FINAL REPORT

ADVANCED SYSTEMS FOR PRODUCING SUPERCLEAN COAL

by

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EXECUTIVE SUMMARY

The purpose of this project was to develop several advanced separation processes for producing superclean coal containing 0.4-2.0% ash and very little pyritic sulfur. Three physical and physico-chemical processes were studied, i.e.,

- microbubble flotation,
- selective hydrophobic coagulation,
- electrochemical coal cleaning.

The first two, i.e., microbubble flotation and selective hydrophobic coagulation, require that the feed coal be pulverized to micron sizes for mineral matter liberation while the third, electrochemical coal cleaning, does not.

In this investigation, fundamental information has been collected from bench-scale experiments in order to determine the basic mechanisms of all three processes. Additionally, because microbubble flotation has already been proven on a bench scale, preliminary scale-up models have been developed for this process. A fundamental study of the electrochemistry of coal pyrite has also been conducted in conjunction with this scale-up effort in order to provide information useful for improving sulfur rejection.

As a result of this work, fundamental information is now available for future pilot-scale testing of each of the proposed coal cleaning processes. Microbubble flotation has proven to be the most viable of the three processes, followed by electrochemical coal cleaning and selective hydrophobic coagulation, both of which will require additional work to determine their commercial viability.

INTRODUCTION

In the face of volatile energy costs, dwindling energy resources and increased environmental concerns, it has become increasingly more important to

utilize the vast U.S. coal reserves to the greatest extent possible. Recent studies indicate that the U.S. possesses 483 billion tons of economically mineable coal reserves. This is equivalent to more than two-and-one-half times the known world oil supplies. Yet, the U.S. is a net importer of approximately 50% of its oil needs. When considered in light of the total U.S. trade picture, this amounts to nearly half of the U.S. trade imbalance (Ingersol-Rand, 1984). Clearly, development of these vast coal reserves would not only help the U.S. achieve energy independence, but would improve economic conditions and greatly help a depressed domestic coal industry.

In the past, oil has had the advantage of being a convenient, clean and relatively inexpensive fuel source. In recent years, however, a great deal of interest has been generated in the production of gaseous and liquid forms of coal, including coal-water mixtures (CWM), which could be used as substitute fuel sources in utility plants and industrial boilers. The Department of Energy estimates that approximately 4.8 million bbl/day of oil, about 25% of the total daily domestic consumption, could be saved if oil-burning boilers were converted to coal (Green, 1982). It appears that CWM technology is well advanced in terms of producing stable, low-viscosity suspensions with maximum coal loading. The major problem that remains, however, is that the coal used as a feedstock for CWM contains much larger amounts of impurities than does fuel oil. This factor, combined with the politically sensitive acid rain issue, appears to be a major handicap for CWM in its competition with oil. If the impurities in coal can be reduced to the levels present in oil, however, CWM could be an excellent fuel source, costing substantially less than oil.

To produce CWM having impurity levels comparable to oil, superclean coal (i.e., containing < 2% ash) must be used as the feedstock. Unfortunately, very few coals can be directly utilized as feedstocks for CWM. Most coals must be cleaned to reduce their ash content to the desired level.

In producing superclean coal, both chemical and physical coal cleaning techniques are employed. While chemical processes can be very efficient, the operating costs tend to be prohibitively high and some of them generate toxic wastes. Therefore, a significant amount of attention is being given to the development of advanced physical coal cleaning techniques. The major advantage of a physical coal cleaning technique is that the operating costs are intrinsically less than those of a chemical process, although the ash and sulfur removal may not be as efficient. By incorporating a mild chemical process with a physical separation technique, however, it may be possible to improve the ash and sulfur rejections of the physical process without substantially adding to the cost.

Physical processes for producing superclean coal require that the feed coal be micronized prior to separation in order to liberate the mineral matter. This may require grinding to sizes of 5 μm or less. Unfortunately, grinding to these fine sizes can be a significant part of the expense in the physical separation processes. Much effort has been devoted in the past several years to the study and development of novel size reduction techniques, such as ultrasonic grinding and attrition grinding, which could result in much lower energy costs for producing micronized coal. Additional work is needed, however, to further reduce the energy consumption. In addition, a detailed liberation analysis of coal would be very useful in determining the extent of grinding required for sufficient liberation of mineral matter.

Once the mineral matter has been sufficiently liberated, the micronized coal must be recovered. Unfortunately, micronized coal is difficult to process using any of the conventional physical coal cleaning techniques. While froth flotation is generally recognized as the best method of beneficiating fine coals (Fourie, 1977), it becomes less efficient in making a clean separation as particle size is decreased (Trahar and Warren, 1976; Fuerstenau, 1980). Many investigators have shown from hydrodynamic analyses

that the inefficiency of fine particle flotation can be partly attributed to the fact that the air bubbles generated in conventional flotation machines are too large to capture small particles (Flint and Howarth, 1971; Reay and Ratcliff, 1973; Collins and Jameson, 1976; Anfruns and Kitchener, 1977).

Waste treatment engineers have long realized that smaller bubbles are required for the flotation of ultrafine particles, and have actively utilized techniques such as vacuum flotation, dissolved air flotation and electro-flotation. Bubble sizes in these operations are generally no larger than 200 μm , whereas the top size of bubbles used in conventional mineral separations are usually larger by at least an order of magnitude.

In 1980, the contract's PI's started using bubbles having diameters of 300-400 μm for the flotation of coal, and termed the process *microbubble flotation*. They demonstrated that the benefits of using microbubbles could be found both in recovery and in selectivity (Yoon et al., 1984) and, under DOE's AR & TD University Coal Research Program (FG22-80PC30234 and FG22-83PC60806), developed microbubble flotation to the point where bench-scale testing could begin. Preliminary results showed that some coals can be cleaned to less than 0.4% ash with high recovery.

More recently, the group has developed a process called *selective hydrophobic coagulation*. In this process, ultrafine coal particles are coagulated by a hydrophobic interaction which has recently been recognized as an important surface force. The flocs (or coagula) are then removed from the dispersed ash particles by simple sedimentation or by elutriation. Of the two, it has been found that elutriation is a better route to producing superclean coal.

While microbubble flotation and selective hydrophobic coagulation provide efficient means of producing superclean coal, they do have the distinct disadvantage, as do all other physical separation processes, of

requiring a micronized feed coal. Since the energy costs associated with fine grinding can be substantial, and since fines can contribute significantly to subsequent handling and dewatering problems, a method of producing superclean coal using a coarser sized feed would be desirable.

For this reason, a third process has been developed to produce superclean coal via an entirely new concept. This process involves the electrolysis of coal in an acidic medium, during which ash-forming minerals are liberated into solution. The liberated ash can then be removed from the processed coal by a simple technique such as washing on a screen. Thus, the electrochemical coal cleaning process has the distinct advantage that coals can be cleaned without fine grinding. It also removes pyrite by an electrochemical dissolution mechanism. In fact, the presence of a small amount of pyrite helps remove the ash from coal. Previous work (Yoon and Paul, 1984) shows that a variety of coals can be cleaned to less than 1 or 2% ash.

All three of these processes are proprietary to Virginia Tech and are the subjects of patents and/or patent applications.

CONTRACT OBJECTIVES

The main objective of this contract was to further develop these processes, and/or a combination of these processes, to the point where their suitability for the production of superclean coal (containing 0.4-1.0% ash and very little sulfur) from a wide range of different coals could be established.

It was also an objective of this contract to gather fundamental information for processing fine coal and to distribute the findings to the industrial and the scientific communities through publications and formal reports.

TASK 1: GRINDING/LIBERATION STUDY

Introduction

As with all physical separation techniques, the microbubble flotation and selective shear coagulation processes require that the coal be finely pulverized in order to sufficiently liberate ash-forming mineral matter and pyrite. Although the degree of liberation is rarely well quantified for most coals, recent investigations by Mathieu and Mainwaring (1986) have suggested that grinding to sizes of 5 μm or less is required for adequate liberation. Unfortunately, grinding to these sizes by conventional ball milling requires a very long retention time and a high energy input.

A number of studies carried out in recent years suggest that stirred ball milling may be superior to conventional ball milling for producing ultrafine particles (Herbst and Sepulveda, 1978; Davis et al., 1980). The advantages of stirred ball milling, as reported in these articles, include improved energy utilization and faster grinding kinetics. Sepulveda (1981), for example, demonstrated an energy savings greater than 60% for the micronizing of a Lower Freeport seam coal using a stirred ball mill.

Recent work at Virginia Tech has shown that the size of the grinding media used in stirred ball milling can greatly affect grinding kinetics (Brown, 1986; Mankosa et al., 1986), with the optimum breakage rate occurring at a ball/particle diameter ratio of 20:1. Test work has shown that a 5- μm mean product size can be obtained for as little as 70 kwh/ton if 1/16-inch grinding media is used in the stirred ball mill. This is nearly an order of magnitude less than what would be required in a conventional ball mill to achieve the same product size. Continuing research at Virginia Tech indicates that a proper manipulation of operating conditions can further reduce energy consumption in fine coal grinding. Experimental studies on the effect of

stirring speed (Brown et al., 1984) suggest that low stirring speeds (200-300 rpm) are more energy efficient than high stirring speeds (600-800 rpm). Finally, the solids content seems to be very important in fine coal grinding when slurries in excess of 50% solids are used. Experiments conducted at 20 and 43% solids showed very little effect on the final size distribution produced by the mill. However, tests conducted at 50% solids or higher showed a significant reduction in the efficiency and size reduction capability of the stirred ball mill. These results suggest that viscosity-reducing reagents may significantly improve the performance of the stirred ball mill. Additional study of the stirred ball milling operation may make it possible to reduce the energy consumption further and provide an economical means for producing micronized coal.

Task 1.1.1: Fine Grinding

All tests completed under this task were conducted using a 5-inch diameter stainless steel stirred ball mill which was constructed for a previously funded Department of Energy project (DE-FG22-83PC60806). A schematic of this equipment is shown in Figure 1.1. The mill was equipped with a torque sensor from which energy input to the mill could be monitored. The coal sample used in the test work was a bituminous coal obtained from the Elkhorn No. 3 coal seam in southwestern Virginia.

a. Effect of Grinding Aids

A series of grinding experiments were conducted at various grinding aid additions and a constant specific energy input of 94 kwh/ton. In each test, the feed pulp density was adjusted to 50% solids, and a stirring speed of 330 rpm was employed. Figure 1.2 shows the mean product sizes obtained at various reagent additions for sodium silicate, Dow XDR and Lomar-D. As shown, Lomar-D was the most effective grinding aid for this particular coal sample. By adding 10 lb/ton of Lomar-D, the mean product size could be reduced from 7.8

Figure 1.1 Schematic representation of the stirred ball mill and drive used in the present work.

Figure 1.2 Effect of grinding aid addition on the mean product size at a constant energy input of 94 kwh/ton for stirred ball milling of Elkhorn No. 3 seam coal.

to 4.2 μm with the same energy input. The Dow XDR reagent produced similar results to Lomar-D, although higher dosages were generally required to achieve the same level of performance. Sodium silicate appeared to show little effect even at dosages as high as 50 lb/ton.

The improvement in grinding efficiency with the addition of various grinding aids can be explained by change in mill power draw. As shown in Figure 1.3, the addition of Lomar-D can produce a reduction in the torque requirement up to 25%. This appears to be a result of a decrease in slurry viscosity, rather than a reduction of the surface free energy as suggested by the Rebinder theory (Rebinder, 1931; Rebinder et al., 1940). With each increase in reagent addition, the region of constant torque input is extended. As grinding proceeds, the particle size in the mill is continually reduced. This requires that higher reagent additions be utilized in order to maintain the same viscosity within the mill. Beyond a certain critical size, the reagents are no longer capable of maintaining the viscosity, and the torque readings (i.e., energy requirements) begin to increase. Thus, the major role of the grinding aid appears to be that of a viscosity modifier.

b. Effect of Media Type

A major part of the energy requirement for stirred ball milling involves stirring and lifting of the ball charge itself. Therefore, one might expect a lower energy consumption if the density of the grinding media can be reduced without significantly affecting the grinding performance. In order to test this possibility, grinding experiments were conducted with steel and glass media to determine whether changes in media density would impact grinding performance.

Figure 1.4 shows a comparison between the performance of steel and glass media over a range of media sizes. In this comparison, tests were conducted at a pulp density of 30% solids and a stirring speed of 330 rpm. A relatively

Figure 1.3 Effect of grinding aid addition on torque draw for stirred ball milling of Elkhorn No. 3 seam coal.

Figure 1.4 Effect of media type on grinding rate for stirred ball milling of Elkhorn No. 3 seam coal.

low energy input of 8.5 kwh/ton was used in each test. The grinding performance was measured by the percent of monosized feed remaining in the mill after 8.5 kwh/ton of energy input. As shown, steel balls were found to be more efficient than glass balls. This result was contrary to the original expectation that low-density media would provide an improvement in grinding performance. This finding suggests that the mass of the individual grinding media is important in determining the attrition force operating in the mill.

c. Effect of Stirring Speed

The effect of stirring speed on the product particle size distribution was determined by conducting a series of tests at equal energy input while varying the speed of the impeller. Two sets of tests were conducted at specific energy inputs of 63.5 and 94 kwh/ton, respectively. The pulp density was held constant at 43% solids by weight. A ball mixture consisting of equal weights of 1/4-, 1/8- and 3/32-inch balls was used for this series of experiments.

The test results presented in Figures 1.5 and 1.6 indicate that slower stirring speeds are more energy efficient in stirred ball mill grinding. This effect is more pronounced at high energy inputs when very fine micronization is desired. A possible explanation for the changes in grinding performance with stirring speed may be that the breakage mechanism changes as the stirring speed changes. At low speeds, the media are moving in the mill in a gentle rolling action which allows particles to be trapped between balls and crushed in compression. This mechanism may be much like particles crushed in a roll mill. However, as the stirring speed is increased, the grinding action becomes more violent and particles break by impaction from the media. At the higher speeds, a significant amount of energy is lost during the collision between media. These findings are in agreement with suggestions by Schonert (1988) that breakage by slow compression is more efficient than impact.

Figure 1.5 Effect of stirring speed on product size distribution at a constant energy input of 65 kwh/ton for stirred ball milling of Elkhorn No. 3 seam coal.

Figure 1.6 Effect of stirring speed on product size distribution at a constant energy input of 94 kwh/ton for stirred ball milling of Elkhorn No. 3 seam coal.

breakage. Thus, low-speed stirred milling should result in more efficient use of energy in the fine grinding of coal.

The effect of high-speed attrition grinding was also studied by conducting a series of tests in an attrition scrubber that has been shown to be very efficient for grinding soft materials (such as clay) to very fine sizes. A comparison between the standard stirred ball mill and the high-speed attrition scrubber is shown in Figure 1.7. In order to normalize the effect of ball size, the standard Charles' plot has been modified by plotting energy consumption versus dimensionless particle/ball diameter. The data indicates that the energy consumption required to micronize the coal was an order of magnitude higher for the attrition scrubber than for the stirred ball mill. In addition, the data confirm an earlier conclusion that smaller balls can significantly reduce the energy of micronization (Mankosa et al., 1986). The data demonstrate that by decreasing the ball size by half, the energy requirement can be reduced by approximately one order of magnitude for either the attrition scrubber or the stirred ball mill. This is a tremendous incentive for using small media to micronize coal.

The data shown in Figure 1.7 also indicate that the amount of energy required to produce a specific product size appears to be independent of media type. For this reason, it may be desirable to use nonferrous media that is significantly less expensive. One disadvantage, however, is that a longer period of grinding is required to achieve the same energy input with the lighter nonferrous media. Another disadvantage is that the wear rate appears to be higher for the nonferrous media. In some cases, the noncombustible material in the coal more than doubled when ceramic or glass media was used.

Task 1.1.2: Liberation Analysis

The overall objective of fine grinding is to liberate ash- and sulfur-bearing mineral matter from the coal matrix. Unfortunately, only a limited

Figure 1.7 Specific energy input versus normalized product size/ball diameter ratio for various types and sizes of grinding media.

amount of data has been published in recent years concerning the liberation characteristics of various coal types. In the present work, liberation studies have been conducted to establish proper guidelines for fine coal grinding, to estimate the ultimate limits for physical cleaning, and to characterize the various feed and product streams from the various processes under investigation in the present work.

Liberation data are typically obtained from the microscopic examination of polished particle mounts. A number of techniques are available to determine the amount of a given mineral contained in a composite particle. These include linear intercept methods (Rosiwoj, 1898), area tracing methods (Delesse, 1848), and point counting methods (Thompson, 1930). More recently, advances in computerized image analysis have made it possible to gather more detailed information on the distribution of free and composite particles. A software package called GIPSY (General Image Processing System) has been used extensively at Virginia Tech for making area-based liberation measurements (Craig et al., 1982). To complement this existing system, another automatic image analysis system developed by Kontron (SEM-IPS) has recently been installed in the coal preparation/mineral processing laboratory at Virginia Tech. This system is one of the most advanced image analysis systems available today and can be interfaced to a scanning electron microscope or a petrographic microscope.

Along with the recent advancement in image processing technology has come an increased effort to understand and quantify the liberation process during comminution. A simple model for liberation was first proposed by Gaudin (1939) and later modified by Wiegel and Li (1967). With the advent of image processing equipment, King (1979) developed a model relating the distribution of linear intercept lengths through mineral grains in an ore to the fractional liberation of those minerals. More recently, a Monte-Carlo simulation technique has been used in modeling the liberation of mineral matter from coal

(Klimpel and Austin, 1983; Bagga and Luckie, 1983).

Any of the above models can be used to quantify the extent of liberation for a given grind, but for the purposes of simulating actual grinding processes, a combined model for size reduction and mineral liberation is required. A few attempts have been made to simultaneously account for liberation and breakage during comminution (Andrews and Mika, 1975; Wiegel, 1976; Ruebush et al., 1980). The major limitation in using these models, however, has been the difficulty in estimating the necessary breakage parameters for composite particles.

A combined size reduction and liberation model has been developed at Virginia Tech for use in predicting the complete size/mineral content distribution from a grinding mill on the basis of the image analysis data of the feed material. The model development and experimental determination of breakage parameters is described elsewhere (Choi et al., 1985, 1987). For mineral systems, excellent agreement between computer-simulated and experimental results has been obtained. With this model, the size distributions of the ash-forming minerals, pyrite and each maceral can be predicted. For this to be possible, the breakage and liberation parameters have to be determined by extensive image analysis work. The usefulness of such a comprehensive model is that one can predict the washability behavior of coal as a function of particle size for both ash and pyrite. In addition, one can predict the changing maceral compositions with particle size, which is very useful information for blending and coke making.

a. Characterization of Coals

The spatial distribution of the pyrite and mineral matter contained in the various coals used in this study has been examined with a Zeiss ICM 405 optical microscope interfaced to an image processing system (Kontron SEM-IPS). Coal samples from the Cedar Grove and Elkhorn No. 3 seams in Virginia, the

Upper Freeport seam in Pennsylvania, and the Pittsburgh No. 8 seam in Ohio have been analyzed.

The various coal samples were prepared by grinding each coal to minus 100-mesh followed by screening to obtain the desired size fractions. The samples examined in this study included 100x200, 200x270 and 270x400 mesh size fractions. The powdered samples were mounted in epoxy briquettes and polished prior to examination. The image processing system was used to determine the areal fraction of a given constituent (i.e., coal, mineral matter or pyrite) in each coal particle. The areal fraction provides a measure of the volume fraction of a given constituent present in the coal.

The results of the image analysis characterization of the four minus 100-mesh coals studied in this investigation are shown in Figures 1.8-1.11. In general, it can be seen that a large portion of the mineral matter present in each coal is liberated, in contrast to the pyrite which largely occurs in the composite form. The Pittsburgh No. 8 and Cedar Grove seam coals both show increasing amounts of free pyrite and mineral matter in the finer size fractions. A similar trend can be seen for the pyrite in the Elkhorn No. 3 coal, although the mineral matter distribution appears to remain nearly constant with size. In the case of the Upper Freeport coal, both the mineral matter distribution and the pyrite distribution remain nearly constant with size, indicating that the pyrite and mineral matter in this sample are relatively finely disseminated.

A better overview of the characterization of these samples is shown in Figures 1.12 and 1.13 in terms of overall degree of liberation for mineral matter and pyrite. In this work, the degree of liberation refers to the weight percent of a given component that appears as free particles (Gaudin, 1939). A locking factor of unity has been assumed for all composite particles. As shown in Figure 1.12, the degree of liberation for mineral

Figure 1.8 Degree of liberation of mineral matter and pyrite in various size fractions of Pittsburgh No. 8 seam coal.

Figure 1.9 Degree of liberation of mineral matter and pyrite in various size fractions of Cedar Grove seam coal.

Figure 1.10 Degree of liberation of mineral matter and pyrite in various size fractions of Elkhorn No. 3 seam coal.

Figure 1.11 Degree of liberation of mineral matter and pyrite in various size fractions of Upper Freeport seam coal.

Figure 1.12 Overall degree of liberation of mineral matter in minus 100-mesh samples from various coal seams.

Figure 1.13 Overall degree of liberation of pyrite in minus 100-mesh samples from various coal seams.

matter in minus 100-mesh Elkhorn No. 3 coal is nearly 70%. This is substantially greater than any of the other coals studied. This is not surprising since it is routinely possible to produce coal containing less than 2% ash at 90% combustible recovery using the MCF process on Elkhorn No. 3 seam coal. The remaining coal samples show mineral matter liberation of approximately 30-40%, with the Pittsburgh No. 8 seam coal having the higher value.

Pyrite liberation, on the other hand, is quite low at this size, as shown in Figure 1.13. Once again, the Elkhorn No. 3 seam coal shows the highest degree of liberation at approximately 15%, while the Cedar Grove coal shows a pyrite liberation of just 2%. It should be noted, however, that both of these samples contain very little pyrite. Of the two high-sulfur coals, the Pittsburgh No. 8 sample has the higher degree of liberation at approximately 10%, while the Upper Freeport has only 5% liberated pyrite at the minus 100-mesh size.

The back-scattered scanning electron microscope images of the four coal samples analyzed here are shown in Figure 1.14. Since these photographs were all taken at the same magnification, this figure illustrates quite clearly that the Upper Freeport and the Pittsburgh No. 8 coal samples have much more finely disseminated mineral matter than do the Cedar Grove or Elkhorn No. 3 samples. In fact, most of the mineral matter present in the Elkhorn No. 3 coal exists as large discrete particles which can be easily removed by physical separation processes. These results demonstrate that fine grinding will be required in order for the advanced physical coal cleaning processes outlined in the present work to be effective. This is particularly true when sulfur reduction is desired, since pyrite was found to be difficult to liberate.

Upper Freeport

Pittsburgh No. 8

Elkhorn No. 3

Cedar Grove

Figure 1.14 SEM photomicrographs of back-scattered electron images of minus 100-mesh samples from various coal seams.

b. Breakage Behavior of Macerals and Minerals

The effectiveness of any physical coal cleaning process is highly dependent on the degree of liberation of the feed coal. For example, finely disseminated mineral matter in the feed coal matrix will often result in a high ash content in the product. Pyrite, in particular, often occurs as submicron-sized framboids in the coal matrix. In addition, many coal cleaning processes are affected by maceral content of the feed coal, which can control the coal's grindability, reactivity, floatability, etc. The purpose of this task is to characterize the liberation of macerals and mineral matter during comminution, and to determine the effect of liberation on the coal cleaning processes being studied under this contract.

The procedure being used to characterize mineral and maceral liberation from coal is the same as that which was developed at Virginia Tech for characterizing mineral liberation from ores (Choi et al., 1985, 1987). With this approach, a narrow size fraction of coal is ground in a batch-operated ball mill (10-inch diameter) for a short time period, usually less than 10 minutes. The mill product is then removed, separated into size fractions, mounted in epoxy briquettes, polished, and examined with an optical microscope (Zeiss ICM 405) which is connected to an automatic image analysis system (Kontron SEM-IPS). Each of the briquettes is placed on a computer-driven scanning stage and a series of images are digitized from the microscope and then discriminated on the basis of grey level for each maceral and mineral component.

One source of error with this procedure lies in the determination of exinite. The procedure tends to lump the pits in the sample surface, the holes in the fusinite structure and some mineral matter into the measurement of exinite. As a result, the exinite value is overestimated and the fusinite value is slightly underestimated. Because of this difficulty, a semi-automated technique has been developed that allows user interaction with the

program to measure these components. A comparison of the data obtained from these two procedures is provided in Table 1.1 for a 28x35 mesh Taggart seam coal cleaned at a specific gravity of 1.3. The image analysis system determines the areal fraction of a given maceral constituent in each coal particle. This areal fraction can then be used directly as the volume fraction of a given maceral constituent, or it can be related to the volume fraction through the use of appropriate transformation functions. This has not been done here.

The coal sample used in this work was from the Taggart seam in Virginia. The coal was cleaned to approximately 2% ash and very low sulfur. The cleaned coal was hammer-milled and dry-screened at various sizes to produce monosized feeds of 10x14 mesh, 14x20 mesh, 20x28 mesh and 28x35 mesh for the grinding tests. Preliminary estimates of breakage rates for several of the macerals present in the 10x14 mesh sample were determined from a semi-log plot of the fraction of each group remaining as a function of time, i.e., the standard first-order disappearance plot (Herbst and Fuerstenau, 1968). The groups were classified as free inert (fusinite and semifusinite), free reactive (vitrinite and exinite) and composite. Mineral matter was not considered in this analysis since the coal had been cleaned to below 3% ash prior to the grinding tests. The breakage rates for each of these groups, along with the percentage distribution of each group as grinding proceeds, are shown in Table 1.2. As can be seen, the free inert macerals and composite particles tend to grind faster than the free reactive macerals. As a result of the different breakage rates, there is a preferential concentration of reactive macerals in the 10x14 mesh size class as grinding proceeds. Since inert macerals are known to be more difficult to float than reactive macerals, the implication of these data is that a large portion of the poorly-floating fine fraction may consist of inert macerals.

Table 1.1

Comparison of Image Analysis Results for Taggart Seam Coal

Component	Semi-Automatic (Volume %)	Automatic (Volume %)
Pyrite	Trace	Trace
Fusinite	4.4	3.2
Semifusinite	0.7	1.1
Vitrinite	92.4	91.6
Exinite	2.0	4.1
Mineral Matter	0.5	Trace

Table 1.2

Breakage Rates for Various Maceral Groups for Taggart Seam Coal

Group	Feed	Grind Time (min)			Breakage Rate (min ⁻¹)
		1	2	4	
Free Reactive	87.7	88.0	91.2	91.8	0.83
Free Inert	1.2	1.3	1.0	0.2	--
Composite	11.0	10.7	7.0	7.5	0.92

Table 1.3 shows the maceral composition of the 14x20 mesh feed before and after grinding for 4 minutes in a 10-inch ball mill. The Taggart seam coal contains a high proportion of reactive macerals (i.e., vitrinite and exinite) and a minor concentration of the unreactive inertinite. As shown, a substantial portion of the reactive macerals are already in a liberated form (79.1% for free vitrinite and vitrinite/exinite). It is interesting to note that after four minutes of grinding, the percentage of free reactive material increased to 81.1%, while that of the maceral composites decreased. After a longer grinding time, the liberation of reactive macerals would have been more significant.

The pyrite size analysis of the monosized 28x35 mesh Taggart seam coal is shown in Table 1.4. The mean equivalent diameter of pyrite grains was found to be approximately 8.4 μm . Thus, it is necessary to grind the coal to below this size in order to substantially liberate the pyrite. However, some of the pyrite occurs as framboids, the size of the individual grains being approximately 0.35 μm . In any case, this data indicates that very fine grinding will be required in order to completely liberate the finely disseminated grains of pyrite from the coal matrix.

c. Combined Size Reduction/Liberation Model

The concepts of breakage of a binary mineral system with respect to both size and mineral content are schematically illustrated in Figure 1.15. This diagram considers the breakage of A, B and AB type particles. For the case of coal, type A can be considered as free coal, type B as free mineral matter and type AB as composite particles of mineral matter and coal. Free A and B particles are represented by a simple size reduction process. The breakage of AB particles, on the other hand, must include liberation to A, B and any of several classes of composite AB combinations, in addition to simple size reduction within the same AB class. Conceptually, therefore, it is possible

Table 1.3

Petrographic Composition of the 14x20 Mesh Taggart Seam Coal
Before and After Grinding for Four Minutes in a Ball Mill

Maceral Group*	Free		Locked				
	V	F&SF	V+E	V+F+E	V+SF+E	V+F+SF+E	V+SF
Before Volume (%)	41.6	1.1	37.5	3.0	13.7	3.0	0.2
After Volume (%)	42.6	0.9	38.5	1.7	13.2	2.7	0.3

*V: Vitrinite; F: Fusinite; SF: Semifusinite; E: Exinite

Table 1.4

Pyrite Size Distribution for the 28x35 Mesh Taggart Seam Coal

Particle Size (Microns)	Cumulative Percent Finer
1.16	0.4
1.74	1.6
2.32	2.5
3.47	5.6
4.62	18.5
6.98	30.5
9.25	56.0
13.88	100.0

Figure 1.15 Schematic representation of the breakage/liberation of coal and mineral matter.

to consider the change in the amount of material of any type and size to be represented by two processes: size reduction and liberation.

Using the above approach, a grinding model has been developed which accomodates liberation. Considering separately the breakage and production of A, B and multiple classes of AB type particles, the matrix form of the mass balance model for batch grinding becomes:

$$\frac{d\hat{M}_a}{dt} = (\underline{B}_a - \underline{I})\underline{S}_a\hat{M}_a + \underline{L}_a \sum_{i=1}^J (\underline{S}_{ab,i}\hat{M}_{ab,i}) \quad [1.1]$$

$$\frac{d\hat{M}_b}{dt} = (\underline{B}_b - \underline{I})\underline{S}_b\hat{M}_b + \underline{L}_b \sum_{i=1}^J (\underline{S}_{ab,i}\hat{M}_{ab,i}) \quad [1.2]$$

$$\frac{d\hat{M}_{ab,j}}{dt} = (\underline{B}_{ab,j} - \underline{I})\underline{S}_{ab,j}\hat{M}_{ab,j} + \sum_{\substack{i=1 \\ i \neq j}}^J (\underline{L}_{ab,j-i}\underline{S}_{ab,i}\hat{M}_{ab,i}) \quad [1.3]$$

where the variables are defined as:

$\hat{M}_a, \hat{M}_b, \hat{M}_{ab,j}$ = mass fraction of particle type A, B, or AB_j contained in each size class.

$\underline{B}_a, \underline{B}_b, \underline{B}_{ab,j}$ = breakage distribution matrix for A, B, or AB_j type particles (i.e., the fraction of primary breakage product of type A, B, or AB_j reporting to each size class).

$\underline{S}_a, \underline{S}_b, \underline{S}_{ab,j}$ = selection function (breakage rate) matrix for A, B, or AB_j type particles (i.e., the rate at which material breaks out of each composition class).

$\underline{L}_a, \underline{L}_b, \underline{L}_{ab,j-i}$ = liberation distribution matrix for A, B, or AB_j type particles (i.e., the fraction of primary breakage product of type AB_j which liberates into another size and composition class).

i, j = a specific composite particle class.

J = total number of composite particle classes.

In Equations [1.1] and [1.2] describing the breakage of free particles, the first term in each equation represents appearance and disappearance in

each size class due to breakage, and the second term represents appearance in each size class due to liberation from composite particles. The same terms can also be found in Equation [1.3] representing the fate of the composite particles, i.e., the first term describes appearance and disappearance due to breakage and the second term describes appearance due to liberation. Thus, all possible changes in size and mineral content are accounted for by these equations. Furthermore, it should be noted that when only one class of composite particles is considered, the $L_{ab,j \leftarrow i}$ terms drop out and the above three equations reduce to the form described in published reports (Choi et al., 1985, 1987).

Equation [1.3] can actually be considered as the basis for a general form of the entire model. For example, by considering free A and B particles as extreme cases of the AB composite class, Equation [1.3] can be modified to give:

$$\frac{d\hat{M}_k}{dt} = (B_k - I)S_k\hat{M}_k + \sum_{\substack{i=2 \\ i \neq k}}^{K-1} L_{k \leftarrow i} S_i \hat{M}_i \quad [1.4]$$

which encompasses all cases in one matrix equation. In this representation, k is the specific mineral content class out of a total of K classes. All other terms are as defined previously.

The determination of breakage parameters for the above model is a significant task. With the advent of modern image analysis equipment, however, direct determination of many of the model parameters from experimental data is no longer beyond the realm of possibility. The basic approach used in this investigation has been to directly measure as many of the parameters as possible using the technique of batch grinding monosized feeds (Herbst and Fuerstenau, 1969). Breakage rate functions for all components and breakage distribution functions for the two free components can

be determined in this manner. Furthermore, by using image analysis it is not necessary to separately grind individual components. In fact, it has been found that measuring breakage parameters from separately ground components will produce incorrect results (Choi et al., 1985, 1987).

