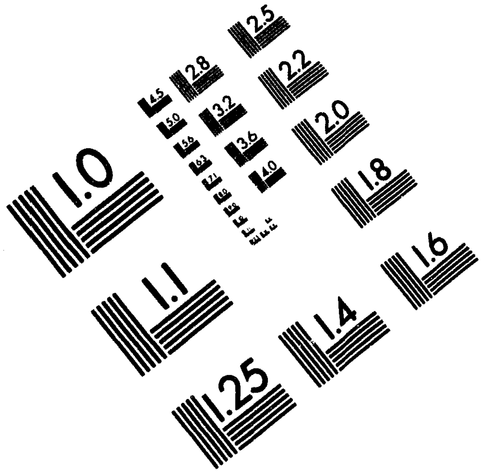
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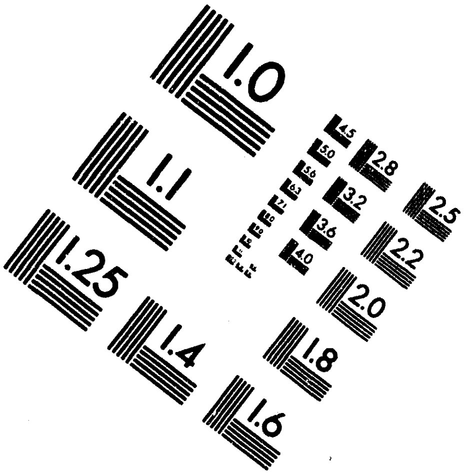
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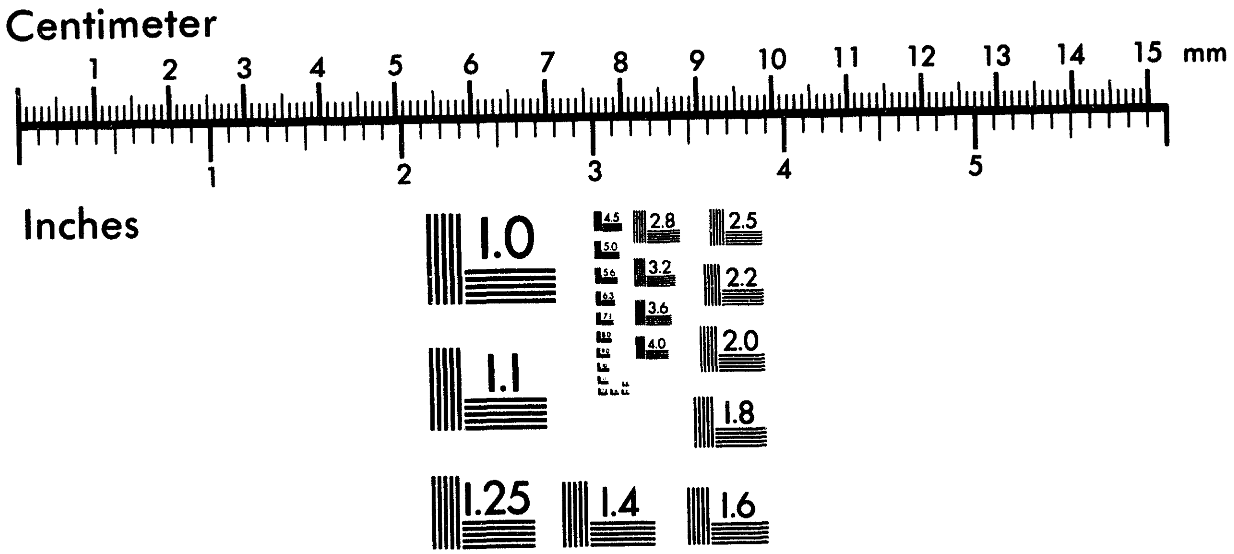
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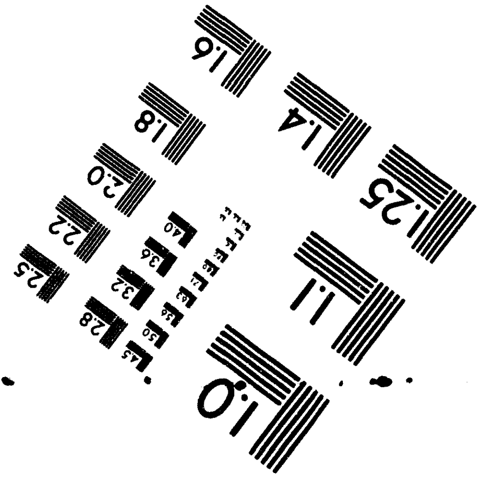
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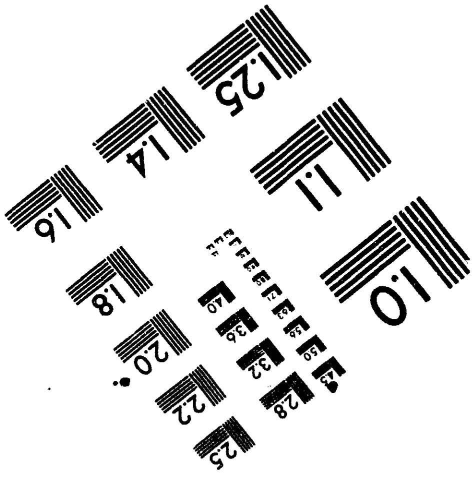
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1 of 2

Coal Desulfurization by Bacterial Treatment and Column Flotation

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Final Report

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Table of Contents:

12 APPENDICES

CHAPTER 1: INTRODUCTION

In order to improve the marketability of the fine coal produced during mining, it is desirable to remove as much sulfur and ash as possible. Numerous methods have been devised for this purpose, but many techniques are too expensive, produce objectionable waste products, or are not sufficiently selective. A discussion of the various methods for removing sulfur from coal before combustion is presented.

The criteria for selecting processes for further study were:

1. Capital and operating cost: The process costs must be low enough for the cleaned coal to be sold profitably at $50/ton.
2. Coal recovery: the process should recover at least 80% of the heating value of the feed coal.
3. Pyrite removal: the process should remove at least 50% of the pyritic sulfur, or reduce the pyrite content to less than 1%.
4. Coal quality: the quality of the coal (heating value per unit weight, ash content, moisture) should be equal to or better than the feed coal quality.

A review of the literature showed that bacterial leaching, using the microorganism *Thiobacillus ferrooxidans*, was a very effective technique for removing pyrite from coal, as it could dissolve even the finest pyrite particles without the need for expensive reagents or extreme processing conditions. Unfortunately, bacterial leaching is also rather slow, and so the initial goal of this research was to decrease the leaching time as much as possible, preferably to less than two days. By using a more thoroughly aerated reactor, it was found to be possible to approximately double the leaching rate. However, this still left the bacteria needing approximately a week to remove half of the pyritic sulfur, and so a faster technique was sought.

Since it had been reported in the literature that *T. ferrooxidans* could be used to depress the flotation of pyrite during froth flotation of coal, this was investigated further. The intent was that bacteria could be used to partially leach the coal for a short time to dissolve the finest pyrite and improve the liberation of the coarser pyrite. The organisms would then act as a depressant for the remaining pyrite during subsequent froth flotation of the coal. But, when this was tried, the microorganisms had no effect on the amount of pyrite reaching the froth.

There were two possible reasons why the bacteria had no effect: either 1. the bacteria were unable to make floatable pyrite stop floating, or 2. the pyrite in the coals tested was not floatable in the first place. By studying the recovery mechanisms of coal-pyrite in froth flotation, it was found that the second possibility was the correct one, and that pyrite was being recovered by entrainment and by locking to coal particles, not by true flotation of hydrophobic pyrite. Therefore, no pyrite depressant could be of any significant benefit for keeping pyrite out of the coal froth product, and it was much more important to prevent entrainment from occurring.

Countercurrent flotation columns were invented to essentially eliminate entrainment effects, by washing the froth and reducing mixing of the froth and tailings products. Existing flotation columns tend to be quite simple, and in order to give reasonable product quality they must be very tall (typically 30-45 feet). As a result, they have difficulty in handling the high froth volumes which occur in coal flotation, and are awkward to install in existing plants. The bulk of this project therefore concentrated on developing an improved coal flotation column, and testing it under actual plant conditions.

CHAPTER 2: LITERATURE REVIEW

2.1 INTRODUCTION

One of the primary problems with the use of coal as a fuel is its sometimes excessive sulfur content, which causes the emissions from power plants to be acidic and corrosive. While it is possible to use scrubber technology to remove the sulfur oxides from power plant exhausts, the installation, operating, and waste disposal costs from this technology are significant, and so lower-cost alternatives are being sought. In addition to improvements in scrubber design and alternative combustion techniques, there is considerable interest in removing the sulfur-containing compounds from the coal before it is ever burned. A truly effective technique for accomplishing this at a cost of no more than a few dollars per ton could allow high-sulfur coals to be desulfurized to the point where scrubbers are no longer necessary. Even moderate reductions in sulfur content before burning will reduce the load on the power plant scrubbers, and allow reductions in scrubber operating costs and waste disposal requirements.

An additional benefit of desulfurizing coal is that in many cases, the ash content is reduced simultaneously with the sulfur content. This reduces the production of fly ash, minimizes boiler fouling, and reduces the amount of ash which must be disposed of by the power plant. If the ash is removed at the mine site, there is the added benefit that the weight of material which must be shipped in order to deliver the same BTU content is reduced, thus reducing shipping costs.

While coal desulfurization before combustion can be very beneficial, there are several factors which combine to make complete desulfurization impractical on an industrial scale with current technology and existing energy prices. The most important of these is the physical structure of the coal, and the fashion in which the sulfur is bound into the structure. In general, the sulfur in coal is present in three forms: organic sulfur, sulfide sulfur, and sulfate sulfur. The organic sulfur is the most resistant to removal, as it consists of organic compounds which contain sulfur as part of their molecular structure. Removing these compounds involves chemically breaking down the coal to liberate the sulfur atoms into a removable form, while maintaining the rest of the structure in a form which is sufficiently intact to still possess most of its original heating value. Current techniques mostly involve heating to several hundred degrees, which introduces a rather significant processing cost. The sulfide sulfur, which is almost entirely in the form of pyrite or marcasite, is in the form of discrete mineral inclusions ranging from massive lumps to sub-micron particles. These particles can, at least in theory, be physically broken away from the coal matrix and separated, and are also amenable to selective dissolution by a variety of techniques. Processes for physically removing the pyrite from coal generally remove a great deal of ash as well, while chemical dissolution methods frequently have little or no effect on the ash content. Sulfate sulfur, which is typically present in much lower concentrations than the other two forms, can be easily dissolved by acidic solutions, and also generally is removed by physical separation techniques. Since the sulfates are primarily the result of oxidation of the sulfides, the two forms are closely associated and the sulfates are generally removed by any process which removes pyrite.

A second consideration in coal processing is the extreme heterogeneity of the coal. Coal is not a single, fixed substance. Rather, it is a mixture of organic compounds formed from the organic detrius in ancient bogs (McClung and Geer, 1979). As a result, the variability from seam to seam, or from point to point in the same seam, is very large. Coal formed from tree trunks will obviously be different than that formed from algae, and a salt bog will be different from one formed in fresh water. As a result, there is no guarantee that a process which is effective for desulfurizing a particular coal sample will be equally effective with a sample taken from the next seam down, or a point on the same seam a few hundred feet distant. This is particularly critical for processes which depend on differences in the surface chemistry between coal and mineral matter, as surface chemistry is one of the more variable coal properties. As a result, highly sophisticated processes which require precise operating conditions in order to work properly are usually not well suited for coal cleaning, as a change in the properties of coal being processed can render them unworkable at any time.

The existing technologies for removing sulfur can be loosely classified into chemical, biological, and physical desulfurization. Chemical techniques involve chemical reaction with one or more forms of sulfur to convert it into a form which can be easily removed. Biological desulfurization is a form of chemical desulfurization, but instead of using high temperatures or reactive reagents to cause the sulfur to react, microorganisms are used to catalyze the reaction under relatively gentle conditions. Physical separation of the sulfur simply consists of sorting high-sulfur particles from low-sulfur particles by differences in their properties, such as density or hydrophobicity, and is generally the least expensive alternative.

2.2 CHEMICAL DESULFURIZATION TECHNIQUES

In general, any process which can remove organic sulfur to any extent is capable of nearly complete removal of the pyrite as well. This is particularly true of oxidative processes. It is reported that certain bacteria remove only the organic sulfur and not the pyrite (Isbister and Kobylinski, 1985), but the level of organic sulfur removal by these organisms is somewhat low (approximately 20%). While organic sulfur removal is the most desirable, the greater simplicity of pyrite removal has resulted in the investigation of a number of processes which only remove this form.

2.2.1 Molten-Caustic Leach

The molten-caustic leach process is generally considered to be the most effective means for cleaning all forms of sulfur and most ash from coal without completely dismantling the coal structure.(Hayashi et al, 1990; Kusakabe et al, 1989;Gala et al, 1989; Meyers and McClanathan, 1990, and Markuszewski and Chriswell, 1990) The basis of the process is the reaction of sulfur compounds, silicates, and metal oxides with molten sodium and potassium hydroxides at a temperature of 300-400 degrees C. Originally the mixture of salts was selected simply to reduce the melting point of the caustic bath. However, it has since been found that the minimum temperature needed to remove organic sulfur is sufficiently high to melt NaOH alone. As a result, the more expensive potassium hydroxide is not needed for coals where the higher reactivity of the K ion is not needed to break bonds in highly refractory sulfur compounds.

Molten-caustic leaching consists of the following process steps: First, the coal is reacted with molten caustic at elevated temperatures, for times ranging from 30 minutes to 2 hours. This results in the breaking of C-S bonds (apparently forming alkali metal sulfides), the conversion of pyrite to iron hydroxides and soluble sulfides, and the conversion of silicates and aluminosilicates to soluble sodium salts. Following reaction, the material is quenched, and the alkali recovered as far as possible by countercurrent washing with water. This is followed by water washing to remove the water-soluble reaction products and residual alkali. Since some of the reaction products (particularly the iron compounds) are not soluble in water or alkaline solutions, an acid wash is needed to remove these materials from the coal residue. The resulting acid waste stream is then neutralized with lime to precipitate the dissolved salts for disposal.

The critical economic factor for molten-caustic leaching is recovery of the caustic, as the volume of caustic needed in the leach reactor is typically greater than that of the coal being processed. While some work has been done to reduce the ratio of caustic to coal needed, approximately 65% of the reactor charge must still be caustic even in the leanest mixtures. It has also been found that in order to maximize coal recovery, oxygen must be excluded from the reactor, as otherwise volatile organic compounds are oxidized before the reaction can repolymerize them back into the solid product. The need for heating the coal is an additional expense which will tend to keep the cost of this process high. The product is changed from its original state by the processing, with volatile matter either lost or converted to solid compounds. Coal losses are higher when reaction is attempted at lower temperatures, due to the volatile and soluble compounds not reaching a sufficient temperature to re-integrate with the mass of the product. There is also a loss of specific heating value in the product which results from an increase in the number of oxidized functional groups.

2.2.2 Chlorination

Chlorination of coal consists of reacting coal with chlorine gas, usually dissolved in methyl chloroform, at near ambient temperature.(Hsu et al, 1977;Cho, 1989; Bayrakceken et al, 1990) This is primarily effective for removing pyritic sulfur, although it is reported to be capable of removing up to 40% of the organic sulfur as well. A drawback to this method is that in the course of chlorination, a great deal of chlorine combines with the coal, reaching levels as high as 20% by weight. While much of this chlorine can be removed by simple hydrolysis, enough would remain to cause serious corrosion and emissions problems when the coal is burned. The coal requires heating to approximately 600 degrees C under a reducing or inert atmosphere to remove the remaining chlorine.

While the chlorinization process requires less reagent than the molten-caustic leach process, this is offset somewhat by the higher cost of the reagents. Similarly, the savings due to the low reaction temperature are offset by the need for high-temperature dechlorinization. Since this technique is not completely effective for removing organic sulfur, and does not remove a significant amount of mineral matter, it is generally considered to be inferior to the molten-caustic process at this time.

2.2.3 Microwave Treatment

Microwave heating provides a selective method for preferentially heating the portion of the coal which contains the sulfur, and can ideally be tuned to heat primarily the C-S bonds and the pyrite (Yang and Wu, 1987). This is used to improve the rate and effectiveness of the molten alkali leach process. The result is that the bulk reaction temperature can be reduced, which decreases the degree of heat alteration of the product. It is reported that organic sulfur removal of 50-75% can be achieved in one minute of microwave treatment for a variety of coals, with pyritic and sulfate sulfur removals being nearly complete in the same treatment time. The main obstacles to use of this process are the cost of the alkali, and the expense of high-power microwave generators.

2.2.4 Aqueous Alkali

Alkali in aqueous solution at near ambient temperature have been found to be capable of reacting with a portion of the organic sulfur, particularly the mercaptans (Sareen, 1977; Tai et al, 1977; Meyers, 1977; Eliot, 1978). Unfortunately, at room temperature the alkali is not able to cleave the more strongly-bonded sulfur compounds without an added energy input.

Electrolysis appears to be capable of supplying the energy for the alkali reaction (Lalvani and Hines, 1987; Wapner et al, 1988). At approximately ambient temperature, the reaction removes the pyritic sulfur and roughly 40% of the organic sulfur. In addition, hydrogen is generated with about half the energy consumption which would be required by water electrolysis, and would therefore be a useful by-product of the process. However, the increased complexity of the cell as compared with other techniques, coupled with the difficulty of finding a suitably long-lived anode material, is likely to cause some difficulty on an industrial scale.

2.2.5 Oxidative Desulfurization

If coal is lightly oxidized using any of a variety of oxidizing agents, such as hydrogen peroxide, ferric sulfate, or hot air, many of the sulfur bearing compounds will be oxidized to soluble forms, particularly the pyrite (Friedman et al,1977; Hamersma et al, 1977; Ahnonkitpanit and Prasassakich, 1989). This however does not have a significant effect on either the organic sulfur content or the ash content, and oxidation reduces the calorific value of the coal. The cost of the reagents, along with the expense of recovering the sulfur-bearing compounds, generally keep this process from being widely considered as a possible industrial process. Processes which produce oxidizing agents in situ, such as gamma-ray irradiation (Tripathi et al, 1991) have also been tested on a laboratory scale.

2.2.6 Hydrogenation reactions

Cracking and hydrogenation, roughly analogous to the processes used in petrochemical manufacture, can be used to convert coal into liquid, gas, and a high-carbon residue (Huang and Pulsifer, 1977; Eliot, 1978; Ellington, 1977; McMillen and Malhotra, 1989; Anderson and Jaturapitpornsakul,1989; Nowok et al, 1989). The sulfur can then be removed using techniques which have already been highly developed for processing crude oil (Perry's Chemical Engineers Handbook, 1984). Since the sulfur tends to concentrate in the volatile fractions, the solid char is essentially sulfur-free, although it contains the ash originally present in the feed. The basic drawback is that the liquid and gaseous fuels produced must be treated as if they are high-grade crude fuels, and thus require further purification. This makes them uncompetitive with existing crude fuels which can be pumped from reservoirs more cheaply than coal can be mined and converted.

Simple hydropyrolysis consists of heating the coal to approximately 800°C with hydrogen, often in a fluidized bed. A gas such as nitrogen can be added as well to improve the fluidization, and also to reduce the explosion hazard somewhat. The high temperature is believed to cause bond breakage in the coal, with the hydrogen being taken up by the dangling bonds. Without the presence of hydrogen, the coal would rapidly be converted to a refractory mass of coke which would plug the reactor, and would be more conveniently produced by a conventional coke oven. The result is a wide selection of volatile hydrocarbons which are recovered and purified.

The coal can also be pyrolyzed with water. However, this produces a gas product which is high in CO and CO_2, and reduces the calorific value of the various products. The major benefit of this is that the process is more nearly self-heating, and that water is much less expensive than hydrogen.

Solvent extraction allows the liquefaction of the coal at much lower temperatures, and less gas is evolved. An organic solvent, typically naphthalenic, is used to dissolve the coal at moderately elevated temperatures. The broken bonds are stabilized by a hydrogen donor molecule, such as Tetralin, which allows the normally highly stable molecular structure of the coal to be dissolved. While the temperatures are less extreme, the higher cost of the reagents greatly affects the cost-effectiveness of this process.

2.3 MICROBIAL COAL DESULFURIZATION

Microbial coal desulfurization makes use of the abilities of certain bacteria to metabolize the sulfur forms contained in the coal and, in the process, convert it to a form that can be more easily removed (Dugan, 1986). A variety of bacteria can be used for this purpose, to remove particular types of sulfur under various sets of conditions (Ehrlich, 1986).

In general, pyrite and organic sulfur require differing types of bacteria for their removal. Bacteria for pyrite dissolution use pyrite oxidation as their primary energy source, whereas bacteria that remove organic sulfur typically do so as a secondary portion of their metabolism.

The most important microorganisms in desulfurizing coal fall into several general classes: (1) acidophilic bacteria growing at ambient or slightly elevated temperatures, such as certain *Thiobacillus* species (Hoffmann et al., 1981); (2) acidophilic bacteria growing at extremely elevated temperatures, such as the various *Sulfolobus* species (Murphy et al., 1985); (3) altered soil bacteria, which grow at ambient temperatures and approximately neutral pH, such as the mutant strain CB1 of the Atlantic Research Corp. (Isbister and Kobylinski, 1985); and (4) coal solubilizing organisms, which are typically bacteria or fungi adapted for decomposing wood (Klein and Wellek, 1989).

2.3.1 Thiobacillus

The most frequently used bacterium of this genus is the species *T. ferrooxidans*, which oxidizes pyrite to soluble sulfates. This species has no confirmed ability to remove organic sulfur compounds. The dissolution of pyrite by *T. ferrooxidans* proceeds by both an indirect and a direct mechanism, of which the indirect is better understood (Silverman, 1967). In indirect oxidation, pyrite oxidation occurs as a result of the action of the Fe ion, according to the equation (Hoffmann et al., 1981)

$$FeS_2 + 14Fe^{+3} + 8H_2O \longrightarrow 15Fe^{+2} + 2SO_4^{-2} + 16H^+ \qquad (1)$$

which proceeds spontaneously when the Fe^{+3}/Fe^{+2} ratio is greater than 2:1 (Singer and Stumm, 1970). While Fe^{+2} can be oxidized to Fe^{+3} by free oxygen, the uncatalyzed reaction is extremely slow. However, if *T. ferrooxidans* is present, the rate of the regeneration reaction (Hoffman et al., 1981)

$$4Fe^{+2} + O_2 + 4H^+ \xrightarrow{\text{Bacteria}} 4Fe^{+3} + 2H\ O \qquad (2)$$

can be accelerated by a factor of as much as 10^6 (Singer and Stumm, 1970). So, in the presence of these bacteria, the overall reaction for indirect oxidation of pyrite is

$$FeS_2 + {}^7/_2O_2 + H_2O \xrightarrow{\text{Bacteria}} Fe^{+2} + 2SO_4^{-2} + 2H^+ \qquad (3)$$

Since the actual pyrite oxidation is carried out by the Fe^{+3} ion, the bacteria need not be in intimate contact with the pyrite, as long as transport of ions to and from the pyrite surface is fairly unobstructed. Indirect oxidation can only occur at pH values less than 4, as at higher pH values the Fe^{+3} ions will precipitate as insoluble iron hydroxides (Baker and Miller, 1971).

The direct oxidation mechanism requires intimate contact between pyrite and bacteria, as in this case the disulfide is being oxidized without a soluble intermediate. Direct oxidation by *T. ferrooxidans* proceeds at only about one-seventh the rate of indirect oxidation, provided that sufficient Fe is present for the indirect process to occur. However, when little dissolved iron is present, only direct oxidation is possible. It is then the dominant process until oxidation of pyrite has released sufficient iron into solution for indirect oxidation to be practical (Singer and Stumm, 1970).

Another acidophilic *Thiobacillus* species, *T. thiooxidans*, is also capable of dissolving pyrite, although not as rapidly as *T. ferrooxidans*. However, mixed cultures of these two species dissolve pyrite at a substantially greater rate than either bacterium alone. This is apparently due to the ability of *T. thiooxidans* to catalyze the oxidation of pyrite by Fe^{+3}, while *T. ferrooxidans* regenerates the oxidizing agent (Hoffmann et al., 1981). Other bacterial species may also be used to regenerate Fe^{+3}, although they may lack the capability of *T. ferrooxidans* for direct sulfur oxidation and, hence, may not be as effective for this purpose (Norris et al., 1986).

2.3.2 Sulfolobus

Bacteria of the *Sulfolobus* genus are acidophiles and extreme thermophiles, requiring pH in the range of 1.5 to 4 and temperatures in the range of 50° to 80° C. These bacteria are native to sulfurous hot springs worldwide (Brock, 1978). Their primary advantage is their ability to catalyze pyrite oxidation at elevated temperatures, shortening the time required for oxidation to occur.

Unlike *T. ferrooxidans* and *T. thiooxidans*, *Sulfolobus* species are capable of extracting metabolic energy from sources other than oxidation of inorganic material. For this reason, it has been considered possible that removal of organic sulfur may be accomplished using *Sulfolobus*. While some researchers have reported that *S. acidocaldarius* is indeed capable of removing a portion of the organic sulfur (Kargi and Robinson, 1986), this has not yet been proven (Dugan, 1986). This uncertainty is due to the difficulties involved in accurately determining the organic sulfur content of coal, and to the possibility that some organic sulfur dissolves naturally at elevated temperatures.

At present, little meaningful comparative data for sulfur removal by *T. ferrooxidans* and *S. acidocaldarius* exists. This lack is due to the extreme heterogeneity of coal, which ensures that unless investigators have taken care to use identical coal samples for both bacteria, results are not directly comparable. However, it appears that *S. acidocaldarius* can remove pyrite approximately twice as fast as *T. ferrooxidans*.

2.3.3 Mutated Soil Bacteria

Atlantic Research Corp. has developed a mutant bacteria strain from certain soil bacteria that were originally minimally capable of oxidizing organic sulfur compounds, particularly thiophenes. The mutant, labeled CB1, has considerably enhanced thiophene-oxidizing capabilities over its parent culture (Isbister and Kobylinski, 1985). Experimentation with radioisotope- labeled dibenzothiophene showed that CB1 oxidizes sulfur from thiophene compounds without breaking the carbon ring structure. This is in contrast with other thiophene-oxidizing microbes that break the rings but do not release the sulfur.

The strain CB1 oxidizes the thiophenes over a temperature range of 25° to 40° C and at approximately neutral pH. This strain is reported to be capable of removing up to 47% of the organic sulfur from certain coals. However, it has not been effective in dissolution of pyritic sulfur (Isbister and Kobylinski, 1985) and, therefore, requires that pyrite be removed by some other means. There is also some question whether these bacteria were actually acting to remove sulfur from coal, as the quantity of organic sulfur removed during leaching experiments was not much greater than the normal uncertainty in the measurements of organic sulfur. Since CB1 cannot survive at the low pH values required by *T. ferrooxidans* and *S. acidocaldarius*, it cannot be used in mixed cultures with pyrite-removing bacteria.

2.3.4 Coal Solubilizing Organisms

It has recently been discovered that several microorganisms are capable of converting certain low-rank coals into liquid or water-soluble products, and may therefore be able to produce high-energy, clean liquid fuels from these coals. Research in this area is not yet advanced, but initial work has been done to identify suitable microorganisms and determine their capabilities (Klein and Wellek, 1989). The most effective organisms appear to be those which efficiently degrade lignin in wood, and are most useful for solubilizing low- rank, highly oxidized coals. At present, high-rank coals appear to be impervious to biosolubilization, and results on sub-bituminous coal and lignite tend to be spotty and somewhat unpredictable. The products produced are generally water-soluble, highly aromatic, high-molecular-weight compounds which are at present poorly characterized. While no direct use of these compounds is evident, their solubility in water raises the possibility that they can be used as chemical feedstocks for manufacturing consistent-quality fuels. This type of treatment still requires a great deal of work before it will be suitable for industrial use.

2.3.5 Microbial Leaching Techniques

Sulfur removal by bacterially catalyzed oxidation imposes the following requirements on any process that makes use of it: (1) the leaching unit must have sufficient residence time for dissolution to be carried out, generally a period ranging from several days to over a week; (2) the solution temperature and pH must be closely controlled at the optimum values for bacterial growth; (3) supplemental nutrients and oxygen must be supplied to the bacteria; and (4) the coal must be reduced to a fine size, as leaching rates increase rapidly with decreasing particle size (Beier, 1985). In addition, means must be provided for removing and neutralizing the sulfate produced by the leaching process and for supplying seed bacteria to the beginning of the process.

Handling of the bacteria is of critical importance in maintaining the bacteria in the proper growth phase for optimum pyrite removal. The various growth phases are illustrated in Figure 2.1 (Murphy et al., 1985). The lag phase is the time required for the bacteria to acclimate themselves to conditions, while the stationary and death phases result from depletion of nutrients or accumulation of toxins. For best results in continuous processing, bacteria should be maintained as much as possible in the exponential phase, as they are then multiplying and metabolizing sulfur at their maximum rate (Murphy et al., 1985).

Maintaining bacteria at the exponential growth phase in a continuous reactor is often difficult, primarily due to the possibility of "washout". If material is fed to the bacterial reactor too rapidly, then the microorganisms can be swept out before they can reproduce and backmix with the fresh feed. When this happens, the number of cells available for leaching falls off rapidly, and the process stops. Because of this, bioleaching processes frequently maintain a seed culture in a separate fermenter. This supplies bacteria to the desulfurization process as needed. A related problem can occur if the feed enters too slowly, or if there is too much backmixing. If this happens, then the nutrients can be depleted and toxins can accumulate in the reactor until bacterial

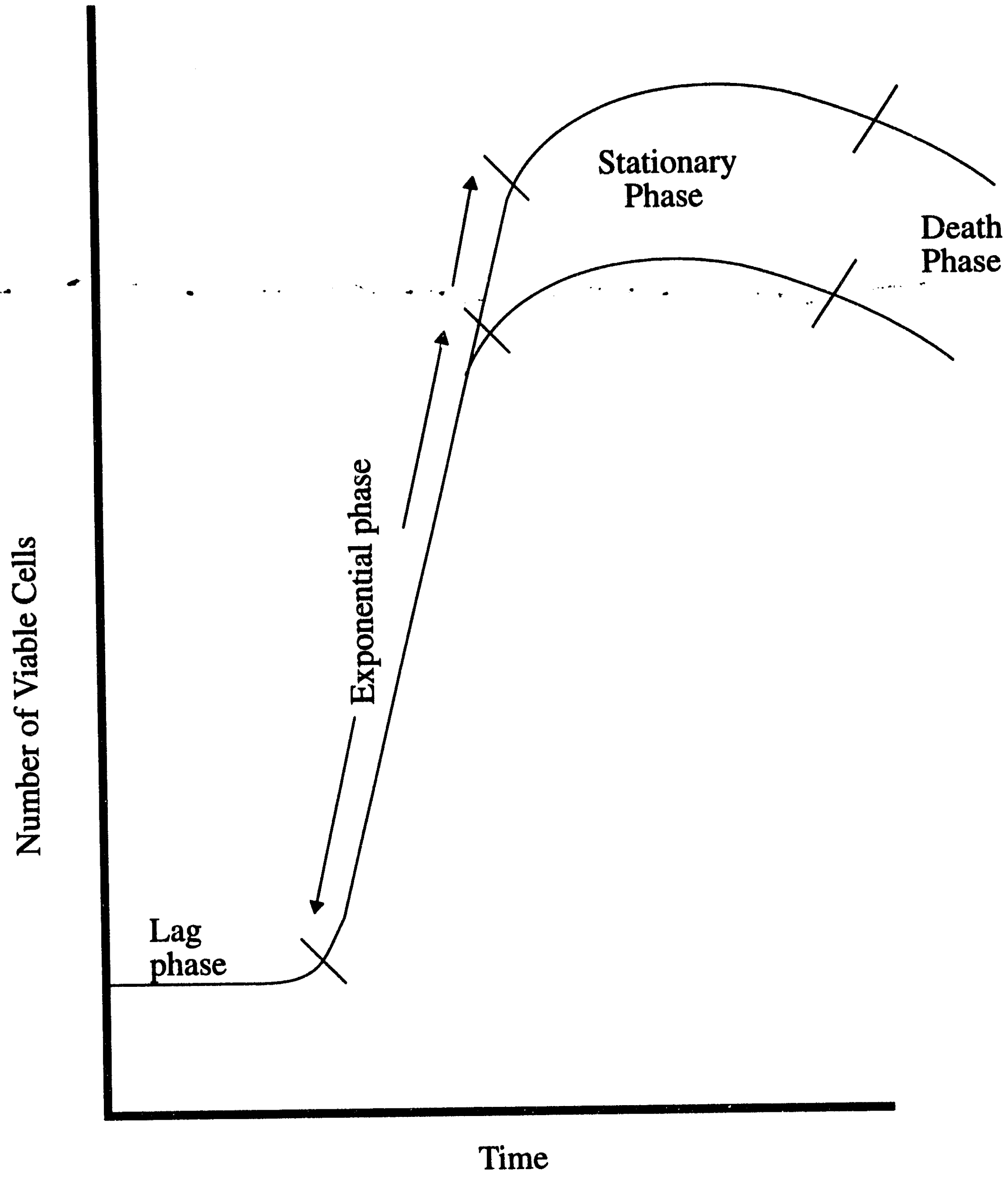


FIGURE 2.1. Generalized growth curve for batch bacterial cultures. The lag phase represents the time required for the organisms to adapt to specific conditions, and the stationary and death phases are result of nutrient depletion and buildup of wastes. In general, it is desirable to maintain the exponential growth phase as long as possible, as that is the period of greatest bacterial activity.

growth ceases, and again the process stops.

Since bacterial growth rates can vary for a number of reasons, preventing the cells from being washed out or dying off is not trivial. For example, if the reactor is initially fed too slowly, then the cells will run out of nutrients and begin to die back. If the feedrate is then rapidly increased, the cells can then be washed out before they can go through the lag phase and begin to grow again, and so washout can occur even at feedrates that would normally be acceptable.

A typical process flowsheet for continuous microbial coal desulfurization is illustrated in Figure 2.2 (Murphy et al., 1985). Ground coal, air, bacteria, and heat (if required) are added to any of a variety of reactor types. Treated coal slurry is withdrawn from the reactor and thickened, with the solids filtered, washed, and dried to produce a desulfurized product. Also, the exhaust air from the reactor is scrubbed to remove acid fumes that would otherwise be released in the immediate vicinity of the process. The solutions from the thickener, filter, and exhaust gas scrubber, which contain the products of the sulfur oxidation, are then sent to the precipitator, where the sulfates are removed by addition of lime and occasionally aluminum salts. The resulting sulfate precipitate is then disposed of, and the cleaned water is returned to the reactor. The major variation in bioleaching circuits is in the design of the reactor. The reactor used must provide long residence times at reasonable cost, should approach plug flow to maximize kinetics, and yet should have sufficient backmixing to prevent "washout" of the bacteria. In the case of pyrite dissolution, the reactor should also be resistant to corrosion by acidic slurries and, hence, use a minimum number of moving parts.

There are three basic configurations for practical bioleaching reactors: cascades of continuously stirred tanks, pipelines, and horizontal rotating drums (Vaseen, 1985).

Cascades of stirred tanks have the advantage of being highly controllable, with leaching being carried out in discrete steps. Either mechanically or pneumatically agitated tanks may be used, as air must be supplied to the bacteria in any case. However, the requirement of long residence times ensures that plants of this type must be extremely large (Vaseen, 1985).

Bioleaching in a coal-slurry transport pipeline has the major advantage that coal is being transported to the end use while leaching is being carried out, and that the transportation and reactor time costs are combined (Beier, 1985). However, such a system provides little control of residence time, which is primarily determined by the distance to the end user. Also, addition of air to the slurry is somewhat difficult, and the lifetime of the pipeline is reduced by the corrosive nature of the slurry.

The horizontal rotating drum reactor consists of a very long horizontal drum, equipped with slurry lifters and means for supplying air to the slurry all along the drum length. The drum is rotated at from 1 to 20 rpm to provide agitation. Such a reactor provides a compromise between plug flow and backmixing suitable for maintaining a good bacterial distribution (Vaseen, 1985). Again, a reactor of this type must be very large, requiring a 20:1 length to diameter ratio to provide sufficient residence time for leaching by *T. ferrooxidans* (Vaseen, 1985).

A bioleaching system could either be located at the plant where the coal will be burned or at the mine, depending on the circumstances. Locating the leaching operation at the plant allows the use of waste heat for maintaining the slurry at the proper temperature and for drying the cleaned coal (Murphy et al., 1985). However, if the plant receives coal from a variety of suppliers, the need to adjust the process for great variations in feed character may make this arrangement impractical. Locating the operation at the mine will ensure a fairly consistent coal quality, but, here, heating and drying costs will be greater. These costs may be reduced if a coal-water fuel (60% to 75% by weight coal) is produced because thermal drying is then unnecessary.

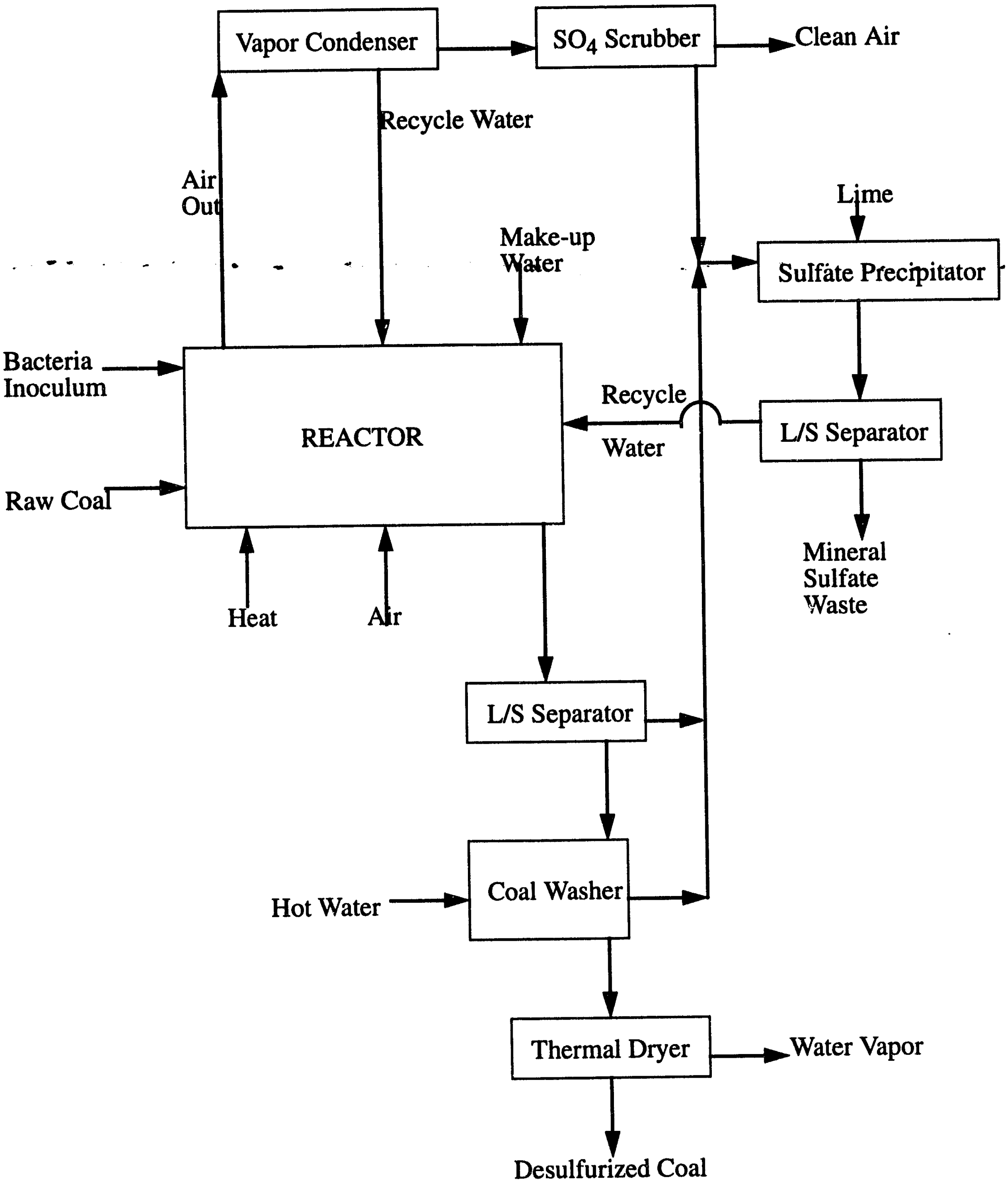


FIGURE 2.2. A basic flowsheet for bacterial coal desulfurization, suitable for both low and high-temperature organisms.

The bioleaching process is therefore most suitable either (1) located at the power plant when coal is received from a single source, or (2) located at the mine if a coal-water fuel is the desired product.

2.3.6 Bacterially Assisted Coal Cleaning

The primary disadvantage of microbially catalyzed sulfur oxidation is the long residence time required for sulfur removal to be completed, which makes for large installations and high capital costs. If bacterial treatment times can be reduced, processing will obviously become much more cost-effective. One method for reducing treatment time is to use bacteria to assist more conventional, physical separation processes.

Separation techniques that depend on differences in surface chemistry, such as froth flotation and oil agglomeration, have a limited ability to remove pyrite particles from coal (Baker and Miller, 1971). This is due to the formation of elemental sulfur on the surface of pyrite when it is gently oxidized (Stock and Wolny, 1990). Since elemental sulfur is naturally hydrophobic (Davis, 1985), this makes the pyrite in some oxidized coals floatable under the same conditions which float coal. Improving the pyrite-rejection capability of these processes therefore rests on rendering the surfaces of the pyrite particles uniformly hydrophilic.

While complete oxidation of pyrite by *S. acidocaldarius* or *T. ferrooxidans* is very time-consuming, the bacteria effectively alter the pyrite surface within a short time, on the order of 30 minutes. This is believed to be a result both of oxidation of the pyrite surface and of the direct attachment of the bacteria to the pyrite. Since the bacteria have a hydrophilic surface and the oxidation products of pyrite are also often hydrophilic, the net result of the short-term bacterial action is to destroy the hydrophobicity of the pyrite surface. However, it has been reported that under certain circumstances microorganisms produce elemental sulfur (Chou, 1990), which is naturally hydrophobic. Elemental sulfur is formed when oxidation is sufficient to alter the pyrite, but not sufficient to oxidize the sulfur, such as when oxidation occurs at low temperatures or in oxygen-depleted water. It is therefore possible that under the right conditions, the action of bacteria could enhance the hydrophobicity of pyrite rather than reducing it.

The effect of bacterial treatment on physical pyrite removal was first noted for the oil agglomeration process (Kempton et al., 1980; Capes et al., 1973), where conditioning with bacteria produced a 50% decrease in product sulfur content (Kempton et al., 1980). Since oil agglomeration is itself not a particularly economical process due to the cost of the oil, attention has shifted to bacterially assisted froth flotation. Work by Attia and Elzeky (1985) and Dogan et al. (1985) has indicated that this technique does improve pyrite rejection, without producing notable decreases in coal recovery. This is a failing of many chemical pyrite depressants (Baker and Miller, 1971).

2.3.7 Confounding Factors

A number of considerations complicate the use of microorganisms for coal desulfurization. One of these is the presence of toxic substances released by the coal (Klein and Wellek, 1989). A microorganism which is adapted to the environment of, for example, a copper tailings dump can be poisoned by the numerous organic compounds present in coal leaching liquors. If this happens, a lengthy period of adaptation will be needed in order to select a bacteria strain which can tolerate these toxins. Unfortunately, each coal has its own chemical peculiarities, and so there is no guarantee that a bacteria strain adapted to a particular coal will be able to thrive in a different one. While this can be handled by selecting a strain which is highly tolerant of a wide variety of toxins, this tends to increase the metabolic overhead of the organism, and reduces the amount of energy which it can devote to desulfurization and reproduction (Brock et al, 1984). Therefore, it is most efficient for a microbe to be resistant only to those chemicals which are actually present, and thus to be fairly coal-specific.

Another, more important, difficulty is contamination by foreign organisms. Since microorganisms are ubiquitous, maintaining a pure culture of a particular organism can be quite difficult. Contaminating organisms will produce major process disruptions if they compete for nutrients with, secrete products which are toxic to, or actively feed on the organisms which are actually desulfurizing the coal. While these foreign microbes may also be useful for coal desulfurization, they will generally not be as effective as the carefully selected culture which they displace. In laboratory experimentation, careful sterilization of water, equipment, and coal will prevent contamination. However, complete sterilization of the coal is likely to produce chemical changes, and in any case would not be practical on an industrial scale. Therefore, a suitable bacteria culture should be able to out-compete contaminants in the desulfurization reactor if it is to produce acceptable results. This can be accomplished either by using robust, proven natural strains, or by selecting organisms that function under severe conditions, thereby thinning out the competition. An additional factor which must frequently be considered is the form and quantity of mineral matter associated with the coal. The presence of large amounts of clay or alkali compounds will greatly increase the quantity of acid needed to adjust the slurry pH, as well as reacting with or adsorbing nutrients needed by the bacteria. Additionally, clays may cause mechanical problems by forming plugs in the reactor. Since bacterial reactors must be large with long residence time, clay deposition must be specifically prevented, preferably by removing the clay before bacterial processing.

2.4 PHYSICAL COAL DESULFURIZATION

Physical desulfurization of coal consists of liberation of the pyrite particles from the coal matrix, followed by a sorting process of some type to separate the pyrite from the coal particles. Sulfur removal by such processes is limited to the pyritic and sulfate sulfur, as the organic sulfur is an integral part of the molecular structure of the coal and can only be liberated if a chemical reaction occurs. This limitation of physical separation is largely offset by two factors. First, physical removal of pyrite will typically remove all liberated mineral particles as well, which will reduce the ash content and thus increase the heating value and overall quality of the coal. This is in contrast to chemical treatments, which often have no effect on the ash content and often degrade the heating value of the coal. Second, physical separations are typically very rapid, inexpensive, and produce little in the way of environmentally objectionable waste products. As a result, physical separations often produce much greater improvements in the product quality per dollar spent than do chemical processes. They will therefore continue to be the primary means of coal treatment for the foreseeable future, although they may ultimately be used as pretreatment techniques to reduce the operating costs of subsequent chemical treatments.

Physical separations can be carried out using a variety of differences in physical properties, primarily differences in density, electromagnetic properties, or surface chemistry. For coarser particles, particularly those larger than 28 mesh, separations based on density differences are the most effective for removing pyrite. This is a result of the density of pyrite being over three times that of coal, providing an ideal situation for nearly any density separation which has ever been devised. However, much of the pyrite present in coal is not liberated at 28 mesh, which makes it necessary to grind the coal to a finer size to remove what remains.

Gravity separations which function well for moderately fine coal include certain types of jigs, spirals, tables, and hydraulic classifiers. However, these processes all have a minimum size limit which is coarser than approximately 0.1 mm, and have little effectiveness for finer coal particles (Luckie,1987; Deurbrouck and Palowitch, 1979). Nevertheless, for the intermediate sizes these devices are the most effective means for removing pyrite from coal. Modern spirals are particularly useful, as they have a low water consumption, minimal maintenance, no moving parts, and are quite compact due to nesting of several spirals onto a single center shaft.

As particles become progressively finer, the ratio of surface area to volume of each particle increases, which in turn increases the ratio of the magnitude of the drag forces to the magnitude of the gravitational forces. Since density separations depend on these two sets of forces being of approximately equal magnitudes, such processes become more difficult and ultimately impractical with decreasing particle size, particularly when the working fluid is water or a liquid of similar or greater viscosity. The use of centrifugal effects to increase particle settling rates, by means such as cycloning, allow density separations to be made on particles as fine as 400 mesh in some cases, but any finer is generally considered impractical.

2.4.1 Water-Only Cyclones

Water-only cyclones are extremely common devices in coal cleaning plants, as they are simple, inexpensive to operate, and have a high capacity while taking up little space (O'Brien and Sharpeta, 1978). A water-only cyclone is essentially the same as a classifying cyclone, except that the apex cone angle is typically greater than 90 degrees and the vortex finder is more than half the length of the separating chamber. The large cone angle is believed to increase the quantity of high-density particles which are held up in the cyclone body, thus increasing the slurry density sufficiently to force the coal particles to float out the vortex finder. As a result, it is believed that the water-only cyclone is essentially an autogenous heavy-media separator. They are highly effective for removing pyritic sulfur from coal, and can clean coals which are too oxidized for treatment by froth flotation. However, they cannot simultaneously produce a highly-cleaned coal product and a low-calorific-value tailings, due to their low selectivity (Hochscheid, 1981). They are therefore generally used as precleaners before a more selective process, such as heavy-media cycloning or froth flotation. For this reason, they are generally operated with little attempt at optimization or control and designed on a largely empirical basis. However, improved efficiency and product consistency from these cyclones would reduce the demands on later processing, and would therefore produce a substantial improvement in circuit performance (Bull et al., 1987).

2.4.2 Heavy-Media Cycloning

Heavy-media cycloning consists of cycloning the fine coal in a suspension with its density adjusted to cause coal particles to tend to float while mineral particles tend to sink. The use of cycloning allows a reasonable separation to be achieved even at fairly fine sizes. Normally, the density of the suspension is adjusted by the addition of finely ground magnetite. Magnetite is preferred for this purpose due to the ease with which it can be recovered from the cyclone products by wet magnetic separation, and also due to its low cost and nontoxic nature. However, magnetite much finer than 400 mesh is not practical to use in normal applications, due to excessive viscosity and difficult recovery. Some work has been done with true heavy liquids, but these tend to be toxic or excessively expensive halogenated hydrocarbons, and so such technologies are not considered to be industrially practical compared to other techniques.

A relatively recent development in heavy-media coal cleaning is the use of ferrofluids. A ferrofluid is a suspension of submicron magnetic particles which, when subjected to a magnetic field, is affected as a bulk fluid rather than as discrete particles. With such a fluid, it is possible to select any desired specific gravity of separation by simply using a magnetic field to increase the apparent force of "gravity" on the ferrofluid. Since the magnet attracts the fluid but not the nonmagnetic coal, ash, or pyrite particles, the particles being separated see a density higher than what the fluid would have when no magnetic field was present. The sensitivity of the fluid to magnetic fields also aids in its recovery from the separated products. Since the magnetic particles are submicron size, this technique can be used on coal which is much finer than would be practical using more conventional heavy media cycloning. However, the cost of producing the submicron magnetics and the inevitable losses of ferrofluid in the finished products again makes this process excessively expensive.

2.4.3 Electrostatic separation

Electrostatic separation can be divided into two general categories: separation by magnitude and sign of charge, and separation by particle conductivity.

Conductivity separations make use of the fact that a charged particle will adhere to a grounded, conductive surface due to induced charging of the surface. If the particle is conductive, its charge will rapidly leak away into the grounded surface and it will no longer adhere, whereas an insulator will hold its charge and remain attached for some time. The most common type of separator which makes use of this effect is the corona-discharge drum separator. This device uses a high-voltage corona discharge to transfer a charge of the same sign and approximately the same magnitude to the particles of the feed. These particles then contact a rotating, grounded drum. Conductive particles rapidly lose their charge and are flung off by the drum's rotation, while nonconductive particles adhere until they are brushed off. Intermediate particles adhere briefly, and are collected as middlings. This device produces a rapid separation, and is best suited for particles which are large enough not to be seriously affected by air currents. However, the capacity is somewhat low, and more than a trace of moisture frequently causes the particles to either all become conductive, or to cake up in the system. When used for cleaning coal, it has been found that a small amount of moisture will render the clay minerals conductive before the coal does so, thus allowing clays and pyrite to be removed from the coal.

Separators which make use of differences in the sign and magnitude of the charges on particles must first selectively charge the particles of interest. Since corona discharges produce a charge of the same sign on all affected particles, this charging method is not suitable for this type of separator. For this reason, triboelectric charging is the preferred method for selectively charging particles.

Triboelectric charging occurs when two dissimilar materials are brought into contact. Because of the differing conductivities and surface work functions of the materials, electrons are exchanged, leaving the surfaces oppositely charged. If coal is brought in contact with copper it receives a positive charge, while most ash minerals charge negatively on contact with copper. Therefore, if a mixture of ash minerals and coal are caused to rub against a grounded copper surface, the desired selective charging will occur.

Once charged, the particles are allowed to fall between two oppositely charged plates. This causes the particles to separate according to the sign of their surface charge. Provided that air turbulence in the separator is minimized, this technique is capable of separating particles finer than 40 microns. Like the drum separator, this device works best if the feed is kept quite dry.

The primary drawback of the parallel-plate separator is its low separation efficiency on a single pass. This is a result of the fact that oppositely charged particles attract each other, and attach until they have neutralized their charges. These particles which have lost charge account for a large proportion of the feed (30 to 70%), and must be recirculated. There is therefore a large circulating load present, which restricts separator capacity. Since increasing the particle throughput only increases the particle discharge rate and therefore increases the circulating load, the capacity of plate separators is restricted to about the same degree as for the drum-type separators.

The utility of either type of electrostatic separator for coal desulfurization is somewhat limited, due to the need for a dry feed and the limited capacity. However, such techniques may be useful for treating dry pulverized coal, which would be prohibitively expensive to clean by wet methods due to high dewatering costs. This could be particularly important for low-rank coals, which have insufficient calorific value to be useful as fuels if their moisture content is high.

Another type of electrostatic separation is electrophoresis. This depends on the tendency of particles in suspension to develop a surface charge by exchange of ions with the surrounding solution. By altering the solution chemistry, it is possible to cause coal and pyrite particles to have different surface charges, and then to separate them using a DC field of 250-500 volts. The process is reported to be effective (Miller and Baker, 1974; Null, 1987), but unfortunately the process is currently uneconomical due to the high current consumption and to scaleup difficulties.

2.4.4 Magnetic Separation

In its as-mined state, the pyrite in coal is not strongly magnetic, which would seem to preclude magnetic separation. However, if the pyrite is properly oxidized it can be converted to pyrrhotite, which is magnetic. Standard wet or dry magnetic separators can then be used to remove it from the coal. Methods which have been used to convert the pyrite to pyrrhotite include thermal treatment and microwave heating. Another means for rendering pyrite magnetic is reaction with iron pentacarbonyl, which results in the formation of a ferromagnetic layer on the pyrite surface.(Luckie, 1987)

The development of high-intensity magnetic separators has allowed the separation of pyrite to be carried out without recourse to pretreatment, as the natural paramagnetism of pyrite is sufficient for these machines to operate. Current high-intensity magnetic separators consist of a chamber filled with small-diameter ferromagnetic material, such as stainless-steel wool, which is subjected to a powerful magnetic field. A high magnetic field gradient is produced in the vicinity of the fibers, which is strong enough to attract the paramagnetic pyrite particles. When the quantity of pyrite attached to the steel wool becomes too high, the chamber is removed from the field and flushed to remove the particles. As a result, the process is not continuous, and cannot easily handle coal which contains a high proportion of pyrite. The characteristics of this type of separator make it most suitable as a final cleaner after some other process, such as froth flotation. However, the high capital cost of the equipment and the relatively marginal improvement gained by use of this technique make it unlikely to be adopted.(Luckie, 1987)

2.4.5 Conventional Froth Flotation

Froth flotation is generally considered to be the most suitable method for physical cleaning of fine coal, as it is rapid, high capacity, inexpensive, and produces a reasonably good separation of coal from ash (Zimmerman, 1979). It is based on the natural difference in wettability of the coal and mineral particles. Since coal is composed of hydrophobic organic compounds, it can often be recovered by froth flotation without the need for any reagents other than a frother. Flotation of coals which are not naturally sufficiently hydrophobic to be floated can be accomplished by adding a neutral oil such as kerosene or fuel oil as a collector.

2.4.5.1 Pyrite Depressants: While flotation is generally acceptable for ash removal, it often is not highly effective for removing the pyritic sulfur from the coal. It is often hypothesized that this is due to the pyrite being naturally hydrophobic, and therefore floated along with the coal. A great number of chemical and biological pyrite depressants have been proposed by several investigators, as shown in Table 2.1. However, while they have often been claimed to be effective

TABLE 2.1: Representative depressants for coal-pyrite which have been reported in the literature.

Reagent	Action	Reference
Lime, CaO	pH, Hydrolyzed ion adsorption	Chander & Aplan, 1989
Potassium Dichromate, $K_2Cr_2O_7$	Oxidizing agent	"
Sodium Hypochlorite, NaClO	Oxidizing agent	"
Sodium Sulfide, Na_2S	Potential-determining ion/ reducing agent	"
Sodium Sulfite, Na_2SO_3	Reducing agent	"
Corn Starch	Physically adsorbed colloid	"
High-Amylose Starch	Physically adsorbed colloid	"
Cationic Starch	Physically adsorbed colloid	"
Xanthated Cationic Starch	Physically adsorbed colloid	"
Congo Red	Dye	"
Nigrosine	Dye, chelating agent	Raleigh & Aplan, 1990
Sodium Silicate	Dispersing agent	"
Ferric Chloride, $FeCl_3$	Hydrolyzed ion adsorption	Baker & Miller, 1971
Aluminum Chloride, $AlCl_3$	Hydrolyzed ion adsorption	"
Chromium Chloride, $CrCl_3$	Hydrolyzed ion adsorption	"
Copper Sulfate, $CuSO_4$	Hydrolyzed ion adsorption	"
Calcium Chloride, $CaCl_2$	Hydrolyzed ion adsorption	"
Sodium Cyanide, NaCN	Complexing agent	Yancey & Taylor, 1935
Ferrous Sulfate, $FeSO_4$	Hydrolyzed ion adsorption	"
Ferric Sulfate, $Fe_2(SO_4)_3$	Hydrolyzed ion adsorption	"
Para-Aminophenol	Complexing agent	"
Carboxymethyl Cellulose	Physically adsorbed colloid	Laskowski et al., 1985
Thiobacillus ferrooxidans	Oxidation, surface attachment	Elzeky & Attia, 1987
Other microorganisms	Surface attachment	Townsley & Atkins, 1986

in laboratory experiments, none have been adopted on a plant scale (Fonseca, 1991). This is due to minimal benefits seen in the plants, probably resulting from the unpredictable nature of pyrite hydrophobicity, which varies a great deal upon relatively mild oxidation. Also, pyrite depressants require good control of the slurry pH in order to work properly (Baker and Miller, 1971) and existing coal flotation circuits typically are not equipped for more than the coarsest control of this parameter.

2.4.5.2 Reverse Flotation: A different approach to removal of sulfur by flotation is the reverse flotation process (Miller and Baker, 1972; Miller, 1973; Baker, Miller, and Deurbrouck, 1973; Miller, Lin, and Chang, 1984) This consists of first conventionally floating the coal to remove the ash and larger pyrite particles. This is followed by a second stage where the coal flotation is depressed by addition of an appropriate reagent. A xanthate collector is then added to make the remaining pyrite floatable, and the pyrite is floated from the coal. The benefit of this technique is its handling of locked particles. A significant fraction of the pyrite is locked with floatable coal particles, and so tends to be recovered along with the floatable coal in the first stage of flotation. In the reverse flotation second stage, such particles will remain floatable due to the hydrophobicity of the pyrite, and will therefore be effectively removed from the coal which has been depressed. The drawbacks of the reverse flotation technique include high reagent costs, a need for two sets of flotation machines, difficulty in depressing coal particles finer than about 100 mesh in the second stage of flotation, and froth stability problems if the coal contains insufficient pyrite to stabilize the second-stage froth (Miller, 1973, 1985).

2.4.6 Column Flotation

Conventional froth flotation is generally considered to be insufficiently selective to be used for desulfurizing coal, as conventional machines are incapable of removing all of the liberated mineral matter in a single pass (Aplan, 1978). Since froth flotation is only a secondary means of coal recovery in most plants, the investment in floor space and equipment is kept to a minimum, which means that in general only a single stage of flotation is used. It is therefore desirable to redesign the flotation process to produce the effect of multistage cleaning, while maintaining the low capital and operating costs of a single stage.

Countercurrent column flotation has been shown to be very effective for fine coal cleaning. A column essentially performs as if it were a multistage flotation circuit arranged vertically (Dell, 1985). Since the flotation column is a single machine with no more mechanical overhead than a conventional machine, its installation and operating costs are comparable to those of a single stage of conventional flotation cells.

2.4.6.1 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 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, to the tailings outlet. This flow pattern is in direct contrast to that found in conventional cells, where both the air and the solid particles are driven in the same directions. The result is that columns provide improved hydrodynamic conditions for flotation, and thus produce a cleaner product while maintaining high recovery and low power consumption. The performance differences between columns and conventional cells may best be described in terms of the following factors: collection zone size, particle/bubble contact efficiency, and fines entrainment.

The collection zone, the volume where particle/bubble contact occurs, differs greatly in size between column and conventional flotation. In conventional cells, contact occurs primarily in the region surrounding the mechanical impeller. The remainder of the cell acts mainly as a storage volume for material which has not yet been through the collection zone. This creates a bottleneck which keeps the flotation rate down. In contrast, flotation columns have a collection zone which fills the entire volume of the machine, which offsets the gentle bubble/particle contact conditions present in the column. The reduced level of turbulence needed to achieve a good rate of recovery in columns also reduces the tendency of coarse particles to be torn away from the bubbles which they attach to, and therefore columns are more effective for floating coarser coal particles.

Columns exhibit a higher particle/bubble contact efficiency than conventional machines, due to the particles colliding with the bubbles head-on. As a result, the energy intensity needed to promote contact is less, and so power consumption is reduced. A second beneficial effect in certain types of flotation column is the reduction of bubble diameter. As bubble diameter is reduced, the flotation rate of both the coarser and finer particles is improved. The effects producing the improvement are illustrated in Figure 2.2. Coarse particles can attach to more than one bubble if they are small, and therefore the chances of the particle being torn loose and sinking again is reduced. For fine particles, the probability of collision with the bubble is improved if the bubble is small, as then the hydrodynamic forces tending to sweep the particle away from a collision are reduced. The reduction of bubble diameter has the added benefit of increasing the available bubble surface area for the same amount of injected air. It is therefore desirable to produce bubbles as fine as possible (Yoon and Luttrell, 1986).

