ABSTRACT

One of the primary concerns in coal utilization is the emission of sulfur dioxide (SO₂). Fifty-five to 80% of the sulfur in most coals is in the form of pyrite. If a significant portion of pyritic sulfur could be removed by advanced coal cleaning techniques, total sulfur emissions in the U.S. could be cut by as much as 50%. Total liberation of pyrite and other minerals from the organic components requires grinding to a top size of 325 mesh. At this fine particle size, advanced beneficiation processes are necessary, and even then difficulties are encountered due to surface related phenomena. This project has utilized a new, novel process which circumvents surface phenomena and takes advantage of the natural porosity of the organic fraction of the coal, encouraging bubbles to form from the pore openings, and floating the coal away from the non-porous minerals. During this initial phase of the project, it has been shown that clean coal can be floated by intrinsic bubble formation. Frothers and frother-collectors are the most promising group of additives for the process, although very good recoveries and ash reductions have been obtained using no additives. It has also been noted that pressurization appears to increase the hydrophobicity and decrease the wettability of coals, the extent of which increases with decreased particle size. Tests using octanol with low ash Colchester No. 2 suggest that the preferable pH range is 1.5 to 2, while for Herrin No. 6, preferable pH range is 4 to 4.5. Lower pulp densities improve surface wetting, while higher pulp densities enhance float recovery. Even though the process has not been optimized, very good recoveries and ash rejections have been obtained, even for weathered samples. The system uses very low additive dosages, and once the coal enters the flotation column, float production is almost instantaneous. This process has a high potential for cleaning fines which would be otherwise uncleanable, and opening up new markets for Illinois coals.
EXECUTIVE SUMMARY

One of the primary concerns in coal utilization is the emission of sulfur dioxide (SO₂). Presently, the major alternatives for the prevention of SO₂ emissions are pre-combustion coal cleaning and post-combustion scrubbing. Post-combustion scrubbing has been proven to be technically feasible, but costly. Therefore, incentives exist to explore pre-combustion cleaning. In most coals, 55 to 80% of the sulfur is in the form of pyrite. If a significant portion of pyritic sulfur could be removed by advanced coal cleaning techniques, total sulfur emissions in the U.S. could be cut by as much as 50%.

The minerals in coal erode and corrode equipment, decrease heat transfer in boilers, prohibit coal use in magnetohydrodynamics (MHD) and diesel engines, cause particulate emissions, and lower the efficiency of coal conversion processes. Pyrite and marcasite are the dominant inorganic sulfur species found in coal. Some of the pyrite and other minerals can be removed by conventional coal cleaning techniques, but significant mineral reduction requires total liberation of minerals from the organic components. To accomplish total liberation, most coals must be ground to a top size of 325 mesh.

Conventional coal cleaning methods which are based on gravity separation become inefficient due to the attractive forces that are greater than the differences in the gravity forces exerted on fine and ultrafine particles. Recently, advanced physical beneficiation processes (flotation, agglomeration, and heavy-liquid cycloning) have been explored. However, sufficient Btu recoveries and mineral reductions have not been achieved. The difficulties encountered in advanced coal cleaning techniques appear to be surface related. Coal-mineral interactions, surface wetting, and weathering all reduce the efficiencies of advanced coal cleaning processes. Coal flotation by intrinsic bubble formation is an advanced, novel, physical coal cleaning process, aimed at circumventing these surface phenomena which reduce the efficiencies of advanced coal cleaning processes involving fine and ultrafine coal.

This process takes advantage of the natural porosity of the organic material in the coal, encouraging bubbles to form at the pore openings, thereby floating the organic material away from the non-porous minerals. Since the process does not require particle-bubble collision and attachment as with other flotation processes, the probability of flotation of an organic particle should be close to 100%.

The initial phase of the project involves a preliminary scoping of the process, including the variables which may affect it. Cleanability of two Illinois coals is being determined in a batch process. The effects of weathering and various additives were also examined.

After fine-tuning the process, time to commercialization as a continuous process is anticipated to be short, as the process could be easily retrofitted to existing types of flotation equipment, particularly column flotation.

