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NOVEL SEPARATION PROCESSES FOR SOLID/LIQUID SEPARATIONS IN COAL DERIVED LIQUIDS

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I. INTRODUCTION

The removal of the mineral matter found in coal derived liquids is a very difficult solid/liquid separation process. Clays, pyrites and other minerals that occur in coal ultimately find their way into the liquefied product. This is the case, e.g., for both the solvent refined coal (SRC-I) and H-Coal processes. The ash content of bituminous coals which may be fed to coal liquefaction processes normally ranges from 6 to 17 wt.%. The ash content of the coal liquid product can range from 4 to 20 wt.% depending upon the liquefaction process. Ash levels must be reduced to, e.g., 0.4 wt.% in the case of boiler fuel and less than 0.1 wt.% for gas turbine fuels.

The solid/liquid separation is complicated by a hydrocarbon coating associated with the mineral matter particles. In many cases, this coating is composed of an asphaltic material. A more detailed discussion of the characteristics of the minerals and this coating is presented in a later section. There are similarities between the behavior of mineral matter particles in coal derived liquids and other synthetic liquid fuels such as tar sand produced oils and shale oil retort liquids. The discussion here will be limited to particle removal from coal derived liquids.

The primary objective of this review paper is to present and discuss current results relating to novel solid/liquid separation processes that would be reasonable alternatives to the more conventional processes such as filtration. The discussion will center on two classes of processes. These are:

1. Techniques which rely on the precipitation of asphaltic materials from the oil phase which in turn promote the agglomeration of the mineral matter in coal derived liquids and
2. Processes which exploit the surface characteristics of the mineral matter, or the mineral matter with its asphaltic coating, by use of either a liquid phase or a gas phase as a separating agent.

II. BACKGROUND

A. Particle Characteristics

The mineral matter found in coal has various origins. Some was intrinsic to the original plants while the remainder was added to the coal deposits from outside sources such as dust or silt from a stream. The mineral matter content varies widely among coals from different seams and can even vary significantly from sample to sample of coal from the same seam. The mineral matter content of coal usually varies from 1 to 30 wt.%. This mineral matter ultimately is found in the coal liquid product. Coal liquids for solids removal processing can contain 4 to 20 wt.% mineral matter depending on the liquefaction scheme used. Organic insolubles from incomplete dissolution of the coal or coking of the coal liquids are also present.

Typical analyses[1,2,3] of coal ash show that from 80 to 90 percent of the ash is made up of common constituents of which silica constitutes 40 to 50 percent, ferric oxide 15 to 25 percent, and alumina 15 to 25 percent. Distinction should be made between the mineral matter originally in the coal and coal liquids and the ash which results after high-temperature oxidation. Briggs and Stirling[4] list pyrite, calcite, and kaolinite as being common disseminated minerals in coal and have reported particles in the size range from 10 to 80μ. Other minerals which have been identified in coal include quartz, garnet, tourmaline, feldspar, rutile, hornblende, and many more. Minerals from clays, rocks, and soil are found in coal in the 5 to 250μ size range.

The removal of such small particles of mineral matter from the coal derived liquids is further complicated by the crushing of the coal in preparation for liquefaction processing. This crushing of the coal often further reduces the size of the mineral matter particles. Many coal liquefaction processes have utilized coal crushed to minus 200 mesh ($\leq$ 74μ). The mean particle size (by volume) of solids in coal derived liquids generally varies between 1 and 10μ[5,6] depending on both the liquid sample analyzed and the analytical technique used in particle sizing.

Many of the previously mentioned minerals found in coal derived liquids are hydrophilic (water wet) in nature. However, these particles obtain a hydrophobic, carbonaceous matter coating (Figure 1) in liquefaction processing preceding the solid/liquid separation step.[6] It is believed that this coating consists of the asphaltene and preasphaltene fractions of the coal liquid. Briggs and Smith[5] have shown that the asphaltene fraction exhibits surface active characteristics. Futhermore, they have shown that asphaltenes are strongly adsorbed to mineral matter surfaces. Henry and Jacques[7] have presented evidence to the effect that this coating is composed of asphaltenes by showing that the coated particles and the asphaltenes are both positively charged in the presence of a hydrogen donor solvent such as that present in solvent refined coal (SRC-I) filter feed.

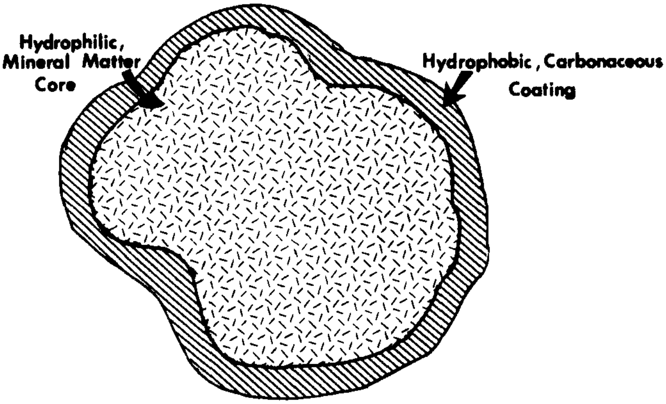


FIGURE 1
Mineral matter particle with hydrophobic, carbonaceous coating.

B. Conventional Processes

Particle removal from coal derived liquids by conventional processes is complicated by properties of the coal liquid/particulate solid system. The small size of the particles and the presence of the surface active asphaltenes lead to very high cake resistances in the case of filtration[5]. This, in turn, necessitates a rather high filter-aid consumption. The small particle size also impedes the effectiveness of hydrocloning and centrifugation. Often as much as 50 percent of the coal liquid product exits with the solids-rich underflow in these processes.

Batchelor and Shih[8] have reviewed the economics of particle removal from coal derived liquids by filtration and centrifugation. Their economics are based on the performance data of operating pilot plants. The cost of these processes are summarized in Table I.

These very high particle removal costs provide an incentive for the evaluation of alternative solid/liquid separations for the problem of removing mineral matter from coal derived liquids.

A detailed review of the techniques previously studied for the removal of mineral matter from coal derived liquids is beyond the scope of this paper. Briggs and Stirling[4] have summarized the results of much of this previous work.

TABLE I.

Comparison of costs of solid/liquid separation processes for removal of mineral matter from coal derived liquids (Batchelor et. al.[8])

Solid/Liquid Separation Processes	Coal Liquid	Ash Removal Cost[1] $/bbl
Precoat Rotary Pressure Filter	SRC	$2.16
Pressure Leaf Filtration	SRC	$3.24
Centrifugation[2]	H-Coal	$2.91

[1] Includes capital and operating cost, 15% DCF.

[2] Ash content of product greater than 0.7 wt.%.

III. A SEPARATION TECHNIQUE INVOLVING ANTI-SOLVENT AGGLOMERATION AND SEDIMENTATION

The addition of anti-solvents to coal derived liquids causes the asphaltene and/or preasphaltene fractions in the oil to precipitate. The precipitated asphaltenes then agglomerate the mineral matter causing an increase in the sedimentation rate. The sedimentation velocity depends upon three parameters which can vary with anti-solvent addition. The diameter of the particle increases as the precipitation on the solid occurs. This increasing diameter leads to faster sedimentation velocities. The viscosity of the coal liquid solution will decrease with the addition of an anti-solvent causing an increase in the sedimentation velocity. Verhoff et al.[9] have shown that the precipitation of lower density asphaltenes on the solid particles can produce a lower sedimentation velocity by giving the agglomerate a lower total density than the original mineral matter solid. Thus, upon the precipitation of material by an anti-solvent, the sedimentation velocity of the particles could increase or decrease depending upon the relative importance of the three effects discussed above.

A series of batch experiments conducted near the proposed separation process conditions and the availability of information regarding the sedimentation rate and compression zone would enable the scale-up of this separation process. There are a number of system variables such as temperature, anti-solvent type, anti-solvent dose, and mixing parameters that would influence the agglomeration and settling rate. Both direct and indirect measurement techniques have been used to observe mineral matter-asphaltene agglomerate settling in coal derived liquids.

A. Measurement of Particle Settling Rates

1. Direct Measurement Techniques

Several investigators at various laboratories, for example, Conoco Coal Development Corporation (Gorin et al.[10], Burke[11]), Argonne National Laboratories (Huang and Fischer[12]), Oak Ridge National Laboratories (Fodgers et al.[13]), have used direct sampling and subsequent chemical analysis for ash and sulfur to determine settling rate.

Gorin et al.[10] mixed coal liquid and anti-solvent in a 3.75 liter autoclave at constant impeller speeds of 600 rpm or 890 rpm for 40 minutes. After the mixing was stopped, the contents of the autoclave were sampled with a travelling probe while settling occurred. The experimental conditions were selected to match the proposed solid/liquid separation processing conditions. The effect of mixing and the relative effects of various anti-solvents on settling rate were not studied extensively.