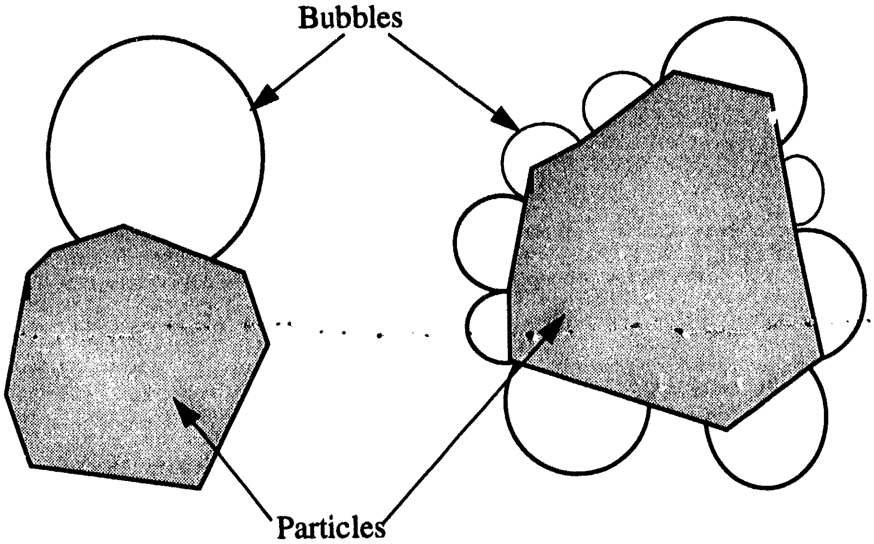
The entrainment of fine waste material in the froth product is a serious failing of conventional flotation machines. It results from the need for a certain amount of water to be carried into the froth as the film surrounding the air bubbles. As a result, fine suspended particles are swept into the froth with this water, even though they are not physically attached to the air bubbles. In most column flotation machines, the entrainment problem is addressed through the use of washwater, as shown in Figure 2.2. Where the conventional cell must allow a certain amount of feed water to enter the froth, the washwater in the column cell displaces this feed water to the tailings, thus preventing entrained contaminants from reaching the froth. The only drawback to the use of froth washing is that the demand for clean water is increased, which may cause water problems in some situations.

The net effect of the relatively gentle mixing, countercurrent flow, and use of washwater in columns is that there is a physical separation of several meters between the clean coal in the froth and the concentrated gangue at the tailings, with a gradual gradient of concentration between the two extremes, as shown in Figure 2.5. There is therefore a reduced possibility of coal being misplaced into the tails, or of gangue short-circuiting to the froth. The result is that a column is typically equivalent to between three and five stages of conventional flotation, depending on the column design.

2.4.6.2 Types of Flotation Columns: Flotation columns can be most easily divided into two general categories: unobstructed designs, and partially or fully packed designs. While the first flotation columns were predominantly of the unobstructed type, there are certain situations where the somewhat more complex packed or partially packed columns have advantages.

2.4.6.2.1 Basic Unobstructed Columns: The unobstructed column types are essentially nearly identical, consisting of open chambers approximately 10-14 meters tall with washwater added at

A. LARGE PARTICLES



B. SMALL PARTICLES

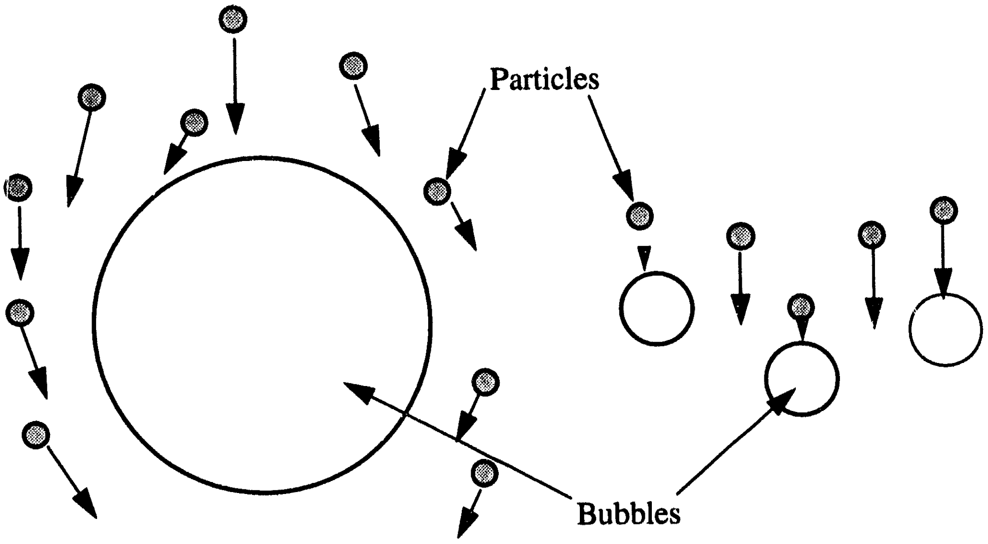
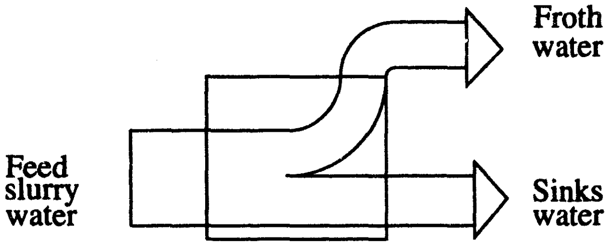
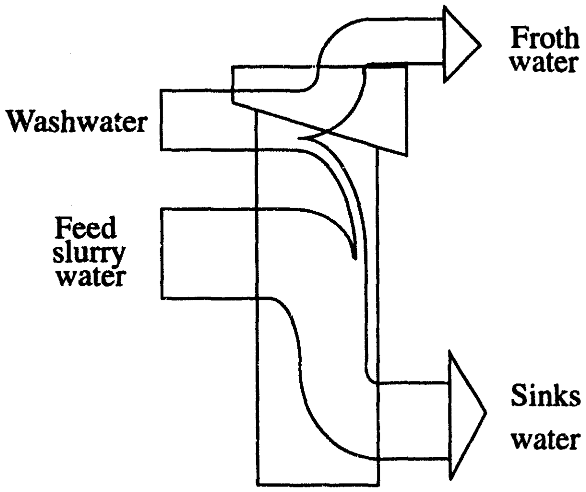


FIGURE 2.3. Effect of bubble size on flotation. Smaller bubbles are more effective due to their greater surface area, which provides more attachment surface for large articles, and reduces the probability that hydrodynamic effects will prevent contact with small particles.



CONVENTIONAL FLOTATION



COUNTERCURRENT COLUMN

FIGURE 2.4. Effect of washwater on the entrainment of feed water into the froth. By displacing feed water with clean water, mechanical entrainment of hydrophilic particles into column froth products is largely eliminated.

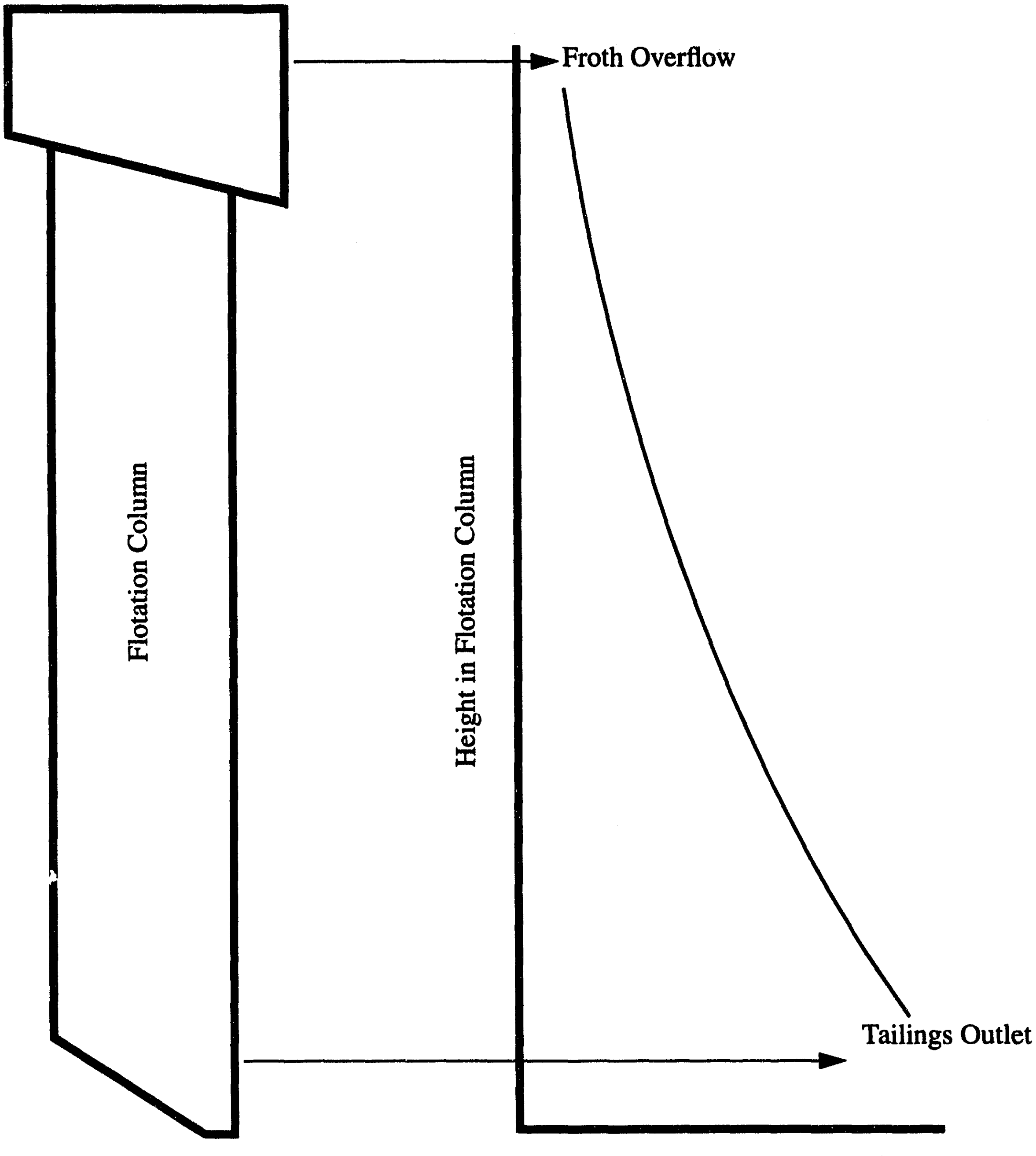


FIGURE 2.5. Concentration gradient as a function of the depth below the froth overflow in a flotation column. The ash concentration in the pulp is lowest near the froth overflow, and highest near the tailings outlet. The necessary column height to achieve the desired froth and tailings grades is a function of the steepness of this gradient.

the top and air bubbles introduced at the bottom. The major differences between unobstructed columns from various manufacturers are mainly in the nature of the bubble generators and in the degree of instrumentation and control with which they are equipped. Currently, the major manufacturers are the Column Flotation Corporation of Canada (CFCC), and Deister Concentrator Co., although the columns are simple enough that many mineral processing plants and research organizations have built their own units. While columns of this type have become very common in metallic ore concentrators, they are not yet widely introduced in coal cleaning plants.

The basic configuration of unobstructed columns is illustrated by Figure 2.6, which illustrates a CFCC column. Air is injected through a diffuser at the base, and the level is controlled using a level sensor and an automatic control valve on the tailings line. A froth depth of 2-4 feet is maintained, and feed is introduced a short distance below the base of the froth layer. In the original design, the diffuser was sintered ceramic which produced very fine air bubbles. However, this was found to suffer from plugging problems, particularly in hard water, and so cloth and perforated rubber sheeting were adopted instead (Dobby et al, 1985; Boutin and Wheeler, 1967). The flexible diffuser materials resist plugging due to the flexing which they undergo during operation, which breaks loose the mineral incrustations. Nevertheless, internal spargers will eventually plug over a period of weeks, requiring that the column be drained so that they can be replaced.

The Deister Flotaire column, which was originally developed for phosphate flotation, originally had a number of important differences from the CFCC column, although the two types of machine have become steadily more similar over the years. The early Flotaire machines were less than 5 meters tall, did not use washwater, and introduced the use of an external bubble generator rather than internal spargers. Current versions have added washwater sprays similar to the CFCC design and have increased in height, and the external bubble generator has evolved to a type which uses less water than the simple aspirators which were used originally. The external bubble generators can be serviced without draining the column, thus greatly simplifying column maintenance. A schematic diagram of the Flotaire bubble generator is shown in Figure 2.7. Air is diffused through the porous plastic sleeve, and the bubbles are sheared off by the water flowing through the center of the sleeve. The air/water mixture is then injected directly into the column immediately after leaving the generator, in order to minimize bubble coalescence. The volume ratio of air to water for this system can be as high as 8:1, which is a considerable improvement over aspirators which have an air to water ratio on the order of 0.15:1. Similar systems are used by the Bureau of Mines external bubble generator (McKay et al, 1988), and by the Virginia Polytechnic Institute microbubble generator (Yoon et al, 1990).

Most research work with unobstructed columns uses some type of external bubble generator, due to the greater flexibility, ease of servicing, and finer bubble size distribution produced by these units. The primary drawback of the external bubble generators is that they require the addition of clean water to form the bubbles and convey them to the column. While recycled water can be used for aspirator-type bubble generators, the recycled water in coal plants is often too dirty to be used in the more sophisticated bubble generators which have a lower water demand. The use of these devices can therefore result in a high plant water consumption, and also may produce excessively dilute column tailings products which can be difficult to thicken.

2.4.6.2.2 Packed and Baffled Columns: While the standard unobstructed column designs are quite well-accepted, their great height is somewhat inconvenient, both due to headspace requirements and to the large amount of water which is held up in them. This height is necessary to produce

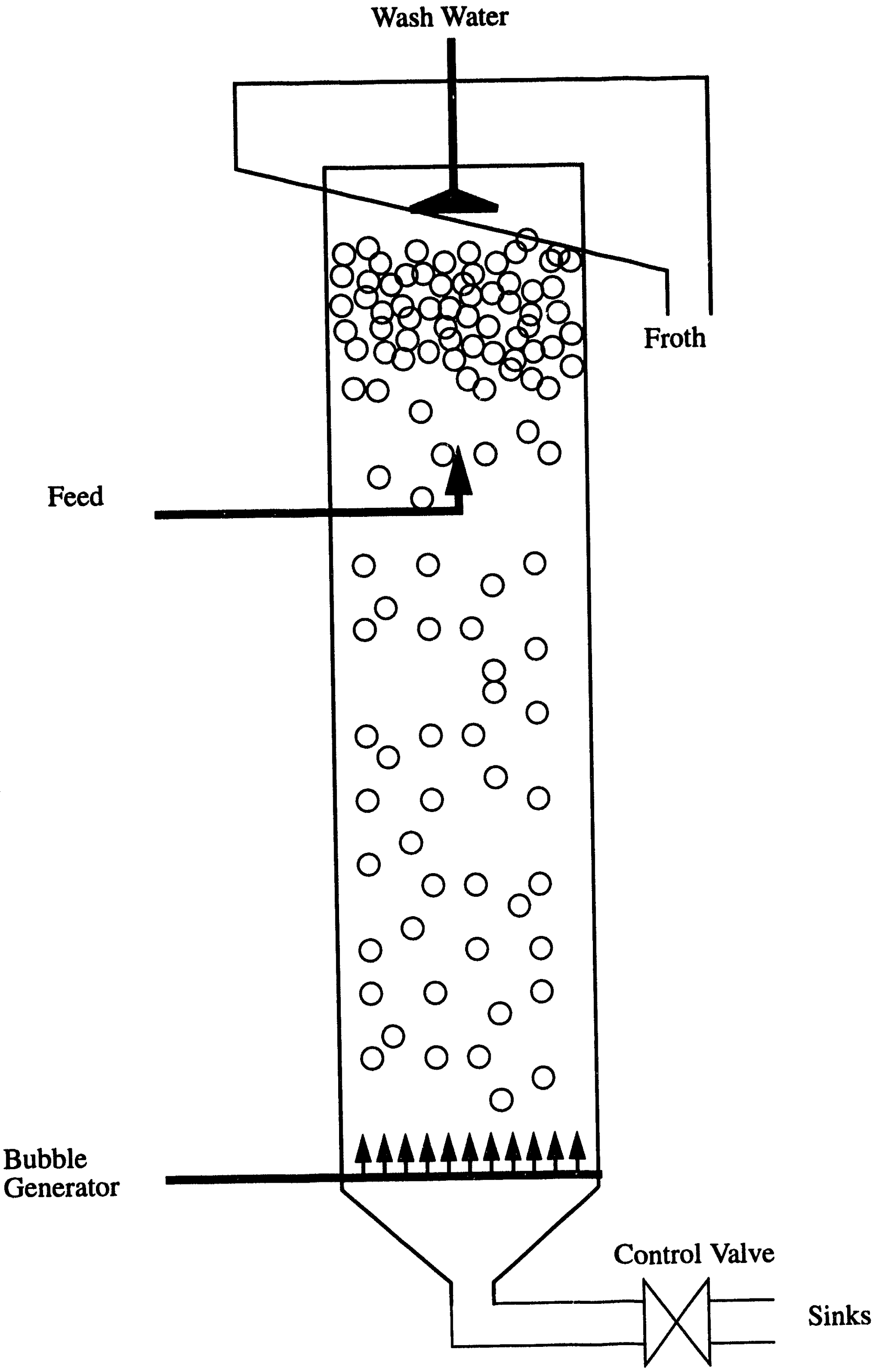


FIGURE 2.6. Schematic of the CFCC column, which shows all of the basic features of a flotation column.

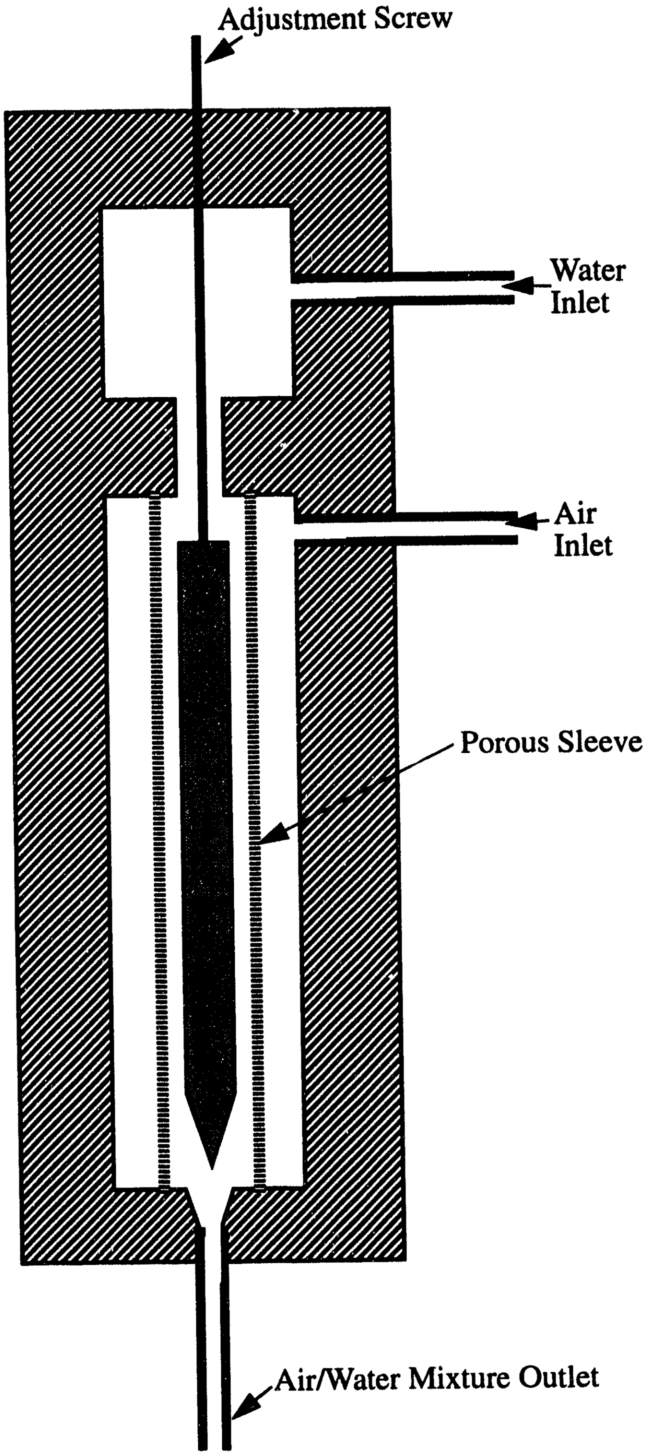


FIGURE 2.7. Schematic of the Deister Flotaire external bubble generator. This generator has a much higher air/water ratio than the original aspirator types, and is much easier to service than generators inside the column.

good froth grades and product recoveries, as otherwise backmixing of gangue into the froth would degrade product quality, while short-circuiting of coal to the tailings would reduce recovery. However, if the hydrodynamics of the column are changed by introducing flow obstructions of various types, backmixing and short-circuiting can be reduced considerably. Flow obstructions can also improve particle-bubble contact efficiency, and thus increase the flotation rate of very fine particles, which is of great importance for producing super-clean coals. However, such obstructions also tend to increase the likelihood that the column will plug. To date, only two types of obstructed column have been considered, the Wemco-Leeds column (Dell, 1985), and the Static Tube (Yang, 1984).

The Wemco-Leeds column was originally designed with the specific goal of approximating the operation of a multi-stage flotation circuit with less space and lower mechanical overhead. It resembles a very deep conventional flotation cell bank, as shown in Figure 2.8. The upper portion of the cell is divided into a series of chambers by several horizontal barriers. Each barrier consists of a rack of fixed rods supporting a set of movable plastic rods, as shown in Figure 2.9. The intent of this barrier design is to trap a thin layer of froth underneath each, with the movable rods lifting to allow froth into the upper chambers when the froth depth

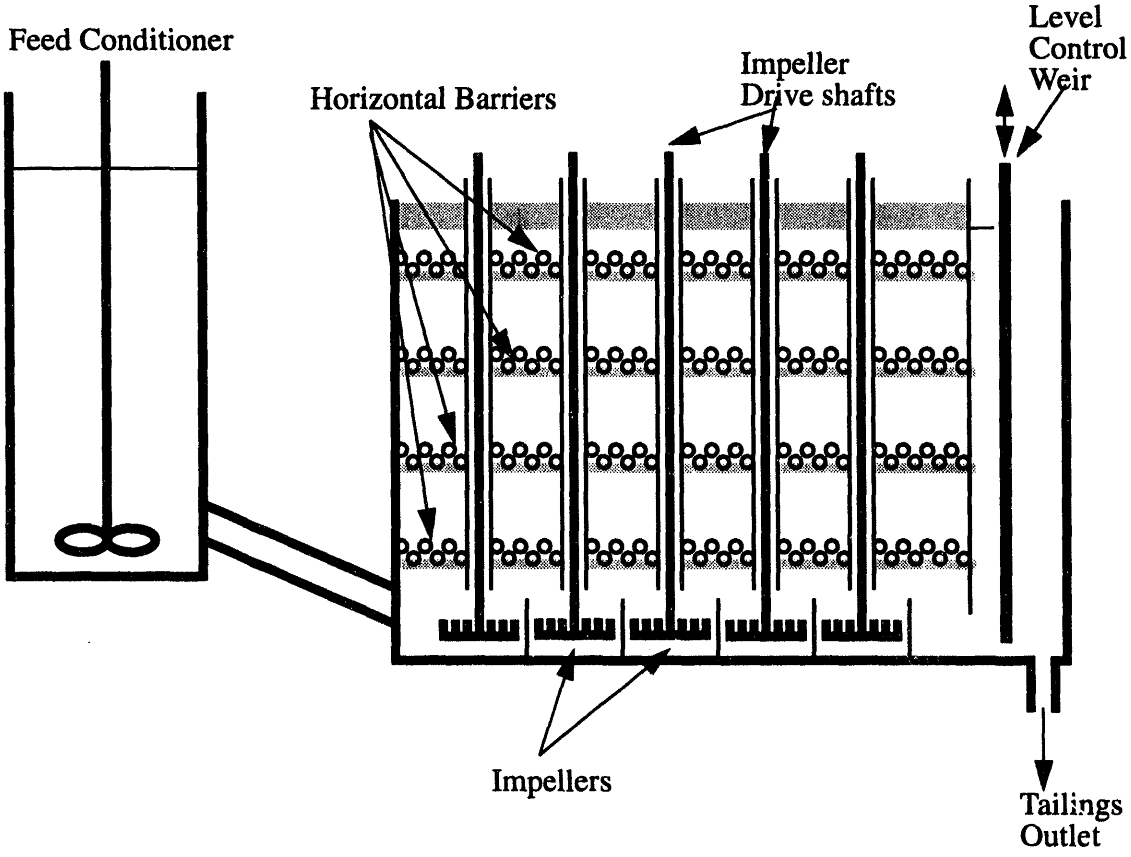


FIGURE 2.8. Schematic of the Wemco-Leeds flotation machine.

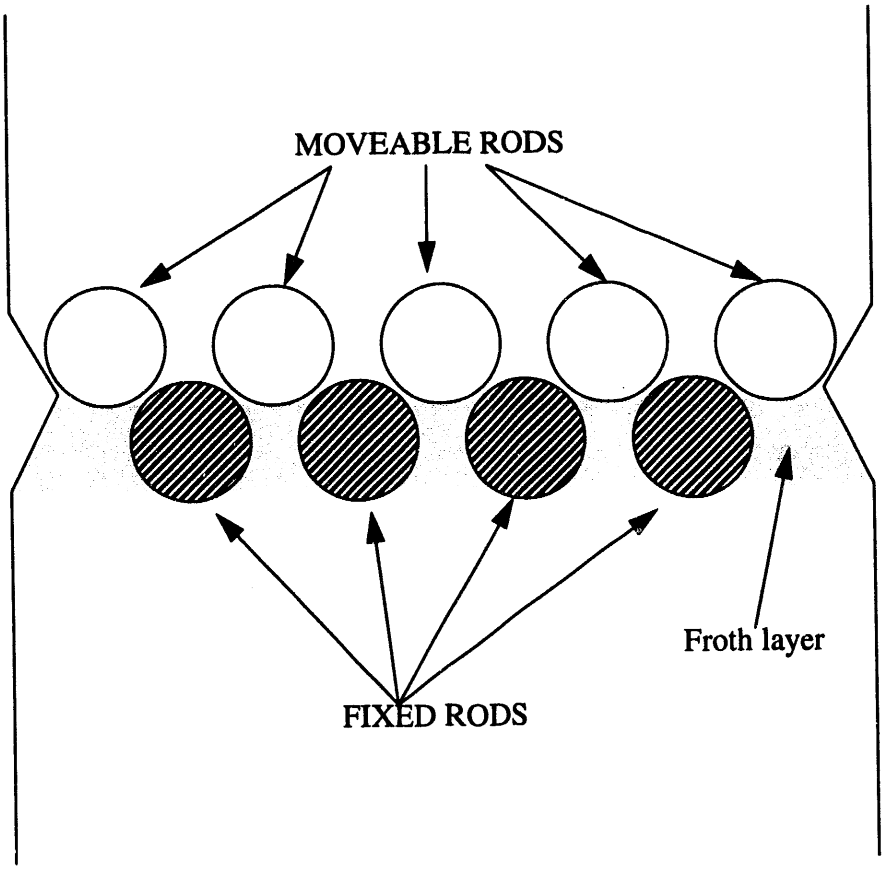


FIGURE 2.9. Detail of the Wemco-Leeds froth barrier design. The movable rods act as valves to restrict the flow of froth and thus improve the cleaning action.

underneath them is sufficiently great. Washwater is added to the uppermost chamber of this machine, which descends to wash each froth layer in succession. Since bubbles only remain in the froth layers beneath the barriers for a short time, the bubbles do not coalesce significantly. Also, the action of the rods will tend to break up any bubbles which do become too large.

Aside from the horizontal barriers and the washwater, the Wemco-Leeds column is operated in essentially the same fashion as a conventional bank of flotation cells. The large available surface area for removing froth is also beneficial, as this reduces the chances of the machine becoming choked with froth, which can be a problem with flotation of coal using other types of column.

The Static Tube carries the introduction of flow restriction to an extreme case, in order to provide high collection efficiency and selectivity for micron-sized particles. The collection zone is completely packed with corrugated plates, which produces very tortuous flow channels only a few millimeters across. Due to the small diameter of the channels, no diffuser or bubble generator is needed, as the mere act of travelling through the packing breaks up the air bubbles. The presence of the packing prevents hydrodynamic forces from sweeping bubbles and particles apart, and so forces bubble-particle contact regardless of the size of the particle. While performance is good for coal which is ground to sizes finer than 20 micrometers, coarser particles tend to abrade and plug the column. Also, if the froth layer at the top of the column becomes too dry, it can solidify and plug the machine, making it necessary to backwash the packing periodically (Woody, 1989).

2.4.6.3 Flotation Column Control: The control of flotation columns can be as simple as for conventional flotation machines, or sufficiently complex to extract the maximum benefit from using a flotation column. The CFCC columns use the highest degree of instrumentation and control, although the same level of monitoring could be used on the other types of column.

A complete control scheme for the CFCC column is shown in Figure 2.10 (Dobby et al, 1985). Three distinct control loops are used. The tailings bias control loop measures the feed slurry flowrate, and adjusts the tailings flowrate to a slightly higher level. This insures that the feed water will be completely displaced from the froth by the washwater, rather than having feed water forced into the froth by a too-restricted tailings flow. Pulp level control is accomplished by the second control loop, with level measured by a differential-pressure sensor, and washwater flowrate adjusted to maintain the level setpoint. The third control loop maintains the air holdup (volume percent air) in the column at some preset value. The air hold-up is measured by determining the pulp density using pressure sensors at two different depths. The controller then uses both the pulp density and the washwater addition rate to adjust the air flowrate and thus maintain the air holdup setpoint.

2.4.7 Agglomeration

When very fine coal is being cleaned, dewatering of the fine coal product becomes quite important. While filters and solid-bowl centrifuges can recover the fine coal, the high surface area of the coal particles results in a high level of adsorbed water, which in turn reduces the calorific value and introduces problems such as freezing in the winter and a tendency for spontaneous combustion. A cleaning process which can alleviate these problems with the cleaned product is therefore desirable. In oil agglomeration, coal is recovered by mixing the fine coal slurry with a quantity of oil. The oil droplets preferentially wet the coal particles, causing them to agglomerate together into a mass which can be recovered either by froth flotation or by screening. Since the oil displaces water from the coal surface, the moisture content of the product is greatly reduced. The presence of the oil also increases the calorific value of the product, which can be as much as 10-15% oil. This process also allows recovery of coal down to micrometer sizes. Unfortunately, the selectivity is lower than froth flotation, particularly when the conditions are right to make the pyrite particles mildly hydrophobic. Also, the high oil consumption partially defeats the purpose of coal cleaning, as cleaned coal is intended to compete with petroleum fuels.

2.4.8 Selective Flocculation

Selective flocculation is intended for cleaning very fine coals with minimal use of reagents. Long-chain polymers are used to selectively flocculate the coal particles, which increases their settling rate relative to the unflocculated mineral matter. At present, a high degree of selectivity is not achieved by this technique, due to unselective bridging of particles by the flocculant, occlusion of mineral particles by settling flocs, and settling of unflocculated dense particles such as pyrite. As a result, it is more likely to be useful as a precleaning treatment than as a final cleaning step. The effectiveness of the process can be considerably enhanced if more selective flocculants are devised, and if the heavy minerals are flocculated and settled while leaving the coal dispersed. However, this would introduce serious problems in thickening the unflocculated coal, unless it is being used as feed for a second cleaning process. Pyrite in particular can potentially be removed by selective flocculation, as a xanthate-based flocculant

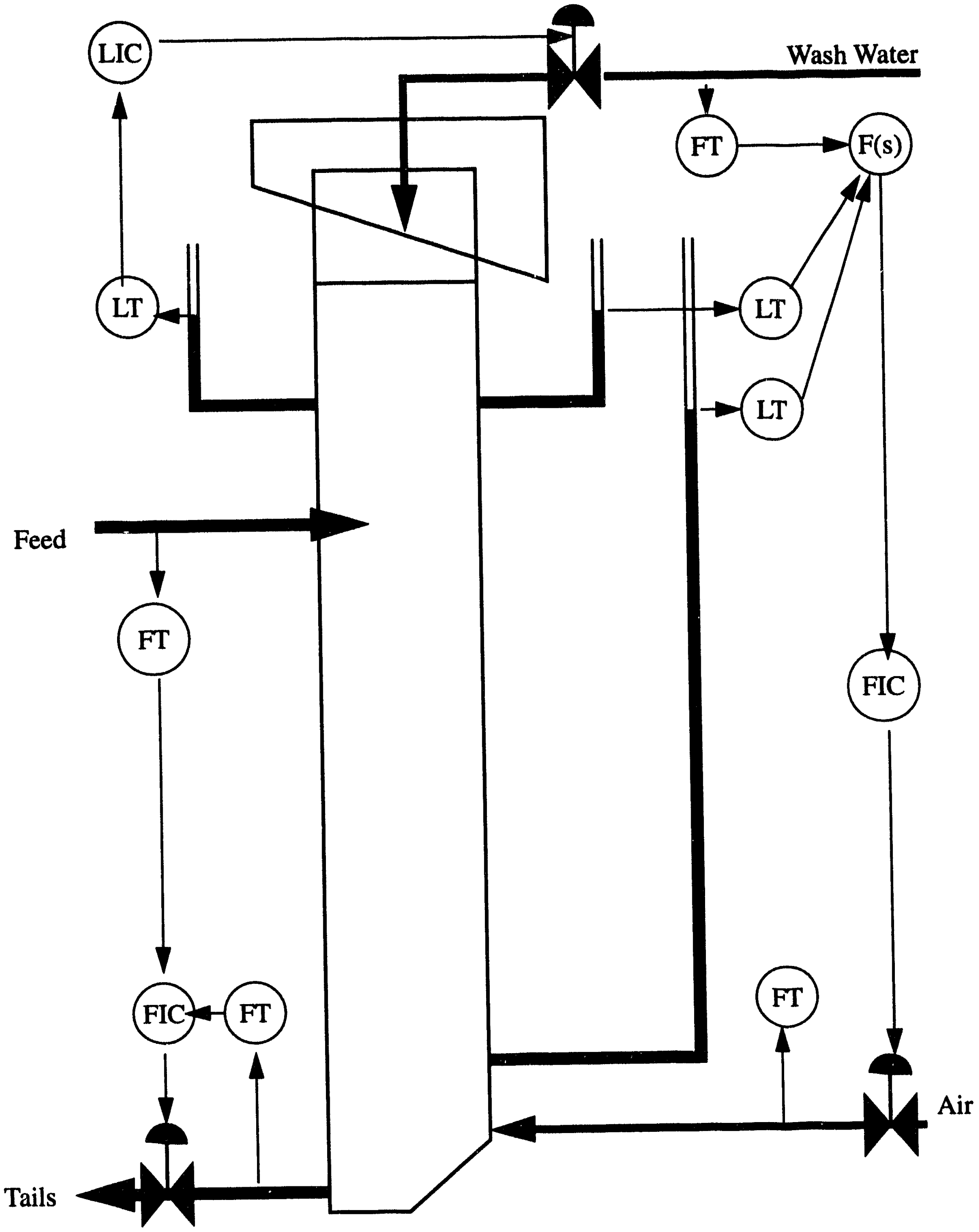


FIGURE 2.10. Control loops used by the CFCC column. FT= flow transmitter; LT= level transmitter; LIC= level controller; FIC= flow controller; F(s)= air hold-up control program.

would be highly selective for pyrite and its high density would give the pyrite flocs a considerably faster settling rate than the other particles.

2.4.9 LICADO Process

The LICADO (LIquid CArbon DiOxide) process is based on the affinity of coal for carbon dioxide (He et al, 1989). A coal slurry is mixed with liquid CO_2 under pressure at room temperature, and the coal particles are selectively wetted by the carbon dioxide phase. The coal-laden carbon dioxide, which is less dense than water, is then skimmed off. The coal is then separated by thickening and filtration. After processing, the clean coal is reduced to atmospheric pressure, and any residual CO_2 immediately boils off. Since the water was displaced from the coal particles during the separation, the moisture content of the fine coal is not high, and filtering and drying are not necessary. The major expense is the need for maintaining a high pressure in the separator, in order to keep the CO_2 in the liquid phase. The selectivity appears to be similar to that of oil agglomeration, which it resembles in its principle of operation.

2.5 DISCUSSION AND CONCLUSIONS

While there is an extremely wide variety of possible techniques for desulfurizing coal, the practical choices are highly restricted by both cost considerations and process effectiveness. While the chemical techniques such as molten caustic leaching present a potential means for highly cleaning coals, economics rule them out at current coal prices. While these processes may be useful at some point for coal desulfurization, in the short term they are essentially limited to the laboratory. It was therefore decided that the best route to take for desulfurizing coal would be either physical or biological rather than chemical. An additional consideration was that reducing the ash and sulfur content as far as possible by an inexpensive means will often reduce the demands on a later, more expensive process, thus reducing the overall processing costs (Prudich and Henry, 1989).

Physical coal-cleaning processes use a wide range of principles, and are generally low-cost. However, process limitations rule out many of them for desulfurizing coal which is ground finely enough to liberate the pyrite. Density-based processes in particular, such as jigs, spirals, tables, and cyclones, cannot effectively separate coal from pyrite at sizes finer than about 200-400 mesh. Magnetic separation processes require either pretreatment of the coal or the use of expensive high-intensity magnets, and in any case cannot remove the ash minerals from the coal along with the pyrite. Electrostatic and electrodynamic separations do not have sufficient capacity when fine particles are being separated, and processes such as electrophoresis have a high power consumption which makes them too expensive for this application. This leaves the physico-chemical separation processes of agglomeration, selective flocculation, and froth flotation. Of these, froth flotation has a lower operating cost than agglomeration, and better selectivity than selective flocculation.

Biological coal desulfurization is not as highly developed as the chemical and physical desulfurization techniques, but shows promise as a technique which can supplement other methods for upgrading coal quality. Since there is considerable doubt as to whether microorganisms are actually effective for removing organic sulfur from coal, their use is primarily limited to removing pyritic sulfur. Their inability to remove ash-forming minerals makes it unlikely that bacterial leaching alone will be a useful process for cleaning fine coal. Of the pyrite solubilizing organisms which are known, the various strains of *Thiobacillus* are the most likely to be immediately useful, as they grow at ambient temperatures and therefore avoid the expense of heating the leaching reactor.

The following criteria were used to select processes for further study in this project, based on the information found in the literature review:

1. The process costs must be low enough for the cleaned coal to be sold profitably at $50/ ton.
2. The process should recover at least 80% of the heating value of the feed coal.
3. The process should remove at least 50% of the pyritic sulfur, or reduce the pyrite content to less than 1%.
4. The quality of the coal (heating value per unit weight, ash content, moisture) should be equal to or better than the feed coal quality.

Three processes were selected for further study which were judged to be capable of achieving the above criteria: bacterial pyrite dissolution by *Thiobacillus ferrooxidans*, column flotation, and froth flotation with bacterial depression of pyrite.

CHAPTER 3: BACTERIAL LEACHING EXPERIMENTS

3.1 INTRODUCTION

From the review of the literature, the potential benefits claimed for bacterial leaching over other processing techniques included process simplicity, high removal effectiveness for locked pyrite particles, and relatively mild processing conditions. The primary problem with bacterial leaching of coal with *Thiobacillus* species was found to be the long processing times required, generally on the order of one to two weeks to remove 90% of the pyritic sulfur. In this phase of the project, experiments were carried out to determine the extent to which improving the aeration of the slurry would increase the leaching rate of the bacteria, and whether the use of pachuca reactors rather than shaken or stirred reactors would produce sufficient improvement to make *Thiobacillus* leaching more nearly practical on an industrial scale. It was decided that bacterial leaching would be pursued further if initial tests with the pachuca tanks could remove 80% of the pyritic sulfur in less than a week.

3.2 EXPERIMENTAL PROCEDURE

Initial leaching experiments were carried out using a bituminous coal from the Meigs Creek Seam, Ohio. This coal contained 4.4% sulfur, 2.0% pyritic sulfur, and 18% ash. It was ground in a rod mill at 37% solids to the particle size distribution given in Table 3.1. For grinding, the pH was adjusted to 12.5 with NaOH to kill naturally-occurring acidophilic microorganisms. Strong alkali is an effective sterilant for *Thiobacillus ferrooxidans* and other related acidophiles, since they cannot survive at high pH. This is because an acid environment is needed to stabilize their cell walls (Bagley, 1987). When the solution approaches neutral pH, the cell wall is weakened and osmotic pressure causes the cells to burst open, or lyse. While there are

TABLE 3.1: Size distributions for the two coals used in the leaching experiments, after rod-mill grinding.

	AEP-Pittsburgh Seam			Meigs Creek Seam
Size Fraction	% Weight	% Ash	% Sulfur	% Weight
+ 65 mesh	--	--	--	0.25
65 x 100 mesh	0.35	--	2.42	2.63
100 x 150 mesh	2.47	21.8	2.55	35.11
150 x 200 mesh	10.91	24.5	3.06	16.84
200 x 270 mesh	15.43	24.7	3.54	12.29
270 x 400 mesh	16.41	25.4	4.12	9.28
400 x 500 mesh	11.79	34.1	5.30	5.85
- 500 mesh	42.64	53.5	2.21	7.75
Total	100.00	38.02	3.19	100.00

organisms which can survive in alkaline environments, they cannot survive at the pH of 2 to 3 where *T. ferrooxidans* thrives.

For all leaching experiments, the coal was suspended in iron-free Tuovinen and Kelly medium (Tuovinen and Kelly, 1973), with the pH adjusted to 2 with sulfuric acid. This medium provides the necessary nutrients, such as phosphorus, potassium, and nitrogen, for the bacteria to grow. It is a standard growth medium which is widely used for culturing *T. ferrooxidans*. The composition of the medium is given in Table 3.2, along with the composition of 9K medium which the literature reports is also widely used. The T&K medium was preferred for the leaching experiments, as it is simpler to make than 9K medium.

TABLE 3.2: Composition and preparation of Tuovinen and Kelly (T&K) and 9K Nutrient Media for culturing iron-oxidizing bacteria such as *T. ferrooxidans*.

Compound	Quantity, grams T&K	Quantity, grams 9K
Ammonium Sulfate, $(NH_4)_2SO_4$	0.4	3.0
Potassium Chloride, KCl	---	0.1
Potassium Phosphate, Dibasic, K_2HPO_4	0.4	0.4
Magnesium Sulfate, $MgSO_4$-$7H_2O$	0.4	0.5
Calcium Nitrate, $Ca(NO_3)_2$	---	0.01
Ferrous Sulfate, $FeSO_4$-$7H_2O$	33.3	55.7
Distilled, sterilized water	1000	1000
Sulfuric Acid to pH=2.0		

Media Preparation:

Growth Media- Combine all salts except the ferrous sulfate with 700 ml of water, adjust pH to 2.0, and autoclave to sterilize. Dissolve ferrous sulfate in 300 ml water, filter-sterilize, and add aseptically to cooled salt solution. This medium is used for growing cultures of *T. ferrooxidans*, with the dissolved ferrous iron acting as the energy source.

Basal Salts- Combine all salts except ferrous sulfate with 1000 ml water, adjust pH, and autoclave. This solution is used for tests where pyrite is available to serve as the energy source for growth, or where large amounts of dissolved iron will be troublesome.

Both pachuca tanks, as shown in Figure 3.1, and shake flasks were used in this experiment. Pachuca tanks, being air-agitated reactors, are more thoroughly aerated than shake flasks, which are the standard reactor used in most laboratory investigations of bacterial leaching. Pachuca tanks are also widely used in industrial oxidative leaching operations, as they are simple to build and operate, and produce minimal size degradation of the particles being leached due to the gentleness of the mixing action.The pachuca tanks had a working volume of 1.25 liters, and the working volume of the shake flasks was 125 ml. The coal suspensions for both the tanks and flasks were 26% solids by weight.

The experiment comprised 24 pachuca tanks and 24 shake flasks, each set divided into

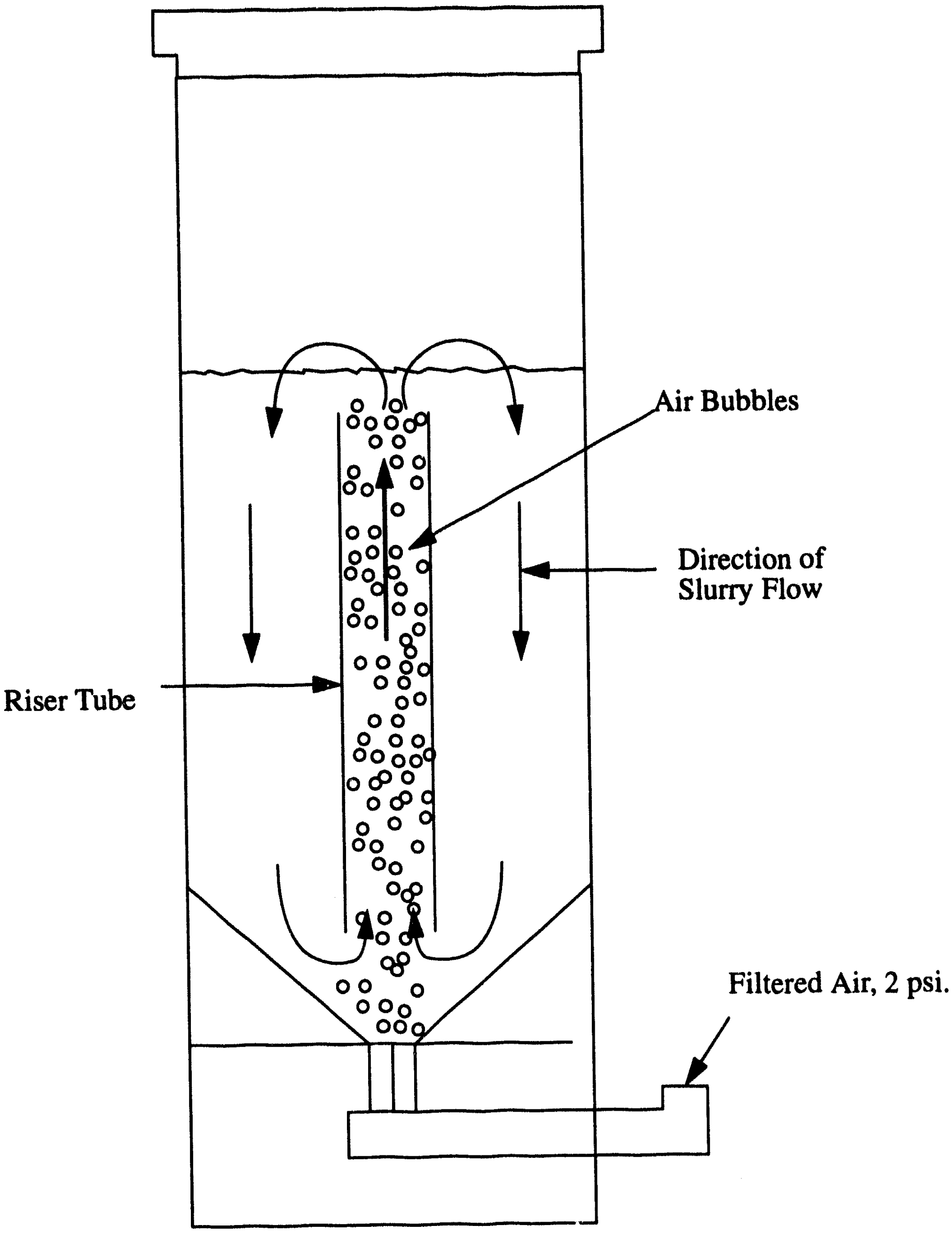


FIGURE 3.1. Schematic diagram of laboratory-scale pachuca tank. Operating pressure is 2 psi.

eight groups of three. Each group consisted of one tank or flask which was sterilized by adding 0.07% by weight $HgCl_2$, and two tanks or flasks which were inoculated with 10% by volume *Thiobacillus ferrooxidans*, washed and suspended to 2 x 10^8 cells/ml. Every three days, one group of tanks and the corresponding group of flasks were removed, filtered, dried, and analyzed for total sulfur content of the leached coal. The solution pH was measured at the time of removal, and the filtrate from the pachuca tanks was oxidized with hydrogen peroxide to decompose dissolved organic material, then titrated using dichromate to determine the concentration of dissolved iron (ASTM, 1987).

A second leaching experiment used bituminous coal mined from the Pittsburgh seam, which contained 3.2% total sulfur, 2.2% pyritic sulfur, and 38% ash. This coal was ground under the same conditions as for the Meigs Creek coal to give the size, ash, and sulfur distributions shown in Table 3.1. Duplicate pachuca tanks and flasks were prepared at 23% solids and pH=1.95, and inoculated with *T. ferrooxidans* prepared in the same manner as in the initial test. Bacterial activity and pyrite dissolution were monitored by daily determination of the quantity of dissolved iron. Iron was measured photometrically using 1,10 phenanthroline, as this method is more rapid and sensitive than dichromate titration, and required a much smaller sample (Sandell, 1959). This made it practical to monitor the progress of the leaching without removing an entire flask or pachuca tank for analysis.

3.3 EXPERIMENTAL RESULTS AND DISCUSSION

The results for the Meigs Creek coal leaching experiments are given in Table 3.3 and Table 3.4, where the results labeled "control" are for the tanks and flasks which were sterilized by

TABLE 3.3: Meigs Creek coal leaching experiment: pH and total sulfur content of coal for pachuca tanks and shake flasks. The columns labeled "control" were sterilized with $HgCl_2$, and those labeled "Inoc. 1" and "Inoc. 2" were for pairs of reactors run in duplicate. The sulfur content of the coal was measured using a Leco SC-132 sulfur determinator.

Leaching time (days)	Tanks						Flasks					
	Control		Inoc. 1		Inoc. 2		Control		Inoc. 1		Inoc. 2	
	pH	%S	pH	%S	pH	%S	pH	%S	pH	%S	pH	%S
3	2.3	4.63	2.2	4.81	2.2	4.88	2.4	4.77	2.6	4.76	2.6	4.78
6	2.4	4.35	2.2	4.28	2.3	4.35	2.7	4.53	2.6	4.53	2.6	4.51
9	2.5	4.55	2.1	4.35	2.3	4.51	2.8	4.67	2.4	4.63	2.4	4.62
12	2.5	4.66	1.9	3.68	1.9	3.95	2.7	4.70	2.2	4.62	2.2	4.59
15	2.5	4.79	1.8	3.59	1.9	3.71	2.7	4.81	2.1	4.33	2.0	4.09
18	2.5	4.51	1.8	3.40	1.8	3.23	2.6	4.50	1.9	3.56	2.0	3.53
21	2.5	4.51	1.8	3.22	1.8	3.28	2.6	4.61	1.8	3.32	1.8	3.45
24	2.5	4.52	1.8	3.10	1.8	3.08	2.6	4.61	1.8	3.27	1.8	3.21

TABLE 3.4: Total dissolved iron in pachuca tanks for Meigs Creek coal leaching experiment, as determined by titration, and pyritic sulfur content, calculated by subtracting 2.8 from the total sulfur content (the coal contains 2.8% organic sulfur, which is not affected by these bacteria). The cause of the fluctuations in the sulfur content and the dissolved iron in the control tanks is not known, but it is probably due to sulfates dissolving and reprecipitating as the pH shifts

Leaching	Controls		Inoc. 1		Inoc. 2	
time (days)	Fe, g/l	%Py. S	Fe, g/l	%Py. S	Fe, g/l	%Py. S
0	0	2.00	0	2.00	0	2.00
3	0.05	1.83	0.03	2.01	0.03	2.08
6	0.07	1.55	0.11	1.48	0.11	1.55
9	0.07	1.75	0.19	1.55	0.11	1.71
12	0.08	1.86	0.36	0.88	0.31	1.15
15	0.07	1.99	0.40	0.79	0.39	0.91
18	0.07	1.71	0.40	0.60	0.49	0.43
21	0.07	1.71	0.45	0.42	0.45	0.48
24	0.06	1.72	0.46	0.30	0.46	0.28

addition of $HgCl_2$. The columns labeled "Inoc. 1" and "Inoc. 2" are results from duplicate tanks and flasks which were inoculated with bacteria at the beginning of the test. Results are given for a total of 24 tanks and 24 flasks.

Figure 3.2 shows that for the Meigs Creek coal, the pachuca tanks reach the end of the bacterial adaptation phase and begin exponential leaching of the sulfur after eight days, roughly three days before the shake flasks do, and reduce the final sulfur content to a lower level. The initial feed contained 2.0% pyritic sulfur as determined by the ASTM nitric-acid leach method, and 2.8% organic sulfur, and if it is assumed that pyrite is the only form removed then the pachuca tanks removed 90% of the pyritic sulfur in 24 days, while the shake flasks removed only 80% of the pyrite in the same time period. This is likely due to the more thorough mixing and aeration in the pachuca tanks. Both pachuca tanks and shake flasks show similar behavior in the sulfur content of the controls.

The water originally added with the coal and bacteria contained no iron. Therefore, any iron in solution in the slurry must come from the coal. Since the primary source of iron will be from dissolving pyrite, there should be a linear correlation between dissolved iron concentration and pyrite removal. When the calculated pyritic sulfur content of the coal is plotted against the concentration of dissolved iron as shown in Figure 3.3, linear regression gives a best-fit line of

$$Fe = (-0.2686)(P) + 0.5759 \tag{4}$$

where Fe = concentration of dissolved iron in the slurry (gms/l), and
P = pyritic sulfur assay of the coal, calculated by subtracting the 2.8% organic sulfur from the total sulfur measurements.

The correlation coefficient of this line is -0.9771, with a chi-squared value of 0.01949. This shows that there is a strong linear correlation between the amount of pyrite removed and the amount of iron in solution. Measurements of dissolved iron concentration in the slurry can there-

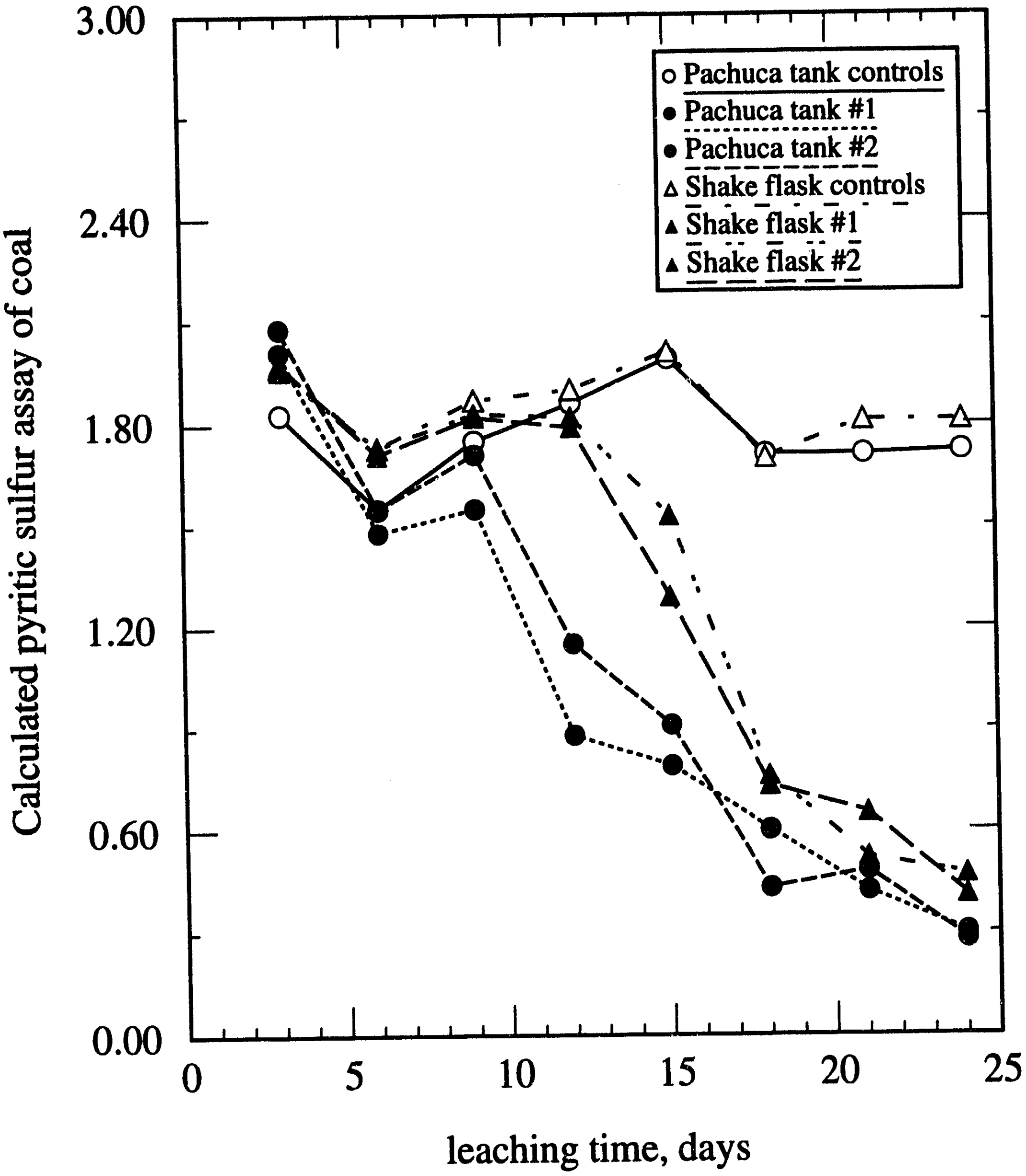


FIGURE 3.2. Leaching results for the Meigs Creek coal. Controls were poisoned with mercuric chloride to kill natural bacteria. Tests with live bacteria were run in duplicate, and each set is plotted separately (so pachuca tank set #2 is a duplicate of pachuca tank set #1). Pyritic sulfur was calculated from total sulfur values by subtracting the organic sulfur content from the total sulfur measurement (the coal contained 2.8% organic sulfur). This shows that the pachuca tanks finish their lag phase and begin leaching approximately three days before the shake flasks do.

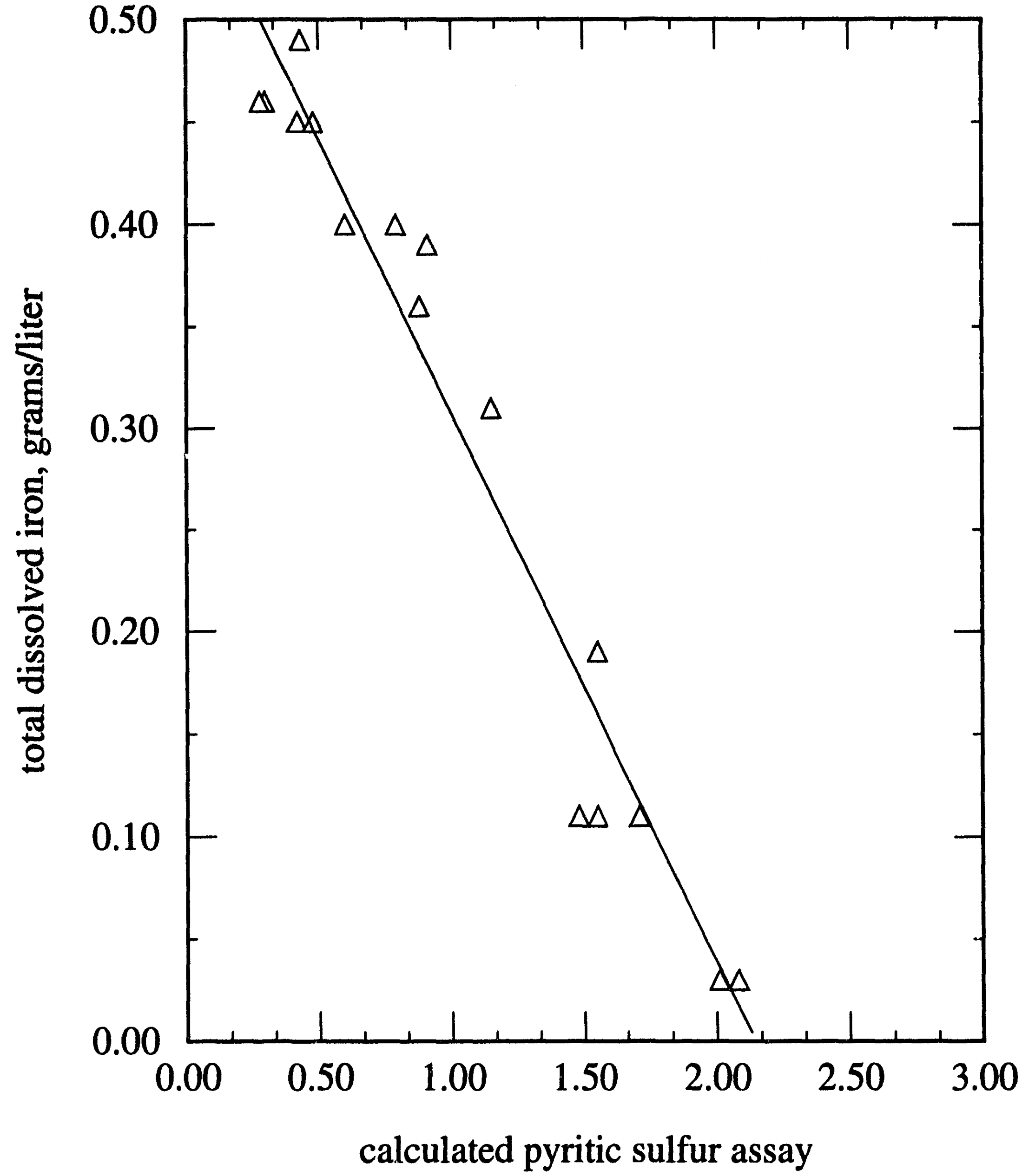


FIGURE 3.3. Correlation of pyritic sulfur remaining in the Meigs Creek coal with the concentration of dissolved iron in the slurry. Linear regression gives the best-fit line shown, (y = (-0.2686)x + 0.5759) with a correlation coefficient of -0.9771 and a chi-squared value of 0.01949. Since the correlation between dissolved iron and sulfur removal is linear, dissolved iron can be used to calculate sulfur removal for a test in progress.

fore be used to estimate the amount of pyrite which has dissolved during a test, without having to stop the test prematurely to do it.