The remaining parameters (i.e., the liberation functions and the breakage functions for composite particles) can be determined from the cumulative form of the model given below as:

$$\frac{d\hat{\gamma}_a}{dt} = \bar{B}_a S_a \hat{M}_a + \bar{L}_a \sum_{i=1}^J (S_{ab,i} \hat{M}_{ab,i}) \quad [1.5]$$

$$\frac{d\hat{\gamma}_b}{dt} = \bar{B}_b S_b \hat{M}_b + \bar{L}_b \sum_{i=1}^J (S_{ab,i} \hat{M}_{ab,i}) \quad [1.6]$$

$$\frac{d\hat{\gamma}_{ab,j}}{dt} = (\bar{B}_{ab,j} S_{ab,j} \hat{M}_{ab,j} + \sum_{\substack{i=1 \\ i \neq j}}^J (\bar{L}_{ab,j-i} S_{ab,i} \hat{M}_{ab,i})) \quad [1.7]$$

where:

$\hat{\gamma}_a, \hat{\gamma}_b, \hat{\gamma}_{ab,j}$ = the cumulative mass fraction of A, B, or AB_j type material finer than a given size.

$\bar{B}_a, \bar{B}_b, \bar{B}_{ab,j}$ = the cumulative breakage function matrix.

$\bar{L}_a, \bar{L}_b, \bar{L}_{ab,j}$ = the cumulative liberation function matrix.

For the case of one composite class, all parameters are known except for $\bar{L}_a, \bar{L}_b$ and $\bar{B}_{ab}$. These three matrices can be determined directly from Equations [1.5]-[1.7] if feed size normalizability is assumed. This is the only assumption needed other than those inherent in the model derivation. For the case of two composite classes, the values determined previously for $\bar{L}_a$ and $\bar{L}_b$ are still valid. Therefore, the two equations arising out of Equation [1.7] must be used to determine the remaining four parameters: $\bar{L}_{ab,1-2}, \bar{L}_{ab,2-1}, \bar{B}_{ab,1}$ and $\bar{B}_{ab,2}$. In this preliminary application of the model for

multiple composite classes, it has been assumed that the cumulative breakage functions and liberation functions for composite particles can be estimated from their component parts in proportion to the volume fraction of each part present in the composite particle. This procedure can be used for handling all cases with more than one composite class.

The goal of this work has been to develop a combined size reduction-mineral liberation model for coal grinding. This goal has been achieved, but difficulties still remain in the experimental determination of the parameters necessary for detailed modeling of the grinding process. This may be an area for future research activities. Once an extensive data base can be established, the model developed in the present work, which combines both size reduction and liberation, should be useful in the design of grinding circuits for meeting specific coal cleaning requirements.

d. Characterization of Process Streams

The purpose of this effort was to apply image analysis and computer-controlled scanning electron microscopy to the characterization of feed and product streams around the microbubble column flotation and electrochemical coal cleaning processes developed at Virginia Tech. For the microbubble column flotation process, the work primarily focuses on the determination of the degree of liberation of pyrite and other mineral matter in each stream and in the selectivity of the MCF process for rejecting liberated pyrite. The image analysis and electron microscopy work conducted for the electrochemical coal cleaning process was directed at identifying the phenomena and/or mechanisms responsible for the liberation of mineral matter by this process.

Microbubble Column Flotation

In the first series of image analysis studies, the feed and clean coal streams from the microbubble column flotation process were analyzed to

determine the selectivity of the process for removing liberated pyrite and mineral matter. In this case, a minus 100-mesh sample of Upper Freeport coal was pulverized to minus 20- μm by grinding for 15 minutes in a Union Process stirred ball mill. The sample was then treated using microbubble column flotation and the products were collected. The minus 20- μm feed and clean coal samples were each mounted in epoxy briquettes. Particles were pretreated with a dilute bromine solution prior to mounting in order to enhance the image contrast. The samples were then analyzed to determine degree of liberation for pyrite.

After micronizing the Upper Freeport sample in a stirred ball mill for 15 minutes, a minus 20- μm sample was produced having a mean size of approximately 3.5 μm . Under this condition, the degree of liberation for pyrite in the Upper Freeport sample was increased from 5% at minus 100-mesh to 25% at minus 20- μm . This information is presented in Figure 1.16 as cumulative degree of liberation versus particle size. It is interesting to note that a significant quantity of liberated pyrite does not appear until the particle size is approximately 3.3 μm , even though over half of the total particle size distribution is greater than this size. It appears that since the pyrite is harder and more brittle than the coal, it grinds to a finer size. Thus, particles of pyrite which may be liberated at a coarser size continue to grind as the coal is reduced in size.

In the case of the concentrate from the microbubble column flotation process, the cumulative degree of liberation plot showed a rather surprising result. As seen in Figure 1.16, the amount of liberated pyrite present on a percentage basis actually increased from 25% in the feed to 40% in the concentrate. However, this increase in the percentage of liberated pyrite present was primarily in the fine sizes below 2 μm . Almost none of the liberated pyrite present in the feed which was greater than 2 μm appeared in the concentrate. Furthermore, the overall rejection of pyrite was quite good,

Figure 1.16 Cumulative degree of liberation for micronized Upper Freeport seam coal treated by microbubble column flotation.

as can be seen in Figure 1.17, which shows the cumulative volume percent of pyrite present versus the particle size. Based on this result, approximately 96% of the pyritic sulfur was rejected as compared to 89% which was calculated from the sulfur analysis of the feed and concentrate.

It is difficult to draw many conclusions from the data at this time since the analysis techniques for micronized coal are very new and need further refinement. For example, the edges of the coal particles tend to be difficult to distinguish from the mounting material. This results in an underestimation of the amount of coal present and, thus, an overestimation of the pyrite present. Furthermore, it is well known that a locked particle containing pyrite can appear as free pyrite while a free particle cannot appear to be locked. Thus, there is a natural tendency to overestimate the amount of pyrite present and the degree of liberation. Clearly, there is a considerable amount of error in the pyritic sulfur estimated by image analysis for the feed sample. Work is continuing in order to improve the analysis techniques for micronized coal. In any case, regardless of the possible errors inherent in the analysis, there is a clear indication that a substantial amount of pyrite was rejected in the form of composite particles. This is most likely due to the short retention time (3 minutes) used in this test, which allowed only the most liberated coal to float.

The data obtained from this task clearly demonstrates that computer-controlled image analysis is a useful tool for characterizing the response of coal, mineral matter and pyrite during physical cleaning by flotation. However, further refinements must be made in the analysis procedures for micronized coal before any major conclusions can be drawn regarding the physical cleaning of very finely pulverized coal.

Figure 1.17 Cumulative volume percent of pyrite for micronized Upper Freeport seam coal treated by microbubble column flotation.

Electrochemical Coal Cleaning

Scanning electron photomicrographs of coal were taken to show the changes in surface morphology before and after processing by the electrochemical coal cleaning process. Tests were conducted by splitting the feed coal into two representative samples by repeated riffing. One sample was treated by the ECC process while the second was treated in acid media without an applied potential. After processing, the coals were wet-screened, dried and riffled to obtain representative samples for analysis.

Photomicrographs were taken of the feed coal and the two product coals.

Figure 1.18a shows the surface morphology of the feed coal from the Jacob Ranch mine in the Middle Wyodak seam. The large gray inclusion near the center of the photomicrograph is a clay mineral consisting of aluminum, silicon and calcium. Smaller mineral inclusions are scattered throughout the photomicrograph. These minerals appear to be adhering to the coal surface, but are more likely to be included inside tiny cracks within the coal. The minerals shown may be only as large as they appear on the photomicrograph, or they may extend deep into the coal pore with their remaining portions hidden beneath their visible sections.

Figure 1.18b shows the surface of this coal when treated with hydrochloric acid. The fine particulates of mineral matter seen on the surface of the feed coal were not present, indicating that the acid treatment may have dissolved or liberated these particles from the coal. However, large inclusions of mineral matter were still visible on the surface (shown by arrows). Further analysis by EDAX showed the presence of aluminum, silicon and calcium.

Figure 1.19a shows the surface of the Jacob Ranch coal after treatment by the electrochemical coal cleaning process. This coal was processed with 1.0 mM of ferric ions added to the acid electrolyte. A characteristic surface of the coal showed that pits and cracks had formed on the coal surface. The pits

(a)

(b)

Figure 1.18 Photomicrographs showing typical surface morphology of a feed sample from the Jacob Ranch coal from the Middle Wyodak seam before (a) and after (b) treatment with hydrochloric acid.

Figure 1.19 Photomicrographs showing pits (a) and cracks (b) in the surface of Jacob Ranch coal from the Middle Wyodak seam after treatment by the electrochemical coal cleaning process.

may have been locations where mineral matter once resided in the coal (similar to that observed in the photomicrographs of the feed coal). Although the surface of the coal was marked with large cracks, there was no significant size reduction of the coal. The cracks, therefore, did not penetrate deep enough to cause complete particle breakage. The areas marked in Figure 1.19b show the beginning stages of some smaller cracks on the surface of the coal.

Photomicrographs were also taken of samples of coal obtained from the Widow Kennedy coal seam. The Widow Kennedy feed coal was observed to have a large number of mineral particles on its surface, as shown in Figure 1.20a. These particles may be held in place on the coal surface by mechanisms of adhesion or by compressive forces. A sample of the acid-treated coal showed a similar pattern of mineral particles remaining on the surface. As seen in Figure 1.20b, however, the observed frequency of these mineral particles is much lower than in the original feed coal. The same feed coal treated by the ECC process (Figure 1.21a) showed a much cleaner surface than either the feed coal or the acid-treated coal, even at a higher magnification.

Acid treatment alone is apparently not sufficient to remove many of the large clusters of pyrite present in the feed coal (Figure 1.21b). This is not totally unexpected since pyrite is insoluble under the acid conditions tested. On the other hand, the ECC process has been shown to remove a significant portion of the pyrite framboids that are present in the feed coal (Figure 1.22a). The surface morphology of the treated coal is also markedly changed as evidenced by the presence of pits and cracks on the coal surface.

Arrow "A" in Figure 1.22a points to a pyrite framboid that was not removed after electrochemical treatment. Apparently, the compressive stresses holding this framboid in place are larger than the osmotic pressure developed between it and the coal surface, thereby preventing its liberation. Arrow "B" points to three empty sites where pyrite inclusions were located. This section is shown enlarged in Figure 1.22b. This work provides direct physical

Figure 1.20 Photomicrographs of Widow Kennedy coal showing typical surface morphology of a feed sample (140x270 mesh) before (a) and after (b) treatment with hydrochloric acid.

(a)

(b)

Figure 1.21 Photomicrographs of the surface of Widow Kennedy coal. (a) shows the surface after electrochemical treatment; (b) shows pyrite clusters after acid treatment.

Figure 1.22 Photomicrographs of the surface of electrochemically-treated Widow Kennedy coal showing: (a) unremoved coal pyrite (A) and former pyrite sites (B); and (b) enlargement of former pyrite sites.

TASK 2: MICROBUBBLE COLUMN FLOTATION

Introduction

The work completed in Task 1 demonstrates that the mineral matter and pyrite present in most coals are very finely disseminated. As a result, any physical cleaning process for producing superclean coal must involve a step in which the coal is pulverized to micron sizes in order to liberate these impurities. Once liberation is achieved, the micronized coal must be recovered. Froth flotation, which was developed at the beginning of this century, is widely considered the best available technology for upgrading finely pulverized coal. Unfortunately, the efficiency of froth flotation deteriorates rapidly with decreasing particle size below approximately 100 mesh. A number of studies have identified various reasons for this decrease in efficiency, including slime coatings, nonselective reagent consumption by fines, and morphological and surface chemical changes during fine grinding. One of the major difficulties in floating fine particles, however, is the unfavorable hydrodynamic conditions surrounding the bubbles generated in conventional flotation machines. It has been shown that when bubbles are too large, fine particles follow the streamlines around the bubbles due to their small inertial force and do not collide with the bubbles. The consequence of this low probability of collision would be a low flotation rate and, hence, poor recovery.

From a fundamental viewpoint, the capture of particles by a rising air bubble can be described by:

$$P = P_c P_a (1 - P_d), \quad [2.1]$$

where P is the overall probability of collection, P_c is the probability of collision between the bubble and particle, P_a is the probability of successful adhesion after the particle collides with the bubble, and P_d is the

probability that the particle will become detached. Much of the hydrodynamic analysis carried out in the past has been concerned with the prediction of P_C . One of the most noteworthy studies on this topic was conducted by Reay and Ratcliff (1973) who modeled the flotation process using numerical techniques. Their data suggested that the probability of collision (P_C) was given by:

$$P_C \propto (D_p/D_b)^2, \quad [2.2]$$

where D_p and D_b are the particle and bubble diameters, respectively. This relationship explains why the flotation recovery should decrease with decreasing particle size. More importantly, this relationship also suggests that the problems associated with the capture of fine particles can be alleviated by decreasing the size of bubbles used during flotation.

More recently, a quantitative expression for particle capture by a nondeformable spherical object has been derived by Weber (1981) and Weber and Paddock (1983). In their analysis, the probability of collision (P_C) was determined analytically for the case of low Reynolds numbers. For larger Reynolds numbers, the expression was modified by applying a curve-fitting technique to the numerical solutions to the Navier-Stokes equations obtained by Masliyah (1970) and Woo (1971). In this manner, Weber and Paddock derived an expression for P_C as follows:

$$P_C = \frac{3}{2} \left[\frac{D_p}{D_b} \right]^2 \left[1 + \frac{(3/16) \text{ Re}}{1 + 0.249 \text{ Re}^{0.56}} \right], \quad [2.3]$$

in which Re is the Reynolds number of the bubble. Unlike previous studies, this work was the first of its kind in which a single expression can predict P_C for a wide range of bubble and particle sizes. This work also demonstrates the important contribution of bubble size in determining the efficiency of fine particle capture. Unfortunately, Weber and Paddock made no experimental

measurements to support their analysis.

It is also generally recognized that physical parameters such as bubble and particle size can also impact flotation selectivity. A quantitative account of this phenomena was originally presented by Sutherland (1948). He considered that upon collision, a particle slides over the bubble surface for a finite period of time, and this "sliding time" is determined by the velocity of the liquid flowing past the rising bubble and the size of the bubble. In cases where bubble-particle attachment is thermodynamically possible, adhesion occurs only when the sliding time is longer than the time required to thin and rupture the intervening film, known as the *disjoining film*, between the bubble and the particle. The minimum time that is required to thin and rupture the film is known as the *induction time*.

The sliding/induction time concept provides a convenient framework for quantifying the probability of bubble-particle adhesion (P_a). This type of analysis has recently been utilized by Dobby and Finch (1985) for modeling fine particle flotation. Although their model is identical conceptionally to that proposed by Sutherland, the availability of improved expressions for describing the flow conditions around a bubble made their predictions more realistic. Two major findings have been made from the work of Dobby and Finch (1985). First, their model suggests that the decrease in floatability with increasing particle size beyond the upper flotation limit is due to a decrease in P_a . Previously, it was explained by an increase in the inertial force with increasing particle size, which in turn increases the detachment force and, hence, decreases P_d . Secondly, the model suggests that P_a for very small particles, e.g., less than 10 μm , is very high and somewhat independent of the hydrophobic/hydrophilic nature of particle surfaces. This finding implies that selectivity will be very poor when floating fine particles. However, many investigators have shown in experiments that ultrafine particles can be selectively recovered by flotation (Gaudin, 1932; Fuerstenau, 1980; Kelvall

et al., 1974; Sennett and Young, 1979; Yang, 1984).

The poor selectivity of fine particle flotation has also been attributed to other factors such as the high surface energy of fine particles, fine particles stabilizing froth and nonselective entrainment (Fuerstenau, 1980; Warren, 1984). The hydraulic entrainment of mineral fines, which is largely controlled by the behavior of the froth phase, is generally recognized as playing a major role in determining flotation selectivity. Past flotation tests conducted at Virginia Tech have shown that by decreasing the bubble size the froth becomes more stable and the entrainment of fine particles becomes more of a problem. However, test work has also shown that mineral matter entrapped in the froth can be readily removed by adding a countercurrent flow of wash water to the froth phase, e.g., column flotation. In this case, a stable froth helps retain most of the clean coal while the mineral fines are rinsed back into the pulp. As yet, very little work has been done to study the properties of the froth phase and utilization of the froth as a means of upgrading the flotation product. Nevertheless, this is an important part of the flotation process which must be studied in more detail. Furthermore, it was recognized early in the present study that the use of a column as the vehicle for the flotation process resulted in superior ash rejection at high recoveries. Thus, microbubble column flotation (MCF) was used throughout the current project.

Because of the theoretical benefits of utilizing small bubbles for flotation, the *microbubble flotation process* was developed at Virginia Tech as an effective means for upgrading fine particles. Numerous publications have been made on this topic since 1981. The indications from the initial work conducted on minus 100-mesh coal samples from the Pittsburgh No. 8 seam were that microbubble flotation gave consistently higher recoveries with higher separation efficiencies than the conventional flotation technique (Yoon,

1982). However, the improvement was rather marginal since the conventional process, when operated properly, is reasonably capable of upgrading minus 100-mesh coals. However, when the two processes were compared in terms of their effectiveness in cleaning micronized coal samples, microbubble flotation substantially outperformed conventional froth flotation. In some cases, microbubble flotation was found to produce results superior to the well-known oil agglomeration process. Although some coals responded better to the oil agglomeration process, the microbubble flotation process has the distinct advantage that the required dosage of reagents is less by two orders of magnitude.

One intriguing observation made from this earlier work with microbubble flotation was that the ash rejection improved significantly with increasing grinding time to improve liberation. This finding led to the concept of producing superclean coal using the microbubble flotation technique (DOE Project No. FG22-83PC60806, 1983). Some of the results obtained in this project showed that various coals can be cleaned by the microbubble flotation process to below 2% ash. With several select coals, ash contents below less than 0.5% were attainable with high recoveries. It is also anticipated that the use of a water sprinkling technique during continuous flotation can remove the entrapped ash particles and help further reduce the ash content while maintaining high recoveries.

In the following sections, various factors that contribute to the overall efficiency of the microbubble flotation process have been examined to provide the basic information required to develop a comprehensive understanding of the microbubble flotation process. These include detailed studies related to microbubble generation, bubble-particle hydrodynamics, bubble-particle adhesion and froth phase phenomena. This is followed by a summary of the laboratory-scale test work done to quantify the effects of changes in the operating variables on process performance. In addition, work

to characterize the surface chemistry of coal pyrite has been initiated because of the recent emphasis on reducing the sulfur content of coal.

Task 1.2.1: Bubble Generation

a. Bubble Generator Characterization

Efficient bubble generation is a key requirement of the microbubble flotation technology. There are several well-known techniques for generating small bubbles, including pressure-release, electrolysis and high-shear agitation. A novel approach developed at Virginia Tech and reported previously under DOE Contract No. DE-FG22-83PC60806 involves the use of a porous venturi tube. As a surfactant solution passes through the venturi tube, the venturi increases the fluid velocity and, in accordance with Bernoulli's equation, creates a low-pressure zone which draws air into the system. Bubbles formed at the pore sites are removed by the force exerted by the moving fluid. This bubble generator is shown in Figure 2.1. The housing and air valve around the porous tube permit the air intake rate to be controlled, while the pumping rate controls the fluid velocity. The apparatus used to determine the size of the bubbles produced by the generator is provided in Figure 2.2. The system allowed direct measurement of the bubble size distribution from a slip-stream of freshly-generated microbubble suspension. Bubble size distributions were determined from photographs which were viewed under a Kontron SEM-IPS image analyzer. In general, bubble diameters ranged from 50 to 125 μm , with a standard deviation of usually no more than approximately 25-50 μm . A typical bubble size distribution is given in Figure 2.3.

The parameters investigated to date include fluid velocity, pore size and generator geometry. The effect of pump speed on the mean bubble size is shown in Figure 2.4. In general, a substantial decrease in bubble size occurred as the pump speed was increased from 1440 to 3800 rpm. Notice,

Figure 2.1 Schematic of the porous venturi-tube microbubble generator.

Figure 2.2 Schematic of the apparatus used for the photographic measurement of bubble size.

Figure 2.3 Typical bubble size distribution produced using the porous venturi-tube microbubble generator.

Figure 2.4 The effect of pump speed on the mean bubble size and volumetric air hold-up.

however, that the shape of the curve appears to be a step function with a sharp change in bubble size from about 2200 to 2500 rpm. The air content of the microbubble suspension was also found to increase with increasing pump speed. Figure 2.5 shows the effect of pore size on the bubble size and percent air in the microbubble suspension. As expected, an increase in pore size results in a corresponding increase in bubble diameter. Furthermore, the increased pore diameter makes it easier to draw more air into the generator, thereby resulting in an increase in the air content of the microbubble suspension. The effects of generator geometry, i.e., porous tube diameter and length, are shown in Figures 2.6 and 2.7, respectively. As shown, bubble size is observed to increase as the length and diameter of the porous tube increase. The increase in bubble size with increasing tube length is most likely due to the higher percent air drawn into the solution. Since there is more surface area for bubble generation in the longer porous tube, more air is drawn into the generator. The increase in bubble size with increased diameter is due to a decrease in superficial fluid velocity through the generator. The decrease in percent air with increasing diameter can be attributed to the decrease in pressure drop as described by Bernoulli's equation. The final design variable examined in this study was the wall thickness of the porous tube. As shown in Figure 2.8, both the bubble size and the air content decreased with an increase in wall thickness. Both of these trends can be explained by the increased resistance of air flow through the thicker walls which, in turn, reduces the flow rate of air into the suspension.

The impact of using different frothing agents for microbubble generation is shown in Table 2.1. In general, Dowfroth M150 was found to produce the smallest bubbles of the three frothers examined, while MIBC gave the largest. The differences in bubble size can be explained in terms of the greater surface activity of Dowfroth M150 compared to the other frothers. The surface excess (i.e., the amount of frother adsorbed at the air-water interface per

Figure 2.5 The effect of porous tube pore diameter on the mean bubble size and volumetric air hold-up.

Figure 2.6 The effect of generator diameter on the mean bubble size and volumetric air hold-up.

Figure 2.7 The effect of generator length on the mean bubble size and volumetric air hold-up.

Figure 2.8 The effect of porous tube wall thickness on the mean bubble size and volumetric air hold-up.

Table 2.1

Characteristics of Microbubbles Produced by Various Commercial Frothing Agents

Reagent	Bubble Diameter (μm)	Air Content (%)	Frother Dosage (mg/l)	Surface Excess (moles/cm ²)
Dowfroth M150	65	13	50	2.6×10^{-10}
Nalco 8836	78	--	50	--
MIBC	80	11	50	5.4×10^{-11}

unit area) of Dowfroth M150 and MIBC has been calculated from surface tension measurements using the Gibbs adsorption equation. It was not possible to calculate these values for Nalco 8836 since the molecular weight for this reagent is not published. As shown in Table 2.1, Dowfroth M150 displays a much greater degree of adsorption than does MIBC. These findings may explain the superior performance of Dowfroth M150 for producing microbubbles.

b. Bubble Generation Model

Because of the complexity of bubble formation processes, few models are available to predict bubble size distribution. Recently, Johnson et al. (1982) demonstrated that an analysis of the form-drag on a bubble emerging from a submerged orifice in a shear field can successfully predict the size distribution of bubbles produced from a shear-type generator. The fundamental concept in development of the model is that the bubble leaves the pore surface when it grows large enough to have a drag force equal to the surface tension force. The drag force may be calculated from a hydrodynamic analysis of flows within the venturi generator. Since the velocity distribution within the generator varies in the radial direction, the fluid force acting on a bubble must also vary with bubble size. Theoretical considerations can be used to show that the drag force acting on a growing bubble can be expressed by:

$$F_{\text{drag}} = \frac{4CSQ_1^2}{\pi^2} \int_0^{R_b+\delta} \left[\frac{2Ry - y^2}{R^4} \right]^2 (2\delta y - y^2 + R_p^2)^{0.5} dy, \quad [2.4]$$

in which,

R_b = bubble radius,

R_p = pore radius,

R = porous tube radius,

Q_1 = liquid flowrate,

C = drag constant (determined experimentally),

S = liquid density,

y = distance from the porous tube wall, and

δ = distance to the bubble center from the tube wall.

From simple geometric considerations, it can be shown that the value of δ can be calculated from:

$$\delta = \sqrt{R_b^2 - R_p^2}. \quad [2.5]$$

Equation [2.4] can be solved by using numerical integration techniques such as Simpson's method.

The surface tension force (F_{surf}), which offers a resistance for the bubble leaving the nucleation site, can be determined from Tate's law:

$$F_{surf} = 2\pi\sigma R_p, \quad [2.6]$$

where σ is the surface tension of the solution. The above analysis suggests that as the bubble grows, the value of F_{drag} increases until it becomes equal to F_{surf} , at which point the bubble is sheared from the nucleation site with a finite size. This equilibrium establishes the size of the bubbles produced by the generator.

Once the bubble size has been determined, the number of bubbles generated per unit time (N) can easily be calculated from:

$$N = \frac{3Q_g}{4\pi R_b^3}, \quad [2.7]$$

where Q_g is the air flow rate. The value of Q_g can be predicted using Bernoulli's equation to calculate the pressure drop in the venturi tube and by correlating this value with the characteristic pressure drop versus flow rate curve for the porous tube supplied by the manufacturer. The model can predict the mean bubble size as a function of a number of important operating

parameters, e.g., porous tube length, tube diameter, fluid flow velocity, pore size, surface tension, etc. The model can also predict the bubble size distribution if the pore size distribution of the porous tube is known.

Figure 2.9 provides experimental results for changes in bubble size as a function of flow rate through the bubble generator. For the same range of flow rates, Equations [2.4]-[2.6] have been used to predict the bubble size from the generator. The predicted values are represented in Figure 2.9 by the dashed line. As shown, the experimental and predicted results are in close agreement. As a result, the bubble generation model provides an ideal tool for scale-up applications since it is based on first principles.

Task 1.2.2: Bubble-Particle Hydrodynamics

Of the various subprocesses which contribute to the overall rate of flotation, the elementary step of particle capture by a rising bubble is the most important. In the present work, an attempt has been made to quantify the bubble-particle capture process by considering the case of an isolated bubble rising through a suspension of particles. As liquid sweeps past the bubble, a flow pattern develops that can be represented by an infinite series of streamlines. As discussed previously, these streamlines influence both the collision and adhesion between particles and bubbles. As a result, the influence of various parameters on flotation performance cannot be established until an adequate understanding of this phenomenon has been developed. An analysis of the bubble-particle attachment process as it relates to fine coal particles is presented in the following sections.

a. Flow Pattern Around a Bubble

Figure 2.10 shows the case of a small particle approaching a bubble surface under the influence of streamline flow. As the liquid sweeps past the bubble, a flow pattern represented by an infinite series of streamlines

Figure 2.9 Predicted (dashed line) and experimentally-measured (data points) mean bubble size as a function of fluid flow rate through the generator.

Figure 2.10 Polar coordinate system used to describe the trajectory of a particle moving past a bubble in streamline flow.

develops. Because of its importance in a wide range of disciplines, the study of fluid flow around a spherical obstruction (such as a bubble) is a classical problem with extensive literature. Particularly detailed in the literature is the case of low Reynolds numbers for which analytical solutions to the Navier-Stokes and continuity equations are possible. Under these conditions, the streamlines are described by the well-known Stokes stream function (ϕ_s), which may be expressed mathematically as,

$$\phi_s = U_b R_b^2 \sin^2 \theta \left[\frac{1}{2} x^2 - \frac{3}{4} x + \frac{1}{4x} \right], \quad [2.8]$$

where U_b is the bubble rise velocity, θ and r are the respective angular and radial coordinates, and x the dimensionless radial distance (i.e., r/R_b).

For the case of higher Reynolds numbers, several approximate numerical solutions have also been presented in the literature (Rimon and Cheng, 1969; Pruppacher et al., 1970). Flow conditions representative of very high Reynolds numbers (i.e., inviscid flow) can be approximated by the potential flow solution to the Navier-Stokes equations. Under these conditions, the streamline flow pattern can be described by:

$$\phi_p = U_b R_b^2 \sin^2 \theta \left[\frac{1}{2} x^2 - \frac{1}{2x} \right]. \quad [2.9]$$

Unfortunately, the Stokes and potential flow solutions are useful for quantifying the streamline patterns at extremely small and large Reynolds numbers. However, the range of Reynolds numbers encountered for the sizes of bubbles typically employed during flotation fall into a range between 0.2 and 100. As a result, neither of the previous solutions is appropriate for describing the flotation process.

Therefore, a new stream function for intermediate Reynolds numbers (ϕ) has been developed in the present investigation by combining the Stokes and

potential flow equations. These two equations are special cases of the expression:

$$\phi = U_b R_b^2 \sin^2 \theta \left[\frac{1}{2} x^2 - \frac{3}{4} \alpha x - \frac{1}{2x} + \frac{3\alpha}{4x} \right], \quad [2.10]$$

where α is a dimensionless parameter which varies between 0 and 1. If the value of α is set equal to 0, this equation becomes the potential flow stream function, while if α is set equal to 1, the Stokes stream function is obtained. Thus, the values of α between 0 and 1 represent cases of intermediate Reynolds numbers which can be used to represent flotation.

In order to determine the values of α as a function of Re for intermediate flow conditions, streamline patterns around a spherical obstruction have been collected from literature for a wide range of Reynolds numbers. Far ahead of the spherical obstruction, a given streamline can be uniquely identified by a fixed value of R_0 which is related to r and θ by:

$$\sin \theta = R_0 / r. \quad [2.11]$$

At an infinite distance ahead of the bubble (i.e., $R \rightarrow \infty$), Equation [2.11] can be substituted into Equation [2.10] to yield:

$$R_0^2 = 2\phi / U_b. \quad [2.12]$$

Therefore, by directly measuring the values of R_0 from the streamline patterns obtained at a given Reynolds number and knowing U_b , one can determine ϕ for each streamline using Equation [2.12]. Once the values of ϕ are known, the values of α can then be determined from Equation [2.10] for any combination of r and θ . The α values obtained as such are plotted as a function of $(1-1/x)$ for Reynolds numbers of 1, 10, 50 and 100, as shown in Figure 2.11. It was found that the α values can be normalized with respect to Reynolds number

Figure 2.11 Back-calculated values of α as a function of $1-1/X$ for a range of Reynolds numbers.

using the relationship:

$$\alpha = 1 - (\text{Re}^{.72}/15) [1 - 1/x], \quad [2.13]$$

for Reynolds numbers between 0 and 100. This expression may also be applicable for $\text{Re} > 100$, although no experimental streamline data are available in the present work.

Substitution of Equation [2.13] into Equation [2.10] yields a generalized stream function for intermediate Reynolds numbers as follows:

$$\Phi = \Phi_s + U_b R_b^2 \sin^2 \theta \left[\frac{\text{Re}^{.72}}{15} \right] \left[\frac{1}{x^2} - \frac{1}{x} + x - 1 \right]. \quad [2.14]$$

This expression provides a general description of the streamline flow pattern around a rising air bubble in the low to intermediate flow regime. As a result, this expression can be used to predict the trajectory of particles as they flow past a bubble under the influence of streamline flow.

b. Bubble-Particle Collision

If inertial forces are neglected, the probability of collision (P_c) between small particles and an air bubble can be calculated from the streamline flow pattern by assuming that the particle trajectory is determined by the streamline which passes through its center. For obvious reasons, this assumption becomes less valid as the ratio of particle diameter to bubble diameter increases. Assuming that the streamlines come closest to the bubble at its equator, a grazing streamline is defined as the one passing through the distance of a particle radius (R_p) at the equator and the distance of R_0 at an infinite distance from the bubble. It is clear, then, that of the particles located in the path of the bubble, only those within the limiting radius (R_0), will collide with the bubble. Those which lie outside this area will sweep past the bubble without having an opportunity for contact. The probability of

collision, which is defined as the fraction of particles in the path of the bubble that actually collide with it, is therefore determined by the ratio of the area (A_o) inscribed by the limiting radius (R_o) to the area (A_b) inscribed by the bubble radius (R_b). Thus, the probability of collision (P_c) is given as:

$$P_c = \frac{A_o}{A_b} = \left[\frac{R_o}{R_b} \right]^2. \quad [2.15]$$

The value of R_o is unknown and must be determined from the mathematical description of the grazing streamline. It should also be noted that the denominator of Equation [2.15] should actually be $(R_b + R_p)$, but this expression holds when $R_b \gg R_p$.

By combining Equations [2.12], [2.14] and [2.15], the probability of particle collision (P_c) can be derived as:

$$P_c = \frac{2\phi}{U_b R_b^2} = \sin^2 \theta \left[x^2 - \frac{3}{2} x + \frac{1}{2x} \right]. \quad [2.16]$$

For the limiting case of the particle just grazing off the bubble equator,

$$r = R_p + R_b \quad [2.17]$$

$$x = 1 + R_p/R_b, \text{ and} \quad [2.18]$$

$$\theta = 90^\circ. \quad [2.19]$$

By substituting Equations [2.18] and [2.19] into [2.16], it is possible to show that:

$$P_c = \left[\frac{3}{2} + \frac{4Re^{.72}}{15} \right] \left[\frac{R_p}{R_b} \right]^2. \quad [2.20]$$

This expression shows that P_c varies directly with R_p^2 and inversely with D_b^2 .

However, P_c is also a function of the Reynolds number of the bubble, so that P_c does not vary exactly as the inverse square of the bubble size.

c. Bubble-Particle Adhesion

Clearly, not all of the particles which collide with bubbles become attached. Otherwise, no separation would be possible by flotation. Qualitatively, only those particles that are hydrophobic enough attach themselves to the bubble by forming a three-phase contact with a finite contact angle. To be able to accurately predict flotation response, it is therefore necessary to evaluate the probability of adhesion in addition to the P_c term that has been considered in the foregoing section. For the small particles considered in the present work, detachment need not be considered (Dobby and Finch, 1985).