Rodgers et al.[13] performed a considerable number of preliminary experiments using a variety of anti-solvents and flocculating agents. The coal liquid (SRC-I) and anti-solvent were mixed at room temperature, charged into a tube, heated rapidly to the selected operating temperature (about a 10 minute heating time) and maintained at temperature for 60 minutes. The tube was then cooled and sampled from the top down for chemical analysis. The results of these experiments suggested that toluene was an effective anti-solvent at a dose of 20 percent by weight of oil.

Rodgers also reported some settling experiments using a modified settler (3.75 cm diameter and 125 cm height). In these experiments, the anti-solvent was injected into a stirred autoclave charged with SRC-I filter feed. The contents of the autoclave were then heated for about 45 minutes and transferred to the settler which was held at the same temperature. Samples were withdrawn from six sampling ports at predetermined times for chemical analysis.

Huang and Fischer[12] also have investigated additives for the separation of solids from Synthoil. Oil and additive were shaken together at 80°C in a copper tube. The tube was then quickly removed, quenched first in ice water and then in liquid nitrogen. The Synthoil solidified in 10 minutes. The copper tube was cut into segments and the Synthoil removed from each section for chemical analysis. Kerosene was found to be an effective anti-solvent for the Synthoil gross product.

Burke[11] used a two liter autoclave which was charged with SRC-I filter feed and heated to the desired operating temperature. An anti-solvent, Soltrol-130, was added unheated, mixed at 400 rpm for 30 minutes and transferred to the settling chamber. Four samples were taken at predetermined times, from sample ports located 6 to 25 cm below the liquid surface, for chemical analysis.

The principal difficulty associated with the techniques described above has been the problem of observing the settling velocity of agglomerated particles. In virtually all cases, this has been accomplished by using a settling column and directly sampling the mineral matter at various positions along the column as a function of time. Direct sampling is time consuming in that one sample is required for each settling time studied. A variety of settling times must be observed in order to yield a reliable settling rate. Direct sampling techniques can also cause disturbances of the settling particles themselves.

2. Indirect Measurement Techniques

Ondeyka et al.[14] have developed an experimental technique which utilizes time sequenced x-ray photographs to characterize mineral matter settling in a chamber at high temperature and pressure. This system has the capability of high temperature (up to 400°C) and high pressure (up to 1000 psig) so that experiments can be performed at proposed process conditions. Using this technique, it is possible to rapidly study system variables such as anti-solvent type and dose, temperature, and mixing which would be time consuming and expensive with direct sampling techniques.

Vaidyanathan[15] utilized the above technique to study the important variables that affect the anti-solvent induced agglomeration and settling process. A 300 ml Parr autoclave was charged with 80 ml of SRC-I filter feed and then heated. Unheated anti-solvent is added to the heated coal liquid under different mixing conditions. It was then transferred to a sedimentation cell which was heated to the selected operating temperature. The sedimentation process was then monitored by x-ray photography. The interface heights were then located as a function of time using a film densitometer and plotted. The slope of the constant-rate settling period gives the initial settling rate. The influence of temperature, mixing, and anti-solvent type and dose on the initial settling rate are discussed below.

B. Influence of Process Parameters on the Settling Rate

1. Influence of Temperature

The influence of temperature on the initial settling rate of mineral matter in SRC-I filter feed was studied with and without anti-solvent present. The four operating temperatures considered were 150°C, 205°C, 260°C, and 315°C. In the absence of anti-solvent, the increase in the initial settling rate with increase in temperature can be explained by the reduction in oil viscosity with temperature.

In the presence of anti-solvent, the interaction between the asphaltene and preasphaltene precipitates and mineral matter was found to be the dominant mechanism rather than the reduction in fluid viscosity.

2. Effect of Mixing

The effect of mixing on settling rate was studied at 285°C with a Soltrol-130 to oil ratio of 0.64 by volume. At a constant mixing speed of 250 rpm, increasing the mixing time from 2 to 30 minutes decreased the initial settling rate from 117 cm/hr to 98 cm/hr. Vaidyanathan et al.[16] used an unsteady state breakage model to explain these results.

Increasing the mixing speed from 100 rpm to 440 rpm in steps of 150 rpm, at a constant mixing time of 30 minutes, the initial settling rate decreased from 110 cm/hr to 70 cm/hr. These results indicate that the impeller speed is more influencial than the mixing time. Shinnar and Church's[17] coalescence and breakage stabilized models are used to explain the effect of mixing speed.

Further improvements in the mixing effect were achieved by using sequential mixing. At first, a high impeller speed was used for a short time (550 rpm, two minutes) to promote a rapid dispersion of the anti-solvent and secondly, a slow mixing speed was used for a long time (250 rpm, 28 minutes) to promote agglomeration. Vaidyanathan et al.[16] developed an unsteady state agglomeration model based on binary collisions to interpret the results. From Figure 2, it can be seen that the experimental data compare favorable with the model. There is a two fold increase in the initial settling rate due to employing sequential mixing.

3. Influence of Anti-Solvent Type

The twelve anti-solvents studied were selected based on their solubility parameters [6.6-11.3 $(\mathrm{cal/cm}^3)^{1/2}$], hydrogen bonding (0-4.5), dipole moment (0-4.3 Debye), dielectric constant (2-35), and carbon to hydrogen ratio (0.42-1.2). Filtration and sedimenta-

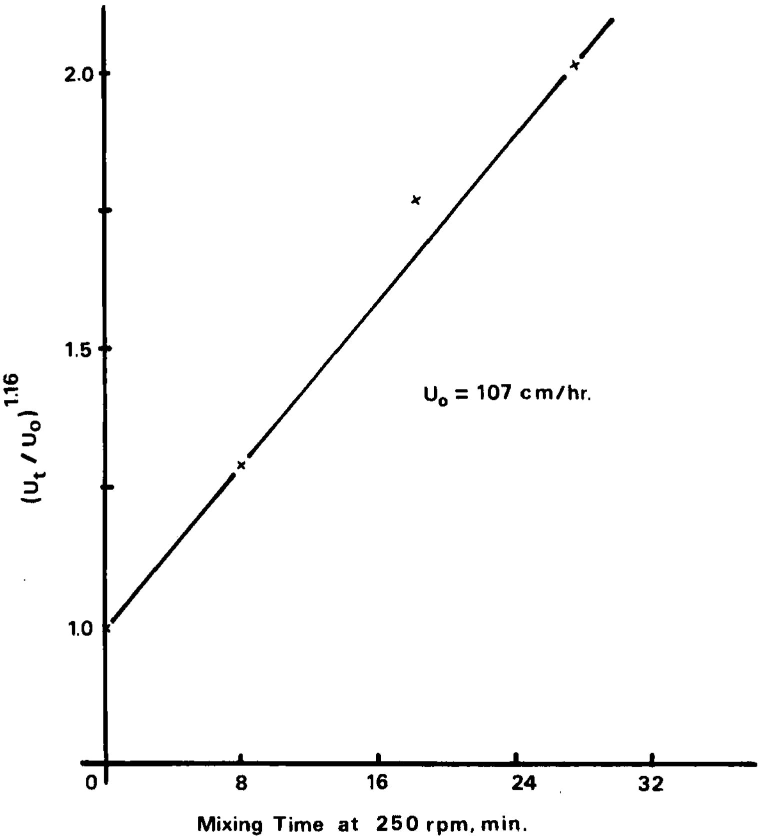


FIGURE 2
Unsteady state agglomeration model, effect of sequential mixing on the initial settling rate for SRC-Soltrol system at 285°C with a two minute mixing at 550 rpm followed by mixing at 250 rpm.

tion experiments were carried out at 205°C, with a two minute mixing period at 550 rpm followed by an eight minute mixing period at 250 rpm. An anti-solvent to oil ratio of 0.25 by volume was used. A blank experiment with SRC-I filter feed was also performed.