Experiments indicate that frothers and frother-collectors are the most promising additives, although very good results have been obtained using no additives. It has also been noted that pressurization increases hydrophobicity and decreases wettability of coals, the extent of which increases with
decreasing particle size. Tests using octanol with low-ash Colchester No. 2 indicate that a low pH range of 1.5 to 2 is preferable, while for Herrin No. 6, preferable pH range is 4 to 4.5. Lower pulp densities improve surface wetting, while higher pulp densities enhance float recovery.

Even though the process is not yet optimized, recovery and ash rejection are very good in some cases, even for weathered samples, especially considering the low maximum yield of 1933 coal. The system uses very low additive dosages (usually less than 2 pounds per ton). Once the coal enters the flotation column, float production is almost instantaneous, which becomes important with large continuous operations.

This is a new and novel process with a high potential for cleaning fines which would be otherwise uncleanable. This process could open up new markets for Illinois coal.
OBJECTIVES

The initial phase of the project involved a preliminary scoping of the process, including the variables which may affect it. Cleanability of two Illinois coals was determined in a batch process. These were Illinois Basin Coal Sample Program Nos. 2 and 4. These coals were chosen because of their differing rank (reflectance), clay, ash, and pyrite/organic sulfur ratio values. This allowed for the determination of the process effectiveness on different mineral constituents. The effects of oxidation and various additives and conditions were also determined.

Because of positive results obtained during this phase of the project, additional funding has been requested for work using different coals, additives, and conditions. Future funding may be requested for application of the process to a continuous mode of operation and, eventually, for proof of concept.

INTRODUCTION AND BACKGROUND

This project has been an exploratory investigation of an advanced, novel, physical coal cleaning process which uses intrinsic bubble formation for fine and ultrafine coal flotation. Conventional coal cleaning methods based on gravity separation become inefficient due to the attractive forces between the particles which are greater than the gravitational forces exerted on these fine particles. Advanced surface-related processes (including flotation, agglomeration, and heavy-liquid cycloning) have received increased attention, but sufficient Btu recoveries and mineral reductions have not yet been achieved. The difficulties encountered in these advanced coal cleaning techniques appear to be surface related. Coal-mineral interactions, surface wetting, and weathering are major factors in reducing the efficiencies of advanced coal cleaning processes. This project is aimed at circumventing the surface phenomena which reduce the efficiencies of advanced coal cleaning processes.

Successful applications of this concept would:

1. develop new markets for Illinois coals (MHD, diesel engines);
2. increase the efficiency of combustion, decrease fouling and corrosion in boilers, and decrease operating costs;
3. decrease acid rain concerns on present markets; and
4. provide good feedstocks for blending control to ensure steady operations.

To develop new coal markets, it is necessary to decrease the mineral content of the coal. Development of coal usage in MHD, gasification, and internal combustion engines has been hindered by the presence of mineral matter which causes slagging and corrosion with all of these systems.

With appropriate staging, the process may be capable of generating feedstocks that have controlled composition and properties. This has several advantages. First, controlled composition would decrease excursions in oper-
ations which may account for the heaviest fouling and emission. Second, by making blending possible, the utilities could become less dependent on a single coal source. Third, the blending of uniform feedstocks could make utility design and construction more modular, thus reducing the cost of new plants. Also, carbon emissions might be reduced. Recent work at SIUC has shown that particulate carbon emissions may be the result of incomplete combustion of liptinites and not inertinites as previously thought. By controlling compositions, decreased concentrations of undesirable organic components can be accomplished, with the result of producing by-products that can be used in producing chemical or material feedstocks.

Coal flotation processes are based on the principle that most organic coal constituents are hydrophobic, while most of the inorganic minerals are hydrophilic. Froth flotation involves the injection of air bubbles and pulp mixture together into the contact chamber. Column flotation is a modification of froth flotation which uses a counter-current flow of air bubbles and pulp (bubbles injected at the base and pulp injected at the top of the chamber) (Kawatra et al. 1987). The organic particles and bubbles attach to one another and travel to the upper froth layer where they are removed, while the minerals remain in the aqueous media (Zimmerman 1968).