As soon as a particle collides with a bubble, it begins to slide over the surface of the bubble and resides on it for a finite period of time, which is generally referred to as the "sliding time". The magnitude of the sliding time is determined by the velocity at which the liquid sweeps the particle along the bubble surface. During this time period, the intervening film of water must be thinned and ruptured if the particle is to be attached to the surface of the bubble and eventually collected in the froth phase. Attachment occurs when the sliding time is longer than the induction time. Therefore, the particle must slide a finite distance over the bubble surface before the attachment occurs. For a given bubble and particle size, the distance traveled by a particle along the surface of a bubble is a function of the angle of incidence (θ_i) at which the particle strikes the bubble. Only when θ_i is smaller than the limiting angle (θ_0) will the particle have a sliding time longer than the induction time and become attached.

The probability of bubble-particle adhesion (P_a) can now be defined as the fraction of particles in the path of the bubble that actually adhere to

the bubble. In reference to Figure 2.12, P_a should be the ratio of the area inscribed by the limiting radius (R_c) to the area inscribed by the bubble and particle radius ($R_b + R_p$). Using this concept, P_a can be expressed as:

$$P_a = \frac{\pi R_c^2}{\pi (R_b + R_p)^2}, \quad [2.21]$$

or

$$P_a = \sin^2 \theta_o. \quad [2.22]$$

The value of the limiting angle (θ_o) is determined by the magnitude of the tangential velocity of the particle as it slides over the bubble surface. Therefore, the sliding velocity of a particle is determined by the tangential velocity of the streamline (U_t) at a distance of one particle radius from the bubble surface. The particle sliding time (τ_s) can then be calculated by dividing the arc length traveled by the particle by the velocity of the particle, i.e.,

$$\tau_s = \int_{\theta_o}^{\pi/2} \frac{R_b + R_p}{U_t} d\theta. \quad [2.23]$$

An upper integration limit of $\pi/2$ is used since the streamline flow will move a particle away from the bubble surface after it passes the bubble equator.

For axisymmetric flow around a rigid sphere, the instantaneous tangential velocity of the fluid (U_t) can be determined from the stream function (Φ) by:

$$U_t = \frac{1}{R \sin \theta} \frac{d\Phi}{dr}, \quad [2.24]$$

in which r is the radial distance between the center of the bubble and the streamline in question and θ is the angular coordinate. By substituting Equation [2.14] into [2.24] followed by integration, U_t of the fluid can be

Figure 2.12 Polar coordinate system used in determining the critical angle of incidence and probability of adhesion.

determined at any point in the vicinity of the bubble. By substituting U_t into Equation [2.23], an expression for the particle sliding time (τ_s) can be derived as a function of Θ_0 . Solving for Θ_0 , and substituting it into Equation [2.22], an expression for P_a can be obtained. The τ_s term in this expression can be substituted directly by induction time (τ_i) since $\tau_s = \tau_i$ when $\Theta_i = \Theta_0$. This procedure provides an expression for P_a which is given by:

$$P_a = \sin^2 \theta \left[2 \arctan \exp \frac{-(45+8Re^{.72})U_b\tau_i}{30R_b(R_b/R_b+1)} \right]. \quad [2.25]$$

Since this expression is a sine function, the value of P_a always falls between zero and unity. This is an improvement over the numerical solutions obtained by Dobby and Finch (1985) whose P_a values exceed 1 when the bubble size is very small or the induction time is short. A sample calculation for using Equation [2.29] may be given here: a weakly floating particle whose $\tau_i = 100$ msec and $D_p = 10 \mu\text{m}$, will have its $P_a = 0.08$. If τ_i is reduced to 10 msec by increasing the collector addition, for example, P_a will increase to 0.98.

To demonstrate the utility of Equation [2.25], P_a is plotted in Figure 2.13 as a function of particle size (D_p) for the case when using 1-mm diameter bubbles and when the particles have induction time (τ_i) values of 10, 20, 30 and 50 msec. As expected, the smaller the induction time, the higher the value of P_a for a given particle size. More importantly, P_a is shown to increase with decreasing particle size, which is a result of the lower tangential velocity (U_t) of the fluid and hence the longer sliding time for smaller particles. Thus, Equation [2.25] suggests that small particles become attached more readily than large particles once the collision has taken place.

In Figure 2.14, Equation [2.25] is plotted as a function of bubble size (D_b) for the case of floating 20- μm diameter particles having τ_i values of 10, 20, 30 and 50 msec. As has been shown to be the case in Figure 2.13, a decrease in τ_i results in an increase in P_a , which requires no further

Figure 2.13 Theoretical effect of particle size on the probability of adhesion for induction time values of 10, 20, 30 and 50 msec.

Figure 2.14 Theoretical effect of bubble size on the probability of adhesion for induction time values of 10, 20, 30 and 50 msec.

explanation. At a given τ_i , P_a is shown to decrease with decreasing D_b until a bubble size of approximately 350 μm is reached. This is due to the fact that as the bubble size is reduced, the bubble rise velocity (U_b) is also reduced, which in turn results in an increased sliding time (τ_i). A further decrease in D_b , however, causes a decrease in the sliding distance, which results in a decrease in τ_i and hence a decreased P_a .

d. Bubble-Particle Modeling Incorporating Viscous Film Thinning

In the previous sections, the probability of adhesion (P_a) for bubble-particle attachment has been quantified using the induction time concept originally presented by Sutherland (1948). This model is useful if the critical induction time (τ_i) for film rupture is known. Unfortunately, τ_i is difficult to quantify since it depends on both physical and chemical parameters. Chemical phenomena are controlled by reagent additions and the surface characteristics of the materials to be separated. Physical phenomena, on the other hand, are largely controlled by the hydrodynamic interactions between bubbles and particles which are determined by such factors as bubble size, particle size, turbulence, etc. Therefore, a better approach to modeling of the bubble-particle attachment process would be to completely separate the physical and chemical parameters which affect flotation response.

As shown previously in Figure 2.10, the approach of a small particle toward a bubble can be defined in terms of a cylindrical coordinate system described by r and θ . The instantaneous radial velocity (U_r) and tangential velocity (U_t) of the fluid flowing around the bubble can be determined from the stream function (Φ) by the expressions:

$$U_r = \frac{1}{R^2 \sin \theta} \frac{d\Phi}{d\theta}, \quad [2.20]$$

and

$$U_t = \frac{1}{R \sin \theta} \frac{d\phi}{dr}. \quad [2.27]$$

The stream function (ϕ), which is simply a mathematical description of the streamlines, is given by Equation [2.14] for the case of flow conditions found in froth flotation.

Since the only factor which influences the movement of the particle in the tangential direction is that of the streamline flow, the tangential velocity of the particle (U_{tp}) is equal to that of the fluid flow, i.e.,

$$U_{tp} = U_t. \quad [2.28]$$

At large distances from the bubble surface, the radial velocity of the particle (U_{rp}) may, likewise, be approximated by the radial velocity of the fluid flow (U_r). However, as the separation distance between the bubble and particle (H) becomes smaller, the viscous thinning of the intervening film begins to show resistance and inhibit further movement of the particle toward the bubble. The resistance force (F_r) against the film thinning can be calculated from lubrication theory by:

$$F_r = 6\pi\mu R_p U_{rp} \beta, \quad [2.29]$$

where μ is the liquid viscosity, R_p is the particle radius and β is the Stokes correction factor. The magnitude of β approaches unity as H approaches infinity, and increases rapidly as the value of H decreases (Maude, 1961; Brenner, 1964; Goren and O'Neill, 1971). The force which presses the particle against the bubble (F_p) is a result of the hydrodynamic drag acting on the particle. For a spherical particle, F_p is, therefore, given by:

$$F_p = 6\pi\mu R_p U_r. \quad [2.30]$$

A dynamic equilibrium requires that Equations [2.29] and [2.30] be

equal. Thus, upon elimination of like terms, the radial velocity of the particle (U_{rp}) is given by:

$$U_{rp} = U_r/\beta. \quad [2.31]$$

Using Equations [2.28] and [2.31], the trajectory of a particle can be simulated numerically. The numerical technique employed in the present work assumes that the position of the particle as it approaches from a great distance ahead of the bubble can be estimated by:

$$\theta_{new} = \theta_{old} + U_t \Delta t / r, \quad [2.32]$$

and

$$r_{new} = r_{old} + U_r \Delta t / \beta, \quad [2.33]$$

in which Δt is the time step used in the simulation. The value of β has been determined using an analysis presented by Goren and O'Neill (1971).

For the case under consideration, the overall probability of collection (P) for fine particles can be quantified using:

$$P = [R_0/R_b]^2, \quad [2.34]$$

in which R_0 is the radius of the tube of liquid that is actually swept by the bubble and R_b is the bubble radius. It is considered that particle attachment occurs when its approach to the bubble surface is within a certain critical distance at which the thin intervening film of liquid becomes unstable and spontaneously ruptures. This critical film thickness (H_c) is a function of particle hydrophobicity, interfacial tensions at the various interfaces involved, and interfacial viscosity. H_c should provide a much better measure of hydrophobicity than induction time (τ_i) since it does not depend on the physical parameters related to the thinning of the viscous film between the bubble and particle.

Given the value of H_C , a value of R_0 can be determined uniquely from the particle trajectory simulation for a given bubble size (D_b) and particle size (D_p). Equation [2.34] can then be used to obtain the values of P . Thus, P is a function of D_b , D_p and H_C . Figure 2.15 shows the results of such an analysis for a bubble diameter of 100 μm and a range of particle sizes. As shown, P increases with H_C and decreases with D_p . The simulation results obtained for other bubble sizes have been normalized with respect to the curves drawn for the 100- μm diameter bubble. The normalization factor plotted in Figure 2.16 shows that P increases exponentially with decreasing D_b , demonstrating the benefits of microbubble flotation.

e. Modifications for Particle Inertia

The analyses presented above may not apply in all cases since inertial forces may cause particles of very large size or high density to deviate from the streamlines. The Stokes number (St), which represents the ratio of inertial to drag forces, is useful for determining the tendency of a particle to adjust to changes in fluid flow. Particles having small values of St will follow the streamlines closely, while those having larger values of St will deviate from the streamlines. The following expression can be used to calculate Stokes number:

$$St = \frac{1}{9} \frac{S_p}{S_l} \left[\frac{D_p}{D_b} \right] Re, \quad [2.35]$$

as a function of the Reynolds number (Re) of the bubble, particle diameter (D_p), bubble diameter (D_b), particle density (S_p) and liquid density (S_l). As shown, the tendency of a particle to follow a streamline around the bubble depends on both the bubble and particle sizes. It can be readily shown that for a D_b of 1 mm and an S_p of 1.3 gm/cm³, the inertial forces need not be considered for particles smaller than approximately 100-125 μm in diameter.

Figure 2.15 Theoretically determined relationship between the probability of collection (P) and critical film rupture thickness (H_c) for a bubble diameter of $100\ \mu\text{m}$ and particle diameters of 1 - $40\ \mu\text{m}$.

Figure 2.16 Normalization plot for determining the probability of collection (P) at various bubble sizes.

Thus, for most cases when fine coal ($< 100 \mu\text{m}$) is to be floated, inertial forces need not be considered and the preceding analyses should apply.

f. Validation of Bubble-Particle Collection Model

Two series of experiments were undertaken to establish the validity of the preceding theoretical analyses. In the first set of tests, the probability of collection (P) was determined for a single bubble rising through a suspension of very hydrophobic coal particles. The value of P determined as such may closely approximate the probability of collision (P_C) since the probability of adhesion (P_a) for very hydrophobic particles should approach unity. In the second set of tests, P_a values were determined from experimentally measured values of induction time (τ_i) for a run-of-mine coal sample, and compared with microflotation results. The particles used in the flotation experiments were so large that the probability of collision (P_C) may be considered unity. This will allow a direct comparison between P_a and floatability.

Probability of Collision

Figure 2.17 shows the results of probability of collection (P) measurements conducted on the Buller seam coal, New Zealand, as a function of bubble size. This coal contained only 0.13% ash and was very hydrophobic as mined. The apparatus and experimental procedure used in the determination of P have been described in a previous DOE project (Grant No. DE-FG22-83PC60806). Tests were carried out using samples having 40.1-, 31.0- and 11.4- μm mean diameters. The solid lines in this figure represent the theoretical probability of collision (P_C) calculated using Equation [2.20]. The P values measured experimentally should be equal to P_C since this coal is strongly hydrophobic ($P_a \approx 1$).

As shown in Figure 2.17, both the experimental P and the calculated P_C values show a drastic increase as the bubble diameter is reduced. Considering

Figure 2.17 Comparison of experimentally-measured probability of collection (points) and theoretical probability of collision for different bubble and particle sizes.

the log-scale used for plotting P , the benefits of using small bubbles for fine particle flotation are quite substantial. In general, there is excellent agreement between the theoretical and the experimental values. Note, however, that the experimental P values are considerably higher than predicted when collecting large particles with large bubbles. This discrepancy may be attributed to the likelihood that the large particles deviate from the streamlines due to inertial force. The lack of fit observed when using small bubbles to collect the 11.4- μm particles may be due to some sort of surface force which becomes more predominant as particle size becomes very small.

Probability of Adhesion

A run-of-mine Elkhorn No. 3 seam coal, Virginia, having a feed ash of 15.5% was used for both the microflotation tests and the induction time measurements. Flotation tests were conducted using a 22-mm diameter microflotation cell. The induction time apparatus employed in these experiments has been described elsewhere by Yordan and Yoon (1986), and is similar to that used by Eigeles and Volova (1960).

Figure 2.18 shows the results of the microflotation tests and the induction time measurements carried out on the coal sample aged (or oxidized) in water at ambient temperature for varied lengths of time. In general, prolonged oxidation resulted in an increase in induction time and a corresponding decrease in floatability. When the coal sample was unoxidized, the recovery was approximately 70%, while after 20 days of oxidation, the floatability was reduced to approximately 20%. Also shown in Figure 2.18 is the probability of adhesion (P_a) predicted using Equation [2.25]. The prediction was made by substituting the measured induction time values into the equation along with the experimental variables, such as particle size and bubble size, employed in the flotation experiments. As shown, the P_a values calculated as such decrease rapidly as the induction time increases and show

Figure 2.18 Effect of oxidation time on recovery, induction time and theoretical probability of adhesion.

reasonable agreement with experimental floatabilities. The calculated P_a values are considerably smaller than the fractional floatabilities (percent floatability deviated by 100), but the trend is the same. If the flotation time had been shorter than actually employed (1 minute), the calculated P_a values would have more closely matched the flotation results.

As another example, a series of microflotation experiments were conducted on the Elkhorn seam coal at various pH values, and the results are compared in Figure 2.19 with the P_a values calculated from the induction times measured concurrently and the particle and bubble sizes employed in the flotation experiments. The floatability is shown to reach a maximum at approximately pH 8, where the induction time is minimum. Although the predicted P_a values are significantly higher than the fractional floatabilities, the P_a values calculated using Equation [2.25] can predict the trend and the maximum flotation pH reasonably well. In this case, the predicted P_a values would have been closer to the flotation results if the flotation time had been longer than actually employed. The results given in Figures 2.18 and 2.19 demonstrate that results of microflotation experiments can be predicted from induction time, particle size and bubble size, and by considering the flotation time as an adjustable parameter.

g. Flotation Rate Model

Quiescent Conditions

Columns typically employ very quiescent conditions since there is no mechanical agitator used to disperse air bubbles or mix the pulp. Under these conditions, the flotation rate constant (k) for bubble-particle attachment can be calculated using:

$$k = \frac{3P}{2D_b} V_g, \quad [2.36]$$

in which P is the probability of bubble-particle collection, V_g is the

Figure 2.19 Effect of pH on recovery, induction time and theoretical probability of adhesion.

superficial aeration rate, and D_b is the bubble diameter. The derivation of this expression has been detailed in a previous DOE project (Grant No. DE-FG22-83PC60806). If particle detachment is neglected (a reasonable assumption for the flotation of fine coal particles), this expression can be combined with Equations [2.1] and [2.20] to yield:

$$k = \left[\frac{9}{4} + \frac{2Re^{.72}}{5} \right] \left[\frac{D_p^2}{D_b^3} \right] v_g P_a. \quad [2.37]$$

Values of k predicted using this relationship are shown in Figure 2.20 as a function of bubble size for a range of P_a values. This plot indicates a very strong relationship between flotation rate constant (k) and bubble diameter (D_b).

Turbulent Conditions

Unlike a flotation column, a conventional flotation cell is turbulent due to intense mechanical agitation. As a result, the expression for k given in Equation [2.36] may not be valid and a new expression for k must be derived. Under turbulent conditions, the collision rate between two types of particles can be estimated using a modified form of Smoluchowski's equation. By applying this expression to the case of flotation, the number of bubble-particle collisions per unit volume per unit time (Z) is given by:

$$Z = (4/3) N_p N_b (R_p + R_b)^3 \sqrt{W/v}, \quad [2.38]$$

where N_p is the number of particles per unit volume, N_b the number of bubbles per unit volume, R_p the particle radius, R_b the bubble radius, W the energy dissipation rate per unit mass and v the kinematic viscosity. Thus, the total number of particles captured by bubbles per unit time can be calculated from:

$$- \frac{dN_t}{dt} = (4/3) N_p N_b (R_p + R_b)^3 \sqrt{W/v} v_c P_a, \quad [2.39]$$

Figure 2.20 Predicted relationship for flotation rate constant (k) versus bubble size (D_b) under quiescent conditions.

where N_t is the total number of particles in the cell, t the time, V_c the total pulp volume and P_a the probability of bubble-particle adhesion. Values for N_p and N_b can be calculated from:

$$N_p = N_t/V_c, \quad [2.40]$$

and,

$$N_b = 3\epsilon/(4\pi R_b^3), \quad [2.41]$$

in which ϵ is the fractional air holdup. By substituting Equations [2.40] and [2.41] into [2.39], it can be shown that:

$$-dN_t/dt = (\epsilon/\pi) \sqrt{W/V} P_a (1+R_p/R_b)^3 N_t. \quad [2.42]$$

Examination of this expression indicates a first-order process with a rate constant given by:

$$k = (\epsilon/\pi) \sqrt{W/V} P_a (1+R_p/R_b)^3, \quad [2.43]$$

or,

$$k = C (1+R_p/R_b)^3, \quad [2.44]$$

where C is a constant for a fixed air fraction and mixing environment. Values of k predicted using this relationship are shown in Figure 2.21 as a function of bubble size for a range of C values. An air-balance around a perfectly mixed flotation cell was used to estimate values of ϵ . As shown, Equation [2.44] indicates a much weaker dependence of k on D_b than the case derived previously for quiescent conditions.

In order to support the results predicted by Equations [2.37] and [2.44], a series of flotation tests were conducted using various degrees of pulp agitation. The flotation tests were performed using a column-type cell equipped with a variable-speed impeller along its length. Bubble size was varied by using different porous frit sizes. A narrow size fraction of quartz particles (10- μ m mean diameter) was used in all tests.

Figure 2.21 Predicted relationship for flotation rate constant (k) versus bubble size (D_b) under turbulent conditions.

Figure 2.22 shows the results of the flotation tests conducted at different levels of pulp agitation. At a low level of agitation (100 rpm), k increases rapidly with decreasing D_b . However, as the agitation increases, the dependence of k on D_b becomes less significant. This result tends to support the predictions made by Equations [2.37] and [2.44]. Thus, the flotation rate constant for fine particles may be enhanced by agitation when large bubble sizes are used; however, for very fine bubbles, agitation may result in a decrease in the flotation rate constant.

Task 1.2.3: Bubble-Particle Adhesion

a. Induction Time Measurements

Induction time measurements for coal particle capture on a bubble were carried out using an Elkhorn No. 3 seam coal containing 15.5% ash. The coal was ground to -1/4 inch in an agate mortar and then pulverized in a micro-grinder. This product was then wet-screened to collect a 60x100 mesh sample. Variables tested included particle size, kerosene addition, frother concentration, pH and oxidation time.

Figure 2.23 shows the results of induction time measurements conducted as a function of particle size. As shown, the induction time increases as a power function with particle size over the size range examined. Similar trends have been observed by other investigators (Eigeles and Volva, 1960). The rapid increase in induction time with particle size may explain the difficulty in recovering very large particles by flotation.

The effect of kerosene addition on induction time is shown in Figure 2.24. As expected, the induction time decreases sharply with increasing kerosene addition. It is likely that the droplets of hydrocarbon oil adsorb on the coal surface and bridge the hydrophobic sites, masking the hydrophilic sites in-between. The net result is that the hydrocarbon makes the coal surface more hydrophobic and causes the disjoining film to be less

Figure 2.22 Experimentally-measured flotation rate constants (k) as a function of bubble diameter for agitation speeds of 100, 300 and 600 rpm.

Figure 2.23 Effect of particle size on the induction time of an Elkhorn No. 3 seam coal.

Figure 2.24 Effect of kerosene addition on the induction time of an Elkhorn No. 3 seam coal.

stable, making it easier for the approaching air bubble to displace the liquid film and result in bubble-particle adhesion.

Figure 2.25 shows the results of induction time measurements conducted in the presence of various concentrations of Dowfroth M150. In general, the measured induction time values decrease steadily with increasing frother dosage. This suggests that the presence of Dowfroth M150 in the solution favors the bubble-particle adhesion process. Adsorption studies have shown that nonionic surfactants adsorb on coal via hydrophobic bonding. The results obtained in the present work support this possibility and suggest that frother adsorption makes the coal surface more hydrophobic.

Solution pH is also known to impact the performance of coal flotation. Figure 2.26 shows the results of induction time and microflotation experiments conducted as a function of pH. The maximum flotation occurs at the pH where the induction time is minimum, i.e., pH 7-8. Numerous studies have shown that the flotation maxima of various minerals occur at pH values where the minerals have minimum zeta-potentials. This phenomenon can be explained by the fact that at such pH values, the electrostatic repulsion between the coal surface and the bubble is minimum. However, zeta-potential measurements carried out in the present work showed that the iso-electric point for this coal occurs at pH 3.5-4.0, which is far removed from the pH of maximum floatability. This suggests that forces other than the electrostatic phenomenon play an important role in this case.

Induction time measurements were also conducted to determine the effect of oxidation on bubble-particle attachment. Figure 2.27 shows the effect of oxidation time on induction time measurements. These experiments were conducted in a solution of pH 6.0 with no surfactants present. Oxidation was achieved by placing the ground coal particles in Pyrex beakers open to the atmosphere. As shown, induction time increases rapidly over the first 8 to 10 days of oxidation and then levels off through day 24. In terms of flotation,

Figure 2.25 Effect of frother concentration (polypropylene glycol) on the induction time of an Elkhorn No. 3 seam coal.

Figure 2.26 Effect of pH on the induction time and flotation recovery of an Elkhorn No. 3 seam coal.

Figure 2.27 Effect of oxidation time on the induction time and flotation recovery of an Elkhorn No. 3 seam coal.

this suggests that the coal particles are effectively oxidized within ten days of exposure. Figure 2.27 also shows the results of salt microflotation experiments conducted as a function of oxidation time using 10^{-3} M NaCl solution. As shown, the flotation recovery steadily decreases with increasing oxidation time, indicating that the natural hydrophobicity of the coal particles is reduced by the oxidation process. For coal oxidation beyond 10 days, however, the flotation recovery remains unchanged suggesting that further oxidation has no greater impact on the flotation characteristics of the coal.

b. Bubble Charge Measurements

It is generally recognized that the rate of flotation is maximum when the charge on the surface of the particles is minimum. The explanation for this phenomenon is that the particles can approach the bubbles, which are also charged, more readily when there is no electrostatic repulsion. In fact, Derjaguin and Dukhin (1981) have shown that oppositely-charged bubbles and particles attach almost instantaneously. Unfortunately, while there is an abundance of information related to the charging of particles, there is a general lack of knowledge concerning the charging of bubbles.

In light of the above, tests were conducted in the present work to determine the zeta potentials of bubbles in the presence of various surfactants. Tests were carried out using a streaming current apparatus described previously by Usui and Sasaki (1978). This apparatus measures the sedimentation potential created when charged particles (or bubbles) move through a liquid. This phenomenon is commonly referred to as the Dorn effect. The streaming current apparatus was modified to allow the influence of bubble size to be investigated. This was made possible by using interchangeable frits of different porosities for gas sparging. Experiments were conducted as a function of pH, surfactant concentration and bubble size. The three

surfactants examined in this study are listed in Table 2.2. Research-grade reagents were used in all of the experiments.

Figure 2.28 shows the results of charge measurements obtained with each of the surfactants as a function of concentration at pH 6. The bubbles generated using the anionic (SLS) surfactant were negatively charged, while those generated with the cationic (DAH) surfactant were positively charged. These results demonstrate that the sign of the bubble charge is determined by the polar group of the surfactant molecule adsorbed on the bubble surface. These data also show that the magnitude of the bubble charge increases as the concentration of surfactant increases. The charge increase is due to increased adsorption of surfactant on the bubble surface in accordance with the Gibbs adsorption equation. The nonionic surfactant (PPG) produced bubbles having a slightly negative charge which remained constant with changes in reagent dosage.

The effects of pH on the zeta potential of bubbles produced using the various surfactants are shown in Figure 2.29. The surfactant dosage was maintained at a concentration of 5×10^{-5} M in each test. As shown, bubble charge was found to be relatively insensitive to pH over the range of pH 4 to 9. This pH range covers any practical range of values expected in coal flotation.

Figure 2.30 shows the effect of bubble size on bubble charge. In general, a decrease in bubble size produced a considerable increase in the magnitude of the bubble charge for both the anionic and cationic surfactants. Since bubble charge plays a key role in bubble-particle attachment, the results shown in Figure 2.30 may help to explain the differences in flotation selectivity when microbubbles are utilized. The charge of bubbles produced using the nonionic surfactant was much less sensitive to changes in bubble size. The mechanism(s) responsible for the observed changes in bubble charge with bubble size are unexplained at this time.

Table 2.2
Surfactants Used in the Zeta Potential Measurements

Surfactant	Type	Formula
Dodecylamine Hydrochloride (DAH)	Cationic	$\text{CH}_3(\text{CH}_2)_{11}\text{NH}_2\text{HCl}$
Sodium Lauryl Sulfate (SLS)	Anionic	$\text{C}_{12}\text{H}_{25}\text{OSO}_3\text{Na}$
Polypropylene Glycol (PPG)	Nonionic	$\text{H}[\text{OCH}(\text{CH}_3)\text{CH}_2]_{11}\text{HCl}$

Figure 2.28 The zeta potential of bubbles generated using various surfactants as a function of concentration at pH 6.0.

Figure 2.29 The zeta potential of bubbles generated using various surfactants as a function of pH at a concentration of $5 \times 10^{-5} \text{ M}$.

Figure 2.30 The zeta potential of bubbles generated using various surfactants as a function of bubble diameter at pH 6 and a concentration of $5 \times 10^{-5} \text{ M}$.

c. Critical Film Rupture Thickness Measurements

As discussed in Task 1.2.2, the probability of particle capture (P) is critically dependent upon the critical rupture thickness of the intervening film (H_c). In order to determine the value of H_c experimentally, an optical device was constructed (Figure 2.31) which allows a captive bubble to be slowly pressed against a smooth transparent plate while the changes in film thickness are monitored. An optical interferometry technique is being used to measure the thickness (H_c) at which the aqueous thin film between a hydrophobic quartz plate and an approaching air bubble ruptures. The unit employed is similar to that used by Read and Kitchener (1969), but the images are analyzed on-line with a Zeiss Kontron image processing system rather than by photographic means. This approach increases the speed of data acquisition and reduces the errors involved in developing photographic material. In this technique, a monochromatic light passing through the film results in the formation of interference patterns. The relationship between the reflectance of the interference bands (R) and the thickness of the film (H) is given by the Raleigh equation, i.e.:

$$R = \frac{A^2 + B^2 + 2AB \cos\theta}{1 + A^2B^2 + 2AB \cos\theta}, \quad [2.45]$$

$$A = (n_1 - n_0)/(n_1 + n_0), \quad [2.46]$$

$$B = (n_0 - n_2)/(n_0 + n_2), \quad [2.47]$$

$$\theta = 4\pi n_0 H / \Omega, \quad [2.48]$$

in which Ω is the wavelength of the incident light and n_0 , n_1 and n_2 are the respective refractive indices of the solution, solid and gas phases. For the case of fused silica immersed in water, the theoretical values of reflectivity can be calculated as a function of film thickness using Equations [2.45] - [2.48]. An example of these calculations is provided in Figure 2.32, which

Figure 2.31 Optical interference apparatus used for the determination of disjoining film thickness. A-movable stage, B-enclosure, C-cell, D-bubble holder, E-solution, F-smooth solid surface, G-viewing port, H-microscope.

Figure 2.32 Calculated reflectivity versus film thickness for incident light of wavelengths of 700, 666 and 633 nm.

shows reflectivity as a function of film thickness for monochromatic light sources of 700, 666 and 633 nm.

Table 2.3 shows the experimental results for H_C measurements conducted on hydrophilic fused quartz and mica in distilled water. The results indicate that aqueous films on hydrophilic surfaces are very stable and do not rupture. This condition prevents flotation of the mineral by preventing the attachment of air bubbles to the mineral surfaces. In contrast, Figures 2.33 and 2.34 show the results obtained when the surface of fused quartz is rendered hydrophobic by methylation. H_C is shown to increase with increasing degree of methylation, which renders the silica plate hydrophobic. Methylation destabilizes the aqueous films and allows rupture, with H_C varying from 50 nm for the least hydrophobic plate (1% w/w) to 150 nm for the very hydrophobic one. It is interesting to note that the H_C values do not exceed 150 nm even after extensive methylation.

Figures 2.35 and 2.36 show H_C for the collector-coated quartz plate-water-bubble system. Here, the quartz is rendered hydrophobic by the absorption of dodecylamine hydrochloride (DAH) on the plate. Figure 2.35 indicates that H_C increases with increasing DAH addition. Also note that Figure 2.36 shows that H_C increases with increasing pH, suggesting that H_C is a function of the system pH and that hydrophobicity increases with pH.

The results obtained indicate that H_C is a function of the chemistry of the system and varies from 50 nm for a weakly hydrophobic quartz plate to 150 nm for a very hydrophobic one. H_C increases with increasing pH at a given surfactant (dodecylamine hydrochloride) addition. This finding indicates that the hydrophobicity of the surface increases with increasing pH, which correlates well with flotation and induction time results previously reported (Yordan and Yoon, 1986).

Table 2.3

 H_c Measurements on Hydrophilic Mineral Surfaces

Mineral Surface	Liquid	Results
Fused Quartz	Water	No rupture
Fused Quartz	$1 \times 10^{-3} M$ KCl	No rupture
Fused Quartz	$1 \times 10^{-4} M$ Sodium Dodecyl Sulfate	No rupture
Mica Plate	Water	No rupture

Figure 2.33 Measured values of critical rupture film thickness (H_c) as a function of chloromethylsilane additions for a smooth quartz surface.

Figure 2.34 Measured values of critical rupture film thickness (H_c) on quartz as a function of pH for two levels of methylation.

Figure 2.35 Measured values of critical rupture film thickness (H_c) on quartz as a function of dodecylamine hydrochloride (DAH) addition at pH 5.6.

Figure 2.36 Measured values of critical rupture film thickness (H_c) on quartz as a function of pH for a dodecylamine hydrochloride (DAH) concentration of $5 \times 10^{-4} \text{ M}$.

Task 1.2.4: Froth Phase Studies

In the early years of flotation, little attention was given to the study of froth behavior. However, results obtained over the past two decades indicate that the froth phase plays a much more important role in determining the effectiveness of flotation.

a. Froth Stability Measurements

A froth of adequate stability is required in order to obtain good flotation performance. If the froth is not sufficiently stable, mineralized bubbles which enter the froth layer rupture prematurely, causing valuable particles to pass back into the pulp. On the other hand, too stable a froth may result in a large volume of liquid reporting to the product that may adversely affect product grade by nonselectively entraining fine particles. Yet, despite the importance of froth stability in flotation, only a limited amount of data has been reported on this topic. Furthermore, much of the work performed in this area has been qualitative in nature. Information of this type is useful for characterizing froth behavior, but makes the translation of data to actual flotation conditions nearly impossible.

In the present work, froth stability measurements have been performed using the specially designed flotation cell shown in Figure 2.37. The degree of stability of a froth has been determined by measuring the rate at which water is recovered in the froth product. A high water recovery rate would indicate a more stable froth, whereas a lower water recovery rate would indicate a less stable froth. Coal samples used for froth stability studies were obtained from the Elkhorn No. 3 seam of Kentucky, the Upper Cedar Grove and Lower Cedar Grove seams of Virginia, and the Blair seam of West Virginia. Prior to flotation, the coal samples were pulverized in a laboratory hammer mill and screened to obtain minus 100-mesh samples. The coal was slurried and then fed to the cell via a peristaltic pump. A variable-speed impeller was

Figure 2.37 Schematic of the flotation cell used for conducting the froth stability studies.

used to maintain completely mixed conditions within the pulp region. The cell design allowed the froth height to be varied by adding Plexiglas tubes of different lengths. Nitrogen gas was introduced through a fritted glass plate at the bottom of the column. Bubble size was controlled using interchangeable sparging frits with different porosities. Dowfroth M150 was used as the frothing agent in all of the tests.