Snell and Simone[18] correlated the ash removal efficiency of the anti-solvents with the Watson characterization factor[19]. The Watson characterization factor is a measure of the aromaticity/ paraffinicity of an anti-solvent. Recently, Kleinpeter et al.[20]

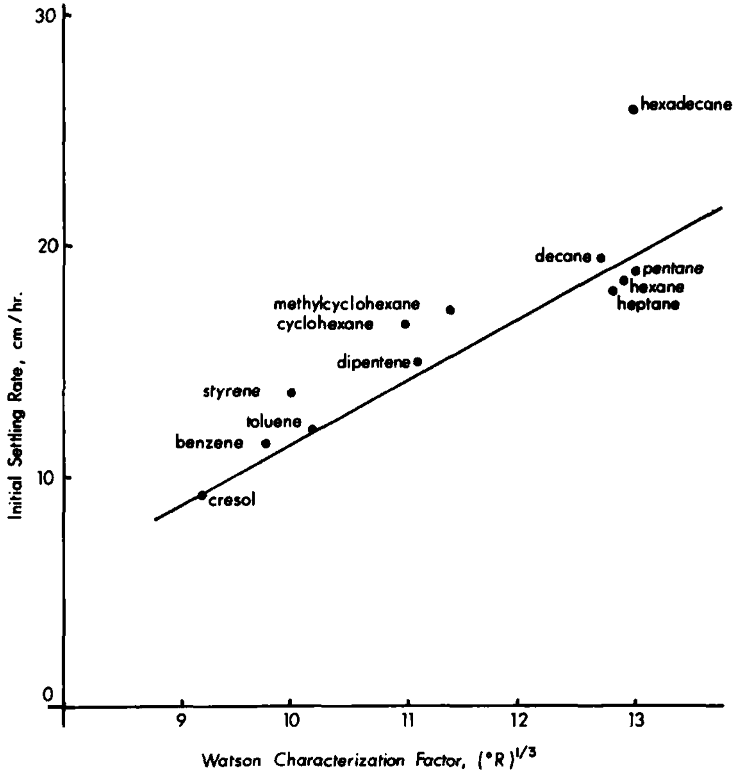


FIGURE 3
Correlation of initial settling rate with watson characterization factor of the anti-solvent at 205°C with a two minute mixing at 550 rpm followed by eight minute mixing at 250 rpm for anti-solvent to oil ratio of 0.25 by volume.

proposed a correlation between the initial settling rate and the Kauri-butanol value of the anti-solvent. The Kauri-butanol value[21] is a measure of the relative solvent power of hydrocarbon solvents having a boiling point over 40°C. The initial settling rate as a function of Watson characterization factor and Kauri-butanol number is shown in Figures 3 and 4. Vaidyanathan et al.[22] correlated the initial settling rate with a linear combination of carbon to hydrogen ratio and solubility parameter as shown in Figure 5. Their correlation is of the form,

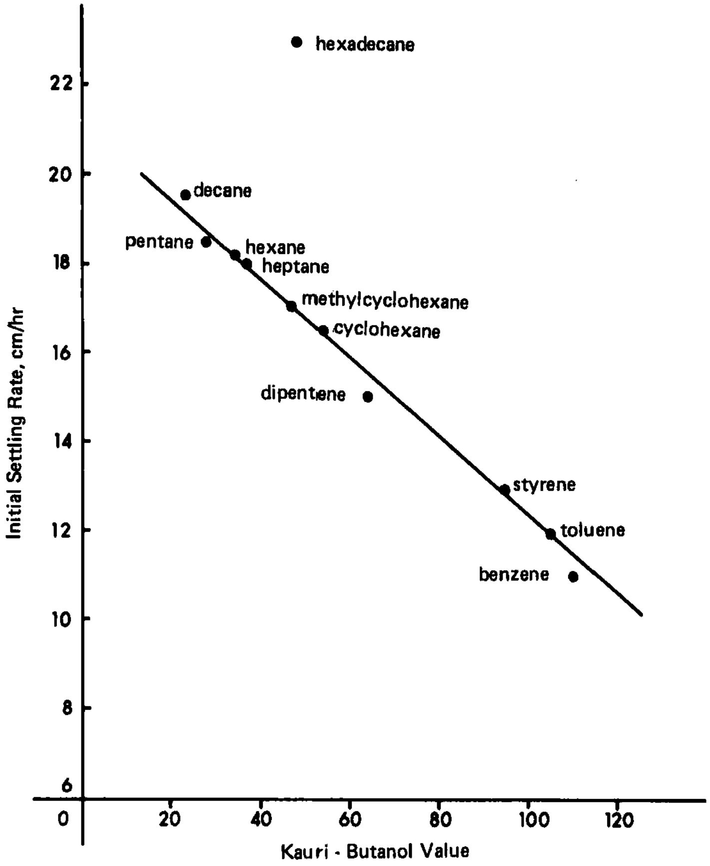


FIGURE 4
Influence of Kauri-butanol value on the initial settling rate at 205°C with a two minute mixing at 550 rpm followed by eight minute mixing at 250 rpm for anti-solvent to oil ratio of 0.25 by volume.

$$\text{Calculated initial settling rate} = 33.5-8(C/H)-1.6(\delta) \qquad (1)$$

The advantage of this correlation over the ones presented earlier is that it involves the use of more fundamental and readily available properties of the anti-solvents.

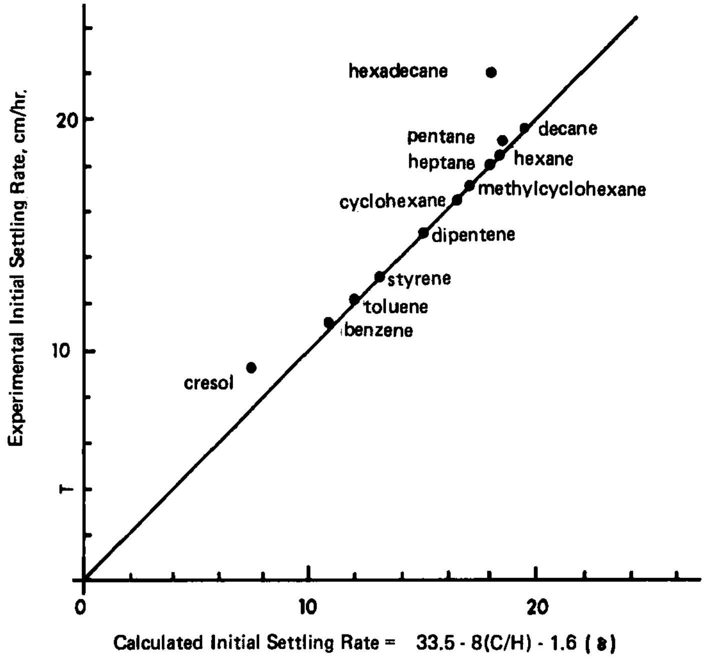


FIGURE 5
Correlation of initial settling rate with a linear combination of carbon to hydrogen ratio and solubility parameter of anti-solvent. (Conditions the same as in Figure 3).

4. Influence of Anti-Solvent Concentration

The influence of anti-solvent concentration was studied for toluene, decane, and Soltrol-130. Typically, the initial settling rate was increased by a factor of five (from 18 cm/hr to 90 cm/hr) when the anti-solvent to oil ratio was increased from 0.1 to 0.5 by volume[22]. This supports the fact that increased anti-solvent concentration causes more precipitation and agglomeration which in turn increases the initial settling rate. The influence of anti-solvent concentration on the initial settling rate is shown in Figure 6.

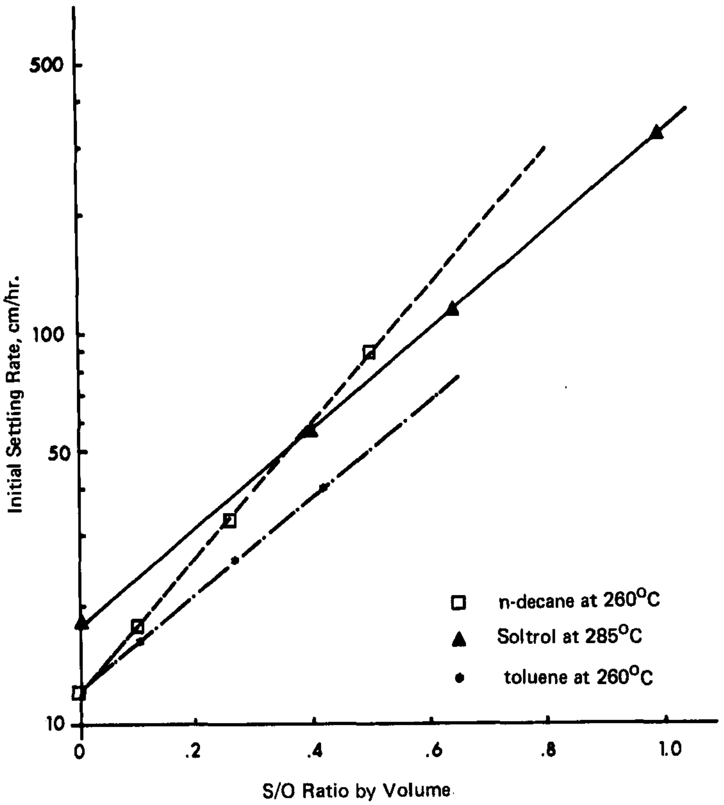


FIGURE 6
Influence of anti-solvent concentration on the initial settling rate with a two minute mixing at 550 rpm followed by eight minute mixing at 250 rpm for n-decane and toluene and a thirty minute mixing at 550 rpm for Soltrol-130.

C. Commercial Deashing Units

Anti-solvent deashing technology is presently moving from bench scale to large pilot plant level. Efforts are underway to couple anti-solvent induced agglomeration with hydroclones and centrifuges in addition to a continuous thickener.