Flotation reagents are usually added to the pulp mixture to ensure air bubble attachment to the appropriate particles. These flotation reagents fall into three main groups: frothers, collectors (or promoters), and modifying reagents. Frothers are used to develop a good stable bubble layer, or froth. They are usually characterized by the presence of two opposing constituents, one polar and one non-polar. Collectors are used to promote contact between coal particles and air bubbles. Some common frothers, such as MIBC and kerosene, have both frothing and collecting characteristics. For most coals, one of these frother-collectors is all that is necessary, although for oxidized or low rank coals, addition of a pure collector is necessary for effective flotation. Modifying agents are those reagents which are used for purposes other than frothing and collecting. These include depressing agents to inhibit flotation of unwanted materials, activation agents to alter a surface to aid in air bubble attachment, pH regulators, and dispersing agents to counteract the effect of slime adsorption or to deflocculate clay and carbonaceous shales (Zimmerman 1968). These modifying agents must be used selectively, as some pyrite depressants, for example, also depress the organic fraction of the coal (Perry and Aplan 1985).

Miller and Misra (1987) have patented a process which utilizes gaseous carbon dioxide (CO₂) to improve the hydrophobic characteristics of coal for froth flotation. The CO₂ adsorbs to the external coal surface, changing the surface characteristics of the coal. This process involves wet milling of a coal, conditioning the coal by pressure filtering with CO₂, repulping in a CO₂ saturated aqueous solution, and then running standard froth flotation procedures using either air or CO₂ bubbles with staged additions of frother and promoter (Miller and Misra 1987, 1985).

Current flotation processes, including the Miller process, require coal particle-bubble collision and attachment. Collision and attachment depend on particle size, oxidation and rank of coal, pulp density, pH and water characteristics, flotation reagents, and flotation equipment (Zimmerman 1968). The probability of flotation can be expressed by the following equation:
\[ P_f = P_c \times P_a \times (1 - P_d) \]

where:

- \( P_c \) = the probability of particle-bubble collision which is controlled by cell hydrodynamics and pulp density,
- \( P_a \) = the probability of attachment which depends on surface forces, and
- \( (1 - P_d) \) = the probability of retaining the particle-bubble attachment which depends on adhesion forces and the turbulent interaction forces which favor detachment (Gala 1987).

The above equation holds for both organic and mineral components. Each type of particle has its own unique probability factors. Since coal and mineral surfaces are vastly different, they have different attachment probabilities. Because mineral concentrations are lower than coal concentrations, the probability of organic particles colliding with bubbles is greater than the probability of minerals colliding with bubbles. As particle size is reduced, finer bubble size is required in order to obtain optimum selectivity; therefore, many small bubbles are preferred over one large bubble. This is especially true for ultrafine coal.

Coal is composed of organic and inorganic components. Most geologists believe that the origin of mineral matter in coal is the result of two parallel genetic lines, either organic or inorganic in origin (Gluskoter et al. 1981), where minerals are deposited in the coal swamp or adsorbed at some time during the coalification process after the accumulation of the organic coal debris (Figure 1). Many types of minerals are found in coal, including quartz, clays, pyrites, and carbonates, and may vary in size from microns to inches. Inorganic salts are also present in coals and usually appear as highly divided discreet particles. Most minerals can potentially be removed from coal by physical coal cleaning, although there are some organically derived elements

<table>
<thead>
<tr>
<th>Organic</th>
<th>Time</th>
<th>Inorganic</th>
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<tbody>
<tr>
<td>Coal swamp flora (C, H, O, N, S, Se)</td>
<td>Detrital minerals (clay minerals, quartz, zircon, tourmaline)</td>
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<tr>
<td>Epigenetic (early) (first stage of coalification) (B, Ge)</td>
<td>Syngenetic minerals (pyrite, calcite, ankerite, clay minerals)</td>
<td></td>
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<tr>
<td>Epigenetic (later) (second stage of coalification) (Ge, U, Br, Cl)</td>
<td>Epigenetic minerals (pyrite, calcite, kaolinite, sphalerite)</td>
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<tr>
<td>Coal</td>
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Figure 1. Parallel genetic lines in the development of coal (Gluskoter et al. 1981).
which contribute to ash production which are not removable by physical coal cleaning.