In the subsequent experiment with AEP-Pittsburgh seam coal, using more frequent monitoring of the dissolved iron, it was confirmed that pachuca tank leaching is more rapid and complete than shake-flask leaching. After leaching for 16 days, analysis of the leached coal showed a final sulfur content of 2.05% for the pachuca tanks as compared to 2.50% for the shake flasks, as shown in Table 3.5. The initial sulfur content of this coal was 3.2% sulfur, and 2.24% pyritic sulfur as determined by the ASTM nitric-acid leach method. If the bacteria were only

TABLE 3.5: Leaching results for Pittsburgh seam coal, comparing pachuca tanks and shake flasks. Dissolved iron concentrations were measured photometrically with 1,10 phenanthroline, from 5 ml liquid samples removed from the leaching reactors in the course of the experiment. The initial pH was 1.95 for all. The last lines of this table are the total sulfur content of the coal when it was removed from the reactors after 16 days, as measured by a Leco SC-132 sulfur determinator, and the final pH for each reactor. The initial sulfur content of the coal was 3.2% total sulfur, and 2.24% pyritic sulfur. The intermediate pyritic sulfur levels given are calculated from the dissolved iron concentrations, using the equation: (%pyritic sulfur) = 2.24 -0.53(dissolved iron, g/l) which was calculated from the initial and final sulfur and dissolved iron measurements.

Leaching time (days)	Dissolved Iron Concentration, g/l				Average Calculated Pyritic Sulfur	
	Pachuca tanks		Shake flasks			
	Inoc. 1	Inoc. 2	Inoc. 1	Inoc. 2	Tanks	Flasks
1	0.11	0.11	0.13	0.13	2.18	2.17
2	0.15	0.15	0.17	0.19	2.16	2.15
3	0.08	0.10	0.09	0.10	2.19	2.19
4	0.17	0.17	0.19	0.20	2.15	2.14
6	0.18	0.22	0.24	0.22	2.14	2.12
7	0.19	0.23	0.27	0.28	2.13	2.09
8	0.20	0.33	0.27	0.28	2.10	2.09
9	0.25	0.50	0.28	0.30	2.04	2.09
10	0.54	0.90	0.36	0.34	1.86	2.05
11	0.80	1.00	0.47	0.43	1.76	2.00
12	0.98	1.32	0.58	0.54	1.63	1.94
13	1.40	1.50	0.74	0.62	1.47	1.88
14	1.67	1.73	0.87	0.78	1.34	1.80
15	1.97	2.09	1.00	0.95	1.16	1.72
16	2.30	2.30	1.30	1.15	1.02	1.59
Final %S	2.05	2.08	2.50	2.50	1.06	1.51
Final pH	1.97	1.97	1.96	1.95		

dissolving the pyritic sulfur, then 43% of the pyrite was dissolved in the pachuca tanks while only 23% of the pyrite was dissolved in the shake flasks. Plotting the calculated pyritic sulfur content for this coal in Figure 3.4 shows results similar to those for the Meigs Creek data, with the lag period being shorter for the pachuca tanks than for the shake flasks. The leaching tests with the Pittsburgh seam were started at the same pH as the Meigs Creek tests ended at, and as a result the pH did not change noticeably during the Pittsburgh seam tests. The constant pH seems to have prevented the Pittsburgh coal from showing the early fluctuation in sulfur content and dissolved iron that is seen for the Meigs Creek coal.

Aside from the decrease in the lag period, the pachuca tanks also increase the rate of leaching, as is shown by linear regression in Figure 3.4. The best-fit line for the pachuca tank curve after eight days of leaching had a slope of -0.1436, while the shake-flask results have a slope of only -0.0743. This shows that the shake-flask leaching was about 50% slower than pachuca tank leaching for these conditions.

3.4 CONCLUSIONS

From this work, it was concluded that pachuca tanks do reduce the time needed for leaching coal using the bacteria *Thiobacillus ferrooxidans*. This is due to the improved aeration in air-agitated reactors such as pachuca tanks, as compared to more conventional laboratory apparatus such as shake flasks. However, removal of 90% of the pyrite from the coals tested required 24 days of leaching. Even reducing the 8-9 day adaptation period would still leave a 16 day leaching requirement, which would result in a prohibitive amount of reactor volume in any industrial application. Since the pachuca reactors required three times the target of one week to remove 80% of the pyritic sulfur, it was decided not to pursue bacterial leaching further for this project.

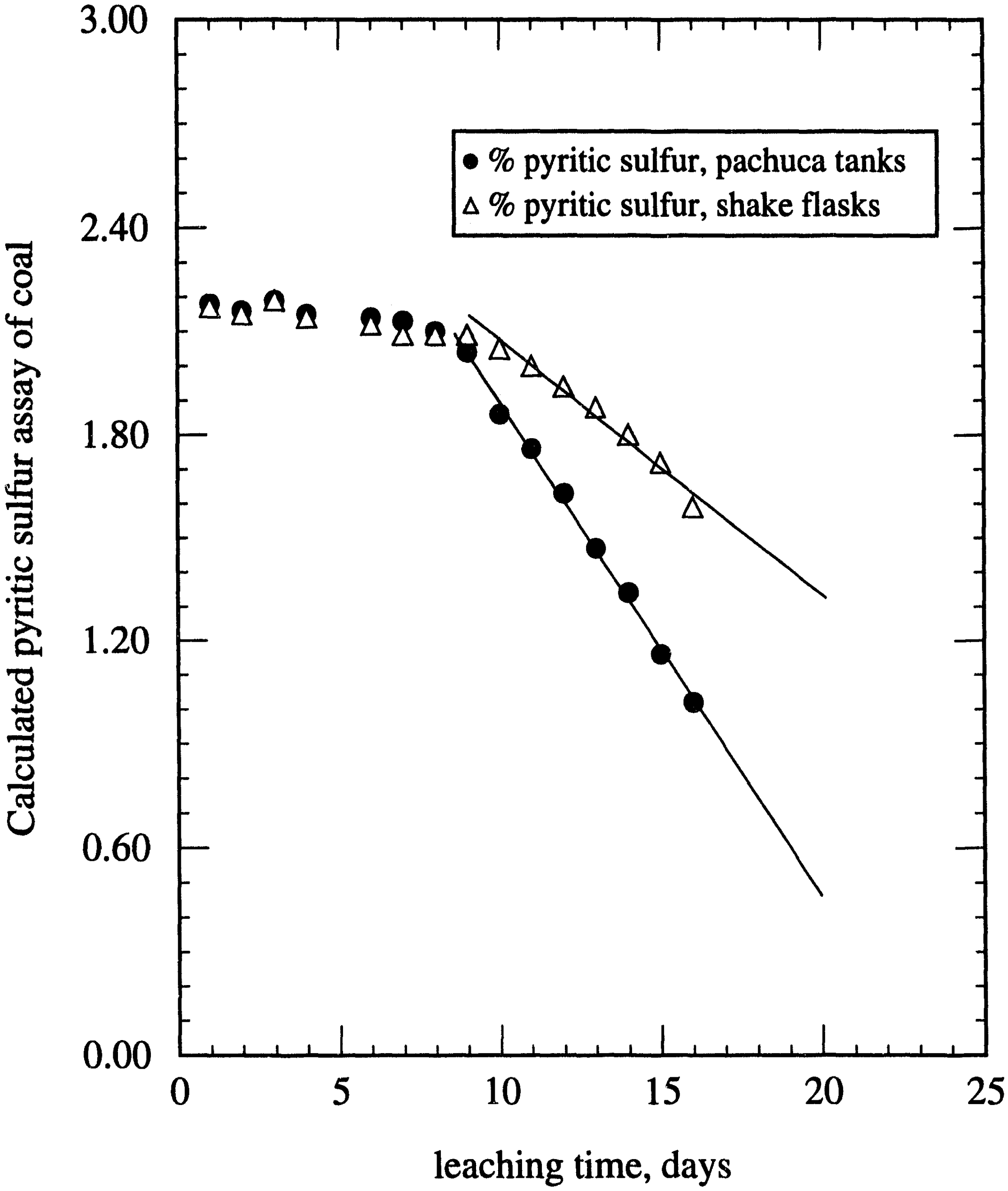


FIGURE 3.4. Calculated pyritic sulfur content of AEP-Pittsburgh seam coal as a function of time. Linear regression was done for both reactor types after the lag phase had passed. Pachuca tanks: y = (-0.1436)x + 3.3296 (correlation coefficient =-0.9984, chi-squared = 0.00266). Shake flasks: y = (-0.0743)x + 2.82 (correlation coefficient = -0.9877, chi-squared = 0.00386) The pachuca tank leaching is therefore almost exactly twice as fast as for the shake flasks in the early part of the leach.

CHAPTER 4: BACTERIAL PYRITE DEPRESSION

4.1 INTRODUCTION

As shown in Chapter 3, the major problem with direct bacterial leaching is the very long leaching times required. Since an industrial application would require a more rapid process in order to keep the needed equipment volume down, it was decided to investigate the possibility of using bacteria as a pyrite depressant in coal flotation. Two independent sets of experiments were conducted. The first set was carried out to replicate experiments conducted by others (Elzeky and Attia, 1987) in order to confirm whether the process actually worked as well as claimed. The second series of experiments was to evaluate a number of microorganisms as pyrite depressants, in order to determine whether pyrite depression would only occur with lithotrophic organisms such as *Thiobacillus ferrooxidans*, or if it could be caused by microorganisms in general.

4.2 THEORETICAL DISCUSSION

The flotation of pyrite from both synthetic coal/pyrite mixtures and high-sulfur coals has been reported to be depressed by *Thiobacillus ferrooxidans* (Elzeky and Attia, 1987; Townsley, Atkins, and Davis, 1987; Atkins, 1990). Elzeky and Attia carried out their experiments by conditioning a synthetic coal/pyrite slurry with bacteria at pH=2, followed by flotation of the coal at pH=7-9. The rationale was that the bacteria, which live best at pH=2, would be most able to attach to pyrite surfaces at this pH, while coal is most floatable at near-neutral pH. Townsley *et al.* conducted both the bacterial contacting and the flotation at a pH near 2 in most experiments, as this is the pH where pyrite flotation by neutral oils is most pronounced. Atkins (1990) and Stainthorpe (1989) have reported that in addition to *T. ferrooxidans*, many other organisms are equally effective for depressing pyrite flotation, as are a number of miscellaneous proteins, such as from whey.

When the pH is higher than about 4, the cell wall of *Thiobacillus ferrooxidans* loses its structural integrity. As a result, these bacteria lyse and die at neutral pH (Bagley, 1987). When these bacteria were used for pyrite depression at near-neutral pH, they were therefore dead and any pyrite depression would have been caused by proteins released by the dying cells rather than attachment of whole cells to the pyrite.

4.3 DEPRESSION OF PYRITE FROM COAL

4.3.1 Experimental Procedure

4.3.1.1 Preliminary tests: Preliminary experiments were carried out in a conventional flotation machine, using a procedure reported by Elzeky and Attia (1987) to be effective for depressing coal-pyrite flotation. The bacteria used was a *Thiobacillus ferrooxidans* strain obtained from EG&G Idaho. Flotation was carried out in a conventional 1.9 liter Denver flotation cell. The coal used for these conventional experiments was the Quarto-4 coal, which was mined from the Pittsburgh seam in Ohio. This coal contained 13.6% ash, 3.9% total sulfur, and 2.5% pyritic sulfur. The coal was riffled into 100 gram charges, which were rod-milled in 150 ml of tap water for 5 minutes to give a size distribution of approximately 80% passing 150 mesh. The pulp was then diluted to 1.65 liters with tap water (approximately 150 ppm hardness); the pH was adjusted to 2.5; 250 ml of either 9K basal salts or bacteria suspended in the 9K growth media which they had been cultured in were added; and the pulp was conditioned for 30 minutes. The *Thiobacillus* culture had a cell concentration of 2.6×10^8 cells/ml. After conditioning the pH was raised to 8.5 with sodium hydroxide, the slurry was conditioned with collector and frother for 3 minutes, and the coal was floated for 3 minutes. The reagents used were Dowfroth 250 (0.2 kg/mt) and #2 fuel oil (as noted in Table 4.1).

4.3.1.2 Long-term bacterial contacting: The next experiments were conducted with a different coal, using longer bacterial contact times. Additional, related experiments are given in Appendix 6. These tests used Meigs Creek seam coal, ground to 80% passing 92 micrometers (the complete size distribution has been given earlier, in Table 3.1). The coal was contacted with bacteria in pachuca tanks at 26% solids and a pH of 2.1 in Tuovinen and Kelly basal salts. Bacteria were added as a suspension of 2×10^8 cells/ml in Tuovinen and Kelly media (with dissolved iron), providing 7.5×10^7 cells/gram coal. The coal/bacteria mixture was agitated in the pachuca tanks for periods of 2, 23, 47, 70, 94, and 118 hours, with bacteria-free controls also run for 2 and 118 hours. After pachuca tank treatment, the coal from each tank was filtered, divided into a head sample and three 100 gram flotation charges. Each charge was resuspended in tap water in a 1.9 liter Denver flotation cell and conditioned for 3 minutes with MIBC as frother (0.3 kg/mt) and #2 fuel oil as collector (0.22, 0.43, and 0.86 kg/mt for each set of three charges) and floated for 3 minutes. Flotation was carried out at natural pH for the resuspended coal, which was between 5.5 and 6.0 for each test.

4.3.2 Experimental Results

The preliminary experiments with Quarto-4 coal showed no significant difference between flotation with and without bacteria, as shown in Table 4.1, below.

TABLE 4.1: Conventional flotation results in the presence and absence of *T. ferrooxidans,* at varying collector dosages. Coal was from the Quarto-4 mine (see Appendix 7), the collector was #2 fuel oil, and the frother was Dowfroth 250 (0.2 kg/mt). The coal was conditioned with bacteria for 30 minutes at pH=2 to give the bacteria the opportunity to attach to the pyrite. This was followed by flotation at pH=8-9, which is the pH range where coals are typically most floatable. The coal was 80% passing 150 mesh, and 100 gram flotation charges were used, giving 5% solids.

No Bacteria Added			Bacteria Added		
collector	%wt	%S	collector	%wt	%S
0.5 kg/mt	71.4	3.40	0.5 kg/mt	72.1	3.43
0.75 kg/mt	72.1	3.46	0.75 kg/mt	71.6	3.44
1.0 kg/mt	72.1	3.43	1.0 kg/mt	72.3	3.52
1.5 kg/mt	74.0	3.49	1.5 kg/mt	73.7	3.52

These results were surprising, since not only were bacteria expected to depress pyrite, but Fe had also been reported to be a strong pyrite depressant at this pH (Baker and Miller, 1971) and the 9K growth media contained a great deal of dissolved iron. Yet, not only were the bacteria not reducing pyrite flotation, but the large quantity of Fe^{+3} dissolved in the nutrient medium had no effect on the pyrite either. Since many investigators have reported true flotation of pyrite to be a problem in coal flotation, the lack of effect from these reported depressants required further investigation.

The second set of experiments, using the Meigs Creek coal and pachuca tanks for the bacterial contact phase, was intended to determine whether a different coal and longer contact time would show significant pyrite depression by bacteria. The frother was switched to MIBC because it was possible that the DF250, which is a strong frother, might have been somehow cancelling the depressant. Since the natural pH for the resuspended Meigs Creek filter cake was between 5.5 and 6, tests were run at this pH so that there would be less chance that the pH modifier was acting as a depressant. These results are given in Table 4.2, and show that even after 118 hours of leaching the froth sulfur contents were not significantly different between the tanks containing bacteria and the bacteria-free controls, in spite of the fact that the sulfur content of the head samples dropped from 4.8% sulfur down to 4.5% sulfur. This shows that the bacteria are not particularly effective pyrite depressants in the pH range of 5-9 for either of the coals tested.

4.4 BACTERIAL DEPRESSION OF PURE PYRITE FLOTATION

4.4.1 Experimental Procedure

4.4.1.1 Microflotation tests:

Initial pyrite flotation experiments were carried out using pure mineral pyrite mined in Rico, Colorado (see Appendix 7 for details), which was obtained from Wards Natural Science Establishment. This pyrite was stage ground (dry) in a stainless steel rod mill and sized to 150 by 200 mesh. Five gram charges were floated in a 100 milliliter pyrex flotation cell, using fuel oil as a collector and methyl isobutyl carbinol (MIBC) as a frother, and air added at a rate of 100 ml/second. MIBC was used to keep the froth from being excessively voluminous, as stronger frothers such as DF 250 tended to cause most of the liquid in the cell to report to the froth, and made the microflotation cell difficult to use. The pH was adjusted with 1.0 N H_2SO_4 to pH = 2. Tests were not carried out at neutral pH, as the pyrite used was only floatable at acid pH (this is shown by the results in Appendix 7, and this phenomenon is pursued in more detail in Chapter 5). Each test used 80 ml of bacteria suspended in distilled water with 5 grams of pyrite, giving 5.88 wt.% solids. The microorganisms used are listed in Table 4.3, and were selected to cover a wide range of microbial properties (Van Loosdrecht *et al.*, 1987). The flotation tests used pyrite which had been freshly ground and stored in sealed plastic bags at -15°C until use.

Bacteria were grown in appropriate culture media, and were washed and rinsed by centrifuging 20 minutes at 15,000 gravities and resuspended in distilled water at 4°C. Following the second rinse the cells were diluted to 2×10^8 cells/ml, based on cell counts using a Petroff-Hauser counting chamber under a phase-contrast microscope at 400x magnification. Since the *Thiobacillus* strains lyse due to breakdown of their cell walls if the pH is much higher than 4, the washwater for these bacteria was adjusted to pH = 2 with sulfuric acid.

Before floating, the Rico pyrite charges were mixed with 80 ml of bacterial suspension, which had been adjusted to pH = 2, for 15 minutes. Controls were mixed with pH = 2 distilled water for the same length of time. Each charge was then conditioned for an additional minute with 0.005 ml (0.86 kg/mt) of #1-1/2 fuel oil and 0.003 ml (0.60 kg/mt) of MIBC, and floated for one minute. The flotation products were then dried at 75°C, weighed, and the percent of the total pyrite reporting to the froth was calculated, with the results as given in Table 4.3.

TABLE 4.2: Flotation results for Meigs Creek Coal after various periods of bacterial treatment in pachuca tanks. The feeds for the control tests were also treated in pachuca tanks, but without any bacteria added. The pachuca tank treatment was at pH=2, and flotation was in the pH range of 5.5-6. The frother was MIBC (0.3 kg/mt) and the collector was #2 fuel oil. The coal was 80% passing 92 micrometers, and 100 gram flotation charges were used, giving 5% solids.

Contact time (hours)	Collector (Kg/mt)	Froth % weight	Froth % ash	% ash rejection	Froth % sulfur	%Sulfur rejection
2 (control)	0.22	72.8	9.8	56.5	4.3	31.9
	0.43	78.8	10.0	52.1	4.2	28.1
	0.86	86.9	10.9	43.4	4.3	18.6
2	0.22	75.8	9.8	54.0	4.3	28.6
	0.43	83.6	10.2	45.6	4.3	21.8
	0.86	87.8	11.0	40.0	4.4	16.8
23	0.22	56.8	9.2	66.9	4.4	49.6
	0.43	76.4	9.4	54.5	4.2	28.0
	0.86	85.5	9.7	46.1	4.2	18.7
47	0.22	58.6	9.4	65.4	4.2	45.7
	0.43	71.4	9.5	57.3	4.3	34.3
	0.86	84.7	10.1	46.5	4.3	19.3
70	0.22	57.4	9.6	65.8	4.3	49.6
	0.43	75.4	10.1	53.2	4.3	31.6
	0.86	85.6	10.1	45.8	4.2	17.8
94	0.22	53.4	9.2	68.0	4.1	50.5
	0.43	75.2	9.5	54.6	4.2	28.6
	0.86	82.8	10.3	46.9	4.3	23.3
118	0.22	57.9	9.7	65.0	4.2	47.4
	0.43	76.4	10.0	52.7	4.3	28.3
	0.86	85.4	10.2	46.0	4.2	17.7
118 (control)	0.22	64.1	9.8	59.9	4.2	40.9
	0.43	73.0	9.8	54.8	4.2	31.4
	0.86	84.6	10.2	45.8	4.2	20.4

4.4.1.2 Larger-Scale Flotation: Since microflotation results frequently are quite variable, a second series of experiments was conducted using larger sample sizes and a 1.9 liter Denver flotation cell, and using distilled water rather than tap water. These tests used the Rico pyrite (30 gram charges), AEP-Pittsburgh seam coal (150 gram charges), and a synthetic coal/pyrite mixture (30 grams Rico pyrite, and 150 grams Pittsburgh coal). The Rico pyrite was prepared by rod-milling 120 grams of pyrite (approximately 80% passing 65 mesh) in 500 ml water for 5 minutes, filtering, and dividing into quarters. The coal was prepared by grinding 300 grams of -20 mesh

TABLE 4.3: Results of pyrite flotation with various microorganisms at pH = 2. Tests were run in triplicate, and the results averaged. The range of uncertainty is equal to the difference between the highest and lowest values for each test set.
Bacteria Dosage: $3.2\text{x}10^9$ cells/gram
Feed: Rico pyrite, 5 grams, 150x200 mesh
Flotation cell working volume: 80 ml
Air flowrate: 100 cc/sec.
Frother: MIBC, 0.60 kg/mt
Collector: #1-1/2 fuel oil, 0.86 kg/mt
Percent solids: 5.88%
Temperature: 25°C

Organisms	Source	Percentage of pyrite reporting to froth
Pseudomonas fluorescens	MTU stock culture	2.0 0.25
Lactobacillus acidophilus	MTU stock culture	2.4 1.4
Staphylococcus epidermis	MTU stock culture	2.3 0.6
Klebsiella terrigena	MTU stock culture	4.4 0.4
Saccharomyces cerevisiae	MTU stock culture	1.8 0.02
Thiobacillus ferrooxidans	EG&G Idaho, Culture	9.4 1.8
T. ferrooxidans strain Pa-1	Pyrite-adapted strain derived from DSM-83	39.9 2.7
Distilled water controls		76.5 2.5

coal in 500 ml water for five minutes, filtering, and dividing in half. The synthetic mixture was prepared by grinding 360 grams (300 grams coal and 60 grams pyrite) in 500 ml water for five minutes, filtering, and dividing in half.

Three species of bacteria were used in these experiments: *Thiobacillus ferrooxidans*, *Pseudomonas fluorescens*, and *Klebsiella terrigena*. The *P. fluorescens* was chosen because it was one of the most effective organisms in the microflotation tests, the *T.ferrooxidans* was chosen because it was the organism which was widely reported as a depressant in the literature, and the K. terrigena was selected because it was intermediate between the two other organisms. A series of control experiments with no bacteria were also run for comparison purposes. The bacteria were prepared as for the microflotation tests, and 500 ml of suspension was used for each test. The samples were adjusted to the desired pH, and conditioned with the bacteria for 5 minutes. The collector was then added, the sample was conditioned for an additional 2.5 minutes, frother was added and conditioned for 0.5 minutes, and the sample was then floated for 2 minutes. Each test used 0.1 ml of #2 fuel oil and 0.05 ml of MIBC, which corresponds to dosages of 0.57 and 0.33 kg/mt respectively for the AEP-Pittsburgh coal, 0.48 and 0.28 kg/mt for the synthetic mixture, and 2.87 and 1.67kg/mt for the Rico pyrite. The tests were conducted at pH=6 for the coal and synthetic mixture tests and at pH=2 for the pyrite alone, since these are the pH levels where each was found to be most floatable. The results are given in Table 4.4.

TABLE 4.4: Results of larger-scale flotation experiments with three microorganisms, using Pittsburgh coal, Rico pyrite, and synthetic mixtures of the two. The values given are for the froth products. The reagents were #2 fuel oil and MIBC. Coal is AEP-Pittsburgh coal (150 gram charges, 7.3% solids, fuel oil 0.57 kg/mt, MIBC 0.33 kg/mt), Pyrite is Rico pyrite (30 gram charges, 1.6% solids, fuel oil 2.87 kg/mt, MIBC 1.67 kg/mt), and Mix is a synthetic mixture of the two (150 grams coal + 30 grams pyrite, 8.6% solids, fuel oil 0.48 kg/mt, MIBC 0.28 kg/mt)

Material	Klebsiella		Pseudomonas		Thiobacillus		Control	
	%wt	%S	%wt	%S	%wt	%S	%wt	%S
Coal, pH=6	68.84	3.15	67.64	2.96	66.38	2.75	67.54	3.10
Coal, pH=6	69.43	3.28	62.57	2.85	65.06	2.78	63.77	2.85
Mix, pH=6	60.03	3.62	54.19	3.16	55.85	3.15	53.26	3.16
Mix, pH=6	56.24	3.76	54.94	3.21	54.62	3.19	56.23	3.28
Pyrite, pH=2	4.96		12.97		55.38		45.25	
Pyrite, pH=2	9.70		10.06		64.67		38.31	

4.4.1.3 Comparison of Mineral and Coal Pyrite Flotation: This series of tests used two pyrites, which had each been stage-ground to 150x200 mesh in a dry rod mill. The mineral pyrite used was from Custer, South Dakota (Custer-2, purchased from Ward's Natural Science Establishment, see Appendix 7) rather than the Rico pyrite, because the Rico pyrite was no longer available from Ward's. The coal pyrite (Empire pyrite, see Appendix 7) was collected as sulfur balls (large nodules of pyrite) from the jig tailings at the Empire Coal Mine, Gnadenhutten, Ohio. The size of 150x200 mesh was selected so the results would be comparable to the microflotation tests, and to keep entrainment low. Each test used 150 gram charges, suspended in 1.9 liters of distilled water. The machine used was a Denver laboratory flotation machine, running at 1500 rpm.

The flotation procedure was as follows:

1. suspend 150 grams pyrite in sufficient distilled water so that when the bacteria were added, the total liquid volume was 1.9 liters, adjust to the desired pH with either H_2SO_4 or NaOH.
2. add the desired microorganism, and condition for 10 minutes. The water temperature was 20°C.
3. add #2 fuel oil (3.0 kg/mt) and condition 2 minutes
4. add 15 ml of a 0.2% solution of MIBC (0.2 kg/mt) and condition for 30 seconds
5. float for 5 minutes, scraping froth by hand.

The microorganisms used were *Thiobacillus ferrooxidans* and *Saccharomyces cerevisiae.* The *S. cerevisiae* was selected for these tests because it was the most effective organism in the microflotation tests, and because it was more readily available in a standard form than any other microorganism. The *T. ferrooxidans* was added along with the T&K media that it had been grown in, at a cell concentration of 3.4x10 cells/ml. The *S. cerevisiae* was added as dry active cells (Red Star® All-Natural Baker's Yeast) which were weighed dry before addition to the flotation cell. Tests were conducted at pH values ranging from 2 to 11 with both pyrites, and results are given in Table 4.5.

TABLE 4.5: Flotation results for the Custer-2 mineral pyrite and the Empire coal pyrite, which were stage-ground to 150x200 mesh for these tests (the 150x200 mesh Empire pyrite contained 69.8% pyrite, and the 150x200 mesh Custer-2 pyrite contained 52.4% pyrite, as determined by Hydrochloric acid and Nitric acid leaching).
Flotation conditions were:
Sample weight: 150 grams
Cell volume: 1.9 liters
Percent Solids: 7.3%
Water: distilled
Collector: #2 fuel oil, 3.0 kg/mt
Frother: MIBC, 0.2 kg/mt
Impeller speed: 1500 rpm, Denver machine

Pyrite	Microorganism	pH	%wt yield (recovery)	%Pyrite	%Py.Recovery
Empire	None	2.15	25.95	66.9	22.03
Empire	*S.cer.*, 13.3kg/mt	2.2	16.06	54.2	11.16
Empire	None	6.0	66.18	77.0	66.29
Empire	*S.cer.*, 13.3kg/mt	6.05	44.03	72.7	41.90
Empire	None	12.3	20.14	66.8	17.96
Empire	*S.cer.*, 13.3kg/mt	12.3	9.93	49.1	6.57
Custer	None	2.2	64.5	85.4	100.0
Custer	*S.cer.*, 13.3kg/mt	2.15	3.4	31.9	1.9
Custer	*S.cer.*, 6.6 kg/mt	2.1	4.1	47.2	3.6
Custer	*S.cer.*, 3.3 kg/mt	2.22	40.9	81.6	61.6
Custer	*T.fer.*, 1500 ml	2.15	57.2	86.5	99.6
Custer	*T.fer.*, 500 ml	2.4	60.3	83.4	100.0
Custer	None	6.3	4.1	40.6	3.0
Custer	*S.cer.*, 13.3 kg/mt	6.2	3.3	26.0	1.7
Custer	None	11.8	4.2	25.9	2.1
Custer	S.cer., 13.3 kg/mt	11.8	9.4	65.2	11.8

S. cer. = *Saccharomyces cerevisiae*, added as dry active yeast

T. fer. = *Thiobacillus ferrooxidans*, added as a suspension of 3.4x10^8 cells/ml in T&K growth media. 1500 ml is approximately 3.3 kg/mt, and 500 ml is approximately 1.1 kg/mt (dry cell wt.)

4.4.2 Results and Discussion

From the microflotation results (Table 4.3), it is immediately obvious that all of the microbes evaluated are capable of effectively preventing the flotation of pure Rico mineral pyrite. This indicates that pyrite depression is a general property of microorganisms, and not a specific action of lithotrophic bacteria such as *Thiobacillus ferrooxidans*. Indeed, when the pyrite surface is completely fresh and unoxidized, *T. ferrooxidans* strains are the least effective of the microbes tested, and pyrite-adapted *T. ferrooxidans* is even less effective than the parent strain.

In the results for the larger-scale flotation experiments with coal, pyrite, and synthetic mixtures of the two (given in Table 4.4), the results are not nearly as clear-cut. While the *Klebsiella* is the most effective for depressing pure Rico pyrite at pH=2, it appears to increase the sulfur content for both the AEP-Pittsburgh coal and the synthetic coal/pyrite mixture at pH=6. The *Pseudomonas* is not quite as effective for depressing the pure pyrite, and seems to have no effect one way or the other on the coal and synthetic mixture. Finally, the *Thiobacillus* is completely ineffective for depressing the pure pyrite, but gives a slightly lower sulfur content for the coal and synthetic mixture.Unfortunately, the variation between duplicate tests with the coal and synthetic mixture is nearly as large as the differences between the control tests and the tests with the various bacteria, so it is difficult to say for certain whether the *Thiobacillus* was actually improving the sulfur removal for the coal. Any benefit from the bacteria at this pH is small, in any event.

The larger-scale flotation results for the 150 x 200 mesh Empire and Custer-2 pyrites are listed in Table 4.5. The goal of these experiments was to determine two things; how much coal pyrite differed from mineral pyrite in its pH dependency, and whether microorganisms have any effect on the floatability of pyrite at neutral or high pH. Figure 4.1 shows the effect of changing pH and adding microorganisms on the flotation of the Custer-2 pyrite. Most obviously, this pyrite loses its floatability almost completely when the pH is higher than about 4-5. At pH=2, the pyrite is strongly floatable, with the flotation tailings composed mainly of silicate and oxide impurities in the original pyrite. Adding the *T. ferrooxidans* culture to the cell had no noticeable effect on the pyrite flotation at any pH, probably because the cell concentration was not very high. The *S. cerevisiae* weakly depressed the acid flotation of Custer-2 pyrite at a dosage of 3.33 kg/mt, and strongly depressed the flotation at 6.67 kg/mt or higher. The yeast did not have any large effect on the pyrite at neutral or alkaline pH, for the obvious reason that the pyrite was not floating in the first place. The slight increase in the pyrite recovery from adding *S. cerevisiae* to alkaline pulp was because the yeast was a weak foaming agent in alkaline solution.

Figure 4.2 shows that the Empire coal pyrite behaved completely differently from the Custer-2 mineral pyrite. The Empire pyrite was most floatable at near-neutral pH, with much lower floatability in acid and alkaline solution. This is the type of flotation behavior which is expected from coal, implying that the attached coal is making the pyrite float and not the other way around. When *S. cerevisiae* was added, the total weight % yield (recovery) was depressed at all pH levels. When the products were assayed for pyrite (material which is soluble in nitric acid but not in hydrochloric acid), and the pyrite recovery at varying pH was plotted, it was found that the relationship of pyrite recovery to total weight % yield was unchanged by the yeast. If the yeast was a selective pyrite depressant, then the pyrite recovery should have decreased more than the total weight % yield decreased. Since it did not, then either the yeast unselectively depresses both coal and pyrite, or the coal pyrite was floating because of attached floatable coal. This is further shown by the grade-recovery curve of Figure 4.3, where the tests with and without yeast both follow approximately the same curve.

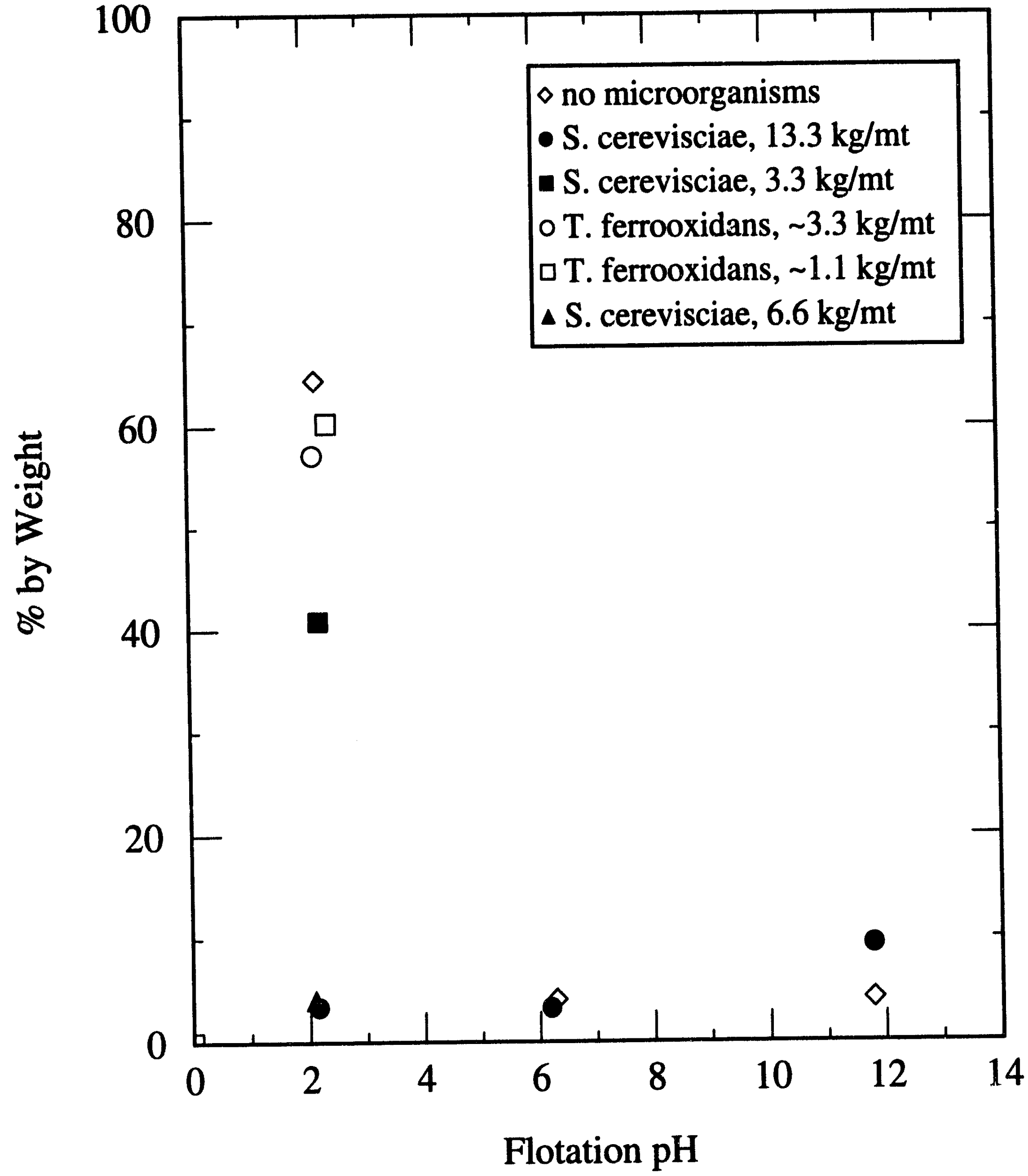


FIGURE 4.1. Flotation of 150x200 mesh Custer-2 pyrite in Denver flotation cell, over a wide pH range, with two different microorganisms added. The Thiobacillus dosage is only approximate, as it was calculated from the cell counts in the culture media. The flotation of the pyrite is extremely pH dependent, and yeast must be added at a rather high dosage to depress its flotation at acid pH. The slight increase in pyrite recovery with yeast at pH=12 is due to the yeast being a weak foaming agent at this pH. At acid pH, high microorganism dosages will depress pyrite, but not at high pH. Test temp. was 20 °C

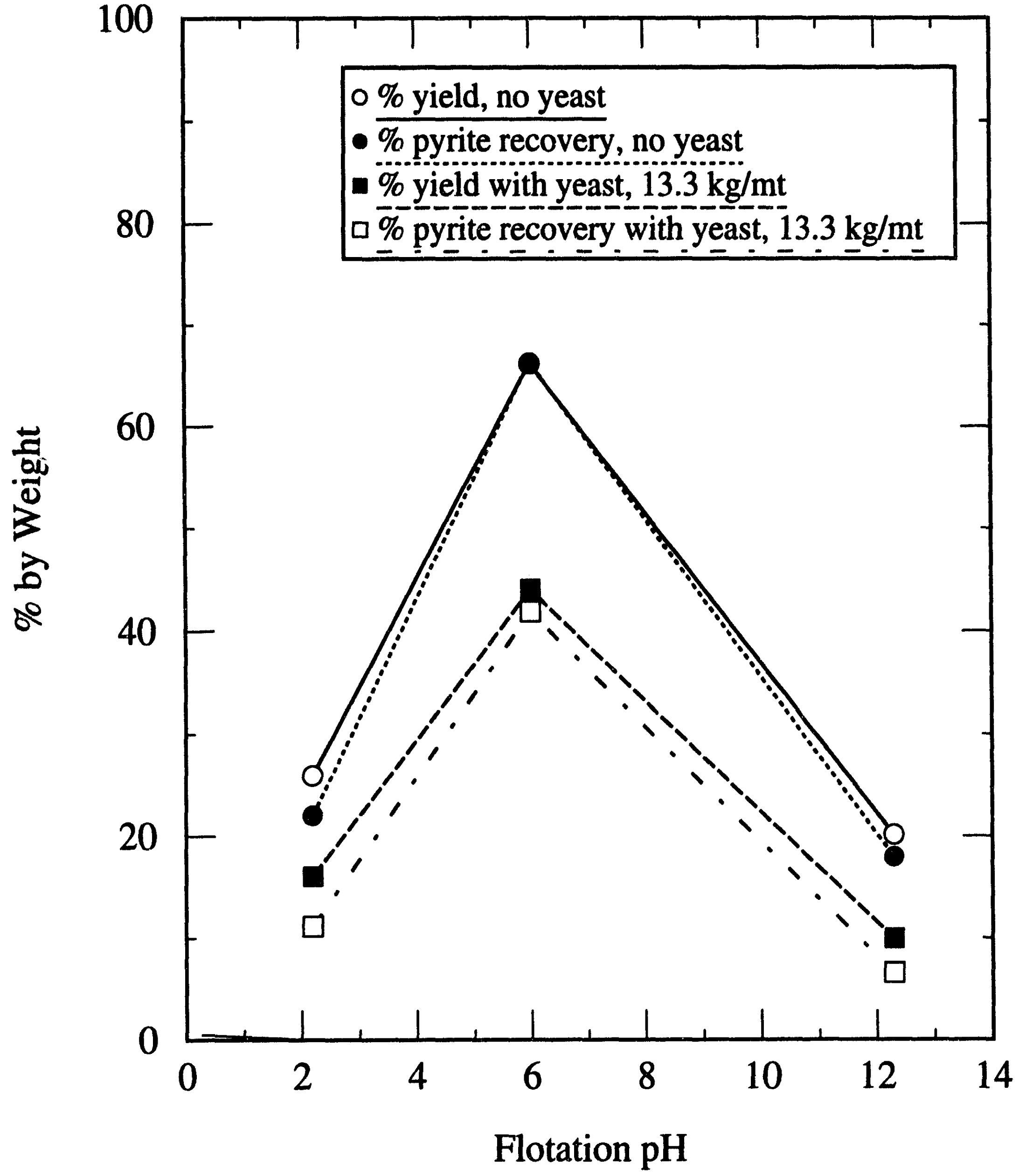


FIGURE 4.2. Flotation of 150x200 mesh Empire coal-pyrite in the Denver flotation cell, over a wide pH range, with and without added yeast. While the yeast does depress the weight % yield (recovery) of the coal-pyrite to the froth, the pyrite is not being significantly more depressed than the bulk material (much of which is coal). This indicates that the yeast is probably a general flotation depressant, and not a selective pyrite depressant.

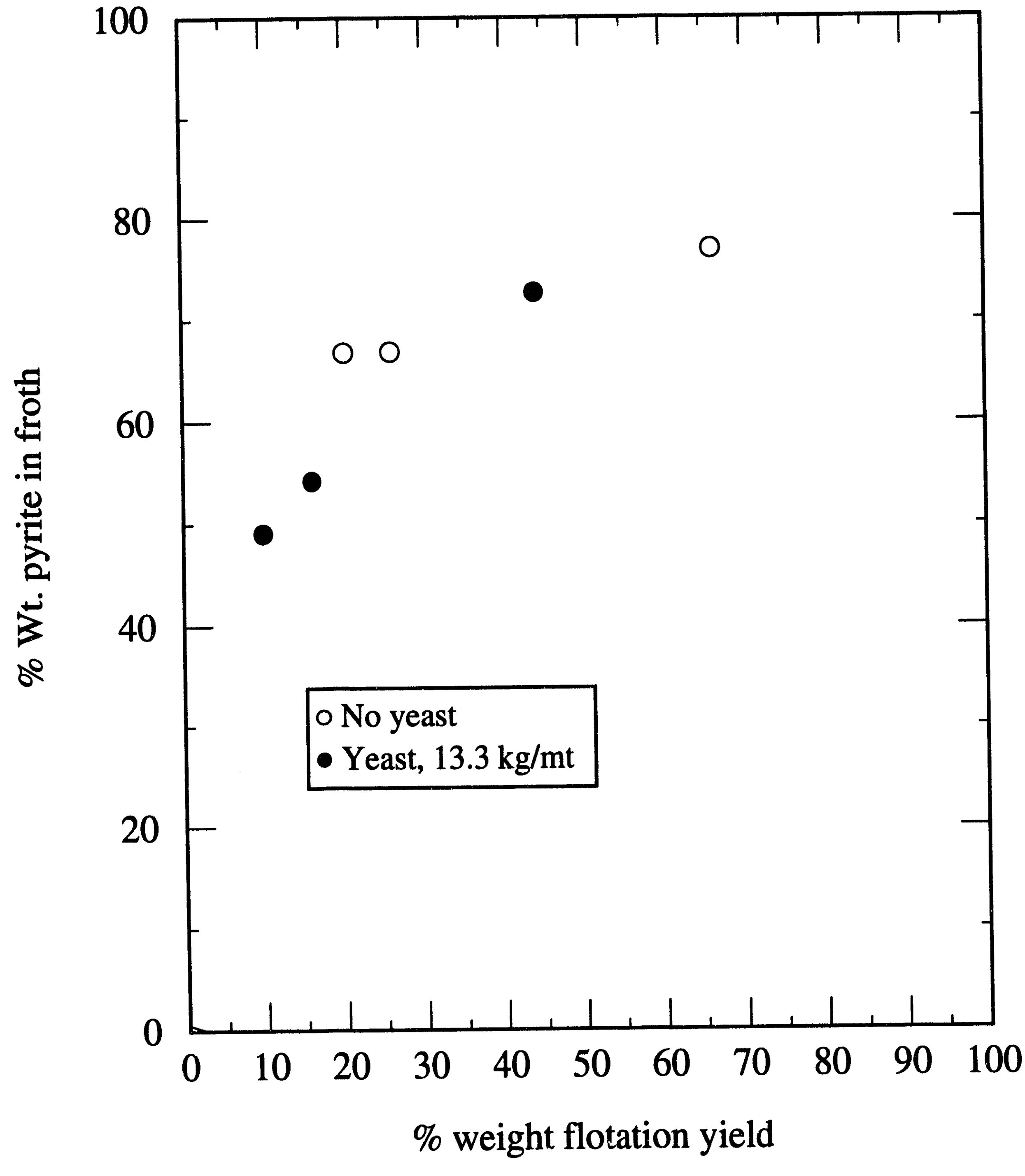


FIGURE 4.3. Grade-recovery curve for the 150x200 mesh Empire pyrite, with and without yeast added. The lack of a clear separation between the curves for flotation with and without yeast indicates that the yeast was not selectively depressing pyrite, but instead was uniformly depressing all of the floatable material.

4.5 CONCLUSIONS

From the attempt to replicate the results of other researchers, it was found that bacteria do not necessarily depress pyrite flotation for all coals, as the coals tested showed no change in froth sulfur content regardless of whether bacteria were present. However, it was not certain whether this was due to the bacteria not being active, or to there being no floatable pyrite available in the coal to be depressed. Microflotation experiments with pure pyrite showed that all of the microorganisms tested were effective for depressing pyrite flotation, and that the strains of *Thiobacillus ferrooxidans* tested were actually the least effective for this purpose. Larger-scale experiments with pure pyrite, coal, and synthetic mixtures of the two confirmed that at pH=2, the non-*Thiobacillus* organisms were more effective pyrite depressants than the *Thiobacillus*. However, this behavior may have reversed at higher pH, with the *Thiobacillus* apparently producing a small reduction in the froth sulfur content for the coal. This is consistent with the hypothesis that it is the proteins released by dying cells that produces the pyrite depression, and not the action of living cells. At pH=2, *Thiobacillus* thrives, but other organisms die, and it is the other organisms which are the most effective pyrite depressants at this pH. At pH=6, *Thiobacillus* will die while the other organisms survive, and at this pH the *Thiobacillus* appear to be producing a small amount of pyrite depression while the other organisms do not.

While bacteria were effective for depressing mineral pyrite at pH=2, tests with Custer-2 mineral pyrite showed no major effect of bacteria on pyrite flotation when the pH was near neutral or alkaline. The most likely explanation for this is that at near-neutral pH, the pyrite in the coals tested was not significantly floatable in the first place. Experiments with the Empire coal pyrite did show significant floatability at neutral pH, with the yeast depressing this flotation. However, the pyrite appeared to be floating because of locked coal particles, not because the pyrite was hydrophobic.

CHAPTER 5: INHERENT FLOATABILITY OF PYRITE

5.1 INTRODUCTION

These experiments were intended to determine the conditions under which finely-ground pyrite is floatable by a neutral oil collector such as #2 fuel oil. This was made necessary by the observation that pyrite did not appear to be significantly floatable at the pH levels where coal flotation is normally carried out, and it was beginning to appear that true flotation of pyrite might not be as major of a problem in froth flotation as had been believed. These tests also compared two different mineral pyrites to two different coal pyrites to determine whether mineral pyrite is at all suitable as a model for coal pyrite.

5.2 THEORETICAL DISCUSSION

Over the years there has been considerable controversy over whether pyrite is naturally hydrophobic (Kocabag et al, 1990). Apparently, pyrite is very near the borderline between hydrophobic and hydrophilic behavior, and as result small changes in the surface chemistry can easily push it one way or the other. One hypothesis is that pyrite becomes hydrophobic when conditions are right to form elemental sulfur on its surface, and that floatability is highest in acid solution, although the degree of pH dependence varies from coal to coal (Townsley et al, 1987; Kocabag et al, 1990). Determining exactly what is happening on the pyrite surface is further complicated by the complex chemistry of sulfur (Greenwood and Earnshaw, 1984), which makes it difficult to be certain what chemical species are actually present under a given set of conditions. It is also generally accepted that the properties of coal pyrite are very different from the properties of pyrites from other sources (Lyon, 1969).

5.3 EXPERIMENTAL PROCEDURE

Relatively pure pyrites from four sources were used: mineral pyrites from Custer, SD, and Rico, CO, purchased from Ward's Natural Science Establishment; and coal pyrites collected as sulfur balls from Panther Valley, PA (anthracite), and Empire Coal, OH (bituminous) (see Appendix 7 for details). The Custer pyrite was purchased in two lots (Custer-1 and Custer-2), and while Custer-1 was essentially pure pyrite, Custer-2 contained a great deal of impurities, mostly silicates and carbonates. These pyrites were ground to the size distributions given in Table 5.1, using a steel rod mill, at 37.5% solids and a pH adjusted to 12 with NaOH to prevent corrosion and subsequent dissolution of iron, which is reported to be a pyrite depressant (Baker and Miller,1971). The pyrite was then filtered, divided into charges of the desired weight, repulped in a Denver laboratory flotation cell (volume of 1.9 liters), and the pH was adjusted to the desired level with sulfuric acid. The noted quantities of #2 fuel oil were then added, and the pulp conditioned for 2 minutes. Finally, 0.03 gm MIBC/liter (0.38 kg/mt) was added as frother, the pulp was conditioned for an additional 30 seconds, and floated for 5 minutes at an impeller speed of 1500 rpm with froth removed manually.

5.4 EXPERIMENTAL RESULTS

The results of these experiments are given in Table 5.2. The pH values were selected on the basis of earlier tests, which showed that mineral pyrite floats well below pH=4, and poorly at higher pH values.

TABLE 5.1: Size distributions for the samples used in the pyrite flotation experiments, determined by Microtrac particle size analyzer. The pyrites were stage-crushed to pass 20 mesh and divided into 300 gram charges. Each charge was rod-milled with 450 ml distilled water and 50 ml of 1 N sodium hydroxide solution for 30 minutes, and filtered.

	Cumulative weight% passing			
Size, µm	Rico	Custer-2	Panther Valley	Empire
62	100.0	98.1	100.0	99.8
44	97.4	92.5	100.0	98.5
31	88.3	81.2	97.3	94.5
22	73.5	66.7	89.6	87.6
16	56.5	50.7	75.8	75.2
11	42.2	37.3	59.6	59.7
7.8	31.7	28.8	45.2	45.8
5.5	23.0	21.6	32.7	33.7
3.9	16.1	11.4	22.1	18.5
2.8	10.0	10.1	13.1	15.9
1.9	4.3	10.1	5.4	15.9
1.4	1.8	6.8	2.2	10.4
0.9	0.3	2.9	0.4	4.3

The mineral pyrites strongly buffered the pH at pH = 4, consuming approximately 3 grams sulfuric acid per kilogram of pyrite to reduce pH below this level. As a result, intermediate pH values were difficult to achieve. Upon lowering the pH below 4, the pyrite became strongly floatable, simultaneously releasing a strong odor of H_2S.

Unlike the two mineral pyrites, the two coal pyrites never became as strongly floatable at acid pH, and their floatability did not decrease as sharply as the pH was raised. The coal pyrites also never released the characteristic H_2S odor in acid solution. A froth product from the Empire coal pyrite was mounted, polished, and examined at 500x magnification, and was found to be predominantly locked coal/pyrite particles, as shown in the photomicrographs of Figure 5.1. This is supported by Figure 5.2, which shows the dependence of total weight % yield, pyrite recovery, and froth pyrite assay on pH for the Empire coal pyrite. The pyrite content of the froth was slightly higher at acid pH than at alkaline pH, but the change was much smaller than the change in the total weight % yield. Likewise, the pyrite recovery followed the total recovery extremely closely. If the pyrite surfaces were hydrophobic, pyrite should have had a higher recovery than the total weight % yield at low pH, then have become lower than the total weight % yield as the pH was raised. Since this did not happen, the best explanation is that the pyrite was floating mainly because it was locked with floatable coal particles, with a smaller amount of hydrophobic pyrite being present at acid pH.

Some time after the experiments were originally done, it was decided to repeat selected experiments in order to confirm the original results. The pyrite used was the Custer-1 pyrite, which had been stored at -15 °C for over a year as material stage-crushed to pass 20 mesh.

TABLE 5.2: Conditions and results for pure pyrite experiments. The pyrites are described in Appendix 7.

Frother: MIBC, 0.38 kg/mt
Charge Weight: 150 grams
Cell Volume: 1.9 liters (giving 7.3% solids)
Water: Distilled
Impeller speed: 1500 rpm

Test	Pyrite	#2 fuel oil, kg/mt	pH	% Floats
1	Rico	3.0	2.1	98.62
2	“	3.0	5.0	9.56
3	“	0.0	8.4	3.9
4	“	0.0	2.1	14.2
5	Custer-1	3.0	7.5	3.34
6	“	3.0	7.5	4.34
7	“	3.0	8.3	4.65
8	“	3.0	2.0	98.57
9	“	3.0	2.3	98.01
10	“	3.0	2.2	97.57
11	Panther Valley	3.0	8.8	31.64
12	“	3.0	3.5	36.47
13	“	3.0	2.2	43.00
14	“	3.0	2.0	35.22
15	Empire	0.0	5.1	15.6
16	“	3.0	12.3	20.6
17	“	3.0	10.4	36.8
18	“	3.0	8.2	40
19	“	3.0	6.2	40.8
20	“	3.0	5.3	44.8
21	“	3.0	4.7	52.7
22	“	3.0	2.6	56.7
23	Custer-2	0.0	9.8	7.6
24	“	0.6	6.8	10.0
25	“	3.0	11.7	20.7
26	“	3.0	9.7	11.4
27	“	3.0	5.7	14.9
28	“	3.0	2.3	68.3
29	“	3.0	1.8	69.7

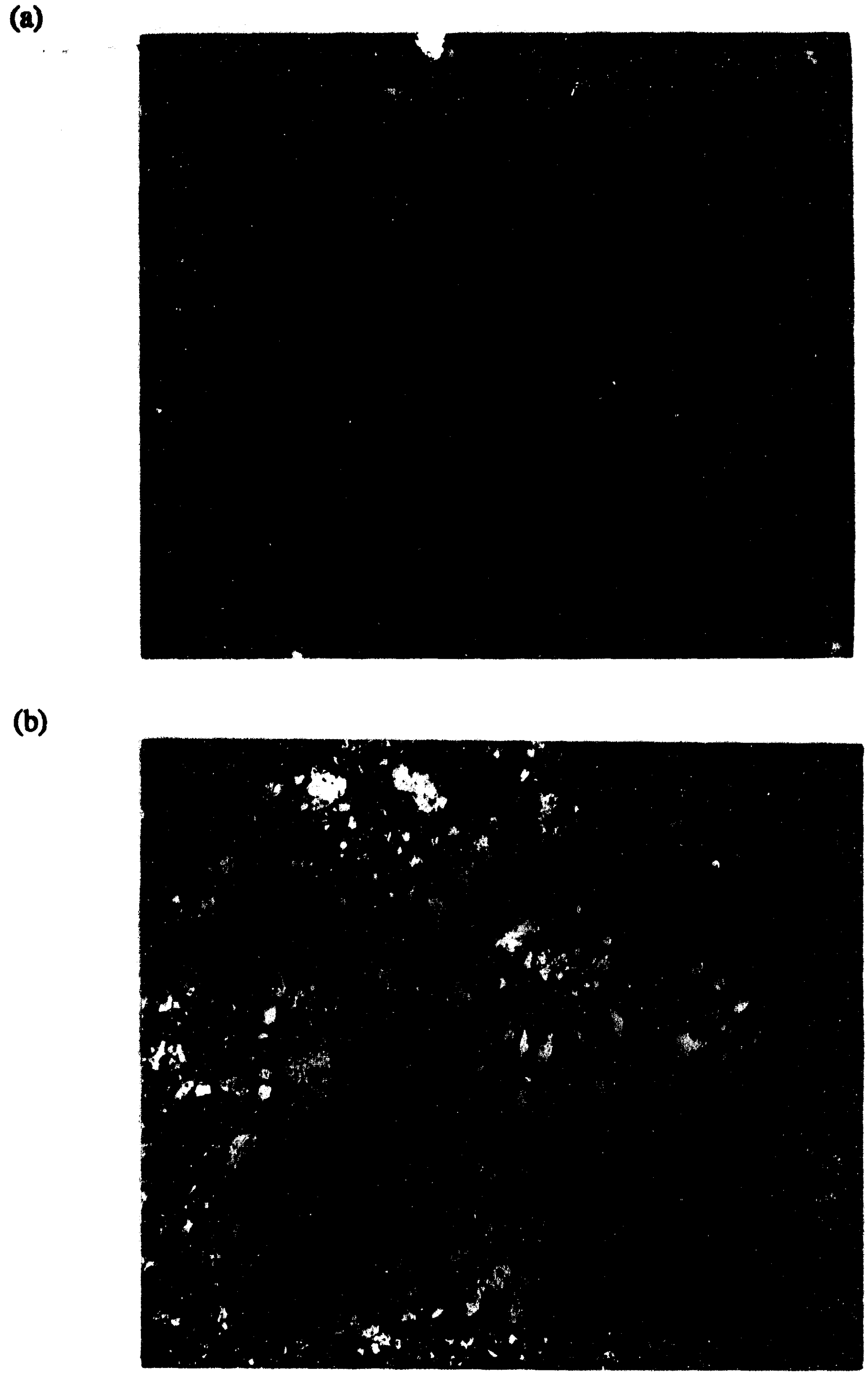


FIGURE 5.1. Photomicrographs of the products from floating Empire coal-pyrite at pH=5.3 with #2 fuel oil (3.0 kg/mt) and 80% passing 18 microns. (a) froth product; (b) tails product. (scale: 1 cm = 27 microns). Bright particles are pyrite, and dark particles are mostly coal. In the froth sample, pyrite particles are heavily locked to coal, while in the tailings the pyrite is well liberated, showing that only locked coal/pyrite floats well.

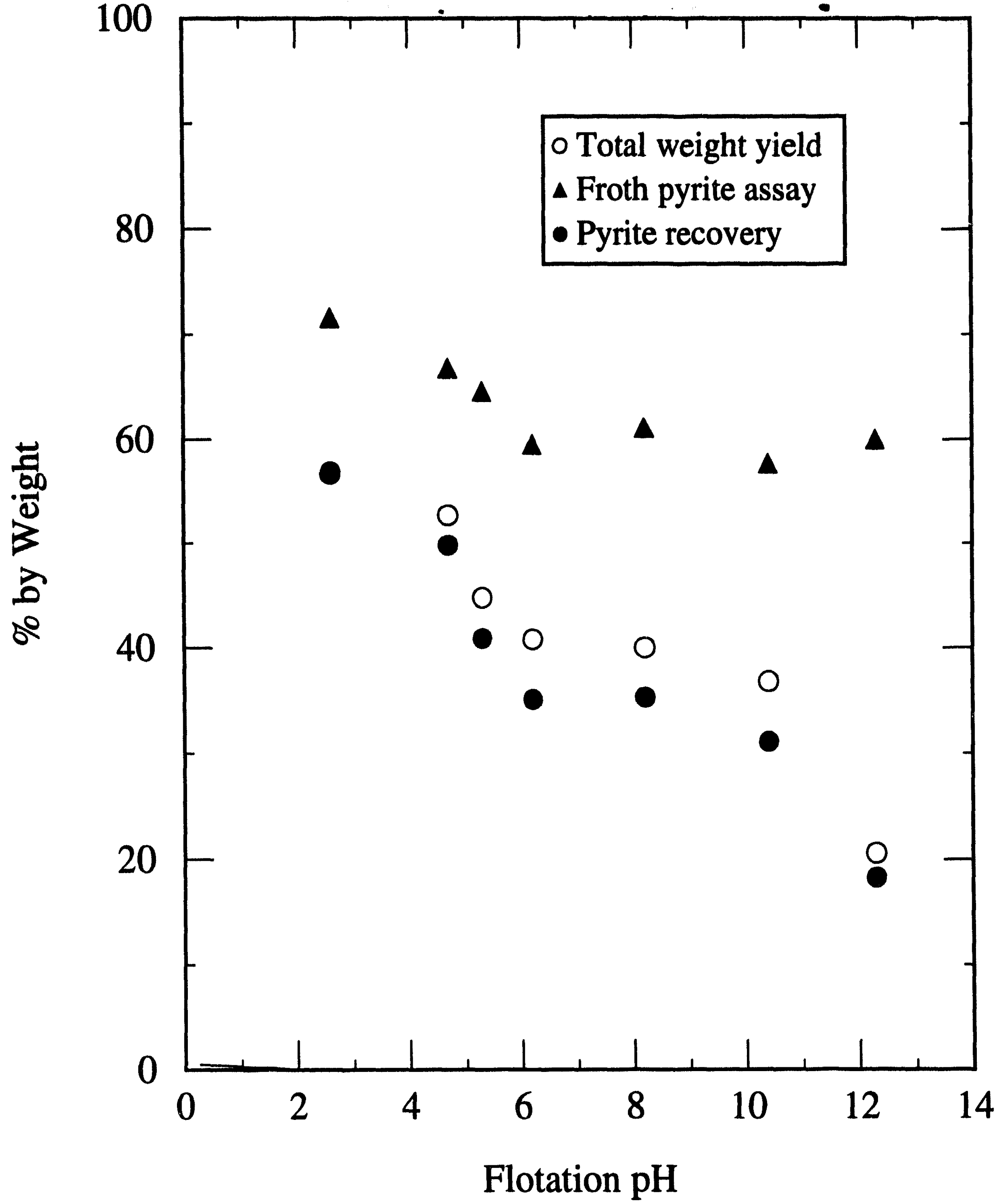


FIGURE 5.2. Total weight recovery, froth pyrite grade, and pyrite recovery as a function of pH for flotation of finely-ground Empire pyrite with #2 fuel oil as collector. Below about pH=5, some of the pyrite appears to be hydrophobic, but at higher pH the pyrite that floats is mainly locked to coal, and is floating only because the coal is floating.