Snell and Simone[18] of Lummus Company have developed a process for the removal of ash from coal liquids by the addition of kerosene distillates. Their pilot plant studies have involved heating the coal liquids and anti-solvents to operating temperatures in the range of 150 to 315°C. The two streams were than fed continuously to a thickener. After about 20 hours of continuous operation, the overflow and underflow were collected and then analyzed for solids. The solids content of the overflow was found to satisfy most ash removal criteria with little or no further processing.

Weber and Agrawal[23] of the Wilsonville SRC-I Pilot Plant have reported results of anti-solvent deashing by centrifugation. The anti-solvent Soltrol-130 was mixed with SRC-I filter feed sequentially in an in-line mixer and in a mixing tank. The stream was then fed to a P-850 Sharples solid-bowl centrifuge. At an anti-solvent to oil ratio of 0.4, the ash content of SRC was less than 0.1% at almost two times the rated plant throughput of 1500 lbs/hr.

Hydrocarbon Research Institute is developing the H-Coal process. They also face the solids separation problem. They have employed anti-solvent deashing coupled with a continuous thickener, hydroclone, and centrifuge[24]. A hydroclone and a two-stage centrifugation system was effective in meeting the product ash specification. However, the flow capacity was very low. The solvent precipitation and subsequent settling seems to be the most promising solid/liquid separation technique for the H-Coal process.

D. Summary

Considering the complexity of the experimental conditions (high temperature and pressure), it can be readily appreciated that the indirect x-ray measurement technique is a better and an easier technique when compared to direct sampling. By using this technique, it is possible to study rapidly process variables such as anti-solvent type and dose, temperature, and mixing. Various types of coal derived liquids can be studied and the influence of the above mentioned variables on anti-solvent induced agglomeration and subsequent settling can be obtained in order to optimize the separation process.

IV. SEPARATION TECHNIQUES INVOLVING PARTICLE SURFACE CHARACTERISTICS

Several techniques presently under investigation for the removal of mineral matter from coal derived liquids involve the exploitation of the surface characteristics of the coal liquid/solid/fluid system. The techniques described below include coal liquid/gas interfacial collection, coal liquid/water interfacial collection, and distribution of the mineral matter solids to a water phase. The work which utilizes a gas to provide the collecting interface has been performed by Bhattacharyya and Kermode at at the University of Kentucky while the work utilizing an aqueous phase was performed by Henry at West Virginia University.

A. Regimes of Separation

Three possible regimes of separation exist when a second immiscible fluid phase is added to a coal liquid in order to affect the removal of the mineral matter. These regimes are:

1. Collection of the solid at the fluid/coal liquid interface.
2. Distribution of the solid into the bulk fluid phase.
3. Bridging or clumping of the solids by the fluid in order to form an agglomerate, followed by settling.

Only regimes (I) and (II) are discussed in this paper.

While the surface chemical differences involved in each of these regimes is only a matter of degree, the applied processing (equipment configurations) can be very different. Collection at the interface would normally take place in something similar to a flotation cell with a solids laden "foam" or "emulsion" phase being removed, while distribution to the bulk phase fluid would behave as an extraction analog with the solids being removed along with the bulk fluid phase. The ability to determine, in advance, which of these separation regimes is optimal or most likely to occur in a particular liquid/fluid/solid is desirable. While no set criteria presently exist with which to make this judgment, some thought has been given to the identification of the system para-

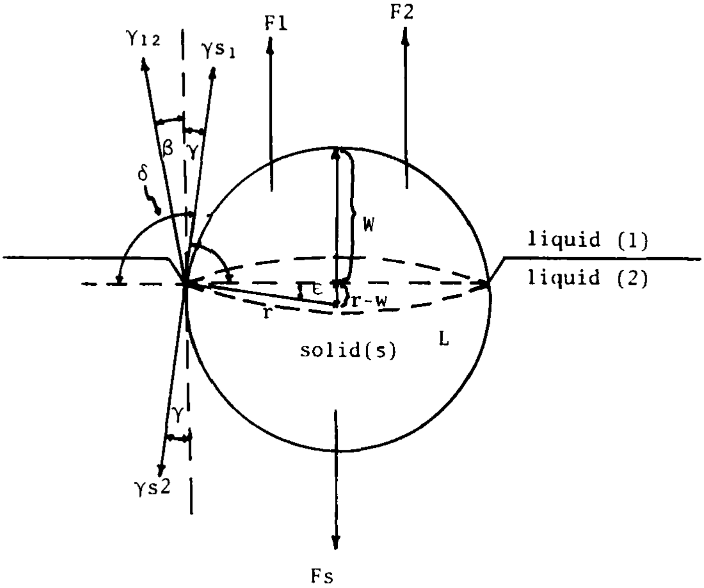


FIGURE 7
Solid sphere suspended at the liquid-liquid interface. (F_1 and F_2 are buoyancy forces; F_s is gravity).[25]

meters which make each regime feasible. This feasibility has been defined on the basis of force balances or free energy studies. A brief summary of this work is presented below.

Analysis of a spherical particle suspended in a planar interface (or a spherical interface whose radius of curvature is sufficiently greater than that of the particle as to make a planar interface assumption valid) have appeared in the literature for quite some time, the most commonly presented form being a free energy balance in the absence of all external body forces. The results of this type of study concludes that for a spherical particle possessing a three phase contact angle, measured through the receiving or collecting phase, between 0° and 180°, collection at the interface would be favored over residence in either bulk phase. The results of this work are commonly summarized, using Young's equation, as:

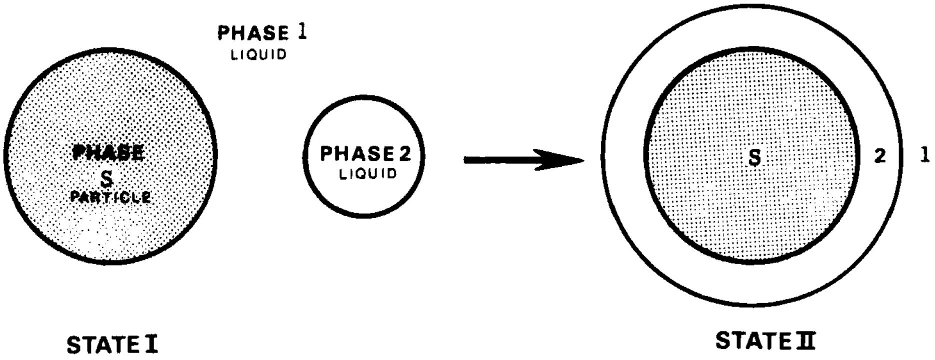


FIGURE 8
Process of particle (phase S) distribution from continuous liquid phase 1 into dispersed liquid phase 2, showing phase relationship between initial state I and final state II configurations.[29]

$$\frac{\gamma_{s2} - \gamma_{s1}}{\gamma_{12}} > 1 \qquad \text{particle wet to phase 1} \tag{2}$$

$$\frac{\gamma_{s2} - \gamma_{s1}}{\gamma_{12}} < 1 \qquad \text{particle wet to phase 2} \tag{3}$$

$$\left| \frac{\gamma_{s2} - \gamma_{s1}}{\gamma_{12}} \right| \leq 1 \qquad \text{particle at interface} \tag{4}$$

It can be seen that this set of equations also states the criteria for particle distribution from one fluid phase to another.

Many additional studies[25,26,27,28] have been made on spherical and cylindrical particles at a planar interface, which include body forces such as gravitational acceleration and buoyancy. A typical example was a study performed by Winitzer[25,26]. A force balance on his system (Figure 7) resulted in the following force balance, where V_1 is the volume of the particle in phase one, V_2 the volume in phase two, and L is the circumference of the contact line where the particle is intercepted by the liquid/fluid interface. This force balance is shown in Equation 5.

$$[(\gamma_{s1}-\gamma_{s2})\cos\delta+\gamma_{12}\cos\beta]\,L=g[V_{TOTAL}\,\rho_s-V_1\,\rho_1-V_2\,\rho_2] \qquad (5)$$

The left hand side of the equation represents the surface forces acting on the particle while the right hand side represents the gravitational and buoyancy terms. This example illustrates that body forces have a significant effect on the particle behavior. In addition, particle size as well as the densities of all three phases are introduced as important variables.

Jacques et al.[29] have extended this work to cases where the radii of curvature of the solid and the liquid/fluid interface are of the same order of magnitude. They have presented results for the case of particle distribution (Figure 8). This study assumes spherical particles and interfaces while neglecting body forces. Differences between the final and initial surface free energies are used to analyze this system. Results demonstrate that the ratio of the particle radius to the liquid/fluid interface radius, n, is an important system parameter (Figure 9). Distribution of the particle from one phase to the other is favored when the free energy difference is negative. The curve corresponding to n equal to 100 approximates the condition of a planar interface. Collection at the liquid/fluid interface is not considered in this analysis.