The organic subcomponents of coal are microporous substances, while the inorganic components are nonporous crystalline or amorphous substances (Gan et al. 1976). According to these authors, mineral free coal from the Illinois Basin should have a particle density range of 1.0 to 1.06 g/cm³. They also have 20 to 30% porosity, most of which is found in a narrow distribution of transitional sized pores. For fine and ultrafine particles, most of this porosity would be open to gas penetration. The minerals range in density from 2.7 to 4.5 g/cm³, depending on the percentage of pyrite in the sample. The minerals also have a very low porosity (O’Gorman and Walker 1973). Because of these properties, this process is uniquely suited to Illinois Basin coals. The particle densities are smaller for Illinois Basin coals than for coals from any other U.S. coal bearing region. In addition, the porosity is larger for Illinois coals than for other coals. The narrow distribution of transitional pores will aid in optimizing the process requirements and in obtaining uniform bubble size. Higher rank coals have smaller pore diameters and volumes which limit bubble size and floatability. They also have increased particle density. Lower rank coals have a higher porosity and the pore openings are large. Because of the larger pore openings, bubble size would be large and uncontrollable. The larger bubbles would result in mineral attachment. Also particle densities are much larger than in the case of Illinois coals.

Intrinsic bubble formation takes advantage of the different porosities and densities between macerals and minerals. In this process, dry micronized coal is fed to a pressurized chamber and then mixed with a flotation liquid (with an appropriate wetting action). The flotation media is water or water with a minimum amount of additives. The slurry is discharged into a depressurization column. The pressurized gas expands through the capillary pores of the organic coal and forms micro-bubbles according to the capillary relationships determined by Sugden (Adamson 1967). Each pore opening forms a bubble whose volume is dependent on the pore radius, the total pore volume, and the elevated pressure of the process. Since the density of the organic coal material is nearly one to begin with, only a small volume increase (porous particle + capillary bubble) is required to float the coal particle. Therefore, the coal particle floats to the top of the column while the mineral particles settle to the bottom of the column.

Intrinsic bubble flotation depends on the formation of bubbles from the pores of the organic material by capillary action. Probabilities of collision and attachment, $P_c$ and $P_a$, may be eliminated from the flotation equation, and since the probability of detachment may be controlled by system overpressure, as $P_d$ approaches 0, the probability of flotation $P_f$ approaches 1. This should make collectors for contact promotion unnecessary. Since pore volume and capillary action are the key factors with intrinsic bubble flotation, oxidation should have less effect on floatability, and flotation should be independent of mineral depressants and other additives. This should allow them to work more effectively, as long as the appropriate wetting/contact angle is preserved between the surface and the flotation media.

A higher solids capacity should exist in the foam layer, as every bubble is attached to a coal particle. Without the need for a stable froth development,
the use of a frother should be unnecessary, allowing mineral slimes entrained in the film water to drain from the froth more efficiently. This is supported by the good recoveries and ash reductions obtained using no additives. Since water would not be entering the coal pores, the moisture content of the cake should be decreased, the only moisture being from the film water.

Macerals might be separated from each other by staged pressure reduction. The three macerals are known to have different densities. While little has been documented with regards to relative porosity and pore size distribution, it is expected that these properties will vary between macerals. Thus, separation of coal into components might become commercially feasible. The advantage of blending has been discussed previously. New markets, such as diesel engines, may require controls on C-tane indexes that could be modulated employing a staged process. Finally, recovery of liptinites for pitch feedstocks might pay for the cleaning process. For example, a high quality feedstock for pitch production could be sold for $300/ton. Thus, 5% liptinites in the coal could be separated and sold for $15/ton of the whole coal, adding to the value of the coal by 50%. Three hundred dollars/ton is a reasonable cost for specialty materials used in the production of pitch fibers and pitch-based matrix composites.

