Studies Relating to Removal of Pyritic Sulfur from Coal by Column Flotation

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ABSTRACT

Although column flotation is known to be more effective than conventional flotation for cleaning fine coal, little attention has been paid to the considerable sulfur removal potential of this process. Whereas conventional flotation can only with difficulty remove pyritic sulfur from coal, flotation columns can make this separation readily due to their greater selectivity. This project has used a modified flotation column to remove pyrite from fine coal. This column has been shown to be capable of removing 70 to 85 percent of the pyritic sulfur from coal while recovering 80 to 85 percent of the total calorific value. However, the remaining pyrite is too finely disseminated to be readily removed by physical means. Currently, experimentation is in progress using bacterially-catalyzed dissolution of pyrite in acid solution to remove ultrafine pyrite and aid in the removal of coarser pyrite inclusions.

INTRODUCTION

Due to the severe environmental effects resulting from release of sulfur oxides into the atmosphere, it is necessary to limit the emissions of sulfur resulting from coal combustion. Since the majority of eastern and midwestern coals exceed the federal emission standards, these coals cannot be utilized without some form of sulfur removal before, during, or after combustion. A cost-effective method for removing sulfur prior to combustion would therefore have considerable utility.

The bulk of the sulfur present in coal is in the form of either inclusions of pyrite, or is covalently bonded into the coal structure as organic compounds such as thiophenes and mercaptans. The sulfur is typically distributed between the pyritic and organic forms in roughly equal amounts. Since the organic sulfur is an intimate part of the coal molecular structure, it cannot be effectively removed without extensive chemical processing, which is presently prohibitively expensive. However, since the pyrite is present as discrete inclusions it is amenable to removal by a physical separation of the pyrite particles from the coal. Since physical separations are less expensive than chemical techniques in most cases, and many coals can be made to meet emission standards by complete removal of the pyritic sulfur, a physical pyrite removal process is the preferred technique.

A major difficulty in the removal of pyrite by physical means is the size of the pyrite particles, a substantial quantity of which are finer than 25 micrometers. Liberation of the pyrite inclusions from the coal matrix therefore requires that the coal be ground to a fine particle size. The most effective processes for separation of very fine particles are those based on differences in surface chemistry.

Flotation is normally the most effective and efficient of the surface chemistry based separation technologies. It is particularly applicable to coal, as coal particles are naturally hydrophobic and therefore attach to air bubbles readily after addition of small amounts of a neutral oil. However, pyrite is also slightly hydrophobic, and conventional flotation is insufficiently selective to prevent flotation of much of the fine pyrite along with the coal. The use of various agents to depress pyrite flotation has generally not produced satisfactory results, and so column flotation has been adopted in order to improve flotation selectivity.

COLUMN FLOTATION PRINCIPLES

The basic principle of column flotation is the use of countercurrent flow of air bubbles and solid particles. This is achieved by injecting air at the base of the column, and allowing the bubbles to rise through a downward-flowing slurry. Countercurrent flow is accentuated in most columns by the addition of washwater at the top of the column, which forces all of the water which entered with the feed downward. This flow pattern is in direct contrast to that found in conventional cells, where air, water, and solids are all driven in the same directions. The result
is that columns exhibit improved hydrodynamic conditions for flotation, and thus produce a cleaner product at higher recoveries and lower power consumption. The performance differences between columns and conventional cells may best be described in terms of the collection zone size, particle-bubble contact efficiency, and fines entrainment.

Collection Zone Size

A major difference between conventional and column flotation is the size of the collection zone. Whereas in a conventional cell, particle-bubble contact occurs primarily in the high-shear region around the impeller, in a column contact occurs throughout the entire volume. A flotation column therefore provides a greater number of opportunities for particle collection, and thus provides an increased flotation rate.