Surprisingly, when this pyrite was ground and floated as for the previous tests, it was found to be floatable at near neutral pH. When a portion of the aged Custer-1 pyrite was oxidized at 100 °C for 44 days in a forced-air drying oven before grinding for flotation, the behavior returned to nearly that seen for the fresh pyrite, although no odor of H_2S was noted when the oxidized pyrite slurry was made acid. Results of the flotation experiments using the aged pyrites are given in Table 5.3.

TABLE 5.3: Results of floating Custer-1 pyrite after ageing at -15 °C for over one year, and after oxidizing at 100 °C for 44 days. The pyrite was rod-milled as for the previous tests.
Frother: MIBC, 0.38 kg/mt
Cell Volume: 1.9 liters (giving 7.3% solids)
Water: Distilled
Impeller speed: 1500 rpm

Treatment	pH	% Floats
Aged at -15 °C	9.0	46
Aged at -15 °C	6.8	37
Aged at -15 °C	6.0	35
Aged at -15 °C	1.9	92
Oxidized at 100 °C	6.2	7
Oxidized at 100 °C	2.0	82

5.5 DISCUSSION

These results indicate that the natural hydrophobicity of pyrite near neutral pH is a result of partial oxidation of the surface. Fresh completely unoxidized pyrite is floatable with fuel oil as collector, but only in acid solution. However, upon mild oxidation the pyrite apparently forms a small quantity of elemental sulfur on its surface (Stock and Wolny, 1990), which is a naturally hydrophobic material and acts essentially as a collector for the pyrite particle. One mechanism for this to occur in aqueous solution is as follows (Chou,1990):

$$2Fe^{+3} + FeS_2 \Longrightarrow 3Fe^{+2} + 2S^0$$

Upon further oxidation, this is converted to sulfate and the hydrophobicity is lost. As a result, it is fairly unpredictable whether pyrite will or will not be floatable at neutral pH due to the fact that floatability comes and goes with small changes in the degree of oxidation. Pyrite is apparently most likely to become hydrophobic under conditions of mild oxidation, such as at very low temperatures in air. Similarly, it is likely that pyrite will become floatable when submerged in water during the early stages of bacterial oxidation. This is a possible explanation for why, in the results presented in Chapter 4, the *Thiobacillus* strains were the least effective for depressing pyrite flotation, and why the pyrite-adapted strain was even less effective than the parent strain. While the bacteria probably do attach to the pyrite surface, they also may rapidly produce traces of elemental sulfur upon their initial reaction with the pyrite. This would tend to counteract the effect of the hydrophilic surface of the bacteria, and give rise to the observed low depression effectiveness.

The role of elemental sulfur in pyrite flotation also provides an explanation for the observed strong dependence of floatability on pH. When the pyrite is in acid solution, the solubility of iron oxides formed on the surface becomes much higher than at neutral pH. When the oxides dissolve, they leave a residue of insoluble elemental sulfur. Since the hydrophilic oxides are then no longer present to counteract the hydrophobicity of the elemental sulfur, the pyrite becomes strongly floatable. If the pH is then raised again, the oxides will reprecipitate on the surface, and floatability will be reduced.

5.6 CONCLUSIONS

The use of microorganisms for depression of pyrite in coal flotation appears to be of little or no practical use, as flotation of pyrite is usually not significant at near-neutral pH. Pyrite can become naturally hydrophobic under certain specific conditions of oxidation, such as gradual oxidation at low temperatures or in oxygen-depleted environments, probably as a result of elemental sulfur forming on the surface. The floatability of pyrite is also greatest when the pH is less than about 4. While freshly-ground coal pyrite is more readily floatable at neutral pH than is freshly-ground mineral pyrite, this appears to be primarily due to locking of floatable coal particles to the pyrite.

Since coal pyrites are widely reported to be greatly different chemically from mineral pyrites, the next phase of the project was begun in order to attempt to separate the effects of mechanical locking, entrainment, and true flotation on the recovery of pyrite particles during flotation of a high-pyritic-sulfur coal.

CHAPTER 6: PYRITE RECOVERY MECHANISMS IN COAL FLOTATION

6.1 INTRODUCTION

In many coal flotation operations, a significant amount of apparently liberated pyrite is seen to report to the froth, thus raising the sulfur content of the clean product and reducing its economic value. Prevention of this unwanted recovery of pyrite is therefore desirable.

Before the best means for preventing liberated coal pyrite recovery can be selected, it is necessary to determine how it is actually being recovered. Separation of particle entrainment and bubble attachment effects in a real experiment is very difficult, especially when locked particles are being floated as well. Since coal pyrite does not have the same properties as pure mineral pyrite [Chernosky and Lyon, 1972], and it is not practical to produce coal pyrite which is completely free of locked coal particles, experiments to demonstrate conclusively whether pyrite from a given coal either does or does not float by hydrophobic bubble attachment are impractical, and the best which can be done is to estimate the relative probable quantity of liberated pyrite which can be accounted for by the two mechanisms.

For this chapter, experiments were carried out to attempt to measure the floatability of liberated pyrite in coal using both a conventional cell and a laboratory-scale flotation column, using reagents which are commonly selected in current industrial practice.

6.2 THEORETICAL DISCUSSION

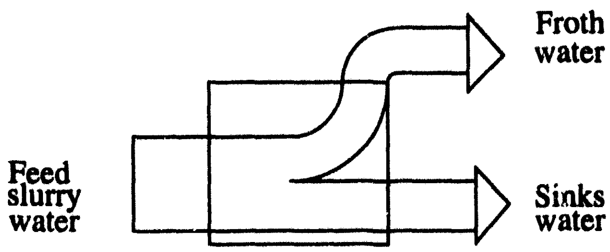
Determination of the quantity of entrained material in a flotation froth is based on correlation of the amount of water in the froth with the quantity of the entrained species in the froth. Since entrainment is, in theory, directly related to water recovery [Lynch et al., 1981], a correlation between percent recovery of purely hydrophilic particles and of water will be linear; the percent recovery of particles will be equal to or lower than the percent recovery of water, with the finest particles most closely approaching the behavior of the water. Since a range of particle sizes will be present in flotation experiments, this tends to introduce a small amount of scatter and curvature to the data. However, the linear trend will still be evident. Deviations from linearity, or a solids recovery rate which is faster than the water recovery rate, are due to particles which are either recovered by direct bubble attachment, or by mechanical locking with hydrophobic particles.

6.3 EXPERIMENTAL PROCEDURES

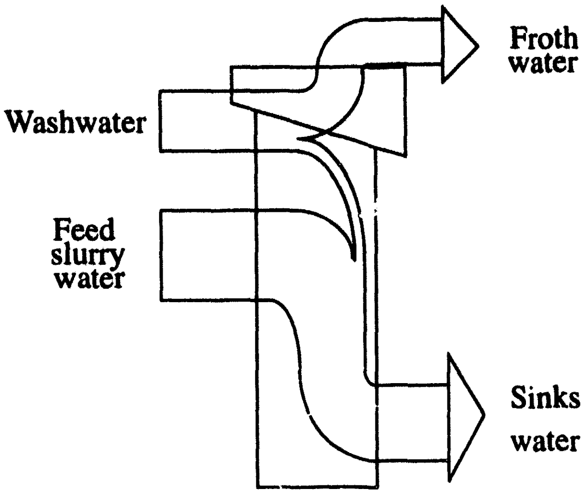
In order to determine whether the pyrite in a particular Pittsburgh Seam coal was floating by locking/entrainment or by true flotation, two sets of experiments were carried out. These experiments provided data on the extent to which coal pyrite flotation occurs during normal flotation of coal, its correlation to the quantity of water entrained in the froth, and the quantity of pyrite reporting to the froth in a flotation column designed to reduce entrainment, as shown in Figure 6.1.

6.3.1 Pittsburgh Coal Conventional Flotation

The first objective was to attempt to estimate the relative proportions of sulfur reporting to a coal froth by entrainment and true flotation. To accomplish this, it was necessary to measure the



CONVENTIONAL FLOTATION



COUNTERCURRENT COLUMN

FIGURE 6.1. Mechanism of entrainment reduction in flotation columns as compared to conventional flotation. Since entrainment is caused by solids being carried into the froth by the feed water, columns replace the feed water with clean washwater before the froth is removed.

recovery of coal, ash, water, and the various forms of sulfur as a function of time. Variations in collector dosage were intended to vary the coal flotation rate, and determine whether pyrite flotation was or was not sensitive to collector dosage.

These experiments used 250 gram charges of AEP Pittsburgh seam coal (described in Appendix 7) which had been stored at -20 °C prior to use, to retard oxidation. For experiments, this coal was ground in a steel rod mill to the size distribution given in Table 6.1. The freshly ground coal was then divided into 250 gm charges for flotation, and floated as soon thereafter as possible. Timed flotation experiments were carried out in a 4-liter flotation cell, with gravity-feed

TABLE 6.1: Size distribution of Pittsburgh seam coal used in the coal flotation experiments, produced by grinding 900 g charges of coal at 40% solids in a steel rod mill for 45 minutes. Size distribution was measured using a Microtrac particle size analyzer. Charges for flotation (three 250 gram charges for conventional flotation, and two 400 gram charges for column flotation) were removed, with the remainder used as a head sample.

Size, μm	Cumulative % Passing
88	100.0
62	96.0
44	87.5
31	74.7
22	61.7
16	49.2
11	37.6
7.8	28.4
5.5	20.3
3.9	13.7
2.8	8.1
1.9	3.1
1.4	1.1
0.9	0.0

pulp level control and mechanical froth scrapers (Figure 6.2). The frother was Dowfroth 200, added at a rate of 0.03 g/liter (0.5 kg/mt). Froth was collected over the time intervals 0-30 sec, 30 sec-1 min, 1 min-2min, 2 min-3 min, 3 min-5 min, and 5min-9 min, filtered, dried, and weighed. All products were analyzed for ash content by the standard ASTM method, and total sulfur content was determined using a LECO SC-132 sulfur determinator. Pyritic sulfur was measured using the ASTM leach technique, with the nitric acid dissolution step carried out by leaching at room temperature overnight (16 hrs.), followed by boiling for 30 minutes to ensure complete dissolution.

6.3.2 Column Flotation Experiments

Experiments with column flotation were intended to determine the behavior of the coal components when entrainment was minimized by froth washing. Flotation experiments were carried out in a laboratory-scale coal flotation column, using coal prepared in the same manner as that used in the conventional coal flotation tests. A modified Deister 3" diameter column 6' high was used for these experiments. This column is further described in Chapter 7. A froth depth of 18" was maintained, with 1 liter/minute of washwater. Aeration was provided by an aspirator, with a water pressure of 15 psi and a flowrate of 5 liters/minute. The frother was Dowfroth 200, introduced with the aspirated air as a 1% solution to give a concentration of 0.03 g/liter (0.5 kg/mt coal), and also added to the washwater at the same concentration. Tracer experiments conducted

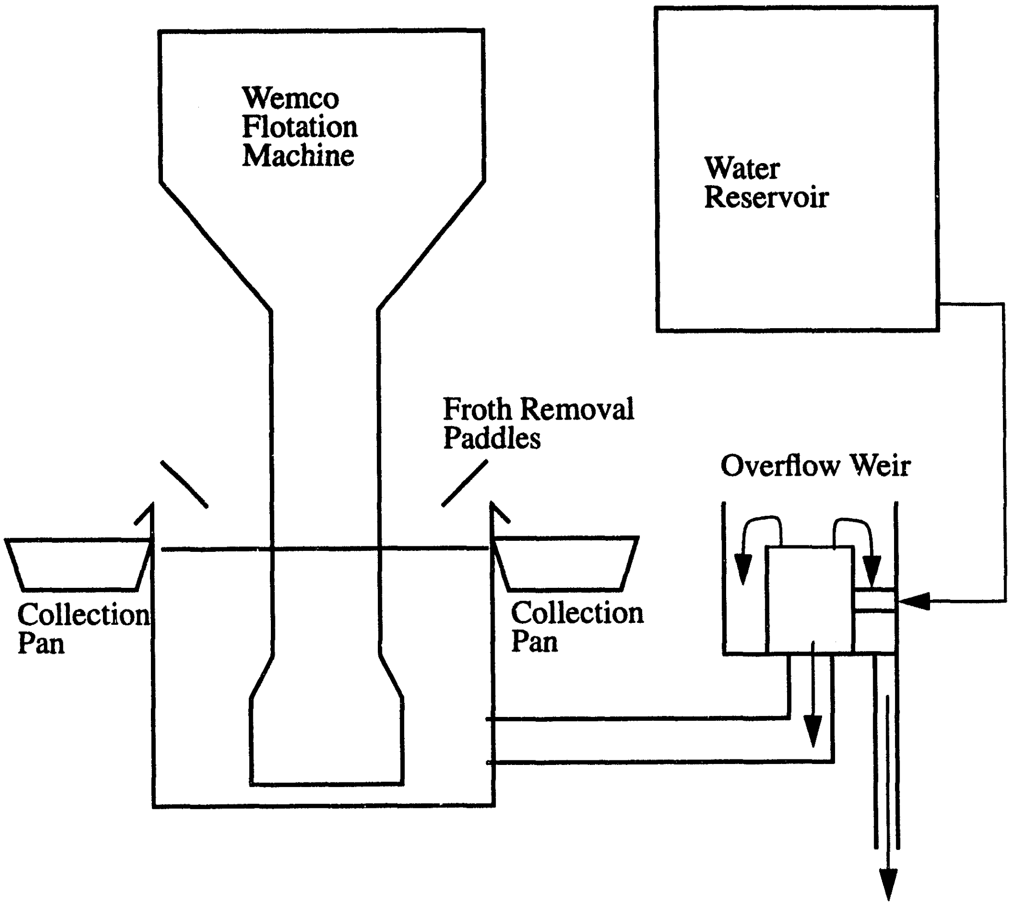


FIGURE 6.2. Schematic diagram of the conventional flotation cell used in the timed flotation experiments, showing the motorized froth scrapers and the pulp level control. Froth paddle speed=18.75 rpm. Cell volume = 4.25 liters. Air flowrate to cell = 15.7 liters./min. Impeller speed = 1086 rpm.

using sodium fluorescein dye (described in Chapter 7) showed that less than 4% of the feed water was entrained in the froth product using this column.

Timed flotation experiments were carried out by adding a 400 gm charge of the coal in slurry form as a single increment. After adding the feed, 30 seconds were required before coal began flowing into the overflow launder. From this time, froth increments were removed over the 0-30 sec, 30 sec-1 min, 1 min-2 min, 2 min-3 min, 3 min-5 min, and 5 min-9 min time intervals. These samples were analyzed in the same fashion as for the conventional flotation tests.

6.4 EXPERIMENTAL RESULTS

The results from the conventional and column flotation experiments are given in Table 6.2 and Table 6.3. In Table 6.2, results are given both for conventional tests with no collector added (tests 1-3) and with increasing levels of collector (tests 4-6). For each set of three tests, a 900

TABLE 6.2: Results from timed flotation experiments using a constant- level conventional flotation cell. The measured heads were determined from incremental samples taken from the feeds for the three tests preceding each. Collector was #2 fuel oil, and the frother was Dowfroth 200 (0.5 kg/mt), with a charge weight of 250 grams (cell volume 4 liters, %solids=5.9%). Water was Houghton tap water, with hardness in the range of 90-150 ppm $CaCO_3$ equivalent. At flotation times longer than 3 minutes, most of the solids in the froth were being recovered by entrainment, which caused the very high ash and sulfur contents of the 3, 5, and 9 minute froth products.

	Product	% Wt	% Ash	% S	% Py. S	%Solids
pH = 7.6						
Collector Dosage (fuel oil) = 0.0 kg/mt						
Test 1	30 sec Froth	31.24	11.1	2.14	0.9	15.14
	1 min Froth	26.60	13.2	2.59	1.6	16.04
	2 min Froth	8.83	26.8	3.64	2.5	8.88
	3 min Froth	4.83	61.1	5.17	4.4	2.41
	5 min Froth	5.70	82.5	5.08	4.5	1.15
	9 min Froth	6.73	88.1	4.22	3.7	0.70
	Final Tails	16.07	88.2	4.55	4.2	
pH = 7.7						
Collector = 0.0 kg/mt						
Test 2	30 sec Froth	44.37	12.7	2.37	1.1	15.70
	1 min Froth	18.19	17.5	2.86	1.7	13.73
	2 min Froth	8.47	42.5	4.33	3.3	4.01
	3 min Froth	3.88	79.5	5.27	4.7	1.37
	5 min Froth	4.70	87.4	4.56	4.0	0.90
	9 min Froth	4.66	89.0	3.91	3.7	0.59
	Final Tails	15.72	84.2	4.54	4.2	
pH = 7.7						
Collector = 0.0 kg/mt						
Test 3	30 sec Froth	43.82	12.4	2.26	1.1	16.00
	1 min Froth	19.00	17.1	2.69	1.7	13.90
	2 min Froth	8.73	43.3	3.81	3.3	3.95
	3 min Froth	3.91	79.1	4.67	4.6	1.33
	5 min Froth	4.90	86.3	4.06	4.0	0.90
	9 min Froth	6.01	88.6	3.49	3.4	0.56
	Final Tails	13.63	87.0	3.98	4.0	
Measured Head (Tests 1-3)			37.2	2.90		

TABLE 6.2: Results from timed flotation experiments using a constant- level conventional flotation cell. The measured heads were determined from incremental samples taken from the feeds for the three tests preceding each. Collector was #2 fuel oil, and the frother was Dowfroth 200 (0.5 kg/mt), with a charge weight of 250 grams (cell volume 4 liters, %solids=5.9%). Water was Houghton tap water, with hardness in the range of 90-150 ppm $CaCO_3$ equivalent. At flotation times longer than 3 minutes, most of the solids in the froth were being recovered by entrainment, which caused the very high ash and sulfur contents of the 3, 5, and 9 minute froth products.

	Product	% Wt	% Ash	% S	% Py. S	%Solids
pH = 7.5						
Collector = 0.18 kg/mt						
Test 4	30 sec Froth	23.1	10.3	1.85	0.8	16.21
	1 min Froth	14.3	9.4	1.89	0.9	19.41
	2 min Froth	19.9	12.9	2.39	1.5	21.83
	3 min Froth	9.8	35.3	3.94	3.3	6.08
	5 min Froth	7.7	73.9	4.51	4.4	1.46
	9 min Froth	6.6	86.7	3.76	3.7	0.77
	Final Tails	18.4	85.6	3.86	3.8	
pH = 7.5						
Collector = 0.35 kg/mt						
Test 5	30 sec Froth	55.4	14.0	2.24	1.3	14.73
	1 min Froth	10.9	27.1	3.13	2.3	7.78
	2 min Froth	7.2	58.2	4.20	3.7	2.09
	3 min Froth	4.1	72.3	3.84	3.7	1.16
	5 min Froth	4.9	84.2	3.63	3.7	0.73
	9 min Froth	5.2	87.5	3.30	3.3	0.47
	Final Tails	12.3	84.4	4.10	4.1	
pH = 7.6						
Collector = 0.70 kg/mt						
Test 6	30 sec Froth	56.0	15.0	2.33	1.4	14.50
	1 min Froth	8.9	33.0	3.51	2.8	5.96
	2 min Froth	6.9	63.2	4.10	3.7	1.77
	3 min Froth	5.4	64.4	3.48	3.3	1.26
	5 min Froth	5.6	77.4	3.36	3.4	0.73
	9 min Froth	5.5	81.4	3.19	3.2	0.43
	Final Tails	11.7	75.7	4.02	4.0	
Measured Head (Tests 4-6)			37.3	2.99		

TABLE 6.3: Timed column flotation results, using the same coal as for the conventional flotation cell experiments in Table 6.2 (Frother Dowfroth 200, 0.5 kg/mt; no collector; 400 gram flotation charge (7 liter working volume, nominal %solids=5.4%), nominal pH=7. Water was Houghton tap water, with hardness in the range of 90-150 ppm $CaCO_3$ equivalent.

	Product	% Wt	% Ash	% S
Test 1	30 Sec Froth	0.61	7.78	2.35
	1 min Froth	1.07	2.91	1.72
	2 min Froth	3.42	2.85	1.67
	3 min Froth	6.05	3.13	1.74
	5 min Froth	24.11	4.52	1.96
	9 min Froth	22.29	11.74	2.73
	Final Holdup	7.41	56.68	7.45
	2 min Tails	12.79	76.38	4.32
	2 min Tails	22.24	83.91	3.92
Test 2	30 sec Froth	0.00	0.00	0.00
	1 min Froth	0.86	3.42	1.71
	2 min Froth	3.57	3.11	1.66
	3 min Froth	7.97	3.38	1.73
	5 min Froth	21.59	4.51	1.93
	9 min Froth	23.29	11.54	2.68
	Final Holdup	8.25	57.04	6.99
	2 min Tails	11.39	75.02	4.17
	9 min Tails	23.06	83.87	3.86
Measured Head (Tests 1-2)			36.85	3.36

gram sample of coal was ground, and divided into three 250 gram flotation charges and a 150 gram head sample. Similarly, for the flotation test results in Table 6.3, the 900 gram sample was divided into two 400 gram flotation charges and a 100 gram head sample. In the column experiments, timed tailing samples were collected in addition to timed froth samples, since the column produced a continuous tailings product in addition to a continuous froth product. The final holdup product is the material that remained in the column at the end of the test.

6.5 DISCUSSION

Determining conclusively whether pyrite is being recovered by true flotation, locking of particles, or entrainment is not practical at present. A rough approximation of entrainment can be made by correlating the recovery of a given component (coal, ash, etc.) with the recovery of water in the froth. In addition to water recovery data, a method is needed to distinguish liberated pyrite particles from other sulfur forms. Sulfur is predominantly in the form of organic sulfur, liberated pyritic sulfur, and pyritic sulfur intermixed with coal (i.e., locked particles), best described by Equation 6.1:

$$\text{Total sulfur} = \text{organic sulfur} + \text{liberated pyritic sulfur} + \text{unliberated pyritic sulfur} \qquad (6.1)$$

Sulfate sulfur is also present, but typically in trace amounts. For purposes of this discussion, sulfates will be considered to be part of the pyritic sulfur.

Standard analysis techniques allow for quantitative measurement of total sulfur and pyritic sulfur, but no practical methods are available for differentiating between liberated and unliberated pyritic sulfur for large numbers of particles. By making the following simplifying assumptions, it is possible to use Equation 6.1 to develop a method of determining a numerical value for organic sulfur plus unliberated pyritic sulfur for a particular coal:

1. The liberated pyrite is always less floatable than the most floatable coal particles when no collector is added, and therefore the fastest-floating coal in the absence of collector will be free of liberated pyrite if entrainment is minimized.
2. The locked pyrite and organic sulfur are uniformly distributed throughout the combustible fraction of the coal.

Given these assumptions, a quantitative value for organic sulfur plus unliberated pyritic sulfur in the combustible fraction of the coal sample can be determined by either of two methods. The coal can be successively refloated several times by conventional flotation to recover only the fastest floating particles, or it may be floated using column flotation with the initial, fastest-floating, lowest-sulfur product being considered free of liberated pyritic sulfur. Once this value has been determined for the sample, it is possible to use Equation 6.2 to calculate the liberated pyritic sulfur content:

$$\%S_{LP} = \%S_T - \%S_{LO}\,(W_C) \qquad (6.2)$$

where $\%S_{LP}$ = liberated pyritic sulfur content of the sample,
S_T = total sulfur content of the sample,
W_C = weight fraction of combustible matter in the sample,
$\%S_{LO}$ = locked and organic sulfur content of the combustible fraction,

which was determined for this coal to be 1.7%, using the flotation column technique described above.

This value of 1.7% locked and organic sulfur is further supported by a heavy-liquid separation of the feed, at a specific gravity of 1.35. The low-gravity float product was found to have a total sulfur content of 1.79 wt.%, at a recovery of 20% wt.

A second correction was made necessary by the constant-level feature of the conventional cell. While a constant froth depth is needed to reduce variations in the entrainment constant, the addition of make-up water makes the cell continuous with respect to water, while remaining batch with respect to solids. The effect of this can be seen in Figure 6.3, which plots the cumulative percent recovery of various components against the cumulative weight recovery of water. All of the plots exhibit a pronounced curvature, even the ash, which is known to be predominantly clay and therefore mainly recovered by entrainment. If the cell is assumed to be a well-mixed system, however, a simple residence-time calculation can be used to correct for makeup water dilution, as follows (Dankwerts, 1953):

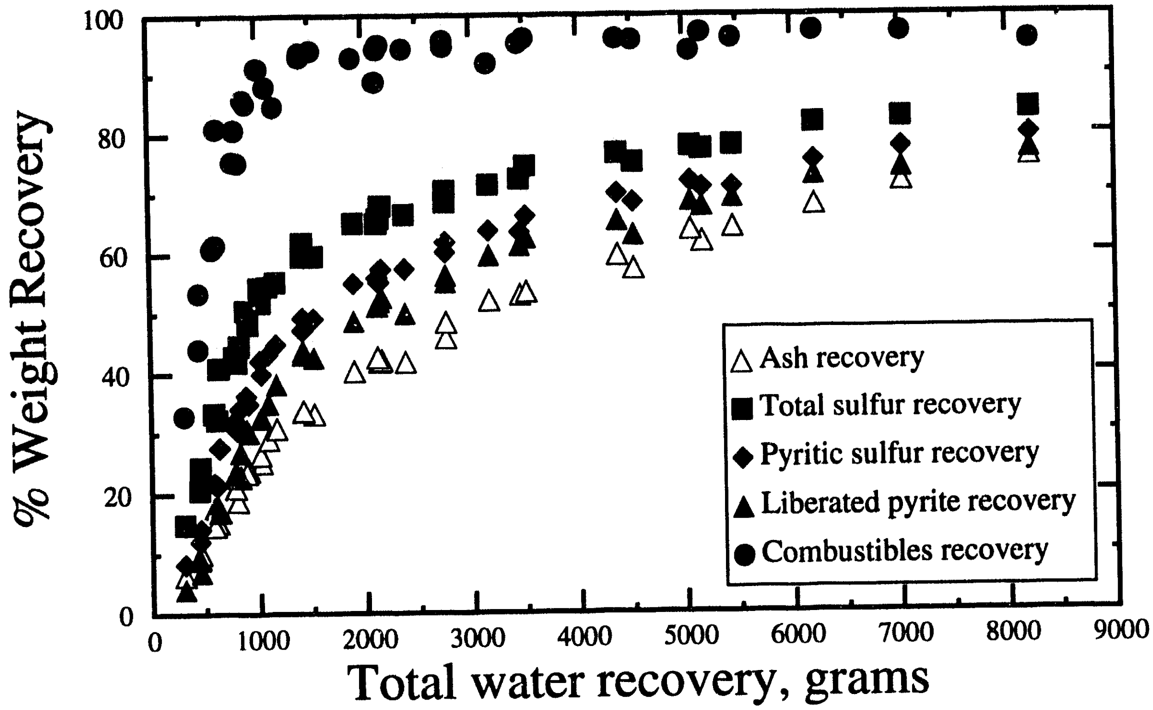


FIGURE 6.3. Comparison of cumulative recoveries of liberated pyritic sulfur, combustible matter, ash, and total sulfur with recovery of total water in the froth for all six timed tests using the conventional flotation cell. The curves are all convex upwards mainly because of the dilution effect of the makeup water added in the course of the tests.

$$F(T) = 1 - e^{-R/V} \tag{6.3}$$

where F(T) = the volume fraction of the water originally in the cell which is recovered by time T,

R = total volume of water which is removed and replaced by makeup water by time T, and

V = total cell volume.

Using this formula to correct for makeup water dilution, the cumulative percent recovery of the water originally in the cell can be calculated. This corrected water recovery can now be used to distinguish between entrainment and true flotation.

Figure 6.4 shows the correlations of combustible matter, ash, and total pyritic sulfur with the corrected water recovery for all six conventional tests. It is immediately evident that the ash shows behavior strongly characteristic of entrainment, while the combustible matter behaves as a strongly floatable species. The pyritic sulfur behaves in an intermediate fashion, with recovery

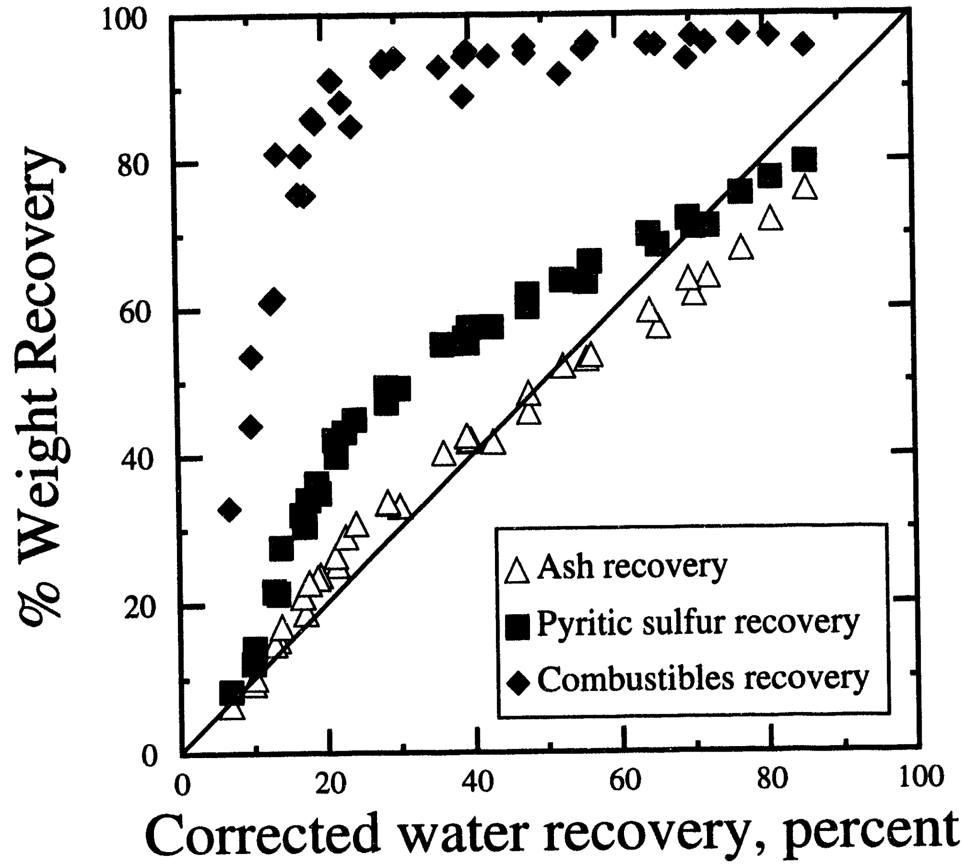


FIGURE 6.4. Correlations of combustible matter, ash, and total pyritic sulfur recovery with water recovery corrected for make-up water addition, according to Equation 6.2. Perfect entrainment would follow the 45° line.

being initially slightly faster than that of water, then abruptly becoming slightly slower. It is of interest to note that, within the limits of accuracy of the data, this inflection occurs at precisely the same water recovery as the abrupt slope decrease in the combustibles curve, which occurs due to exhaustion of the floatable coal particles in the cell. The fact that the slope of the pyrite curve tracks the combustibles curve this closely, in spite of the substantial variations in coal flotation rate produced by changing the collector addition, strongly implies that the pyrite which floats by bubble attachment does so due to mechanical locking with floatable coal particles.

When liberated pyritic sulfur, calculated using Equation 6.2, is plotted against corrected water recovery in Figure 6.5, it is seen that the curve more closely approaches linearity than the total pyritic sulfur does. Further, the behavior of the liberated pyrite closely approximates that of the ash, indicating that the recovery mechanism for the two components is similar. The degree of

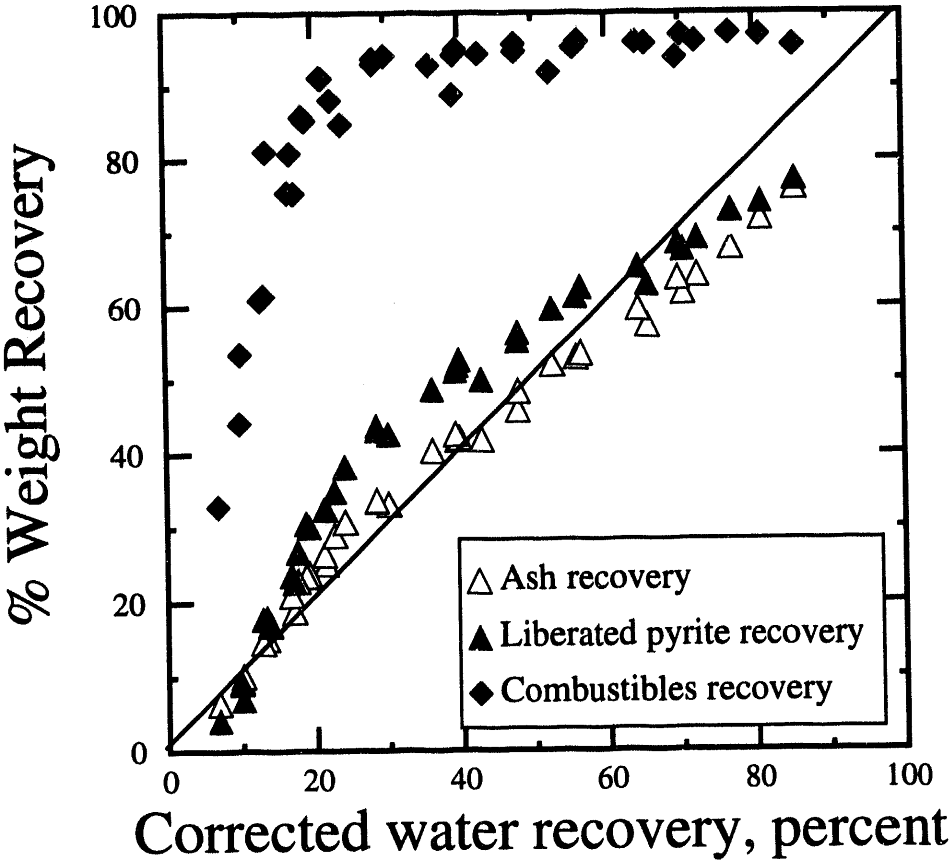


FIGURE 6.5. Correlation of combustibles, ash, and liberated pyritic sulfur recovery with water recovery corrected for make-up water addition.

similarity is shown further by Figure 6.6, where the plot of liberated pyritic sulfur recovery versus ash recovery follows very closely the 45° line.

The ash is primarily composed of fine clay particles which are expected to be strongly hydrophilic, and are well-liberated due to the high feed ash content. This correlation, combined with the correlation with water recovery, strongly implies that entrainment is by far the most important recovery mechanism for liberated pyrite.

The column flotation results represent a flotation separation where entrainment is reduced to very low levels, and thus all pyrite which is recovered under these conditions does so as a result of either locking or true flotation. Comparison of the results for conventional tests 1-3 and the column flotation tests are given in Figure 6.7 and Figure 6.8, and the shift in the grade/recovery curves is most consistent with liberated pyrite being recovered primarily by entrainment. As a result, it is probable that when this particular coal exhibits excessive pyrite recovery, it is more effective to switch to column flotation (thus minimizing entrainment) than to attempt to use chemical depressants to prevent hydrophobic flotation which does not appear to be occurring.

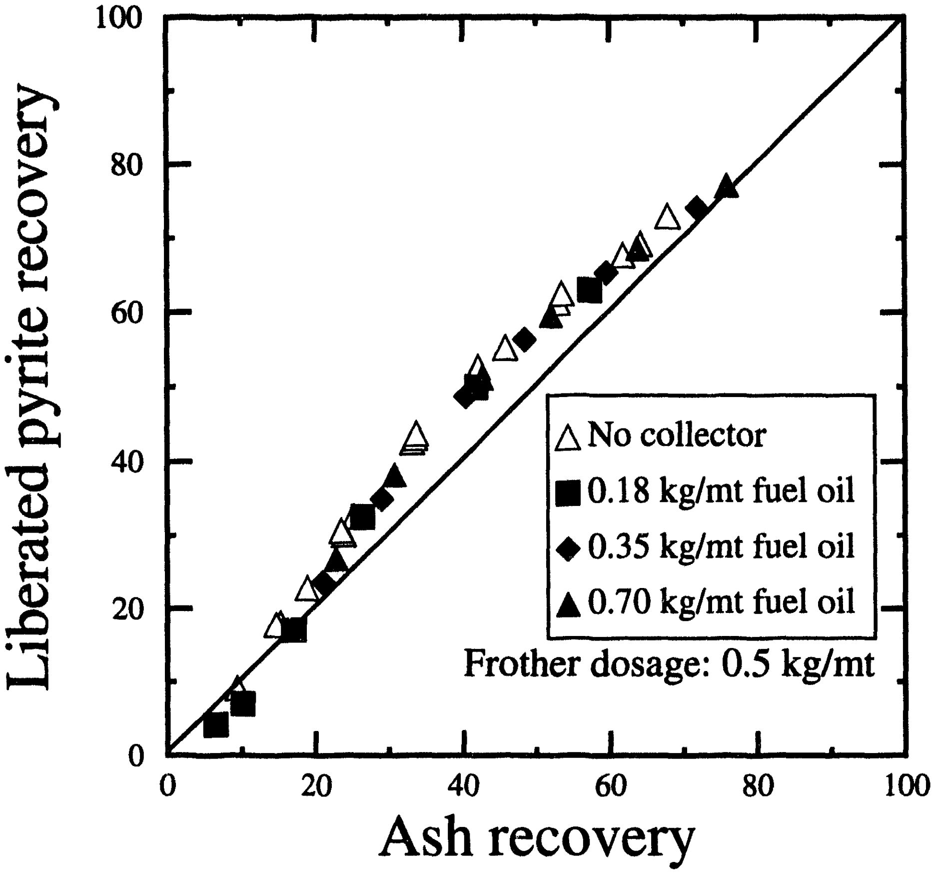


FIGURE 6.6. Correlation of pyritic sulfur recovery with ash recovery in the conventional flotation tests.

Unfortunately, there does not appear to be any available method for conclusively measuring the relative quantities of locked and liberated pyrite particles in coal flotation, nor is there an effective method for isolating coal-free pyrite from coal which does not also either contaminate or oxidize the pyrite surfaces. At the present time, it is therefore not possible to prove that coal pyrite either does or does not enter the froth as a result of true hydrophobic attachment. Based on the data given here, it is hypothesized that, in this case, the coal pyrite is floating due to attachment to coal. This hypothesis is supported by recent work by Chander and Aplan (1989), where great care was taken to isolate liberated pyrite from seven coal sources for a variety of detailed analyses. The pyrite was concentrated from the coals by hindered settling and tabling of single size fractions, followed by crushing to 100 x 400 mesh and repeated hand-vanning and ultrasonic treatment to remove adhering coal particles from the pyrite. Using a microflotation cell aerated with nitrogen gas, all of the purified pyrites were found to show very little inherent floatability (average = 1.9% wt. floating, range = 0-7% wt.). The procedure which Chander and Aplan describe for purifying the pyrites does provide opportunity for the pyrite to

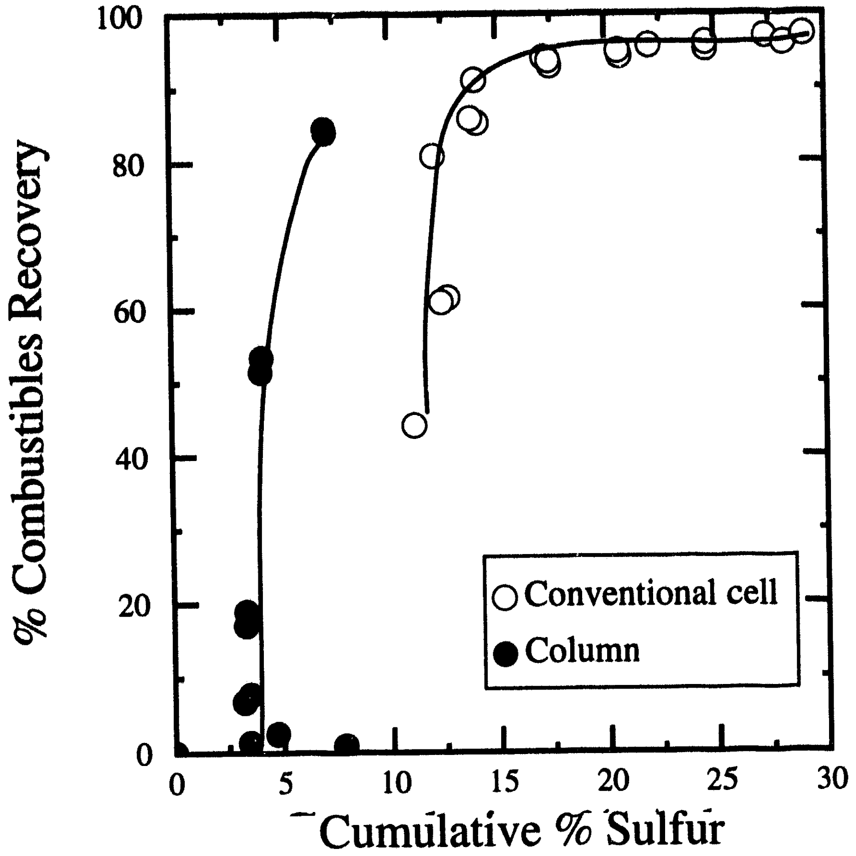


FIGURE 6.7. Comparison of the grade-recovery curves with respect to ash for the flotation column and the conventional cell. Only the conventional results for tests using no collector are plotted, for consistency with the column results.

oxidize somewhat, which may conceivably destroy its inherent floatability. Nevertheless, it appears likely that coal pyrites have a very low inherent floatability, and are therefore floated primarily as either locked or entrained particles, or due to formation of elemental sulfur on the pyrite surface.

This is further supported by reported results that sodium silicate dispersant was under certain circumstances able to reduce the amount of sulfur recovered in coal flotation to about the same degree as chemical pyrite depressants (Raleigh and Aplan, 1990). Since dispersants act to reduce entrainment by preventing flocculation and improving froth drainage (Leja, 1982), this implies that much of the pyrite originally being carried into the froth is not doing so by direct bubble attachment.

Although pyrite depressants have often been shown in the laboratory to reduce pyrite recovery, this may be a result of factors other than depression of floatable liberated pyrite

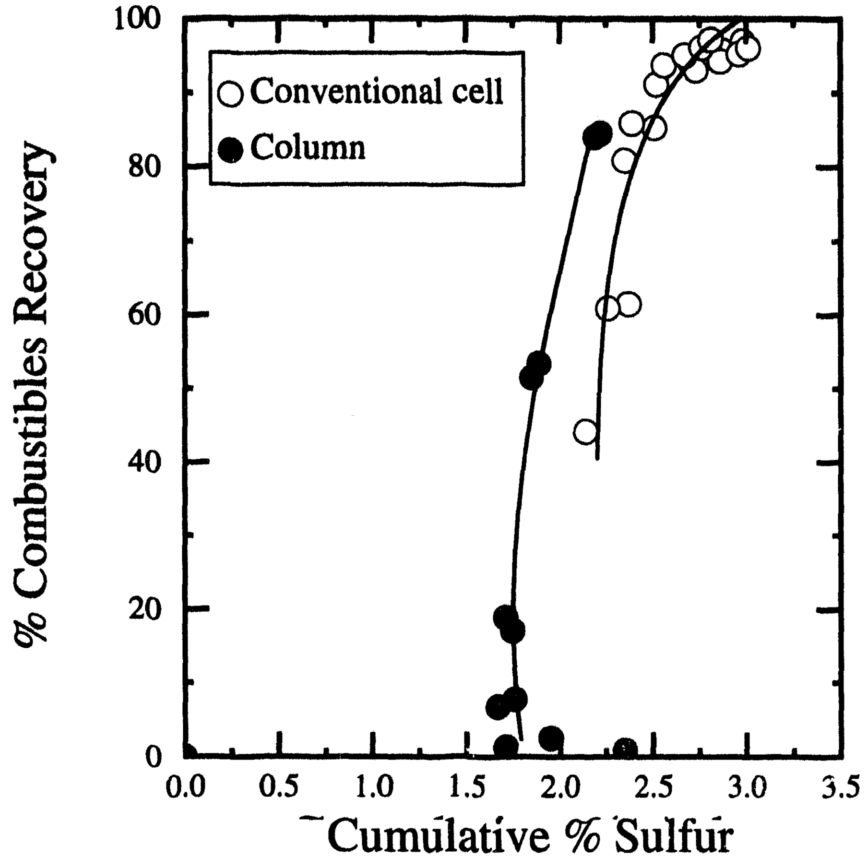


FIGURE 6.8. Comparison of the grade-recovery curves with respect to total sulfur for the column and the conventional cell. The scatter of points at the extreme low recovery of the column curve is due to the initial turbulence of the froth when the feed is added to the column.

particles. In general, pyrite depressants also act as mild coal depressants (Chander and Aplan, 1989). The coal particles which will be depressed first are the locked particles which include the greatest amount of gangue, since these particle have the least available surface area for bubble attachment. This is indicated by the grade/recovery profile for the conventional flotation cell given in Figure 6.8, which shows that the last few percent of coal recovered carries a disproportionate amount of the total sulfur. Small decreases in the combustibles recovery will therefore be of significant benefit in reducing the sulfur recovery.

If it is assumed that pyrite is indeed primarily recovered by locking and entrainment, then it should be expected that sulfur rejection would be poorest for the finer coal sizes. This is a result both of entrainment being most important for the fine particles due to their low settling rates, and of the low solids content of fine-particle flotation froths, which increases the quantity of entrained water for a given solids recovery. Drastically poorer selectivity at the finest sizes is indeed what is observed (Raleigh and Aplan, 1990), so entrainment is likely to be a major problem in such cases, with specific pyrite depressants being of relatively minor benefit.

6.6 CONCLUSIONS

From the results presented, the following conclusions may be drawn:

1. Timed flotation of a Pittsburgh seam coal in a conventional cell produced results consistent with the pyrite being recovered in the froth predominantly by entrainment and mechanical locking with floatable coal particles. Any contribution from hydrophobic flotation of liberated pyrite appears to be minimal.
2. The use of a flotation column, which is specifically designed to reduce entrainment of hydrophilic particles in the froth, allows a significant reduction of the sulfur content of the froth. The shift in the grade-recovery curve for this coal produced by switching from conventional to column flotation is consistent with the assumption that pyrite was primarily reaching the froth by entrainment during conventional flotation.
3. Since chemical pyrite depressants can only reduce the froth sulfur content in coal flotation if a significant amount of pyrite is floating due to hydrophobic bubble attachment, investigators should first be certain that pyrite is being recovered by this mechanism and not simply being entrained before using such reagents. The contribution of entrainment can be estimated, but only if the water recovery is measured as carefully as the recovery of the other species. Such water recovery measurements should therefore be a routine part of coal flotation studies.

CHAPTER 7: HORIZONTAL BAFFLING IN COAL FLOTATION COLUMNS

7.1 INTRODUCTION

In existing coal-cleaning plants, a single stage of froth flotation is generally all that is used, as the price advantage of highly cleaned coals is not sufficient to pay for multiple cleaning stages or for a great deal of pretreatment. For this reason, cleaned coal fines contain a substantial amount of liberated ash-forming and sulfur-bearing minerals which were misplaced into the froth by entrainment. This gives coal fines a reputation for low quality, and keeps the demand for fine coal low.

Currently, a considerable amount of work is being done to introduce flotation columns into coal-cleaning plants, as described in Chapter 2. Since columns accomplish in a single stage a degree of cleaning that would require three or more stages in conventional flotation, the mechanical overhead and floor space requirements of a column are less than for an equivalent conventional flotation circuit. However, flotation columns have two problems which discourage their widespread use in coal washeries. First, in order to maintain good separating efficiency, columns are generally very tall, on the order of eight to ten meters. This requires that a plant have sufficient headspace for their installation, catwalks to allow easy access to the top of the column, and sufficient pumping capacity to lift the feed slurry to the appropriate height. Second, modern columns tend to be very responsive to changes in operating parameters. While this is a desirable characteristic from the point of view of controllability, operating flexibility, and adaptation to changes in feed characteristics, it also makes their operation very difficult unless fairly sophisticated automatic control is used. As a result of these two factors, the capital costs of coal flotation columns are often perceived as being high, and existing plants are reluctant to retrofit their fine coal circuits with these machines. However, these difficulties can be minimized if column heights can be reduced to a more reasonable level of about two meters (Jameson, 1988), and if the need for control is reduced by stabilizing the column operation.

With these points in mind, a flotation column was developed at Michigan Technological University which uses horizontal baffling both to reduce the needed column height and to increase the reproducibility of the column's performance with minimal control.

7.2 THEORETICAL DISCUSSION

A flotation column is a countercurrent separator. Water travels downward through the column, carrying hydrophilic particles, while hydrophobic particles are carried upward by air bubbles. This ideally forms a concentration gradient, as described in Chapter 2. The sharper this gradient can be made, the shorter the column can be and still produce a clean separation. Normally, a column consists of an unobstructed pipe over most of its length, and so there is nothing to prevent turbulence and backmixing from blurring the concentration gradient. In addition, air bubbles rising through the slurry produce a pumping action which tends to carry water from bottom to top, resulting in a great deal of vertical mixing. In most existing columns, this mixing problem is solved by increasing the column height until the very gradual concentration gradient builds up a large-enough grade difference to make a good separation. Since the height necessary to do this becomes greater as the column diameter is increased, plant-scale columns tend to be very tall, and are sometimes sectioned by vertical dividers in order to reduce the apparent diameter of the machine.

A more direct way to prevent backmixing is by breaking up the vertical mixing currents with baffles, as shown in Figure 7.1. Different approaches to this were taken by Dell (1976) and Yang (1984), which are described in detail in Chapter 2. Both investigators used flow baffles to suppress vertical mixing and improve washing efficiency. Dell used a combination of fixed and movable rods in discrete racks to produce a machine which could clean coal as coarse as 28 mesh, while Yang used a packing similar to that used in packed distillation columns with the goal of improving separation of particles finer than 20 microns. For most coal-cleaning operations, a compromise between the two types of baffle described is desirable. Simple perforated-plate baffles can be placed much closer together than the more complex rod-racks, while having sufficiently large openings to prevent the plugging which plagues the packed column. This type of baffle is also much more suitable for retrofitting or redesigning existing columns, as they are easy to make and install.

Before such baffles could be used on a production scale, it was necessary to determine their effect on column performance, and to select the baffle design which provided the best results. With this in mind, two sets of experiments were carried out using a laboratory-scale column. The first set of experiments were carried out to determine the effects of changing the amount of open area in the baffles while floating a high-clay Pittsburgh seam coal. The second set of experiments was conducted to determine the effects of the baffles above and below the feed entry point while floating a plant sample consisting of a blend of coals from the Lower and Middle Kittanning seams. Fluorescein dye was used as a water tracer in the second series of experiments, so that the feed water could be tracked.

7.3 EXPERIMENTAL PROCEDURE

7.3.1 Equipment

The column used was a modified Deister Flotaire 7.6 cm diameter laboratory column, with an aspirator-type bubble generator, and a washwater spray 8 cm below the froth overflow lip, shown schematically in Figure 7.2. The level was controlled by an overflow weir so that an expensive active controller would not be needed. Frother (Dowfroth200) was metered directly into the aspirator to give a concentration of 0.03 g/liter (0.5 kg/mt for 400 gram coal charges, and 0.83 kg/mt for 250 gram coal charges), and the resulting air/water/frother mixture was injected into the column base at a flowrate of 6 liters/minute. The washwater spray contained the same frother concentration as the rest of the water used, and was introduced at a flowrate of 1 liter/minute. The froth depth was maintained at 0.5 meters, and feed was introduced at a depth of 1 meter. The basic column design included three permanent baffles, at heights above the tailings outlet of 0.3, 0.9, and 1.2 meters. Removable baffles, with effective open areas of 14%, 19%, 29%, and 38%, were used to vary the degree of baffling in the column. The total column height was two meters, and feed was introduced between the 0.9 and 1.2 meter baffles. As a result, there were two permanent baffles below the feed inlet, and one permanent baffle above the feed inlet. The column was operated in batch mode, with 1600 ml of feed slurry added at the beginning of each test.

7.3.2 Effects of Baffle Open Area

The first set of experiments focused on determining the best design for the baffles and consisted of five pairs of experiments, one pair for each baffle type and one pair with only the

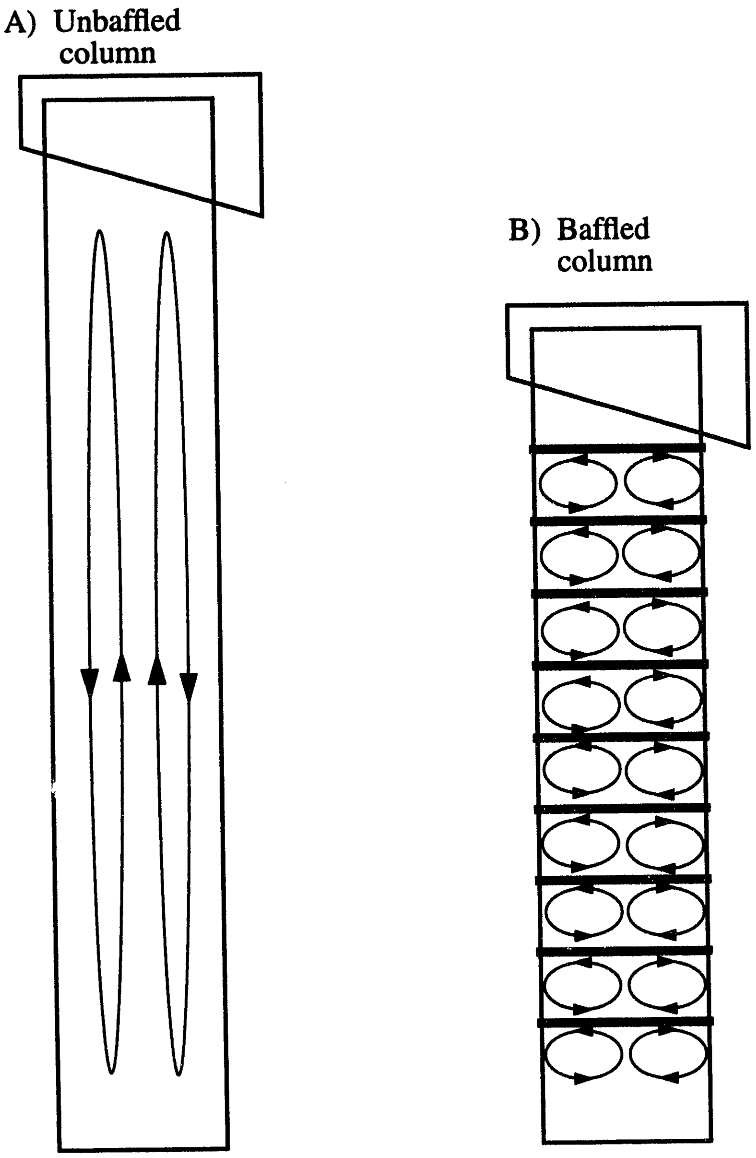


FIGURE 7.1. Without baffles, rising air bubbles carry water upward in the center of a flotation column, producing vertical mixing which reduces the separation efficiency. Horizontal baffles break up the mixing currents so that material cannot short-circuit directly to either the froth or tailings. This makes it possible for a baffled column to produce a better-quality separation with less height.

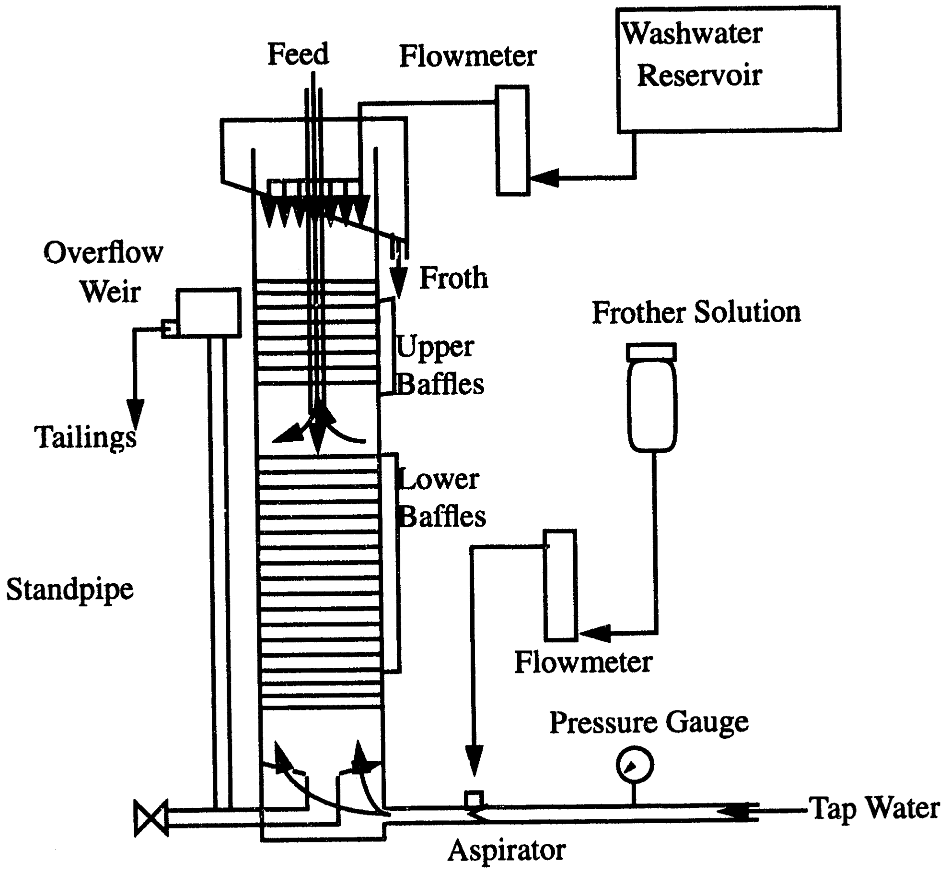


FIGURE 7.2. Schematic of the basic column used in these experiments. The column was 6' tall and 3" in diameter, with the froth depth held constant using an overflowing standpipe on the tailings line. Air bubbles were injected at the base using an aspirator, with frother solution added directly to the aspirator air inlet.

three permanent baffles. Each pair consisted of duplicate experiments, in order to determine the variability of the results.

7.3.2.1 Materials and Reagents: The coal used for the first set of experiments was a Pittsburgh Seam coal provided by American Electric Power Co. This coal was stage-crushed to pass 20 mesh and stored at -20 °C to prevent surface oxidation. Column feed was prepared by grinding 900 grams of the stage-crushed coal in 1500 ml distilled water in an 8" diameter rod mill for 45 minutes, producing the size distribution given in Table 7.1. Each 900 gram lot was then divided into two 400 gram flotation charges and a 100 gram head sample. The only reagent used was Dowfroth 200 as a frother, at a concentration of 0.03 ml DF 200/liter of water (0.5 kg/mt coal). No collector was used, as the natural hydrophobicity of the coal was sufficient for easy flotation in the column. Tap water was used in the column, at a pH of 6.5-7.0 and a hardness of 150 ppm.

TABLE 7.1: Representative size distribution for coal feeds to column, as determined by Leeds and Northrup Microtrac analysis of flotation feed head samples. The coals are described further in Appendix 7. The Empire coal used in these lab tests was collected from the Empire coal cleaning plant in March of 1989.

	Cumulative % Passing	
Size, µm	AEP-Pittsburgh	Empire
88	100.0	99.0
62	96.0	94.8
44	87.5	84.1
31	74.7	68.9
22	61.7	53.9
16	49.2	40.4
11	37.6	28.6
7.8	28.4	19.8
5.5	20.3	13.0
3.9	13.7	8.0
2.8	8.1	4.3
1.9	3.1	1.3
1.4	1.1	0.0
0.9	0.0	0.0
% Ash	38.0	13.5
% Sulfur	3.23	3.41
BTU/lb	8119	12100

7.3.2.2 Procedure: After grinding, flotation charges were repulped to 1600 ml with distilled water, and mixed with the desired reagents for 1 minute. The flowrates in the column were adjusted to the desired level, with the drain valve open to keep the column from filling prematurely. The drain valve was then closed, and the timer was started. At 30 seconds, the feed was added to the column over a 15 second time interval, with the froth overflow beginning at 1 minute after closing the drain valve. Froth samples were collected covering the time intervals 0-1.5 min, 1.5-2 min, 2-3 min, 3-4 min, 4-6 min, and 6-10 min, and tailings samples covering the intervals 0-3 min and 3-10 min. After 10 minutes, the column was shut down, and the holdup product collected separately. The products were then weighed to determine water content, filtered, dried, reweighed, and both ash and total sulfur contents determined.

7.3.3 Effects of Baffle Position

The second set of experiments was intended to determine the effects of baffles positioned above and below the feed inlet, and consisted of experiments with: 1) 8 upper baffles, and 18 lower baffles; 2) 1 upper baffle, and 2 lower baffles; 3) 8 upper baffles, and 2 lower baffles; and 4) 1 upper baffle, and 18 lower baffles. A tracer dye was used to track the water entering with the feed.

7.3.3.1 Materials: These experiments used a coal sample which had been collected from the Empire coal processing plant, consisting of a blend of coals from the Lower and Middle Kittanning seams. This sample was prepared in the same fashion as the Pittsburgh seam sample, except that each 900 gram lot was divided into three 250 gram flotation charges and a 150 gram head sample. The size distribution and assay information is given in Table 7.1. The flotation charge weight for these tests was only 250 grams because greater charge weights with this coal produced an overloaded froth and reduced the recovery.

7.3.3.2 Procedures: Since this coal was too oxidized to be easily floatable with only fuel oil as collector, a mixture of 80% #2 fuel oil and 20% Dow M210 froth conditioner was used. The froth conditioner is an agent to improve the wetting of oxidized coal by oils, and therefore reduces the reagent requirements in flotation of these coals. The collector mixture dosage was 3.4 kg/metric ton coal, and the nominal frother dosage was 0.83 kg/metric ton coal (0.03 g/liter).