While these thermodynamic stability studies can be valuable in evaluating the feasibility of a process, they are presently inadequate in showing which regime will actually dominate the efficiency of the process. The mechanism of fluid encounter with the solid particle is ignored. Also, the strength of the particle attachment as well as the relative energy inputs to the system are not taken into account. On the other hand, theoretical studies of the method of particle/interface encounter[30] generally neglect the above surface considerations. A study which successfully weds the two approaches would be valuable.

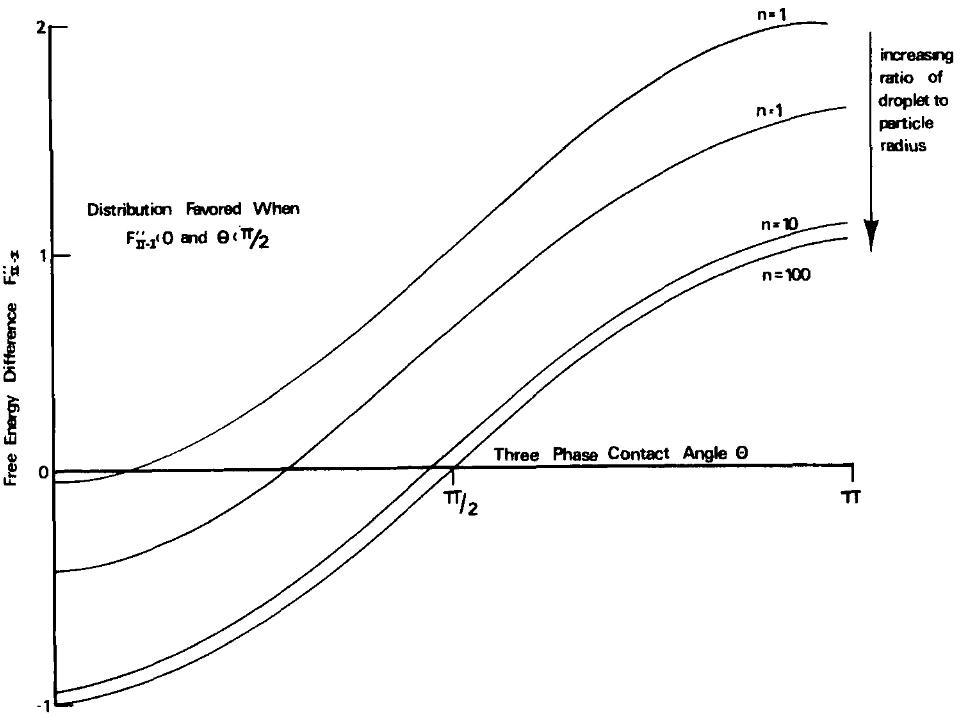


FIGURE 9
Difference in free energy between states II and I (particle distribution) showing significance of θ and n when the particle is preferentially wetted by phase 2 liquid.[29] $\Delta F''_{II-I}$ is dimensionless, i.e. it is the free energy divided by the interfacial tension, γ_{12}.

B. Gas/Liquid Interfacial Collection

Gas/liquid interfacial collection is an example of separation regime (I), collection at a liquid/fluid interface. Much work on this type of separation has been performed in conjunction with the concentration of ores in the mineral industries. A majority of this flotation work has taken place in aqueous systems. In the case of coal liquids, the oil is the continuous liquid phase. The information presented below represents a summary of currently published results on an ongoing evaluation of gas/liquid flotation being performed by Bhattacharyya, Kermode, and others[31,32] at the University of Kentucky.

1. Experimental System

The gas flotation studies were performed in a 3.4-cm i.d. glass flotation column. Heating tapes were wrapped around the column in such a way as to allow the independent control of both the foam and liquid temperatures. The column was operated in a semi-batch mode at constant volume. The system variables discussed below include oil phase composition, oil temperature, solids type, solids size, and gas composition. Unless otherwise noted, the flotation gas used was CO_2. The degree of flotation was measured as percent ash separation. This measurement was defined as:

$$\%\ \text{ash separation} = \frac{\begin{array}{c}\text{initial ash concen-}\\ \text{tration in the liquid}\end{array} - \begin{array}{c}\text{ash concentration in}\\ \text{the liquid at time } t\end{array}}{\text{initial ash concentration in the liquid}} \times 100 \qquad (6)$$

2. Oil Phase Composition

Three different oil phases were evaluated in conjunction with the flotation studies. They include a light cycle oil (LCO) with 6% cresol added, a filtered solvent refined coal (SRC) liquid, and an H-Coal liquid. All of the liquids were initially free of solids. The LCO was petroleum derived and was chosen because its boiling point, density, and viscosity were similar to those of the product from a coal liquefaction atmospheric still. This model liquid was used because of its superior stability with time (as compared with the coal derived liquids) and its ability to give good reproducibility. No qualitative or quantitative differences in flotability were observed in runs using either LCO or SRC liquids, however, runs using H-Coal liquid showed zero percent ash separation (Figure 10).

3. Oil Phase Temperature

Experimental runs were made at 70, 95, and 125°C using an LCO oil phase. The results were inconclusive in that statistically different values of percent ash separation were not achieved due to a large amount of scattering in the data.

The temperature gradient between the bulk liquid and the foam was found to be an important system parameter (Figure 11). A series

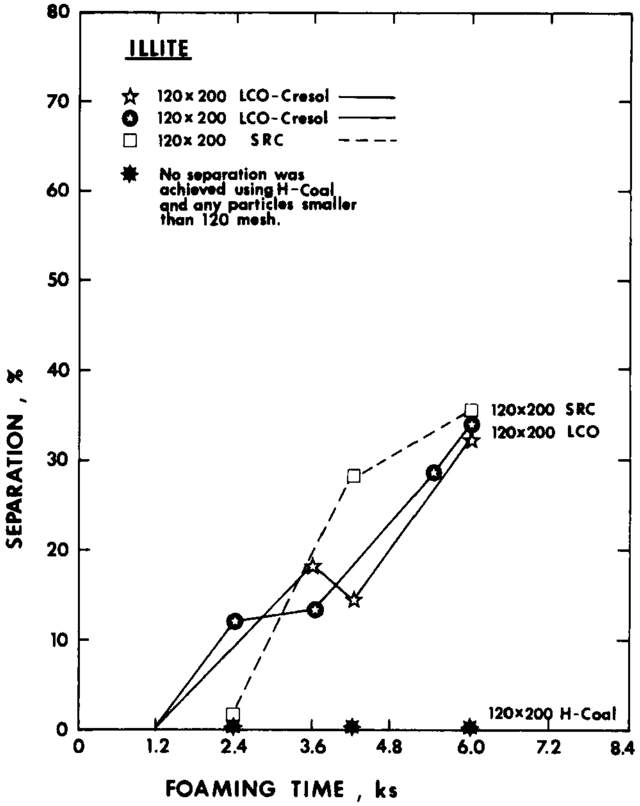


FIGURE 10
Separation of 120 x 200 mesh illite particles in three solvents.[32]

of experiments were performed holding the liquid temperature constant (110°C) and varying the foam temperature. No ash separation occurred in the isothermal system. When the foam temperature was lowered to 75°C, a temperature difference of 35°C, an ash separation of 40 percent was observed. No explanation was offered for this phenomena.

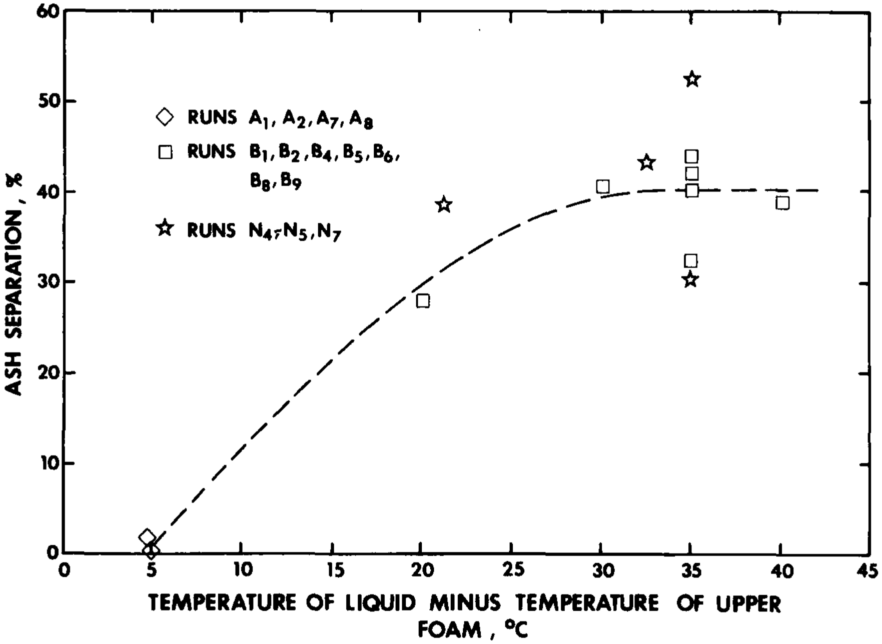


FIGURE 11
The effect of the difference in foam and liquid temperatures on the extent of ash separation.[31]

4. Solids Type

Flotability experiments were made using several clays and minerals which have been found in coal liquefaction residues. Among the solids studied were calcite, quartz, kaolinite, illite, montmorillonite, and wollastonite. These minerals were added to the coal liquid to test their flotability. All, with the exception of illite and kaolinite, showed good flotability. Kaolinite particles were observed to break up into smaller particles due to temperature as the run progressed. This reduction in particle size caused a decrease in kaolinite flotability with time.