The circuit arrangement used in the flotation testing is shown in Figure 2.38. As shown, both the froth product and the reject streams were recycled back through the system in order to continuously provide feed slurry. The recycling procedure dramatically reduced the amount of slurry needed to perform each test. Prior to sampling the product and reject streams, the feed slurry was fed to the column for 15 minutes to allow the process to reach steady-state conditions. The froth product was permitted to flow naturally over the top of the column via an overflow lip. The flotation tailings was removed through a tailings port at the bottom of the column. The level of the froth-pulp interface was controlled by means of a variable height weir.

Bubble Size

The effects of bubble size on froth stability, and the corresponding impact of these changes on flotation performance are shown in Figures 2.39 and 2.40. Bubble sizes were calculated from air hold-up using a method outlined by Mankosa (1990). As shown in Figure 2.39, a decrease in bubble size produces a corresponding increase in combustible recovery and product ash content. One explanation for the increased recovery is the higher rate of bubble-particle collisions which take place as the bubble size decreases. Entrainment mechanisms can also be used to explain the higher recovery of combustibles as well as the increase in ash recovery, since smaller bubbles produce a more stable froth. As shown in Figure 2.40, an increase in the mass rate of ash and water reporting to the product also occurs with decreasing

Figure 2.38 Schematic of the recirculation system used in the froth stability studies.

Figure 2.39 The effect of bubble size on combustible recovery and product ash content.

Figure 2.40 The effect of bubble size on mass rate of water and mass rate of ash reporting to the froth product.

bubble size. As bubble size decreases and the number of bubbles increases, there is more surface area available to carry water and entrained ash particles into the froth. These data clearly stress the need for adding wash water to the froth to prevent entrainment when microbubbles are used for fine particle flotation.

Frother Addition

Figure 2.41 shows the effect of frother addition on product ash content and combustible recovery. An increase in frother concentration from 1.5 to 6 lb/ton produced only a slight increase in recovery, while the product ash content changed more dramatically. The relationship between product ash content and frother dosage can be explained in light of the froth stability measurements given in Figure 2.42. At low frother dosages, an increase in the frother dosage produces a lower product ash content by recovering larger amounts of coal relative to the nonselective recovery of mineral matter. As the frother concentration is further increased, the stability of the froth becomes too high, recovery due to entrainment begins to dominate, and the ash content of the product rises. These results show that the product quality is largely controlled by froth characteristics.

Froth Height

Another parameter that was examined in the froth stability measurements conducted in the present work was froth height. Froth height was varied from 0 to 30 cm via the addition of Plexiglas column sections above the pulp level. Figure 2.43 demonstrates that the combustible recovery decreases as the froth height increases. The results also indicate a significant decrease in product ash content with increasing froth height. As shown in Figure 2.44, the change in product ash with froth height is due to variations in froth stability. As the froth depth was increased, the amount of water per unit time reporting to the product stream decreased, i.e., the froth became drier. This behavior is

Figure 2.41 The effect of frother (Dowfroth M150) addition on combustible recovery and product ash content.

Figure 2.42 The effect of frother (Dowfroth M150) addition on the mass rate of water and mass rate of ash reporting to the froth product.

Figure 2.43 The effect of froth height on combustible recovery and product ash content.

Figure 2.44 The effect of froth height on the mass rate of water and mass rate of ash reporting to the froth product.

due to an increase in amount of time available for liquid to drain from the froth phase back into the pulp. As a result of the less-stable froth, fewer particles were nonselectively recovered with the clean coal and the ash content decreased. Since both coal and mineral matter can be entrained, this phenomena can be used to explain both the decrease in recovery and product ash with increasing froth height.

Aeration Rate

Variations in the flow rate of gas to the flotation cell were studied by following the same procedure as described in the previous sections. As shown in Figure 2.45, an increase in gas flow rate caused an increase in combustible recovery and product ash. The increase in product ash content with gas rate can be attributed to an increase in water recovery. The froth stability measurements shown in Figure 2.46, which indicate an increase in both water recovery and ash rate, support this conclusion.

Feed Rate

Figures 2.47 and 2.48 show the effects of increasing the feed rate on product recovery and grade, and on the mass rate of coal and ash reporting to the product, respectively. Figure 2.47 reveals that as the feed rate is increased, the product recovery decreases. One possible reason for this is that the slurry retention time decreases with increasing feed rate. It is also interesting to note that the increased feed rate had an unexpected detrimental effect on product ash content, i.e., a reduction in the amount of coal recovered in the product should coincide with a decrease in product ash. This may be attributed to the increased froth stability with increasing feed rate shown in Figure 2.48. An explanation for the enhanced stability has to do with the presence of a higher concentration of particles in the froth. These particles inhibit the drainage of water from the froth back into the pulp by "blocking" the lamella. At very low feed rates, the froth contains

Figure 2.45 The effect of gas flow rate on combustible recovery and product ash content.

Figure 2.46 The effect of gas flow rate on the mass rate of water and mass rate of ash reporting to the froth product.

Figure 2.47 The effect of slurry feed rate on combustible recovery and product ash content.

Figure 2.48 The effect of slurry feed rate on the mass rate of water and mass rate of ash reporting to the froth product.

only a few particles and water drains back to the pulp very easily. As the feed rate is increased, more particles are carried into the froth and the drainage rate is slowed (i.e., a more stable froth is produced). These results demonstrate that the characteristics of the froth phase and their impact on flotation performance are strongly dependent on the rate at which particles become attached to bubbles in the pulp and are transported to the froth. Thus, in order to develop an adequate model of the froth, a good description of the events which take place in the pulp should first be obtained.

b. Froth Profile Measurements

Because of the importance of the froth phase in determining the product grade, a series of small-scale flotation tests were carried out to examine the profile of ash and solids along the height of the froth zone. The column shown previously in Figure 2.37 was used for this test work, although it was modified slightly so that wash water could be added just below the cell lip. A sampling lance was used to take samples at various points along the column height, as well as in the radial direction across the column cross-section. Two locations were sampled across the column, i.e., at the discharge lip and at the back of the cell opposite the discharge lip. The test work was carried out at various wash water addition rates so that the impact of adding wash water to reduce entrainment could be investigated.

Figure 2.49 shows the profiles of ash and solids in the froth at a relatively low wash water rate of 0.4 lpm. As shown, the ash content drops sharply at the pulp-froth interface for both the front and back sampling points. The sharp decrease in ash content at the interface can be largely attributed to the action of wash water which prevents ash-bearing minerals from entering the froth by hydraulic entrainment. The ash content decreases only slightly with height in the region just above the pulp interface up to

Figure 2.49 Froth profiles obtained at a wash water rate of 0.4 lpm.

the wash water inlet. This section of the froth is referred to as the stabilized froth zone since the flow of wash water through this region retards bubble coalescence and stabilizes the froth. Bubbles in this zone are relatively uniform in size and coalesce very slowly. Above the wash water inlet, the ash content again takes a sharp decrease with height. This section of the froth, which is called the drained froth zone, is similar to the froth typically found in conventional flotation cells. The cleaning action in this region of the froth is a result of bubble coalescence. The drop in bubble surface area causes middlings particles which are less hydrophobic to detach and return to the pulp phase. It should also be noted that the data shown in Figure 2.49 indicate that the ash content of the froth was somewhat lower at the back of the cell. This is probably due to the lower product flow rate and improved drainage in this section of the cell.

Also shown in Figure 2.49 is the profile of the solids content expressed in terms of solid/liquid ratio in the froth. As shown, the solids content remained relatively constant up to the wash water inlet. This suggests that the cleaning action in the stabilized froth was probably not due to changes in bubble surface area. Above the wash water inlet, the solid/liquid ratio increased very rapidly because of bubble coalescence and froth drainage. The solid/liquid ratio obtained at the front sampling point seemed to be slightly lower than that obtained at the back one. This finding also suggests that the froth in the back of the cell drained better than the froth near the front discharge lip.

Froth profiles obtained at a higher wash water rate of 0.8 lpm are shown in Figure 2.50. As before, the ash content dropped sharply at the froth pulp interface. However, at this higher wash water flow rate, the ash profile remained relatively constant all the way up to the top of the cell. There was no additional upgrading apparent in the drained froth zone above the wash water inlet, despite the fact that the solids content increased sharply in

Figure 2.50 Froth profiles obtained at a wash water rate of 0.8 lpm.

this zone. This finding suggests that the higher wash water rate may have resulted in the rejection of middlings particles prior to their entering the drained froth zone. This possibility would also explain the relatively sharper ash profile obtained at this higher wash water flow rate.

Tests were also conducted at a relatively high wash water rate of 1.2 lpm. These data, shown in Figure 2.51, also demonstrate that most of the cleaning action in the froth occurred close to the pulp-froth interface. Upgrading in the drained froth above the wash water inlet was essentially negligible for this relatively high wash water rate. In addition, the solids content profile was almost identical to that obtained at a wash water flow rate of 0.8 lpm. These results indicate that flow rates greater than 0.8 lpm are sufficient to prevent entrainment of feed water into the froth product under the given experimental conditions.

The test work outlined above indicates that the primary cleaning action of the froth phase occurred just above the pulp-froth interface. At this point, there is a sharp increase in the bubble size and air fraction associated with the transition from the pulp phase to the froth phase. The flow of wash water across this interface prevents the hydraulic entrainment of fine particles into the froth phase. These results clearly demonstrate the importance of utilizing wash water when intensive cleaning of fine coal particles by flotation is required.

c. Froth Phase Modeling

Process models can be very useful for the design, optimization and control of unit operations. Furthermore, models which are developed from fundamental principles serve as excellent tools for investigating process behavior since they provide a great deal of conceptual information. Modeling is particularly attractive for applications related to flotation since the numerous combinations of process variables make these systems very difficult

Figure 2.51 Froth profiles obtained at a wash water rate of 1.2 lpm.

to study without exhaustive experimentation.

Because of the aforementioned advantages, considerable interest has been placed in recent years on developing theoretical models which describe flotation. Some success has been achieved using models that predict flotation response from the calculation of the probability of capture of fine particles in the pulp. However, a satisfactory model which describes the behavior of the froth phase in terms of its elementary parameters has not yet been achieved. For this reason, an attempt has been made in the present work to develop a phenomenological model of the froth region using the population balance modeling technique. Because of the complexities associated with three-phase froths, the work carried out in this project has concerned studies of two-phase froth behavior.

Model Development

The two-phase froth flotation model is based on a combination of flow balances around a particular flotation system and population balance modeling techniques. The froth flotation cell has been divided into two distinct regions, the pulp zone and the froth zone. In the present work, flow balance equations are used to describe the pulp zone and the flotation cell as an entire system. A combination of population balance model equations and flow balances around the froth zone have been used to describe the froth phase. The volume and number balances around each zone consider only transport terms, i.e., fluid flow and bubble buoyancy. Transport terms are used to describe the movement of air or liquid due to volumetric flows, settling or rising velocities, and entrainment.

The completed model contains three equations and three unknowns which can be solved simultaneously. In the present work, a combination of search techniques and numerical resubstitutions have been utilized. The resultant froth model is capable of simulating the relationship of various parameters,

such as pulp and froth bubble size and volumetric flow rate, on the air fraction in the pulp and froth and the water and air mass recovery rates.

Total System Balance

The schematic shown in Figure 2.52 represents the volumetric flows of air and liquid passing through the overall flotation column. All flow balances are assumed to be at steady state and all fluids are considered to be incompressible. This assumption is valid for the liquid phase and, for the cell geometries considered in the present work, should also be reasonable for the gas phase. The total volume balance around the flotation column requires that at steady state, input flows equal output flows. This can be stated mathematically as:

$$Q_f + Q_g = Q_c + Q_t, \quad [2.49]$$

where Q_f , Q_g , Q_c and Q_t are the flow rates of feed, air, concentrate and reject streams, respectively. Both Q_f and Q_g are known operating parameters. By dividing each term by the cross-sectional area of the flotation column, this equation can be written in terms of superficial velocities, i.e.,

$$V_f + V_g = V_c + V_t. \quad [2.50]$$

An air flow balance can also be conducted around the total column system.

This balance is given by:

$$Q_f \epsilon_f + Q_g \epsilon_g = Q_t \epsilon_t + Q_c \epsilon_c + V_b A \epsilon_c, \quad [2.51]$$

where V_b is the superficial velocity of the air bubbles rising through the froth phase and ϵ_f , ϵ_g , ϵ_t and ϵ_c are the respective fractional contents of air in the feed, air, reject and concentrate streams. The term $V_b A \epsilon_c$ represents the flow of air into the product due to bubble buoyancy in the froth.

Figure 2.52 Schematic representation of the volumetric flow balance around a flotation cell.

In order for Equation [2.51] to be useful, a value must be determined for V_b . Using Richardson and Zaki's generalized equation for hindered settling conditions, a standard expression for the rise velocity of bubbles can be derived as:

$$V_b = U_b [1 - \epsilon_c]^{N_c}, \quad [2.52]$$

where U_b is the terminal rise velocity of a single bubble under free rising conditions and N_c is the order of the hindered rise. The value for N_c is unknown. For this model a value of 2 was used to represent large bubbles. Luttrell (1986) has shown that U_b can be determined from the expression:

$$U_b = Z (D_b)^{1.14}, \quad [2.53]$$

where Z is a proportionality constant obtained for a given set of experimental conditions. For the sizes of bubbles typically used in flotation, Z can be approximated as 148 when U_b is given in units of cm/sec and D_b is given in units of cm.

In order to further simplify Equation [2.51], one can assume that the air stream entering the cell contains no liquid and that the feed stream contains no entrained air, i.e., $\epsilon_f = 0$ and $\epsilon_g = 1$. Furthermore, if the cell is assumed to be perfectly mixed, then the fraction of air leaving the cell should be equal to the air hold-up within the cell. Mathematically, this would require that $\epsilon_t = \epsilon_p$. From these assumptions, Equation [2.51] can be simplified to yield:

$$Q_g = Q_t \epsilon_p + Q_c \epsilon_c + V_b A \epsilon_c. \quad [2.54]$$

By substituting Equations [2.49] and [2.52] into Equation [2.54], the superficial flow rate of concentrate (V_c) can be determined as:

$$V_C = \frac{V_g - (V_f + V_g)\epsilon_p - U_b\epsilon_C(1 - \epsilon_C)^{N_C}}{\epsilon_C - \epsilon_p} \quad [2.55]$$

The unknown terms in this expression are V_C , ϵ_C and ϵ_p .

Froth Phase Equations

The froth zone can be considered a steady-state environment with an input stream from the pulp and an output stream that comprises the flotation product. Internal flows through the froth zone must be represented by a population balance model. According to Figure 2.52, only the flow of the concentrate (Q_C) need be considered. If air fraction (ϵ_C) in the froth becomes the general property of interest, the general form of the population balance model can be used to show that:

$$d(V_z, \epsilon_C)/dz = 0, \quad [2.56]$$

assuming that (a) the model system is at steady-state, i.e., there is no change in the froth air fraction with time, (b) the froth phase is completely mixed in the horizontal x- and y-directions but is plug flow in the vertical z-direction, (c) bubble size does not change continuously with froth height, and (d) there is no discrete appearance or disappearance of bubbles after they initially pass the pulp-froth interface.

The total rise velocity in the vertical z-direction can be expressed by:

$$V_z = V_C + U_b [1 - \epsilon_C]^{N_C}. \quad [2.57]$$

This equation for the rise velocity of the air phase is a combination of an overall flow balance and a modified version of Richardson and Zaki's equation for hindered settling. The parameter, N_C , is an empirical number related to the particular hindered system. A value of $N_C = 2$ has been found to be reasonable for the size of bubbles commonly found in flotation columns (Griffith and Wallis, 1961). However, further study is needed before this

value can be fully quantified for the froth phase. The determination of V_c is important since it dictates the net magnitude of the flow of solid, gas and liquid to the product stream. This value, combined with the relative velocity at which particles settle through the froth, ultimately determines whether particles in the froth have a net upward or downward velocity (Moys, 1978).

By substituting Equation [2.57] into [2.56] and taking the derivative with respect to z , it is possible to obtain a second expression for the superficial flow rate of concentrate to the product stream, i.e.,

$$V_c = U_b [(N_c \epsilon_c (1 - \epsilon_c)^{N_c - 1} - (1 - \epsilon_c)^{N_c})]. \quad [2.58]$$

As with Equation [2.55], this expression includes V_c and ϵ_c as unknown parameters. However, in order to solve these expressions, an independent expression must also be derived for ϵ_p .

Pulp Phase Balance Equations

The description of the pulp phase process as a perfectly mixed system has become widely accepted in the flotation research community (Moys, 1978), and was therefore employed in this work. In order to determine the external flows of the flotation column, the internal flows of the pulp and froth phases were once again considered. Volumetric flow balances for total flow and air around the flotation pulp are given by Equations [2.50] and [2.51]. As before, it can be assumed that the air fraction of gas entering the column is unity (i.e., $\epsilon_g = 1$) and that the feed contains no air ($\epsilon_f = 0$). It can also be assumed that at the pulp/froth interface, the air fractions in the pulp, tailings, and concentrate are equal ($\epsilon_c = \epsilon_t = \epsilon_p$).

By using Richardson and Zaki's equation to describe the hindered rise of bubbles in the pulp phase, the rise velocity of bubbles in the pulp can be determined from:

$$v_b = U_b [1 - \epsilon_p]^{N_p}, \quad [2.59]$$

where U_b is the terminal rise velocity of a single bubble under free rising conditions and N_p is the order of the hindered rise of bubbles in the pulp. Again, N_p is unknown and has been assumed to be 2 for large bubbles. U_b can be determined as a function of bubble size using Equation [4.8].

By simultaneously solving Equations [2.50], [2.51] and [2.59], the final pulp balance equation can be derived as:

$$\epsilon_p = \frac{v_g}{v_f + v_g + U_b(1 - \epsilon_p)^{N_p}}. \quad [2.60]$$

The expressions which describe the pulp phase, froth phase and the total system provide us with three equations (i.e., [2.55], [2.58] and [2.60]) and three unknowns (i.e., V_c , ϵ_c and ϵ_p). These expressions can be solved simultaneously to calculate the value for these unknowns for a particular set of column geometries and operating conditions.

Parameter Estimation

The two-phase froth flotation simulator requires a number of input operating parameters which describe the column geometry and flow characteristics. The input data required to run a simulation include aeration and feed flow rates, pulp bubble size, froth bubble size, hindered rise coefficient for the pulp, and hindered rise coefficient for the froth. After determining these values, the first step of the solution procedure is to determine the pulp air fraction (ϵ_p) using Equation [2.60]. Since this is a nonlinear equation, a resubstitution technique is required to solve this expression. Once the air fraction in the pulp has been determined, Equations [2.55] and [2.58] must be solved simultaneously for values of V_c and ϵ_c . Simulations were carried out using a set of "standard" conditions, i.e.: $N_p = 2$ (pulp), $N_c = 2$ (froth), $D_b = 0.08$ cm (pulp), $D_b = 0.15$ cm (froth), $V_g = 2$

cm/s, and $V_f = 0.5$ cm/s.

Model Predictions

Aeration Rate: Figure 2.53 shows the predicted results for the superficial flow rate of air and liquid to the product stream as a function of aeration rate. As shown, the rate of both liquid and air reporting to the product increases with increases in the superficial gas rate. This trend coincides with the experimental results found for the three-phase froth flotation studies described previously in Figure 2.46, i.e., the mass rate of water reporting to the product also increases with increasing gas flow rate.

Figure 2.54 describes the effects of gas rate on the air fractions in the pulp and froth phases. In the pulp, an increase in superficial gas rate causes an increase in pulp air fraction. It is commonly known that an increase in gas flow rate will introduce a greater number of bubbles into the pulp, thereby increasing the amount of air in the pulp. An increase in superficial gas rate also causes a decrease in the froth air fraction. In practice, as more bubbles rise from the pulp into the froth, more water is carried upward into the product stream creating a "wetter" froth. Therefore, the results predicted by the simulator seem to reasonably predict trends commonly observed in actual flotation practice.

Froth Bubble Size: Figure 2.55 illustrates the effect of increasing froth bubble size on the superficial product rates of liquid and air. In general, the model predicts that an increase in froth bubble diameter causes a decrease in the rate at which liquid reports to the product. The experimental results shown previously in Figure 2.40 also show that smaller bubbles result in a wetter, more stable froth. Although the effects of increasing froth bubble size have not actually been measured via experimental studies, it has been shown that as bubbles in the froth coalesce and increase in size, the

Figure 2.53 Model predictions of the effect of superficial gas rate on the superficial rate of liquid and air reporting to the product.

Figure 2.54 Model predictions of the effect of superficial gas rate on the fractional air hold-up in the pulp and froth phases.

Figure 2.55 Model predictions of the effect of froth bubble size on the superficial rate of liquid and air reporting to the product.

rate of drainage of water through the froth increases. This produces a less stable froth, causing a lower mass rate of water and a lower combustible recovery.

The effects of froth bubble size on the air fractions in the pulp and froth phases are shown in Figure 2.56. These results show that the froth bubble size has a dramatic influence on the air fraction in the froth phase. As is to be expected, froth bubble size has no effect on air hold-up in the pulp phase.

Pulp Bubble Size: Figure 2.57 illustrates the model's predictions regarding the effects of increasing pulp bubble diameter on the superficial product rate of liquid and air. As shown, an increase in the size of the bubbles in the pulp only slightly increases the rate at which liquid and air report to the product. However, experimental studies on a three-phase froth flotation system have shown that an increase in pulp bubble size does cause a decrease in the mass rate of water reporting to product (Figure 2.40).

As previously discussed, an increase in froth bubble size would cause a decrease in the amount of water reporting to the froth. As larger bubbles report to the froth, coalescence would occur, resulting in even less water reporting to the product. However, because model simulations were performed by varying the pulp bubble size but keeping the froth bubble size constant, the effects of increasing the pulp bubble size on the froth bubble size are not observed. Therefore, the simulator predicted little change in the liquid and air flow rates reporting to product.

Figure 2.58 shows the effects of increasing the pulp bubble size on the pulp and froth air fractions. An increase in the pulp bubble size is shown to decrease the air fraction in the pulp. This is primarily due to a change in the rise velocity of the bubbles with bubble size. Since pulp geometry does not change, an increase in bubble rise velocity produces fewer bubbles in the pulp and, as a result, a lower net air hold-up. Since the model equations do not link the froth and pulp bubble sizes, the simulator predicts little change

Figure 2.56 Model predictions of the effect of froth bubble size on the fractional air hold-up in the pulp and froth phases.

Figure 2.57 Model predictions of the effect of pulp bubble size on the superficial rate of liquid and air reporting to the product.

Figure 2.58 Model predictions of the effect of pulp bubble size on the fractional air hold-up in the pulp and froth phases.

in the froth characteristics with changing pulp bubble size.

Feed Rate: Figures 2.59 and 2.60 describe the effects of increasing the superficial feed rate on the superficial product rates of liquid and air, and on the pulp and froth air fractions. Figure 2.59 shows how both the rate of liquid and of air reporting to the product are reduced when the superficial feed rate is increased. This can be explained by a decrease in the amount of air reporting to the reject stream when the volumetric flow of feed to the cell is increased. Since less air enters the product stream, less water is carried into the froth. Figure 2.60 shows a similar trend for the froth and pulp air fractions. According to the model, an increase in the superficial feed rate produces a decrease in the pulp air fraction. This slight decrease can also be attributed to the reduction in the amount of air flowing into the reject stream. Once again, little or no effect is seen on the froth air fraction since the pulp and froth bubble sizes are independent in the present form of the model.

Unfortunately, the trends shown in Figures 2.59 and 2.60 contradict those obtained in actual experimental studies (Figure 2.48). In a three-phase flotation process, an increase in feed rate generally causes an increase in the mass rate of water reporting to the product. This discrepancy can be explained by the realization that the simulation model does not consider particle-bubble interactions in the pulp and froth phases. It is well known that particles trapped between bubbles can retard the drainage of water from the froth and result in a net increase in the liquid hold-up. At present, there is no manner in which this type of phenomena can be included into the simulation model. Additional studies in this area are probably warranted.

Task 1.2.5: Batch Flotation

Microbubble flotation has been shown to be an effective method for cleaning very fine coal (Yoon and Miller, 1982; Yoon, 1982; Yoon et al.,

Figure 2.59 Model predictions of the effect of superficial feed rate on the superficial rate of liquid and air reporting to the product.

Figure 2.60 Model predictions of the effect of superficial feed rate on the fractional air hold-up in the pulp and froth phases.

1984). From a fundamental point of view, microbubbles are capable of improving both the recovery and selectivity of fine coal flotation (Luttrell et al., 1985; Yoon and Luttrell, 1986). Since most coals must be finely pulverized in order to liberate finely distributed mineral matter, the microbubble flotation process is ideally suited for producing superclean coal.

a. Preliminary Batch Tests

In the present work, batch microbubble flotation tests were performed on a wide range of coal samples. Most of the samples are run-of-mine, although a few have been obtained as cleaned products from preparation plants. Since the primary interest of this work is the production of superclean coal, all of the samples were wet-ground to ultrafine sizes for the purpose of liberating mineral matter. A detailed description of the experimental procedure used in this study has been presented elsewhere (DOE Grant DE-FG22-83PC60806). A summary of the batch testing results are provided in Table 2.4. As can be seen, the microbubble flotation technique is capable of producing superclean coals from a variety of the samples tested. However, multiple cleaning stages were generally required in order to obtain acceptable results. Recent test work has demonstrated that single-stage continuous microbubble flotation tests (Task 1.2.6) tend to produce superior results compared to multiple-stage batch microbubble flotation tests. For this reason, this phase has been truncated in favor of comparable test work in the continuous flotation column.

b. Oil Emulsion Studies

Although most coals can be readily floated with only a frother, the recovery of these coals can be enhanced by the addition of hydrocarbon oils which increase the coal's hydrophobicity. The most common oil collectors for coal include pine oil, creosol, kerosene and diesel fuel. Recently, pure hydrocarbons and oil mixtures have also been investigated.

Table 2.4

Summary of Test Results from Batch Microbubble Flotation Experiments

Coal Sample	Number Stages	Ash (%)		Combustible Recovery
		Feed	Product	
Jellico Seam	4	23	1.2	62
Upper Freeport	4	23	1.8	73
Taggart	3	28	1.2	75
Elkhorn No. 3	3	15	1.8	86
Splash Dam	3	7	1.6	67

In order for the oil to be effective, it must first adsorb on the coal surface. One important factor which may influence this adsorption is the electrokinetic potential of the oil droplets and coal particles. Although a number of studies have been conducted to determine the electrokinetic behavior of coal particles, relatively little work of this type has been carried out using oil droplets. Therefore, the objective of this subtask was to measure the zeta potentials of oil droplets and coal particles and to study the effect of the surface charges on flotation response.

Pure Hydrocarbon Oils

Figure 2.61 shows the zeta potentials of various pure hydrocarbon oils as a function of pH. As shown, the oil droplets are negatively charged throughout the pH range studied. A possible explanation for the negative surface charge is the preferential adsorption of OH^- ions due to differences in the hydration energies of H^+ and OH^- ions (Yordan and Yoon, 1986). The data collected in this study also indicate that the surface charge increases as the hydrocarbon chain length increases. This suggests that CH_2 groups are less electronegative than CH_3 groups.

Figure 2.62 shows the results of microflotation tests conducted on the Elkhorn No. 3 seam coal as a function of pH using various pure hydrocarbon oils. Flotation in the absence of collector produced the lowest yield over the entire pH range examined. After adding the oils, the flotation yield improved. The results also demonstrate that by increasing the hydrocarbon chain length of the collector, the coal floatability increases. The increase in yield below pH 4 was attributed to the fact that the zeta-potentials of both coal and hydrocarbons are minimum at this pH. Since air bubbles are usually negatively charged in the absence of frother, their adhesion to particles would be favored when the particles have a minimum charge. It is also possible that the adhesion and spreading of the oil droplet over the

Figure 2.61 Zeta potentials of pure hydrocarbon oils (hexane, octane, decane, undecane) as a function of pH.

Figure 2.62 Flotation yield versus pH for the Elkhorn No. 3 seam coal using pure hydrocarbons (hexane, octane, decane, undecane) as collectors.

surfaces of the coal particles are favored near the point of zero charge.

Industrial Collectors

The zeta potentials of various industrial coal collectors are shown in Figure 2.63. As shown, kerosene, white kerosene and No. 3 fuel oil display the same charging behavior over the entire pH range. However, a mixture of No. 3 and No. 6 fuel oil possesses an overall less negative zeta potential. The No. 6 fuel oil could not be studied independently since its characteristics were such that it could not be emulsified in distilled water.

The effects of pH on flotation yield for various commercial fuel oils were also examined. Figure 2.64 shows the results of these tests conducted using kerosene as a collector. As shown, maximum recovery occurs in the neutral pH region. The decrease in flotation recovery at acidic pH may be attributed to the formation of humic acid which is promoted under these conditions (Firth and Nicol, 1981). The decrease in floatability above pH 10 may be due to the high surface charges of coal, oil and air bubbles.

The results shown in Figure 2.65 show the flotation recoveries obtained with No. 3 fuel oil (diesel). The flotation behavior in the presence of No. 3 fuel oil displayed a similar trend to that obtained with kerosene. However, the overall flotation yield for diesel fuel was higher than for kerosene. This may be attributed to the presence of impurities or the longer average hydrocarbon chain length for the diesel fuel. The results obtained with a mixture of No. 3 and No. 6 fuel oils are shown in Figure 2.66. As shown, the highest overall floatabilities were obtained using the oil mixture. The improved performance of the fuel oil mixture may be attributed to the fact that the zeta potential of the mixture is lower than that of the individual oils, particularly in the acidic pH region.

The data collected in the present work suggests that the characteristics of the hydrocarbon collector can have a definite impact on the floatability of

Figure 2.63 Zeta potentials of industrial oils as functions of pH.

Figure 2.64 Flotation yield and zeta potential as functions of pH in the presence of kerosene collector.

Figure 2.65 Flotation yield and zeta potential as functions of pH in the presence of No. 3 fuel oil.

Figure 2.66 Flotation yield and zeta potential as functions of pH in the presence of a mixture of No. 3 and No. 6 fuel oils.

coal. For example, the floatability can be increased by increasing the length of the hydrocarbon collector. Also, the flotation of coal with industrial oils was found to be superior to that obtained using pure hydrocarbon oils. In particular, mixtures of No. 3 and No. 6 fuel oils appear to produce the best performance of all the oils tested. The higher recoveries obtained with the mixtures may be due to the presence of impurities in the No. 6 fuel oil which may alter the electrokinetic behavior of the oil droplet.

Task 1.2.6: Continuous Flotation

Batch experiments have demonstrated that the microbubble flotation process is capable of recovering very fine coal with a marked improvement in selectivity. However, little information has been reported concerning the development and operation of a continuous microbubble column. For this reason, a series of continuous microbubble flotation tests have been performed to refine the column design and to develop a better understanding of the operating variables.

a. Preliminary Testing

Table 2.5 shows some of the preliminary results that have been obtained for various coal samples using a 78-inch tall and 2-inch diameter continuous microbubble flotation column. The data demonstrate that the microbubble flotation process is capable of producing superclean coals ($< 2\%$ ash) with high recovery levels from several run-of-mine samples. Also shown in this table are the results of flotation tests conducted using an Elkhorn No. 3 seam coal which had been cleaned to 0.93% ash using a heavy media cyclone at 1.3 specific gravity. At a froth height of 12 inches, an ultraclean coal ($< 0.8\%$ ash) containing 0.50% ash has been obtained with 83% coal recovery. By increasing the froth height to 18 inches, the ash content was further reduced to 0.41%, although the recovery also fell slightly to 74%.

Table 2.5

Summary of Test Results from Continuous Microbubble Column Flotation Experiments

Coal Seam	Feed		Product		Yield	Recovery
	Ash	Sulfur	Ash	Sulfur		
Elkhorn No. 3	9.12	0.81	1.73	0.75	78.8	84.7
Upper Cedar Grove	7.80	0.81	1.87	0.69	64.4	68.5
Pittsburgh No. 8	5.10	1.46	1.87	1.05	72.9	75.3
Coalburg	39.2	--	6.77	--	60.3	92.4
Elkhorn No. 3 [*]	0.93	0.60	0.50	0.59	83.3	83.3
Elkhorn No. 3 ^{**}	0.93	0.58	0.41	0.57	73.6	74.0

*12-inch froth height

**18-inch froth height

b. Characterization of Operating Variables

A series of microbubble flotation tests were conducted to quantitatively evaluate the effects of various operating parameters on column performance. The list of parameters studied includes countercurrent wash addition, aeration rate, slurry feed rate and length-to-diameter ratio. In these experiments, the parameter under study was varied while all others were held constant at predetermined settings.