**EXPERIMENTAL PROCEDURES**

**Preparation and Characterization**

**Coals Chosen.** The coals which were chosen for use in this study were chosen because of their differing rank (reflectance), clay and ash contents, and pyrite/organic sulfur ratios. This allowed for the determination of the process effectiveness on different mineral constituents. The coals used in this project were from the Illinois Basin Coal Sample Program. They were:

| IBCSP No. 2 | Colchester No. 2 | (also referred to as SIU 1934) |
| IBCSP No. 4 | Herrin No. 6     | (also referred to as SIU 1933) |

**Coal Preparation.** Each of the coal samples was split. Half of each sample was then stored under nitrogen and the other half crushed to −1/8" with a Chipmunk jaw grinder and then to −32 mesh (U. S. Standard) using a Straub grinder. The crushed material was again split, one quarter being reserved as a head sample, one quarter for flotation studies at −32 mesh, and half being ground to −60 mesh with a Holmes pulverizer and then ball-milled to −100 mesh. The −100 mesh material was split, half for flotation studies at −100 mesh, and the other half run through a fluid energy mill for flotation studies at −400 mesh.

**Coal Characterization.** Particle size distributions were determined on the −32-mesh and −100-mesh coals by wet sieving using a set of three-inch U. S. Standard screens. Particle size distributions for the −400-mesh material were performed using a Microtrack Analyzer. The coals were also characterized by proximate analysis using a LECO MAC-400 proximate analyzer, ultimate analysis using a Carlo Erba elemental analyzer, total sulfur using a LECO total
sulfur analyzer, sulfur forms using standard ASTM procedures, and Btu analysis using a bomb calorimeter.

It was decided that additional characterization studies would provide valuable information with regard to the flotation process. Therefore, a washability study was conducted using the Density Gradient Centrifugation (DGC) technique described in several publications by Dyrkacz and others. The process involved the establishment of a liquid density gradient, centrifugation of the sample into the gradient, and collection, filtration, washing, and drying of the various density fractions (Dyrkacz et al. 1987; Dyrkacz et al. 1984a,b,c,d; Dyrkacz and Horwitz 1982). Fractions from various density ranges were then combined and ash values were determined using a Perkin Elmer TGA7 thermogravimetric analyzer.

Additives

Flotation. Dry coal sample was placed in the mixing chamber, which was then sealed and pressurized with nitrogen. The system pressure was controlled by the tank regulator. After pressurization, flotation media was pumped in through the bottom of the mixing chamber with the impeller running. Once mixing was completed, the slurry was slowly drained through the bottom of the mixing chamber into a cylinder containing flotation media. The float and sink (and sometimes suspension) materials were collected, and the mixing chamber was again filled and drained, once again collecting the different fractions. The chamber was then opened and residual material was washed out of the system, with fractions collected as necessary. Occasionally material did not pass out of the mixing chamber due to lack of slurrying. In this case, depressurization and sample collection were done in the mixing chamber. (flotation system shown in Figure 2.). All fractions were filtered, dried in a vacuum oven, and weighed.

For the additive portion of the project, the conditions used were 5% pulp density and 75 psig, using −100-mesh material.

Product testing. Ash values were determined on all collected fractions using a Perkin Elmer TGA7 thermogravimetric analyzer.

Conditions

Flotation and product testing procedures are described under the Additive section. Variations in pH were made using sodium hydroxide (NaOH) and hydrochloric acid (HCl). For pH tests, pressure and pulp density were held constant at 75 psig and 5%. For pressure tests, pH and pulp density were held constant. For particle size effects, the three mesh sizes were tested, holding pH, pressure, and pulp density constant. For pulp density tests, pressure and pH were held constant.