The water tracer used in these experiments was five milliliters of standardized solution of sodium fluorescein dye. This was added to the feed slurry in order to allow photometric tracing of the feed water, so that the amount of entrainment in the column could be estimated. During the tests, samples of the filtrate from each sample were collected and filtered a second time through a micropore syringe filter to remove any remaining suspended solids. The concentration of dye was then measured by comparison with standardized solutions using a spectrophotometer.

7.4 EXPERIMENTAL RESULTS

7.4.1 Baffle Open Area

Results from the first ten experiments, using the Pittsburgh seam coal sample, are given in Table 7.2. The 1.5 minute froth product in each case contained a much higher percentage of ash and sulfur than was present in the immediately following froth fractions. This was a result of froth column instabilities at the beginning of experiments, caused by the addition of the feed slurry. However, these instabilities persisted for only a few seconds, and the quantity of material involved was only a few grams. The cumulative grade-recovery curves for percent ash and percent sulfur for all tests are shown in Figure 7.3 and Figure 7.4, respectively, and the overall

TABLE 7.2: Column flotation results for various degrees of baffling. Times are measured from the closure of the drain valve, and the first froth overflow occurred at approximately 1 minute.

Flotation Conditions:
Charge weight: 400 gms
Collector: none
Frother: Dowfroth 200, 0.03 g/liter in all water streams. Nominal 0.5 kg/mt coal
pH: 6-7 (nominal tap water pH)
Water Hardness: 90-150 ppm (Houghton tap water)
Temperature: 15 ^{o}C
Washwater flowrate: 1 liter/min
Aspirator water: 5 liters/min @ 15 psi

A. 14% open area, duplicate experiments

		%Wt.	% Ash	% S	% Wt.	% Ash	% S
Froth	1.5 m	2.08	6.39	1.88	--	--	--
	2 m	1.33	3.07	1.59	0.23	5.10	1.62
	3 m	2.38	2.71	1.58	1.44	3.01	1.56
	4 m	3.31	2.97	1.60	2.41	2.68	1.54
	6 m	8.18	2.84	1.63	4.67	2.76	1.55
	10 m	19.67	3.71	1.74	13.63	2.90	1.60
Holdup		25.82	24.59	4.27	32.84	19.82	3.63
Tails	3 m	5.90	81.88	3.85	3.77	78.64	3.71
Tails	10 m	31.33	77.05	3.64	41.00	65.49	3.47
		(100.00)	(36.62)	3.10	(99.99)	(36.97)	(3.11)
Head sample for both tests			36.95	3.09			

B. 19% open area, duplicate experiments

		%Wt.	% Ash	% S	% Wt.	% Ash	% S
Froth	1.5 m	1.45	4.84	1.83	1.28	10.84	2.05
	2 m	1.79	2.91	1.58	0.91	5.24	1.61
	3 m	4.49	2.98	1.62	2.79	3.62	1.68
	4 m	6.29	3.17	1.67	4.04	3.30	1.67
	6 m	15.80	3.92	1.82	12.31	3.57	1.67
	10 m	28.16	9.22	2.44	31.85	7.02	2.07
Holdup		10.16	51.93	6.77	12.83	42.57	5.79
Tails	3 m	8.91	84.70	4.15	6.10	75.83	4.16
Tails	10 m	22.94	86.34	3.77	27.88	83.04	3.84
		99.99	36.30	3.13	(99.99)	(36.34)	(3.09)
Head sample for both tests			37.19	3.23			

TABLE 7.2: Column flotation results for various degrees of baffling. Times are measured from the closure of the drain valve, and the first froth overflow occurred at approximately 1 minute.

Flotation Conditions:
Charge weight: 400 gms
Collector: none
Frother: Dowfroth 200, 0.03 g/liter in all water streams. Nominal 0.5 kg/mt coal
pH: 6-7 (nominal tap water pH)
Water Hardness: 90-150 ppm (Houghton tap water)
Temperature: 15 ^{o}C
Washwater flowrate: 1 liter/min
Aspirator water: 5 liters/min @ 15 psi

C. 29% open area, duplicate experiments

		%Wt.	% Ash	% S	% Wt.	% Ash	% S
Froth	1.5 m	0.61	7.78	2.35	--	--	--
	2 m	1.07	2.91	1.72	0.86	3.42	1.71
	3 m	3.42	2.85	1.67	3.57	3.11	1.66
	4 m	6.05	3.13	1.74	7.97	3.38	1.73
	6 m	24.11	4.52	1.96	21.59	4.51	1.93
	10 m	22.29	11.74	2.73	23.29	11.54	2.68
Holdup		7.41	56.68	7.45	8.25	57.04	6.99
Tails	3 m	12.79	76.38	4.32	11.39	75.02	4.17
Tails	10 m	22.24	83.91	3.92	23.06	83.87	3.86
		(99.99)	(36.70)	(3.25)	(99.98)	(36.68)	(3.19)
Head sample for both tests			36.85	3.36			

D. 38% open area, duplicate experiments

		%Wt.	% Ash	% S	% Wt.	% Ash	% S
Froth	1.5 m	2.21	7.78	2.03	1.08	4.47	1.75
	2 m	2.85	3.26	1.59	3.03	3.42	1.62
	3 m	8.47	3.83	1.71	10.39	4.18	1.74
	4 m	14.02	4.87	1.88	17.60	5.40	1.87
	6 m	28.17	9.04	2.37	28.47	12.09	2.64
	10 m	7.61	21.95	3.60	3.35	44.37	5.25
Holdup		6.79	71.93	6.98	6.40	64.98	6.36
Tails	3 m	7.61	83.91	4.04	9.48	83.35	4.14
Tails	10 m	22.26	87.79	3.51	20.20	87.70	3.51
		(99.99)	(36.30)	(3.00)	(100.00)	(36.24)	(3.01)
Head sample for both tests			36.78	3.14			

TABLE 7.2: Column flotation results for various degrees of baffling. Times are measured from the closure of the drain valve, and the first froth overflow occurred at approximately 1 minute.

Flotation Conditions:
Charge weight: 400 gms
Collector: none
Frother: Dowfroth 200, 0.03 g/liter in all water streams. Nominal 0.5 kg/mt coal
pH: 6-7 (nominal tap water pH)
Water Hardness: 90-150 ppm (Houghton tap water)
Temperature: 15 °C
Washwater flowrate: 1 liter/min
Aspirator water: 5 liters/min @ 15 psi

E. 100% open area, 3 permanent baffles only, duplicate experiments

		%Wt.	% Ash	% S	% Wt.	% Ash	% S
Froth	1.5 m	2.26	9.37	2.02	4.90	13.67	2.18
	2 m	1.57	3.59	1.65	6.32	4.75	1.86
	3 m	12.54	5.70	2.07	31.50	11.00	2.36
	4 m	18.99	8.50	2.35	15.72	19.31	2.93
	6 m	20.23	10.11	2.58	5.41	9.62	2.49
	10 m	4.39	9.10	2.61	0.74	14.38	2.98
Holdup		11.28	59.73	5.53	8.94	61.70	5.41
Tails	3 m	9.87	83.72	4.42	8.51	83.47	4.36
Tails	10 m	18.86	87.85	3.98	17.96	88.19	3.95
		(99.99)	(36.61)	(3.22)	(100.00)	(36.56)	(3.15)
Head sample for both tests			36.75	3.33			

combustibles recovery versus time profiles are given in Figure 7.5. From these graphs, two points immediately become evident: first, that the grade at any given recovery in the least baffled column is much worse than in the baffled column tests, with further small improvements produced by decreasing the baffle open area; and second, that decreasing the baffle open area decreases the flotation rate very markedly, but has a much smaller influence on the ultimate recovery.

As a standard for comparison of the flotation rates for each baffle type, the time required for recovery of 50% of the total combustible material was selected. In Table 7.3, the 50% recovery times for each configuration, along with the cumulative % ash and % sulfur at 50% recovery, and the maximum combustibles recovery (including the holdup as part of the froth product) are listed. These results are plotted in the graph of Figure 7.6.

7.4.2 Baffle Position and Tracer Results

Tests using the Empire preparation plant sample to determine the effects of baffles above and below the feed inlet, using tracer dye to follow the water added with the feed, produced the results shown in Table 7.4 and Table 7.5. The baffles used in these experiments were those with 29% open area.

The results from Table 7.4 and Table 7.5 are plotted in Figures 7.7-7.11. Figure 7.7 shows

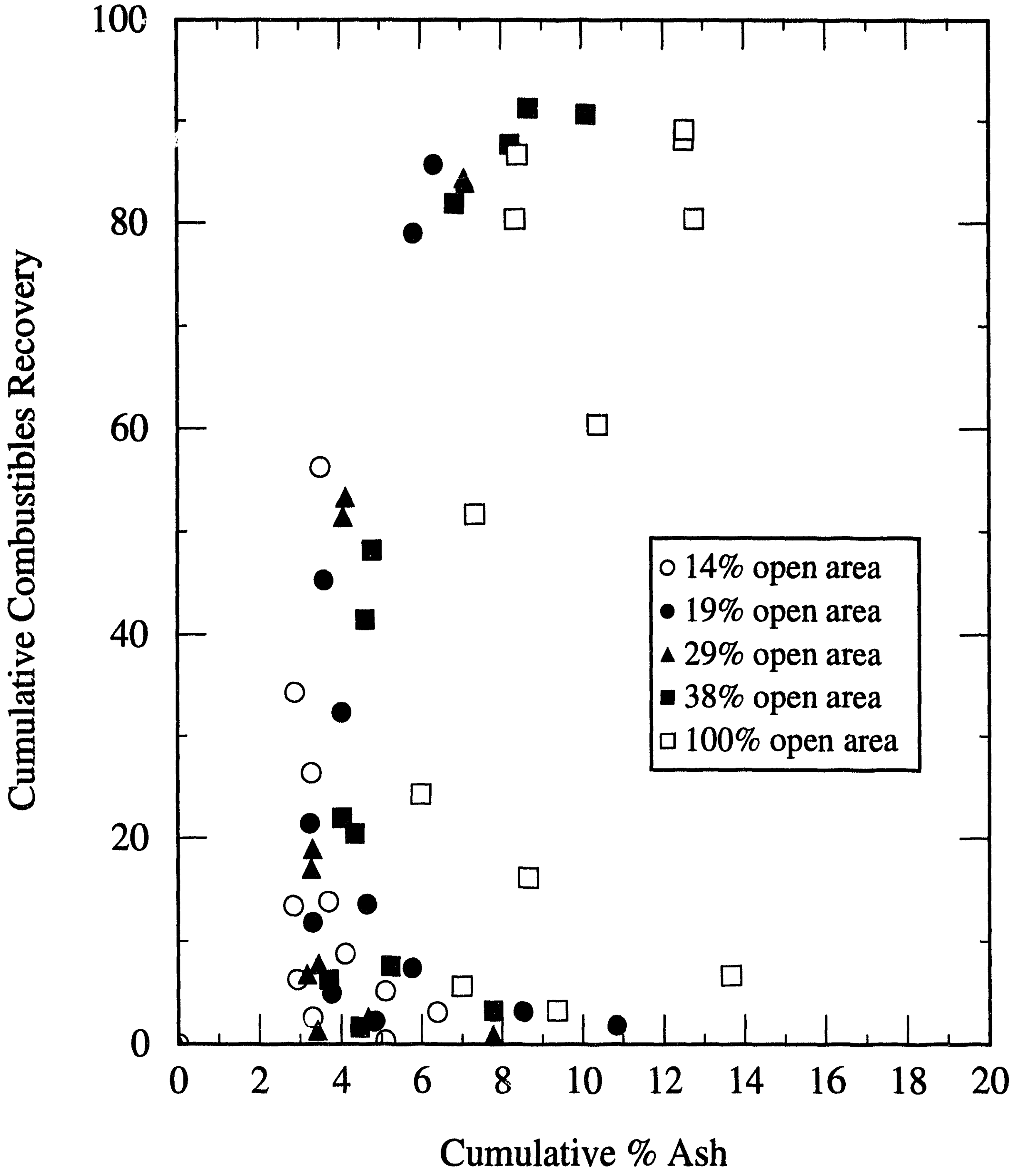


FIGURE 7.3. Grade-recovery performance relative to ash for a 3" diameter floation column with varying amounts of baffle open area. As the open area increases, the amount of ash at a given recovery also increases. The ultimate recovery changes very little when the open area is greater than 19%, but below this value the final recovery falls off very markedly.

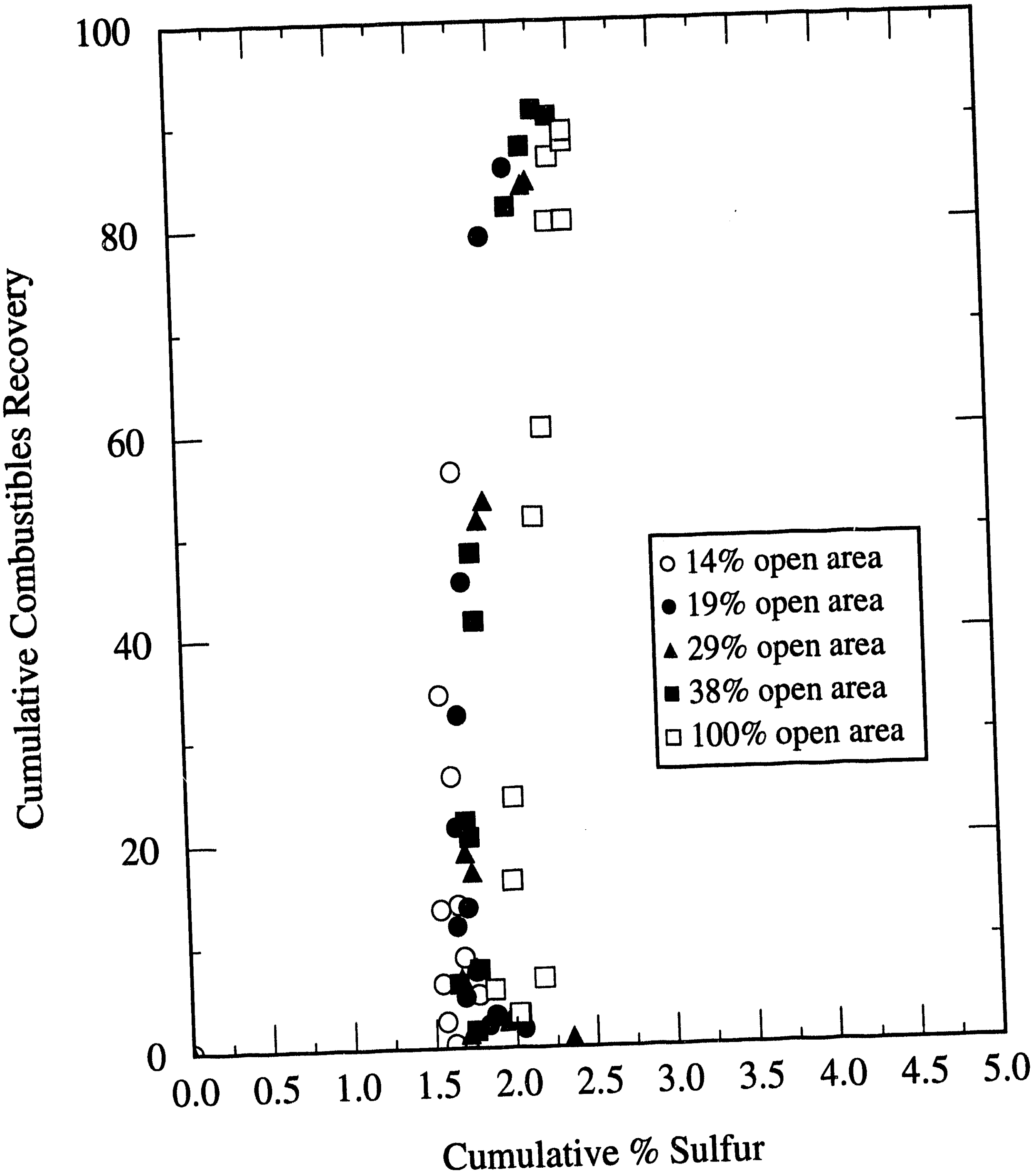


FIGURE 7.4. Grade-recovery curve with respect to total sulfur for a 3" diameter flotation column at various degrees of baffling. Decreasing the baffle open area improves the sulfur removal at any given recovery, but the effect is not as large as for the ash content. This is mainly due to the locked and organic sulfur in this coal (1.7% wt) which cannot be removed by physical separations such as flotation.

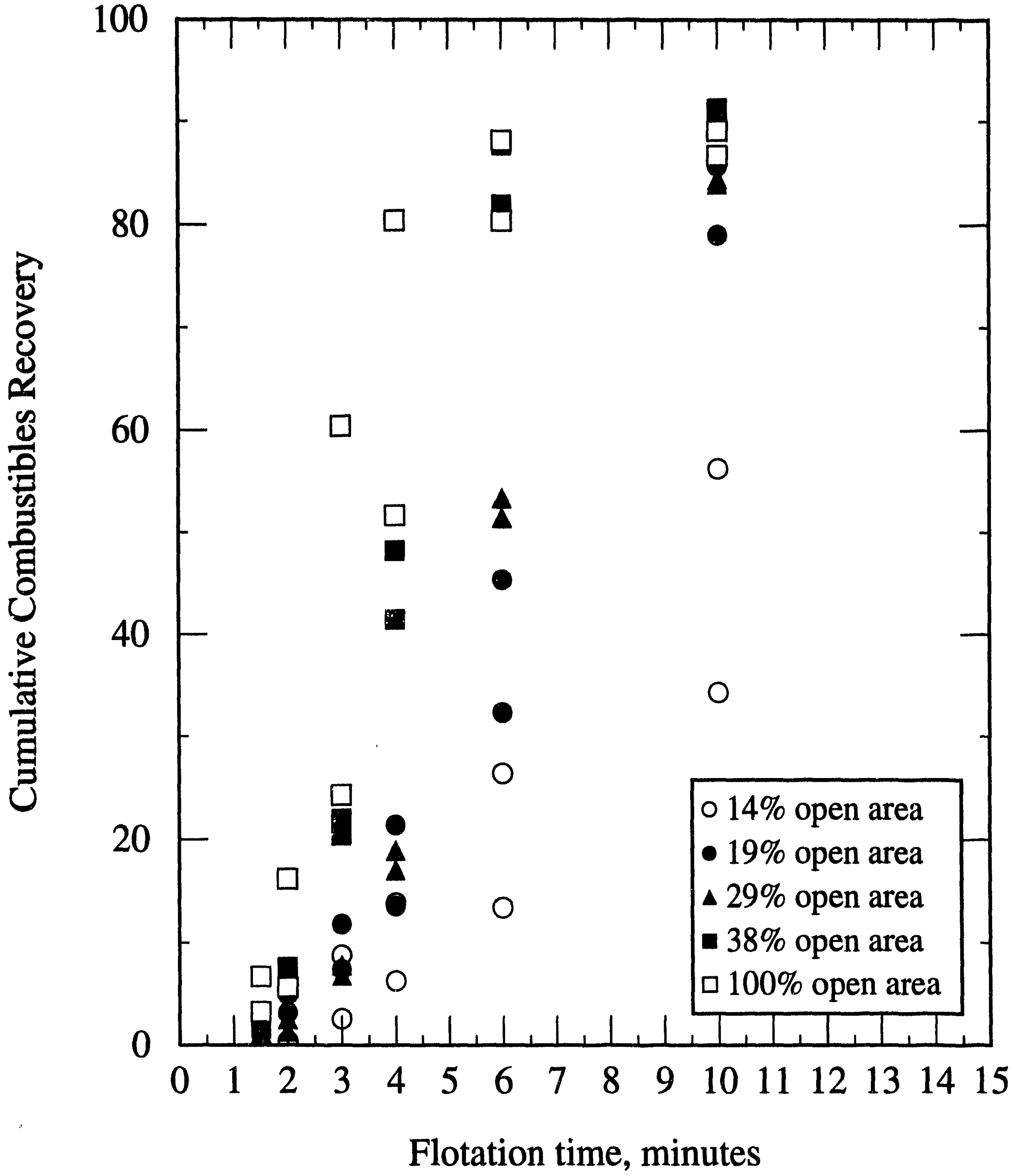


FIGURE 7.5. Combustibles recovery as a function of time at various levels of baffling. Increasing the degree of baffling slows the flotation rate, particularly at 14% open area. However, the baffles do not noticeably reduce the ultimate recovery until there is less than 29% open area.

TABLE 7.3: Summary of column baffling results. The 50% recovery time is the time taken for the column to reach 50% weight recovery. The %Ash and %Sulfur values are the values at 50% weight recovery. The Maximum Combustibles Recovery is the percentage of the total amount of combustible matter that either reached the froth or was still held up in the body of the column at the end of the test.

% Open Area	50% Recovery Time (min)	% Ash	% S	Maximum Combustibles Recovery
100%	3.5+/-0.5	8.5+/-1.3	2.24+/-0.02	89.2+/-1.4
38%	4.2+/-0.2	4.8+/-0.1	1.83+/-0.02	91.3+/-0.7
29%	5.9+/-0.1	4.0+/-0.1	1.85+/-0.01	89.2+/-0.5
19%	7.1+/-0.5	4.0+/-0.2	1.75+/-0.03	89.6+/-1.2
14%	11.2+/-1.6	3.3+/-0.1	1.72+/-0.05	80.1+/-3.8

that the baffles have a profound effect on the entrainment of feed water in the froth phase. With no baffles present over 30% of the feed water was entrained, while with all baffles in place the entrainment was reduced to only 4%. Each set of baffles alone provided very similar results, which were intermediate between the least baffled and the fully baffled tests. Figure 7.8 gives the corresponding coal recoveries as a function of time and degree of baffling, and it is seen that while the baffles do reduce the total recovery and slow the total recovery rate, the effect is much lower than that seen for the tracer recovery.

The grade-recovery curves given in Figures 7.9 and 7.10 show that the presence of baffles either above or below the feed inlet improves the product quality at a given recovery, with the best results seen when both sets of baffles are present. Figure 7.11 shows the change in residence time which occurs as a result of baffling.

7.5 DISCUSSION

7.5.1 Effects of Baffling

The results show that horizontal baffling of a coal column produces a significant improvement in product grade, but only at a cost of reduced capacity. However, Figure 7.6 shows that while the time needed for flotation falls nearly exponentially with increasing baffle open area, the ash and sulfur content at 50% recovery increases essentially linearly. The inflection of the flotation time curve, which occurs at 30-40% open area, shows the region where the drawback of the baffles (reduced capacity) begins to increase faster than the benefit (improved product quality), and so this represents the optimum baffle open area. At larger values of the open area, the column grade can be improved with little loss of capacity by decreasing the open area, while at smaller values of open area the capacity can be improved significantly with little loss of grade.

An additional benefit of baffling is that the reproducibility of the column is markedly improved. This is evident in Table 7.3, where the variation in ash content under least baffled conditions is 1.3% ash, as compared to 0.2% ash or less for all baffled experiments.

From Figures 7.3 and 7.4, which summarize the overall grade-recovery performance, it is

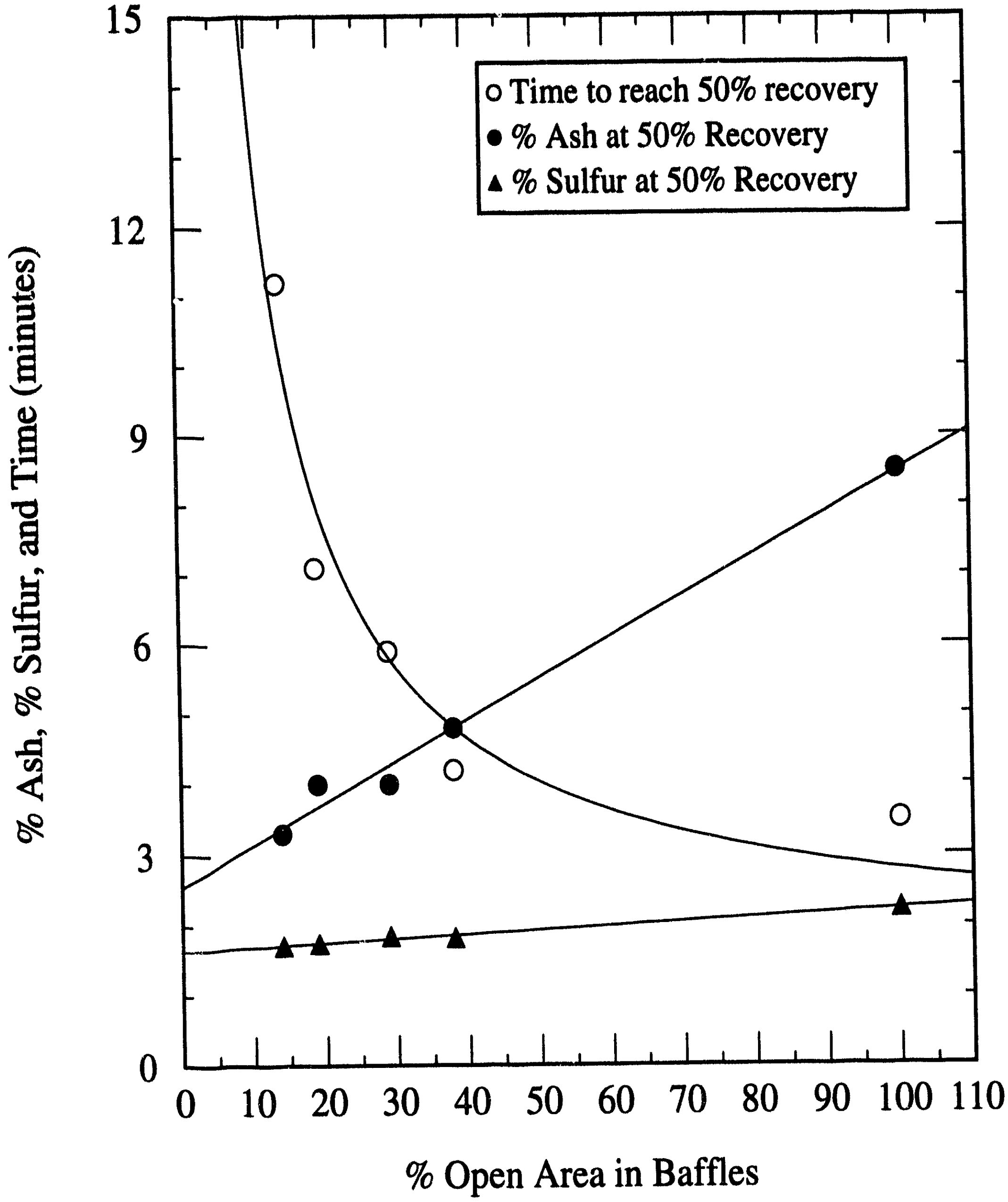


FIGURE 7.6. Composite results, showing the variation of time needed to reach 50% recovery, sulfur content at 50% recovery, and ash content at 50% recovery as a function of baffle open area. At less than 30-40% open area, the floation time increases very markedly, showing that the capacity is being reduced much faster than the ash and sulfur removal is being improved. When the baffle open area is increased beyond 40%, the grade worsens more than the capacity improves. Therefore, the optimum baffle open area is in the range of 30-40%.

TABLE 7.4: Results from flotation tests with the coal from the Empire preparation plant, with no baffles, baffles above the feed inlet, baffles below the feed inlet, and baffles in both positions. The tracer results for the froth products are expressed in terms of the percentage of the fluorescein dye added with the feed that reported to the froth product.

Flotation Conditions:
Charge Size: 250 gms
Collector: 80% #2 fuel oil/20% Dow M210 3.44 Kg/mt coal
Frother: Dowfroth 200, 0.03 g/liter in all water streams. Nominal 0.84 kg/mt
pH: 6-7 (nominal tap water pH)
Temperature: 150 °C
Washwater flowrate: 1 liter/min
Aspirator water: 5 liters/min @ 15 psi
Water in feed: 1444 ml
Tracer Concentrate added: 5 ml
Note: samples without listed BTU values would not burn completely in the calorimeter bomb.

A. Test 1: 8 baffles above feed inlet; 18 baffles below feed inlet

Time	% weight	% Ash	% Sulfur	BTU/lb	% Tracer Recovery
2 min	13.98	3.20	2.30	13885	1.8
3	39.56	3.94	2.58	13723	4.4
4	20.84	6.39	2.86	13399	2.2
6	3.64	13.70	3.87	12079	0.4
10	0.51	--	5.05		0.2
Holdup	4.49	44.25	11.4		
Tails	16.98	37.80	4.05		

B. Test 2: 8 baffles above feed inlet; 2 permanent baffles below feed inlet

Time	% weight	% Ash	% Sulfur	BTU/lb	% Tracer Recovery
2 min	30.35	3.9	2.37	13617	8.28
3	38.96	5.3	2.78	13474	6.10
4	10.29	9.2	3.40	12778	0.92
6	1.85	13.6	4.30	12089	0.26
10	0.55	--	4.04		0.11
Holdup	1.30	44.2	11.2		
Tails	16.71	43.1	5.05	6936	

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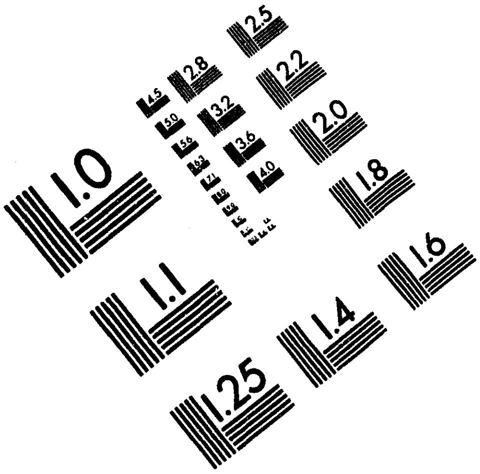

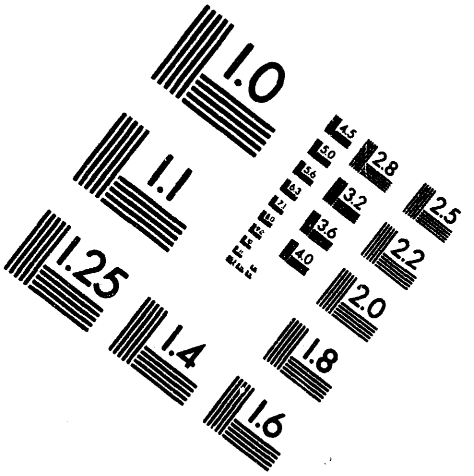

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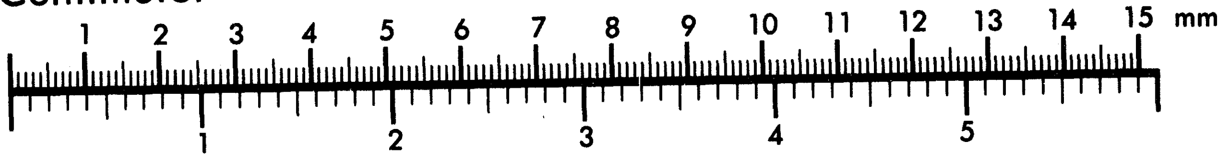

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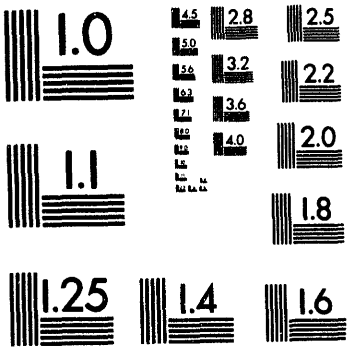

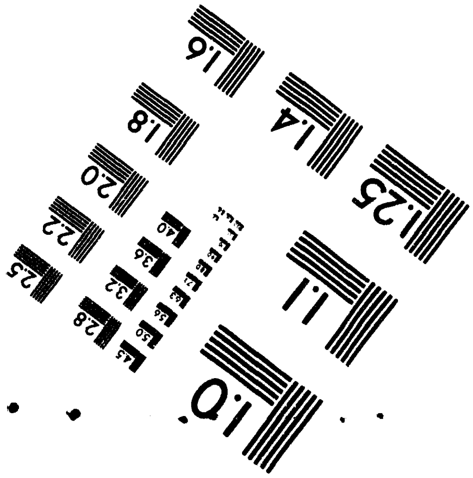

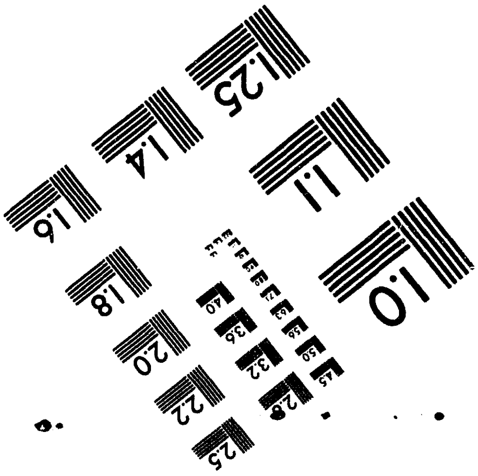

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TABLE 7.4: Results from flotation tests with the coal from the Empire preparation plant, with no baffles, baffles above the feed inlet, baffles below the feed inlet, and baffles in both positions. The tracer results for the froth products are expressed in terms of the percentage of the fluorescein dye added with the feed that reported to the froth product.

Flotation Conditions:
Charge Size: 250 gms
Collector: 80% #2 fuel oil/20% Dow M210 3.44 Kg/mt coal
Frother: Dowfroth 200, 0.03 g/liter in all water streams. Nominal 0.84 kg/mt
pH: 6-7 (nominal tap water pH)
Temperature: 150 °C
Washwater flowrate: 1 liter/min
Aspirator water: 5 liters/min @ 15 psi
Water in feed: 1444 ml
Tracer Concentrate added: 5 ml
Note: samples without listed BTU values would not burn completely in the calorimeter bomb.

C. Test 3: Permanent baffles only (one above feed inlet; two below feed inlet)

Time	% weight	% Ash	% Sulfur	BTU/lb	% Tracer Recovery
2 min	65.25	6.4	2.87	13332	24.56
3	19.45	8.4	3.23	12917	7.60
4	2.75	14.2	4.15	11944	0.26
6	1.15	17.1	4.87	11362	0.18
10	0.62	--	4.18		0.10
Holdup	1.31	39.6	7.67		
Tails	9.46	58.7	5.42	4376	

D. Test 4: One baffle above feed inlet, 18 baffles below feed inlet

Time	% weight	% Ash	% Sulfur	BTU/lb	% Tracer Recovery
2 min	23.16	4.1	2.56	13695	4.66
3	40.04	5.4	2.78	13527	7.80
4	14.61	6.9	3.01	13217	1.42
6	2.53	15.3	4.18	11771	0.26
10	0.51	--	4.71		0.14
Holdup	3.49	55.9	11.4	5222	
Tails	15.66	38.5	4.14	7758	

TABLE 7.4: Results from flotation tests with the coal from the Empire preparation plant, with no baffles, baffles above the feed inlet, baffles below the feed inlet, and baffles in both positions. The tracer results for the froth products are expressed in terms of the percentage of the fluorescein dye added with the feed that reported to the froth product.

Flotation Conditions:
Charge Size: 250 gms
Collector: 80% #2 fuel oil/20% Dow M210 3.44 Kg/mt coal
Frother: Dowfroth 200, 0.03 g/liter in all water streams. Nominal 0.84 kg/mt
pH: 6-7 (nominal tap water pH)
Temperature: 150 ^{o}C
Washwater flowrate: 1 liter/min
Aspirator water: 5 liters/min @ 15 psi
Water in feed: 1444 ml
Tracer Concentrate added: 5 ml
Note: samples without listed BTU values would not burn completely in the calorimeter bomb.

E. Test 5: 8 baffles above feed inlet; 18 baffles below feed inlet

Time	% weight	% Ash	% Sulfur	BTU/lb	% Tracer Recovery
2 min	12.27	3.1	2.28	13738	1.22
3	29.54	3.3	2.46	13778	1.48
4	24.63	5.8	2.86	13318	1.28
6	9.61	7.9	3.12	13023	0.36
10	2.67	9.0	3.40	12738	0.24
Holdup	7.70	33.9	9.09	9079	
Tails	13.53	45.9	4.33	6366	

immediately evident that baffling moves the grade to lower values of ash and sulfur for any given recovery. The ultimate recovery is not greatly reduced until the baffling becomes extreme, at which point overloading of the cleaning zone begins to force floatable coal into the tailings. Again, it is seen that 30-40% open area is near optimum, as ash and sulfur removal is greater than that achieved by the least baffled column, but losses of recovery are still small.

When the column baffling is extreme, at 15% open area or less, the flow of coal particles in the cleaning zone is much more restricted than the flow in the scavenging zone, due to the great volume of solids recovered in the froth during coal flotation. If extreme baffling of a column is desired, it may be possible to maintain reasonable recovery by decreasing the baffle open area with depth. This will allow the flow in the scavenging zone to be throttled to the same extent as the flow in the cleaning zone, and thus prevent coal from being forced into the tailings.

It would normally be expected that adding baffles above the feed inlet would primarily act to improve the froth grade, while adding baffles below the feed inlet would increase the column residence time and improve recovery. The results of these experiments shows that the division of function is not nearly this specific, with lower baffles acting in part to improve grade to nearly the same extent as the upper baffles do. However, Figure 7.11 shows that the lower baffles are

TABLE 7.5: Concentration of tracer dye in the tailings products from the tests described in Table 7.4. Dye concentrate was a saturated solution of fluorescein in water. Dye levels are expressed as grams of liquid concentrate per liter of filtrate. The nominal tailings flowrate was 6liters/ minute, and the holdup volume was 7 liters. The precise tailings flowrates were not measured in the course of these tests, because the large water volume and the fluctuations in the building water pressure would have made this very difficult.

	Concentration of dye in tailings (g/liter)				
Time	Test 1	Test 2	Test 3	Test 4	Test 5
1.5 min	--	0.14	0.11	0.01	0.00
2.5	0.16	0.18	0.17	0.11	0.13
3.5	0.16	0.20	0.21	0.14	0.19
4.5	0.24	0.21	0.17	0.18	0.20
6.5	0.23	0.12	0.11	0.18	0.23
10	0.09	0.03	0.03	0.08	0.08
Holdup	0.18	0.06	0.06	0.18	0.16

responsible for essentially all of the improvement in residence time, as would be expected. From observation of the froth during these experiments, it was seen that the froth is much more turbulent when no baffles are present, due to the vigorous vertical mixing currents which exist when there are no baffles, and to the increased tendency for very large air bubbles to form when there is nothing in the column to limit their maximum size. As a result, any baffles will act to reduce these effects, and will therefore improve the quality of washing in the froth.

7.5.2 Comparison of the Baffled Column and Conventional Cells

The tracer results for the Empire coal sample can be used to calculate a comparison between entrainment in the baffled column and in a hypothetical conventional cell operating under nominally identical conditions. The theoretical maximum amount of pure entrainment will be determined by the ratio w/c, where w is the weight of feed water which reports to the froth, and c is the weight of coal reporting to the froth. A perfectly entrained particle will go wherever the feed water goes, and so the higher this ratio becomes, the higher entrainment will be.

For Tests 3 (no baffles) and 5 (all baffles) with the Empire coal sample, the tracer results gave the feed water/coal ratios listed in Table 7.6. This table also includes the ratios that would be produced by hypothetical conventional flotation cell operating at the same nominal percent solids, with the froth at 15, 20, 25, 30, 35 and 40% solids in the conventional cell.

Table 7.7 lists the maximum amount of fine, entrained solids that could enter the froth product for various levels of fine gangue in the feed and various w/c ratios. A conventional cell with a pulp density of 3.6% was used for comparison because the column feed is diluted to this level by washwater and bubble-generator water shortly after it enters the column. For the baffled column, at a w/c ratio of 0.36 and a feed percent solids of 17.36%, there is only 43.4% as much entrainment as in a conventional cell with a w/c ratio of 4.0 (froth % solids = 20%) and a feed percent solids of 3.6%. If the entrained species is pyritic sulfur, then, for example, if 2% of the

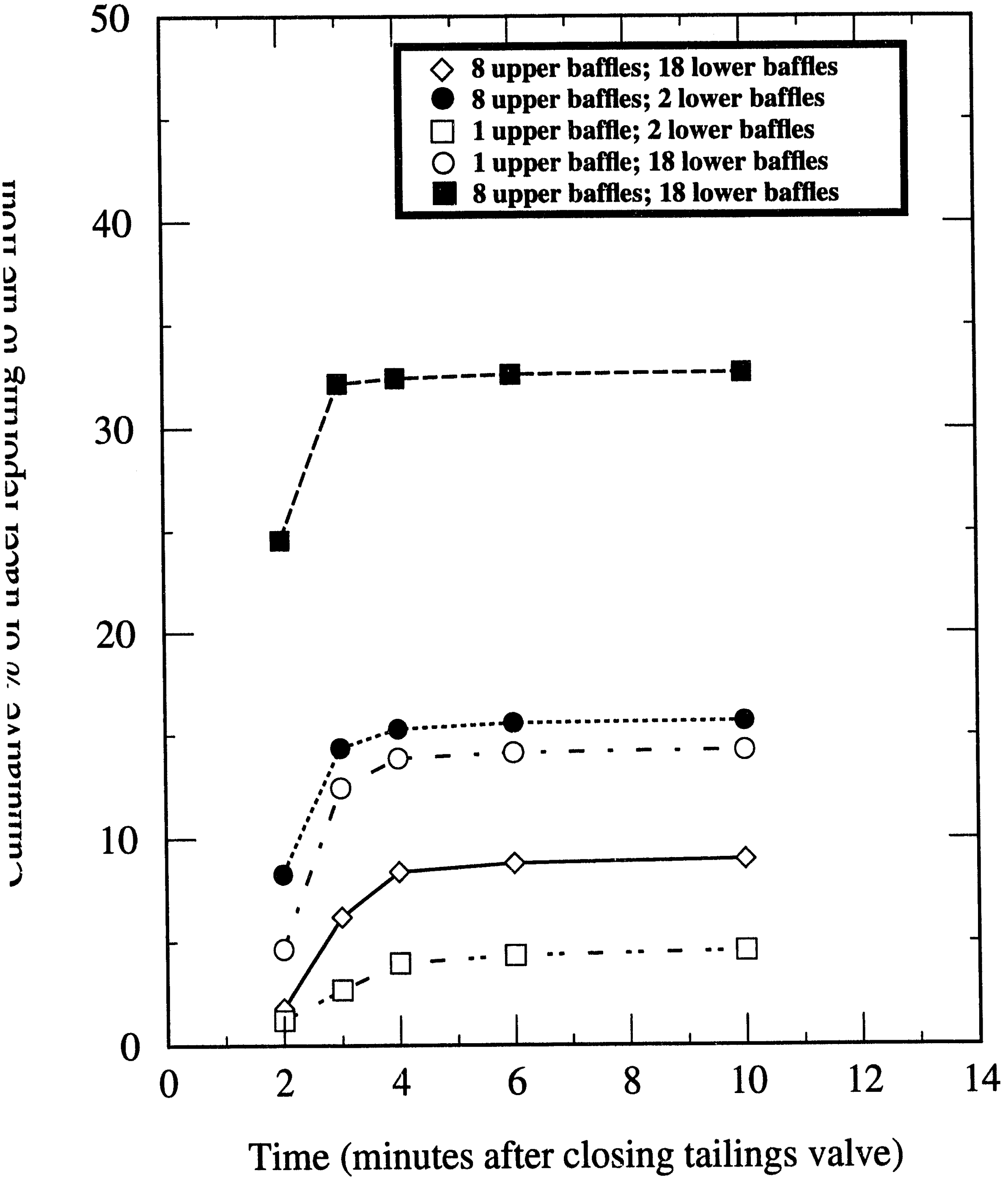

FIGURE 7.7. Effect of the presence of baffles above and below the feed inlet on the recovery of feed water into the froth, as indicated by the recovery of tracer dye (sodium fluorescein). The baffles used had 29% open area, and the coal was collected from the Empire coal processing plant (#5 and #6 seams). These results clearly show that the baffles greatly reduce the entrainment of feed water into the froth.

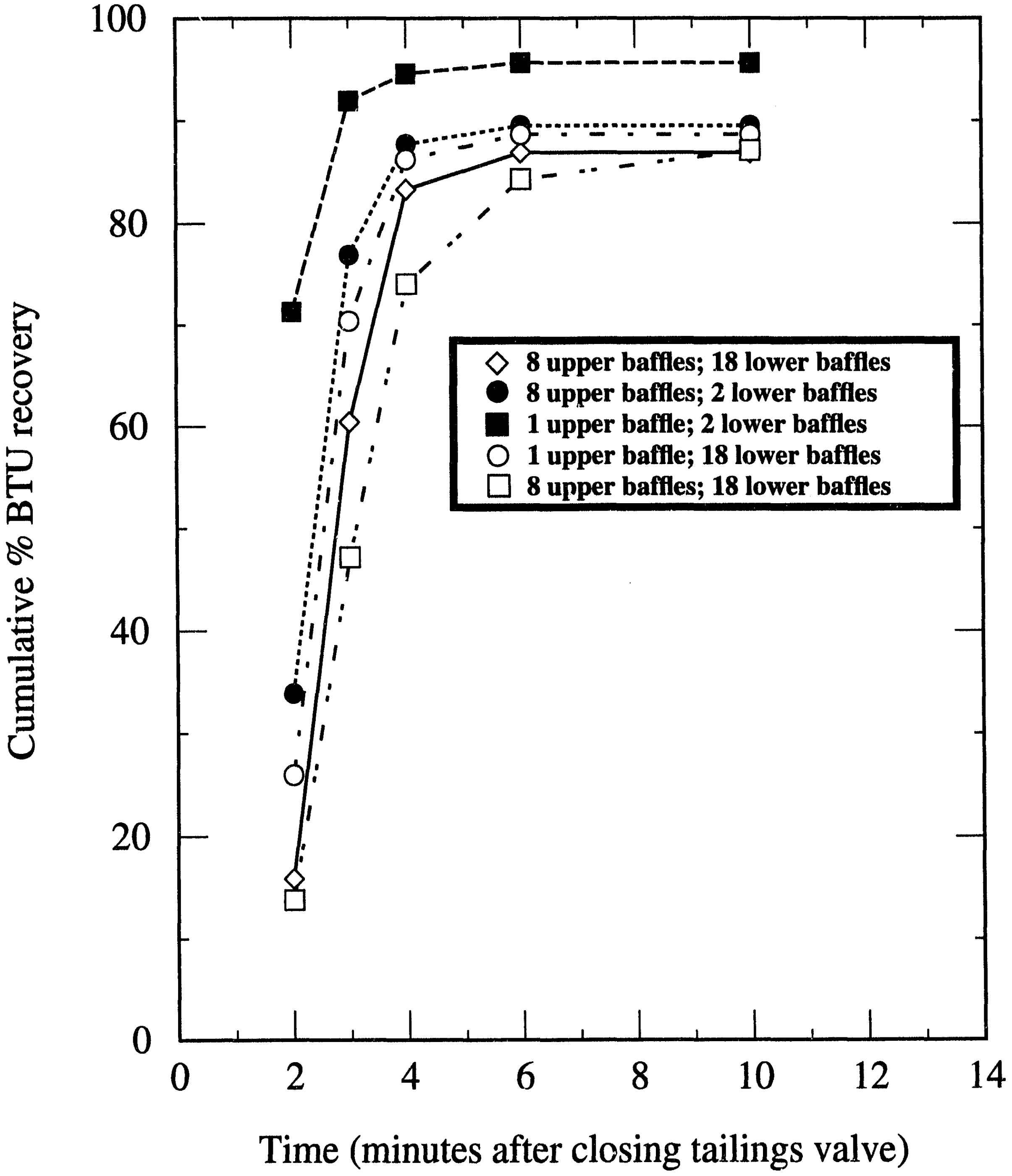

FIGURE 7.8. Effect of baffles above and below the feed inlet on the BTU recovery of the Empire coal. While the recovery is slightly reduced by the presence of the baffles, the reduction is not nearly as large as the reduction in feed water recovery shown in Figure 7.7. This shows that the baffles are indeed reducing the fraction of entrained water, and not simply reducing the recovery of all components equally.

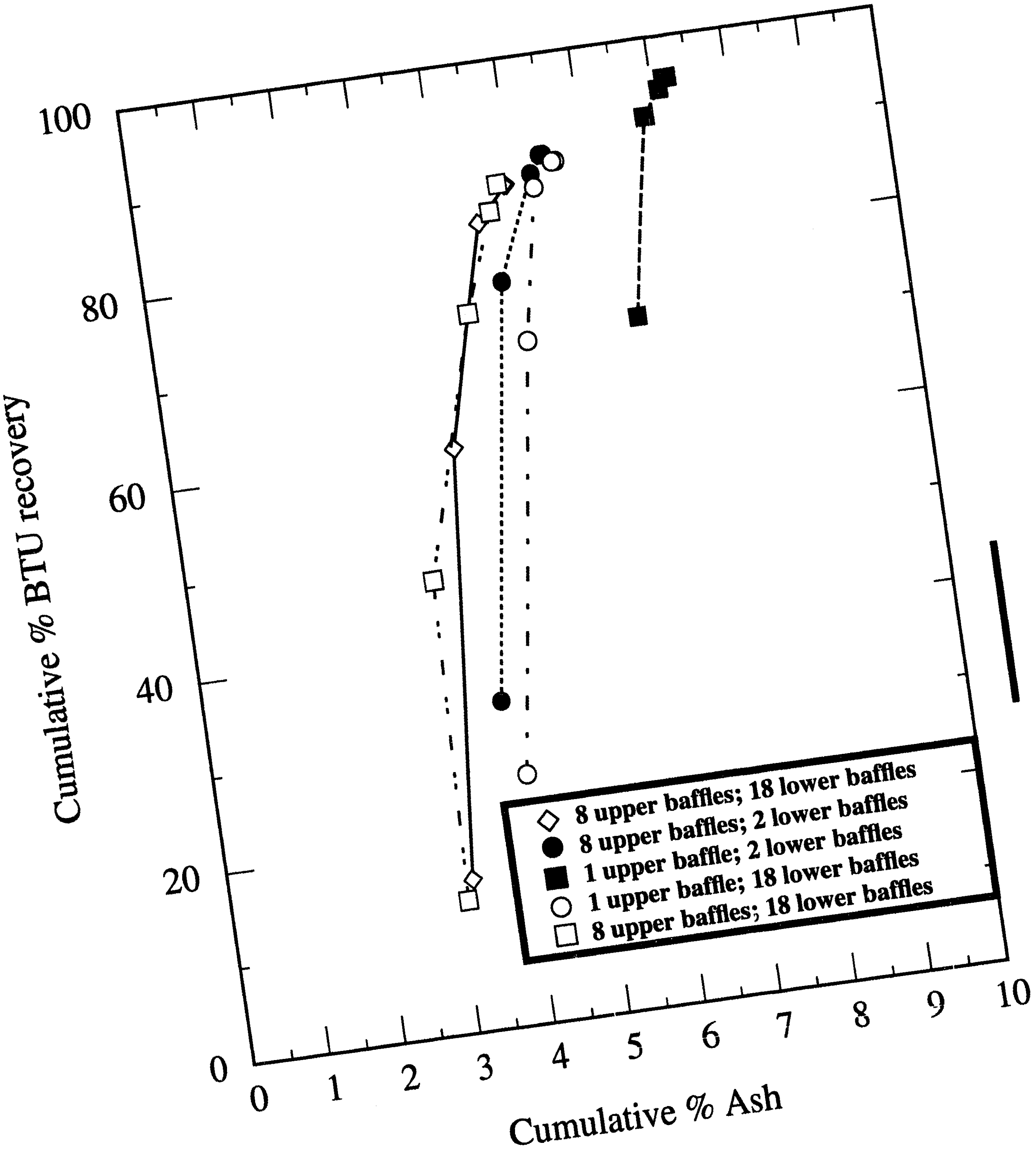

FIGURE 7.9. Grade-recovery performance with respect to ash for the Empire coal sample, showing the effects of baffle position. Baffles either above or below the feed inlet are about equally effective for improving the grade/recovery performance, but baffles in both positions gives better results than either set of baffles alone.

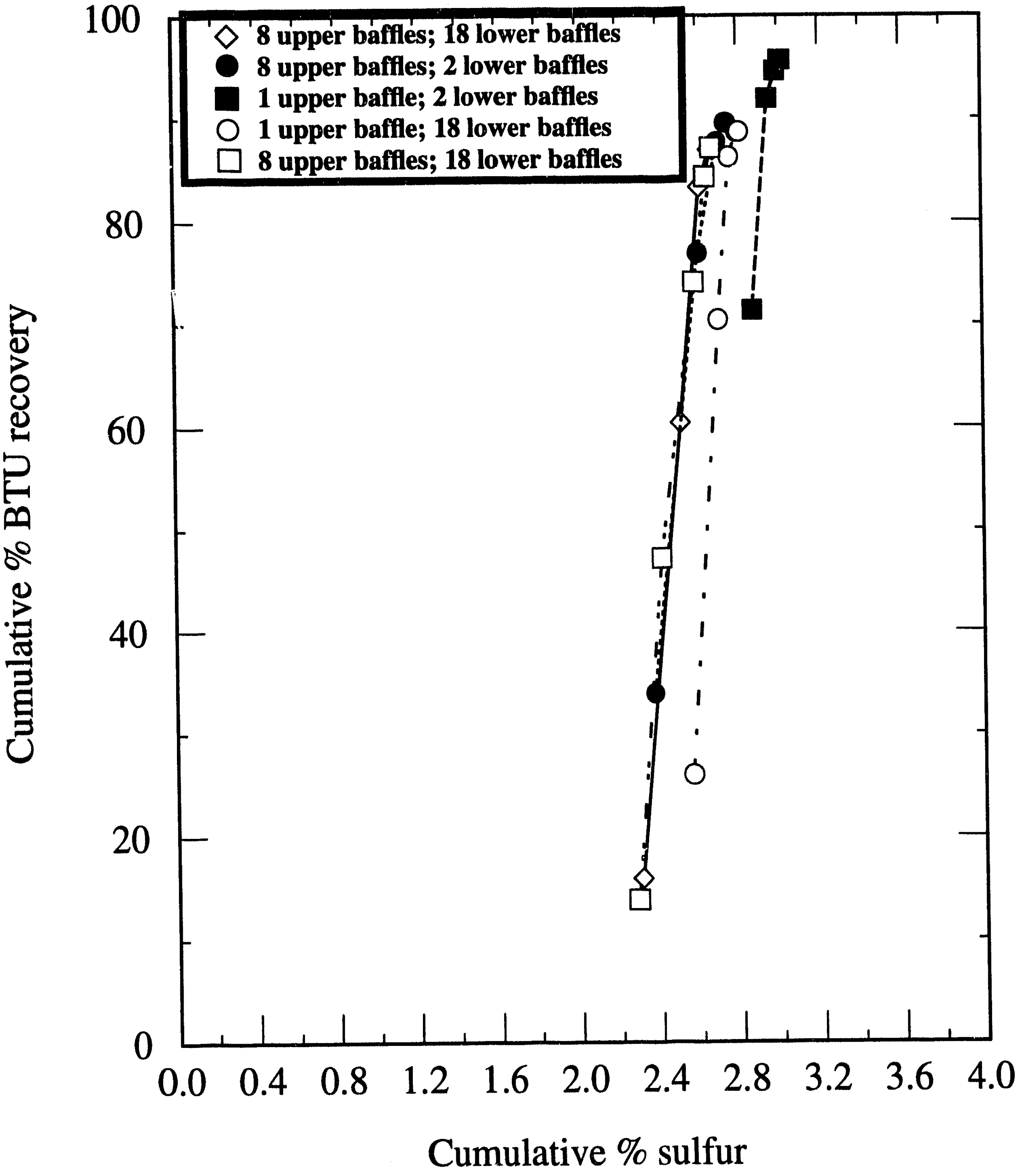

FIGURE 7.10. Grade-recovery performance for the Empire sample with respect to sulfur. As in Figure 7.8 for ash, the baffles improve the quality of the product at any given grade. The change is smaller for the sulfur because of the organic sulfur in the coal, which cannot be removed by froth flotation.

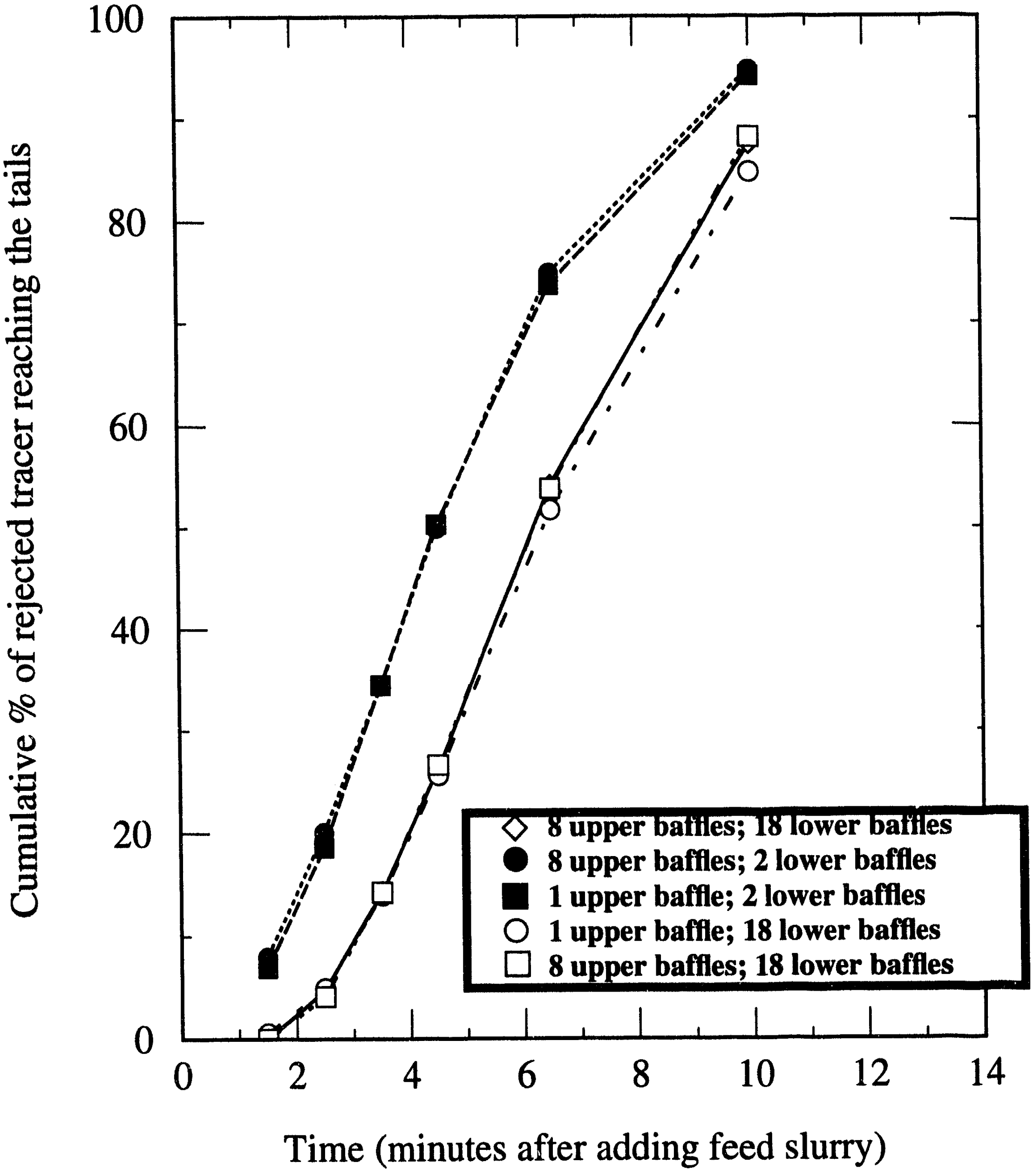

FIGURE 7.11. Effects of baffle position on the retention time of tracer dye in the column. The lower set of baffles account for all of the increase in retention time, as the test with the upper baffles alone showed exactly the same retention as the test with no baffles. The increase in retention from the lower baffles is mainly due to the reduction of short-circuiting of feed directly to the tailings. This ensures that more of the floatable particles have the opportunity to float than would be the case when the lower baffles are not present.

TABLE 7.6: Comparison between the baffled column and a hypothetical conventional flotation cell producing froth at several %solids. The w/c ratio is calculated based on tracer recoveries in the column tests.

	Column Flotation Experiments					
	Test 3 (3 baffles)		Test 5 (all baffles)		Calculated Conventional Cell	
Time	%wt	w/c	% wt	w/c	Froth % Solids	w/c
2 min	65.25	2.18	12.27	0.61	15	5.67
3	19.45	2.26	29.54	0.39	20	4.00
4	2.75	0.54	24.63	0.37	25	3.00
6	1.15	0.90	9.61	0.35	30	2.33
10	0.62	0.93	2.67	0.35	35	1.86
Total	89.22	2.12	78.72	0.36	40	1.50

feed coal is entrainable pyritic sulfur, then the baffled-column froth product will contain no more than 0.125% entrained pyritic sulfur, while a comparable conventional cell with 20% solids in the froth will contain 0.288% entrained pyritic sulfur. For a conventional cell to be comparable to the baffled column, the froth percent solids would have to be increased to nearly 40%, which would introduce serious problems with the froth fluidity.

The least baffled column performs worse than the conventional cell with 20% solids in the froth, which at first glance seems to be contrary to the published literature which says that columns perform better than conventional cells. However, it should be kept in mind that the column used in this work is only six feet tall, which is approximately 1/2 to 1/3 the height which is normally used for columns of comparable diameter. There is also a difficulty in the calculation of pulp % solids for comparison of conventional flotation to column flotation. While the nominal volume of the column was approximately 7 liters, the coal was never uniformly distributed throughout the column. Therefore, the actual percent solids near and above the feed inlet was much higher than the value calculated by dividing the amount of feed by the total pulp volume in the column. The percent solids may have been as high as 10-15% in places, while the nominal value in the whole column was only 3.6%. Therefore, from the standpoint of comparing entrainment levels, the hypothetical conventional cell at 3.6% solids is really too dilute, but there is no really good way to determine what the actual value should be.

7.6 CONCLUSIONS

In the column flotation of coal, a number of benefits are gained by the introduction of baffles. These include:

1. Good performance with less column height
2. Better selectivity due to reduced backmixing and entrainment
3. Increased reproducibility due to reduction of large-scale turbulence and froth churning

As a result of trade-offs between these benefits and the problem of reduced capacity due to increased residence time, the optimum open area in the baffles is between 30 and 40 percent. This achieves most of the benefits of baffling while not greatly reducing the column capacity.