Solids originating in a coal liquid were also used. These solids were produced by grinding the solidified underflow of an H-Coal vacuum distillation column. An analysis of this vacuum bottom material is given in Table II. These solids showed a significant flotability in the LCO liquid (Figure 12).

TABLE II

Analysis of the solid vacuum* bottom[31]

Moisture	0.41% (weight)
Ash (mineral matter)	20.9
Volatile matter	55.8
Fixed carbon	22.9
Sulfur	0.89
Btu/lb value	13,000

*Became liquid (highly viscous) at about 120°C.

5. Solids Size

The percent ash separation was observed to decrease with decreasing particle size (Figure 13). Particles with a diameter smaller than 40 μm were not observed to float.

6. Discussion

This preliminary work shows that solids type and size, gas type, and the particular coal liquid itself are all significant variables in the flotation of solids from coal derived liquids. The determination of the great dependence of flotability on particle size is particularly important since typical coal liquid products contain at least 50% by weight particles smaller than the 40 μm minimum flotable size determined for wallastonite in LCO. The coal feed for liquefaction processes has generally been ground to approximately 200 mesh (70 μm). The utilization of a larger sized feed coal would result in a smaller percentage of mineral matter particles falling under the 40 μm minimum. Additionally, it is not clear that the mineral matter occurring naturally in the coal liquid stream would possess the same flotation characterisitcs as mineral matter added from an outside source.

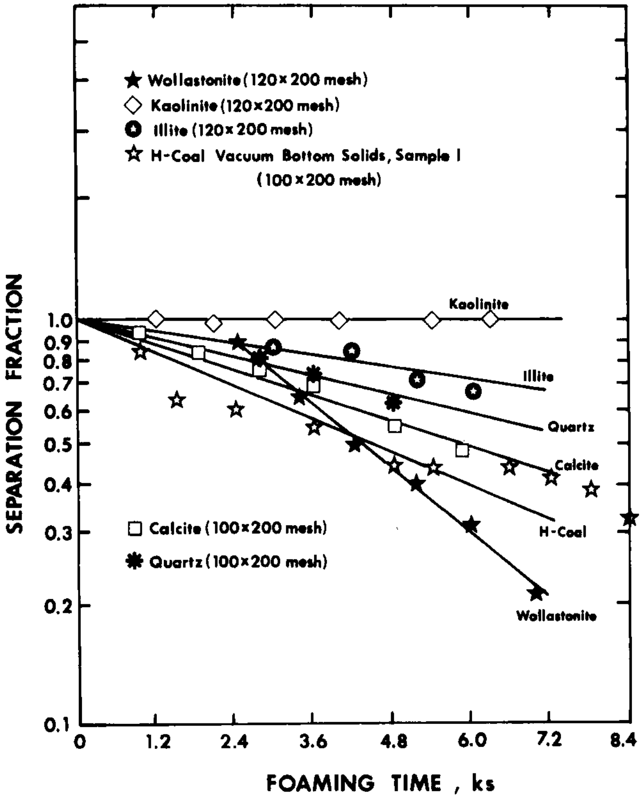


FIGURE 12

Comparison of mineral and clay separation with vacuum bottoms.[32]

(Note: Separation Fraction = $1 - \frac{\%\text{ Ash Separation}}{100}$).

An evaluation of this work points out several interesting areas for future research. Among the research tasks which are suggested are:

1. Surfactant addition in order to enhance particle recovery either by:
    a. Improving the surface characterisitcs (wettability) of the particles with respect to the gas, thus making them easier to float, or

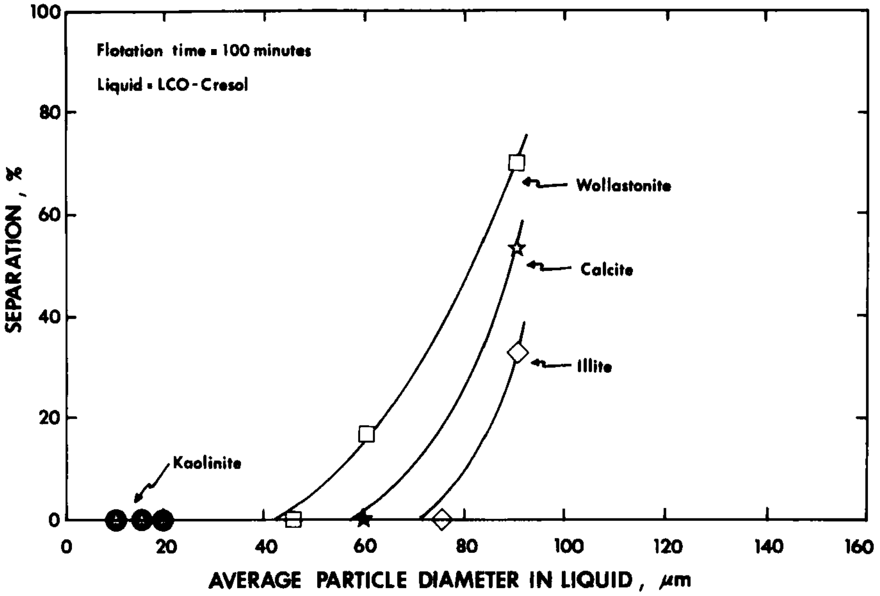


FIGURE 13
Effect of particle size on clay and mineral separation.[32]

   b. Causing particle agglomeration or flocculation, thereby increasing the effective diameter of the collected body.

2. Antisolvent addition in order to increase the effective diameter of the collected body.
3. Work with coal liquids using "in situ" particles.
4. Work at temperatures which would more closely approximate the temperatures which would be found in a coal liquefaction process (400-500°F).

C. Liquid/Liquid Interfacial Collection

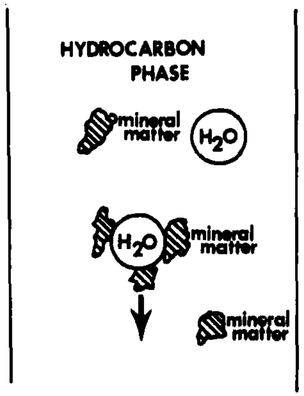
Liquid/liquid interfacial collection, as an analog of gas/liquid collection, is also an example of separation regime (I). In this case a second liquid, instead of a gas, provides the collective interface. The coal liquid is still the continuous phase. Normally, liquid/liquid collection is processed in a manner similar to gas/

liquid flotation, that is, the collecting liquid is introduced at the bottom of the particle-containing liquid and allowed to rise through it, collecting particles as it rises.

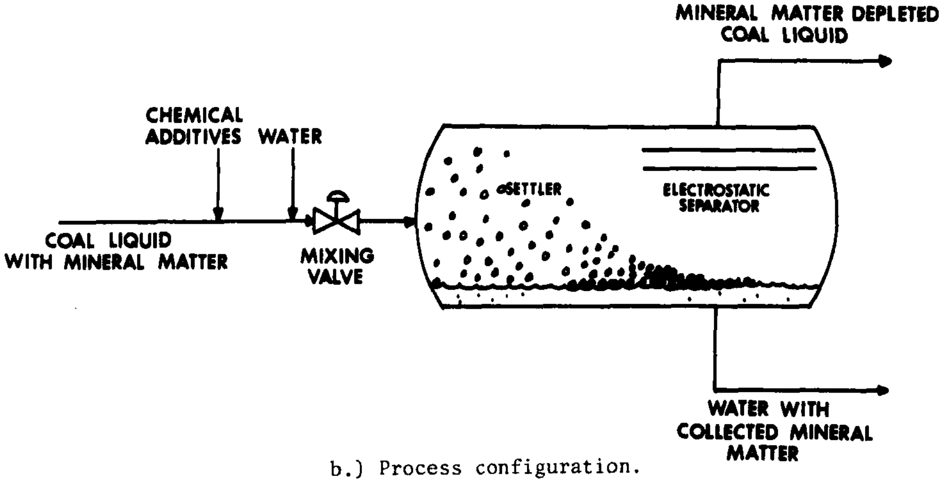
The coal liquid collection work performed by Henry[33] at West Virginia University takes place in a different manner. An aqueous phase, made more dense than the coal liquid by the addition of an inorganic salt, is added to the top of the process vessel and allowed to settle down through the particle laden coal liquid, collecting particles as it goes (Figure 14). A sort of reverse flotation, or enhanced settling, occurs. Regular flotation need not take place in this system because no particle/particle separations are necessary. This enhanced settling takes advantage of the particles' natural propensity to settle in the coal liquid and speeds up this process. A water/particle rich emulsion phase can then be removed from the bottom of the vessel leaving the clean oil to be removed from the top. Further downstream processing, such as an electrostatic coalescence of the emulsion phase may be required.