Weathering

Fifty-gram samples of each coal and size fraction were placed in microporous bags and set out to weather for two months. Weathered samples were floated using conditions which yielded the best results during earlier runs (75 psig and 5% pulp density, with octanol and with no additives) and tested according to procedures described in the Additives section.
Figure 2. Flotation apparatus.
RESULTS AND DISCUSSION

Preparation and Characterization

Particle Size Distributions. Particle size distributions of the three coal sizes are presented graphically in Figures 3 and 4. Most samples followed near log normal distributions, with the exception of -400-mesh 1934 and -100-mesh 1933. The plots of these two samples indicate that the particle size distributions are made up of two types of particle populations, which could be significant if one fraction is predominantly mineral matter. Additional information, such as that obtained from Scanning Electron Microscopy (SEM)/Automated Image Analysis (AIA) is required in order to distinguish the attributes of the particle populations. The -32-mesh 1933 coal has a finer particle size distribution than the 1934, but the width of the distributions are approximately the same. This can be seen by looking at the mean particle size and the characteristic sigma distribution. The -100-mesh samples follow a Rosin-Rammler distribution more closely. Because of the anomalies in the 1933 particle size distribution, a comparison of the two size distributions is difficult. At -400 mesh, the 1933 coal has a coarser distribution than the 1934 coal. The three particle size distributions indicate that 1933 is more resilient to grinding than 1934.

Characterization. Average raw analyses of SIU 1933 and 1934 are presented in Table 1. These data correspond well with the data provided by the Illinois Basin Coal Sample Program.

Washability. Washability curves for -100- and -400-mesh materials are presented in Figures 5 and 6. These data represent the ultimate cleanability of the coal using gravity forces (16,000 x g). These data are similar to ASTM sink/float results, but are more accurate for fine particle size distributions. From the data, the cumulative ash percent vs. cumulative weight recovery are obtained. At low recoveries (below 40%) of the high ash 1933 (Herrin No. 6) coal, the ash content is a constant 3% for both particle size fractions. Recoveries above 40% show a slight difference in washability as a function of particle size. The data indicate that a 55% weight recovery is the maximum attainable recovery for this coal if the ash yield is to remain below 5%. This is because of the high mineral content of the feed, which is approximately 43% of the coal. The maximum separation index is approximately 550, which no commercial process has yet achieved. The best run in this program to date achieves 60% of this efficiency. On the other hand, the ash rejection is better than that of aggregate flotation, while using lower additive dosages (Read et al. 1987). The data also show that only a small benefit can be derived by reducing the particle top size from -100 to -400 mesh. The washability curves for 1934 (Colchester No. 2) demonstrate a difference in liberation of minerals between the -100- and -400-mesh material. This is the opposite for that found with 1933. Also, ash content appears to go through a minimum with increasing density and recovery. This indicates that the inertinites and the liptinites contain a higher inherent ash yield than the vitrinites. Thus, for this coal, ultra-fine ultra-clean product is more likely to be obtained if the inertinite and liptinite fractions can be separated from the vitrinites. Some of the inherent mineral content of the inertinites and liptinites could be due to
Figure 3. Particle size distributions of −32- and −100-mesh materials.
Figure 4. Particle size distribution of -400-mesh material.
higher concentrations of organo-metallics. The ashing properties of the organo-metallics are not known and could present a problem for combustion machinery, such as turbines and piston engines. To reach the ultimate cleanability of around 2%, recovery must remain around 60%.

Additives

The additives used in this project were selected on the basis of a review of the literature and personal communication. The additives include:


3. Depressants: lime (Brown 1962); potassium permanganate, potassium chromate (Zimmerman 1968); and Hylon III (National Starch) (a high amylose corn starch) (Perry and Aplan 1985).

4. Dispersants: Lomar D (Henkel Corporation) and Daxad 32 (W. R. Grace & Co.) (both condensed naphthalene sulfonates) (Simmons and Keller 1984); calcium chloride (Brown 1962); sodium silicate (Zimmerman 1968); Lignosol TSD (Daishowa Chemicals, Inc.) (a
Figure 5. DGC washability curve for SIU 1933 (−100- and −400-mesh).
Figure 6.  DGC washability curve for SIU 1934 (~100- and ~400-mesh).
ligno-sulfonate) (Simmons and Keller 1984); and Goodrite K732 and K752 (B. F. Goodrich Co.) (both ammonium carboxylates) (S. Keller 1988, personal communication).

5. No Additives.

Frothers and Collectors. Of the frother-collectors, MIBC and octanol appear to give the best performance under the conditions studied for 1933, based on separation index. Polypropylene glycol gives a slightly lower performance, and kerosene and oleic acid substantially lower. Octanol gives better ash rejection and MIBC yields better coal recovery.

