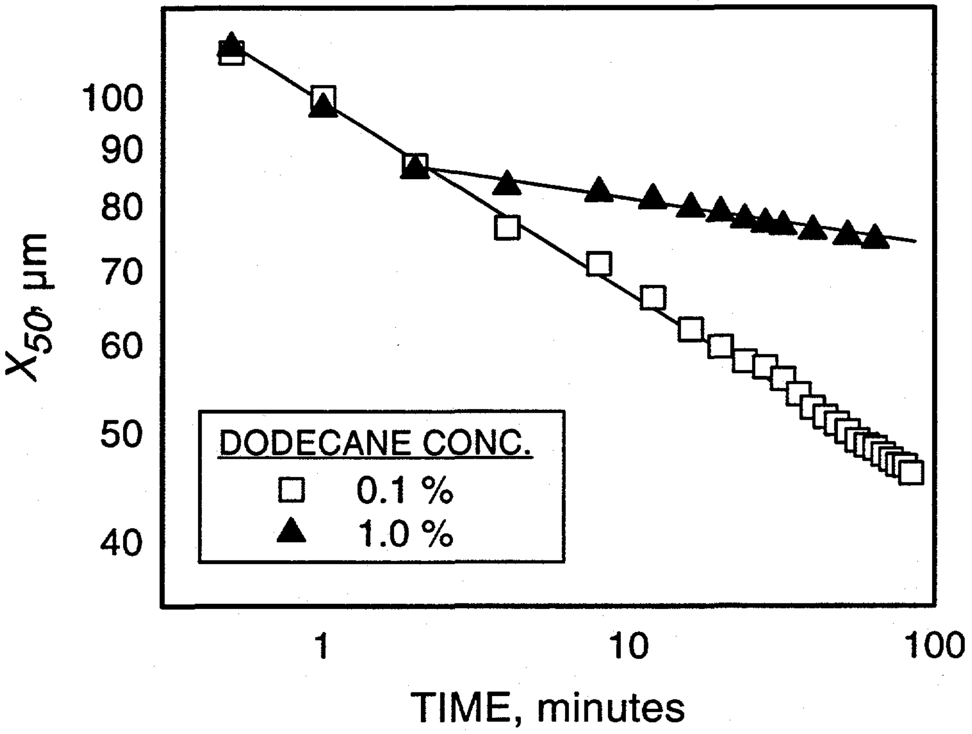

Figure 5. Change in the mean droplet size as a function of time for 0.1 % and 1.0 % dodecane.

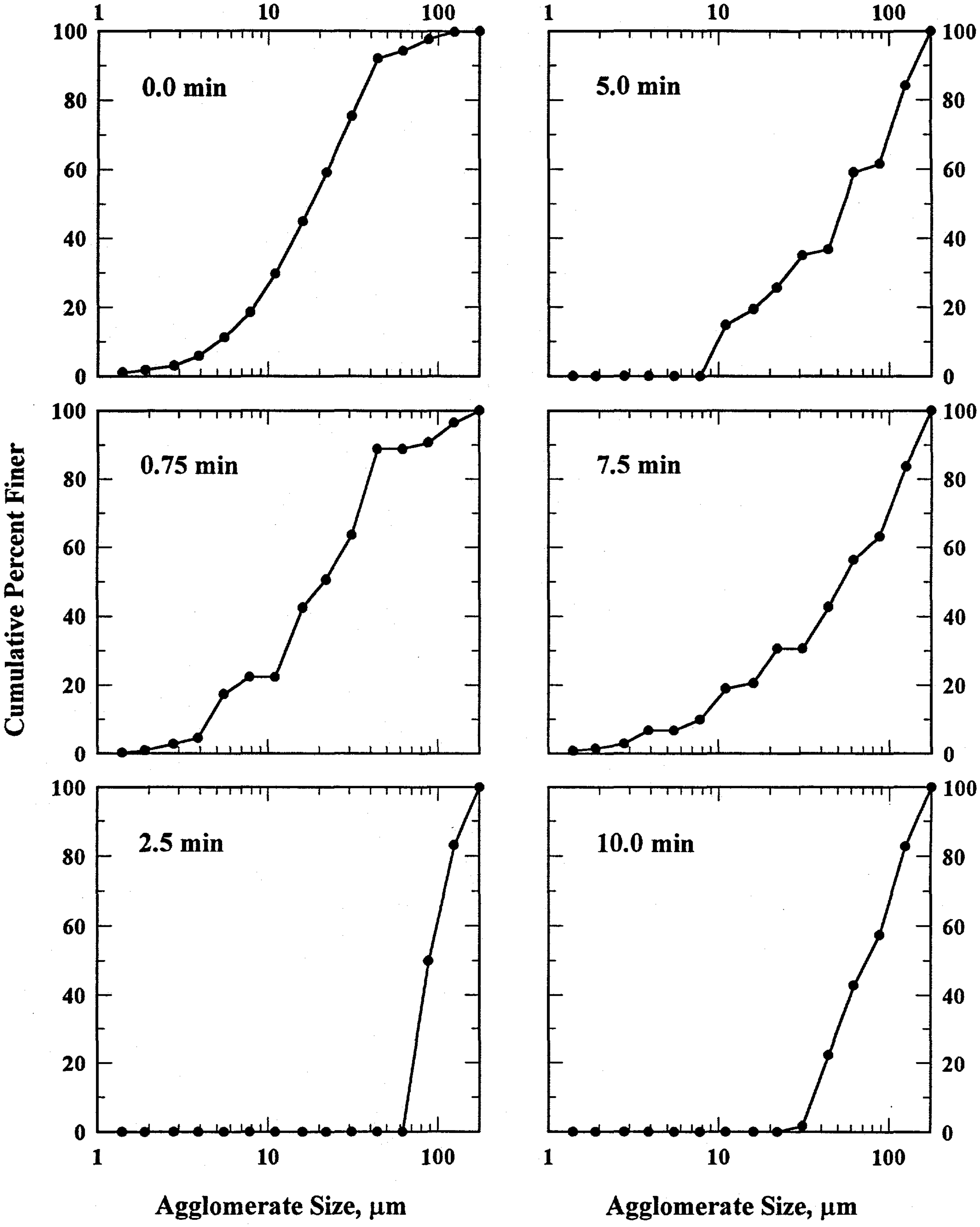

Figure 6. Development of the agglomerate size distribution for 5% oil (dodecane) addition at 1500 rpm.