1. Experimental System

Evaluations of the effectiveness of the reverse water flotation system were done by utilizing a modified Basic Sediment and Water (BS&W) test. This test consisted of batch contacting the SRC-I filter feed with an 18 wt.% aqueous $MgSO_4$ solution. The magnesium sulfate solution was used to insure that the aqueous phase would have a specific gravity greater than that of the coal liquid. After the oil/water contacting was completed, the aqueous phase, along with its collected particles, was allowed to settle out to the bottom of the container. After a predetermined settling time, the top 50 percent of the coal liquid phase was removed and placed in a graduated centrifuge tube. This top 50 percent of the oil represented the clean oil after treatment. This sample was then centrifuged and the amount of sediment compacted in the bottom of the tube was measured. This amount of sediment, when compared with a blank (no water) experimental run, defined the solids removal



a.) Process mechanics.



b.) Process configuration.

FIGURE 14
Liquid/liquid interfacial collection combined with settling as a solid/liquid separation technique.

efficiency. This efficiency was called the percent oil clean-up. Percent oil clean-up was defined as:

$$\text{percent oil clean-up} = \frac{\text{height of compacted solids in blank} - \text{height of compacted solids in run}}{\text{height of compacted solids in blank}} \qquad (7)$$

By defining percent oil clean-up in this manner, only the solids removed due to water collection and surfactant addition were measured. All experiments were carried out at 90°C.

2. Effect of Surfactant Concentration

A number of surfactants were screened for their ability to perform in the coal liquid system. This discussion is limited to the behavior of the most successful of these surfactants. The performance results for this surfactant are illustrated in Figure 15. Basically, the surfactant was found to adsorb onto the mineral matter surface and make it more hydrophilic. This water-loving (hydrophilic) nature can be quantified by the measurement of the coal liquid/aqueous phase/mineral matter three-phase contact angle. The contact angle, as measured through the water phase, decreases with increasing hydrophilicity.. The more hydrophilic the mineral matter particle, the greater its propensity to be collected. The experimental results (Figure 15) show that the effectiveness of this particular surfactant increases with its concentration in the oil phase until oil clean-up levels off at a value of 80 percent (3000 ppm). Additional surfactant beyond this point does not improve the solids removal efficiency. Note that the percent of oil clean-up can be increased to levels approaching 100 percent by sequential addition of the dispersed water phase .

3. Aqueous Phase pH

The results of a series of experiments studying the effect of aqueous phase pH are presented in Figure 16. No surfactant was added to the coal liquid in these experiments. As can be seen, the percent oil clean-up can be increased from nearly zero percent to nearly 100 percent by varying the aqueous phase pH alone. This represents an even greater percent oil clean-up than can be achieved by the use of any of the surfactants studied. This pH effect can be attributed to the behavior of the asphaltic material adsorbed onto the mineral matter particles. Several investigators[34,35] have shown that the surface active fractions of petroleum asphaltenes change from oil wetting promoters to water wetting promoters under

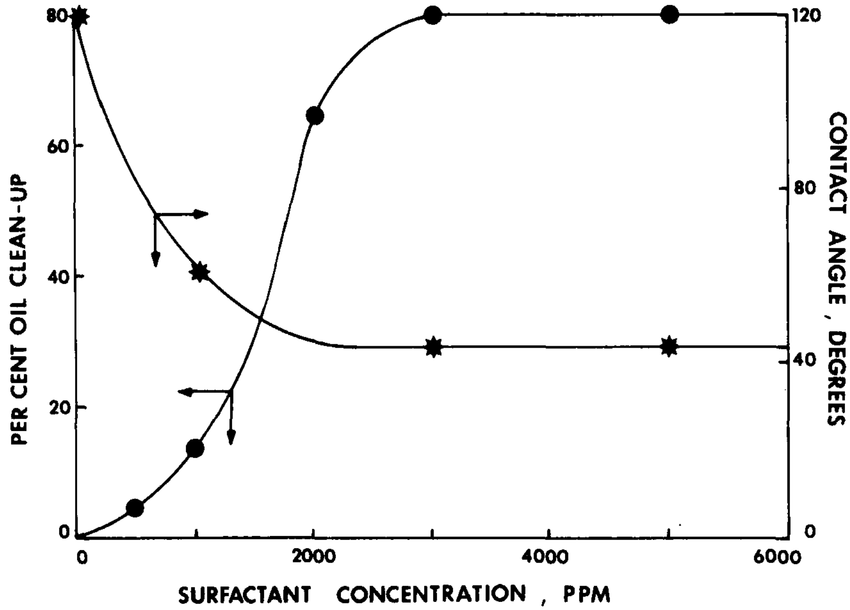


FIGURE 15
The dependence of the contact angle and the percent oil clean-up on changes in the surfactant concentration. (From C. Lau[36]).

basic conditions. Cratin[37] has attributed this behavior to asphaltic zwitterion species. It would appear that this is also the case for coal derived asphaltic surfactants.

4. Discussion

Figures 15 and 16 illustrate that significant percentages of oil phase clean-up (80-100%) can be achieved, in actual coal liquids with naturally occurring mineral matter, by the variation of the surfactant additive concentration and the aqueous phase pH. This percent removal, if equivalent to mineral matter removal, is significantly greater than that reported in the previous section for gas/liquid flotation. Also, this increased removal efficiency is probably adequate to make up for the potential problems present with

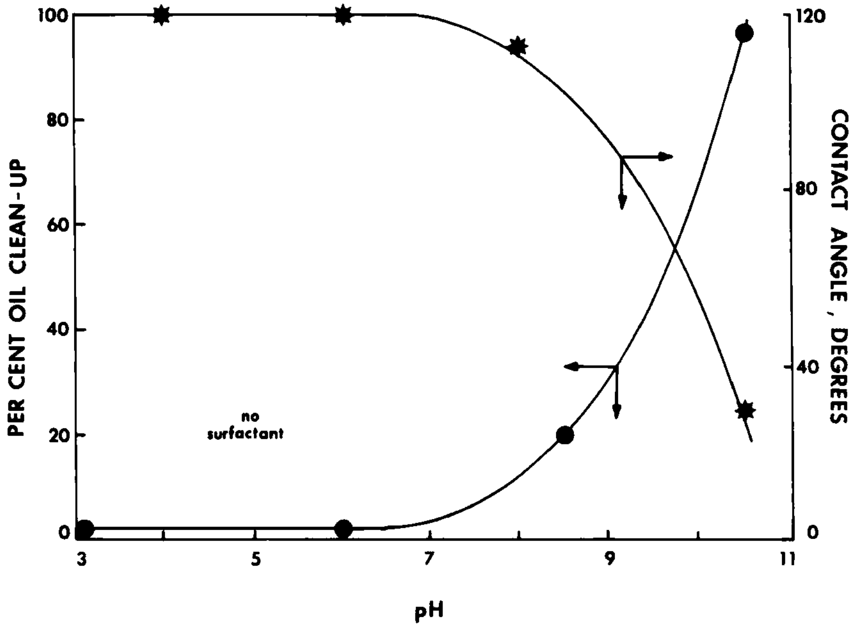


FIGURE16
The dependence of the contact angle and the percent oil clean-up on changes in the aqueous phase pH. (From C. Lau[36]).

water addition to the coal liquid stream which are not inherent to gas/liquid flotation. These problems include the additional water/solids separation step and the need for a higher operating pressure (to provide for a liquid water phase).

As with the previous gas/liquid flotation work, several research areas remain to be explored.

1. Combination of the pH and surfactant effects. A synergistic relationship or tradeoff may exist.
2. Experimentation at higher temperatures more closely approximating those likely to be found in the solid/liquid separation step of a coal liquefaction process.

3. Verification of the measurement percent oil phase clean-up. As presently defined, it may only represent the removal of particles above a certain size range.

D. Particle Distribution

Particle distribution is an example of separation regime (II), distribution of a particle from one liquid phase to another. Separations of this type have normally been limited to the separation of cell particles and macromolecules[38], however, the potential for large scale application exists. As such, exploratory experiments, utilizing surfactants, were performed on a coal derived liquid (Synthoil) using an aqueous phase as the receiving phase[39]. These experiments involved batch contacting of the coal oil and aqueous phase at elevated temperatures followed by batch electrostatic coalescence of the resulting water-in-oil emulsion. The best solids recovery in the liberated water phase represented only four percent of the solids originally in the Synthoil.