Tracer studies showed that the baffled column produced only 43.4% as much entrainment

TABLE 7.7: Calculated maximum percentages of entrained material in flotation froth products, for various feed water/coal ratios in the froth. The actual feed to the column was 17.36% solids. Since the nominal percent solids in the column dropped to 3.6% solids after the feed was diluted by washwater and bubble generator water, this is the value that was used to calculate comparative results for a hypothetical conventional flotation cell.The listed w/c ratios correspond to the following conditions:
0.36 -- fully baffled column;
2.12 -- column with 3 baffles;
1.5-- conventional cell, 40% solids in froth;
2.33-- conventional cell,30%solids in froth;
4.0 -- conventional cell, 20% solids in froth.

Percent of entrainable material in feed	Feed 17.36% solids		Feed 3.60% solids		
	w/c=0.36	w/c=2.12	w/c=1.5	w/c=2.33	w/c=4.0
0.25	0.0156	0.0920	0.0135	0.0210	0.360
0.50	0.0312	0.1840	0.0270	0.0419	0.0720
1.00	0.0625	0.3680	0.540	0.0839	0.1440
1.50	0.0937	0.5520	0.810	0.1258	0.2160
2.00	0.1250	0.7361	0.1080	0.1678	0.2880
2.50	0.1562	0.9201	0.1350	0.2097	0.3600
3.00	0.1875	1.1041	0.1620	0.2516	0.4320
5.00	0.3125	1.8402	0.2700	0.4194	0.7200
10.00	0.6250	3.6803	0.5400	0.8388	1.4400
20.00	1.2499	7.3606	1.0800	1.6776	2.8800
30.00	1.8749	11.0410	1.6200	2.5164	4.3200

as a hypothetical conventional cell would have operating at the same nominal percent solids. The least baffled column did not perform as well as a comparable conventional cell, but this is largely due to the fact that the column is only about 1/2 to 1/3 the height that an unbaffled column should be. Much of the performance difference between the baffled and least baffled column is therefore attributed to the baffles reducing the amount of column height needed for good performance.

CHAPTER 8: PLANT STUDIES AT EMPIRE COAL

8.1 INTRODUCTION

Based on the results given in Chapters 6 and 7 for experiment conducted on a laboratory scale, it was concluded that a baffled flotation column would be considerably more effective than either conventional flotation machines or existing columns for the following reasons:

1. Flotation columns provide a means for washing entrained solids from the froth, thus improving the selectivity between hydrophobic and hydrophilic particles as compared to conventional machines.

2. Existing flotation columns must be very tall in order to provide room for a long separation between the froth and tailings product, which allows for a gradual transition from one to the other rather than the abrupt transition between the pulp and froth which occurs in conventional machines. The introduction of horizontal baffles in a column results in less short-circuiting of floatable material directly to the tailings, and less backmixing of tailings into the froth phase, than in an unbaffled column of the same height.

Laboratory experiments described in Chapters 4-6 also showed that the most important factor causing pyrite to be recovered in coal flotation froths was entrainment, rather than hydrophobicity of the pyrite surface as had previously been believed. As a result, simply reducing the levels of entrainment through the use of column flotation was more effective than attempting to use pyrite depressants to prevent the pyrite from being hydrophobic. It was also found that column flotation was as effective for removing sulfur from fine coal as was bacterial leaching, and could be carried out in a matter of minutes rather than days. The main question remaining was whether the baffled column would still perform well when scaled up. A pilot-scale column was therefore designed and constructed, and trials were conducted at a coal processing plant operated by the Empire Coal Company, Gnadenhutten, Ohio to determine how the column would operate in a plant environment on a larger scale.

8.2 COLUMN DESIGN

The column was based on a basic 8" diameter Flotaire flotation column, as shown in Figure 8.1. The basic column had a maximum height of 30' (9.1 meters), with a pneumatic control system to maintain the pulp at the desired level by regulating the flow through the tailings outlet at the base. A transparent sight glass on the side of the column provided a means for observing the liquid level inside the column, so that the controller could be adjusted to give the desired froth depth. All experiments were conducted with a froth depth of 24 +/- 1 inches (61+/-2.5 cm). Feed was pumped into the column as a slurry with an air-operated diaphragm pump, with the pump speed adjusted using a pressure regulator and a needle valve. Reagents were pumped into the feed stream using a diaphragm reagent pump, and the feed was introduced to the column through a feed funnel which discharged into the column at a depth of 4' (1.22 meters) from the overflow lip. Air bubbles were produced and injected using two Deister bubble generators, which mix air and water at a pressure of 60-70 psi (414-484 KPa) to produce a dispersion of fine bubbles, with a mixing ratio of 1 scfm (28.3 liters) of air per gallon (3.78 liters) of water (volume ratio at atmospheric pressure of 7.5:1). There were two bubble generators, one at the midpoint of the column (15 feet (4.6 meters) from the top), and the other at the column base (30 feet (9.1 meters) from the top). A reagent pump injected frother solution directly into the water supply for the bubble generators. A washwater ring immersed in the upper part of the froth

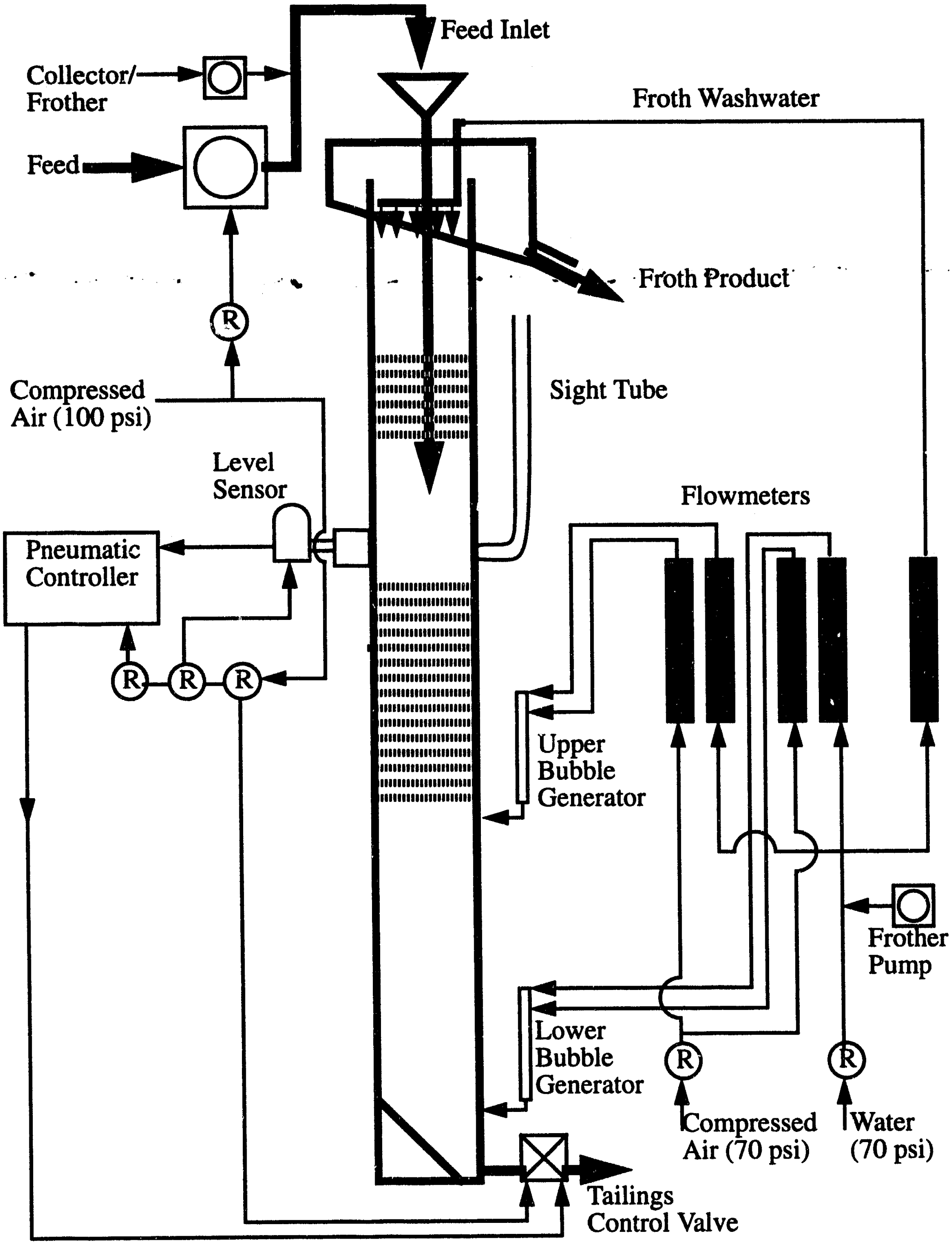

FIGURE 8.1. Basic 8" diameter Deister Flotaire column, showing all necessary fluid supply and control lines.

sprayed clean water into the froth at 2 gallons/minute (7.57 liters/min). Frother was ultimately also added to the washwater at the same dosage as was added to the bubble generator water, to keep the froth from collapsing due to all of the frother being washed out of it. An additional trickle of water was added to the sight glass, in order to keep coal from accumulating in it.

The baffles installed in the column were in two zones: the upper baffle zone was between the feed inlet and the base of the froth, and the lower baffle zone was below the feed inlet. The dimensions of the various zones in the baffled column were as follows:

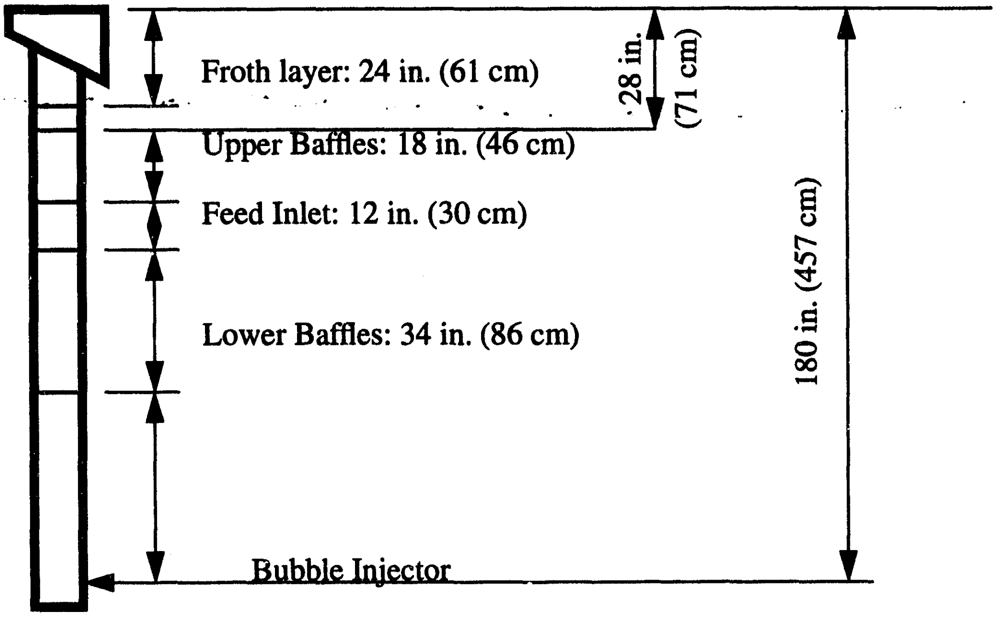

FIGURE 8.2. Dimensions of the important zones in the baffled pilot-scale flotation column.

8.3 PLANT CONDITIONS

The fines cleaning circuit of the Empire Coal preparation plant is shown in Figure 8.3. The fine product from the jigs and the main coal screen was pumped to a bank of twelve classifying cyclones, where the bulk of the -100 mesh fines were removed and sent to the thickener. The cyclone underflow was then distributed through a bank of eight Reichert spirals, and the clean coal product was dewatered on two curved-deck screens. The coarse product from the dewatering screens was then dried with a screen-bowl centrifuge, and sent to the clean coal stockpile. The underflow from the clean coal dewatering screens was selected as the feed for on-line continuous tests with the column. The material sent to the plant thickener consisted primarily of the cyclone overflow and the clean-coal dewatering screen underflow. The spiral tailings were dewatered on an additional curved-deck screen, and the tailings screen underflow was sent to the thickener as well.

Three different seams were processed at Empire Coal: #5, #6, and #7. The #5 and #6 seams (Lower and Middle Kittanning, respectively) are mined on Empire Coal property, while the #7 seam coal (Upper Freeport) is purchased from a neighboring mine which has no preparation plant. The general properties of these seams are as follows (Wizzard et al,1983):

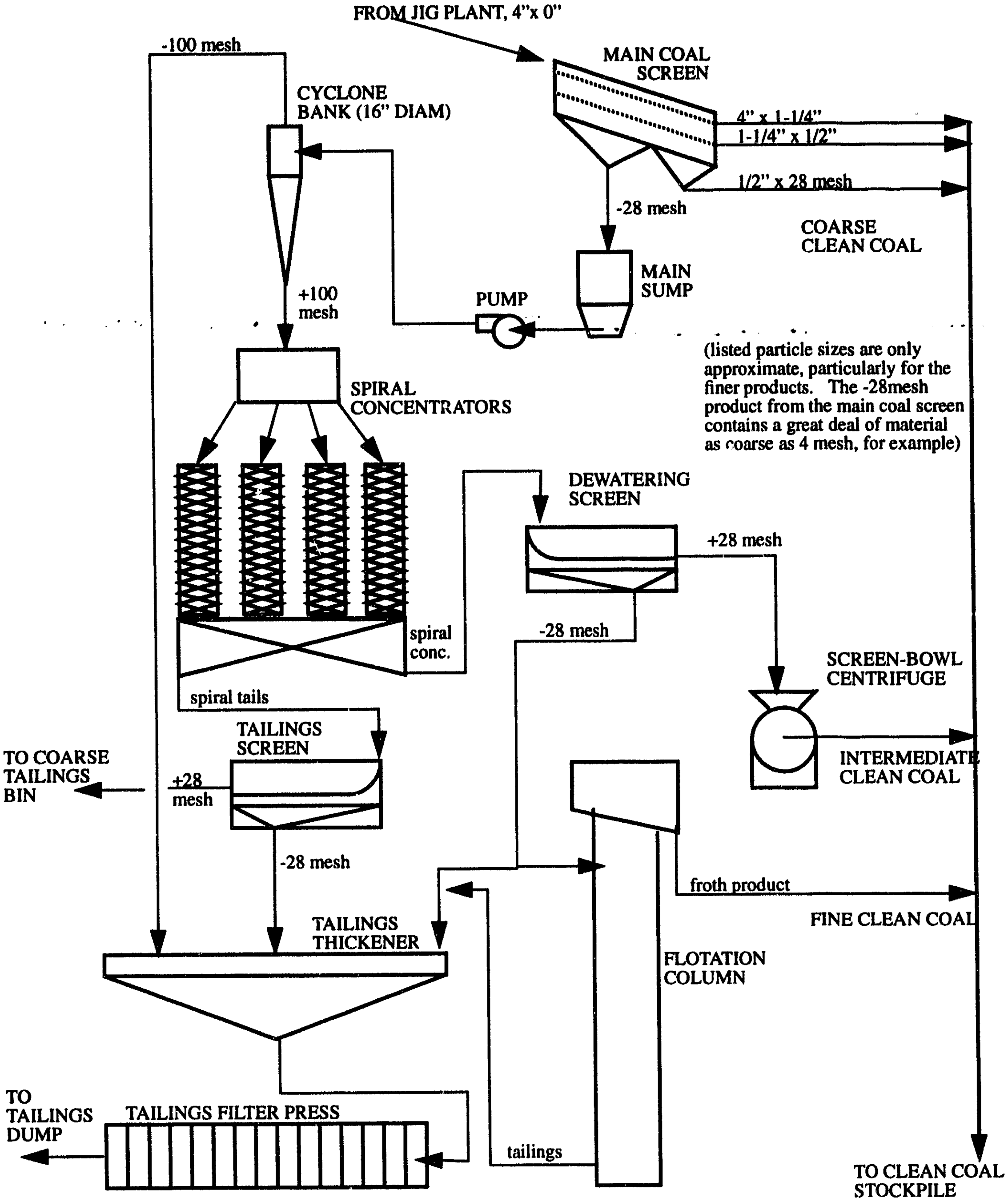

FIGURE 8.3. Flow diagram for the Empire fine coal cleaning circuit. The listed particle sizes are nominal, and there is a considerable amount of material up to about four mesh in the nominal -28 mesh material from the main coal screen. The coal used as column feed for this project is a waste product, since it contains the ash and pyrite that is too fine to be removed by the spirals. The column was also used to treat the cyclone overflow product and the thickener product in the course of experimentation

<u>Lower Kittanning:</u> The Lower Kittanning, or No. 5, coalbed is a generally good-quality, somewhat patchy seam that averages 3.1 feet thick. Statewide, this seam averages 39.7% volatile matter, 45.3% fixed carbon, 12790 BTU/lb (mineral-matter-free basis), 11.0% ash, 4.9% sulfur, and 10.6% oxygen. As shown in Table 8.1, the part of this seam mined at Empire Coal ranged from 12-17% ash and from 6-8% sulfur.

TABLE 8.1: Analyses of the #5 (Lower Kittanning) and #6 (Upper Kittanning) seam coals mined by conventional strip mining and hillside augering at Empire coal. Analyses of the highwall miner product were not available, but it is finer and higher in ash than the augered products.

	#6 Auger				#6 Strip			
Size	% wt	% Ash	%S	BTU/lb	% wt	% Ash	%S	BTU/lb
4" x 2"	9.37	14.85	4.88	12399	9.43	6.81	4.73	13860
2" x 0.5"	23.40	15.33	5.12	12302	41.33	4.80	3.80	14036
0.5" x 0.25"	18.57	19.64	4.70	11596	18.12	5.19	3.07	13755
0.25" x 6m	17.22	17.78	4.30	11274	9.38	6.49	2.79	13155
6m x 28m	19.66	18.79	4.03	11081	13.15	7.53	2.84	12922
28m x 100m	6.06	19.10	4.06	10878	4.01	10.52	3.14	12384
100m x 200m	1.48	18.37	4.81	11465	1.02	12.42	3.79	12080
200m x 325m	0.68	18.38	6.16	11641	0.63	14.23	3.86	12051
325m x 500m	0.49	17.83	5.84	11690	0.46	12.51	3.36	12320
-500m	3.07	53.06	2.21	6024	2.47	45.79	2.19	6842
Total:	100.00	18.65	4.52	11464	100.00	7.71	3.47	13455

	#5 Auger				#5 Strip			
Size	% wt	% Ash	%S	BTU/lb	% wt	% Ash	%S	BTU/lb
4" x 2"	14.30	21.93	10.84	11140	20.02	21.96	11.21	10944
2" x 0.5"	31.30	16.00	7.88	12272	44.88	10.49	5.89	13094
0.5" x 0.25"	19.63	16.93	8.09	12065	13.61	8.87	5.21	13310
0.25" x 6m	15.47	14.33	7.35	12222	6.13	9.02	4.93	13104
6m x 28m	14.09	16.32	7.32	11789	9.01	10.01	4.80	12882
28m x 100m	3.13	17.64	6.59	11378	2.99	13.56	4.72	11823
100m x 200m	0.77	20.54	7.70	9538	0.89	18.54	5.39	11247
200m x 325m	0.27	20.04	8.50	11052	0.33	19.53	5.28	11352
325m x 500m	0.14	26.27	11.24	10055	0.28	20.69	4.92	11326
-500m	0.90	58.38	7.09	4813	1.86	56.45	2.46	5236
Total:	100.00	17.31	8.14	11871	100.00	12.13	6.14	12669

Middle Kittanning: The Middle Kittanning, or No.6, coalbed is the most important coal in Ohio in both quantity and quality, ranging in thickness from 2.5 to 5 feet. It lies about 30 feet above the Lower Kittaning seam. Statewide, this seam averages 38.3% volatile matter, 46.3% fixed carbon, 12860 BTU/lb (mineral-matter-free basis), 11.1% ash, 3.8% sulfur, and 11.4% oxygen. As shown in Table 8.1, the part of this seam mined at Empire Coal ranged from 7-19% ash and from 3-5% sulfur.

Upper Freeport: The Upper Freeport, or No.7, coalbed ranks about ninth in production in Ohio. The quality is generally good, but the occurrence is erratic and irregular. It lies about 60 feet above the Middle Kittanning seam. Statewide, this seam averages 2.77% pyritic sulfur, 3.82% total sulfur, 12.0% ash, and 12626 BTU/lb (mineral-matter-free basis). This seam is not mined directly by the Empire Coal Co, but is purchased from a neighboring mine, and so detailed analyses are not available. The seam is used as the low-sulfur blend component, and consistently runs less than 2% sulfur but more than 15% ash according to plant personnel.

These seams are blended in order to meet the total sulfur and calorific value requirements of the plant's primary customer. Control of the blend was done manually, based on periodic sampling of the plant product to measure the sulfur content. The two primary seams are quite different from each other, as shown in Table 8.1, and the size distribution and ash content varies depending on the mining method used. As a result, the composition of the coal streams in the plant varied quite widely over a very short time. The variability of the coal feed was increased by the fact that three different mining methods were in use: conventional surface mining, hillside augering, and highwall mining. The conventional mining produced primarily coarse lump coal, while the highwall miner performed very much like an underground continuous miner, producing finer coal with a considerable amount of clay gouged out of the ceiling and floor of the seam. Augered coal was intermediate between these two extremes. Finally, the coal was sometimes stockpiled for weeks before it entered the plant, and sometimes fed directly with no delay, and so the degree to which the coal was oxidized was also quite variable.

8.4 OPERATING CONSIDERATIONS

The schematic of the column shown in Figure 8.4 gives the various flowrates of fluids entering the column. The washwater and bubble-generator water flowrates were limited by mechanical constraints, as with the apparatus and water pressure available the 2 gpm (7.57 l/min) washwater rate and the 1 gpm (3.78 l/min) bubble-generator rate were the maximum that could be obtained. The flowrate of the bubble generator water could not be increased beyond 1.25 gpm (4.73 l/min) at the air/water mixing ratios and line pressures recommended by Deister, even with both bubble generators running, since operating one generator reduced the available water pressure enough that the other generator could not be operated at full capacity. Since bubbles from the lower generator coarsened a great deal due to the decrease in hydrostatic pressure as they rose through the column, the column was operated with only the midpoint generator when the lower baffle set was installed in order to maintain a relatively fine-grained froth. This also had the effect of only introducing air into the upper 15 feet (4.6 meters) of the column.

With the original column, Deister personnel recommended that frother be added only to the bubble generator water, as mixing by the rising air bubbles was expected to carry enough frother to the top to stabilize the froth layer. When no baffles were present, the column could be operated this way, but weight recovery in the froth rarely exceeded 30%. However, once the baffles were installed it became impossible to maintain a froth layer regardless of how much

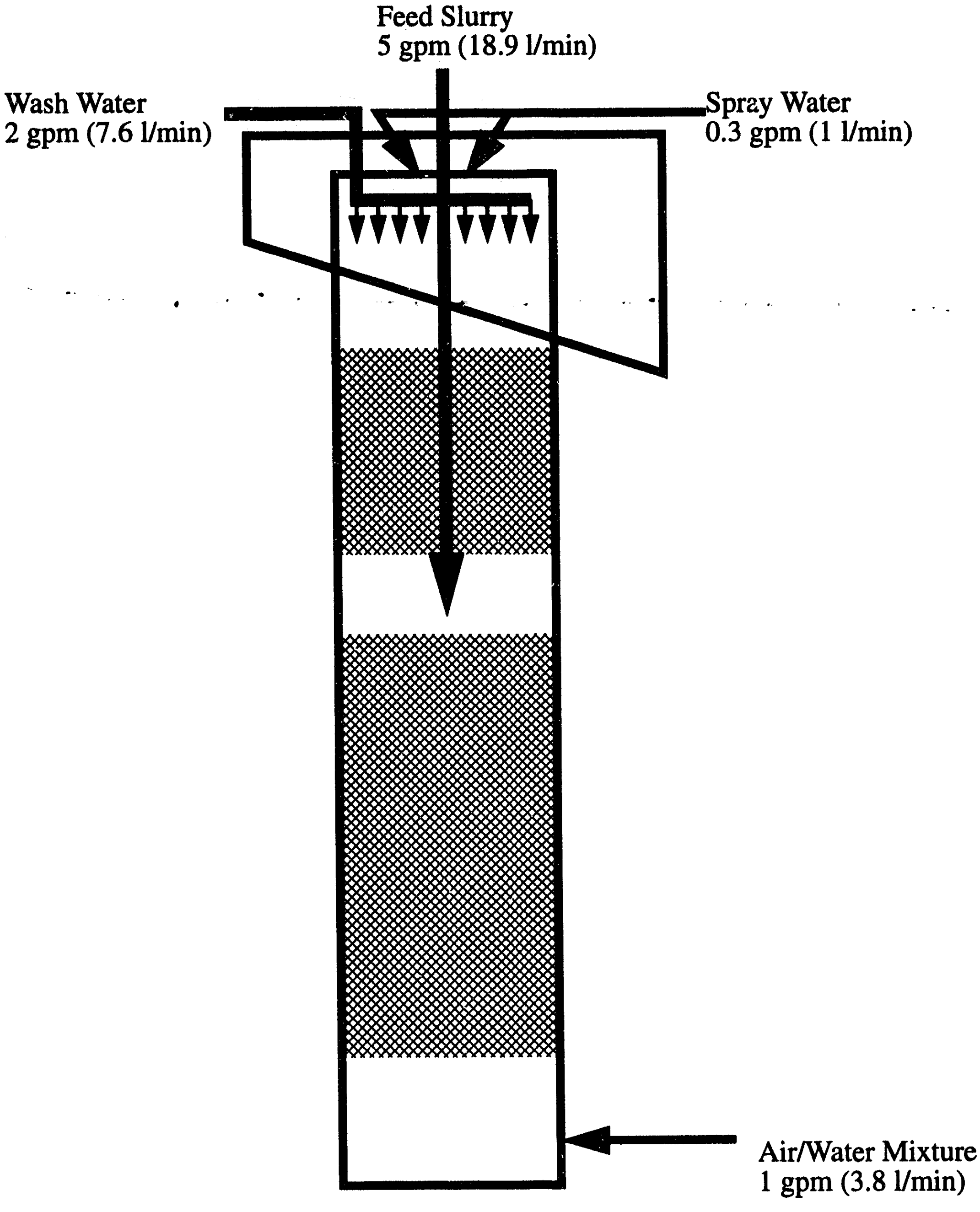

FIGURE 8.4. Flowrates of the main fluid streams entering the column. The high flowrate of water is needed due to the great volume of froth produced in coal flotation.

frother was injected into the bubble generator. This was due to the baffles greatly increasing the efficiency of washing by the washwater, which stripped all of the frother away from the rising air bubbles, causing them to coalesce and collapse the froth. This was partially countered by adding frother to the washwater as well, although recovery was still somewhat low under these conditions (30-50% wt). Eventually, it was found that adding frother to the feed slurry as well would improve the recovery further. Once frother was added to the feed at the same concentration as in the washwater and bubble generator water, recovery was boosted to 80-90% BTU recovery with the dewatering screen underflow product.

When the column was operated continuously for long periods, the top layer of the froth above the washwater ring would drain and stiffen into a mass which adhered to the feed funnel, as shown in Figure 8.5. Over a period of 20-40 minutes, this formed a plug which severely restricted the flow of froth from the column, and had to be removed. It was not practical to simply raise the washwater ring, as it could not break up the plug until it was so high that it would spray over the

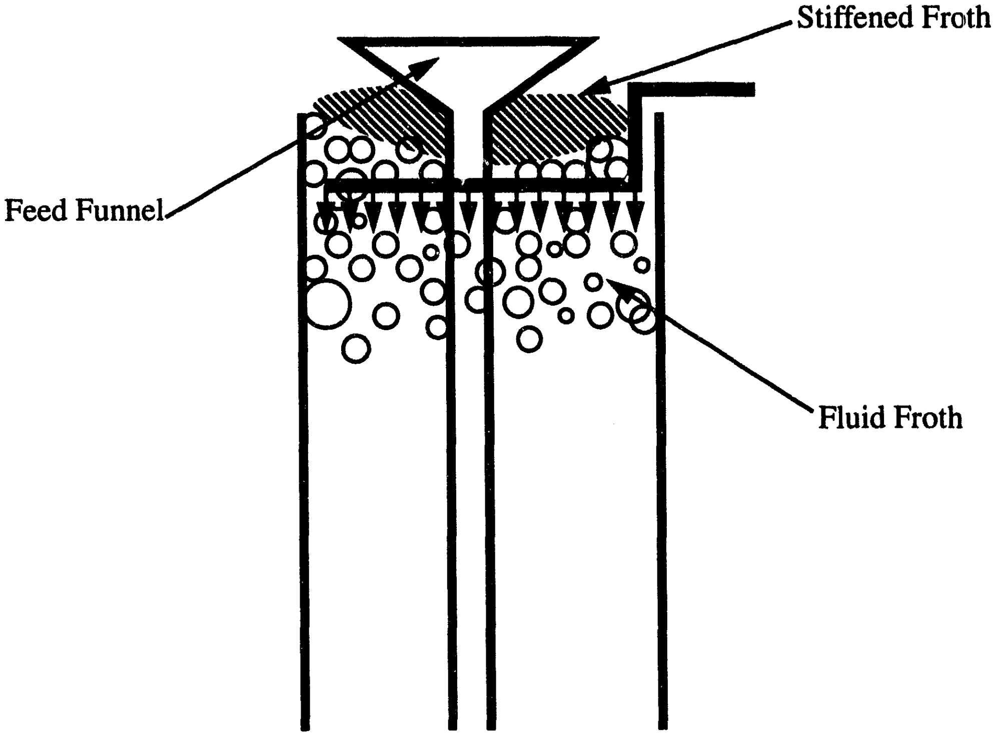

FIGURE 8.5. Formation of the froth plug in continuous tests. This plug could be prevented from forming by using three cone spray nozzles to add water to the froth top, keeping it moist and fluid.

froth lip of the column rather than into the froth as intended.To prevent this plug from forming, a set of three cone-spray nozzles were attached to the feed funnel to keep the top layer of the froth moistened and fluid. The three nozzles had a combined flowrate of 0.3 gpm (1.1 l/min), which was sufficiently low compared to the other flowrates that addition of frother was not necessary.

8.5 REAGENT DETERMINATION FOR ON-LINE TESTS

In earlier laboratory experiments with a sample of the Empire coal, it was found that the coal was poorly floatable when fuel oil alone was used as collector. To improve the effectiveness of the collector, Dow M210 froth conditioner was added to the fuel oil at the rate recommended by Dow Chemical Co (80% #2 fuel oil, 20% M210). This collector mixture was used for all of the plant experiments. Laboratory experiments also showed that when frother was added at near starvation dosages, performance of a flotation column was about the same with stronger polyglycol frothers as with weaker frothers.

Since strong frothers can be added in much lower concentrations than weaker frothers (the column needed approximately 20 times as much Dowfroth 200 as of the much stronger Dowfroth 1012c) and the prices of both stronger and weaker frothers are about the same (Fee, 1991), stronger frothers are more economical to use and are therefore preferred when there is not some overriding reason not to use them, such as excessive entrainment in conventional flotation. For these reasons, Dowfroth 1012c, the strongest glycol frother available, was selected for the bulk of the plant experiments, and is the frother used in all tests described from this point on unless stated otherwise.

Although approximate reagent dosages had been determined in laboratory tests with a sample of Empire coal, it was necessary to run experiments with the pilot-scale column to be certain that scale-up effects did not radically alter the reagent requirements. Since the plant feed variability made systematic studies very difficult while running on-line, a series of off-line batch experiments were conducted in order to examine reagent effects.

For the batch experiments, a large sample of the dewatering screen underflow was collected, and thickened to approximately 65% solids. The size distribution and ash and sulfur content of the feed is given in Table 8.2. Tests were conducted by weighing out 12 pounds (5.44 kg) charges of the wet coal by incremental shoveling, with an additional portion removed as a feed sample and for determination of the precise moisture content of the particular set of charges. Each charge was then suspended in 15 gallons (56.8 liters) of water to make a 6% solids slurry at a pH of approximately 6, and conditioned with the desired reagents for 5 minutes. The column was filled and stabilized without coal added, after which the 15 gallons of slurry was rapidly pumped into the column over a 5 minute time interval. For each test, the rapid addition of feed prevented the froth from building up sufficiently to overflow until after all of the feed had been pumped into the column. The entire froth product was collected for each test, and divided into the following time intervals after the first froth overflow: 0-1 minute, 1-3 minutes, and 3 minutes-end of the test. The collection of froth over timed intervals allowed the results to be plotted as the grade-recovery curves shown in Figures 8.6 and 8.7. Six tests were conducted, at two levels of frother dosage. The collector dosages were intended to be comparable for both frother levels, but differ due to the difficulty of obtaining exactly the same percent solids in the thickened feed from day to day.

In Figure 8.6, it is seen that at the lower frother dosage, increasing the collector dosage has no detectable effect on the grade-recovery curve with respect to ash, which implies that adding

TABLE 8.2: Size distributions and bulk analyses of feed used in the two sets of batch reagent determination flotation experiments. Size distributions were determined using a Leeds and Northrup Microtrac size analyzer.

Size, Microns	(0.45 Kg/mt Frother) % Passing	(0.15 Kg/mt Frother) % Passing
704.00	100.00	100.00
497.80	97.67	94.12
352.00	94.45	89.65
248.90	87.34	78.09
176.00	78.75	64.68
124.45	69.99	52.99
88.00	61.59	43.70
62.23	53.66	36.22
44.00	46.02	29.89
31.11	39.17	24.70
22.00	33.60	20.87
15.56	28.01	17.15
11.00	22.18	13.45
7.78	17.39	10.42
5.50	12.97	7.56
3.89	8.12	4.46
2.75	5.25	2.71
1.94	2.81	1.31
1.38	1.21	0.47
0.97	0.14	0.00
Total % S	3.67	4.09
Total % Ash	41.05	36.30

excess collector does no harm other than wasting reagent. However, at the higher frother dosage the use of a high level of collector improves ash removal. This is probably due to the coal floating faster and with less entrained water at higher collector levels. This reduces the opportunity for gangue to be carried into the froth. The curves in Figure 8.7, showing the grade/recovery curves with respect to total sulfur, shows trends very similar to those for ash, which implies that for this coal, the reagent schemes which are best for ash removal are also best for sulfur removal.

Based on the batch tests, the best collector/frother ratio would be in the neighborhood of 4/1. However, continuous tests which were attempted with high ratios showed that this was not practical. High ratios of collector to frother tended to increase the percent solids of the froth, making it become dry and stiff. This caused the column to plug with stiffened froth, and in extreme cases to collapse the froth entirely. Since the plugging occurred at collector/frother ratios

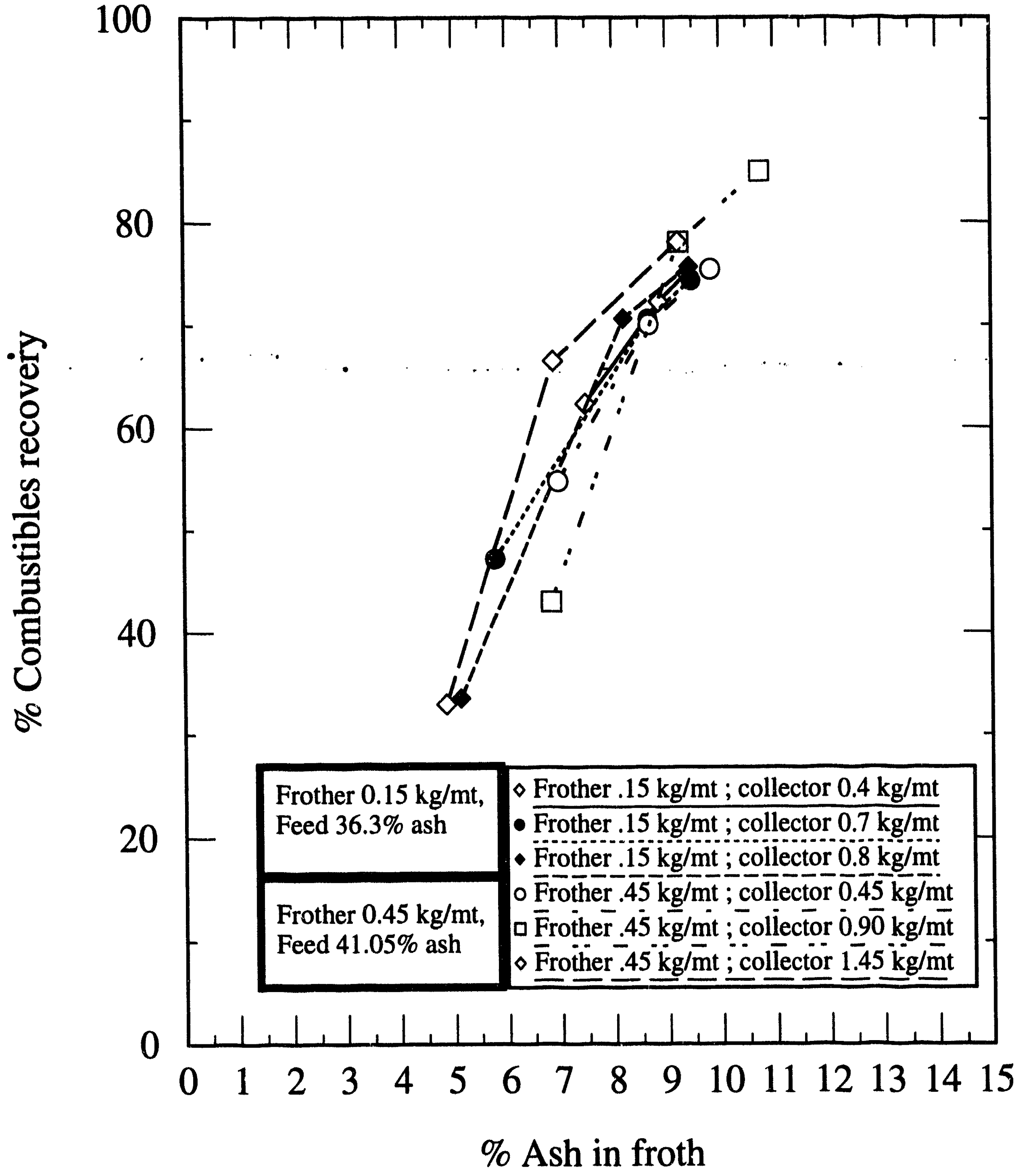

FIGURE 8.6. Grade-recovery curves with respect to ash for batch tests to determine the effects of collector and frother dosage. Frother was Dowfroth 1012c, and collector was 80% #2 fuel oil/20% Dow M210 froth conditioner. Flotation pH was between 6 and 7, and the column was operated in batch mode with all baffles installed and only the upper bubble generator operating (effective column height = 15 feet).

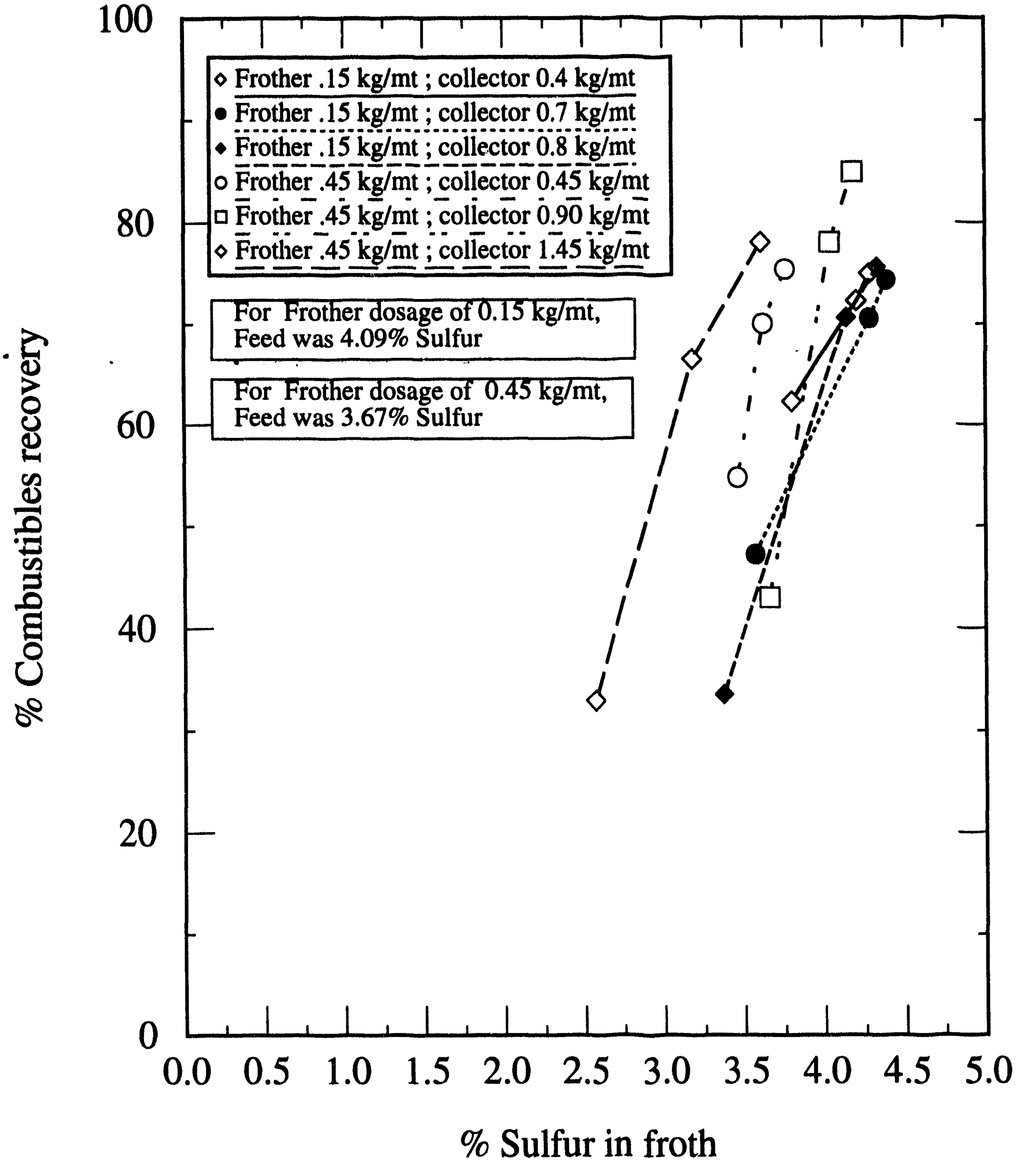

FIGURE 8.7. Grade-recovery curves with respect to sulfur for batch tests to determine the effects of collector and frother dosage. Frother was DF 1012c, and collector was 80% #2 fuel oil/ 20% M210 froth conditioner. The feed pH was between 6 and 7, and the column was operated in batch mode with all baffles installed and only the upper bubble generator operating (effective column height of 15 feet)

higher than approximately 1.5/1, the on-line tests were carried out at a 1/1 ratio to ensure that plugging and froth collapse would not occur.

8.6 CONTINUOUS ON-LINE EXPERIMENTS

Continuous on-line experiments were conducted using the clean coal dewatering screen underflow, with the feed's particle size and composition varying as shown in Table 8.3. Slurry was pumped directly from the dewatering screen underflow at 10% solids and 0.5-0.8 kg of solids per minute. During four of these tests, a dewatering aid (NALCO 89DA038)was added to the plant water, to see what effect this would have on flotation performance. A summary of the results is given in Table 8.4. Ash and pyritic sulfur analysis procedures are given in Appendix 3.

Figure 8.8 shows the grade/recovery performance of the column on-line for removing both ash and pyritic sulfur. The % ash and % pyritic sulfur of the feed for each test is also plotted. This shows that in spite of large variations in the feed quality, the grade of the froth product was very uniform regardless of recovery variations. When no dewatering aid was added, the BTU recovery was consistently greater than 75% and all but two tests were above 80% BTU recovery, with a high of 91.2%. However, the dewatering aid had a severe impact on the column performance. As the dewatering aid gradually built up in the plant water, the recovery rapidly fell to only 55% long before the dewatering aid reached its equilibrium concentration in the plant. This clearly shows that this dewatering aid is not compatible with froth flotation.

From Figure 8.8, it at first appears that the column is not removing pyritic sulfur to any great extent. However, it should be kept in mind that the feed was very high in ash, which was being removed very thoroughly by the column. Since the sulfur is expressed as percent by weight, and much of the weight in the feed was ash, it is seen that in order for the sulfur assay of the froth to be equal to that of the feed, much of the sulfur must have been removed along with the ash. The ability of the column to remove sulfur is clearly shown by Figure 8.9, which plots pyrite and ash rejections against BTU recovery. The rejection values are the percentages of the weights of pyrite and ash originally in the feed which is rejected to the tailings. This figure shows that the column is rejecting between 40% and 62% of the pyritic sulfur from the coal, while simultaneously rejecting from 80% to 93% of the ash.

8.6.1 Pyrite Recovery

The froth product from one on-line test (11/28/90, 86.9% BTU recovery) was screened into +65 mesh, 65 x 150 mesh, and -150 mesh size fractions. Heavy-liquid sink/float assays were run at a specific gravity of 1.9 for all three sizes, and also at 2.96 for the -150 mesh size. Floats and sinks were separated using separatory funnels, allowing the products to segregate in the funnels for one hour before separating. Sink-float separations were run on 10 grams of each size, and an additional separation was run on 40 grams of the -150 mesh product so that enough material would be obtained for sink/float at the 2.96 specific gravity. When enough sample was present, products were analyzed for total sulfur, ash, %moisture, and %volatiles. The results are given in Table 8.5. The -150 mesh size fraction contained a substantial amount of pyrite which was not accompanied by a similar amount of clay, and was therefore probably being recovered by flotation as locked particles. The presence of largely liberated pyrite in the fine 2.96 sinks is confirmed by the photomicrographs of these products given in Figures 8.10--8.12. If these particles could be removed, then the froth sulfur content could be reduced from 3.97% sulfur to between 3.5% (if only the 2.96 sinks were removed) and 3.0% (if 1.9 sinks were also removed).

While the particles denser than 2.96 in Figure 8.12 are predominantly pyrite, close

TABLE 8.3: Average characteristics of the dewatering screen underflow during the final series of on-line experiments, using a Microtrac to determine particle size distributions. This table is a composite of the assays of each feed sample for the on-line tests summarized in Table 8.4. The large standard deviations for ash, sulfur, and pyritic sulfur show that the feed quality was quite variable for these tests.

Size, Microns	% Passing	% In Size Range	Standard Deviation
704.00	100.00	5.92	1.2
497.80	94.08	7.87	0.9
352.00	86.22	14.16	0.6
248.90	72.05	15.59	0.6
176.00	56.47	13.10	0.5
124.45	43.37	9.81	0.4
88.00	33.56	7.33	0.2
62.23	26.23	5.58	0.2
44.00	20.64	4.18	0.2
31.11	16.46	2.82	0.2
22.00	13.65	2.49	0.3
15.56	11.16	2.38	0.3
11.00	8.78	1.88	0.3
7.78	6.89	1.85	0.2
5.50	5.04	2.13	0.2
3.89	2.92	1.26	0.1
2.75	1.65	1.01	0.1
1.94	0.64	0.48	0.1
1.38	0.16	0.16	0.1
0.97	0.00	0.00	0.0

	Mean	Std. Dev.
% Ash	34.8	2.66
% Sulfur	4.41	0.34
% Pyritic Sulfur	3.1	0.50
BTU/lb	9275	365

examination shows that the bright pyrite particles are mostly attached to or rimmed by the darker coal. It is this attached coal which is most likely responsible for floating this pyrite into the froth. The most effective method for removing these pyrite particles from the froth would be some sort of density separation, since any depressant would only work if it also depressed coal.

TABLE 8.4: Summary of on-line tests, using the dewatering screen underflow product. Dewatering aid was being added on 11/16, and caused a progressive loss of recovery as its concentration in the plant water increased. No dewatering aid was added on the other days listed.

		% Py. S	% Ash	BTU/lb	% BTU Rec.	% Py. Rej.	% Ash Rej.
11/15		2.1	7.49	13236	83.9	61.8	87.6
11/16	Test 1	2.4	8.18	13315	77.6	53.7	88.6
	Test 2	2.1	7.10	13366	72.4	57.4	90.6
	Test 3	2.2	7.50	13414	74.7	56.6	89.0
	Test 4	2.2	6.97	13480	55.0	67.2	93.4
	Test 5	2.2	7.38	13401	65.4	61.0	91.1
11/21		2.4	7.49	13308	86.6	56.2	89.0
11/26		2.2	7.22	13411	90.1	48.6	80.3
11/27		2.6	6.78	13460	87.9	51.1	87.8
11/28		2.6	6.96	13420	86.9	56.5	87.9
11/30	Test 1	2.9	7.62	13351	86.7	40.3	85.2
	Test 2	2.7	6.70	13575	85.4	52.9	87.2
	Test 3	2.9	7.19	13391	79.4	54.7	88.2
	Test 4	2.8	7.84	13368	91.2	49.2	84.8
	Test 5	2.4	6.71	13514	88.8	56.1	87.6
	Test 6	2.7	6.90	13506	91.2	49.9	87.2

Reagent addition:	0.5-0.75 ml/min (0.9-1.0 kg/mt)
Reagent mixture:	5 parts DF 1012C frother 4 parts #2 fuel oil 1 part M210 froth conditioner
Feedrate:	0.5-0.8 kg solids/min, at approx. 10% solids
Feed quality:	31-39% ash 3.8-4.8% sulfur

8.6.2 Capacity Effects

One of the concerns with the baffles was that they might unduly restrict the capacity of the column. There was some capacity reduction in laboratory batch tests, and so a set of on-line experiments were conducted with various degrees of baffling to see how the capacity changed. Figure 8.13 shows the variation in the mass flow of coal to the froth as baffles were added and removed, and as the feedrate was changed. Unfortunately, in the course of these experiments the plant was periodically switching between processing freshly-mined coal and processing coal which had been stockpiled for five years, and so the variations in feed quality were even larger than usual.

In Figure 8.13, the mean mass flowrate in the froth for the fully baffled column (15.1 kg/

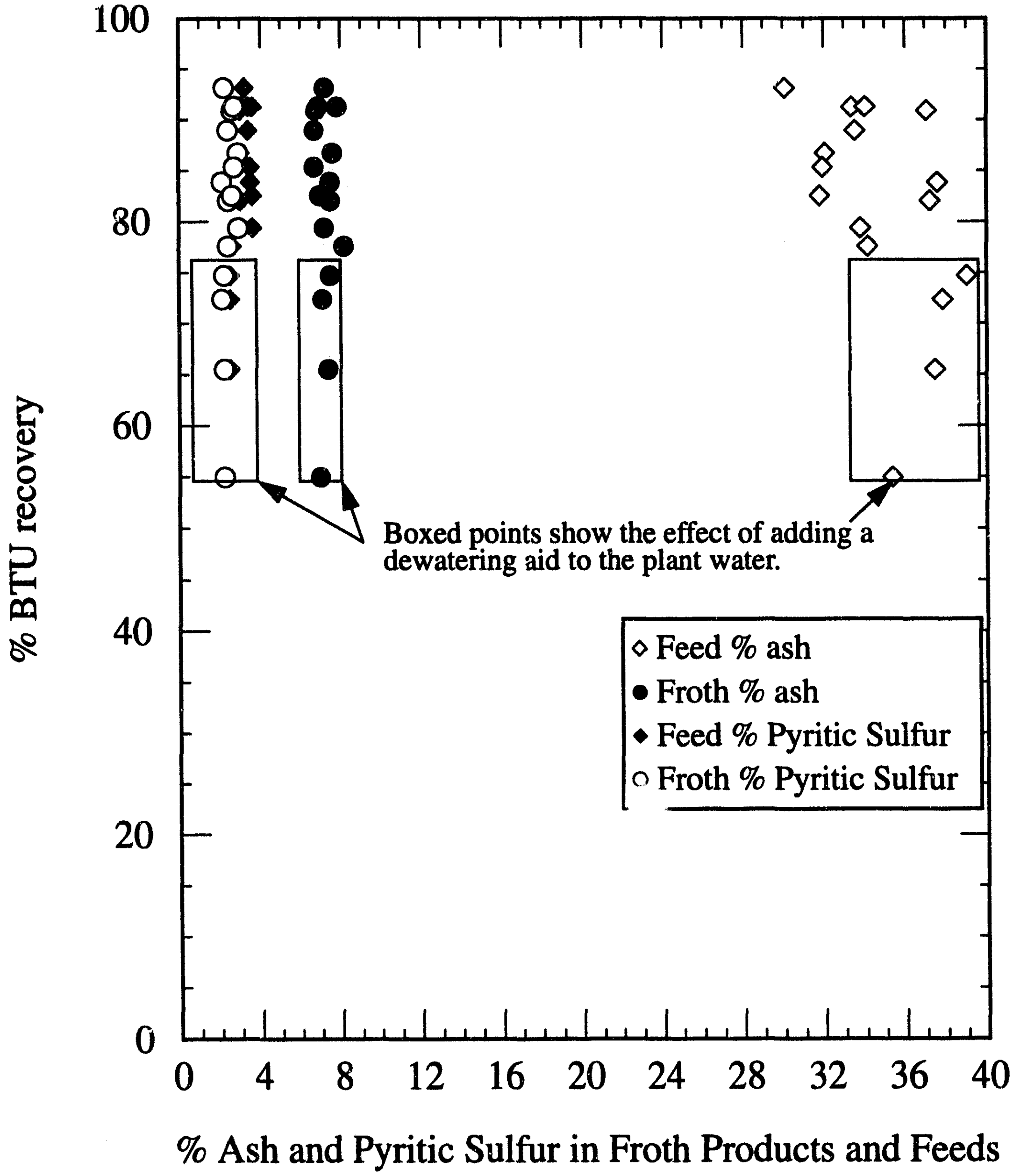

FIGURE 8.8. Grade-recovery results for the on-line continuous flotation tests, all baffles installed, with water sprays on the froth top. The ash and pyritic sulfur content of the feed for each test is also given. In spite of the wide variation in feed ash contents, the ash content of the froth product is quite constant. The boxed data points show the effect of dewatering aid on the column performance. When dewatering aid was added to the plant water, the recovery of clean coal by the column steadily decreased as the dewatering aid build up in the circuit. This chemical is therefore not compatible with coal flotation.

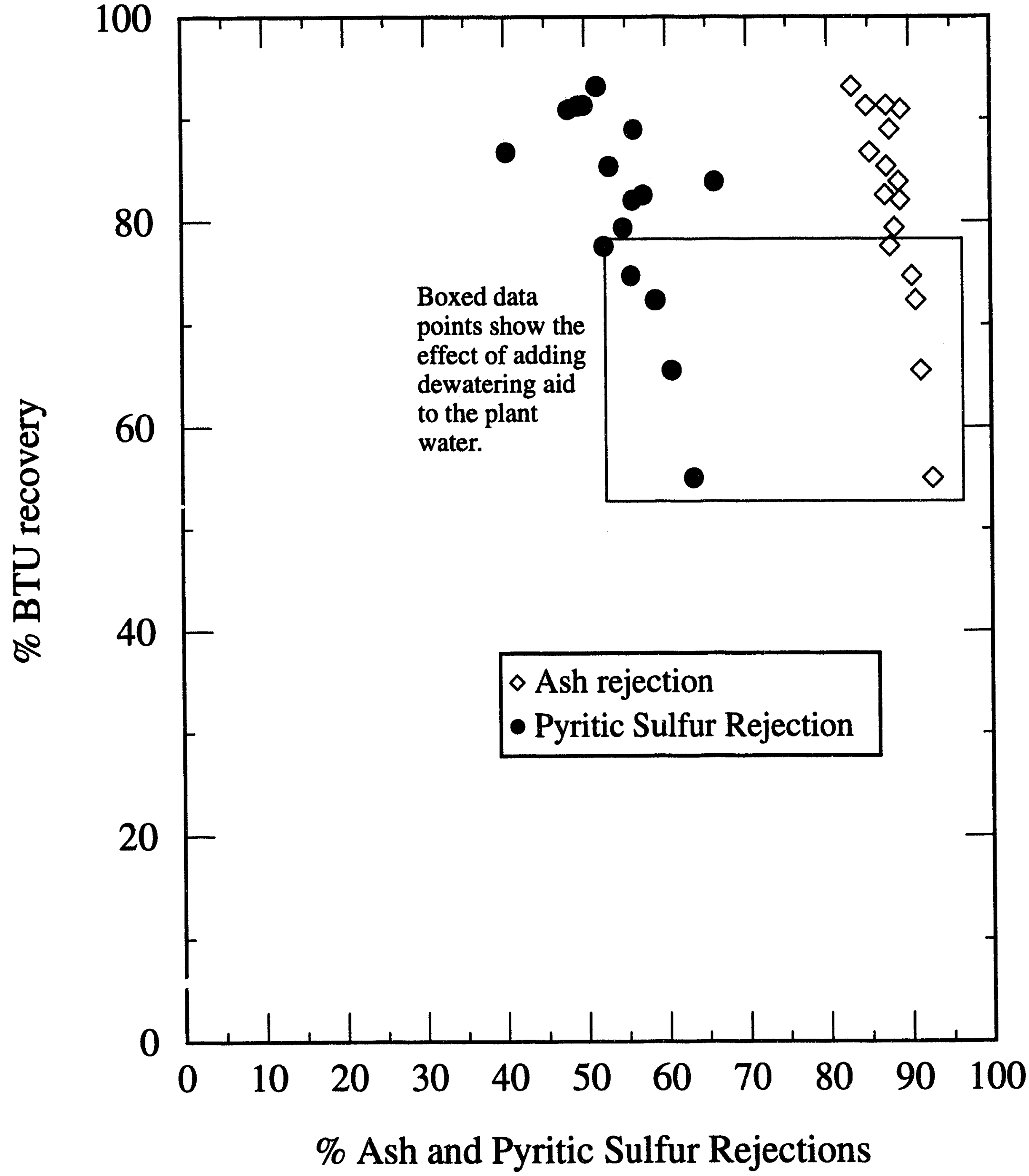

FIGURE 8.9. Pyritic sulfur and ash rejections as a function of BTU recovery in the on-line continuous tests with all baffles installed. This shows that between 40 and 65% of the pyritic sulfur is being rejected by the column, even at high BTU recoveries, and that virtually all of the ash is being rejected.

TABLE 8.5: Results from heavy-liquid assays on a froth product from an on-line continuous column test conducted on November 28, 1990. Particles denser than 2.96 are nearly pure pyrite, as neither coal (specific gravity < 1.5) or clay minerals (specific gravity approx. 2.6) will sink at this density.

Product	% Weight	% Sulfur	% Ash	% Volatiles
+65 mesh	33.02	2.83	3.76	38.86
1.9 floats	33.0	2.72	3.69	38.99
1.9 sinks	(trace)	----	----	-----
65x150 mesh	38.99	3.41	5.18	37.94
1.9 floats	38.01	3.26	3.75	38.67
1.9 sinks	0.98	7.39	----	----
-150 mesh	27.99	6.10	12.00	32.55
1.9 floats	24.75	2.34	5.31	34.65
1.9x2.96	1.75	20.9	----	----
2.96 sinks	1.31	40.3	----	----

hr) is less than that for the unbaffled column (21.0 kg/hr). However, the mean flowrate with the upper baffles installed (25.6 kg/hr) is higher than the unbaffled column, and with only the lower baffles installed and a feedrate less than 100 kg/hr the mean froth flowrate was higher yet (32.0 kg/hr). The effect of baffles on capacity are therefore not entirely clear in these tests, but in any case the reduction in capacity from the complete set of baffles is no more than 28%. Since the capacities with just the upper or lower baffles are both higher than with no baffles, any capacity reduction due to baffling is probably much smaller than this, more on the order of a few percent as was seen in the laboratory tests. The large capacity swings seen on-line are probably due mainly to the substantial changes in the level of oxidation of the coal.

When the feed flowrate was greatly increased to over 180 kg/hr with only the lower baffles, the froth flowrate dropped precipitously. This was due to overloading of the froth, which reduced the froth fluidity and choked off the flow of clean coal. This indicates that the most important factor controlling the column capacity is the fluidity of the froth. This is in agreement with results reported by other researchers (Finch and Dobby, 1990)

8.7 OFF-LINE CONTINUOUS TESTS

Since the plant feed was too variable in quality for running systematic tests, a series of experiments were conducted with a large sample of well-mixed fine waste collected from the plant thickener product. This product was predominantly composed of the cyclone overflow product (~ 75%), mixed with the clean coal dewatering screen underflow (~ 20%) and the fine fraction of the spiral tailings (~ 5%). The size distribution and composition of the sample collected is given in Table 8.6, which shows that the sample was finer, higher in ash, and lower in sulfur than the dewatering screen underflow product.

FIGURE 8.10. Photomicrograph of the 1.9 specific gravity floats, from the -150 mesh size fraction of the 11/28/90 on-line froth. Bright inclusions are pyrite, and the dark and light grey particles are coal. Pyrite particles are thoroughly locked to coal particles, as would be expected for this specific gravity fraction.

8.7.1 Off-Line Continuous Test Procedure

The procedure for the off-line tests was as follows: First, a 60 pound (27.2 kg) charge of the thickener product (which had been filtered by the plant tailings filter to 20% moisture) was incrementally shovelled from a well-mixed stock of plant filter cake. This was then mixed with 50 gallons (189.25 liters) of fresh water in a 55 gallon drum to make an approximately 10% solids suspension, using a side-mounted drum mixer to suspend the solids. The desired levels of reagents were added to the drum of slurry, and conditioned for 5 minutes. The column was filled with water alone, with all water and air flowrates adjusted to the levels used in the on-line experiments, before beginning to pump slurry into the column at a rate of 2 gallons/minute. The feedrate was lower than for the on-line tests because this feed had a finer particle size, which makes the froth overload at a lower mass flowrate. The drum contained enough slurry to continuously feed the column for 25 minutes. Based on initial shakedown tests with the column, the froth was considered to have reached steady state after 15 minutes. Froth and tailing samples were collected 20 minutes after starting the column feed, during steady-state operation, while the feed sample was collected half at the beginning of feeding the column, and half immediately after the froth and tailing samples.