A sample of run-of-mine coal from the Elkhorn No. 3 seam, Kentucky, was obtained for testing in the microbubble flotation column. The ash and sulfur contents of the raw coal sample were determined to be 9.1% and 0.81%, respectively. As soon as the sample was received, it was crushed to minus 6-mm using a laboratory jaw crusher. Prior to flotation, the samples were dry-pulverized in a laboratory hammermill to below 100 mesh. This procedure was followed by wet-grinding at 30% solids in a 13.3-cm diameter stirred ball mill (Union Process) using 3.2-mm diameter stainless steel balls. Each sample was micronized for 30 minutes, which resulted in a mean product diameter of approximately 5 μm . After micronizing, the samples were diluted to an appropriate solids content (5-15%) in a conditioning sump. A kerosene collector addition of 1.5 kg/t of feed coal was employed in all of the experiments. The conditioned slurry was fed to the column at a point approximately 45 cm below the froth overflow lip. Bubbles were generated externally and introduced at the bottom of the column. In most experiments, an aeration rate of 2 lpm was employed. Dowfroth M-150 was added directly into the bubble generation circuit at a constant rate of 17.5 μlpm for all tests. Wash water was introduced at a predetermined rate through a distributor located 10 cm below the product overflow lip. Unless otherwise noted, flotation experiments were conducted using a 5-cm diameter plexiglass column with a length-to-diameter (L/D) ratio of 20. The height of the column was controlled by the removal or addition of 45-cm sections of Plexiglas

tubing. All the results presented here were obtained at steady state, which was determined by monitoring the recovery and ash content of the product and reject streams as functions of time.

Wash Water Addition Rate: One of the major advantages of column flotation is that the entrainment of fine gangue particles can be minimized by utilizing countercurrent wash water. Figure 2.67 shows the effect of wash water addition on the combustible recovery and ash rejection for the Elkhorn (9% ash) and Taggart (28% ash) seam coals. Columns having diameters of 2.5 and 5 cm were used in these tests. In order to normalize the effect of column diameter, wash water addition has been expressed as superficial velocity (i.e., total volumetric flow rate per unit of cross-sectional area).

As shown, ash rejection steadily improves for both coal samples until a superficial velocity (V_w) of approximately 20 cm/min is reached. After this point, no further change in ash rejection is observed. On the other hand, recovery decreases steadily with increasing V_w . Since the objective of using wash water is to achieve maximum ash rejection with minimum loss of recovery, the V_w value should be determined near the plateau of the ash rejection curves. This value is found to be approximately 20 cm/min for both tests using different coals and column diameters. This optimum value can be translated into volumetric flow as follows:

$$Q_w = 0.942 D_c^2, \quad [2.61]$$

where Q_w is the optimum wash water flow rate in lph and D_c is the column diameter in cm.

Aeration Rate: Figure 2.68 shows the effect of aeration rate on combustible recovery and product ash content for the flotation of Elkhorn No. 3 seam coal. The tests were run at the optimum wash water addition rate. As

Figure 2.67 The effect of superficial wash water rate on combustible recovery and product ash content.

Figure 2.68 The effect of superficial aeration rate on combustible recovery and product ash content.

expected, the recovery of coal increases sharply as the superficial gas velocity (V_g) increases until the maximum recovery level is achieved. In contrast, V_g appears to have little influence on the product ash content which remains relatively constant at approximately 2%.

The increase in recovery with increasing V_g can be explained by the increase in the number and total surface area of bubbles introduced into the column. In general, V_g should be as large as possible to ensure a high throughput (i.e., more air is required to carry larger quantities of particles). If V_g becomes too large, on the other hand, the flow pattern in the column becomes disturbed by the presence of large "slugs" of air. Slugging was observed to occur at a V_g corresponding to approximately 150 cm/min. Therefore, the column should be operated just below this critical value. In the present work, a value of approximately 120 cm/min has been chosen as the optimum value of V_g . In terms of volumetric flow, this can be expressed as:

$$Q_g = 6.65 D_c^2, \quad [2.62]$$

where Q_g is the optimum gas flow rate in lph and D_c is the column diameter in cm.

Froth Height: Figure 2.69 shows the results obtained when the froth height was varied from 10 to 110 cm. As shown, an increase in the froth height resulted in a continuous decrease in the ash content from 10 to 30 cm. However, as the froth height increased above 30 cm, the ash content leveled off at approximately 2%. The decrease in ash content may be a result of the froth being less mixed at higher froth heights. As a result, the wash water becomes more efficient. Combustible recovery, on the other hand, was consistently above 85% up to a froth height of 70 cm, after which recovery decreased. This decrease in combustible recovery was possibly due to a decrease in the residence time in the recovery zone, which became shorter as

Figure 2.69 The effect of froth height on combustibles recovery and product ash content.

the froth height decreased.

Frother Addition: The results shown in Figure 2.70 indicate a sharp increase in recovery when the frother addition was increased. However, the increase in recovery above an addition rate of 2.5 kg/ton was less dramatic. The initially low recoveries may be attributed to an insufficient amount of froth in the system. At low frother additions, the number of microbubbles in the column was insufficient to float the coal particles. However, as the addition of frother increased, there was a corresponding increase in the number of microbubbles in the column, which accounts for the increase in recovery. The ash content in the clean coal was also shown to increase with increasing frother concentration. The increased amount of ash may be a result of an increase in froth stability. A froth of greater stability carries more slurry into the final product and a larger quantity of gangue particles with it. This would, in turn, account for the higher ash content in the product. It is interesting to note that there appears to be an optimum frother addition of approximately 2.25 kg/ton for this particular coal sample and grind size.

Kerosene Addition: The results shown in Figure 2.71 indicate that both the product ash and recovery increase with increasing kerosene addition. The product ash increased from 1.14% when no kerosene was added to 3.14% at a kerosene addition rate of 2 kg/ton. Recovery of the combustible product increased from 26.8 to 91.4% with kerosene additions of 0 to 2 kg/ton, respectively. The increase in recovery was probably due to the increased hydrophobicity of the coal surfaces. In addition, the kerosene may help to agglomerate the fine coal particles so that they can be more easily floated. However, as the coal particles agglomerate, fine mineral matter can be entrapped in the flocs. Entrapped mineral matter is probably responsible for the rise in product ash after kerosene is added.

Figure 2.70 The effect of frother (Dowfroth M150) addition on combustible recovery and product ash content.

Figure 2.71 The effect of kerosene addition on combustibles recovery and product ash content.

Bubble Size: Recently, the effect of bubble size on combustible recovery and ash rejection has generated a great deal of interest. Figure 2.72 shows the effect of bubble size on product ash and combustible recovery. As shown, at a bubble diameter of 400 μm , the recovery was 98.6%. After increasing the bubble size to 1200 μm , the recovery decreased to 24.3%. Note, however, that the bubble size seems to have little influence on the product ash content. The increase in recovery at smaller bubble sizes can be attributed to the increase in surface area available for contact and an improvement in the collision efficiency due to enhanced bubble-particle hydrodynamics.

Feed Rate and Column Geometry: A series of flotation tests were performed to determine the effects of feed slurry flow rate and column length-to-diameter ratio (L/D) on flotation performance. As shown in Figure 2.73, combustible recovery decreased sharply with feed slurry flow rate and increased slightly with L/D . Product ash content remained relatively unchanged provided that a sufficient flow rate of countercurrent wash water was utilized.

In order to explain the observed variations in recovery, both the retention time and bubble size were determined for each test. Bubble size was evaluated directly from the gas hold-up. Since some bubble coalescence occurred in the column, this measurement resulted in a slightly larger bubble size than was normally found in the bubble generation circuit. The results of these analyses are given in Figure 2.74. As shown, the variation in flotation recovery with L/D appears to result from the combined influence of increased retention time and decreased bubble size. For example, at a feed flow rate of 40 ml/min, retention time increased from 1.4 to 2.7 minutes as L/D increased from 11 to 20. At the same time, bubble size decreased from 0.6 to 0.3 mm over the same range of L/D . Both the increase in residence time and the decrease in bubble size, which has a significant influence on flotation rate,

Figure 2.72 The effect of bubble size on combustibles recovery and product ash content.

Figure 2.73 The effect of feed on combustible recovery and product ash content at various L/D values.

Figure 2.74 The effect of feed rate on the retention time and mean bubble size in the column at various L/D values.

appear to be responsible for the increase in recovery with L/D.

The sharp decrease in recovery with increasing feed rate appears to be due to an increase in bubble size. As shown in Figure 2.73, coal recovery dropped from over 95% to less than 40% by increasing the feed rate from 40 to 80 ml/min. Over the same range of feed rates, the bubble size increased from approximately 0.35 to over 1.2 mm (Figure 2.74). The increase in bubble size with feed rate was probably due to a depletion of frother (Dowfroth M-150) by adsorption. Since the frother addition rate to the column was held constant, the depletion of frother became more pronounced as the feed rate of slurry to the column increased (i.e., kg/t of frother was reduced). On the other hand, Figure 2.74 shows that residence time changed very little and, in fact, increased slightly as feed rate increased. Under normal circumstances, an increase in feed rate results in a decrease in retention time and a loss of recovery. In the present work, however, the retention time increased due to a decrease in gas hold-up with increasing bubble size. Thus, the results shown in Figures 2.73 and 2.74 suggest that bubble size is the primary factor which determines throughput and recovery in the microbubble flotation column.

c. Comparison with Conventional Flotation

Side-by-side flotation tests were conducted on a continuous basis using a bench-scale conventional flotation circuit. In the column, the zone below the feed point was designated as the collection zone. This zone was considered to be equivalent to a rougher bank in a conventional circuit. The zone above the feed point was considered to be equivalent to a cleaner bank in a conventional circuit. In these comparison tests, the residence time in the conventional circuits were kept identical to those for the corresponding sections in the column.

In all of the tests, 0.75 kg/ton of kerosene was added to the feed slurry, which was diluted to 5% solids. The coal slurry was fed at a rate of

200 ml/min into each process, which resulted in a mean residence time of 10 minutes. The frother addition rates for the microbubble flotation column were 2.2 and 0.12 kg/ton when processing micronized and coarse coals, respectively. Conventional flotation consumed 0.25 kg/ton for both the micronized and coarse coals. The aeration rate was 1 lpm for the column and 6 lpm for the conventional cell.

Figure 2.75 shows the test data obtained with minus 28-mesh Upper Cedar Grove seam coal containing 7.8% ash. As shown, column flotation gave nearly 30% higher combustible recovery than did conventional flotation, although the ash content was slightly lower in the conventional tests. Note, however, that the recovery of conventional flotation was much closer to that of column flotation when the residence time was reduced. This finding suggests that for the flotation of coarse coal, conventional flotation may be acceptable. However, this would be the case only when the coal does not contain significant amounts of clay-like material which can be easily entrained in the froth product. The results of the tests performed on the micronized coal, which are shown in Figure 2.76, indicate that the true advantage of microbubble flotation is found in processing finer coal. At an identical residence time, column flotation gave 80% higher recovery than conventional flotation at a comparable ash content.

d. Column Design

Two types of microbubble injection devices, a one-way plate (Figure 2.77) and a bubble injection tube (Figure 2.78), were tested to determine the most effective method for injecting gas into the microbubble column. The tests were conducted in the absence of coal in the 5-cm diameter column with a length-to-diameter ratio of 18.5. The amount of frother added to both systems was identical and the aeration rate was increased until "slugs" of air began to form in the column.

Figure 2.75 Comparison of the results from microbubble column flotation and conventional flotation tests conducted on a minus 28-mesh Cedar Grove seam coal.

Figure 2.76 Comparison of the results from microbubble column flotation and conventional flotation tests conducted on a micronized Cedar Grove seam coal.

Figure 2.77 Schematic of the microbubble flotation cell utilizing a one-way plate. A-feed sump, B- peristaltic pump, C-feed distributor, D-recovery zone, E-one-way plate, F-cleaning zone, G-wash water distributor, H-overflow spout, I-tailings outlet, J-aeration zone, K-microbubble generator, L-centrifugal pump, M-peristaltic pump, N-frother sump, O-gas inlet.

Figure 2.78 Schematic of the microbubble flotation cell utilizing a bubble injection tube. A-feed sump, B-peristaltic pump, C-feed distributor, D-recovery zone, E-cleaning zone, F-wash water distributor, G-overflow spout, H-tailings outlet, I-gas inlet, J-frother sump, K-peristaltic pump, L-microbubble injection tube, M-microbubble generator, N-centrifugal pump.

Figure 2.79 shows the results of the design evaluation tests. As shown, the inlet tube clearly allowed a larger quantity of air to enter the column before slugs of air appeared. A possible reason for this result is that coalescence of the microbubbles was observed to occur under the one-way plate. Since the microbubble inlet tube was capable of allowing more air into the column, it was used as the method for injecting microbubbles for the remaining test work.

e. Process Modeling

Column Mixing

It is now widely recognized that flotation columns are neither plug flow nor perfectly mixed, but operate somewhere between these limiting conditions (Dobby and Finch, 1986; Yianatos et al., 1987). This characteristic is demonstrated in Figure 2.80 which shows recovery as a function of the dimensionless product of flotation rate constant (k) and mean residence time (τ) for different mixing regimes. The recovery values for plug flow and perfectly mixed conditions were determined from standard equations available in the literature (Lynch, 1981). As shown, plug flow conditions provide nearly a 20% improvement in recovery over perfectly mixed conditions for typical values of $k\tau$. It is, therefore, advantageous to make the column as plug flow as possible.

For intermediate flow conditions, recovery can be determined as a function of $k\tau$ using an axially dispersed reaction model (Levenspiel, 1972). This expression allows mixing to be represented in terms of a dimensionless vessel dispersion number (N_d). A larger value of N_d indicates a greater degree of axial mixing. The magnitude of N_d is primarily determined by column length-to-diameter ratio (L/D), superficial aeration rate (V_g) and interstitial liquid velocity (V_l). Actual values of N_d are usually determined from experimental measurements of residence time distributions. Details of

Figure 2.79 The effect of frother concentration on the maximum allowable aeration rate with and without a one-way plate.

Figure 2.80 Recovery versus $k\tau$ for well-mixed, plug flow and axially-dispersed conditions. The shaded region represents the typical operating region for columns and the dashed line represents the average performance for which $N_d=0.25$.

this technique as it applies to column flotation have been reported in the literature (Dobby and Finch, 1986).

A review of published data indicates that typical values of N_d are between 0.1 and 0.5 for most flotation columns (Rice et al., 1974; Rice et al., 1981; Dobby and Finch, 1985; Mankosa et al., 1987). This range of N_d values was obtained from columns having a wide spectrum of L/D ratios (10-50) and superficial gas velocities (60-180 cm/min), while the results reported by Mankosa et al. (1987) were obtained using microbubble flotation columns. The shaded area in Figure 2.80 represents the relationship between recovery and $k\tau$ for the range of N_d values reported in literature. As has been noted by Mankosa et al. (1987), there is little change in recovery for this range of N_d values. Thus, a value of $N_d = 0.25$ (dashed line) may be considered as a typical representation of mixing in a flotation column. Using this value of N_d , the axially dispersed equation reported by Levenspiel (1972) is reduced to:

$$R = 1 - 4 \frac{A}{B-C}, \quad [2.63]$$

where

$$A = \sqrt{1+k\tau}, \quad [2.64]$$

$$B = (1+A)^2 \exp(2A-2), \quad [2.65]$$

and

$$C = (1-A)^2 \exp(-2A-2). \quad [2.66]$$

Equation [2.63] actually represents the dashed line shown in Figure 2.80, and can be used to predict column flotation recovery within approximately 4%.

Flotation Rate Constant and Mean Residence Time

Although recovery can be improved by decreasing mixing, the extent of improvement is relatively small. Under typical operating conditions, the improvement is usually on the order of a few percent. Therefore, since

recovery is determined only by N_d , k and τ , the increase in recovery commonly observed when L/D is increased (for a fixed volume) must be associated with changes in the latter two factors.

Recent studies have shown that the rate constant (k) for column flotation can be quantitatively expressed by:

$$k = \frac{3P}{2D_b} V_g, \quad [2.67]$$

in which P is the probability of particle capture and D_b is the bubble diameter. A discussion concerning the determination of P has been reported elsewhere (Yoon and Luttrell, 1986).

On the other hand, the mean residence time (τ) of very small particles can be considered to be equivalent to the mean residence time of the liquid in the column. For a cylindrical column of diameter, D_c , and length, L , τ can be expressed as:

$$\tau = \frac{\pi D_c^2 L (1-\epsilon)}{4(Q_f + Q_w)}, \quad [2.68]$$

where ϵ is the fractional gas hold-up, and Q_f and Q_w are the volumetric flow rates of feed slurry and wash water, respectively. Since recovery is a function of the product $k\tau$, Equations [2.67] and [2.68] can be combined to yield:

$$k\tau = \frac{3LP}{2D_b} (1-\epsilon) \frac{V_g}{V_f + V_w}, \quad [2.69]$$

where V_f is the superficial velocity of the feed slurry. With all other factors held constant, this expression suggests that bubble diameter (D_b) plays at least as important a role as column length (L) in determining $k\tau$. In addition, studies have shown that, for fine particles, P is approximately

proportional to the inverse square of bubble size (Reay and Ratcliff, 1973; Collins and Jameson, 1976; Anfruns and Kitchener, 1977; Weber and Paddock, 1983; Yoon and Luttrell, 1986). Thus, the actual relationship between bubble size and kr should be:

$$kr \propto 1/D_b^3. \quad [2.70]$$

Figure 2.81 shows values of kr back-calculated from experimental recovery data using Equations [2.63] and [2.69]. The recovery data were collected using three different flotation columns having diameters of 5, 10 and 20 cm. Variations in kr were obtained by varying V_f and L/D for each column diameter. Average values of D_b were calculated from the air hold-up (ϵ) which was directly measured using a differential manometer. As shown, there is a strong dependence between the value of kr and D_b . For bubbles larger than about 0.6 mm in diameter, kr varies according to D_b^{-3} , as predicted. However, as bubble size is decreased below this value, kr deviates from the cubic relationship. The smaller value of kr is a result of the sharply increasing value of ϵ for smaller bubbles (see Equation [2.69]).

The effects of L/D and D_b are more clearly demonstrated in Figure 2.82. In this figure, kr has been calculated using Equation [2.69] for a fixed column volume and constant volumetric flow rate of feed slurry. Wash water addition rate and aeration rate were set according to Equations [2.61] and [2.62]. The value of P was estimated using a hydrodynamic model for bubble-particle collision (Yoon, Adel and Luttrell, 1987). Bubble loading was not considered in the present analysis, although in reality it may put a limit on the L/D ratios shown here. The results indicate that, at a given feed flow rate and column volume, kr can be improved by increasing L/D and decreasing D_b . Since the superficial wash water velocity (V_w) is fixed, the increase in kr with L/D is a result of the decrease in the volumetric flow of wash water with decreasing column diameter which, in turn, increases the retention time.

Figure 2.81 Back-calculated values of kr as a function of bubble size for column diameters of 1-, 2- and 4-inches.

Figure 2.82 Predicted values of $k\tau$ as functions of L/D and bubble diameter (in mm) for a fixed column volume and feed rate.

For example, at a bubble diameter of 0.5 mm, an increase in L/D from 10 to 20 increases recovery by nearly 10%, which is solely due to an increase in retention time. The decreased volumetric flow of wash water for smaller diameter columns is also beneficial in terms of downstream dewatering since less total water is required. Thus, one of the main advantages in using columns having a large L/D is that it minimizes the wash water addition rate.

Figure 2.82 also indicates some interesting trends regarding the effect of bubble size on k_r . For a given value of L/D , k_r increases very sharply as the bubble size is decreased. The improvement in recovery is due to the greater number of bubbles and enhanced bubble-particle collision when bubble size is decreased. As an example, consider the case for a fixed column volume and L/D of 15. As the bubble diameter is decreased from 1 to 0.3 mm, the recovery increases from approximately 50% to over 95%. This improvement is substantially greater than can be achieved by increasing L/D over any practicable range using larger air bubbles. In addition, the incremental increase in k_r with L/D is more pronounced at the smaller bubble sizes, as is indicated by the increased slope (i.e., L/D has a larger effect when D_b is small). These analyses clearly demonstrate the benefits of processing fine coal in column-type flotation cells using microbubbles.

As a result of the column test work and modeling efforts, three factors have been identified as having the greatest impact on column flotation performance: column mixing, flotation rate and residence time. Although mixing plays a role in controlling column performance, it does not appear to have a large effect on recovery over the range of column geometries and operating conditions normally encountered in column flotation. The results of the present work also suggest that column flotation can be substantially improved by decreasing bubble size (D_b) and increasing the length-to-diameter ratio (L/D) for a fixed column volume and feed flow rate. The increase in recovery with decreasing D_b is the result of an increase in the flotation rate

constant with decreasing bubble size. On the other hand, the improvement in recovery with increasing L/D is largely due to the increase in particle residence time associated with a decrease in the required volumetric flow of wash water with decreasing column diameter. In the modeling effort, simple expressions have also been derived which allow the optimum flow rates of wash water and air to be estimated. In addition, a simplified equation for determining fractional recovery (R) from the flotation rate constant (k) and mean particle residence time (τ) has been presented. These expressions can be used for the design, scale-up and operation of column flotation.

Task 1.2.7: Surface Chemistry of Coal Pyrite

The main objectives of the test work carried out under this subtask were (i) to examine the flotation characteristics of coal pyrite under different conditions, and (ii) to develop methods of depressing coal pyrite effectively in coal flotation. The techniques used to characterize the surfaces of mineral pyrite and coal pyrite included microflotation tests, contact angle measurements under electrochemically controlled conditions, cyclic voltammetry, electron spectroscopy for chemical analysis (ESCA), and infrared spectroscopy (FTIR).

a. Electrochemical/Contact Angle Cell

Figure 2.83 shows a schematic of the electrochemical/contact angle apparatus used to monitor changes in the wetting behavior of pyrite as a function of measured potential. Experiments were carried out as a function of pH using a pure sample of mineral pyrite from Peru and a coal pyrite sample from the Pocahontas No. 3 seam. The control of pH was achieved using standard buffer solutions.

Figures 2.84 and 2.85 show the effects of applied potential on the measured contact angle for the samples of mineral pyrite and coal pyrite,

Figure 2.83 Schematic diagram of the apparatus used to measure contact angle under applied potential conditions.

Figure 2.84 Contact angle measurements as a function of applied potential and pH for mineral pyrite.

Figure 2.85 Contact angle measurements as a function of applied potential and pH for coal pyrite.

respectively. For the neutral and alkaline pH solutions, the contact angle values remained relatively low regardless of the applied potential, which indicates that the surface of the pyrite displayed little hydrophobicity under these conditions. For pH 4.6, the contact angle values remained low for negative potentials, but increased gradually as the potential became more positive. The increase in contact angle may be explained by the formation of hydrophobic oxidation products, such as elemental sulfur or polysulfides, which form when the sample is exposed to oxidizing potentials. Similar behavior was observed at pH 2, but a drop off in contact angle was noted when the potential exceeded 0.5 volts. The decrease in contact angle may be due to the formation of hydrophilic oxidation products, such as sulfate, which occur as oxidation becomes more extensive. The results clearly demonstrate that mineral and coal pyrite can be made either floatable or nonfloatable simply by varying the surface oxidation. The test data also suggest that an effective method for preventing the flotation of pyrite is to float under reducing conditions or using solutions of high pH.

b. Cyclic Voltammetry

Cyclic voltammetry experiments were carried out to examine differences in the electrochemical behavior of pyrite. Three different samples were examined in the study: pure mineral pyrite, coal pyrite containing a very small (< 5%) amount of coal inclusion, and coal pyrite containing approximately 50% coal inclusions. Figure 2.86 shows the results of cyclic voltammetry measurements conducted with each of the three freshly-prepared samples at pH 7. In general, only minor electrochemical differences, if any, exist between the three unoxidized samples. Similar results were also obtained in the acidic and alkaline pH regions.

Figure 2.86 Test results obtained from cyclic voltammetry for mineral pyrite (a), coal pyrite containing < 5% coal inclusions (b), and coal pyrite containing > 50% coal inclusions (c).

c. Electron Spectroscopy for Chemical Analysis (ESCA)

In order to develop a better understanding of the mechanism(s) responsible for the variations in the hydrophobicity of pyrite, the oxidation products formed on the surfaces of mineral and coal pyrite were examined using electron spectroscopy for chemical analysis (ESCA). As before, three different pyrite samples were examined in the study. These included pure mineral pyrite, coal pyrite containing a very small (< 5%) amount of coal inclusion, and coal pyrite containing approximately 50% coal inclusions.

The results of the ESCA measurements are shown in Figure 2.87. The samples were analyzed after being freshly prepared and after 90 hours of oxidation in water. When the samples were not oxidized, the XPS signals for the sulfur 2p were similar in all three cases. The primary peak has been identified with S^{2-} in bulk pyrite. However, after conditioning the three samples in double-distilled water for 90 hours, each of the three samples displayed a peak associated with the formation of sulfate. More importantly, the spectra show a very strong oxidation of the sample containing the most coal inclusions, while the coal pyrite with less than 5% coal inclusion was less severely oxidized. The oxidation of mineral pyrite seems to be much lower than that of either of the coal pyrites samples. These findings suggest that the oxidation kinetics of pyrite may be accelerated by the presence of coal inclusions. Since coal pyrite appears to be oxidize faster, it may be prone to form hydrophobic surface oxidation during the short conditioning periods in commercial flotation circuits. This phenomenon may partly explain why coal pyrite is difficult to reject in coal flotation circuits.

d. Spectroelectrochemical Cell

A specially-designed spectroelectrochemical cell was constructed so that the oxidation behavior of mineral and coal pyrite could be examined *in-situ*. As shown in Figure 2.88, the cell is equipped with a mineral bed working

Figure 2.87 ESCA spectra of pyrite samples before and after 90 hours of oxidation in distilled water. (a) mineral pyrite, (b) coal pyrite containing < 5% coal inclusions, (c) coal pyrite containing > 50% coal inclusions.

Figure 2.88 Schematic diagram of the spectroelectrochemical cell.

electrode, a platinum counter electrode and a reference electrode. The mineral bed electrode consists of finely-ground particles of pyrite embedded in carbon-paste. This three-electrode system allows the mineral bed electrode to be conditioned at an arbitrary potential, after which the FTIR spectrum of the mineral surface is taken by pressing the working mineral bed electrode against the reflection element.

Results of FTIR measurements conducted using the *in-situ* ATR cell are shown in Figure 2.89. For the mineral pyrite sample, a strong adsorption peak occurred at a wavelength of 1080 cm^{-1} . The adsorption spectra of standards conducted using both solid (Figure 2.90) and aqueous forms (Figure 2.91) indicate that the major adsorption peak on mineral pyrite is associated with the presence of ferrous sulfate. A similar shoulder peak was observed for the coal pyrite sample. However, there exists an unknown compound on the coal pyrite which displays adsorption peaks at wavelengths of 1010 and 1032 cm^{-1} . There are several possible explanations for these peaks. As shown in Figure 2.90, these adsorption peaks are similar to that obtained for solid $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$. Therefore, it is possible that the adsorption peak simply reflects the presence of a complex mixture of oxidation products in the surface layer. It is also possible that the adsorption doublet between 1150 and 1085 cm^{-1} is the characteristic peak for C-O-C bonds which have appeared due to the superficial oxidation of the coal inclusions in the pyrite matrix.

e. Microflotation

The data collected to this point indicates that mineral and coal pyrite can become naturally hydrophobic if the surface conditions are not properly controlled. To this end, several possible schemes for manipulating the surface properties of pyrite are examined in the following sections. The performance of these techniques has been assessed from microflotation testing.

Figure 2.89 *In-situ* FTIR spectra of mineral pyrite (a) and coal pyrite (b) in distilled water.

Figure 2.90 Standard FTIR spectra for solid samples of Na₂SO₄ (a), FeSO₄·xH₂O (b) and Fe₂(SO₄)₃·xH₂O (c).

Figure 2.91 Standard FTIR spectra for aqueous samples of Na_2SO_4 (a), FeSO_4 (b) and $\text{Fe}_2(\text{SO}_4)_3$ (c).

Figure 2.92 shows the effect of pH on the floatability of mineral pyrite. In general, this sample shows essentially no floatability over the entire pH range when only an electrolyte is added to the solution. However, the floatability increases sharply after the addition of MIBC, a commercial frothing agent. The increase is particularly pronounced at pH values less than 4. When both kerosene and MIBC are used, the floatability again increases dramatically. As before, the increase is particularly sharp in the acidic pH region. The results of similar test work carried out using samples of coal pyrite are shown in Figure 2.93. These tests reveal that coal pyrite has a considerably different flotation behavior than mineral pyrite. In general, the floatability of coal pyrite was found to be much less sensitive to changes in pH. The coal pyrite was also found to be weakly floatable (10-30%), even in the absence of frother or collector. The use of MIBC significantly increased the recovery of coal pyrite, and when both kerosene and MIBC are used, recovery increased beyond 80-85%.

Microflotation tests were also conducted to study the effect of oxidation on the floatability of coal pyrite. The oxidized sample was prepared by allowing the sample be exposed to air for an extended period of time. Figure 2.94 shows pyrite recovery behavior for the oxidized and unoxidized samples. In general, the freshly-prepared coal pyrite sample behaved in a similar fashion as the mineral pyrite sample shown in Figure 2.92, i.e., the floatability increased sharply with decreasing pH. However, after oxidation, the coal pyrite sample became less floatable and less sensitive to changes in pH. This behavior is similar to that shown previously in Figure 2.93. As before, none of the samples floated well in the absence of frother, suggesting that coal pyrite has some affinity for the frother. These results also support the conclusion that the differences in the floatabilities of mineral and coal pyrite can be attributed to differences in their oxidation behavior. It is also worth noting that the test data indicate that in the presence of

Figure 2.92 Flotation recovery of mineral pyrite as a function of pH using 0.3 M NaCl (a), 0.01 M NaCl and 20 μ l/liter MIBC (b), and 0.01M NaCl, 20 μ l/liter MIBC and 2 μ l/liter kerosene (c).

Figure 2.93 Flotation recovery of coal pyrite as a function of pH using 0.3 M NaCl (a), 0.01 M NaCl and 20 μ l/liter MIBC (b), and 0.01 M NaCl, 20 μ l/liter MIBC and 2 μ l/liter kerosene (c).

Figure 2.94 The effect of pH on the recovery of fresh and oxidized coal pyrite in the presence and absence of frother (Dowfroth M150).

frother, depression through pH control is effective only if the sample is fresh. Oxidized samples display a moderate degree of floatability across the entire pH range.

In order to determine the effect of potential on the floatability of coal pyrite, microflotation experiments were conducted by adding various amounts of oxidizing and reducing agents. Figure 2.95 shows the results obtained using the reducing agents of hydrazine and sodium sulfide. As shown, coal pyrite floats very well at potentials above 0.1 V. When the potential was reduced by adding increasing amounts of hydrazine or sodium sulfide, the floatability was reduced substantially. These results show that the floatability of coal pyrite can be prevented by properly controlling the solution redox conditions. Other redox-controlling agents were also examined to determine their impact on pyrite floatability. Hydrogen peroxide (H_2O_2), which is a strong oxidizing agent, was also tested. This reagent was found to retard the floatability of pyrite through the formation of hydrophilic sulfoxy species, but relatively high dosages were required. Sodium sulfite (Na_2SO_3) was found to be a less effective depressant than either hydrazine or sodium sulfide. The addition of ferric sulfate was found to have relatively no impact on the floatability of coal pyrite.

Figure 2.95 The effects of potential-controlling agents on the flotation recovery of coal pyrite at pH 6 in the presence of 20 μ l/liter MIBC.

TASK 3: SELECTIVE HYDROPHOBIC COAGULATION

Introduction

Considerable interest has been shown in recent years in the application of selective flocculation to fine coal cleaning. Russian and Polish investigators (Blagov, 1970; Blaschke, 1972, 1976) used polymeric flocculants in an attempt to remove ash from coal, but their conclusion was that the process is not selective and the flocculated coal requires further treatment. In the U.S., Hucko (1977) was the first to test this process on a bituminous coal, but his results were also discouraging. In a series of tests conducted on a thickener underflow, he showed that the results of the selective flocculation process using Dowell M172 and Superfloc 315 were not as good as those obtained using the conventional froth flotation process. More recently, however, Attia (1985) claims to have developed more selective flocculants for coal, but the nature of his reagents is not known for proprietary reasons.

Coal particles can also be selectively coagulated from coal-ash mixtures without any reagent. This "autogenous" or "self-coagulation" process has been found to be more selective than the conventional selective flocculation processes using polymeric flocculants. This process was discovered during investigations into microbubble flotation, where coal is wet-ground to below 10 μm in a stirred ball mill. It was found that when a pulverized coal sample was placed in a beaker with some dilution water, the coal particles were flocculated at the bottom of the beaker while the ash particles were dispersed in the supernatant. With repeated decantation of the supernatant, ash particles were removed from the coal to below 1 or 2% ash with very high recovery. Since this process was possible without using any reagent either during grinding or decantation, it provided a means of low-cost coal cleaning.

It should be noted that the coal coagula redisperse approximately 8-12 hours after grinding. However, they can be recoagulated by agitating the pulp

at high speed. This process may be related to the shear flocculation phenomenon observed by Warren (1975, 1977) with scheelite. He found that micron-sized scheelite particles can be flocculated when the slurry is subjected to high-shear agitation in the range of 800-1800 rpm. It is important to point out, however, that shear flocculation does not occur unless the mineral particles become hydrophobic by collector adsorption. For the case of coal, no collector coating is necessary because it is naturally hydrophobic.

Thus, all that is required for the selective coagulation of coal is high-shear agitation (unless the coal has become hydrophilic to some extent by oxidation). Once coagulated, the coal can then be separated from the uncoagulated ash-forming minerals by sedimentation, elutriation and/or screening. Typically, several stages of coagulation and separation are required to produce acceptable ash rejection levels, principally because of mineral particle entrapment during coal coagulum formation.

The work reported below reviews the fundamentals of the coagulation process, describes the results of bench-scale test work conducted to evaluate the technical feasibility of the process, and discusses development of mathematical models of the coagulation and elutriation phases of the process for eventual use in simulation studies.