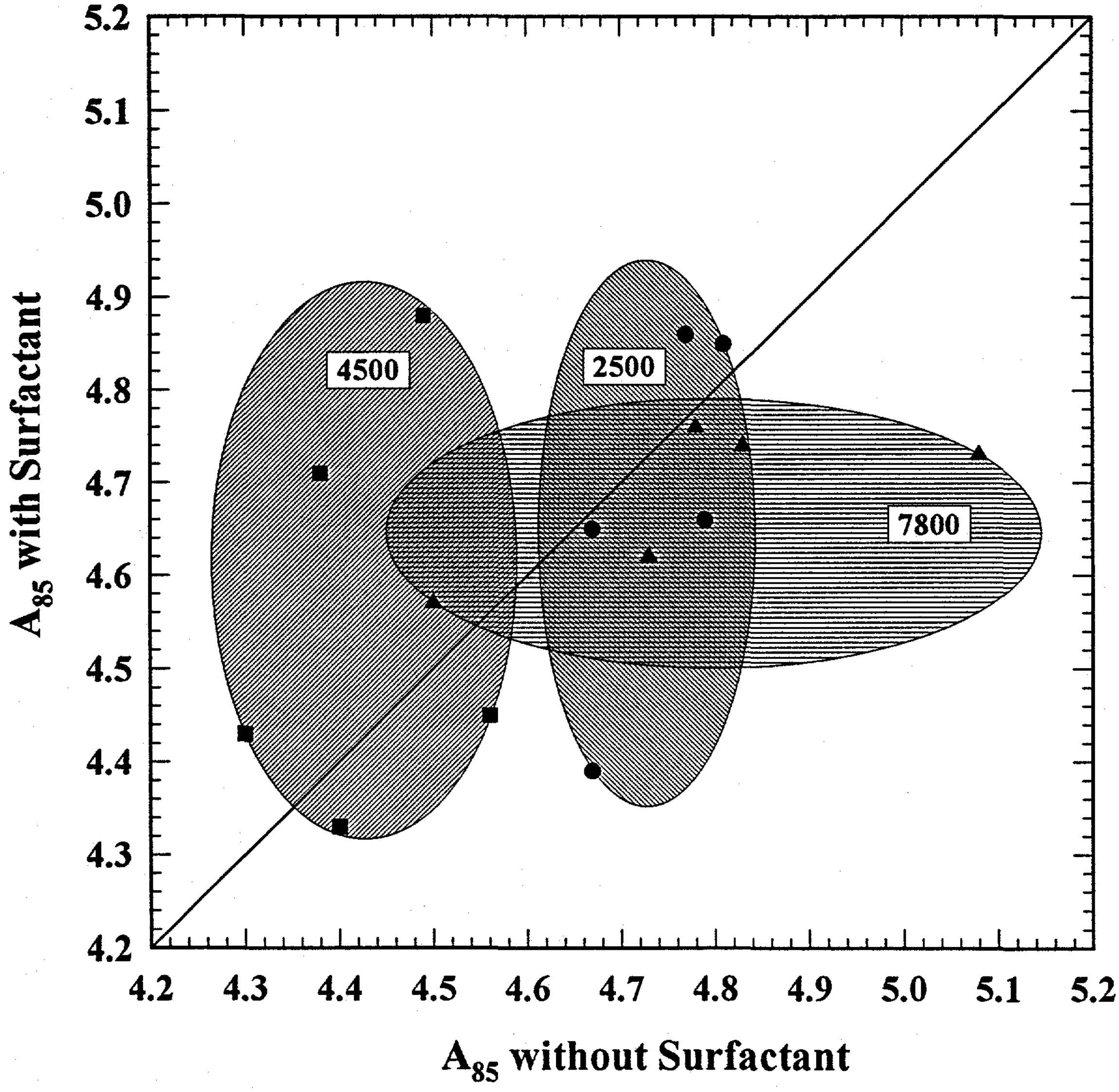

Figure 7. Effect of surfactant addition (10^{-6} mole/ℓ Pluronic L64) on the selectivity of agglomerate flotation.

Table1. Effect of agglomeration conditions on flotation selectivity expressed as product ash content at 85% coal recovery.

Agitator Speed (RPM)	Agglomeration Time	Product Ash at 85% Recovery, A_{85} (%)	
		without Surfactant	with Surfactant
2500	45 sec.	4.67	4.65
	2.5 min.	4.67	4.39
	5.0 min.	4.77	4.86
	7.5 min.	4.81	4.85
	10.0 min.	4.79	4.66
4500	45 sec.	4.38	4.71
	2.5 min.	4.40	4.33
	5.0 min.	4.49	4.88
	7.5 min.	4.30	4.43
	10.0 min.	4.56	4.45
7800	15 sec.	5.08	4.73
	30 sec.	4.78	4.76
	45 sec.	4.83	4.74
	2.5 min.	4.73	4.62
	5.0 min.	4.50	4.57