Particle-Bubble Contact Efficiency

The efficiency of particle-bubble contact in a column is greater than that in a conventional machine due to the difference in the type of collisions. In column flotation, particles and bubbles travel in opposite directions, and so while the absolute velocities are low, the relative velocities are quite high. In contrast, conventional cells drive particles and bubbles in approximately the same direction, providing for high absolute velocities but with collision velocities on the same order as those found in columns. Since less energy is wasted in the column, there is an increase in the efficiency of collection than conventional cells and are therefore less energy-intensive to operate.

Several flotation columns presently in use are capable of producing finer air bubbles than is possible with conventional mechanical air dispersers. This reduction in bubble size allows for improved flotation rate and selectivity, particularly for very coarse or very fine particles (Yoon and Luttrell, 1986). In the case of coarse particles, this is due to the fact that a greater number of bubbles attach to the surface, rather than only one or two (Fig. 1a). This prevents turbulence from tearing loose all of the air bubbles, and hence increases the flotation rate. For fine particles, the flotation rate increase is due to an improved contact probability. If an air bubble is very much larger than a particle, then the liquid flow around the bubble is likely to sweep the particle around, without contact every occurring. The use of smaller bubbles decreases the probability of this, and also increases the bubble surface area available for contact (Fig. 1b).

Fines Entrainment

In conventional flotation cells, a substantial amount of waste is carried into the froth by the water contained in the froth layer, thus degrading the separation. Most column flotation machines prevent this through the use of a deep froth layer which is washed by clean water. The washwater forces all of the water entering with the feed down to the tailings outlet, largely eliminating entrainment, as shown in Figure 2. In addition to preventing feed water from entering the froth, the wash water reduces the quantity of waste material in the upper region of the column, thus establishing a concentration gradient and reducing the probability of waste material entering the froth layer. The net effect of this is that the column froth is as clean as the product obtained by several stages of conventional flotation, while the operation costs are similar to those of a single conventional stage.

The improvement in selectivity obtained with column flotation is of particular importance for the removal of pyritic sulfur from coal. This is due to the slight hydrophobicity of pyrite particles, which causes fine pyrite to tend to float with the clean coal. Addition of fuel oil aggravates this effect, as it increases the floatability of the pyrite in the same fashion as it improves the flotation of coal. The higher selectivity and lower reagent requirements of column flotation were therefore expected to allow removal of pyrite with higher efficiency than is possible with conventional flotation processes.

EXPERIMENTAL PROCEDURE

Materials

Coal samples for this project were collected from the three seams comprising the greatest
REMOVAL OF PYRITIC SULFUR FROM COAL

A. CONVENTIONAL CELL

B. COUNTERCURRENT COLUMN

Figure 2: Distribution of water flow in a countercurrent flotation column.

reserves in Ohio (Wizzard et al., 1983): The Pittsburgh, or No. 8 seam; the Middle Kittaning, or No. 6 seam; and the Meigs Creek, or No. 9 seam. Of these coals, the Meigs Creek is generally considered to be the lowest quality, and the Middle Kittaning is considered to be the highest quality. The coal samples used were collected from the raw coal storage piles of mines operating on these seams, and stored at -20°C until needed. Washability data for the coals used is presented in Table 1.

Analyses were carried out using the methods of ASTM standards D3174-82 and D2492-8 for determination of ash content and pyritic sulfur content, respectively, a LECO SC-132 sulfur analyzer for determination of total sulfur, and a LECO Automatic calorimeter for determination of calorific value.

The column used for this work was a 3" diameter laboratory column, as shown in Figure 3. The height of this column was increased from two feet to seven feet in order to increase the residence time sufficiently for high-efficiency flotation of fines.

Initial experiments showed that, at the size required for liberation of fine pyrite, excessive quantities of ash minerals caused BTU recovery to be low. To reduce this problem a two-stage process was used, consisting of coarse flotation to remove the bulk of the ash followed by fine flotation to remove the remaining ash and the fine pyrite. A flow diagram for the process is given in Figure 4.

Figure 3: Schematic Diagram of a laboratory column.