Task 1.3.1: Fundamentals of Hydrophobic Coagulation

a. Floc Size and Porosity

An Elkhorn No. 3 coal sample (3.5% ash) was used to study coal coagulum characteristics. The coal was prepared for test work by crushing and screening to 400 mesh and then diluting 11 grams of this material to 450 ml with 10^{-3} M KCl solution of appropriate pH. After agitating this suspension at 1000 rpm for 10 minutes, coagulum size distributions were determined by the Andreasen pipette method. To do this, the suspension was first transferred to

a graduated cylinder and diluted to 1000 ml to give a suspension of 2% by weight of solids. This suspension was agitated by inverting the flask 20 times, and then allowed to settle. A 10 ml sample of the suspension was then taken at a fixed depth by pipette according to a predetermined time schedule. Each of the 10-ml samples was dried in an oven set at 75°C and then weighed to determine the solids concentrations at the given height as a function of time. The aggregate size was calculated using the Stokes free settling law as given by:

$$d = 141 \left[\frac{h\eta}{t(S_s - S_l)} \right], \quad [3.1]$$

in which h is the settling height in cm, η is the viscosity of the liquid in poise, t is the settling time in minutes, and S_s and S_l are the densities of solid and liquid, respectively. The diameter found thus is in μm . The solid percent finer was calculated as $100 \times (W_t/W_0)$, where W_t and W_0 are the solid weights of the 10-ml suspensions at time t and time 0, respectively.

To test the technique, aggregate distributions were obtained from three different tests at identical conditions. The pH of the suspension was adjusted to 8.4. As shown in Figure 3.1, the measurements were fairly reproducible over the three different tests. However, it was found experimentally that it was difficult to obtain accurate data in the upper size range of the aggregate distribution due to the rapid settling velocities of the larger aggregates.

Aggregate size distributions obtained at two different solution pH values and in the presence of a popular dispersant for coal, i.e., Lomar-D, are shown in Figure 3.2. The dispersant was used to obtain a particle size distribution of the coal. The resulting size distribution showed that the coal sample used in this study had a very narrow distribution and that 80% of

Figure 3.1 Aggregate size distribution measured from three independent runs using the Andreasen Pipette Technique.

Figure 3.2 Aggregate size distribution of Elkhorn No. 3 coal formed in three different suspension conditions.

the particles were below 25 μm . After the suspension was subjected to coagulation at pH 8.4, the size distribution curve shifted significantly toward the larger size spectrum. The value of d_{50} , defined as 50% finer, increased from 24 to 49 μm , and the distribution became narrower. However, the aggregate size distribution of the coal sample coagulated at pH 10.1 was almost identical to that of the initial particle size distribution, indicating that at this pH, coal particles did not coagulate. The stability of the coal particles at this pH was probably a result of a strong electrostatic force which will be discussed later in this report.

b. Surface Forces

Electrokinetic studies were undertaken in order to better understand the fundamental principles involved in the selective coagulation process. These studies were conducted on a run-of-mine Lower Cedar Grove coal containing 1.4% ash. The sample was crushed to minus 6-mm using a laboratory hammermill and screened. The minus 400-mesh fraction was used for both the electrokinetic measurements and the coagulation experiments. Samples of ash-forming particulates for use in the electrokinetic work were obtained by low-temperature ashing of the coal sample.

Zeta potentials were measured using a Pen Kem Model 501 Laser-Zee meter. The sample dispersion was prepared by dispersing 0.02 g of the 5- μm sample in 500 ml of 10^{-3} M KCL solution. At a given experimental condition, at least three zeta potential readings were taken and averaged.

The coagulation experiments were conducted by suspending 10 g of the minus 400-mesh coal sample in 500 ml of KCL solution (10^{-3} M). The suspension was agitated for 5 minutes at 1000 rpm in a 3-1/2-inch diameter Plexiglas cylinder. The cylinder contained six baffles and a 1-3/4-inch diameter variable speed impeller. After agitation, the suspension was allowed to settle for 3 minutes and then 300 ml of the supernatant was withdrawn by

siphoning. The solids in the supernatant were weighed after filtration and drying. The coagulation efficiency (E_c) was calculated as:

$$E_c = 100(W_i - W_f)/W_i, \quad [3.2]$$

in which W_i refers to the initial weight of solids in a given volume (300 ml) of the suspension before coagulation and W_f refers to that in the supernatant after coagulation.

Figure 3.3 shows the coagulation and zeta potential data obtained as a function of pH on both fresh and oxidized coal (140°C) samples. The fresh coal is shown to coagulate over a wide range of pH values between 3.8 and 8.9. The dotted line in Figure 3.3 shows how the upper critical coagulation pH limit and the corresponding zeta potential are determined. The lower pH limit and zeta potential can be determined likewise. It is interesting to note that at the upper and lower pH limits, the zeta potentials, i.e., -43 and 42 mV, respectively, are of approximately the same magnitude. The fact that fresh coal can coagulate at such high zeta potentials suggests that there exists a highly attractive force which can overcome the strong electrostatic repulsive force. This excess attractive force has come to be known as the hydrophobic interaction force.

Figure 3.3 also shows that oxidation at 140°C did not change the zeta potentials appreciably, while the effect on the pH range for coagulation was reduced significantly. The upper critical coagulation pH limit, which will be designated as pH_c , was lowered to 7.3, at which point the corresponding zeta potential was -23 mV. The fact that no coagulation was possible at higher zeta potentials suggests that oxidation significantly reduces the hydrophobic interaction force.

The results obtained with coal samples oxidized at higher temperatures, i.e., 170 and 200°C, are shown in Figure 3.4. One can see that after severe oxidation, the hydrophobic interaction force was further reduced, so that

Figure 3.3 Coagulation and zeta potential values for fresh and oxidized (140°C) coal samples as functions of pH.

Figure 3.4 Coagulation and zeta potential values for coal samples oxidized at 170 and 200°C as functions of pH.

coagulation only occurred at pH values near the isoelectric point (iep) of the coal sample. The zeta potential values at the pH_C were less than -5 mV. At these low zeta potentials, the dispersion force would be large enough to overcome the electrostatic repulsive force, in which case the DLVO theory may be perfectly applicable. The hydrophobic force could still be there, but it must be smaller in magnitude than the dispersion and electrostatic forces.

Table 3.1 summarizes the results presented in Figures 3.3 and 3.4. It shows that very hydrophobic coals can coagulate at pH values far above their iep's, where the zeta potentials are in excess of -40 mV. This was most probably because of the presence of a large attractive hydrophobic interaction force. As the coal was oxidized, however, the hydrophobic interaction force was reduced and, as a result, the coagulation occurred at pH values closer to its iep, where the zeta potentials were low.

The selective hydrophobic coagulation process not only depends upon coal coagulation, but also upon dispersion of the mineral matter. Therefore, zeta potential measurements were obtained for the mineral particulates present in the Lower Cedar Grove coal. Turbidity measurements of the particulate suspension were used as an indication of coagulation behavior. As shown in Table 3.2, the mineral particles coagulated very readily at pH values corresponding to their iep. As the pH was increased, which resulted in an increase in zeta potentials, the ash-forming particles became more and more dispersed up to a pH of around 7. Beyond pH 7, the turbidity values remained relatively constant, indicating maximum dispersion. Therefore, based on this data, a window of separation exists for this coal between the pH values of 7, where optimum dispersion occurs, and 8.9, where the coagulation efficiency of the coal particles sharply decreases. These values correspond fairly well with the bench-scale results shown later in this report.

Table 3.1

Critical pH and Zeta Potential Values for Coagulation of Coal

Parameter	Oxidation Temperature ($^{\circ}\text{C}$)			
	25	140	170	200
pH_c (exp)	8.9	7.3	3.8	1.5
zpc (exp)	-43.0	-22.0	-5.0	-5.0

Table 3.2

Zeta Potentials and Turbidities of Mineral Matter Particulates
from the Lower Cedar Grove Seam Coal as Functions of pH

pH Value	Zeta Potential (mV)	Turbidity
2.8	3	45
3.0		47
4.0	-7	
4.4		78
6.0	-9	120
6.8		135
7.2	-17	
7.8		145
8.0	-23	
8.8	-31	148
10.4	-38	148

Hamaker Constants

The Hamaker constants for the Lower Cedar Grove coal were determined by experimentally measuring the contact angles and using the angle to calculate the dispersion component of the surface free energy of a solid (G_s^d) using the following equation:

$$G_s^d = \left[\frac{(1 + \cos \theta_m) G_m}{\sqrt{G_m^d}} \right]^2 \quad [3.3]$$

in which θ_m is the contact angle, G_m ($= 50.8 \text{ erg/cm}^2$) is the surface free energy of methylene iodide, and G_m^d ($= 48.5 \text{ erg/cm}^2$) is its dispersion component. The dispersion component of the surface free energy can be used to estimate the Hamaker constant for a material by using the following equation:

$$A_{ii} = 6\pi r_{ii}^2 G_s^d, \quad [3.4]$$

in which r_{ii} is the intermolecular distance within the interacting body of the substance. For most materials, the value of $6\pi r_{ii}^2$ is approximately 1.44×10^{-14} .

The contact angles for the coal were measured at 25°C using a contact angle goniometer (Rame-Hart). The sessile drop technique was employed in a closed container to take the measurements at equilibrium vapor pressure. Typically, at least 20 equilibrium contact angles were measured at different sites and specimens and averaged. The specimens were polished coal chunks.

Table 3.3 shows the measured contact angle values along with the Hamaker constant for the Lower Cedar Grove coal at different degrees of oxidation. Also shown is the maximum interaction energy values calculated from the classical DLVO theory. As discussed in the previous section, the energy barrier as calculated by DLVO theory is much too high for strongly hydrophobic coal to coagulate. Another attractive force having a magnitude much greater

Table 3.3

Potential Energy Barrier at Critical pH of Coagulation
and Hamaker Constants of Coal

Parameter	Oxidation Temperature ($^{\circ}\text{C}$)			
	25	140	170	200
Θ_m	38.8	32.2	26.6	23.3
$A_{ij} \times 10^{13}$ (erg)	6.07	6.51	6.87	7.06
$V_{\max}$ (kT)	2924	548	3.3	2.3

than the van der Waals force must exist. The origin of the force must be related to hydrophobicity since oxidized coals coagulate only near their iep where the van der Waals force is large enough to overcome the repulsive electrostatic force.

c. Coagulation Model Development

A population balance model describing the size distribution evolution of a coagulation process has been developed. The model is a set of simultaneous first-order nonlinear ordinary differential equations for each discrete size spectrum and uses equations for aggregate porosity, growth and breakage to provide details of both aggregation and breakage processes in terms of the physical parameters and operating conditions. The development of the population balance model and the equations associated with the model will be discussed in detail in the following paragraphs.

During the coagulation of solids in a suspension, porous aggregates are formed, with volumes being greater than the sum of the volumes of the individual particles making up the aggregates. It has been found, theoretically and experimentally, that the porosity of the aggregates increases as the aggregate size increases, but in a complicated fashion. Therefore, it is necessary to model the porosity of aggregates as a function of aggregate size for any simulation of the coagulation process to be successful. The equation for porosity, ϵ , used in this model is

$$\epsilon = [p^2(1-p)]/(1-p^5), \quad [3.5]$$

where $p = a_1/a_2$ (a_1, a_2 = particle diameter). For the special case of $a_1 = a_2$, $\epsilon = 0.2$. It is important to realize that Equation [3.5] only gives a new volume-based porosity introduced from binary aggregation. Therefore, the following equation must be used in order to determine the overall porosity for a z th-fold aggregate:

$$\epsilon_z = 1 - \{[z(1-\epsilon_{z-1})(1-\epsilon_{pz})]/(z-\epsilon_{z-1})\}. \quad [3.6]$$

The new porosity, ϵ_{pz} , in Equation [3.6] can be calculated using Equation [3.5] in which p_z is given by Equation [3.7],

$$p_z = a_1/a_{z-1} = [(1-\epsilon_{z-1})/(z-1)]^{1/3}. \quad [3.7]$$

With the overall velocity, the equivalent spherical size of a z th-fold aggregate can be readily calculated using the following equation:

$$a_z = a_1[z/(1-\epsilon_z)]^{1/3}. \quad [3.8]$$

By solving Equations [3.7], [3.5], [3.6] and [3.8] in sequence, the overall porosity and equivalent spherical size of an aggregate can be simulated as a function of aggregate number, z .

Aggregation rate depends upon the frequency of collision and the fraction of collisions which result in adhesion. In the present work, the shear field is applied by intense mixing with the primary particle size being greater than 1 μm . Under these conditions, the fluid flow is the only important mechanism for transporting particles. The suspension used in this study is sufficiently dilute (less than 3% by volume) that aggregation is a free-in-space process to which simple, binary collision free-path concepts may be applied for calculating collision frequency.

As an example of developing an expression for collision frequency, the collision between an i th-fold aggregate and a j th-fold aggregate is considered here. According to the Kolmogorov theory of isotropic turbulence, the relative velocity, U_{ij} , with a separation distance of $(a_i + a_j + H_m)$ in the fluid, depends on the turbulent scale, and its magnitude is given by the relationships:

$$U_{ij} = (1/15)^{1/2}(\epsilon/\nu)^{1/2}(a_1+a_2+H_m) \quad \text{if } (a_1+a_2+H_m) < \tau, \quad [3.8]$$

or

$$U_{ij} = 1.37[\epsilon(a_1+a_2+H_m)]^{1/3} \quad \text{if } (a_1+a_2+H_m) > \tau, \quad [3.9]$$

where ν is the kinematic viscosity of the continuous phase, ϵ is the rate of turbulent energy dissipation per unit mass, H_m is the critical separation corresponding to the maximum interaction energy barrier, $V_{\max}$, upon which two particles will slip together spontaneously, and τ is the Kolmogorov microscale as defined by Equation [3.10]:

$$\tau = (\nu^3/\epsilon)^{1/4}. \quad [3.10]$$

In the present work, the collision efficiency is taken as unity if the kinetic energy is larger than or equal to the interaction energy barrier. Otherwise, an exponential distribution of collision is used, i.e.:

$$\alpha = 1 \quad \text{if } V_k \geq V_{\max}, \quad [3.11]$$

or

$$\alpha = \exp[-\beta(V_{\max} - V_k)] \quad \text{if } V_k < V_{\max}. \quad [3.12]$$

β is an adjustable parameter with a unit of $(kT)^{-1}$, describing the rate at which collision efficiency decreases with increasing $(V_{\max}-V_k)$, where $V_{\max}$ is the interparticle potential energy barrier and V_k is the kinetic energy of the particles at the moment of collision.

Since both the relative velocity and collision efficiency can now be determined, the overall aggregation rate can be calculated using Equation [3.13]:

$$R(i,j) = \alpha\pi(a_1+a_2+H_m)^2 U_{ij} n(i)n(j) \quad \text{if } i \neq j, \quad [3.13]$$

or

$$R(i,j) = (1/2)\alpha\pi(a_1+a_2+H_m)^2 U_{ij} n(i)n(j) \quad \text{if } i=j. \quad [3.14]$$

It is convenient to use rate constants instead of rates in formulating coagulation kinetic equations since the rate constant is an intensive

property, independent of the concentration of the species. It can be readily shown that the aggregation rate constants $k(i,j)$ are given by:

$$k(i,j) = \alpha\pi(a_1+a_2+H_m)^2U_{ij}, \quad \text{if } i \neq j, \quad [3.15]$$

or

$$k(i,j) = (1/2)\alpha\pi(a_1+a_2+H_m)^2U_{ij}, \quad \text{if } i=j. \quad [3.16]$$

Two important roles of mixing in promoting the aggregation rate are illustrated in Equations [3.13] and [3.14]. On one hand, an increase in mixing intensity will increase the kinetic energy and, thus, increase the collision efficiency in the presence of an interaction energy barrier. On the other hand, an increase in mixing intensity increases the collision frequency, as indicated by an increase in U_{ij} . Apparently, shear conditioning of a coagulation system is favorable for aggregation kinetics. However, it should be noted that the shear conditioning will unavoidably create a mechanical force which may be strong enough to break the aggregates of a certain size, as will be discussed in the following section.

It is evident that there are two major forces which control the breakage rate of aggregates or coagula. The surface forces between particles tend to hold them together, forming a stable aggregate, while the hydrodynamic shear force tends to break the bonds between particles so that only random aggregates can form. Therefore, it is reasonable to relate the breakage rate constant to these counteracting forces. These two forces can be determined using the following equations:

$$\text{and} \quad F_b = 2k_1G_{sw}a^2(1-\epsilon)^{2/3}, \quad [3.17]$$

$$\text{or} \quad F_s = (2\pi/15)k_2S_wa^4(\epsilon/v) \quad \text{if } 2a < \tau, \quad [3.18]$$

$$F_s = 1.09k_2\pi S_wa^{8/3}\epsilon^{2/3} \quad \text{if } 2a > \tau, \quad [3.19]$$

where F_b is the binding force, F_s is the shear force, ϵ is the aggregate

porosity, G_{sw} is the solid/water interfacial tension, k_1 and k_2 are model constants, and ϵ is the rate of turbulent energy dissipation per unit mass.

Based on the values of these two forces, the breakage rate constant, $S(a)$, which is defined such that $S(a)n(a)dt$ is the number of aggregates having size a that split per unit volume in the infinitesimal time interval, dt , can be calculated using the following functional formula:

$$S(a) = 0 \quad \text{if } F_b > F_s \quad [3.20]$$

$$\text{or } S(a) = A\{1 - \exp[k_3(F_b - F_s)]\} \quad \text{if } F_b \leq F_s, \quad [3.21]$$

where A and k_3 are adjustable parameters which can be determined by fitting experimental data to the simulation results.

Upon breakage, an aggregate of size a turns into a number of daughter fragments which are distributed in the size space according to a distribution function, $\beta(a', a)$. $\beta(a', a)$ is the number fraction of aggregates of size a that report into a size class of a' after their disintegration. To complete the description of the breakage event, it is necessary to know the distribution function of the fragments resulting from the breakage of a larger aggregate, known as the breakage function.

In this model, the Broadbent and Callcott breakage function is used without significant modification to describe the aggregate breakage function. For convenience, the aggregate number instead of the aggregate size is used in the following:

$$\beta(z', z) = [(e^{-(z'-1)/z} - e^{-z'/z}) / (1 - e^{-1})][z/z'], \quad [3.22]$$

where z and z' refer to the z th- and z' th-fold aggregates, respectively. $\beta(z', z)$ represents the fractional number of z' th-fold aggregates formed by the breakage of a z th-fold aggregate.

From the development of the aforementioned aggregate growth and breakage models, a general model was developed to describe the dynamic behavior of

coagulation under mixing conditions. The model is based on the theorem of population balance which is commonly used for many physical rate processes. The population balance as a basis for describing particulate processes has been developed from the general conservation equation:

$$\text{Accumulation} = \text{Input} - \text{Output} + \text{Net Generation.} \quad [3.23]$$

In coagulation processes, the size evolution in a population of aggregates is of significant interest. Therefore, the aggregate size is the only property considered in this population balance model. Applying the general theorem of Equation [3.23] to a closed system of coagulation processes under proper mixing conditions, the basic deterministic equation for the number balance of any fold aggregates, say zth-fold, is obtained as:

$$\begin{aligned} \frac{dn(z,t)}{dt} = & \frac{1}{2} \sum_{i=1}^{z-1} RC(z-i,i)n(z-i,t)n(i,t) - n(z,t) \sum_{i=1}^{\infty} RC(z,i)n(i,t) \\ & + \sum_{i=z+1}^{\infty} S(i)B(z,i)n(i,t) - S(z)n(z,t) \quad z=3,4,\dots \quad [3.24] \end{aligned}$$

The symbol of $n(z,t)$ for the number concentration of zth-fold aggregate indicates the time dependence of concentration. Other symbol descriptions are the same as described in the text above.

The left side of Equation [3.24] represents the change in number concentration of zth-fold aggregates per unit time. This term is also referred to as an accumulation of zth-fold aggregates, which is equivalent to the left side of Equation [3.23]. On the right side of Equation [3.24], the first term accounts for the increase in the number concentration of zth-fold aggregates which are formed by binary aggregation of smaller aggregates and/or particles in this unit time interval, and the second term describes the decrease in number concentration of zth-fold aggregates due to the binary

combination of a zth-fold aggregate with the aggregate of any class, forming an aggregate larger than the zth-fold aggregate. These two terms in combination describe the aggregate growth behavior, and the other two terms on the right side collectively represent aggregate breakage behavior. The third term shows the appearance of a zth-fold aggregate by the breakage of a larger aggregate, and the fourth term represents the disappearance of the zth-fold aggregate due to its disintegration, forming a spectrum of smaller daughter aggregates. It can be seen that the right side of Equation [3.24] corresponds to the net generation term in Equation [3.23]. Since the system in question is a closed system, both input and output terms must be zero. Thus, Equation [3.24] satisfies the general conservation theorem of Equation [3.23].

In Equation [3.24], it is implicitly assumed that the aggregate can grow without any limitation on the aggregate size, as indicated by the summation to infinity. It has been found experimentally that a characteristic finite maximum aggregate size exists for every coagulation system. It is therefore reasonable and practical to replace the infinity sign in Equation [3.24] with a maximum aggregate number, N , which varies from one system to another.

Applying this general theorem to the primary particle, the dimer and the top aggregate classes yield the following equations:

$$\frac{dn(1,t)}{dt} = -n(1,t) \sum_{i=1}^{z-1} RC(1,i)n(i,t) + \sum_{i=1}^{\infty} S(i)B(1,i)n(i,t), \quad [3.25]$$

$$\frac{dn(2,t)}{dt} = RC(1,1)n(1,t)^2 - n(2,t) \sum_{i=1}^N RC(2,i)n(i,t)$$

$$+ \sum_{i=3}^N S(i)B(2,i)n(i,t) - S(2)n(2,t), \quad [3.26]$$

and

$$\frac{dn(N,t)}{dt} = 1/2 \sum_{i=1}^N RC(i,N-i)n(i,t)n(N-i,t) - n(N,t) \sum_{i=1}^N RC(i,N)n(i,t) - S(N)n(N,t). \quad [3.27]$$

An additional constraint should be imposed on Equations [3.24]-[3.27] in order to complete the description of a closed system of coagulation under mixing conditions:

$$\frac{d \sum_{z=1}^N zn(z,t)}{dt} = 0. \quad [3.28]$$

Equation [3.28] indicates that the total mass of the solids in a system does not change with time, which is a common characteristic of any closed system. It can be written in an integral form as:

$$\sum_{z=1}^N zn(z,t) = n(1,0). \quad [3.29]$$

It should be noted that the above equations (Equations [3.24]-[3.27]) have been derived from a macroscopic viewpoint where spatial dependence is suppressed. However, in the case of batch-operated coagulation, where the system is well mixed, this approach turns out to be exact. These coagulation kinetic equations can be obtained by using the universal microscopic population balance approach if the same assumption of a well-mixed, batch-operated system is made.

In order to solve the coagulation kinetic equation numerically, it is important to define the size classes over the size spectrum of interest. For a system of monosized primary particles, it is convenient to define the size class based on the number of particles composing the aggregates. In the present work, the classes are defined in such a way that the aggregates in each successive class contain one more primary particle than the ones in the

previous class. It is obvious that each class has a constant property of aggregate number. A large number of classes, say 500 classes, is required to cover the size spectrum of interest using this method. However, this scheme of classification is more convenient. This method also gives a more accurate mass balance in the simulation since all the aggregates in the same class have identical solid mass. With the classes being specified, the porosity for each class is calculated using Equations [3.7], [3.5] and [3.6], successively, while the equivalent spherical aggregate size is calculated using Equation [3.8] in which the porosities have been previously obtained.

The interaction energy barrier, $V_{\max}$, and the critical film thickness, H_m , between particles of each pair of classes are then calculated using the modified DLVO theory, consisting of an equation for hydrophobic interactions. In these calculations, the particle sizes are replaced by the corresponding spherical aggregate sizes, and the zeta potentials and Hamaker constants of the aggregates are assumed to be the same as for the primary particles. The kinetic energy, V_k , for the aggregates of each pair of classes at the separation of critical film thickness must be determined using existing equations. The reduced mass of interacting aggregates is calculated from the apparent masses of individual equivalent spherical aggregates, which include the masses of solids and the inclusions of water. The relative velocity between two approaching aggregates is then calculated using Equation [3.9] or [3.10], depending on whether the flow of the suspension is viscous dissipation or inertial convection in nature. With the obtained energy barriers and kinetic energies, the collision efficiency between aggregates of each pair of classes is calculated using Equation [3.11] or [3.12]. Coagulation rate constants for each pair of aggregates in any two different classes is then calculated using Equation [3.15] or [3.16].

In the calculation of the breakage rate constants, the adhesion force and break-up force are calculated using Equations [3.17] and [3.18] or [3.19], respectively. The breakage rate constant is calculated for each class using Equation [3.20] or [3.21] with parameters A and k_3 being fixed at reasonable values. Finally, the daughter aggregation distribution function is calculated for each class using Equation [3.22].

After predetermination and calculation of all parameters and constants, the coagulation kinetic equations, i.e., Equations [3.24]-[3.27], are solved numerically using the backward differentiation method known as Gear's stiff method. The solutions were then tested using the constraint equation, i.e., Equation [3.28], for the acceptance of the results. If the relative error is larger than a given value, the solutions are rejected and the time interval is reduced for another try; otherwise, the solutions are accepted and sent to the output device. The steady state is then checked by comparing the total number of aggregates in two successive runs. If steady state is recognized, the program is terminated. Otherwise, the numerical solution starts again from the ending time of the previous run, unless the desired time range has been covered. This numerical procedure is summarized in the schematic flow chart given as Figure 3.5.

The numerical procedure outlined above has been used to simulate the aggregate size distribution as a function of evolution time for a fine coal particle suspension mixed at 1000 rpm, and the results are given in Figure 3.6. A zeta potential value of -43 mV, a Hamaker constant of 6.07×10^{-20} J, and a hydrophobic interaction parameter of -1.247 mJ/m^2 corresponding to the critical pH have been used in this simulation. A solid/water interfacial tension of 26.72 dyne/cm as determined from contact angle measurements has been used. The values of other model parameters for calculating the collision efficiency and breakage rate have been chosen so that reasonable dynamic equilibrium aggregate size distribution can be determined. They are 0.138

Figure 3.5 Schematic diagram of the computer program for simulating coagulation kinetic behavior.

Figure 3.6 Cumulative aggregate size distributions of fine coal particles at various coagulation times.

$(kT)^{-1}$, 139.89, 507.38 dyne^{-1} and 1×10^5 , respectively, for β , k_1 , k_3 and A .

Figure 3.6 shows that, starting with mono-sized primary particles of 5 μm , three distinct size zones are developed as the coagulation proceeds. The first zone covers a size range of 5-26.7 μm . This zone is characterized by relatively low coagulation rate constants. Its existence is due to the breakage of the larger aggregates of zone 3. Following the first zone, a second zone is developed with evolution of coagulation time, which is characterized by a coagulation rate larger than its breakage rate. This zone covers a wide range of aggregate sizes, from 29.6 to 99 μm . Most aggregates formed fall into this range. The wide range of aggregate sizes covered by this zone shows that the aggregates formed under severe shear conditions differ significantly in size. The last zone starts with an aggregate size of 100 μm . Inside this zone, only random aggregates are formed since the breakage rate of aggregates in this zone is much greater than their formation rate. Therefore, upon formation, the aggregates break into a spectrum of daughter aggregates of smaller size.

Simulations were also conducted and compared with experimental results obtained using an Andreason pipette. The general agreement between aggregate size distributions as measured experimentally and predicted from the coagulation model is illustrated in Figure 3.7. The aggregate top size of approximately 50 μm as measured experimentally is almost the same as that predicted by the simulation. The discrepancy found in the aggregate size range greater than 50 μm may be attributed to the inaccuracy of the aggregate size measurement using this experimental technique. The simulation is also unable to predict a tail in the small size spectrum as measured experimentally due to the nature of the binary breakage function used in this simulation.

The simulated effect of agitation intensity on aggregate size is shown in Figure 3.8. The results were obtained using particles having a mean size of 5 μm as the primary particles. Figure 3.8 shows that by increasing

Figure 3.7 A comparison of aggregate size distributions obtained from computer simulation and experimental measurements at pH 8.4.

Figure 3.8 Equilibrium cumulative aggregate size distributions as functions of coagulation time for three different mixing rates.

the agitation intensity and, hence, the shear rate, the mean aggregate size was reduced quite significantly. For example, the d_{50} of the aggregates after agitation at 500 rpm was approximately 140 μm compared to 25 μm after agitation at 1000 rpm. The large decrease may be due to aggregate breakage after formation in high-shear conditions, which will be discussed later in the report.

The effects of hydrophobicity on aggregate size were investigated by changing the hydrophobic interaction parameter in the coagulation model. The results of the simulation are shown in Figure 3.9. A low parameter value resulted in no coagulation as indicated by the 100% less than 5- μm point shown in the figure. After decreasing the parameter by a fairly small amount, which represents an increase in hydrophobicity, the d_{80} size of the aggregates increased to approximately 75 μm . A further decrease in the hydrophobic parameter had no effect on the aggregate size distribution.

Task 1.3.2: Bench-Scale Tests

Bench-scale coagulation tests were conducted using a 6-inch diameter container which has four 1/2-inch baffles placed vertically along the inside walls at equal distances apart. Initial experiments rotated a 3-inch serrated disk impeller at 1800 rpm. However, after further testing indicated that rotational speeds as low as 250 rpm were sufficient to induce selective coagulation, the mixing speed was reduced to 750 rpm.

Typically, after grinding a coal sample in a stirred ball mill to produce a 5- μm mean particle size, 20 grams of the sample was placed in the mixing container. The sample was diluted to 2% solids by weight using tap or distilled water and the pH was adjusted to the desired value using either sodium hydroxide or hydrochloric acid. Each test was carried out in three steps, shown respectively in Figures 3.10a, 3.10b and 3.10c. Initially, as shown in Figure 3.10a, the coal suspension was agitated for 5 minutes to

Figure 3.9 Equilibrium cumulative aggregate size distributions for different values of hydrophobic interaction parameter C .

Figure 3.10 Schematic representation of the experimental procedure for batch-type selective coagulation tests.

disperse the mineral matter, promote particle-particle collision and produce aggregates. The slurry was then allowed to stand for 5 minutes, as shown in Figure 3.10b, during which time aggregates grew in size and settled to the bottom of the container while the ash-forming particulates remained in suspension. The dispersed phase was siphoned from the mixer, as shown in Figure 3.10c, leaving the settled coal at the bottom.

In most case, it was necessary to repulp the settled material and repeat the process several times to remove both the minerals entrained in the water associated with the product and those entrapped inside each coagulum. A typical plot showing the stage-by-stage product ash content and recovery analysis from the treatment of an Elkhorn No. 3 coal is shown in Figure 3.11.

a. Process Feasibility

Table 3.4 shows the results obtained with various coal samples in multiple stages of batch experiments. The coal samples were attrition ground to 3- to 5- μ m median size (D_{50}). Most of the test results were obtained using tap water as the medium, while de-ionized water was used for some of the coal samples such as the Pittsburgh No. 8, Illinois No. 6, and Upper Freeport coals. No hydrocarbons were used to obtain any of the test results shown in Table 3.4. Depending on the feed ash, washability characteristics, hydrophobicity and the number of cleaning stages employed, the product ash contents varied in the 0.36-7.5% ash range. The pyritic sulfur rejections varied from 57 to 88% for different coals. With the Elkhorn No. 3 coal, which assayed 12.0% ash and 0.25% pyritic sulfur in the feed, the product assayed only 0.03% pyritic sulfur. In general, the selective hydrophobic coagulation process gave very high combustible recovery values.

b. Characterization

Most physical cleaning processes are limited by a lower particle size value due to a sharp drop in recovery as the particle size is further

Figure 3.11 A stage-by-stage analysis of recovery and product ash contents in batch-type selective coagulation experiments.

Table 3.4

Results of Batch Selective Coagulation Tests Conducted on Various Coal Samples

Coal Seam	Ash (%)		Pyritic Sulfur (%)		Combustible Recovery (%)
	Feed	Product	Feed	Product	
U. Cedar Grove	24.0	5.13			89.24
U. Cedar Grove	12.0	2.45			91.08
U. Cedar Grove	3.4	0.98			92.98
L. Cedar Grove	1.44	0.36			79.07
Elkhorn No.3	12.0	1.14	0.25	0.03	85.25
Elkhorn No.3	5.25	1.34			93.91
Splashdam	3.50	2.07			99.11
Upper Freeport	22.2	7.50			82.89
Upper Freeport	12.0	4.84	1.25	0.41	88.48
RL-Consol	5.50	1.84	0.65	0.28	90.49
Illinois No.6	12.0	4.49	1.72	0.55	92.38
Pittsburgh No.8	14.4	3.45	2.31	0.46	88.14

decreased. However, combustible recovery values obtained by the selective hydrophobic coagulation process improved with decreasing particle sizes, as illustrated in Figure 3.12. These results were obtained after 6 cleaning stages using an Elkhorn No. 3 coal sample (12% ash). Combustible recovery linearly increased from 73% at a 14.5- μm mean size to 95% at 4.4 μm . Ash and sulfur rejection values also improved with decreasing particle size as a result of continued liberation of the respective components. Additional tests were conducted over a larger range of particle sizes on an Upper Cedar Grove coal. Figure 3.13 compares the recovery-product ash content curves obtained from three coal slurries having mean particle sizes of 3.7, 5.0 and 75 μm . These results further demonstrate that finer particle sizes yield lower product ash values and that combustible recovery improves with a decrease in particle size for the selective coagulation process.