For the 1934 coal, kerosene gives the highest separation index, but has a slightly lower recovery than polypropylene glycol. Octanol recoveries are lower than those for kerosene or polypropylene glycol, yielding a lower separation index. MIBC gives a separation index which is slightly better than octanol, but the ash reduction is the lowest of the frother-collectors studied. Oleic acid gives the lowest separation index.

Potassium ethylxanthate displays peculiar behavior in the process with the 1933 coal. It selectively wets ash and allows a larger proportion of the minerals, as opposed to coal, to be enveloped in the slurry. The net result is that the ash yields for samples collected from the mixing chamber are lower than the ash yields for the equivalent fractions collected from the flotation column. The separation index based on material left in the mixing chamber is as good as that obtained with polypropylene glycol, but the material found in the flotation column has a separation index closer to kerosene. This indicates that two mechanisms of cleaning are occurring with potassium ethylxanthate. This behavior does not hold for 1934, but the potassium ethylxanthate gives comparable performance to kerosene, the best frother-collector for this coal. Thus, the results clearly indicate that additives can affect process performance and behave differently for different coals.

Depressants. The depressants, with the possible exception of lime, show poor performance, with the primary problem being decreased coal flotation. Lime has shown some results which indicate that it is effective in separating coal and minerals; however, difficulties in analytical testing obscure performance. This is because lime reports to all fractions, increasing the ash yields of all samples. Although the performance is better than that of other depressants, it does not appear worth pursuing because of the increased difficulties in analytical characterization.

Dispersants. Dispersants give slightly lower performance than the best frother-collectors. The Goodrite additives appear to give the best performance for the 1933 coal. The dispersants increase recoveries, but reduce ash reduction for this coal. Calcium chloride, sodium silicate, and Lomar D gave poor recoveries and ash rejections. Again, the calcium chloride data are difficult to interpret because it contributes to ash yields. Daxad 32 seems to plate minerals onto the walls of the mixing chamber, allowing coal to be preferentially enveloped and pass through the mixing chamber. The separation index is difficult to calculate since all fractions contained less ash than the starting coal. As a group, dispersants cause ash rejection to increase with decreasing recovery.
The dispersant behavior with 1934 is different than with 1933. The highest separation index is from Daxad 32, which gives better performance than the frother-collectors because of the high material recovery. The ash rejection for Daxad 32 is low in comparison to the frother-collectors. Again, there is a trend toward decreasing recovery with increasing ash rejection. The Goodrite additives give poorer performance than sodium silicate and Lignosol TSD. However, Goodrite K732 produces lower ash in all the fractions tested. Again, it is apparent that ash plates on the mixing chamber walls with this additive for this coal.

**Combinations.** In general, the dispersants increase recovery while decreasing ash reductions, while the frother-collectors give high ash reductions. Therefore, combinations of frother-collectors and dispersants would seem to be worthwhile. Attempts to combine Lignosol TSD with frother-collectors such as MIBC, polypropylene glycol, and octanol indicate that increased performances can be attained using additive combinations. In specific, increased recoveries are obtained while maintaining the high levels of ash reductions associated with the frother-collectors.

**No Additives.** Runs made with water only yield separation indexes in the middle range of those of the frother-collectors for 1933, indicating that the judicious use of additives could enhance the ash rejection for this coal. For the 1934 coal, the separation indexes are higher than any separation index obtained from the additive studies, indicating that lower dosages or no additives are required (i.e., optimization is necessary). This also shows that additive use and selectivity are coal dependent.