Batch experiments were also performed at room temperature using model oil streams[40]. Up to 100 percent particle distribution was obtained in these systems. The major purpose of the model system work was to elucidate the action of added surfactants in a system containing asphaltic coated mineral matter particles. Toward this end, benzene extracted Synthoil mineral matter particles were used. Xylene was most often used as the model oil phase in order to allow the characteristics of the particle surface to dominate the distribution behavior of the system. This mechanistic work is summarized below. The observations made apply equally well to surfactant action both in liquid/liquid interfacial collection and particle distribution.

1. Fate of the Surfactant

Five asymptotic mechanistic models based on the fate of the surfactant at long time were studied[41]. Surfactant effects modeled include adsorption onto the particle surface, adsorption at the oil/water interface, distribution of the surfactant itself into the bulk aqueous phase, complete detergent removal of the asphaltic layer, and partial detergency. These models were compared with data from batch experiments in which mixing time, mixing speed, surfactant concentration, and water/oil ratio were varied. The partial detergency model was the only model which explained all of the parameter dependences observed in the experimental system.

The partial detergency model itself (Figure 17) includes several phenomena. The surfactant first adsorbs onto the asphaltic

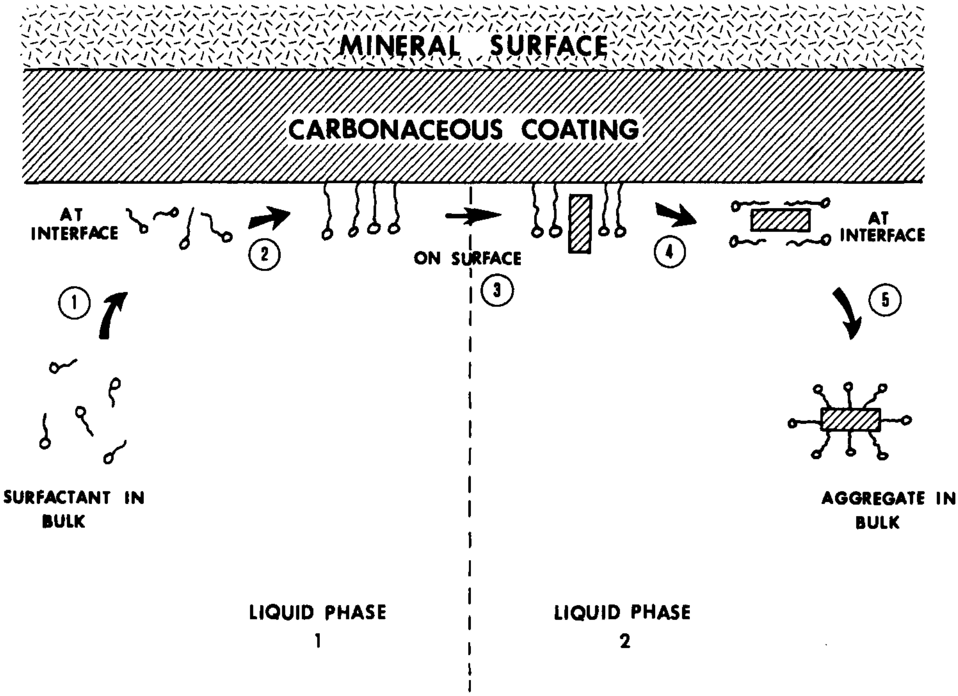


FIGURE 17
Phenomenological model of solubilization detergency: 1-diffusion of the surfactant from the bulk liquid to the particle surface, 2-adsorption of the surfactant onto the surface, 3-surface reaction, 4-desorption of the surfactant-carbonaceous matter aggregate from the surface, 5-diffusion of the surfactant-carbonaceous matter aggregate into the bulk liquid phase.[40]

coating of the particle, making it hydrophilic. Upon contact of the particle with the aqueous phase, detergency occurs. The surfactant is lost to the surface as a result of this detergency and more of the hydrophobic, asphaltic surface is exposed. This accounts for the experimentally observed decrease in the distribution coefficient, defined as the concentration of mineral matter in the aqueous phase divided by the concentration of mineral matter in the oil phase, with increasing time (Figure 18).

2. Aqueous Phase pH

As with the reverse liquid/liquid flotation work[33], the model system studies for particle distribution showed an increase in separation efficiency with increasing aqueous phase pH (Figure 19).

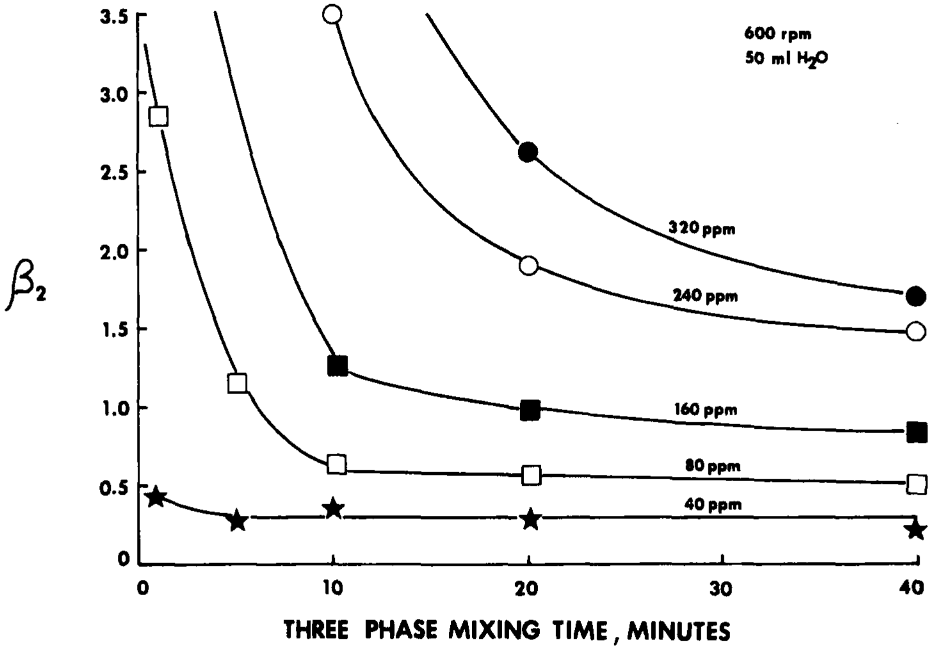


FIGURE 18
The distribution coefficient, β_2, versus mixing time.[40]

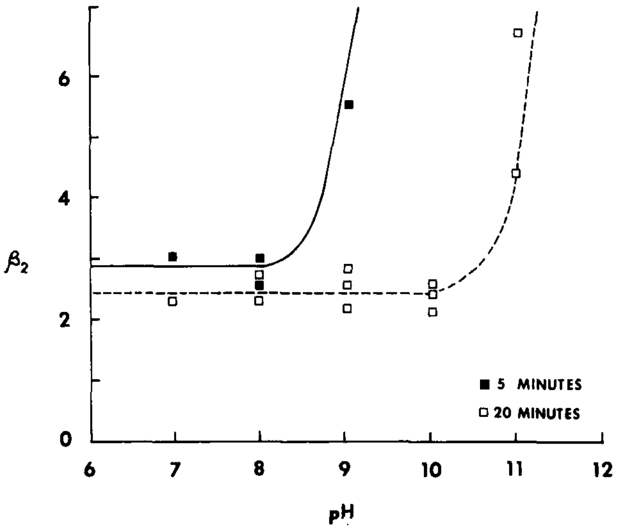


FIGURE 19
Effect of pH on the distribution coefficient, β_2.[40]

E. Summary

The application of surface-based separation techniques to solids separation from coal derived liquids is still in its infancy. Promising results have been shown. More time and work will be required before a final evaluation can be made as to the relative merits and faults of these separation techniques.

V. CONCLUSIONS

Several novel techniques for application to the problem of solids removal from coal derived liquid product streams have been presented. Obviously, the implimentation of these techniques is closer to fruition for some than for others. It is not the purpose of this paper to favor one separation scheme over any other. It is hoped that this presentation will acquaint the reader with work presently under way in this field.

VI. SYMBOLS USED

C/H	carbon-to-hydrogen atomic ratio
F	Force term (Figure 7)
F''_{II-I}	nondimensionalized change in free energy from state II to I
g	gravitational constant
n	radii ratio of solid to liquid
r	radius
S/O	anti-solvent/oil ratio (volume basis)
U_o	reference settling velocity
U_t	initial settling velocity
V_i	volume of phase i

GREEK LETTERS

β_2	distribution coefficient (water/oil)
γ_{ij}	interfacial tension between phases i and j
δ	solubility parameter
ρ_i	density of phase i
θ	three phase contact angle

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