Two sets of off-line continuous tests were conducted. One set used a constant reagent dosage and varying degrees of baffling in the column, while the second set was carried out with all baffles installed and widely varying levels of frother and collector dosage. These experiments were intended to determine how the addition of baffles alters the steady-state column

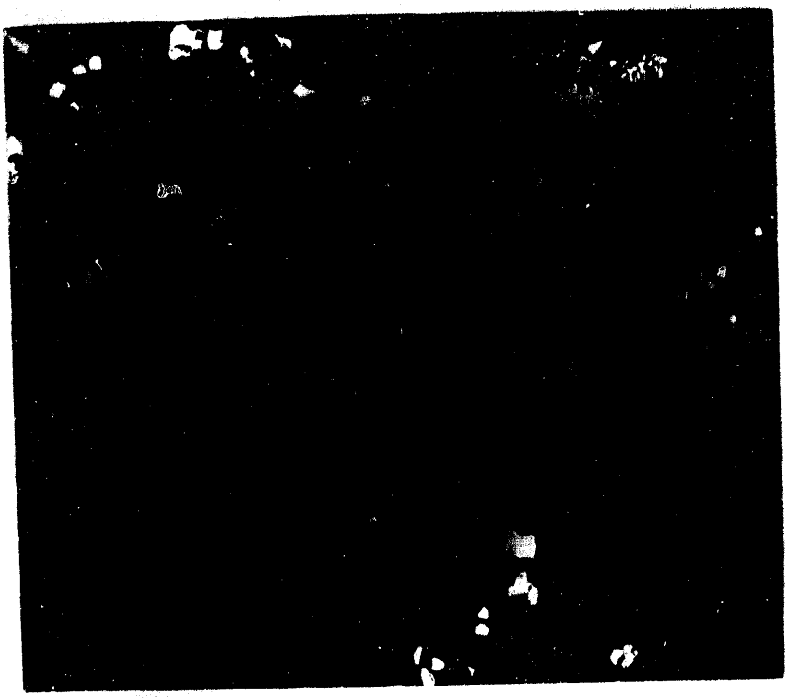

FIGURE 8.11. Photomicrograph of the 1.9 x 2.96 specific gravity particles, from the -150 mesh size fraction of the 11/28/90 on-line froth. Bright inclusions are pyrite, and the dark and light grey particles are coal. Pyrite makes up a large part of this specific gravity range, but it is still thoroughly locked to coal particles. This pyrite is therefore floating because of the hydrophobicity of the attached coal.

performance, and how performance changes with changing reagent dosage.

In order to track the recovery of the water which was present in the feed slurry, and thus to estimate the degree of entrainment of non-floatable particles, five grams of sodium fluorescein dye was added to each barrel of feed slurry. This is a non-toxic dye which can be readily detected using a spectrophotometer at less than 1 part per million concentration, and therefore can be used as a water tracer at a low enough concentration to avoid major changes in the flotation chemistry. Published work to date has generally used potassium chloride or other salts which do not naturally occur in coal, but these salts must be added in amounts approaching 1% of the feed in order to be sufficiently measurable in all of the product streams, and they are harder to detect than the fluorescein dye.

8.7.2 Off-line Continuous Test Results

These experiments were carried out to determine both the effects of variations in the degree of baffling, and of changes in reagent dosages. By carrying them out off-line with a consistent feed, problems with the variability of the feed quality could be avoided. Since the baffle-variation tests were carried out before the reagent-variation tests, the reagent dosage used (collector 1.1 kg/mt, frother 0.36 kg/mt) was not optimum (optimum dosage is closer to: collector 2.25 kg/mt, frother 1.26 kg/mt), and so the recovery was not as good as it might have been. For the baffle-variation tests, Figures 8.14 and 8.15 show the effect on grade-recovery performance in the column which resulted from the addition of baffles. At a single reagent dosage, the recovery

FIGURE 8.12. Photomicrograph of the 2.96 specific gravity sinks, from the -150 mesh size fraction of the 11/28/90 on-line froth. Bright particles are pyrite, and the dark and light grey portions are coal. Pyrite is predominant at this specific gravity, but the majority of the pyrite particles are attached to or rimmed by coal, so that coal is making up much of the available particle surface area for bubble attachment during flotation.

with all of the baffles installed is much higher than with no baffles at all (average of 47.9% combustibles recovery with baffles, and only 19.3% combustibles recovery without baffles), while Figure 8.14 shows that the increase in froth ash content was negligible. Figure 8.15 shows an increase in the sulfur content with increasing recovery, but without exceeding the total sulfur content of the feed.

The reagent-variation experiments were carried out with collector and frother dosages both varying by a factor of four, in order to determine the results of both over and underdosing with frother and collector, as well as performance near the optimum levels (collector 2.25 kg/mt, frother 1.26 kg/mt). The collector and frother dosages and the collector/frother ratios are shown in Table 8.7. The grade-recovery curves shown in Figures 8.16 and 8.17 illustrate that in the case of ash, increasing the collector dosage acts to improve ash removal, and has a similar although smaller effect on sulfur removal.

It was observed that as the collector dosage was increased, a greater quantity of frother was needed to achieve a reasonable level of BTU recovery, as shown in Figure 8.18. This was largely due to an increased stiffness of the froth at increasing collector levels. This increased stiffness is a result of increasing percent solids in the froth, which is probably caused by oil-coated coal particles beginning to agglomerate. Ultimately, the froth stiffened to the point that the froth overflow would halt entirely. Increasing the frother dosage had the effect of making the froth more fluid, and thus more easily removed from the column. Figure 8.18 also shows that

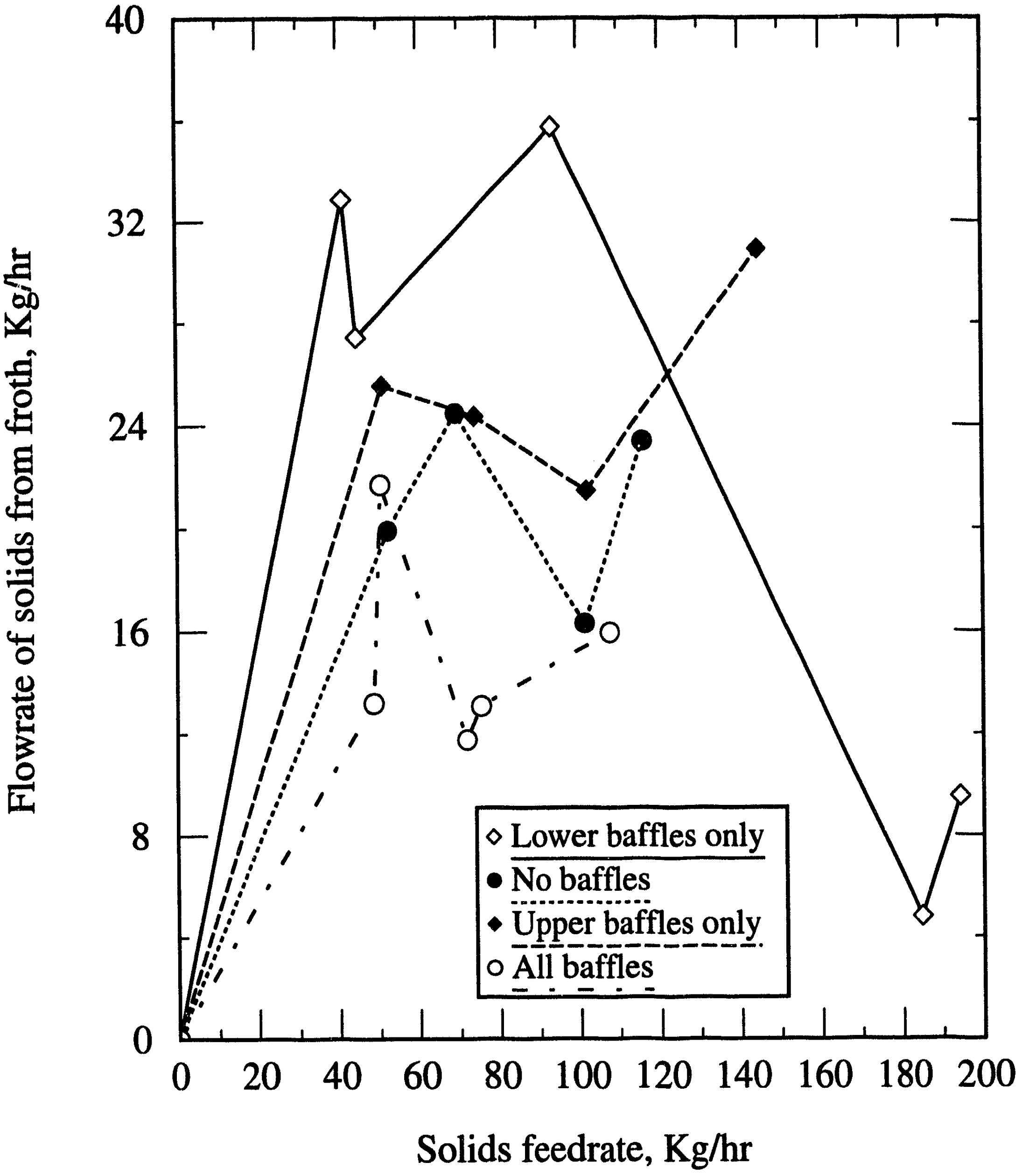

FIGURE 8.13. Rate of froth production over a range of feedrates, with varying degrees of baffling. These are on-line continuous tests. While the mean froth production rate for the fully baffled column is somewhat lower than that for the unbaffled column, the partially baffled column results both average a higher froth flowrate than the unbaffled column. Much of this variation between the varying baffle levels is due to changes in the quality of the feed coal, which in turn altered the character of the froth. To a large extent, the column capacity is controlled by the froth layer. When the froth becomes overloaded, as happened when the feedrate was increased to 180 kg/hr, it stiffens and plugs the column, reducing the froth flowrate to nearly zero.

TABLE 8.6: Size Distribution and composition of the filter press cake used in the off-line continuous experiments. The ash in this product is almost entirely fine clay. The results given are a composite of the feed sample assays for each of the off-line continuous tests, and the small standard deviations show that the feed was well-mixed and uniform.

Size, Microns	% Passing	% In Size Range	Standard Deviation
704.00	100.00	3.72	0.8
497.80	96.28	3.05	0.6
352.00	93.23	6.03	0.4
248.90	87.19	6.33	0.2
176.00	80.87	6.47	0.2
124.45	74.40	6.26	0.2
88.00	68.14	6.07	0.1
62.23	62.07	6.31	0.1
44.00	55.76	6.61	0.1
31.11	49.15	5.77	0.2
22.00	43.38	6.51	0.3
15.56	36.87	7.18	0.3
11.00	29.69	6.30	0.2
7.78	23.39	6.03	0.2
5.50	17.36	6.23	0.3
3.89	11.13	3.97	0.3
2.75	7.16	3.30	0.2
1.94	3.86	2.11	0.2
1.38	1.75	1.43	0.1
0.97	0.32	0.32	0.1

	Mean	Std. Dev.
% Ash	39.80	0.85
% Sulfur	2.83	0.05
% Pyritic Sulfur	2.04	0.08
BTU/lb	8410	134

increasing the frother dosage also tended to increase the % pyritic sulfur and % ash in the froth. In extreme cases, the volume of water from all sources being carried into the froth was nearly as large as the amount that was entering in the feed. However, most of the water that was contained in the froth was actually washwater, and not feed water. As a result, the feed water recovery (as determined from the recovery of tracer dye in the froth) never greatly exceeded 10%, as shown in

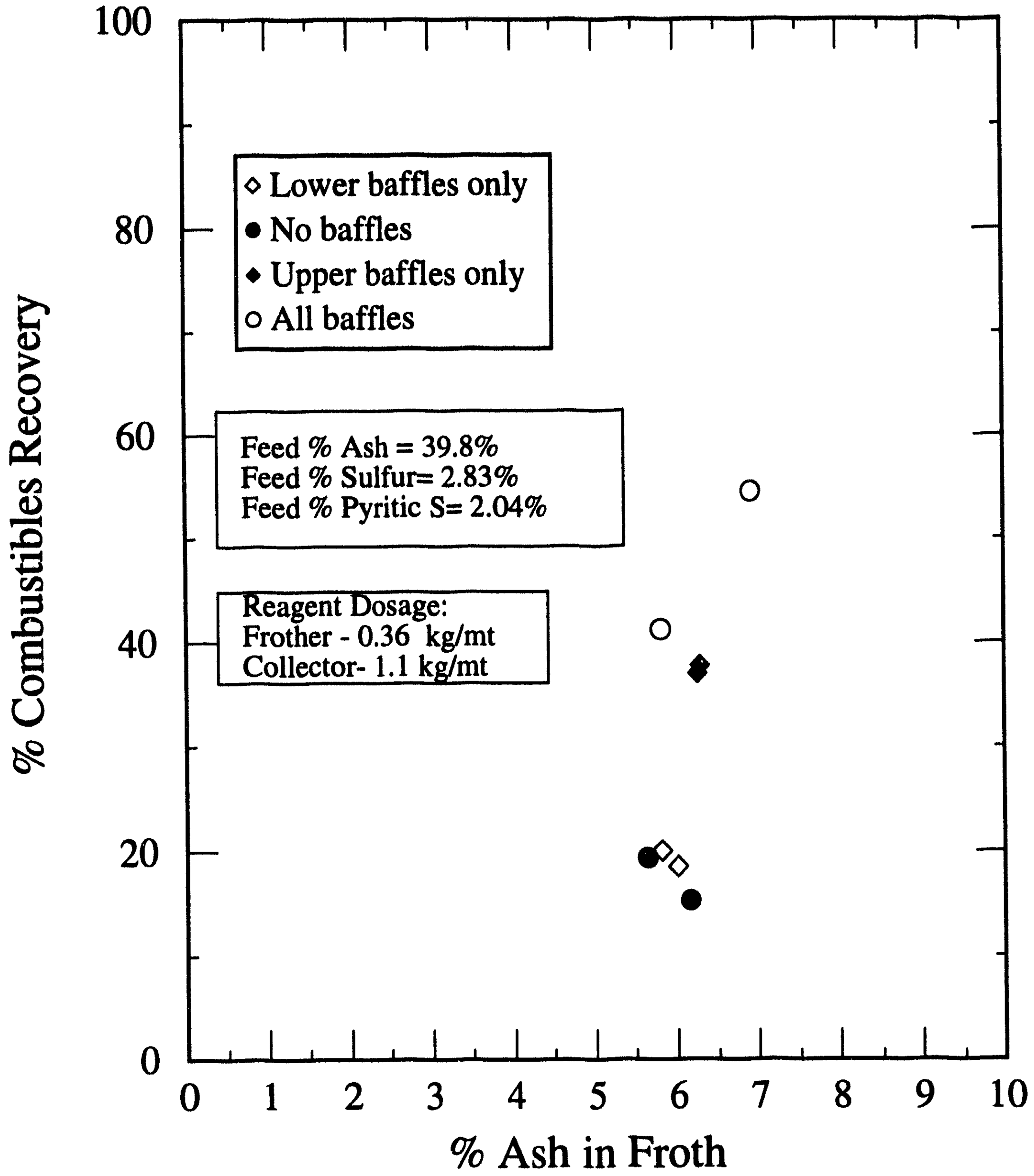

FIGURE 8.14. Effect of baffles on the grade-recovery performance of the column in off-line continuous tests with the filter press cake. This feed is very high in ash, fine, heavily oxidized, and contaminated with flocculant, and would therefore not normally be considered a good feedstock for froth flotation. Nevertheless, the baffled column was able to recover over 50% of the combustible matter as compared to about 20% for the unbaffled column. Since these tests were run before the reagent-variation tests with this feed, the reagent dosages used were not yet optimized. Optimum reagent dosage would have been closer to 2.25 kg collector/mt, and 1.26 kg frother/mt.

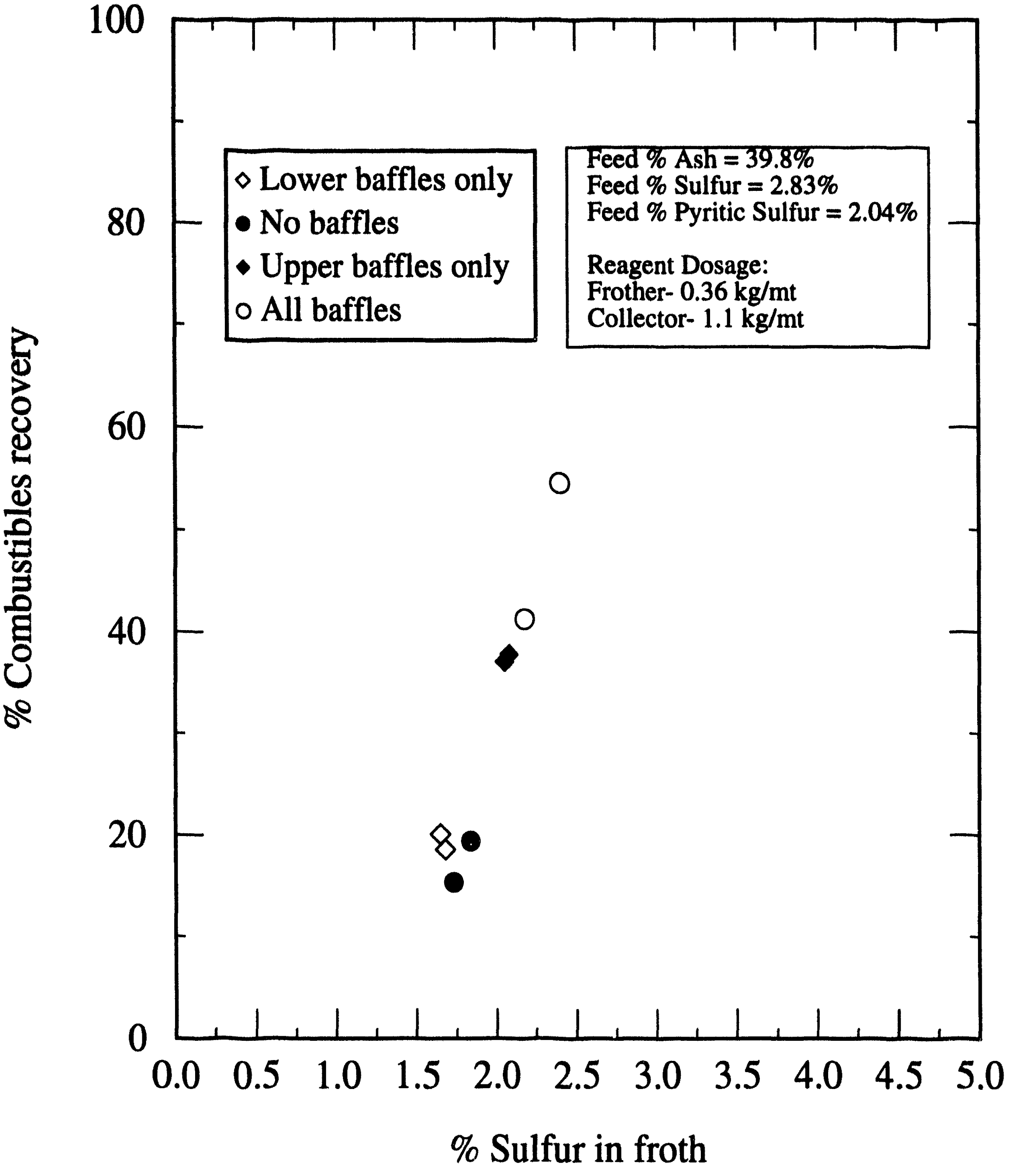

FIGURE 8.15. Effect of baffles on grade/recovery performance with respect to sulfur in off-line continuous tests with the filter press cake. Reagent dosages are not optimized. This is the same test as described in Figure 8.14

TABLE 8.7: Collector and frother dosages, in kg/metric ton coal, for continuous off-line reagent variation tests, using the tailings filter cake as feed. Reagents were conditioned in 55 gallon drums for five minutes before beginning each experiment, and the column was run for 20 minutes before taking samples so that it had a chance to reach steady state operation. The collector was a mixture of 80% #2 fuel oil and 20% Dow M210 froth conditioner, and the frother was Dowfroth 1012c. The collector was dissolved in the frother before adding to the coal slurry, to emulsify the fuel oil and give better spreading over the coal surface. This may have increased the frother dosage needed to reach a particular BTU recovery, while reducing the collector consumption (Laskowski, 1992).

Collector Kg/mt	Frother Kg/mt	Ratio Collector/Frother	% BTU Recovery	% Pyrite Rejected	% Ash Rejected
0.55	0.18	3.06	18.19	94.6	98.1
0.55	0.36	1.53	45.55	81.4	94.5
0.55	1.26	0.44	70.55	65.8	88.2
1.10	0.18	6.11	11.33	98.2	98.9
1.10	0.36	3.06	55.90	80.3	93.9
1.10	1.26	0.87	65.26	70.6	91.0
1.30	0.36	3.61	30.31	92.4	97.3
2.25	0.54	4.17	24.65	94.9	98.0
2.25	0.72	3.13	51.12	84.1	95.6
2.25	1.26	1.78	83.57	53.3	85.3
2.25	2.52	0.89	85.26	51.7	84.0

Figure 8.19. This illustrates that the column was able to maintain a high degree of froth washing even when the froth was excessively voluminous.

At the maximum collector dosage of 2.25 kg/mt, the recoveries of feed water, ash, heating value, total sulfur, and pyritic sulfur as a function of frother addition are as shown in Figure 8.20. Similar trends are seen for each component, implying that they are approximately linearly related. In particular, it is seen that the ash recovery correlates very closely with the feed water recovery, indicating that the high-ash particles were being recovered by entrainment, and can be removed by a second stage of flotation. While the total sulfur and pyritic sulfur were not being recovered as fast as the heating value, and were therefore being largely removed by the flotation column, there was still a significant fraction which was remaining in the clean product. In order to determine whether the pyritic sulfur was being recovered as locked particles or as hydrophobic pyrite, a series of heavy-liquid sink-float tests were carried out on two feed samples and on the 83.57% BTU recovery froth sample. These assays provided a means for measuring the quantity of sulfur which is locked to a significant amount of coal, and therefore gave the maximum degree of sulfur removal which could be achieved at a given BTU recovery. The sink-float results presented in Figure 8.22, along with the total sulfur recovery values from the flotation tests, show that sink-float separation on the column feed gives virtually identical results to those obtained by column flotation. This indicates that the flotation column was functioning as well as what is

TABLE 8.8: Summary of off-line continuous tests, with varying collector/frother dosages

Collector kg/mt	Frother kg/mt	Froth product analyses				
		% Total S	% Py. S	% Ash	BTU/lb	% BTU Rec.
0.55	0.18	2.05	1.00	6.57	13697	18.92
0.55	0.36	2.34	1.31	7.48	13441	45.55
0.55	1.26	2.84	1.63	9.83	13131	70.55
1.10	0.18	1.60	0.54	6.04	13708	11.33
1.10	0.36	2.40	1.19	6.92	13525	55.90
1.10	1.26	2.57	1.52	8.48	13221	65.26
1.30	0.36	1.92	0.91	5.59	13652	30.31
2.25	0.54	1.79	0.79	5.63	13732	24.65
2.25	0.72	2.23	1.14	6.00	13700	51.12
2.25	1.26	2.95	1.86	10.51	12939	83.57
2.25	2.52	2.93	1.80	10.72	12893	85.26

Frother:	DF 1012C
Collector:	4 parts #2 fuel oil 1 part M210 froth conditioner
Feedrate:	0.5-0.6 kg solids/min 9% solids
Feed quality:	38-40% ash 2.7-2.9% total sulfur

normally considered to be a near-perfect separation. However, when a sink-float assay was performed on the 83.57% BTU recovery column froth, and the results were calculated to the same feed basis as for the column results, the sulfur removal was significantly better than for the column alone. It therefore appears that the column floats locked coal/pyrite particles from this feed, particularly when the BTU recovery exceeds about 40%. This implies that the best pyritic sulfur rejection from this feed would be achieved using a combination of column flotation and a density separation, since the two types of process complement each other well. For this coal, a water-only cyclone would be an appropriate density separator, used either to treat the incoming feed to the column, or to remove high-density particles from the column froth product.

8.7.3 Particle Size Effects

The feed used in the off-line steady-state tests consisted primarily of fine clay particles and somewhat coarser coal particles. This is illustrated by the results from a Microtrac particle size analyzer used to determine the particle size distribution of the sink and float products produced from the feed at a specific gravity of 1.9, shown in Figure 8.23. The float product is only 25% finer than 30 microns, while the sink product is over 75% finer than this size. This shows that the column must be able to effectively recover the coarser coal while still remaining selective enough to reject the high-ash fines, which will tend to be easily entrained.

Figure 8.24 shows how the recovery of three size ranges varied as the total % weight recovery of feed by the column varied, based on Microtrac size distribution data. The -11 micron

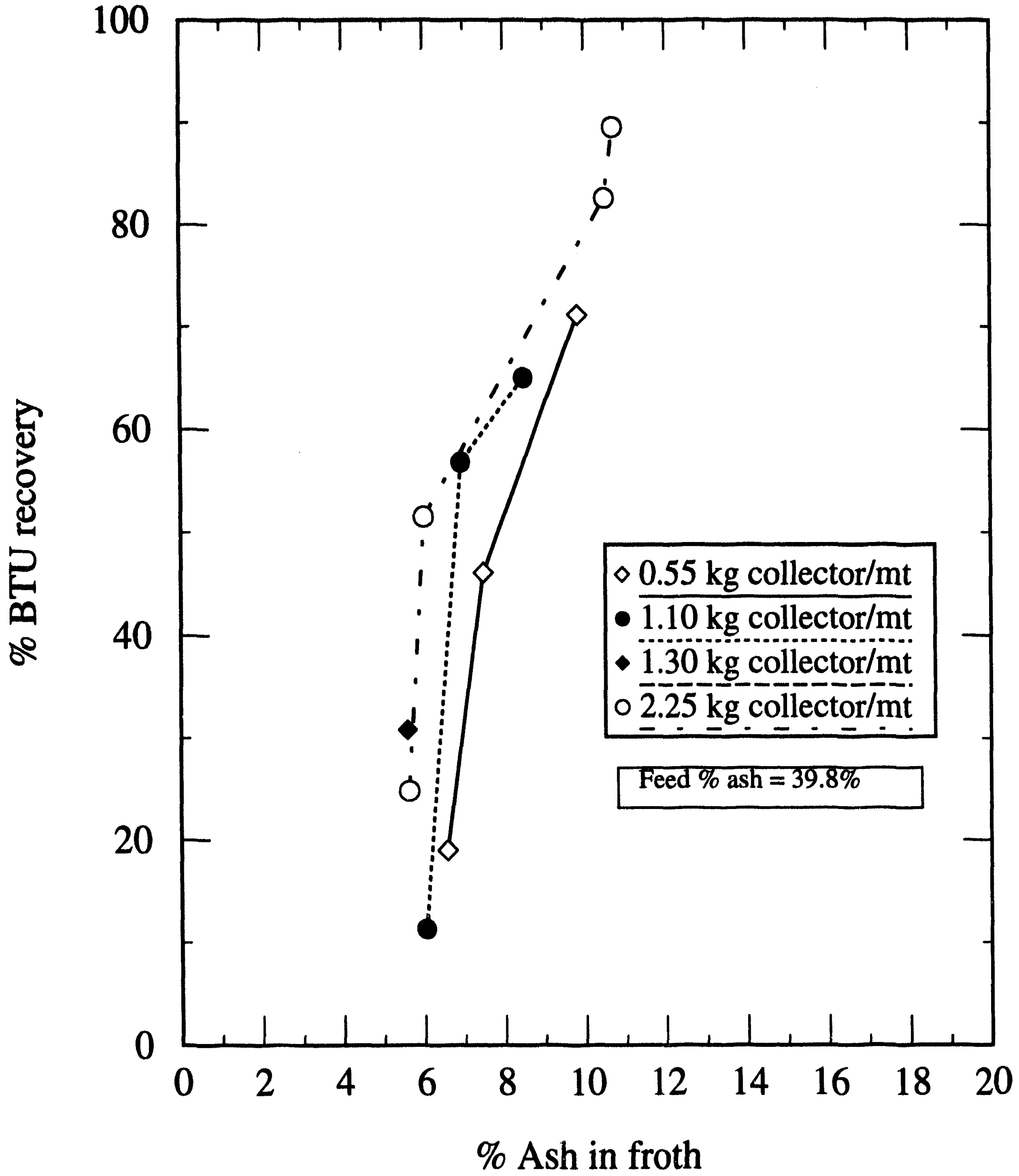

FIGURE 8.16. Effect of reagent dosage on the grade-recovery performance of the column with respect to ash, for continuous off-line experiments with the filter cake. For each collector dosage, the recovery was increased by increasing the frother dosage. Frother dosages are given in Table 8.6. This figure shows that increasing the collector and frother dosage improved the grade/recovery performance of the column, and did not simply move the recovery up along a single grade/recovery curve.

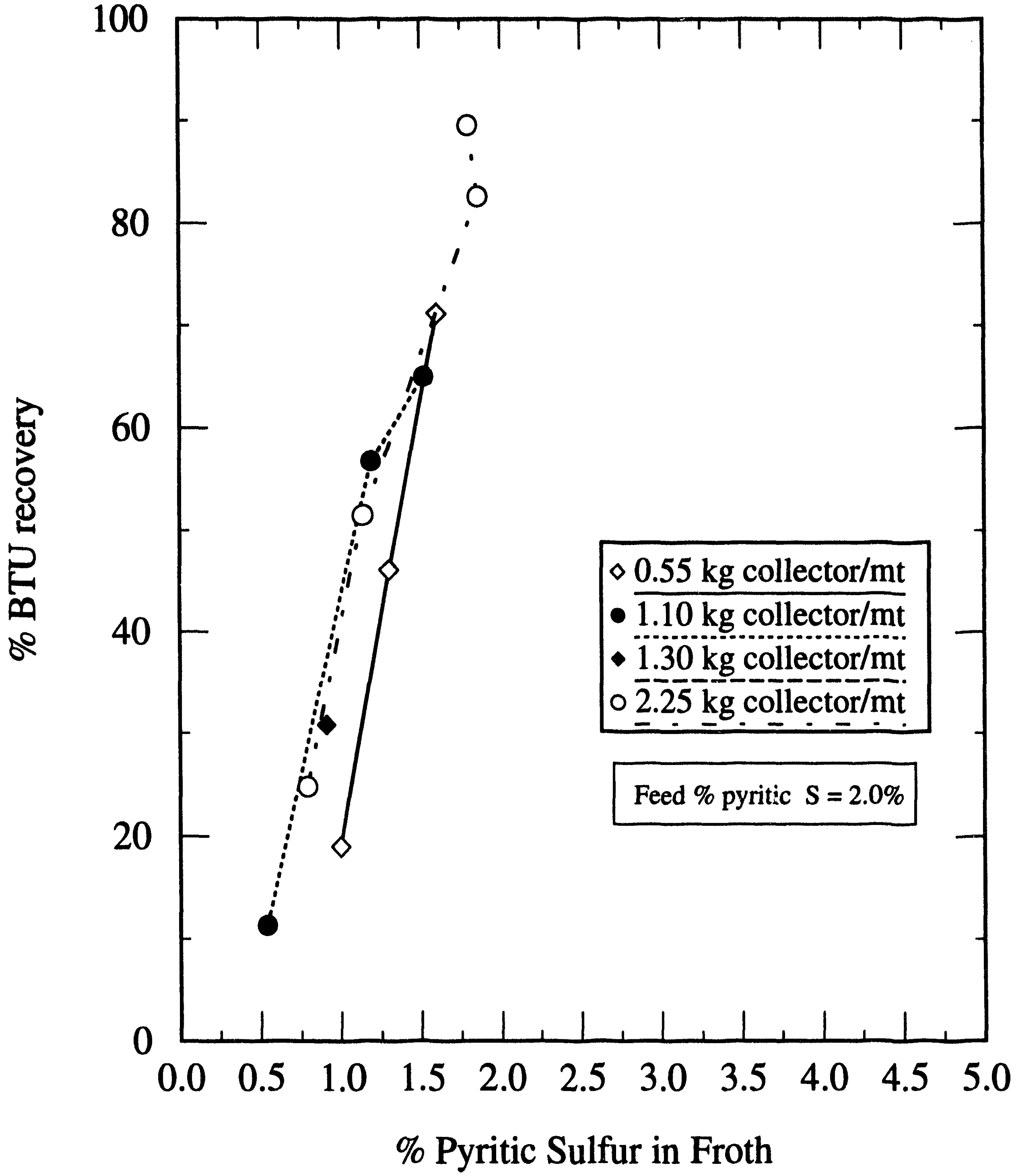

FIGURE 8.17. Effect of reagent dosage on the grade-recovery performance of the column with respect to pyritic sulfur, for continuous off-line experiments with the filter cake. For each collector dosage, the recovery was increased by increasing the frother dosage. Frother dosages are given in Table 8.6. Increasing the reagent dosages did not improve the grade-recovery performance with respect to pyrite as much as it did with respect to ash, and the change in this figure shows that the performance was essentially moving along a single grade/recovery curve.

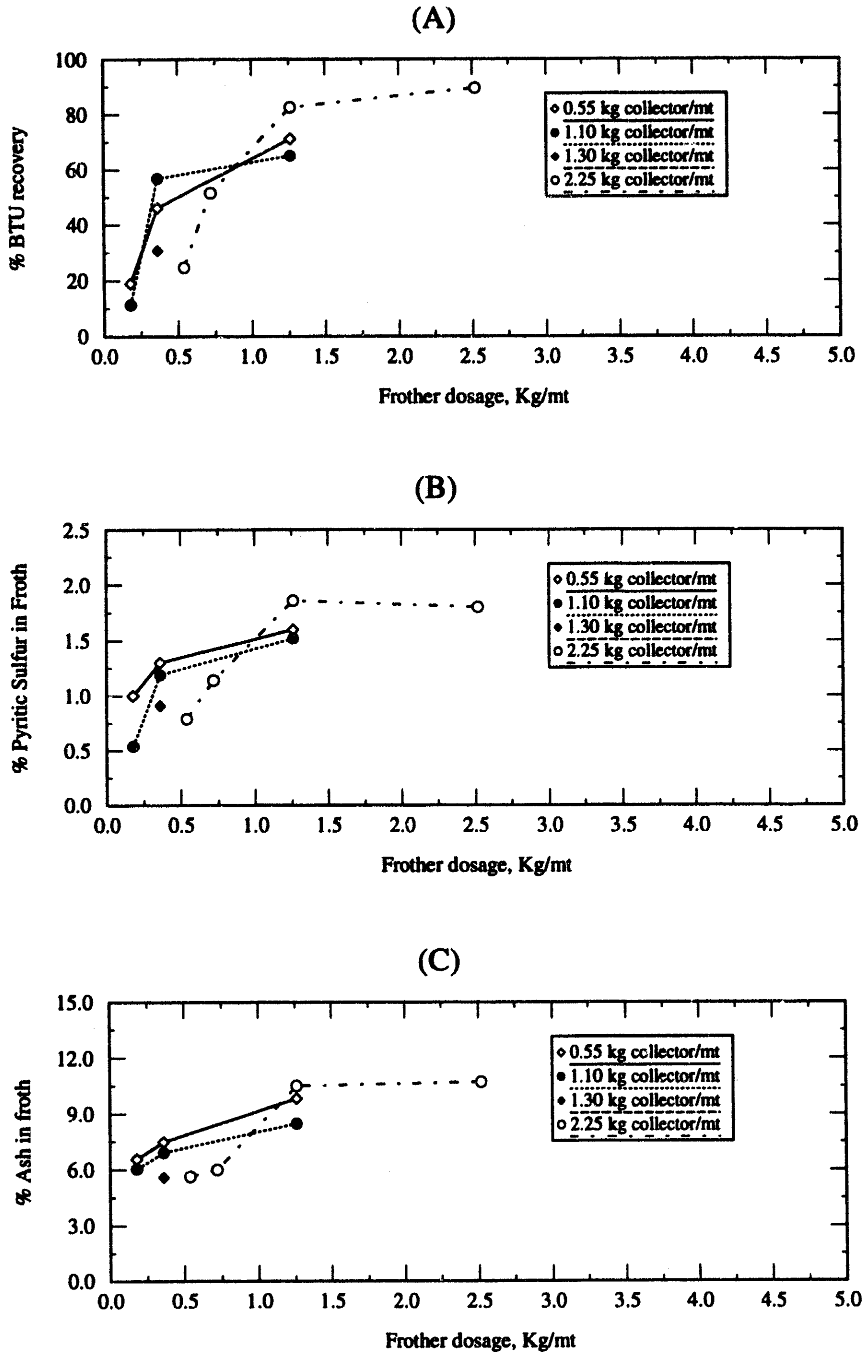

FIGURE 8.18. Dependence of BTU recovery, froth pyritic sulfur content, and froth ash content on frother and collector dosages for the off-line continuous tests with the fully baffled column. The column feed was 2.04% pyritic sulfur and 39.8% ash.

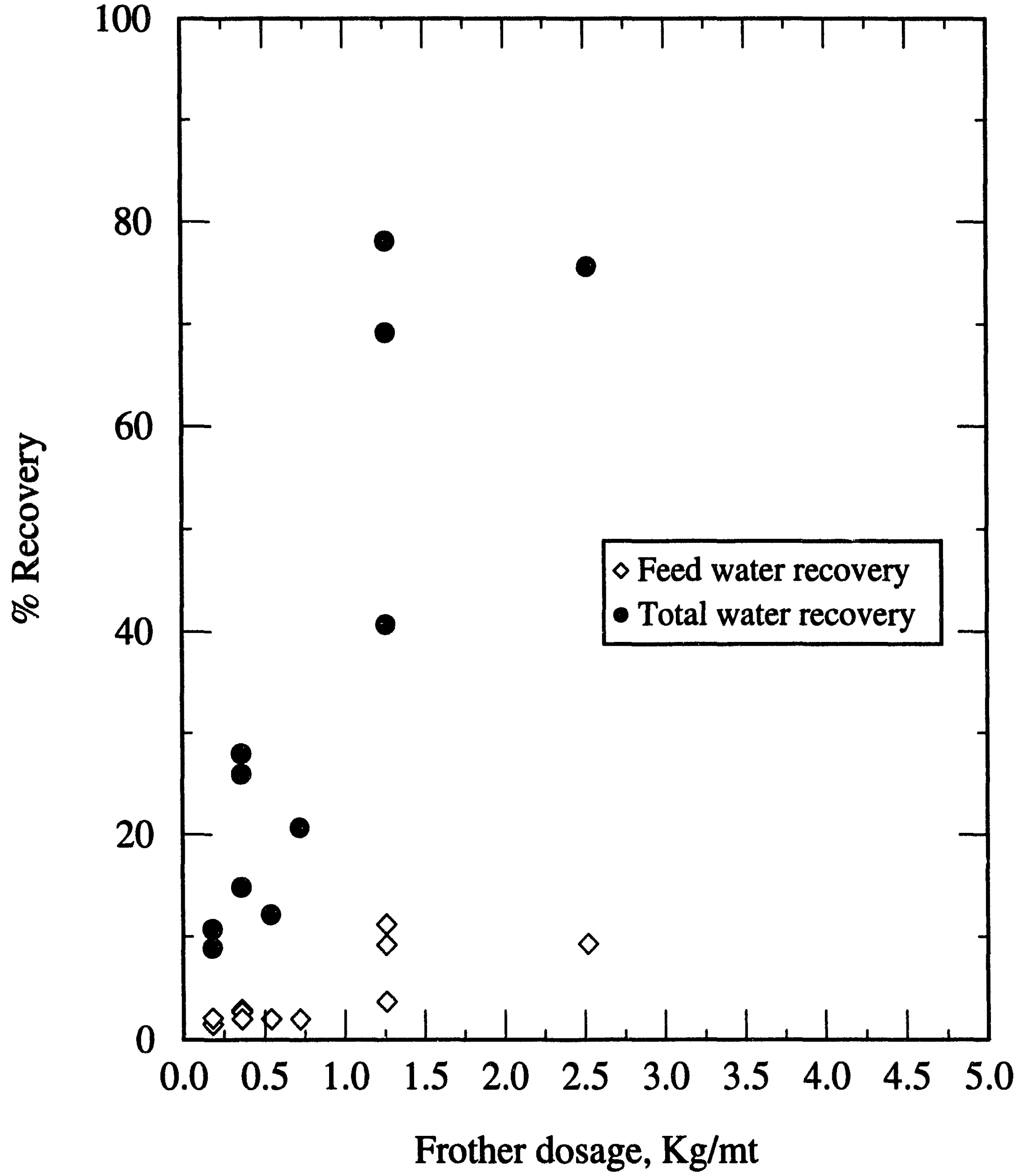

FIGURE 8.19. Comparison of feed water and total water recoveries for the off-line continuous tests. The total water recovery is all of the water that is recovered in the froth, and is mostly washwater (the total water recovery is normalized, to feed water volume = 100). The recovery of just the feed water was measured using sodium fluorescein as a tracer dye. This figure shows that even though increasing the frother dosage boosted the water content of the froth, the entrainment of feed water (and hence of ash and pyrite) was kept below 11% by the washing action of the column.

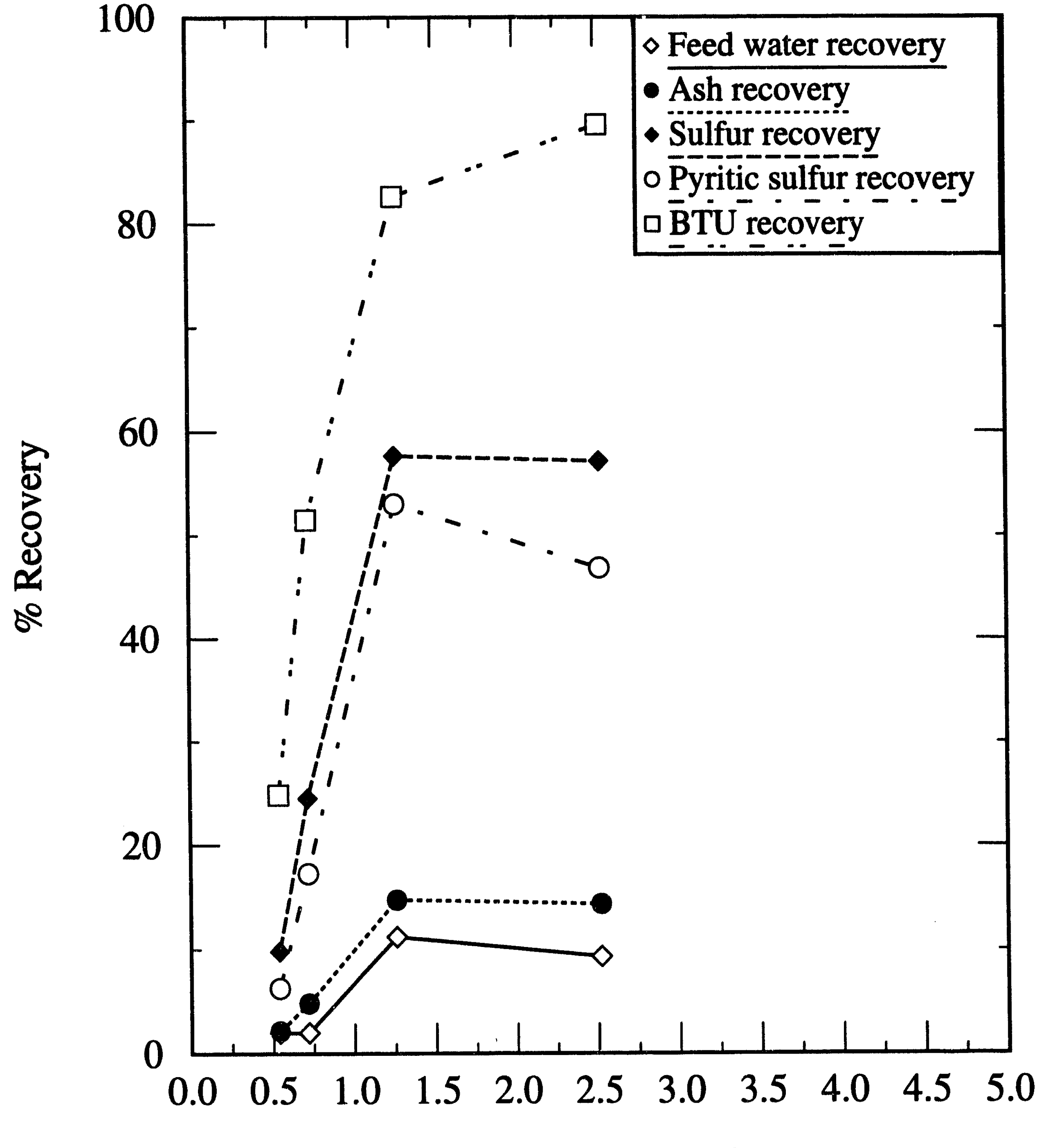

FIGURE 8.20. Recoveries of several components as a function of frother dosage, at a constant collector dosage of 2.25 kg/mt, for the off-line continuous tests with the fully-baffled column.

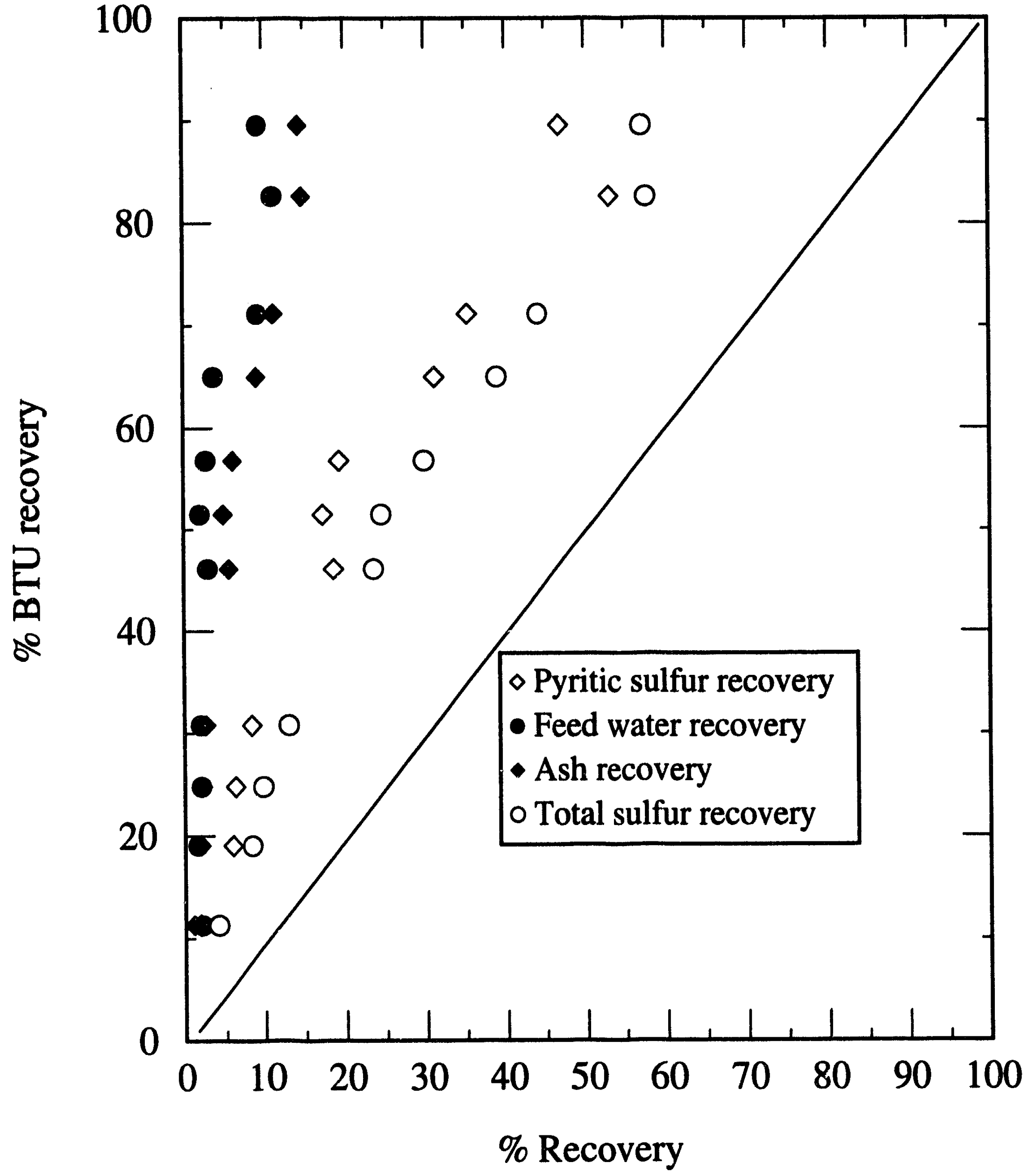

FIGURE 8.21. Comparison of the recoveries of various components with the BTU recovery for all of the off-line continuous reagent tests with the Empire filter cake as feed. All of the listed components are recovered more slowly than the total heating value, showing that the column is acting to remove them. The ash and feed water recoveries are nearly identical, showing that the ash is reaching the froth by entrainment. Both the pyritic sulfur and the total sulfur are recovered faster than the feed water, showing that the pyritic sulfur is being recovered as locked particles with the coal.

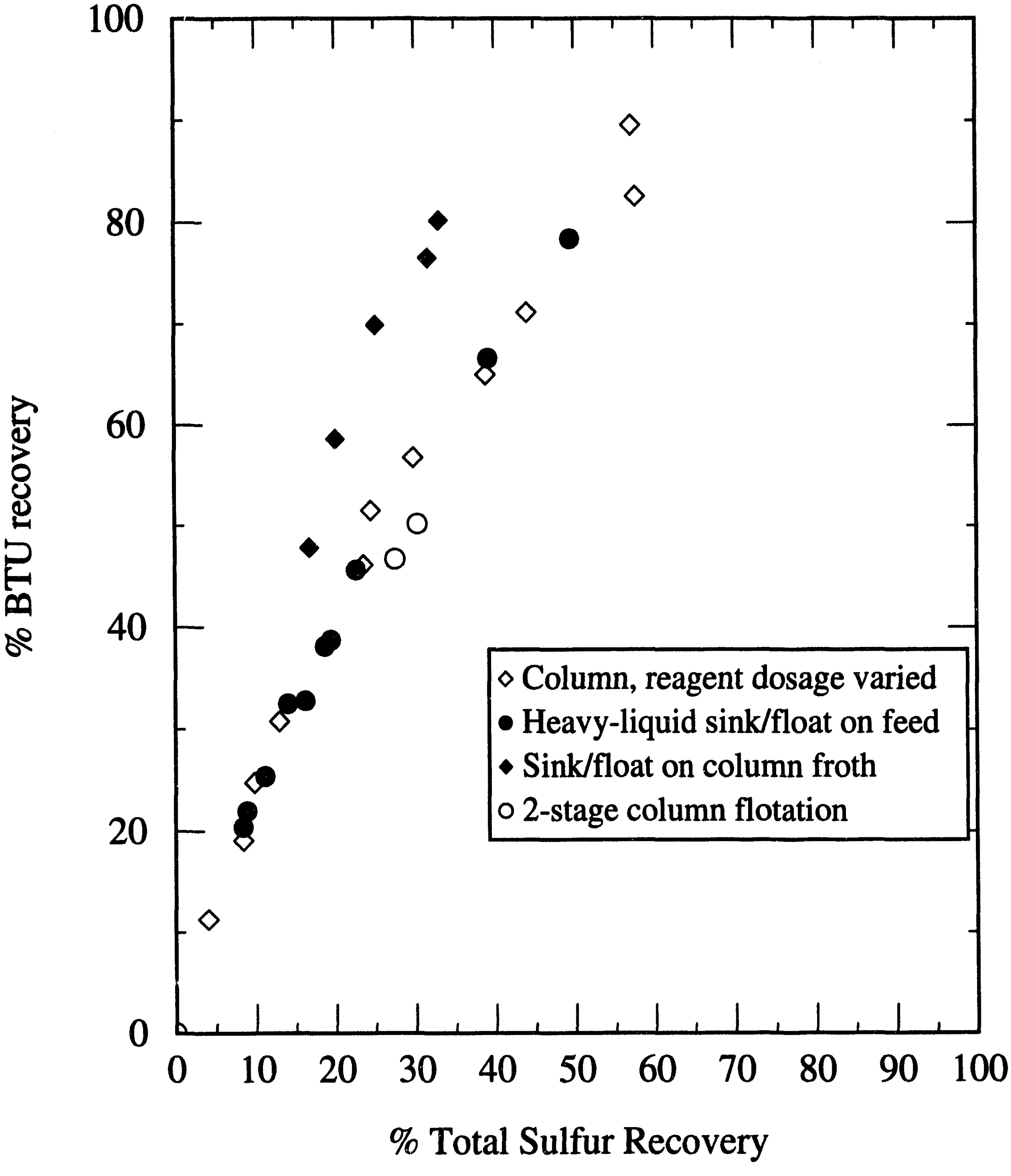

FIGURE 8.22. Comparison of BTU recovery versus sulfur recovery for the column alone, for sink/float separation alone, for column flotation followed by sink/float, and for two stages of column separation. The feed was the filter-press cake used in the off-line continuous tests. This shows that either a density separation alone or column flotation alone will give almost exactly the same sulfur removal, but that the combination of column flotation and density separation is markedly superior.

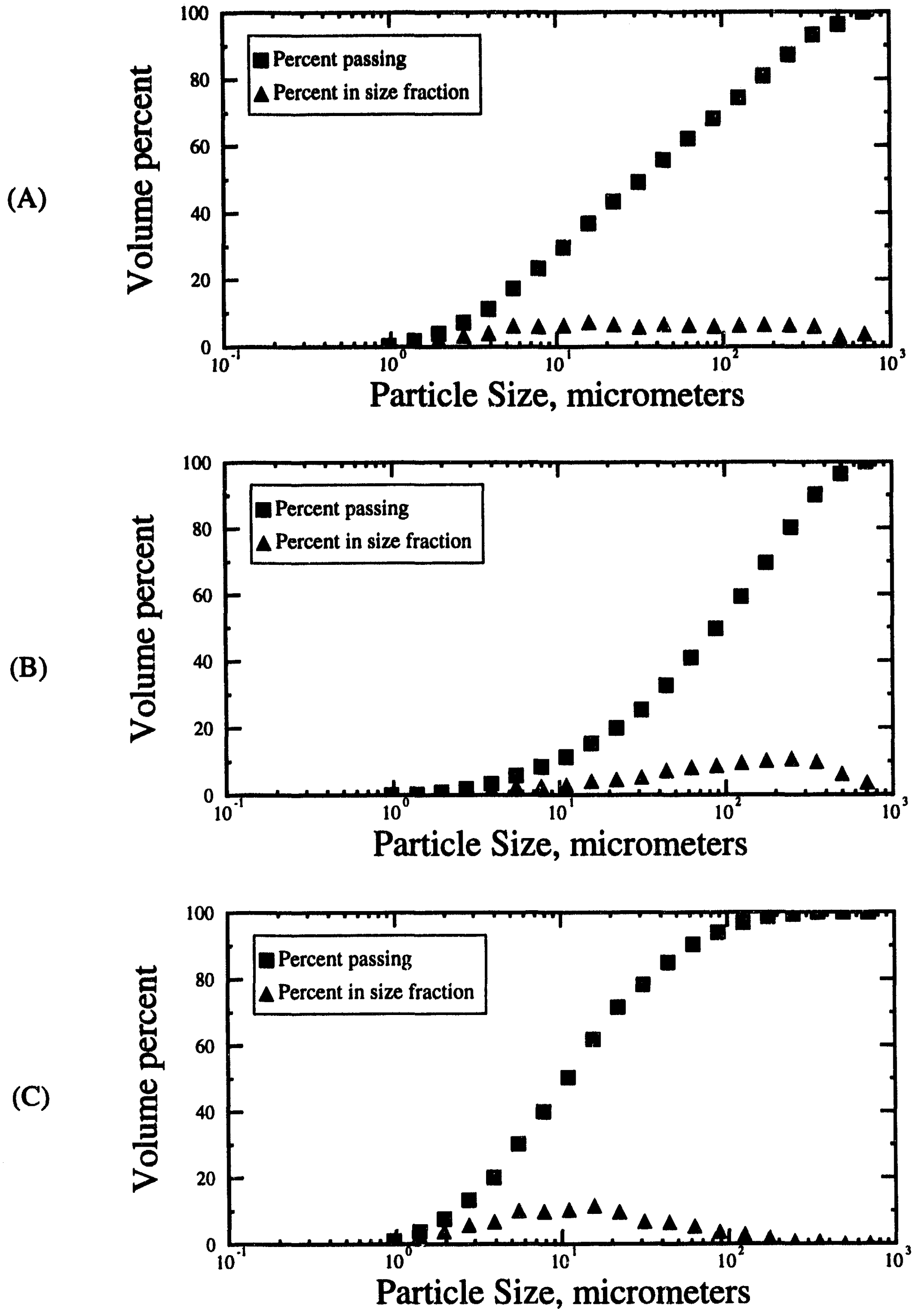

FIGURE 8.23. Microtrac plots of the particle size distributions for: (A) the column feed collected from the tailings filter; (B) the 1.9 specific gravity floats fraction, and (C) the 1.9 specific gravity sink fraction. The float fraction accounts for 50.1% of the column feed.

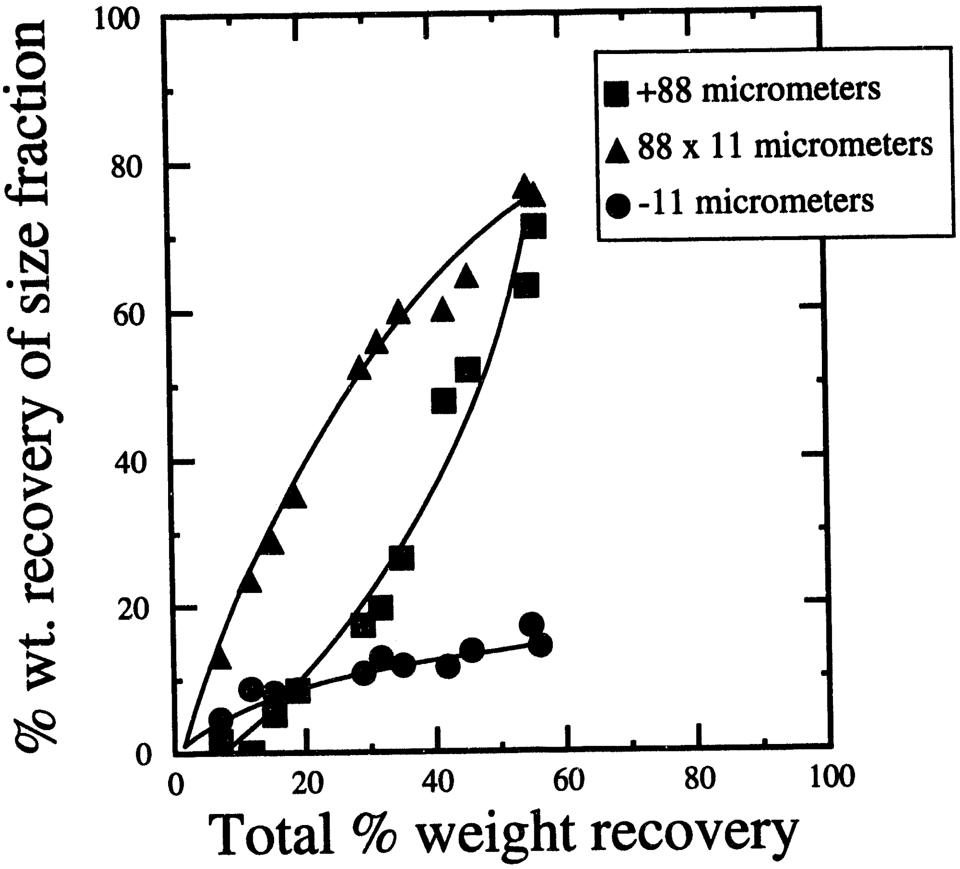

FIGURE 8.24. Recovery of various size ranges as a function of total weight recovery by the column, over a range of reagent dosages and a constant degree of baffling.

particles appear at first glance to be poorly recovered by the column. However, it should be kept in mind that this size fraction contains very little coal, since less than 20% of it floats at a specific gravity of 1.9 (The specific gravity of coal is typically less than 1.5, clay minerals are about 2.6, and pyrite is 5.0). The most easily floated material was in the intermediate size range, and indeed when the total recovery was less than 10% by weight there was no +88 micron material which floated at all. As the recovery was increased, the fraction of the froth which was coarser than 88 microns steadily increased, until a approximately 50% weight recovery the recovery of the coarse fraction finally equaled the recovery of the intermediate size. The fact that these results follow consistent, smooth curves indicates that the proportions of the various sizes which were recovered is a function of the total percent weight recovery to the froth, regardless of what reagent levels are used to achieve this recovery. This is borne out by Figure 8.25, which gives the size recovery results for the baffle variation experiments. These results used a constant reagent dosage and varied the total recovery by changing the degree of baffling, and yet the size-recovery curves

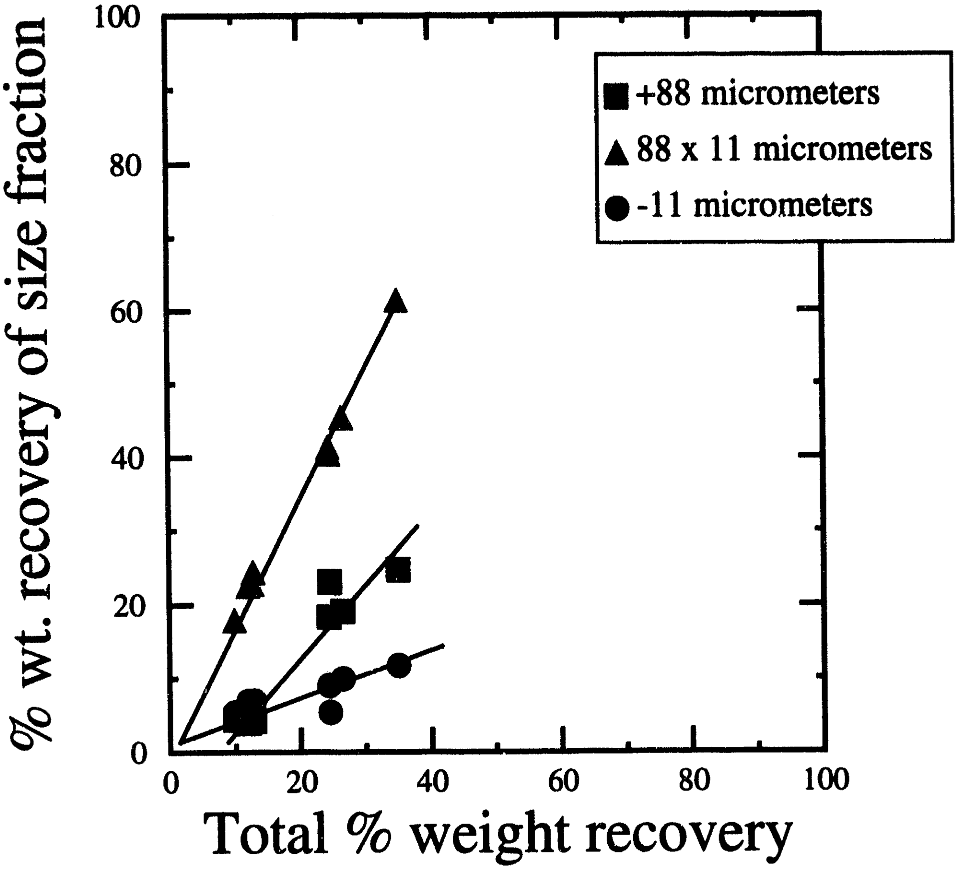

FIGURE 8.25. Recovery of various size ranges as a function of total weight recovery by the column, with various degrees of baffling and constant reagent dosage.

plotted here correspond very closely to the curves of Figure 8.24. The gradual broadening of the froth size distribution with increasing recovery was probably due to the slightly lower floatability of the coarser particles, and to the froth-scrubbing action of the column. At low frother dosages, when the bubbles tended to coarsen and thus reduce the available collecting area, the most floatable particles coated the air bubbles and armored them against attaching to other particles. In addition to this, the thin bubble films at low frother levels meant that the bubble surfaces were being scrubbed thoroughly by other bubbles and by the baffles. Coarse particles were more affected by this scrubbing action because they projected out more from the bubble surface, and were therefore more likely to be removed. As the frother dosage increased, the bubbles became finer and carried a thicker boundary layer, and as a result the scrubbing and armoring effects became less limiting and the recovery of coarser coal particles increased. This is unfortunately accompanied by greater amounts of water being recovered in the froth, but the use of washwater prevents this from being accompanied by an excessive level of gangue entrainment.