A series of experiments were performed to determine the effects of agitation time on recovery and product ash content using an Elkhorn No. 3 coal sample (12% ash). The tests were conducted in distilled water with a slurry pH of 9. As shown in Figure 3.14, agitation of the coal slurry for only 30 seconds at 1800 rpm yielded very low recovery values (38%). However, as the agitation time was increased to 3 minutes, recovery sharply increased to 94% and remained relatively constant for greater agitation times. Therefore, a 3-minute agitation time is all that is required for the efficient coagulation of coal particles in distilled water.

Several coagulation experiments were conducted to determine the difference in required agitation intensity when using distilled water at pH 9 and tap water at pH values of 7 and 9. In the case of distilled water, as shown in Figure 3.15, recovery values were very low for rotational speeds below 750 rpm. Recovery values sharply increased to 88% at an agitation intensity of 750 rpm and remained relatively constant as the impeller speed was increased. For the tests using tap water as the medium, good recovery

Figure 3.12 The effect of particle size on the selective coagulation process. Treatment involved 6 stages of cleaning in distilled water at pH 9.

Figure 3.13 Recovery versus product ash curves for the selective coagulation of Cedar Grove seam coal as a function of mean particle size.

Figure 3.14 Effect of agitation time on coal recovery (three stages).

Figure 3.15 Effect of rotational speed on the coagulation behavior of Elkhorn No. 3 seam coal.

values ($> 90\%$) were obtained at impeller speeds as low as 250 rpm. This may be explained by the presence of ions in the tap water which lower the repulsive electrostatic force and, hence, the potential energy barrier. Thus, the requirement for the minimum impeller speed depends on the height of the potential energy barrier, which in turn is determined by the relative magnitudes of the repulsive electrostatic force and the attractive hydrophobic interaction force prevailing in the system.

Figure 3.16 shows the effect of pH on the treatment of an Elkhorn No. 3 coal using the selective hydrophobic coagulation process. The results were obtained after three cleaning stages in tap water. At pH values between 3 and 5, a very high combustible recovery was obtained, but the products contained a large amount of ash. The high recovery may be attributed to the fact that the isoelectric point (iep) of this coal falls in this pH region, and consequently, that the electrostatic force of these coal particles will also be small. Furthermore, since coal is positively charged below the iep and ash-forming particulates are negatively charged, the coal and mineral particles may heterocoagulate, giving higher recoveries and product ash values. Other possible explanations for the high product ash values in this pH region include self-coagulation of clay particles due to the opposite charge between the face and the edge of the clay particulates and homocoagulation of other ash-forming minerals present due to their iep's. At very high pH values, both coal and mineral matter were well dispersed, resulting in a low coal recovery and a high product ash content. In fact, the settled material had a higher ash content than the feed because the heavier minerals settled faster than the coal. At pH values between 7 and 9, however, there was a window of separation. The combustible recovery was in excess of 95% and the product ash was as low as 3% or less. In this rather narrow pH range, only the hydrophobic coal particles coagulated selectively due to the presence of the strongly attractive hydrophobic interaction force, while the hydrophilic material

Figure 3.16 The effect of pH on coal recovery and product ash content after three cleaning stages in tap water for an Elkhorn No. 3 seam coal (feed ash 12%).

remained dispersed.

The effect of solids concentration on combustible recovery and product ash content for the selective coagulation process is shown in Figure 3.17. The results were obtained using an Elkhorn No. 3 coal (5.25% ash) in tap water and a slurry pH of 9. At a very low solids content of 0.65%, the results were very poor, both in terms of recovery (17%) and product ash content (3.2%), indicating that the probability of collision between the particles was too low. At higher solids concentrations, recovery was very high, but the product contained large amounts of ash-forming material. This result was due to settling and entrapment of mineral particulates in a hindered settling environment. The product ash content was minimized at a solids concentration of around 2%, where recovery reached 80%.

In order to determine the effect that counter ions would have on the process, artificial additions of various multivalent cations were studied. The cations were added to an Upper Cedar Grove coal (24% ash) slurry prior to the initial cleaning stage at a concentration of 10 ppm. Each of these tests were run at a slurry pH value of 9, a solids content of 1.5% by weight and a total of six cleaning stages. As shown in Table 3.5, the higher valence cations, such as Fe^{3+} , produced higher recovery and product ash values, presumably because of a decrease in the surface potentials of the various particulate components which would enhance, in turn, the coagulation ability of the coal and associated mineral matter.

Additional tests were conducted to study the effect of Ca^{2+} concentration on combustible recovery and product ash content using the same Upper Cedar Grove coal. The tests were conducted in distilled water at a slurry pH of 9. As shown in Figure 3.18, Ca^{2+} concentrations below 10 ppm had no effect on recovery and product ash content. However, concentrations around 20 ppm yielded almost 100% coal recovery and product ash content values approximately equal to the feed ash, indicating that the coal and mineral particulates were unstable.

Figure 3.17 Effect of percent solids on coal recovery and product ash percent for Elkhorn No. 3 seam coal (5.25% ash) (three stages).

Table 3.5

Results Illustrating the Effect of Multivalent Cations

Cation	Product Ash (%)	Combustible Recovery (%)
Distilled Water	5.45	89.14
Ca ²⁺	5.88	89.25
Ni ²⁺	5.70	83.88
Zn ²⁺	6.18	87.20
Al ³⁺	16.09	94.93
Fe ³⁺	14.37	95.69

Figure 3.18 Effect of Ca²⁺ concentration on coal recovery and product ash percent in distilled water at pH 9.

If a coal is partially oxidized, it may be beneficial to add a small amount of hydrocarbon oil to enhance the hydrophobicity of the coal particles and, therefore, the hydrophobic interaction force. Figure 3.19 shows the results obtained using an Upper Freeport coal (22.2% ash) with and without kerosene. With no kerosene, the ash content was reduced from 22.2 to 7.5%, with a combustible recovery of 82.9% after several stages of cleaning. Attempts to further reduce the ash content by increasing the number of cleaning stages resulted in a sharp decrease in combustible recovery. When using only 1 lb/ton of kerosene, which amounted to 0.0005% by weight of the coal, coal recovery at comparable product ash contents improved significantly, as shown.

c. Elutriation Column Characterization

The first series of continuous selective coagulation tests were conducted using an elutriation column to separate the coal coagula from the dispersed minerals. The elutriation column shown in Figure 3.20 employed a countercurrent washing action with the upward flow of water controlled so that the upward velocity was less than the settling velocity of the coal coagula, but greater than the settling velocity of the ash-forming particles. With this arrangement, the countercurrent wash water carries the dispersed (mineral) matter out of the top of the cell while the coagulated coal particles settle for collection at the bottom.

Initial tests conducted to study the various process variables involved the treatment of an Elkhorn No. 3 coal containing 12% ash. The coal was ground in a stirred ball mill for 30 minutes prior to each experiment in order to obtain a 5- μ m mean particle size. Tap water was used as the medium and natural pH conditions were used in all the tests. Typical results obtained with the continuous selective coagulation/elutriation process are listed in Table 3.6. These demonstrate that despite the relatively small sizes of the

Figure 3.19 Effect of kerosene addition (1 lb/ton) on coal recovery and product ash content for an Upper Freeport seam coal (22.5% feed ash).

Figure 3.20 Schematic diagram of the counter-current continuous coagulation/elutriation separator.

Table 3.6
Results from Continuous Selective Coagulation Tests

Coal Seam	Feed Ash (%)	Product Ash (%)	Ash Reduction (%)	Coal Recovery
Elkhorn No.3	12.0	4.50	62.5	95
Elkhorn No.3	1.6	1.00	37.5	95
Elkhorn No.3	1.3	0.75	42.3	85

aggregates, estimated to be between 50 and 75 μm , the process can be run continuously.

The effects of increasing the solids content in the feed to the elutriation column were examined by raising the concentration from 2 to 3%. The tests were conducted by varying the elutriation water rate for the two feed solids concentrations. The feed rate for these tests was 50 ml/min. The results shown in Figures 3.21 and 3.22 indicate that a change in solids content from 2 to 3% by weight has little effect on combustible recovery and product ash percent.

Figure 3.23 illustrates the effect of increasing the elutriation water rate on coal recovery, pyritic sulfur reduction, and product ash content. After decreasing gradually with an increase in the elutriation water rate, recovery was found to sharply decrease from a value of 84% at a rate of 450 ml/min to 40% at 550 ml/min. Recovery gradually approached zero as the elutriation water rate was increased beyond 550 ml/min. The product ash content decreased from 7% at 100 ml/min to 4.9% at 450 ml/min, where the ash content began increasing to 7.1% at 800 ml/min. Pyritic sulfur reduction increased with an increase in the wash water rate. For the column design used and a feed rate of 50 ml/min, the optimum elutriation water rate was 450 ml/min, giving rise to a coal recovery of 84%, a product ash content of 4.90%, and a pyritic sulfur reduction of 30%.

The effects of increasing the feed rate were investigated over a range of 25-150 ml/min while maintaining an elutriation water rate of 400 ml/min. Figure 3.24 shows that as the feed rate was increased from 25 to 150 ml/min, coal recovery and pyritic sulfur reduction gradually decreased from 82 to 56% and 36 to 22%, respectively. The product ash content increased linearly from 4.8 to 7.0% over the same range of feed rates. The loss in recovery with increasing feed rate was probably caused by an increase in the upward velocity in the top portion of the column which would, in turn, wash the smaller coal

Figure 3.21 Coal recovery versus elutriation water rate curves for 2 and 3 percent solids.

Figure 3.22 Product ash percent versus elutriation water rate curves for 2 and 3 percent solids.

Figure 3.23 The effect of elutriation water rate on coal recovery, sulfur reduction, and product ash percent at a feed rate of 50 ml/min.

Figure 3.24 The effect of feed rate on coal recovery, sulfur reduction, and product ash percent at an elutriation water rate of 400 ml/min.

coagula out the top with the dispersed minerals.

d. Elutriator Modeling

A population balance model of the elutriation column was developed by first dividing the column into five different zones. From top to bottom, the zones are as follows: overflow zone, upper intermediate zone, feed zone, lower intermediate zone, and product zone. Due to the user's ability to change feed height, the above zones apply to the general case where the feed enters in the middle of the cell.

Mass and flow balances were then generated for each of these zones, as shown in Figure 3.25. For convenience, a complete list of parameter nomenclature for these balances is also given in Table 3.7. A kinetic equation representing mass per unit time was then derived for each zone. For example, the product zone has particles entering by settling from the zone above; their mass per unit time is the product of the particle settling velocity, V_s , the cross-sectional area of the zone above, $A(J+1)$, and the concentration of particles in that zone, $C(J+1)$. The particles leaving the product zone do so either in the upward flow of wash water or via the product stream. The loss due to the upward flow of wash water is given by the product of the net flow rate from the bottom zone, Q_b (which is equal to the elutriation water flow rate minus the product flow rate) and the concentration of that zone, $C(J)$. The loss in the product stream is obtained by multiplying the product flow rate, Q_p , by the zone concentration, $C(J)$. The overall equation for the product zone is therefore as follows:

$$dm(J)/dt = [V_s(J+1)*A(J+1)*C(J+1)] - [Q_b*C(J)] - [Q_p*C(J)]. \quad [3.30]$$

This equation can be simplified to the following form:

$$dm(J)/dt = [V_s(J+1)*A(J+1)*C(J+1)] - [Q_w*C(J)]. \quad [3.31]$$

Figure 3.25 Schematic representation of the mass and volumetric flow balances for the column.

Table 3.7
Modeling Nomenclature

$V_t(J)$	=	particle terminal settling velocity in zone J (cm/sec)
$V_s(J)$	=	particle hindered settling velocity in zone J (cm/sec)
d	=	coagulum or particle diameter (cm)
G	=	gravitation acceleration (981 cm/sec ²)
D_s	=	density of solid (gm/ml)
D_f	=	density of the medium (gm/ml)
N	=	medium viscosity (0.01 dyne sec/cm ²)
$C(J)$	=	solids concentration of zone J (gr/ml)
$m(J)$	=	mass of solids in zone J (grams)
t	=	time (sec)
$A(J)$	=	cross-sectional area of the column in zone J (cm ²)
QF	=	flow rate of feed slurry entering the column (ml/sec)
QW	=	flow rate of elutriation water (ml/sec)
QP	=	flow rate of product stream (ml/sec)
z	=	zone height (cm)
hgt	=	column height (cm)

The equations for the other zones were derived using the same principles and are shown below:

Lower Intermediate Zone:

$$\begin{aligned} dm(J)/dt = & [V_s(J+1)*A(J+1)*C(J+1)] - [V_s(J)*A(J)*C(J)] \\ & + [Q_b*(C(J-1) - C(J))] \end{aligned} \quad [3.32]$$

Feed Zone:

$$\begin{aligned} dm(J)/dt = & [V_s(J+1)*A(J+1)*C(J+1)] - [V_s(J)*A(J)*C(J)] \\ & - [Q_u*C(J)] + [Q_b*C(J-1)] + [QF*C(FEED)] \end{aligned} \quad [3.33]$$

Upper Intermediate Zone:

$$\begin{aligned} dm(J)/dt = & [V_s(J+1)*A(J+1)*C(J+1)] - [V_s(J)*A(J)*C(J)] \\ & - [Q_u*C(J)] + [Q_u*C(J-1)] \end{aligned} \quad [3.34]$$

Overflow Zone:

$$dm(J)/dt = - [V_s(J)*A(J)*C(J)] + [Q_u*C(J-1)] - [Q_u*C(J)], \quad [3.35]$$

where

$$Q_b = QW - QP \quad [3.36]$$

and

$$Q_u = QW + QF - QP. \quad [3.37]$$

Equations [3.31]-[3.35] were divided by their respective zone volumes to convert them to concentration relationships. This modification allowed the model to be dependent upon the column height. The model has been utilized in its steady state form, i.e.:

$$dC(J)/dt = 0, \quad [3.38]$$

which gives five non-linear equations in five unknowns. These were solved simultaneously using an iterative technique based on Newton's method.

Seven important basic assumptions were made during the development of this model. These were:

- i) The elutriation column is completely mixed across any cross-sectional area of the column;

- ii) The column operates in plug flow along the height of the column;
- iii) The column operates under laminar flow conditions, i.e., $Re < 2$. Stoke's equation can therefore be used to determine particle terminal settling velocities;
- iv) Particle size does not change within the column;
- v) The size distributions of the coal and ash particles entering the column are very narrow and can be approximated by a single size;
- vi) Perfect liberation is assumed (no locked particles);
- vii) There are no discrete appearance or disappearance terms, i.e., the coal coagula do not grow or break up in the column.

Simulation, Optimization and Scale-up

The following standard values were used in all of the simulations discussed below:

Solid Concentration = 0.02 gm/ml
 Coal Density = 1.3 gm/ml
 Ash Density = 2.3 gm/ml
 Mean Agglomerate Size = 75 μ m
 Hindered Settling Constant = 3.65.

The initial simulations were run to determine the effect of elutriation water rate and coagulum size on the recovery of coagulated coal. The results are shown in Figure 3.26. Clean coal recovery was found to be very high at low wash water rates. However, as the elutriation water rate was increased, recovery experienced a large decrease. The wash water rate corresponding to the sharp drop in recovery is a function of coagulum size. Using 75- μ m coagula, recovery decreased gradually from 100 to 88% as the wash water rate was increased from 0 to 400 ml/min. Further increases in flow rate caused a drastic drop off in recovery to only 25% at 700 ml/min. For 100- μ m size coagula, recovery gradually decreased to 82% at 700 ml/min and then dropped sharply to 40% at 1000 ml/min.

The model is based on the assumption that the flow of feed slurry entering the column only affects flows in the upper portion of the column

Figure 3.26 Simulation results showing the effect of elutriation water rate on coal recovery as a function of coagulum size.

and, therefore, has little or no effect on recovery. This is shown in Figure 3.27, which summarizes the simulation results for clean coal recovery as a function of feed rate. With 75- μm coagula, recovery decreased from 80% at a feed rate of 25 ml/min to 62% at 200 ml/min. The slopes of the lines for each of the coagulum sizes are almost identical, although the 75- μm material has a slightly larger slope, due to the proximity of the elutriation water velocity to the coagulum settling velocity. The large differences in recoveries for the different agglomerate sizes were caused by the elutriation water rate (which was 400 ml/min).

In order to determine the maximum feed concentration at which the column can efficiently operate, simulations were conducted over a wide range in concentrations at a feed rate of 50 ml/min. Coal recovery was found to gradually decrease from 75% at 0.02 gm/ml to 66% at 0.2 gm/ml, as shown by Figure 3.28. Beyond 0.2 gm/ml, recovery sharply decreased to 22% at 0.60 gm/ml, where it began to level off. Coal recovery is only 12% at 1 gm/ml. Further simulation results showing the effect of solids content are given in Figure 3.29, which is a plot of clean coal recovery versus elutriation water rate for various percent solids. At very low solids concentration (0.02-0.05 gm/ml), recovery was effected only slightly. However, as the feed solids concentration was increased to 0.5 gm/ml, the upper limit on the elutriation water rate decreased as a result of an increase in the effect of hindered settling.

The feed position in the column was found to be very important. Figure 3.30 is a plot showing coal recovery versus elutriation water rate for two feed heights. By placing the feed point 43 cm instead of 63 cm from the bottom of the column, the recovery was increased by approximately 20% when using an elutriation water rate of 400 ml/min. The recovery curve representing the feed height of 63 cm was lower than the 43-cm curve. However, both feed heights resulted in near 100% recovery at low elutriation

Figure 3.27 Simulation results showing the effect of feed rate on coal recovery as a function of coagulum size.

Figure 3.28 Simulation results showing the effect of feed solids concentration on coal recovery.

Figure 3.29 Model predictions showing coal recovery versus elutriation water rate for various feed percent solids values.

Figure 3.30 Simulation results showing the effect of elutriation water rate on recovery as a function of feed inlet location.

water rates and decreased to near zero at high wash water rates. The increased recovery found for a decrease in feed height was a result of a decrease in the settling distance for the coagula.

The effect of changes in upper and lower cell diameters is shown in Figures 3.31 and 3.32. Figure 3.31 illustrates the effect of increasing upper cell diameter using three different elutriation water rates while maintaining the lower diameter at 10.16 cm (4 inches). At all wash water rates, recovery increased sharply with an increase in upper cell diameter. This was due to the fact that increasing the diameter while maintaining a constant column flow rate decreases the wash water velocity, allowing more material to be recovered. A similar result is shown in Figure 3.32, which demonstrates the effect of changing both the lower and upper cell diameter. Increasing the diameter of the two sections resulted in an increase in recovery. This was expected since the upward velocity of wash water decreases with increasing diameter.

After characterizing the elutriation column using the model, previously obtained experimental data were plotted and compared with the model predictions. Figure 3.33 shows both the simulated (solid line) and experimental (points) recoveries of coal as a function of elutriation water rate. The predictions from the simulator correlate well with the experimental results, except that the simulator indicates a perfect separation, or zero percent ash, in the product (underflow), whereas the experimental results show a less perfect separation (Figure 3.34), presumably because of the entrapment of fine ash particles in the coal coagula, the possible presence of coal/ash middlings and/or mixing. The experimental results show an optimum elutriation water rate around 400 ml/min, where the product ash was minimized at 4.9%.

Simulated recovery values for determining the effect of feed rate are compared with experimentally obtained values in Figure 3.35. The simulator

Figure 3.31 Model predictions showing the effect of upper cell diameter on coal recovery for three elutriation water rates.

Figure 3.32 Model predictions showing the effect of both upper and lower cell diameters on coal recovery.

Figure 3.33 A comparison between model predictions and experimental results showing the effect of elutriation water rate on coal recovery.

Figure 3.34 A comparison between model predictions and experimental results showing the effect of elutriation water rate on product ash percent.

Figure 3.35 A comparison between model predictions and experimental results showing the effect of feed rate on coal recovery.

results agree reasonably well with the experimental values, although the experimental recovery dropped off slightly at higher feed rates. The decrease may have been due to an increase in mixing around the feed point as a result of the downward injection of the feed, which would result in the breakage of the coal coagula. Also, an increase in the superficial velocity in the upper section of the column may have caused the coal coagula above the feed point to be washed out the overflow.

Simulator results illustrating the effect of feed solids concentration are compared with experimental results in Figure 3.36. Again, the model predictions correlate well with the experimental values. Both sets of data depict a decrease in recovery as the elutriation water was increased and no effect on recovery when the feed solids concentration was increased from 2 to 5%.

Due to the good agreement between the experimental and predicted data, it can be concluded that the elutriator model is a reasonable representation of the elutriation column used in this analysis.

Figure 3.36 Comparison of experimental (points) and simulated (lines) results obtained using the SSC elutriation column.

TASK 4: ELECTROCHEMICAL COAL CLEANING

Introduction

Many promising advanced physical coal cleaning processes have been suggested in recent years. Two such processes, i.e., microbubble flotation and selective shear coagulation, have been investigated in the foregoing sections of this report. A common denominator in these processes is that the mineral matter must be liberated by an appropriate technique such as a stirred ball mill grinding. Unfortunately, fine grinding is a costly step. Furthermore, due to the small sizes of the particulates involved, separation of the liberated mineral matter from the coal becomes increasingly difficult, and the process of dewatering the coal, if necessary, becomes prohibitively expensive. Development of a novel process that could achieve mineral liberation with a minimum of grinding would, therefore, be of interest. The method presented here describes one such method, in which mineral matter is liberated from coal by means of a surface chemical force. The size of the mineral particles liberated by this method is often much smaller than the coal particles, which makes it possible to remove the mineral particles from the coal by simple screening and/or classification.

Task 1.4.1: Fundamentals of Electrochemical Coal Cleaning

a. Basic Mechanism

It is well-established that osmotic pressure develops in an aqueous medium between two charged plates in close proximity (Schofield, 1966; Blum and Hachisu, 1984). Pressures up to several atmospheres are possible, depending on the distance separating the plates. If such a pressure can be created between the mineral matter and the coal matrix encapsulating it, the mineral matter may be liberated by the osmotic pressure originating from the surface chemical forces.

Figure 4.1 is a schematic representation of the mineral matter located inside a pocket or crevice. The mineral grains are either too large to pass through the opening or are compacted so tightly that a strong physical force is necessary to push them out. When the opening is exposed to a relatively mild acid solution, i.e., $\text{pH} < 2$, both the coal and the mineral surfaces become positively charged because their points of zero charge (pzc) are usually higher than $\text{pH} 2$. The adsorption of H^+ ions is one of the major charging mechanisms for both coal and mineral matter, but for coal there may be an additional charging mechanism, which may be described as follows. In an acidic medium, ferric (Fe^{3+}) ions are released into solution from coal pyrite or other iron-containing minerals in the coal. According to Dhooge and Park (1983), the Fe^{3+} ions are reduced to Fe^{2+} ions on the coal surface as follows:

which, in turn, can oxidize the coal surface slightly by the following reactions:

or

in which the carbon (C) is a simplistic representation of coal. Since electrons are lost from the coal to the Fe^{3+} ions, the coal surface may acquire a positive charge (Anthony and Linge, 1983). Kreysa and Kochanek (1985) suggested that this positive charge is retained by the intermediates formed during the oxidation of the more oxidizable groups, such as hydroquinone, of the coal molecule.

When both the coal and the mineral matter are positively charged in this manner, counter ions will congregate in the vicinity of the surface, setting up electrical double layers. When sulfuric acid is used to lower the pH,

Figure 4.1 Schematic representation of mineral matter entrapped in crevices (or pockets) of coal.

SO_4^{2-} ions will be the counter ions. If the distance between the coal and mineral surfaces is sufficiently small, the double layers will overlap each other, creating a highly concentrated solution inside the pocket where the mineral matter is located. This, in turn, will reduce the chemical potential of the water inside the pocket to below that of the solution outside, and create an osmotic pressure. This situation is akin to the case where a salt solution is separated from fresh water by a semi-permeable membrane.

b. Thermodynamic Model

The osmotic pressure (π) is related to the activities of the species present in the system as follows:

$$\pi = \frac{2RT}{(V_o + V_i)} \ln \frac{A_o}{A_i}, \quad [4.4]$$

in which A_i is the aqueous activity inside the pore, A_o the aqueous activity outside the pore, V_i the partial molar volume of water inside the pore, V_o the same outside, R the universal gas constant and T the temperature. The Gouy-Chapman model of the electrical double layer and the Poisson-Boltzmann equation were used to calculate the concentration of counter ions inside a pore, and then estimate the aqueous activity using the Rard equation (Rard et al., 1976). The partial molar volumes of water were determined using the method described by Smith and Van Ness (1987) and using the semi-empirical relationship established by Paul (1988). As such, the osmotic pressure is a function of the surface potentials of the minerals and coal inside the pore, the sulfuric acid concentration and the distance between the charged walls. Figure 4.2 shows the osmotic pressure calculated for the case of coal and minerals immersed in sulfuric acid solutions. It is shown that the osmotic pressure increases exponentially with decreasing distance between the charged particles. At very small distances, however, the pressure may not be as high

Figure 4.2 Predicted osmotic pressure between two flat plates of coal and mineral matter at various sulfuric acid concentrations.

as predicted because of the strong hydration force of the surfaces involved.

Nevertheless, the calculation shows that the pressure may reach as high as 4-7 atm if the spacing between the coal and the mineral matter is in the range of 100 to 1000 Å. These values are comparable to those measured by Shainberg et al. (1971) and Low (1980) for montmorillonite clays. Note also that the pressure increases with increasing sulfuric acid concentration, although this effect is relatively minor compared to the effects of the crevice spacing and the surface potentials.

Some modifications on the thermodynamic model used to predict osmotic pressure build-up in a coal pore have been made. This model was applied to a less complex system involving hematite/sulfuric acid for validation. Results from this simulation indicate that significant pressure rise occurs only when interparticle spacings are smaller than about 2,000 Å. This suggests that coal particles with large pore/crevice openings may not respond well to the electrochemical coal cleaning treatment.

c. Osmotic Pressure Measurements

An apparatus was constructed for testing the osmotic pressure model and the schematic is shown in Figure 4.3. The sample is placed inside the cylinder and compressed against a polypropylene filter pad supported at the base of the cylinder by screwing the piston downwards.

Two important input parameters for the osmotic pressure model are the surface potential of the solids in the sulfuric acid solution and the average interparticle spacing of the compressed powder. To obtain the first parameter, the zeta potential of a quartz sample was measured in sulfuric acid solutions ranging in concentration from 10^{-4} to 10^{-1} M. It was then assumed that its surface potential was equal to its zeta potential.

To obtain the second parameter, a slurry of the quartz powder previously prepared was placed in the cylinder of the apparatus and compressed to ensure

Figure 4.3 Schematic representation of the apparatus for measuring osmotic pressure developed in compacted mineral slurry exposed to an electrolyte solution.

overlap of the double layers surrounding the quartz particles. The base of the unit was placed in distilled water and the rise in the liquid level in the vertical tube was measured. Figure 4.4 shows the theoretical plot of the osmotic pressure variation with different pore spacing. From this plot, a pore spacing corresponding to 70 Å was determined and used as a representative value for interparticle spacing.

Based on the above information, Figure 4.5 shows the theoretical osmotic pressure build-up predicted by the model corresponding to the measured values at the same acid concentrations. As the acid concentration increases, the value predicted by the model becomes less accurate. There are several possible reasons for this observation. One, the zeta potential of a mineral particle in an isolated state may not be the same when the particle is compressed with other particles of the same charge. Two, there is likely to be some error in substituting the surface potential of the mineral by the zeta potential. Finally, the behavior of the sulfuric acid solution is less ideal at higher concentrations.

d. Ferric Ion Regeneration

The reaction described by Equation [4.1] suggests that Fe^{3+} ions are consumed during the process to become Fe^{2+} ions. The spent Fe^{3+} ions can be regenerated by several different methods. The first is simply to aerate the spent solution before recirculating it. This technique is commonly employed in the process of leaching sulfide and uranium ores using ferric ions as the lixiviant. Secondly, microbes such as *Thiobacillus ferrooxidans* and *Sulfolobus acidocaldarius* may be used (Beyer et al., 1986). The third technique is to use an electrochemical process in which inert electrodes are suspended in the spent solution so that Fe^{2+} ions can be anodically oxidized on their surfaces. The regeneration of ferric ions so far has been achieved by electrochemical means.

Figure 4.4 Calculated osmotic pressure for a particle bed at a zeta potential of 30.3 mv as a function of pore spacing.

Figure 4.5 Comparison between calculated and experimental osmotic pressures for quartz particles as functions of acid concentration.

The experimental apparatus used in these tests consisted of a simple reactor containing a solution rich in ferric ions. The extent of ferric ion regeneration was determined by monitoring the electrochemical potential (E_h) of the Fe^{2+} to Fe^{3+} reaction in solution as a function of time. The first series of measurements were conducted to determine the effectiveness of simple air oxidation. To speed the transfer of air across the air-liquid interface, the contents of the reactor were vigorously agitated using a stirrer. The second set of tests were performed by adding a biomass (*Thiobacillus ferrooxidans*) to the solution. In the final set of experiments, an electrochemical potential of approximately 1 V was applied to the original Fe^{2+} solution to accelerate the conversion process. All other conditions were held constant during the experimental test program.

The results of the regeneration experiments are displayed in Figure 4.6. As shown, the ferric ion conversion rate was relatively slow for the solution treated by simple air oxidation. A much more rapid rate of regeneration was possible after the addition of bacteria. The highest rate of conversion, however, occurred in the solution treated by electrolysis. The solution in which bacteria was added required approximately 20 hours of treatment to reach an E_h of 0.42 V. In contrast, the solution regenerated by electrolysis needed only about six hours to reach 0.42 V. On the basis of these preliminary results, electrolysis appears to be the most promising method in terms of kinetics for regenerating spent ferric ions.

Task 1.4.2: Bench-Scale Electrochemical Coal Cleaning

a. Reaction Vessel Design

The reaction vessels used for the batch electrolysis testing are shown in Figures 4.7 and 4.8. The first is comprised of a water-jacketed, stirred-tank reaction vessel, in which a platinum or graphite working electrode is suspended and a coal slurry is agitated. A Luggin capillary is placed near

Figure 4.6 Measurement of the electrochemical potential of the ferric-to-ferrous reaction as a function of time for various treatment methods.

Figure 4.7 Schematic of the stirred-tank reaction vessel

Figure 4.8 Schematic of the flow-through reaction vessel.

the working electrode to monitor the potential. The counter electrode is separated from the solution by means of a glass frit. The agitation is provided by means of a Teflon-coated magnetic stir bar, which is specially designed so that the breakage of the coal by the spinning action is minimized. The second reactor is designed to regenerate Fe^{3+} ions in a separate compartment in which Fe^{2+} ions are oxidized on the working electrode using the same three-electrode system described above. The electrolyte containing Fe^{3+} ions is then pumped through the flow-through reactor containing a bed of coal particles. In order to obtain desirable flow characteristics, relatively coarse coal samples must be used.

A Widow Kennedy coal sample (20x40 mesh) was treated by the electrochemical coal cleaning process using 3.6 M sulfuric acid solution in the stirred-tank reaction vessel at 65°C. The sample was treated for 15 hours with a potential of 1 V SCE applied to the working electrode. The results show that the ash content was reduced from 23.4 to 8.5% with a coal recovery of 95.5%. In another test, a coarse Widow Kennedy coal sample (3x7 mesh) was precleaned in a laboratory scale dense medium bath to obtain a float product coal assaying 5.3% ash. This precleaned coal was treated using the flow-through reactor with similar conditions as those discussed above. After treating for 7 hours, a product ash content of 0.99% was obtained. This demonstrates that it is not necessary for coal particles to contact the electrodes for the electrochemical coal cleaning process to work. The most important part of the process is to continuously provide ferric ions to the coal surface.

b. Characterization of Operating Parameters

Tests were conducted to examine the effects of different operating parameters on the electrochemical coal cleaning process. Several process parameters were examined including particle size, electrolysis time,

electrolyte type and concentration, applied potential and temperature. Optimization tests were also conducted in which the effects of feed solids, ferric ion addition, acid concentration and solution temperature were studied.

Particle Size: A coal sample from the Glamorgan seam, assaying 1.65% ash and 0.6% sulfur, was tested in the stirred-tank reaction vessel. The experiments were carried out using a 3.6 M sulfuric acid solution at 65°C. The sample was dry-screened into various size fractions and pre-soaked for 12 hours prior to the treatment. A potential of 1 V SCE was applied to the platinum working electrode to regenerate the ferric ions. Figure 4.9 shows that the percentage ash removal improved with decreasing particle size. A product coal assaying less than 0.8% ash could be obtained from a relatively coarse coal. Further tests were conducted using a coarse (16x20 mesh) and a fine (100x140 mesh) fraction with different electrolysis times. Figure 4.10 shows that the mineral matter removal improves with increasing electrolysis time. However, it seemed that most of the mineral matter removal occurred in the first six hours. The mineral matter removal obtained for the coarse coal was also observed to be less than that for the fine coal over the different electrolysis times studied.