Figure 4: Flow diagram for experimental pyrite removal process. First stage feed was 90% passing 100 mesh (65 mesh top size), and second stage feed was 90% passing 400 mesh (270 mesh top size).
TABLE 1. Washability data for coals used in this project. All coals were stage crushed to pass 20 mesh for the washability determination.

A) Meigs Creek Seam

<table>
<thead>
<tr>
<th></th>
<th>% wt.</th>
<th>% Ash</th>
<th>% Pyritic</th>
<th>% Total</th>
<th>BTU/ lb.</th>
<th>Lb. SO₂, MM BTU</th>
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<td>4.3</td>
<td>12786</td>
<td>6.7</td>
</tr>
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Total 100.0 18.0 2.0 4.8 11406 8.4

B) Pittsburgh Seam

<table>
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<th>% wt.</th>
<th>% Ash</th>
<th>% Pyritic</th>
<th>% Total</th>
<th>BTU/ lb.</th>
<th>Lb. SO₂, MM BTU</th>
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<td>14086</td>
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Total 100.0 29.1 2.8 4.3 10059 8.5

C) Middle Kittanning Seam

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<th>% wt.</th>
<th>% Ash</th>
<th>% Pyritic</th>
<th>% Total</th>
<th>BTU/ lb.</th>
<th>Lb. SO₂, MM BTU</th>
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<td>13040</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Total 100.0 7.9 1.1 2.2 12734 3.5
REMOVAL OF PYRITIC SULFUR FROM COAL

1. Raw coal was reduced to 100% -20 mesh by stage crushing with a roll crusher, mixed, split into uniform portions, and frozen.

2. Coal was ground 2.5 minutes at 40% solids in a rod mill to reduce the particle size to 90% passing 100 mesh.

3. Reagents were added as necessary, and the pulp was agitated for 1 minute at 25% solids by weight.

4. The flotation column was started and operated until the water level was uniform.

5. Coal was added to the column at the rate of 200 grams/minute, at 25% solids by weight, for a period of 20 minutes. Froth, tailings, and holdup material were collected and filtered.

6. The froth product was ground in the rod mill at 40% solids for an additional 15 minutes to achieve a particle size of 90% passing 400 mesh.

7. When necessary, additional reagent was added to the reground coal, which was then floated in the column in the manner previously stated.

8. Froth, tailings, and holdup material from each stage were dried, weighed, and analyzed to determine ash content, total sulfur, pyritic sulfur, and calorific value. Mass balances were carried out from this information to determine the precise performance characteristics.

EXPERIMENTAL RESULTS

Results for the flotation of each type of coal are presented in Table 2. Recoveries and sulfur rejections are expressed in terms of the initial feed of the first stage.

From the Stage 1 results, it is readily seen that the flotation column is extremely effective for removing ash minerals from all three coals at a fairly coarse size with excellent BTU recovery rates. In addition, 45 to 65 percent of the total pyrite is also rejected under these flotation conditions. The Stage 2 results show that grinding the coarse flotation froth and reFLOATING allows a substantial increase in pyritic sulfur rejection, while, for the cases of the Pittsburgh and Middle Kittanning coals, maintaining a good BTU recovery rate.

Of the three coals, the Pittsburgh and Middle Kittanning seams show the greatest benefits from column flotation, with substantial ash and sulfur reductions in both stages of flotation and overall BTU recoveries for the entire process of 85-87%. The Meigs Creek sample shows a lesser change in its overall sulfur content due to its large fraction of organic sulfur and low native floatability, which also results in a lower BTU recovery in fine-particle flotation. Nevertheless, it shows acceptable results in coarse-particle flotation from the standpoint of ash removal, with a rejection of 56% of the ash while recovering 96% of the calorific value.

Although the bulk of the pyrite can be removed from the coal by the preceding method, a fairly substantial amount remains in the clean coal. This remaining pyrite is very finely disseminated, and would require grinding to unreasonable particle sizes before liberation could be achieved. Physical separation processes are therefore not suitable for removing this ultrafine pyrite, and some sort of chemical processing is required.