**Conditions**

**Pressure.** Several experiments were made using different system overpressures. Since difficulty was encountered with coal mixing at 75 psig during the additive screening, several additives were mixed with the coals at 0 psig to check wetting action. In these cases, the coal mixed completely, indicating that pressurization increases hydrophobicity and decreases wettability of the coals. This also appears to be particle size dependent, as the finer the particle size, the more difficult the coal is to slurry. This phenomenon is related to the same mechanism that produces the intrinsic bubbles. As coal is enveloped in flotation media, the media will penetrate the capillary pores. As the media proceeds along the capillary pores, the internal gas pressure increases until Young's equation is satisfied. This equation relates the pressure differential between the compressed gas and the system pressure to the media surface tension, wetting angle, and pore radius. With increased pressure, more gas is trapped in the pores, and for a given surface tension and contact angle, flotation media is able to penetrate smaller percentages of the pores. Because media penetrates the pores to a lesser extent at higher pressures, this means that the average particle density is lower at higher pressures, and therefore it is more difficult to envelope particles at high pressures. Increasing particle size provides a stronger gravitational force making large particles more easily enveloped than smaller particles. Additives affect the surface tension and wetting angle; therefore, they affect the particle density and wettability. If the wetting angle is lowered too far, then gas will escape from the pores as the particles are wetted, and decreased flotation will be observed. Fines do not wet in the system because the interstitial voids in the packed bed of coal do not allow
the flotation média to penetrate through the coal bed, even with the high shear rates employed. This makes the whole coal bed act as a single particle, having the tendency to float up and down as the flotation media is pumped in and out. The U/D ratio of the present system is too high. A squatting mixing chamber with a larger diameter is necessary to obtain information on ultra-fine particles.

Initial tests varying pressure using MIBC indicate that pressure has a substantial effect on recovery, but that the different coals have different ideal pressures. With this additive (using ~100-mesh material), the best recovery for the high ash SIU 1933 appears to be around 75 psig, while for the low ash SIU 1934, best recovery appears to be around 30 psig.

Tests using octanol with both coals at 45 and 75 psig showed little difference with respect to recovery or ash reduction, and they indicate that efficiency may go through a maximum between these pressures. Tests using 90 psig with the 1934 coal displayed reduced recovery and ash reduction.

pH. Tests using octanol with ~100-mesh SIU 1934 indicate that a lower pH (1.5 to 2.0) is preferable to a more neutral pH of 6 or 7 in terms of float recovery. At the higher pH levels, no floating of material is achieved. For the higher ash SIU 1933 using octanol, the preferable pH range appears to be 4.0 to 4.5, with float recovery increasing and ash reduction decreasing with decreasing pH.

Pulp Density. Increasing the pulp density using octanol with SIU 1934 causes an increase in float recovery, although ash reduction decreases slightly. Decreasing pulp density with SIU 1933 results in increased recovery, but ash reduction goes through a maximum between 1 and 10% pulp. Slurrying is greatly improved with lower pulp density.

Particle Size. Particle size has a marked effect on recovery and ash reduction for both coals. In general, decreasing particle size decreases both the recovery and ash reduction. This could be due, in part, to the difficulties encountered in slurrying the finer coals under pressure with the current system, as discussed previously. This also indicates that a second cleaning option is available. This option would be equivalent to oil agglomeration, employing air as the agglomeration media.

Weathering. Weathering experiments conducted using either no additives or octanol yielded recoveries and ash reductions which were as good or better than tests run on non-weathered samples, supporting the original hypothesis that intrinsic bubble flotation should be successful on weathered materials.

CONCLUSIONS AND RECOMMENDATIONS

Clean coal can be floated by intrinsic bubble formation.

Frothers and frother-collectors are the most promising primary additives, although very good results have been achieved using no additives. Additional combination studies are necessary toward additive enhancement.
Pressure tests indicate that pressurization increases hydrophobicity and decreases wettability of coals, the extent of which increases with decreasing particle size.

pH tests using octanol as an additive suggest that a more acidic range of 1.5 to 2 for the 1934 coal, and 4 to 4.5 for the 1933 coal is preferable to a more neutral 6 or 7.

Lower pulp densities improve wetting, while higher pulp densities enhance float recovery.

Weathered materials can be floated as successfully as non-weathered materials.

Even though the process is not yet optimized, recovery and ash rejection are very good in some cases, especially considering the low maximum yield of the 1933 coal. The system uses very low additive dosages (usually less than 2 pounds per ton). Once the coal enters the flotation column, float production is almost instantaneous, which becomes important with large continuous operations.

REFERENCES