Electrolysis Time: Tests were conducted on an Elkhorn No. 3 coal from Pennsylvania to study the effects of various electrolysis times on mineral matter removal. A 12x16 mesh sample with an ash content of 7.92% was treated in the stirred-tank reaction vessel using different electrolysis times. The electrolyte contained a mixture of 0.5 M hydrochloric and 1.5 M sulfuric acid at a temperature of 55°C. Figure 4.11 shows that the mineral matter content decreased with increasing electrolysis time. After 5.5 hours, the mineral matter content of the feed coal was reduced to 1.25%. However, the removal of mineral matter seemed to already be marginal after about this time.

Figure 4.9 Effect of particle size on the removal of mineral matter from Glamorgan coal by the ECC process: electrolyte = 3.6 M sulfuric acid; temperature = 65°C; treatment time = 4 hours; potential applied = 1.0 V SCE.

Figure 4.10 Effect of reaction time on the removal of mineral matter from Glamorgan coal by the ECC process: electrolyte = 3.6 M sulfuric acid; temperature = 65°C; potential applied = 1.0 V SCE.

Figure 4.11 Effect of reaction time on the removal of mineral matter from Consol coal.

Electrolyte Type and Concentration: The effect of various acid electrolytes and electrolyte combinations on the removal of mineral matter from Glamorgan seam coal was also studied. A treatment time of 4 hours was used for all of the tests with the temperature set at 60°C. The results of these different tests are given in Table 4.1. Using 3.6 M sulfuric acid, the mineral matter content was reduced from 1.45 to 1.06%. An electrolyte containing 1.5 M sulfuric and 0.5 M hydrochloric acid reduced the mineral matter content from 1.28 to 0.96%. The ash removal was improved further with the use of a mixture of 3.4 M sulfuric and 1.1 M hydrofluoric acid. The addition of 10^{-3} M ferric sulfate monohydrate to this acid mixture resulted in a product ash content of 0.57%. The mixture of sulfuric and hydrofluoric acid proved to be the best electrolyte for this coal. Also, the addition of ferric ions improved the removal of mineral matter from the feed coal.

A Splashdam seam coal (20x40 mesh) was treated by the electrochemical coal cleaning process using different acids and acid concentrations. These samples were treated at 68°C for 6 hours with a potential of 1 V SCE applied in the stirred-tank reactor. The results given in Table 4.2 show that the ash removal improved at a higher sulfuric acid concentration. The synergistic effect of the acid combination of 0.5 M hydrochloric and 1.5 M sulfuric acid is also shown in this table. When only 1.5 M sulfuric acid was used, the product coal assayed 2.5% ash from a feed coal that contained 8.8% ash. With 0.5 M hydrochloric acid, the ash content was reduced to 1.8%. However, a combination of the two acids at these concentrations reduced the ash content of the coal to 0.9%. This observation was also found with several other coal samples.

Applied Potential: The effect of applied potential on the removal of mineral matter from a Widow Kennedy seam coal was also investigated. Tests were conducted on 20x40 mesh samples using an electrolyte containing a mixture

Table 4.1

Effect of Various Electrolyte Combinations
on the ECC Treatment of Glamorgan Seam Coal

Coal Size (Mesh)	Electrolyte Used	Reaction Temperature (°C)	Ash Content (% wt)		Coal Recovery (% wt)
			Feed	Products	
-07 + 12	H ₂ SO ₄ (3.6M)	60	1.45	1.06	98.6
-20 + 60	1.5M H ₂ SO ₄ + 0.5M HCl	60	1.28	0.96	96.5
-20 + 60	3.4M H ₂ SO ₄ + 1.1M HF	60	1.28	0.73	96.0
-20 + 60	3.4M H ₂ SO ₄ + 1.1M HF + 10 ⁻³ M Fe ₂ (SO ₄) ₃	60	1.28	0.57	96.8

Table 4.2

Effect of Electrolyte Concentration on the ECC Treatment of Splashdam Seam Coal

Electrolyte Concentration	Ash Content (% wt)		Coal Recovery (% wt)
	Feed	Products	
H ₂ SO ₄ (1.5M)	8.8	2.5	96.2
H ₂ SO ₄ (3.6M)	8.8	1.5	95.7
HCl (0.5M)	8.8	1.8	95.7
H ₂ SO ₄ (1.5M) + HCl (0.5M)	8.8	0.9	93.6

of 0.5 M hydrochloric and 1.5 M sulfuric acid at a temperature of 60°C. The tests were run at 0.5, 1.0 and 1.3 V SCE with a treatment time of 5 hours. The results of these tests are shown in Table 4.3. The test data indicate that the tests run at 0.5 V SCE gave poorer results than those run at higher potentials. This may be attributed to the very low Fe^{3+} -to- Fe^{2+} ion ratio obtained at this potential. It should be noted that the reversible potential of the $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple is around 0.77 V SCE. Increasing the potential to 1.3 V did not seem to show any significant improvement in the removal of mineral matter. This probably indicates that the efficiency and kinetics of the oxidation of Fe^{2+} to Fe^{3+} does not increase significantly above 1 V.

Neutral Solutions: A sample of Powell Mountain coal, assaying 9% ash and 2.6% sulfur, was treated by the electrochemical coal cleaning process in the absence of any acid. The test was conducted in distilled water at 65°C in the stirred-tank reactor. A potential of 1 V was applied to the working electrode to regenerate the ferric ions. Since this coal contains a significant amount of pyritic sulfur, sufficient ferric ions and sulfuric acid could be generated from the electrochemical dissolution of the coal pyrite. This is evidenced by the corresponding decrease in the pH of the solution during treatment. The charge passed during the initial stage of the process was very low, indicating a slow reaction rate. However, the current measured increased as the amount of ferric ions accumulated in solution increased, presumably through the anodic oxidation of coal pyrite in the oxidizing environment of this process via an autocatalytic pathway. The results given in Table 4.4, show that the ash content was reduced from 8.2 to 5.3%.

Although the ash removal was not as significant as those obtained using acids, it is clear that the removal of ash was possible without using acids. It is likely that the coal pyrite in the coal sample undergoes anodic oxidation to yield a sufficient amount of ferric ions according to the

Table 4.3

Effect of Applied Potential on the ECC Treatment
of 20x40 Mesh Widow Kennedy Seam Coal

Applied Potential (V SCE)	Charge Passed (coulombs)	Ash Content (% wt)	
		Feed	Product
0.5	102.1	23.4	21.6
1.0	525.2	23.4	15.9
1.3	6125.7	23.4	14.7

Table 4.4

Removal of Ash and Sulfur from Powell Mountain Seam Coal
in Neutral Solutions

Particle Size (mesh)	Ash Content (% wt)		Sulfur Content (% wt)		Heating Value (BTU/lb)	
	Feed	Products	Feed	Products	Feed	Product
-60 + 100	8.4	5.7	2.7	2.0	14,832	14,854
-100 + 1140	8.0	5.3	2.5	1.9	14,737	14,828

following reaction:

The ferric ions produced as above will further oxidize the pyrite according to this reaction:

The comparatively poor results may be due to the lack of counter-ions in the aqueous environment needed for the formation of an ionic double layer inside the pores and crevices of the coal. Also, the pH of the solution is probably higher than the pzc of some of the mineral matter present in the coal which means that there would be no ionic double layer formation between these minerals and the coal surface and, therefore, no osmotic pressure build-up.

Temperature: A series of tests were conducted on a Pittsburgh No. 8 coal to study the effect of temperature and time on process performance. For each test, a 65x200 mesh feed sample was processed in the stirred-tank reactor containing 1 M sulfuric acid. The results obtained are shown in Figure 4.12. The removal of ash was found to increase with increasing temperature and time. A maximum ash reduction of nearly 50% was reached with a processing temperature of 70°C and five hours reaction time.

Optimization: The effects of different parameters on the processing of Jacob's Ranch coal from the Middle Wyodak seam were investigated and the optimum operating conditions for removing mineral matter were determined from these tests. The test variables examined in this series included feed solids content (26.7 to 320 gm/l), ferric ion addition (0 to 13.3 mM), acid concentration (0.2 to 3.1 M) and temperature (22 to 70°C). Ferric ions were added to the solution via ferric sulfate. The acid media consisted of 75% sulfuric acid and 25% hydrochloric acid, and the coal used was sized at 80x270

Figure 4.12 Effect of temperature on ash removal from wet-screened Pittsburgh No. 8 seam coal.

mesh. The reaction time for each test was four hours. In total, 25 tests were run in this series.

The test conditions and results obtained are presented in Table 4.5. The data presented reflect ash reductions ranging from 37 to 52%, with most of the results falling between 42 and 49%. The highest ash reduction of 52% was obtained at a temperature of 70°C, while the lowest ash reduction was obtained at a temperature of 22°C. Thus, temperature appears to be a major factor in the ash reduction capabilities of the process. An increase in acid concentration also resulted in an increase in mineral matter removal. The effects of ferric ion addition and solids content were not too significant on the processing of this coal sample.

Using response surface methodology, the optimum conditions for the processing of this coal were determined from the results of these series of tests. The optimum conditions were identified as: 207 gm of coal/l of slurry, 11.3 mM ferric ion addition, 2.61 M acid and 58.5°C. The ash reduction predicted using these conditions was 56.99%.

c. Liberation and Dissolution

The results of electrochemical coal cleaning tests obtained with different coal samples are given in Table 4.6. The experimental conditions employed to obtain these results varied from one test to another. In some experiments, small amounts of ferric sulfate were added to supplement the ferric ions derived from the coal pyrite or other ferruginous impurities present in coal.

A characteristic of the electrochemical coal cleaning (ECC) process is that it gives high combustible recoveries. This may be attributed to the fact that mineral matter is selectively liberated by osmotic pressure. The most commonly employed methods of liberating minerals are based on size reduction, where fractures occur across the grain boundaries (i.e., trans-granular

Table 4.5

Test Conditions and Results for the ECC Treatment
of 80x270 Mesh Middle Wyodak Seam Coal

Coal Weight (grams)	Ferric Ion Addition (mM)	Acid Conc. (M)	Solution Temperature (°C)	Feed Ash (%)	Product Ash (%)	Ash Reduction (%)
75	3.3	1.15	34	7.0	3.7	46.9
185	3.3	1.15	34	6.9	4.0	41.7
75	10.0	1.15	34	7.1	4.0	43.6
185	10.0	1.15	34	7.0	4.3	38.9
75	3.3	3.0	34	7.0	4.3	38.9
185	3.3	3.0	34	7.0	3.9	43.5
75	10.0	3.0	34	7.1	4.4	37.8
185	10.0	3.0	34	7.0	4.1	42.1
75	3.3	1.15	58	7.1	3.4	51.4
185	3.3	1.15	58	7.1	3.3	53.3
75	10.0	1.15	58	7.0	3.6	48.8
185	10.0	1.15	58	7.2	3.6	49.7
75	3.3	3.0	58	6.6	3.3	50.5
185	3.3	3.0	58	6.8	3.8	44.5
75	10.0	3.0	58	7.1	3.3	53.3
185	10.0	3.0	58	7.0	3.7	47.4
130	6.6	2.1	46	6.8	3.6	46.7
20	6.6	2.1	46	7.2	3.6	49.7
240	3.3	2.1	46	6.7	3.5	47.3
130	0	2.1	46	6.8	3.8	44.3
130	13.3	2.1	46	6.9	3.6	48.6
130	6.6	0.2	46	7.0	4.2	39.9
130	6.6	4.0	45	6.9	3.8	44.9
130	6.6	2.1	22	6.9	4.3	37.1
130	6.6	2.1	70	6.9	3.3	52.3

Table 4.6
Summary of ECC Test Results Obtained with Various Coals

Coal Seam	Size (mesh)	Ash Content (wt. %)		Sulfur Content (wt. %)		Combustible Recovery (wt. %)
		Feed	Product	Feed	Product	
<u>Bituminous Coals</u>						
Glamorgan, VA	-270+325	1.2	0.3			97.5
Widow Kennedy, VA ^b	-20+40	23.4	3.5			90.3
Widow Kennedy, VA	-3+7	5.3	0.99			98.0
Powell Mountain, VA ^b	-100+140	8.0	5.3	2.50	1.90	91.2
Splashdam, VA	-20+40	8.8	0.9			93.6
Elkhorn No. 3, VA	-20+60	13.8	7.7			84.6
Pittsburgh No. 8, PA	-100+200	22.68	6.99			93.3
Plant Refuse, VA	-400 ^a	44.0	9.3			52.0
<u>Subbituminous Coals</u>						
Kemmerer, WY	-200+325	3.6	1.4	0.33	0.34	93.8
Middle Wyodak, WY	-20+40	4.7	1.4			89.9
Upper Wyodak, WY	-60+150	8.6	2.3	1.50	0.50	92.3

^acyclone overflow

^bemployed extended reaction times and three stages of cleaning

fractures) and produce large numbers of composite (or middling) particles. If the middlings are rejected to obtain a required grade, recovery will suffer. In the ECC process, the major reason for the loss of coal appears to be abrasive size reduction during mixing, which creates fines that are lost through the screen along with liberated mineral matter during the separation step.

Note in Table 4.6 that processing of the plant refuse (400-mesh x 0 cyclone overflow) reduced the ash content from 44 to 9.3% with 52% combustible recovery. The poor recovery can be attributed to the fact that the sample contained a large amount of coal fines which were lost during the process of removing the liberated mineral matter. In this particular test, a No. 54 Whatman filter paper with an average pore size of 20-25 μm was used to remove the liberated mineral matter. It should be noted, however, that much of the ash removed was simply due to the removal of the fine fractions, which contained a majority of the ash-forming minerals. In order to determine the extent of the ash rejection due to the ECC mechanism and the simple filtration process, the unprocessed plant refuse was filtered through an identical filter paper. In this case, the ash content of the coal remaining on the filter paper was 16.4%, which was significantly higher than that obtained by the ECC process. This difference demonstrates that liberation does occur during the electrolysis.

With the limited number of tests conducted to date, it is difficult to make a strong correlation between the rank of a coal and its response to the ECC process. Nevertheless, the subbituminous coals seemed to respond better than the bituminous coals, although some bituminous coals responded as well as subbituminous coals. Certain eastern bituminous coals such as Sahara, Norton and Blair seam coals responded poorly. One of the reasons that the subbituminous coals tested in the present work responded well was that a large amount of the calcium present in the coal was removed by the acid leaching.

According to Huffman and Huggins (1984), the ash in Wyodak coal is comprised of up to 25% calcium and most of it is in the form of exchangeable ions. The possibility of ion exchange between Ca^{2+} and other cations present in solution, such as H^{+} and Fe^{3+} , has been suggested by Paulson et al. (1981).

In some of the coal cleaning tests involving bituminous coals, the acid was reused several times without affecting the extent of demineralization, suggesting that the ECC process does not consume a significant amount of acid. In one experiment, a dilute (0.01 M) sulfuric acid solution was used while monitoring the pH. It was found that the pH decreased by an order of magnitude over four hours of reaction time, which can be attributed to the dissolution of the coal pyrite. Furthermore, tests conducted with a Virginia coal indicate that an increase in reaction temperature up to 80°C did not produce any significant improvement in the extent of demineralization. These findings may support the view that the main mechanism for demineralization is due to liberation rather than to chemical dissolution, at least for some of the eastern bituminous coals tested in the present work.

In order to determine the relative amount of mineral matter removed by the proposed liberation mechanism and by chemical dissolution, a test was conducted while carefully following the mass flow. The test was conducted using a -20+70-mesh Widow Kennedy coal assaying 27.5% ash in the feed. Following the ECC treatment, the solids were separated from the acid electrolyte by filtration. The residue remaining on the filter paper was washed several times with fresh water to remove the residual acids, and then wet-screened on a 70-mesh screen. The cleaned coal on the screen was dried, weighed and assayed for ash content. The minus 70-mesh fraction containing the liberated mineral matter and some abraded coal particles was collected and allowed to settle overnight. The supernatant was removed by decantation, and the residue was centrifuged to further remove the water. The solid residue

was then dried, weighed and assayed.

Figure 4.1⁷ shows the mass flow diagram of the combustibles and non-combustibles in this test. The mass of the mineral matter was obtained from the weight of ash using a modified form of the Parr formula (Given et al., 1975). Of the 15.14 gm of mineral matter present in the feed coal, 3.91 gm was left in the clean coal product. Therefore, a total of 11.23 gm of the mineral matter was removed from the coal. Of this, 8.29 gm reported to the refuse and the balance (2.94 gm) was either dissolved in the acid or lost during the process. From these numbers, one can see that 73.8% of the mineral matter removed was due to liberation and 26.2% was dissolved and/or lost.

Table 4.7 shows two sets of test results obtained on a 28-mesh x 0 Upper Freeport coal sample assaying 24.5% ash and 1.68% sulfur. In one test, the coal was treated by the ECC process in two stages using a screening technique to remove the liberated mineral matter. In each stage, the coal was contacted with 2 M HCl solution for five hours in the stirred-tank reactor. As shown, the ash and sulfur contents were reduced to 7.7 and 0.64%, respectively, after the first stage. The recovery was only 65% because coal fines present in the feed were lost while washing the electrolyzed coal on a 400-mesh screen to remove the liberated mineral matter. In the second stage, the ash content was further reduced to 3.7%, while the sulfur content remained practically the same. The combustible recovery was high (86%) because most of the fines had already been removed in the first stage.

In the other test described in Table 4.7, the same Upper Freeport coal sample was cleaned to 1.8% ash using a combination of conventional flotation, micronization and microbubble flotation. To reduce the ash further, the coal could have been pulverized again and subjected to another stage of microbubble flotation. However, further grinding of the coal which was already micron-size would have required a lot more energy. An alternative would be to substitute the ECC process for the grinding step and carry out microbubble

Figure 4.13 A mass balance for the ECC processing of a Widow Kennedy coal.
(MM refers to mineral matter)

Table 4.7

Results Obtained with an Upper Freeport Seam Coal
Using Different Methods of Removing Liberated Mineral Matter

Process	Stage	Ash (wt. %)		Sulfur (wt. %)		Combustible Recovery (wt. %)	
		Feed	Product	Feed	Product	Individual	Overall
ECC/Screening (-28 x 0)	1st	24.5	7.7	1.68	0.64	65	65
	2nd	7.7	3.7	0.64	0.63	86	56
ECC/Microbubble (micronized)	1st	24.5	1.8	--	--	73	73
	2nd	1.8	1.1	--	--	82	60

flotation to remove the liberated mineral matter. As shown in Table 4.7, the ash was reduced to 1.1% with 82% recovery by the flotation process.

d. Alternative Methods of Ferric Ion Regeneration

The use of *Thiobacillus ferrooxidans* for regenerating ferric ions was found to be feasible in Task 1.4.1. Based on this ferric ion regeneration strategy, a set-up capable of processing coals using this bacteria was developed. A simplified schematic of the experimental set-up for the electrochemical cleaning of coal using the bacterial regeneration of ferric ions is shown in Figure 4.14. The set-up consists of a biological reactor and a stirred-tank coal reactor. In the coal reactor, the coal is contacted with a known concentration of ferric sulfate solution (for this test work, ferric sulfate concentrations of 9000 mg/l were used). The ferric ions consumed in the process are regenerated in the biological reactor containing the *T. ferrooxidans* bacterial culture. Two filter traps between the two reactors prevented the treated coal from entering the culture medium and the culture medium from entering the coal reactor. The coal reactor was maintained at 70°C while the biological reactor was at 26°C. The data collected, given in Table 4.8, indicate that a solution pH of 2.5 is more efficient in oxidizing the ferrous ions than a pH of 1.5 (about 3 times faster). The blank solution (containing no bacterial cultures) showed very little E_h activity; thus, the trends observed in the pH 1.5 and 2.5 tests using bacteria must be largely accountable to the oxidation of ferrous to ferric ions by *T. ferrooxidans*.

Table 4.9 shows the results obtained when treating an Illinois No. 6 coal using *T. ferrooxidans* to regenerate the ferric ions. The bacteria was grown in an Erlenmeyer flask for 3 days after inoculation, followed by the addition of 3 gm of coal to the medium. The flask was then left on a shaking table for 10 days at 26°C. The results show a marked improvement in sulfur and ash reduction using *T. ferrooxidans*. Most notable is the 40 to 50% reduction in

Figure 4.14 Schematic of the experimental set-up for the regeneration of ferric ions.

Table 4.8

Regeneration of Ferric Ions by *Thiobacillus ferrooxidans*

Time (hours)	TEST CONDITIONS			
	pH 1.5 Eh (volts)	pH 2.5* Eh (volts)	pH 2.5* Eh (volts)	Blank Eh (volts)
0	0.1676	0.2715	0.2768	0.2685
1	0.3859	0.3239		
2	0.3951		0.3538	0.2637
7		0.3977	0.3813	0.2730
15	0.4195			
18			0.4190	0.2936
23		0.4573		
24	0.4628		0.4399	0.3050
30		0.5575	0.4627	0.3181
42	0.5068		0.6309	0.3346
46	0.5119	0.6465		
48			0.6493	0.3409
51		0.6823		
54			0.6496	0.3451
64	0.5433			
70	0.5814			

*Duplicate test conditions.

Table 4.9

ECC Treatment of a Run-of-Mine Illinois No. 6 Coal Sample
Using *Thiobacillus ferrooxidans* to Regenerate the Ferric Ions

Feed Size (Mesh)	Feed Ash (%)	Final Ash (%)	Ash Reduction (%)	Initial Sulfur (%)	Final Sulfur (%)	Sulfur Reduction (%)
100 x 400	15.5	6.98	55.0	---	---	---
100 x 400	15.5	7.72	50.2	---	---	---
325 x 500	13.3	8.96	32.6	4.66	2.45	47.4
325 x 500	13.3	9.62	27.7	4.66	2.65	43.1
325 x 500	13.3	9.24	30.5	4.66	2.67	42.7
100 x 140	13.3	10.60	20.3	4.66	3.04	34.8
140 x 270	13.3	10.90	18.0	4.66	2.87	38.4
270 x 400	13.3	10.80	18.8	4.66	2.75	41.0

sulfur. This has several benefits as applied to the electrochemical coal cleaning process. First, the oxidation of pyrite generates ferric ions which are needed in the ECC process. Thus, there is no need for an external source of ferric ions. Second, the bacteria appear to provide sulfur and ash reductions beyond that achievable by acid treatment alone. Thus, a cleaner coal product can be obtained. Finally, this process is marginally efficient in processing the Midwestern coals. The use of these microorganisms could improve the sulfur and ash removal from these coals.

SUMMARY AND CONCLUSIONS

The objectives of this project are to study the potential applications of the three advanced coal cleaning processes, i.e., microbubble flotation, selective hydrophobic coagulation and electrochemical coal cleaning, for producing superclean coals. Since fine grinding is an integral part of the first two processes, methods of improving stirred ball mill grinding have been studied extensively. The effects of using grinding aids, different types and sizes of grinding media, and different impeller speeds have all been studied. It has been found that grinding aids can indeed reduce energy consumption, but the amounts of reagents needed to give beneficial effects are relatively high. It is believed that the role of grinding aids is essentially one of viscosity modification. The three different types of media studied in the present work, i.e., steel, glass and ceramic, show similar results in terms of energy consumption; however, steel balls give the highest breakage rates. The two most important findings of the present study are that an optimum ball size-to-feed size ratio exists for maximizing breakage rates, and that the slower the speed of the impeller the greater the energy efficiency of comminution in the stirred ball mill.

The purpose of grinding is to liberate mineral matter from coal. Therefore, the mill products have been examined using an image analyzer to determine the degree of liberation achieved under different operating conditions. Of the four coals studied, the Elkhorn No. 3 seam coal shows the highest degree of mineral matter liberation at 100 mesh, followed by the Pittsburgh No. 8, Upper Freeport, and Cedar Grove seam coals. The coal samples analyzed in this study were relatively low-ash coals that were potential feedstocks for the production of superclean coal. The analysis of the breakage behavior of the different macerals showed that the composite particles had higher breakage rates than did the free reactive (vitrinite) or

inert (fusinite) macerals. A combined size reduction/liberation model has been developed for grinding a binary feed. The image analyzer was also used to characterize the feeds and the products of the microbubble and the electrochemical coal cleaning processes.

In the study of the microbubble flotation process, the work was divided into seven subtasks, namely bubble generation, bubble-particle hydrodynamics, bubble-particle adhesion, froth phase studies, batch flotation, continuous flotation, and coal pyrite surface chemistry. The bubble generation studies were conducted on a porous venturi-tube type generator. By calculating the drag force inside the venturi tube and equating it to the surface tension force holding a bubble onto a nucleation site, it has proven possible to predict the average bubble size for any given operating condition. Parameters in the model include length and diameter of the porous tube, fluid velocity, pore size and surface tension. Experimental values are in excellent agreement with predictions.

Perhaps the most important accomplishment of the present work is the derivation of the stream functions around bubbles that are applicable over a wide range of bubble sizes. Using the stream functions derived in the present work, it has been possible to determine the probabilities of both bubble-particle collision and adhesion. Assuming that the probability of detachment is negligible for small particles, which is certainly the case for micronized coals, the product of the collision and the adhesion probabilities gives the overall probability of bubble-particle attachment. This, in turn, can be used to predict the flotation rate constant for a given gas flow rate and bubble size.

Two approaches have been taken to determine the probability of adhesion. In the first, it is assumed that a particle adheres to the surface of a bubble if its closest approach is within a certain critical distance of the bubble. In the second, it is assumed that adhesion takes place if the sliding time of

a particle is longer than the induction time for film thinning. Experimental techniques for determining the critical film thickness and the induction time have been developed in the present work. In general, the critical film thickness increases with increasing hydrophobicity of the particle, and the induction time decreases with increasing hydrophobicity. It is now possible to predict flotation rate constants for given physical and chemical conditions using either of the two approaches. The physical parameters include bubble size, particle size and gas flow rate, while the chemical conditions include collector additions, frother additions, pH and E_h .

The process of bubble-particle adhesion is critically affected by the charge on the air bubbles relative to that of the particles involved. While the techniques for determining the charges of the latter are well established, bubble charge measurements are not. In the present work, bubble charges have been determined using both electrophoresis and Dorn effect apparatus. The results obtained by these two techniques were in reasonable agreement.

As a result of the hydrodynamic studies, it is now possible to predict all of the parameters required to describe the subprocesses that occur in the pulp phase of a flotation column. However, the various phenomena that occur in the froth phase are too complex to model accurately with the present state of knowledge. Nevertheless, a population balance model has been developed in the present work to predict the behavior of two-phase froths. Unfortunately, many of the parameters required by this model, particularly those concerned with coalescence, are not known. Although the mathematical model is still incomplete as far as parameter estimation is concerned, extensive amounts of experimental work have been done to facilitate understanding of the behavior of three-phase froths. By taking samples at different depths in the froth column, the cleaning action taking place in the froth has been analyzed at different gas rates, wash water rates, feed rates, frother addition rates,

froth heights, etc. It has been found that the wash water addition is an important factor in determining the product grade.

Batch flotation tests were carried out on five different U.S. coals from the Jellico, Upper Freeport, Taggart, Elkhorn No. 3 and Splashdam seams. The purpose of these tests was to establish the proper reagent conditions and determine the potential for producing superclean products from these coals. Test results show that all five coals are good candidates for producing superclean coal with high recoveries. As for reagent conditions, the best results were obtained with a 4:1 mixture of No. 3 and No. 6 oils. It appears that the use of the No. 6 oil reduces the negative zeta potential of the emulsions which, in turn, reduce the energy barrier against bubble-particle adhesion.

Continuous microbubble column flotation tests have been conducted using a 2-inch column. The ash contents of the superclean coals produced in this work were in the range of 0.4 to 1.9% with combustible recoveries in the 69-92% range. The performance of the microbubble flotation column was investigated using the Elkhorn No. 3 seam coal, which readily gives superclean coal. Under normal operating conditions, the optimum superficial wash water rate was found to be approximately 20 cm/min, while the optimum superficial gas rate was about 80-100 cm/min; however, these numbers change if either the gas or the wash water addition is not operated at its optimum.

Other operating variables studied include froth height, frother addition rate, collector addition rate, feed rate, bubble size, and column height (or length-to-diameter ratio). Based on the data obtained in these experiments, a process model that can be used for scale-up has been developed. The basis of this model is that the flotation recovery is determined by rate constant, retention time and the degree of mixing in the column, as embodied in the well-known Levenspiel equation. From a survey of the columns operating in plants and in different laboratories, it has been found, however, that the

axial dispersion number representing the degree of mixing in the column does not vary as widely as originally anticipated. Therefore, the process model developed in the present work assumes that the dispersion number does not change significantly with scale-up, in which case the recovery can be expressed as a direct function of the product of rate constant and retention time. Because the rate constant can be predicted from the stream functions derived in the present work, the process model is one based on first principles and, therefore, can be used with confidence for scale-up. The process model also shows that recovery increases as the inverse cube of the bubble size, which is a powerful incentive for using small bubbles for the flotation of fine particles. This inverse cube relationship has been verified in actual flotation experiments conducted in the 2-inch column.

Control of the surface chemistry is potentially useful as means of improving the rejection of coal pyrite during microbubble flotation. In the present work, the comparative electrochemical behaviors of mineral pyrite and coal pyrite have been studied. A contact angle apparatus was designed to permit measurement of contact angles under applied potentials. Both mineral pyrite and coal pyrite exhibit increased contact angle (or hydrophobicity) at oxidizing potentials and with decreasing pH, suggesting that the apparent hydrophobicity of pyrite is due to superficial oxidation. ESCA studies show that, in general, coal pyrite oxidizes faster than mineral pyrite and that the greater the extent of coal inclusion in the grains of coal pyrite, the higher the rate of oxidation. The ESCA spectra also showed that after a prolonged exposure to water, sulfate is formed as the major oxidation product. This was confirmed by work with the spectroelectrochemical FTIR cell developed in the present work. However, the FTIR results show that the nature of the sulfate formed on pyrite is complex, possibly complexed with iron hydroxides.

The microflotation experiments conducted on relatively pure samples of mineral and coal pyrites basically support the findings of the electrochemical studies. The floatability increases with increasing potential and with decreasing pH. However, a more important finding is that the hydrophobicity of coal pyrite acquired through superficial oxidation is magnified substantially in the presence of flotation reagents.

It was found in the work on this project that hydrophobic particles can coagulate spontaneously without significant use of reagents. It was originally thought that this coagulation was induced by high-shear agitation, and thus the term *selective shear coagulation*. It has been found, however, that high-shear agitation is not an essential part of the process. Instead, the driving force is the hydrophobic interaction force, which has not been seriously considered before in coagulation studies. Therefore, a more appropriate term may be *selective hydrophobic coagulation*. In the present work, the extent of hydrophobic coagulation has been measured with micronized Elkhorn No. 3 seam coal. The results show that the size distribution of micronized coal due to hydrophobic coagulation shifts approximately 50 μm .

Attempts have been made to describe the hydrophobic coagulation process in terms of the classical DLVO theory. The electrical energies for coagulation have been determined from the zeta potentials of the particles involved, while the dispersion energies have been estimated from the Hamaker constants determined using the methylene iodide contact angle technique. The results show that the energy barrier against coagulation increases with increasing hydrophobicity of the coal samples used, which is contrary to the experimental observation. Therefore, this finding suggests that there must be a third force that has not been considered in the classical DLVO theory. This force, called the hydrophobic interaction energy, will be studied in future DOE contract work.

A population balance model has been developed to predict the aggregate size distribution due to hydrophobic coagulation. The simulation results are in reasonable agreement with experimental data.

The phenomenon of hydrophobic coagulation has been exploited for separating coal from mineral matter. Typically, the aggregates of coal are separated from the dispersed mineral matter either by settling or by elutriation. Numerous batch separation tests have been conducted to show that superclean coals assaying as low as 0.36% ash can be produced by this technique. The operating parameters studied include particle size, number of cleaning stages, agitation time, stirring speed, pH, feed solids content, divalent cation concentrations, etc. The best separation is usually achieved at pH 7-9.5, where the dispersion of mineral matter is more complete. A series of continuous hydrophobic coagulation tests have been conducted using a specially-designed elutriation column. The test variables studied in the present work include feed percent solids, elutriation water rate, slurry feed rate, etc. A population balance model based on first principles has been developed for the use of an elutriator as the separation device. This simulator has been shown to be capable of successfully predicting the performance of the bench-scale elutriator used in this study. Since this simulator is based on first principles, it can be used for scale-up.

The electrochemical coal cleaning process is based on the premise that Fe^{3+} ions superficially oxidize coal surfaces, during which process an osmotic pressure is set up inside the pockets where the mineral matter is located. If the pressure is large enough, the mineral matter is liberated from the coal matrix without pulverization. A thermodynamic model has been developed to estimate the osmotic pressure as a function of the electrolyte concentration and the distance separating two charged plates. The predicted osmotic pressures have been compared with the experimentally determined values for simplified model systems.

The Fe^{3+} ions are converted to Fe^{2+} ions during the electrochemical coal cleaning process but can be converted back to Fe^{3+} ions by several methods. Of the various techniques studied, the electrochemical technique was the most effective in terms of kinetics, followed by bacterial oxidation and air oxidation in that order. Therefore, the electrochemical technique was studied more extensively. The operating variables studied in the characterization of this process include particle size, reaction time, electrolyte type and concentration, applied potentials, and temperature. Various coals were tested in bench-scale experiments using two different types of reactors. Superclean coals with ash contents as low as 0.3% were obtained with over 90% recovery. Mass-balancing of the test results shows that the majority of the ash rejection from bituminous coals is due to liberation, although some ash is removed by chemical dissolution.

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