While most chemical techniques are prohibitively expensive for use in coal depyritization, bacterially-catalyzed dissolution of pyrite is promising due to its low reagent costs and ability to proceed under ambient temperature and pressure conditions. However, the process is fairly slow, requiring a period of some weeks for pyrite dissolution, as is illustrated by the preliminary results shown in Figure 5. Since the dissolution rate increases as the particle size decreases, a promising approach is to use column flotation to remove the coarser pyrite particles, and bacterial leaching to remove the ultrafine, unliberated pyrite. This would result in more complete pyrite removal in a shorter time than is presently possible with either process alone. Investigation of this technique is presently in progress.
TABLE 2. Two-Stage Column Desulfurization Results

Recoveries and sulfur rejections are expressed in terms of initial feed to first stage.

A. Pittsburgh Seam

<table>
<thead>
<tr>
<th></th>
<th>% Wt.</th>
<th>% Ash</th>
<th>% S</th>
<th>BTU/lb</th>
<th>Pyritic Sulfur</th>
<th>Organic Sulfur</th>
<th>Lb. SO₂</th>
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<tr>
<td>Stage 1 Froth</td>
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<td>6.6</td>
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<td>29.0</td>
<td>84.7</td>
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<td>59.8</td>
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<td>22.3</td>
<td>7.2</td>
<td>11180</td>
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Stage 1: BTU recovery = 97%, % Pyritic Sulfur rejection = 65%
Weight recovery = 71%
Stage 2: BTU recovery = 85%, % Pyritic Sulfur rejection = 87%
Weight recovery = 59.8%
Sulfur emission reduction = 55%

B. Middle Kittaning Seam

<table>
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<tr>
<th></th>
<th>% Wt.</th>
<th>% Ash</th>
<th>% S</th>
<th>BTU/lb</th>
<th>Pyritic Sulfur</th>
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<tr>
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Stage 1: BTU recovery = 96%, % Pyritic Sulfur rejection = 45%
Weight recovery = 92.1%
Stage 2: BTU recovery = 87%, % Pyritic Sulfur rejection = 76%
Weight recovery = 81.0%
Sulfur emission reduction = 37%

C. Meigs Creek Seam

<table>
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<tr>
<th></th>
<th>% Wt.</th>
<th>% Ash</th>
<th>% S</th>
<th>BTU/lb</th>
<th>Pyritic Sulfur</th>
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Stage 1: BTU recovery = 96%, % Pyritic Sulfur rejection = 48%
Weight recovery = 85%
Stage 2: BTU recovery = 67%, % Pyritic Sulfur rejection = 89%
Weight recovery = 56%
Sulfur emission reduction = 36%
SUMMARY

Removal of pyritic sulfur from coal by froth flotation is in general not satisfactory. This is due to the low capability of conventional flotation to distinguish between coal and pyrite particles at the fine sizes commonly necessary for pyrite liberation.

Column flotation exhibits considerably greater selectivity for fine particles than conventional cells, particularly when fine bubbles are used, and therefore has much greater capability for removing pyritic sulfur from coal.

A flotation column was constructed to maximize its ability to reject pyrite particles from coal. The column uses fine air bubbles to produce a deep washed froth while minimizing channeling and turbulence, resulting in high selectivity and the ability to operate on a wide particle size range.

The highest BTU recoveries and pyrite rejections were obtained using a two-stage process. The first stage, carried out at a top size of 90% passing 100 mesh, removed the bulk of the ash minerals, which had been found to interfere with combustibles recovery while attempting to maximize pyrite removal. The second stage was carried out at 90% passing 400 mesh and removed the bulk of the very fine pyrite particles.

Of the three coals tested, the Pittsburgh and Middle Kittaning coals derived the greatest benefits from column flotation, with pyrite rejections of 76-78% and BTU recoveries of 85-87%. Further reduction of the pyrite content by the column is limited by the liberation characteristics of the coal. For complete pyrite removal column flotation must be assisted by a chemical process, such as bacterially catalyzed pyrite dissolution.

ACKNOWLEDGMENTS

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