8.8 COARSE-COAL BATCH EXPERIMENTS

8.8.1 Procedure

A series of batch experiments were carried out with a coarser feed than had been used in earlier tests, in order to determine how the column performed with coal which was largely coarser than 100 mesh. These tests were run to compare the characteristics of the pilot-scale column with the laboratory column described in Chapter 7. The feed was collected from a sandwich screen (nominal sieve size of 150 mesh) which was undergoing trials in the plant for removing the coarse fraction from the thickener underflow, with the goal of removing some of the load from the tailings filter. The size distribution of the feed collected for these experiments is given in Table 8.9. Since this feed was too coarse for the diaphragm pump to handle, the feed was added to the column by hand. For each test, a 10 kg charge of sandwich screen oversize (dry weight approximately 6 kg) was suspended in 4 gallons (15.1 liters) of water (approximately 28% solids), and mixed with the desired amount of reagent. The slurry was then added to the column over a one-minute interval, and the entire froth product was collected over a series of time intervals. For the batch tests with varying amounts of baffling, 1-liter samples of tailings were collected at regular intervals. For the frother experiments, the entire tailing product was collected in a 55 gallon drum for each experiment.

TABLE 8.9: Size and sulfur distribution of the sandwich-screen product used as feed for the coarse-coal batch tests.

Size		% Weight Retained	% Sulfur	% Weight Passing
Mesh	Microns			
28	600	4.73	3.56	95.27
35	425	4.59	4.05	90.68
48	300	14.10	3.68	76.58
65	212	23.23	3.60	53.35
100	150	15.92	3.86	37.43
150	106	10.64	4.39	26.79
200	75	6.53	4.31	20.26
270	53	4.72	5.25	15.54
-270	0	15.54	2.70	---
Total:		100.00	3.74	

8.8.2 Results-Baffle Effects

Figure 8.26 shows the effect which the baffles had on the rate at which material reached the column tailings outlet. The peak percent solids of the tailing slurry occurred at 7 minutes when no baffles were present, but was delayed until 11 minutes when the lower baffles were in place. The upper baffles also delayed the peak percent solids, but only until 9 minutes. Figure 8.26 also shows that while the lower baffles delayed the peak percent solids, they also allowed the

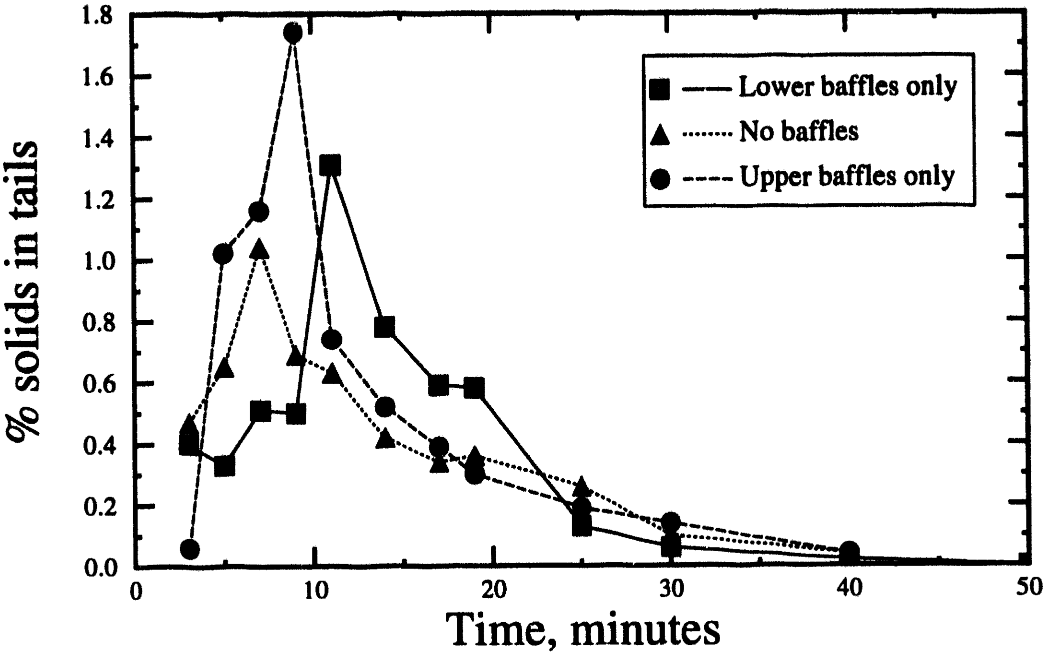

FIGURE 8.26. Effect of baffles on the time required for solids to reach the tailings outlet. These results are consistent with tracer results obtained during column shakedown testing.

column to clear of solids more rapidly. This indicates that the lower baffles acted to provide a closer approach to plug flow, by reducing the probability that a particle will either be swept directly to the tailings or carried back up in the column and delayed on its way to the tailings outlet. The effect of baffles on the froth, as shown in Figure 8.27, was somewhat different. Here, the effect of the baffles was to reduce the amount of time needed for the froth to build up, and increase the flowrate of the froth once the overflow begins. Both the upper and the lower baffles, taken alone, had a very similar effect on the flotation rate. From observation of the froth in the course of each test, the presence of baffles appears to reduce the formation of large air bubbles, which would otherwise cause churning of the froth and make it less stable.

8.8.3 Results-Frother Effects

A second series of batch tests was carried out to determine whether different frothers would have any serious impact on the column performance. The frothers used were Dowfroth 200, Dowfroth 1012c and Dow M420. The structure and characteristics of these frothers are described in Appendix 4, and they were picked in order to give a wide range of frother strengths and some chemical variability. Reagent levels were based on the minimum frother dosage needed to produce a stable froth two feet (0.6 meters) deep when the column was operating with no solids

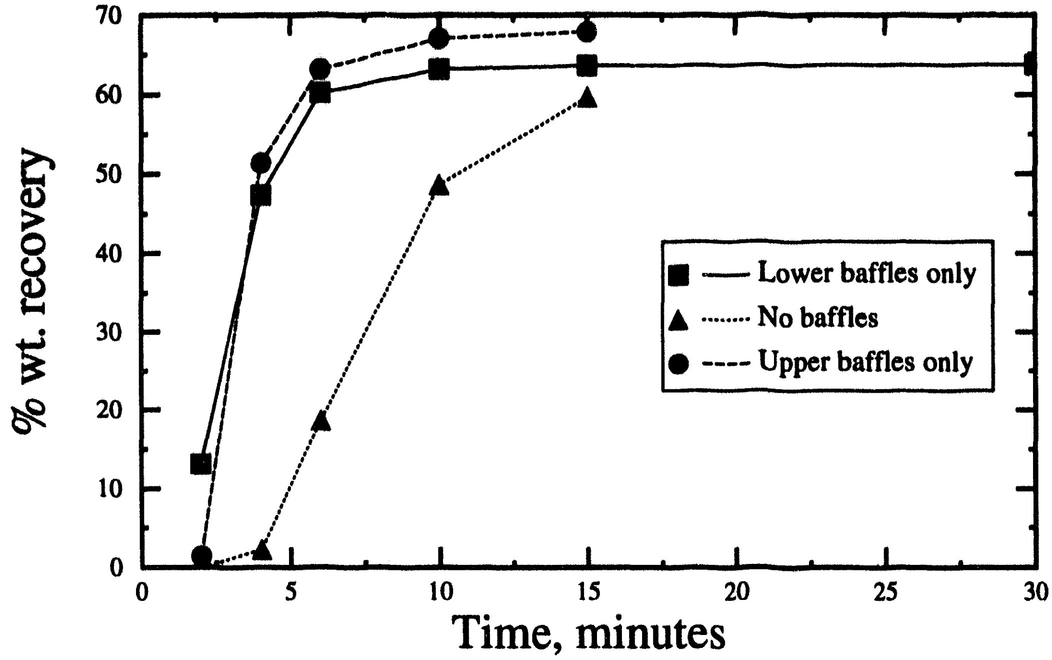

FIGURE 8.27. Effect of baffles on recovery rate of the froth in coarse-coal batch tests. These tests indicate that the baffles can increase the column capacity under certain circumstances.

present. The reagent dosages used are given in Table 8.10 for all nine batch tests.

TABLE 8.10: Reagent Conditions for the coarse-coal batch tests. Since frother was continuously added in the course of each test, the quantity of frother per metric ton coal was not constant. Frother dosage is therefore calculated based on the amount that would be added to a 10% solids feed.

Test Number		DF 1012c	DF 200	M 420
Test 1	Frother	0.04 kg/mt	0.8 kg/mt	0.04 kg/mt
	Collector	0.5 kg/mt	1.0 kg/mt	0.9 kg/mt
Test 2	Frother	0.04 kg/mt	1.6 kg/mt	0.08 kg/mt
	Collector	0.9 kg/mt	0.9 kg/mt	0.9 kg/mt
Test 3	Frother	0.08 kg/mt	0.8 kg/mt	0.04 kg/mt
	Collector	0.9 kg/mt	1.3 kg/mt	0.9 kg/mt

The products from each test were screened into three size fractions and analyzed for sulfur, and the recoveries of total weight and total sulfur for each size were calculated. These results are plotted in Figure 8.28, 8.29, and 8.30. It is immediately seen that for the coal which is coarser than 270 mesh (53 microns) the selectivity between coal and sulfur does not vary, and the recovery of sulfur never exceeds the recovery of coal. Thus, it appears that for the coarser fractions the choice of frother is relatively unimportant for selectivity in column flotation. However, in Figure 8.30 it is seen that the sulfur in the -270 mesh froth product is a strong function of the frother used, with Dowfroth 1012c showing a better selectivity between coal and sulfur than either of the other two frothers tested.

8.9 CONCLUSIONS

From these plant results, the following conclusions may be drawn:

1: In on-line tests, the column was capable of recovering an average of 87.1% (3.45%) of the calorific value in the fine coal waste stream, while rejecting an average of 52.5% (5.64%) of the pyritic sulfur and 86.6% (2.43%) of the ash. The best on-line results were 88.8% BTU recovery with 56.1% pyrite rejection and 87.6% ash rejection. The column is sensitive to the chemistry of the coal slurry, with oxidized coals and surface-active agents such as dewatering aids tending to seriously reduce the recovery.

2: In general, the operation of the column for particles coarser than 270 mesh i insensitive to the specific frother used, with the dosage level being more important than frother type. However, particles finer than 270 mesh appear to be sensitive to frother type.

3: As the collector dosage increases, the increasing particle loading in the froth has the side effect of making the froth less fluid. Ultimately, this causes the column to plug and the froth to collapse at high collector dosages unless the frother dosage is also increased to compensate. As a result, there is a limited range of collector/frother ratios where a coal flotation column will work properly. In the tests conducted, the fluidity of the froth was best at collector/frother ratios between 1:1 and 2:1. In conventional coal flotation which has been reported in the literature, the more usual collector/frother ratio is between 3:1 and 4:1 (Laskowski, 1991). This difference may be a result of excessive conditioning with frother in these column experiments, which would tend to increase the amount of frother adsorbed by the coal and clay particles. It may also be due to the depth of the froth, which makes it necessary to have a very fluid froth in order to let it flow freely from the column.

4: Adding baffles to the column had the effect of increasing the recovery of fine coal, improving the characteristics of the froth, and reducing the necessary column height. The capacity reduction which was expected due to adding baffles was obscured by the variability of the feed quality in the plant, but it appeared that the fluidity of the froth had a more significant effect on column capacity than did the presence of baffles. Since no problems with material plugging the baffles were encountered, there are no serious mechanical problems with using them. Tracer experiments showed that the baffles did significantly reduce the amount of feed water which reached the froth, and that as a result the froth was cleaner. Studies of the residence time of particles in the column confirmed that the baffles reduced the probability of short-circuiting, and caused the flow patterns in the column to more closely approximate plug-flow.

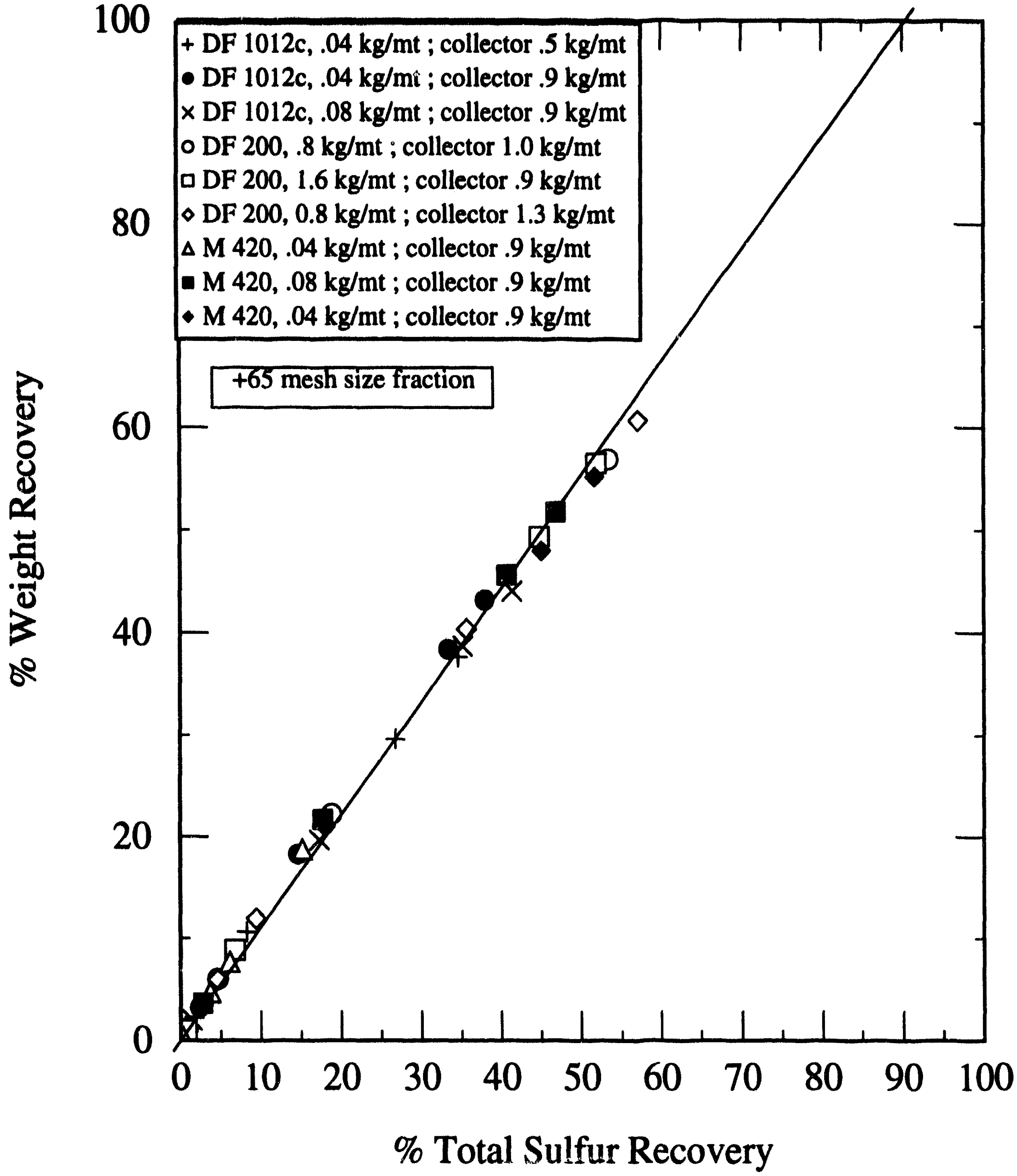

FIGURE 8.28. Relationship of total weight recovery to the total sulfur recovery for the batch tests using the sandwich screen coarse product, for the plus 65 mesh size fraction. These results are for timed batch flotation tests, with all baffles installed.

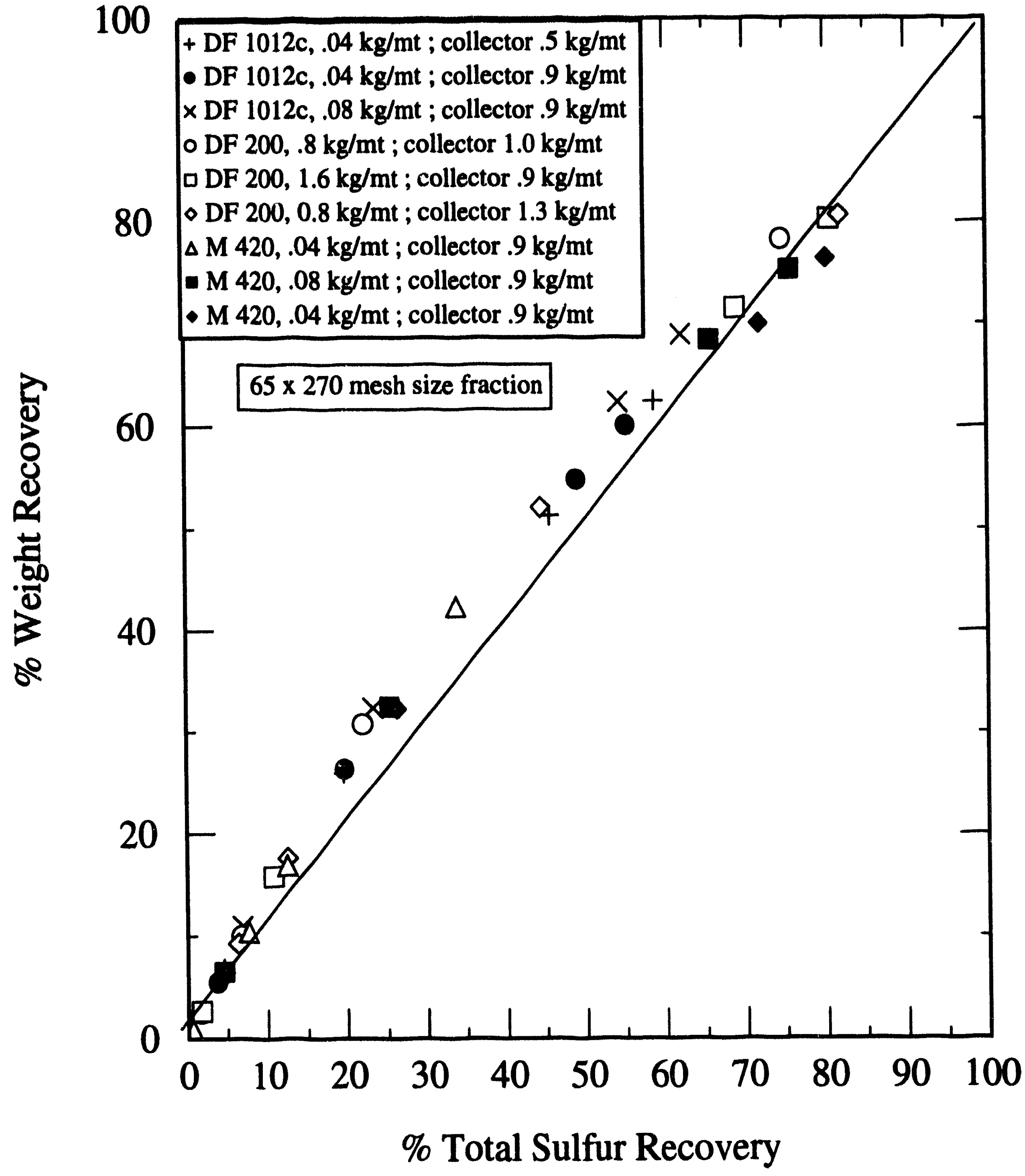

FIGURE 8.29. Relationship of total weight recovery to the total sulfur recovery for the batch tests using sandwich-screen oversize, for the minus 65 mesh/plus 270 mesh size fraction. These results are for timed batch flotation tests, with all baffles installed.

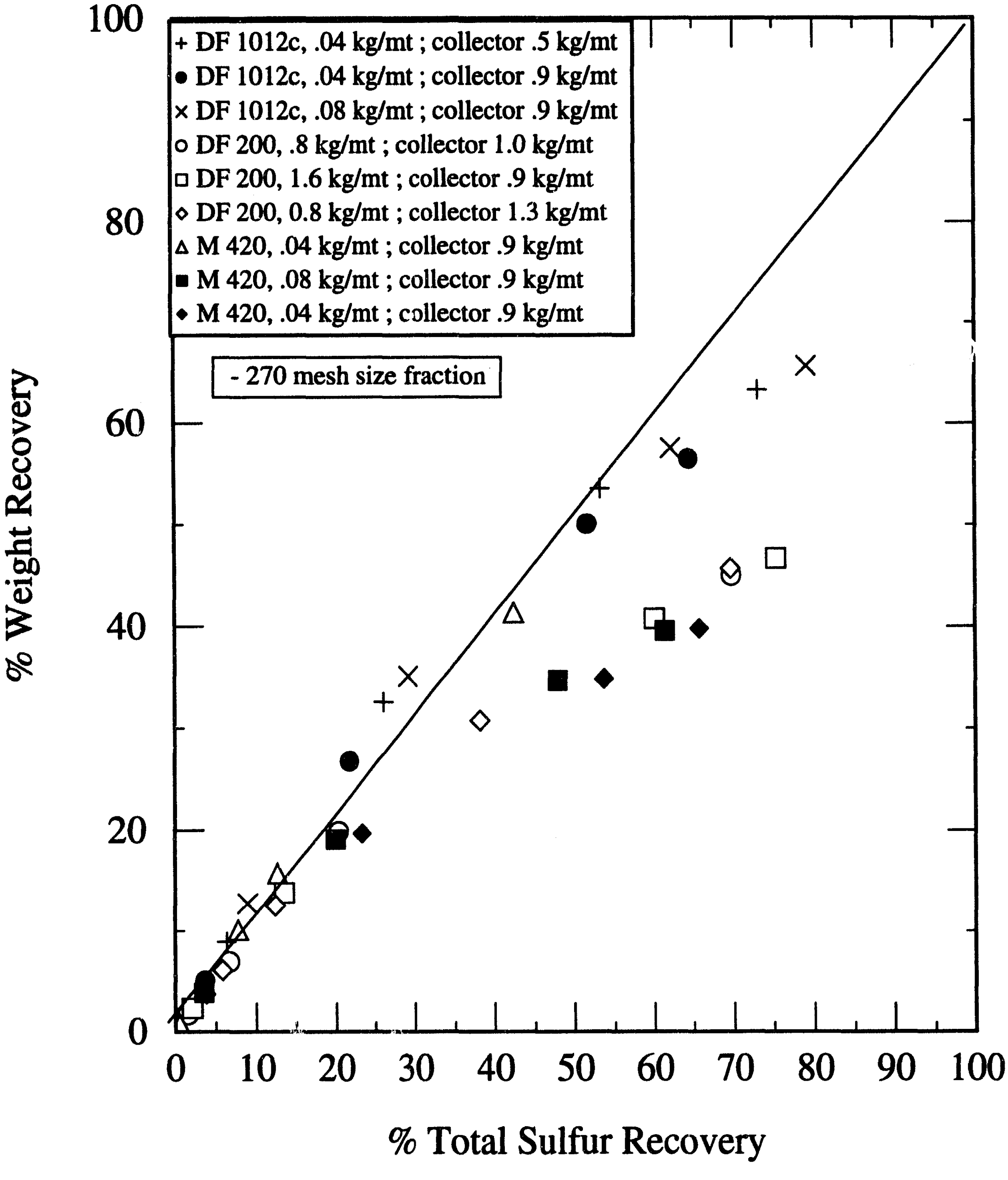

FIGURE 8.30. Relationship of weight recovery and total sulfur recovery for batch tests using sandwich-screen oversize, for the minus 270 mesh size fraction. These results are for timed batch floation tests, with all baffles installed.

CHAPTER 9: MARKETING AND COMMERCIALIZATION

9.1 APPLICATIONS

The market for the column flotation technology developed in this project falls into two categories. The most immediate application is for recovering salable coal from the fine waste stream in existing coal treatment plants, thus reducing the amount of material which must be disposed of and increasing the profitability of the mining operation by reducing BTU losses. This requires a process which is both selective enough to produce a high-quality product from heavily contaminated fine coal, while still being low enough in cost to be profitable. The second application for this process is to deep-clean coals which have been intentionally ground to a fine enough size for good mineral liberation. This deep-cleaned coal can then either be used as fuel directly, or as feedstock for advanced coal processing and utilization schemes. While the demand for such deep-cleaned coal is currently low, it is expected to increase a great deal in the future. These two applications will provide a very wide market for this technology, as most bituminous coals are treatable by column flotation. This will also increase the competitiveness of midwestern coals relative to low-rank western coals, as low-rank coals are generally poorly floatable and must therefore be treated by techniques which are either less effective or more expensive. The commercialization of this project is expected to initially consist of retrofitting existing plants to more effectively treat their fine waste streams. This will be accomplished through existing equipment manufacturers such as the Deister Concentrator Co., which already markets a basic flotation column and can therefore readily adopt the modifications developed in this project.

9.2 PROCESS WASTES

At present, column flotation is most important as a way to reduce the amount of coal being disposed of in tailings dumps, and is therefore already a case of recovering waste for use. The tailings product from column flotation will, for most coals, be predominantly clay which in some cases may be suitable for manufacturing products such as bricks. Since column flotation produces a very clean tailing as well as a highly cleaned froth, the column waste will be easier to find uses for than would be the case using other treatment methods.

9.3 IMPLICATIONS FOR THE EMPIRE COAL PLANT

The results of this project clearly show that a modified flotation column can be installed successfully even in plants where high clay content and coal oxidation make conventional froth flotation impractical. The Empire coal processing plant was originally designed to use froth flotation to recover the fine coal, but the flotation circuit was shut down because the coal produced was too high in ash, sulfur, and moisture to be salable. The product produced by the flotation column on the same coal is of comparable quality to the coal produced by the rest of the plant, and is therefore fully salable. The coal which is currently being lost with the fine tailings is over 10% of the plant's current production, and therefore recovering this coal is an important benefit. For this one plant, this amounts to approximately 12 tons of additional coal production per hour.

9.4 PROCESS IMPLEMENTATION

Since the process is a modification of an existing technology, it can be adopted very quickly. A plant which retrofits with modified flotation columns could be using this technology within six months. As a result, virtually any coal processing plant which is cleaning a floatable coal could realize profits from this technology within a very short time. Since pyritic sulfur and ash removal is more effective at finer particle sizes, the coal produced by column flotation will be at least as salable as the coal currently being sold.

9.5 COST ESTIMATES

These cost estimates are for cleaning the Empire coal waste stream. Deep-cleaning coal would cost more, due to the added grinding and dewatering costs. The cost of dewatering the fine coal is not given, as the waste it is being recovered from is already being filtered, and so dewatering of the coal will have comparable cost to what is already being done.

9.5.1 Baffled Flotation Column

9.5.1.1 Calculations:

9.5.1.1.1 Water pumping costs

$Kw = (H \times Q \times \rho) / (3.67 \times 10^5)$ (Perry, 1984)

where H = pressure head, meters of water;
Q = flowrate, m^3/hr
ρ = density, kg/m^3
Kw = power, kilowatts

For the feed slurry,
$H = 30' = 9.2$ meters;
$Q = 3$ gal/min $= 0.68\ m^3/hr$;
and $\rho = 1000\ kg/m^3$
giving a power draw of 0.017 kw. For the bubble generator and washwater,
$H = 70$ psi $= 49.2$ meters;
$Q = 3$ gal/min $= 0.68\ m^3/hr$;
and $\rho = 1000\ kg/m^3$
for a power draw of 0.091 kw.

9.5.1.1.2 Compressed air pumping cost

$Kw = (9.81 \times 10) \times Q \times p \times X$ (Perry, 1984)

where Q = standard volume flowrate, m^3/hr
p = absolute inlet pressure, kilopascals
$X = 0.5579$, for air when the compression ratio is 4.7 (Perry, 1984)

To run the bubble generator,
$Q = 1.7$ m/hr
$p = 1$ atm. $=100.7$ KPa
$X = 0.5579$
which gives a power consumption of 0.094 kW.
The total power consumption is $0.017 + 0.091 + 0.094 = 0.202$ kW Assuming 70% motor

efficiency, this is 0.288 kW. Since the column produces 30 kg of clean coal per hour, this corresponds to 0.288 kWhr/0.03 mt = 9.6 kWhr/mt

If electricity costs $.06/kWhr, the power cost is $.58/mt

9.5.1.1.3 Reagent costs The reagent costs are as follows: (Fee, 1991)

Table 9.1: Reagent costs for processing the Empire Coal fine waste stream by column flotation.

	$/kg	kg/mt	$/mt
DF 1012c	1.52	0.5	0.76
Dow M210	2.65	0.1	0.26
#2 Fuel Oil	0.26	0.4	0.10
Total			1.12

9.5.1.2 Capital Cost:

An 8' diameter Deister Flotaire column costs $85,000 to $100,000 installed (Woody, 1991). An 8' column will have approximately 144 times the capacity of the 8" pilot column, or 4.3 metric tons/hour. Since the Empire coal plant produces about 27 metric tons of fine waste per hour, and half of this is recoverable coal, this plant would need three columns. The capital and installation cost will therefore be about $300,000.

9.5.1.3 Operating Cost:

The column will use 9.6 kWhr of electricity/metric ton to pump air, water, and feed slurry. At $0.06/kWhr, this costs $0.58/mt. Reagent costs are $1.12/mt. For three columns, at most one more employee will be needed. Assuming labor costs $30/hr, this will be $2.22/mt. The total operating cost is therefore $3.92/mt coal produced.

9.5.1.4 Payback Period:

Since the fines are a waste product, mining and waste disposal costs will not be increased by recovering coal from them. Assuming that coal is worth $40/mt, the payback period for three columns is ($300,000)/[($40/mt-$3.92/mt)x(13.5mt/hr)x(8hr/day)] = 77 days

9.5.1.5 Sulfur and Ash Removal Costs:

This will change depending on the amount of ash and pyrite present in the column feed. At Empire Coal, the feed is approximately 40% ash and 2% pyritic sulfur. 90% of the ash and 60% of the pyritic sulfur is removed by the flotation column. Given an operating cost of $4/mt of clean coal produced, this corresponds to $6.67/mt ash removed, and $222/mt sulfur removed.

9.5.2 Bacterial Leaching

From the laboratory tests with shake flasks and pachuca tanks, it is unlikely that bacterial leaching can remove enough pyrite to be comparable to column flotation in less than a week. At 30% solids, a throughput of one metric ton/hour will require a tank volume of 504 cubic meters in order to get one week of residence time. Comparing directly to an 8' (2.44 m) diameter column

10' (3 m) high with a capacity of 4.3 mt/hr, the column has 14 m of volume, while the bacterial leaching would require 2170 m. Since the bacteria work in acid solution, the leaching tanks will have to be at least stainless-steel, and probably glass-lined. According to Peters and Timmerhaus (1980) 2170 m of stainless-steel mixing tanks with agitators will cost approximately 2 million dollars. This is about twenty times the capital cost of a column with the same capacity. Also, the bacterial leaching is not able to remove clays from the coal, and so the bacterial leaching product is dirtier than the column flotation product. Column flotation is therefore greatly superior to bacterial leaching for floatable coals.

9.6 RECOMMENDED FURTHER WORK

The immediate next step technically is to construct a full-scale plant unit which can be permanently installed in an operating coal cleaning plant. This would preferably be a 6-8 foot diameter unit, with baffles installed with open area and spacing similar to the pilot scale unit used in this project. Such a column would be 10-15 feet tall, rather than the 30-40 feet needed for an unmodified column, and would have a capacity of approximately 4 tons/hour of clean coal. This will conclusively show the benefits of this type of machine in existing operations, and be followed by marketing of the units to the Ohio coal industry.

CHAPTER 10: CONCLUSIONS

1. A review of the literature showed that, although many processes have been developed for desulfurizing coal, there are only a few that are particularly effective for fine coal while still being low enough in cost to produce desulfurized coal at a profit. The processes which were selected for further study in this project were bacterial leaching, bacterial depression of pyrite during froth flotation, and column flotation, as these appeared to give the best combination of low cost and good sulfur removal.

2. Leaching experiments with Thiobacillus ferrooxidans showed that the leaching time could be reduced by improving the aeration in the bacterial reactor. However, the removal of 90% of the pyritic sulfur from the coal still required over two weeks even with well-aerated pachuca tank reactors, and such a long residence time makes the capital and operating costs for bacterial leaching of coal prohibitive.

3. Since it was widely reported in the literature that liberated pyrite in coal is recovered into coal flotation froths by true bubble attachment, work was done to determine whether coating of pyrite particles by microorganisms would depress pyrite flotation. When flotation of coals from two different seams was carried out, the bacteria were not found to have any effect. Experiments with pure pyrite showed that pyrite is sometimes floatable by neutral oil collectors such as fuel oil, but this floatability is mainly seen when the pH is less than 4. At pH values of around 7, which is where coal flotation is normally carried out, freshly ground pyrite was not found to be floatable by fuel oil. If the pyrite was aged at freezing temperatures for an extended period, it was found to be floatable at neutral pH, and this floatability was destroyed when the pyrite was air-oxidized at 100°C. It is believed that the pyrite forms a layer of elemental sulfur on its surface during gentle oxidation, which is naturally hydrophobic and acts as a pyrite collector.

4. Under the acid conditions where pyrite is naturally floatable by fuel oil, a number of microorganisms were found to be effective pyrite depressants. In fact, the least effective organism was the strain of Thiobacillus ferrooxidans which had been adapted to grow on pyrite, which was the organism which was expected to be the most effective. This is probably a result of depression occurring by different mechanisms depending on the organism responsible. The various non-lithotrophic organisms were not capable of living in acid solution, and so they are likely to have lysed. It was therefore the colloidal remains of the dead cells that was causing depression, and not the live organisms. The Thiobacillus, on the other hand, were not killed and were actively metabolizing the pyrite. Since it has been reported that elemental sulfur is formed on the pyrite in the early stages of bacterial leaching in poorly-oxygenated water, the bacteria were probably producing a hydrophobic pyrite collector at the same time as their own attachment to the pyrite surface was acting as a depressant.

5. Based on the pure-pyrite flotation results, it appeared that true flotation of liberated pyrite was not likely to be a general problem in coal flotation, particularly when the coal was not oxidized. This was confirmed for the Pittsburgh seam coal by a series of timed flotation experiments with both a conventional flotation cell and a flotation column. The liberated pyrite particles were found to be recovered almost entirely by entrainment, with true flotation of these particles being negligible. Pyrite is therefore not always hydrophobic, but conventional flotation machines always allow entrained particles to enter the froth. As a result, reducing the level of entrainment in coal flotation is a much more generally useful method for keeping pyrite from entering the froth than is attempting to prevent the pyrite from being hydrophobic. Further work therefore concentrated on using column flotation for coal desulfurization, as the main benefit of

flotation columns is their low level of entrainment compared to conventional machines.

6. Experiments with horizontal perforated-plate baffles showed that they produced a cleaner product with less column height than with the normal unobstructed flotation columns. This was due to a reduction of backmixing and turbulence, which gave a closer approximation to plug flow and thereby reduced the amount of gangue being misplaced into the froth. Based on the laboratory experiments, a pilot-scale column was designed for plant trials.

7. Plant trials of the flotation column at the Empire Coal preparation plant confirmed the benefits of horizontal baffles in coal flotation, although the presence of the baffles introduced some operating peculiarities. The capacity was not noticeably reduced by the baffles, and the ability to recover fine coal was improved, probably due to improved particle/bubble contact. While pyrite was reaching the column froth, heavy-liquid sink/float assays of the feed and froth indicated that most of this pyrite was in the form of locked particles floating due to the hydrophobicity of the attached coal. Significant flotation of liberated pyrite particles was only observed at the finest particle size (less than 150 mesh). There was a substantial proportion of the pyrite in locked particles which were dense enough to be separated by density-based separations, but contained enough coal to be floated by the column. This suggests that combining the column with a separation device such as a water-only cyclone would remove many of these particles from the froth product, which would produce a cleaner product than can be produced by either a density separation alone or flotation alone.

8. Economic analysis of the baffled-column flotation process showed that it can process coal similar to that in the Empire Coal plant at a price of approximately $4/metric ton. Since it was processing a waste stream at this plant, there are no incidental costs to processing this coal and there is an incidental benefit due to reducing the volume of tailings which must be filtered and disposed of. It is therefore an extremely economical process, as coal can typically be sold for $40/metric ton, leaving a profit of $36/metric ton. Since the column is much more rapid than bacterial leaching, it is approximately 20 times cheaper due to lower capital and operating costs. A further benefit of column flotation over bacterial leaching is that flotation removes ash-forming minerals as well as pyrite, which bacterial leaching does not do.

9. The baffled-column flotation process is a useful technique for cheaply removing ash and pyrite from fine coal, provided that the coal is floatable and that interfering reagents are not being added to the plant process water. The technology is ready for full-scale implementation in coal-cleaning plants, barring unforeseen difficulties in the final scale-up from pilot scale to full scale.

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APPENDIX 1: EQUIPMENT FABRICATION CONSIDERATIONS

1.1 A. Pachuca Tanks

With the design of pachuca tank used in these experiments, there were a number of mechanical difficulties and limitations. First, at the particle sizes used in these tests, the tanks could only maintain suspensions of less than 35% solids without plugging. In addition, high clay contents in the coal, as was the case with the Pittsburgh coal, tended to cause gradual accumulations of adhesive clay at the base of the riser, which then eventually plugged the air inlet. This deposit could be cleared by removing the riser and purging with higher-pressure air, but was nevertheless troublesome. Also, evaporation from the tanks was quite rapid, requiring about 50 ml of sterile distilled water to be added as makeup every day. Finally, the tanks were all grouped together onto only a few air pressure regulators, with flows to each tank regulated by needle valves originally designed for home aquarium aerators. As a result, the flowrates were difficult to balance among the tanks, which tended to aggravate the clay plugging problem. Once plugging began, the restriction forced more air into the other tanks while allowing more clay to accumulate in the original tank. To reduce this problem in the future, it will be best to have an individual pressure regulator and flowmeter for each tank. The original tanks were constructed of 3" diameter plexiglas pipe, with 3/4" inside diameter risers. The conical bottoms were made from polyethylene funnels, and unfortunately there do not appear to be any waterproof adhesives which will adhere to both plexiglas and polyethylene. As a result, the epoxy which was used for sealing the tank bases gradually peeled off, and needed regluing periodically. Any additional tanks should be made entirely of easily glued, compatible plastics, such as translucent polyethylene, or should be designed so that incompatible plastics fit together with a solid, mechanical seal.

1.2 B. Laboratory Flotation Column

Like the pachuca tanks, this column was made of plexiglas, but most seals were either chemically-welded plexiglas to plexiglas, or bolted flanges with gaskets. The column as originally recieved from Deister had as a tailings outlet a simple 3/8" line, which did not have enough capacity to handle all of the water which was being injected by the bubble generator, and provided no means for controlling the tailings flow. The column therefore had a tendency to overflow if the bubble generator was running at anything above its bare minimum flowrate. This in turn made the bubble generator very sensitive to small changes in water pressure, and as a result the water level in the column would drop several feet whenever the building water pressure dropped due to transient water demands. To cure this problem, the tailings outlet was enlarged to 1" diameter, and a standpipe with an overflow weir was added to maintain a constant pulp level in the column. A valve was also added at the column base so that it could be easily drained at the end of an experiment. The seal between the new line and the plexiglas of the column wass not very secure, so it had to be periodically resealed with silicone caulk or similar substances. Part of the problem with this seal was that it was in an exposed position, and was easily damaged by accident. Frother was metered into the column with a needle valve and rotameter, using gravity-feed from the frother bottle. The adjustment range of this valve was not large enough for frothers to be metered into the column pure, as this would give a massive frother overdose. Frothers which are not very soluble in water, such as pine oil, MIBC, or cresylic acid, therefore could not be used effectively with this arrangement. Glycol frothers were easiest to use, added as 0.5-5% solutions in water. The rotameter was easiest to operate at a flowrate of 50 mm, which corresponds to 15 ml/minute. If glycol frothers were allowed to stand for too long they apparently formed a scum, which plugged the needle valve and had to be cleaned out periodically. The column baffles were made by drilling holes in a polyethylene rod, and then cutting off slices to make the plates. This was considerably faster than cutting disks from flat stock and drilling holes in each plate individually.

1.3 C. Chemical Welding of Plexiglas

Plexiglas sheets or other smooth surfaces can be quickly welded by coating them with a film of acetone, and pressing together for a few minutes. This can also be done with tetrachloroethylene. If the surfaces to be welded are not smooth or do not fit tightly, or there is a gap to fill, then dissolve plexiglas shavings in a small quantity of tetrachloroethylene until a paste is made, and use like a normal adhesive. Acetone cannot be used to make this paste, as it will skin over too rapidly and will not adhere properly.

APPENDIX 2: OPERATING PROCEDURES

2.1 Procedure for Running Pilot-Scale Column

Startup:

1. Turn on air to bubble generators, and the water supply. Turn on the air first, to prevent wter from backwashing into the air flowmeters.

2. Adjust air and water flowrates to both bubble generators.Flowrates which give a smooth, deep froth without collapse of the froth column or churning are:

Water 0.75 gallons/min Air 50 std.cu.ft./hr

Mixing ratio is 1 cubic foot air per gallon of water, as recommended by Don Zipperian (Deister Co.)

3. Adjust sight glass water to a steady trickle, froth top sprays to 1 liter/minute, and washwater flowrate to 2 gallons/min. The washwater stream did not originally contain frother, as recommended by Deister personnel. However, it was later found that with the baffles in place, frother in the washwater and the feed was critical

4. Move controller set-point to 50, which gives a froth depth of 18-20 inches. Controller regulators should be set to:

Controller and level sensor - 20 psi Control valve - 70 psi

5. Adjust frother pump to desired speed. Starvation dosage has been found to be at a pump speed of 30 with a 10% solution of DF 200 frother, which corresponds to 80 ml/minute of 10% solution, or 0.065 ml frother/liter in the column at a feedrate of 2 gallons/minute.

6. Column takes 22 minutes to fill. Once it has filled, adjust diaphragm pump to give the desired feedrate. Pump operates at 40 psi, with the pulse rate adjusted using a needle valve and stopwatch.

7. Adjust collector pump to desired rate. Excessive collector dosage collapses the froth column, so do not overshoot. Collector consists of 1 part Dow M210 froth conditioner/4 parts #2 fuel oil (by weight). Best results are obtained if the frother being used is mixed with the collector to give a constant frother dosage in all of the streams entering the column. The minimum dependable flowrate from the fuel oil pump is 0.25 ml/min (stroke setting at 5%, speed setting at 2.5). Froth is collapsed at any rate above 2.0 ml/min when a starvation level of frother is used.

8. Column takes at least 15 minutes to stabilize after a disturbance, such as startup or a change in reagent dosage. If the column is being operated with discrete batches of feed, there should be enough to feed the column for at least 20 minutes before samples are taken

2.2 Procedure for running laboratory-scale column

1. Prepare the coal feed sample, and suspend it in 1600 ml water in a two-liter erlenmyer flask, with any collector and frother desired.

2. Fill the washwater head tank, with frother added to give the same frother concentration as the rest of the column. Adjust the washwater valve to give a 1 liter/minute flowrate (30 mm on the flowmeter)

3. Turn on the water, and adjust to 15 psi at the aspirator. Open aspirator, and meter in frother solution. Adjust the frother solution strength so the desired addition rate will be 15 ml/minute (50 on the frother flowmeter) The water flowrate through the bubble generator is 5 liters/minute.

4. When the flows are adjusted, close the outlet valve to start filling the column. After 30 seconds, add the feed slurry through the feed funnel, swirling the flask to keep the solids in

suspension. Add the slurry as rapidly as the funnel will take it. Do not add slurry much more concentrated than 30% solids, as this will plug the funnel.

5. When solids can be seen to be reaching the tailings outlet (about 30 seconds after feed has been added), start collecting tailings in one of the 30-gallon garbage cans. These will be able to collect tailings for up to 20 minutes. The average test will last for 10-15 minutes.

6. To shut down the column, first close the air inlet on the aspirator, followed by the water supply, the frother solution, and the washwater. If the aspirator air inlet is not closed first, water from the column will backwash through it . To collect the holdup product, run a hose from the outlet valve to a 5-gallon pail, and drain into it while washing down the column with several liters of clean water.

7. Since the tailing and holdup products are mostly water, they are easiest to deal with if they are allowed to settle overnight, with most of the water decanted off the next morning before filtering the product. Otherwise, filtering all 15 gallons or so of the tailings can easily take hours, particularly if the coal was high in clay.

2.3 Procedure for timed flotation with the automatic batch cell

1. Fill the makeup water bucket with water, using the desired frother concentration for the test. Close off the clamp valve, and adjust the pH if desired. Adjust the air pressure regulator so that when the air valve is opened, the glass ball in the rotameter reads 100 mm.

2. Prepare sample as desired, and adjust pH if necessary. Add the sample to the cell, and open the clamp valve to start water flowing into the cell. When the water covers the impeller, turn on the impeller to disperse the sample. When the cell finishes filling, close the clamp valve and adjust the pH and other reagents.

3. Have tared pans immediately at hand, and put the first two pans under the overflow lips. Make sure that the froth paddle belts are connected, and turn the froth paddles the right way.

4. Open the clamp valve to keep a small overflow in the level controller, turn on the air, and start the paddles. When the first bit of froth hits the pans, start the timer.

5. Do not wash froth off of the paddles. Swap out pans at the desired time intervals. This is easiest if you slip the next set of pans underneath the set currently filling, then simply pull away the filled pans when the time comes. Recheck the level controller frequently to make sure there is a constant overflow.

6. After the last sample is collected, put a stopper into the line from the level controller to the cell, to prevent backwashing. Weigh and filter all samples, and dry at 75° C.

2.4 Procedure for running Pachuca tanks

1. Grind the feed coal to finer than 35 mesh, as otherwise it will not suspend properly. Clean out the tanks with strong alkali to kill any acidophilic organisms which might be present. If the coal is also ground in strong alkali, this should kill any troublesome organisms which may have gotten in to it.

2. Sterilize all water to be used in the experiment by autoclaving. Use aseptic techniques to prepare the starter culture, so you know what you have.

3. Prepare and sterilize the basal salts for the experiment. There should be enough to provide at least 1 liter for each pachuca tank.

4. Add the ground coal to the pachuca tanks (no more than 400 grams) and fill with basal salts solution to 1.25 liters (the top of the riser tube). Adjust the pH with sulfuric acid. Turn on

the air, and open the needle valves for each tank to provide a good mixing action. Adjust all of the tanks so they are mixing with equal vigor, but not so vigorously as to splash slurry about. Inoculate with either bacteria or with sterilant. Put on the lids.

5. Every day, add sterilized water to compensate for evaporation and wash coal down off of the sides of the tank. Check for plugged tanks regularly, and unplug them with high-pressure air. Plugging becomes worse as the particle size and/or the clay content increases.

6. Leaching activity can be monitored by periodically removing liquid samples and analyzing to determine dissolved iron, or by periodically removing an entire tank and analyzing for sulfur content. Trying to remove small samples of solids from a running tank for sulfur analysis will probably not work unless the coal is very fine, due to sampling problems caused by particle settling.

APPENDIX 3: ANALYTICAL PROCEDURES

ASTM standard analytical techniques described here are taken from the Annual Book of ASTM Standards, 1988, Volume 5.05 (Gaseous Fuels, Coal, and Coke). The spectrophotometric method for determination of dissolved iron is taken from R.A. Day and A.L. Underwood, Quantitative Analysis, Fifth edition, Prentice-Hall, 1986, and the method for determining fluorescein concentration is a standard colorimetric procedure.

3.1 ASTM Method for determining ash content of coal (D 3174)

This procedure is automated by the Leco MAC-300 ash and moisture determinator at Empire coal. Analyses at MTU used a standard muffle furnace, and were done in duplicate.

1. Weigh a small porcelain crucible, and add approximately 1 gram of coal (weighed to the nearest 0.0001 gram). Record both weights.
2. Place the weighed crucibles in an electric muffle furnace, which is purged with sufficient compressed air to give 2-4 changes of air every minute. Gradually heat the furnace to 500° C over a period of one hour.
3. Increase temperature further to 750° C, and hold for two hours at this temperature. Remove the crucibles from the furnace, and allow to cool, preferably in a desiccator.
4. Reweigh the burned crucibles, determine the weight of the ash by subtracting the weight of the empty crucible, divide by the weight of the initial sample, and multiply by 100 to obtain the percent ash.

3.2 ASTM method for determining total sulfur (D 4239)

This procedure is carried out using a Leco SC-132 sulfur determinator, both at MTU and at Empire coal.

1. At the beginning of a set of analyses, calibrate the instrument against a known standard of approximately the same %Sulfur as the samples to be analyzed.
2. In each boat, weigh approximately 0.3 grams of sample, enter the weight, and push the boat into the furnace (2500°F), where it is burned under oxygen. The sulfur dioxide content of the off-gases is measured by an infrared absorption tube, and integrating this value over the entire analysis period allows the sulfur content of the sample to be calculated.

3.3 ASTM method for determining pyritic sulfur (D 2492)

1. Weigh 2 to 5 grams of analysis sample (to nearest 0.0001 gram) and transfer to a 250 ml beaker. Add 50 ml of (2+3) HCl, and make certain sample is thoroughly wetted. A few drops of ethanol aids wetting. Boil gently for 30 minutes, and filter out the remaining solids using a medium texture filter paper. Wash thoroughly with water to remove all of the dissolved non-pyritic iron.
2. Return the solids and filter paper to a 250 ml beaker, and slowly add 50 ml of (1+7) HNO_3. Stir with a glass rod to disintegrate the filter paper and completely wet the coal. Let stand overnight, and on the following morning boil gently for 30 minutes to complete the pyrite dissolution.
3. Filter with a medium-texture filter paper, wash thoroughly to remove all of the dissolved pyritic iron, and discard the solids. To the liquid, add 2 ml of 30% H_2O_2 and boil for 5 minutes to

oxidize organic salts. Be sure to bring the beakers completely to a boil, as otherwise oxidation may not be complete, and the indicator in the titration step will not work properly.

4. Slowly add ammonium hydroxide solution until iron begins to precipitate, and it does not redissolve upon stirring. Add an additional 5 ml of ammonium hydroxide to coagulate the precipitate, and filter with a fast, hardened filter paper. Wash the precipitate several times with hot (1+10) ammoniacal solution, and discard the liquid.

5. Dissolve the iron hydroxide precipitate with 15 to 25 ml of hot (2+3) HCl solution, making certain that all iron is dissolved. Wash thoroughly with hot water until no coloration remains on the filter paper.

6. Heat the solution to boiling, and add $SnCl_2$ solution dropwise until the yellow color disappears, with no more than one or two drops in excess. Cool rapidly to room temperature, and add 10 ml of saturated $HgCl_2$ solution.

7 Combine 150 ml of concentrated $H_2 SO_4$, 150 ml concentrated $H_3 PO_4$, and 700 ml distilled water, and add 20 ml of this mixture to the pyritic iron solution. Dissolve 0.2 g of sodium diphenylamine sulfonate in 100 ml of water, and add 2 to 3 drops of this to the pyritic iron solution to act as indicator.

8. Dissolve exactly 2.4518 grams of standardized potassium dichromate in one liter of water, for use as a titrant. Dilute the pyritic iron solution to 200 ml with water, and titrate until the solution turns violet.

9. Pyritic Sulfur, % = [(C - D) x N x (5.585) / W] x 1.148 where C = milliliters needed to titrate the pyritic iron D = milliliters needed to titrate a blank solution N = Normality of titrant W = original sample weight

3.4 Photometric Determination of Dissolved Iron

1. Prepare the following solutions: 0.1 g of 1,10-phenanthroline monohydrate in 100 ml distilled water; 10 g of hydroxylamine hydrochloride in 100 ml distilled water; 10 g of sodium acetate in 100 ml distilled water; Standard solution: weigh accurately about 0.07 g of pure Iron(II) Ammonium Sulfate, dissolve in water, transfer to a 1-liter volumetric flask, add 2.5 ml concentrated sulfuric acid, and dilute to 1 liter.

2. Into five 100-ml volumetric flasks, pipet 1, 5, 10, 25, and 50 ml of the standard iron solution, and 50 ml of distilled water in a sixth flask to act as a blank. These will be the comparison standards. To each of these, add 1 ml of hydroxylamine solution, 10 ml of phenanthroline solution, and 8 ml of the sodium acetate solution. Dilute all of these to 100 ml and allow to stand for 10 minutes.

3. Add a quantity of each unknown solution to additional 100 ml volumetric flasks, to give a color that falls within the intensity range of the standard solutions. Measure the volumes of unknown to within 0.01 ml, and add reagents as for the standard solutions.

4. Set a spectrophotometer to 508 nm, and use the standards to make a calibration curve. Analyze the unknowns, and use the calibration curve to determine the dissolved iron concentrations.

The standard solutions are very stable, and can be used for a period of several months. It is therefore not necessary to make fresh standards every time an analysis is done.

The samples of water being analyzed for dissolved iron should be thoroughly filtered to remove all particulate matter, as suspended particulates will interfere with the light transmission measurement.

3.5 Determination of Sodium Fluorescein Concentration

1. Prepare standard fluorescein solutions by carefully weighing the powdered dye and dissolving it into volumetric flasks to give concentrations ranging from 100 ppm to 0.1 ppm. Set a spectrophotometer to 493.5 nanometers, and use these solutions to make a calibration curve.

2. Collect water samples containing fluorescein, make sure that the pH is greater than 4, and filter out all particulates. Use the spectrophotometer to compare to the standard solutions. If the solution is too opaque to measure, dilute a carefully measured portion of the solution into a volumetric flask and measure again.

3.6 ASTM Method for determining calorific value of coal (D 2015)

This method is automated with a Leco AC 300 automatic calorimeter.

1. Calibrate the calorimeter with benzoic acid tablets or a similar standard.

2. Weigh samples into tared steel crucibles, and enter weights. Load the crucible into the bomb, install the fuse wire so that it contacts the coal sample, close the bomb, and charge to 440 psi with oxygen.

3. Open the vessel, insert the bomb, and begin the analysis. The calorimeter will fire the bomb, measure the temperature rise of the water jacket, and calculate the calorific value.

4. When the analysis is finished, release the pressure, open the bomb, and wash out the residue thoroughly with water. Let the water drain under gravity for a short time, then load the bomb with the next sample.

APPENDIX 4: REAGENT DATA

4.1 Flotation Reagents

The flotation reagents used in this project were primarily supplied by Dow Chemical Co. in sufficiently large quantity to carry out extended pilot-scale flotation experiments. These were as follows:

1. Dowfroth 200: This is a mixture of polyglycol alkylethers, with an average molecular weight of approximately 200 (CAS #025498-49-1). It is a fully water-soluble frother, which makes wide variations in the frother dosage possible simply by diluting the frother being injected into the column. This is a very helpful feature, as the frother injection pump used had a minimum flowrate which was still much too high for injecting undiluted frother. This frother is somewhat stronger than methyl isobutyl carbinol and forms a finer-grained, more persistent froth.

2. Dowfroth 1012c: This frother is composed of polypropylene glycol methyl ether (CAS #037286-64-9) consisting of a 5-unit propylene chain. This particular formulation is purified to a higher level than earlier products, and is approximately 50 times stronger than DF 200. Otherwise, the two frothers produce quite similar froths, although the DF 1012c froth is somewhat finer grained.

3. Dow M420: This is a frother composed of a mixture of isobutanol (5-10%) with a proprietary polyalkoxyalkanol compound. It is similar in strength to DF1012c, and is also water-soluble. It may assist in the coating of oxidized coal by neutral oil collectors, although this was not confirmed in this project.

4. Dow M210: This reagent is a conditioner, to improve the attachment of neutral oil collectors such as fuel oil to oxidized coal surfaces. It is a proprietary alkanolamide-oil fluid, which is a generic term for a saturated, acyclic hydrocarbon with -OH and -CONH groups attached to improve its affinity for hydrophilic oxidized sites on the coal surface. For the Empire coal, use of this reagent in a mixture of 80% #2 fuel oil/20% M210 reduced the collector consumption by approximately a factor of four while noticeably improving the ultimate recovery. This ratio was selected based on Dow Chemical recommendations, and this collector mixture was used in virtually all experiments with the Empire coal.

5. #2 Fuel Oil. This is a mixture of nonpolar oils with a boiling range of 325-750° F, which is normally used as a home heating oil. While any nonpolar oil could be used as a collector for coal,#2 fuel oil is preferred since it is cheap, readily available, and has a low enough viscosity to spread well over the coal surfaces. The primary constituents are paraffinic, aromatic, naphthenic and olefinic hydrocarbons, typically containing from 13 to 32 carbon atoms. Depending on the crude oil source, and on whether thermal or catalytic cracking is used to increase the yield of distillates, the relative proportions of these components can vary widely. In particular, fuel oils distilled from uncracked crude oils are primarily paraffinic, while cracked oils yield more aromatics and olefins (Schmidt, 1969). The effects of the variable composition on coal flotation has not been well studied, but the primary effect is that fuel oils which are richer in aromatics and olefins seem to be more effective than the paraffinic oils for floating oxidized coals. Given the variability in coal floatability, the effects of changing fuel oil composition on coal flotation are less than the normal variation of the coal, and so there is little concern over this point in the coal industry.

6. Methyl Isobutyl Carbinol (MIBC): $(CH_3)_2\ CHCH_2\ CH(OH)CH_3$, a commonly used frother. This was not used in any of the column flotation experiments, although it was used in the

pyrite flotation experiments where a stronger frother would have made an excessively voluminous froth. MIBC is considerably weaker than any of the glycol frothers, and is not sufficiently soluble in water to make solutions of more than a few tenths of a percent. With the metering equipment available, it was not possible to add enough of such a dilute solution to either column to stabilize a froth, or to add straight MIBC at a sufficiently low rate to avoid a massive overdose. As a result of this purely mechanical problem, MIBC was not used in any column flotation experiment.

4.2 Tracer Dye

In addition to the normal flotation reagents, a tracer dye was used to track the water entering with the column feed. This dye was purchased from Formulabs Inc., Escondido, California: Fluorescein Sodium (or soluble fluorescein): $C_{20} H_{10} Na_2 O_5$. This is a water-soluble orange-red powder, which in solutions more alkaline than pH=4 exhibits an intense yellow-green fluorescence and a strong absorption maximum at a wavelength of 493.5 nanometers. It is a commonly used water-tracing dye, normally used for tracking subterranean waters, currents in large bodies of water, and other large-volume flows. It has a very low toxicity, and is detectable down to a concentration of 0.02 ppm. The yellow-green color is highly visible to the eye at 1 ppm concentration. Accurate determination of the concentration of this dye is straightforward, requiring only a spectrophotometer and a series of standardized solutions. Since only low concentrations are needed, this dye allows effective tracing of water with a minimal impact on the solution chemistry, and the low cost of both the dye ($50/lb) and the measurement apparatus makes it very economical to use.

4.3 Incidental Chemicals

Since the plant recycled over 80% of its water with no treatment other than thickening and filtration, reagents which were added to any part of the circuit ultimately ended up in the flotation feed. The other reagents which were present in the circuit, although they were not being added intentionally to the flotation column, were as follows:

Lime, CaO: This was being added continuously to the plant water to keep the pH above 6, both to prevent excessive corrosion and to keep the thickener functioning properly. Constant addition of lime was needed to neutralize the acid formed by oxidation of the coal. Since the coal pyrite content was high, Thiobacillus ferrooxidans were active in the coal, producing ferric sulfate and sulfuric acid at a rapid rate. On the occasions when the lime feeder was not working properly or the coal was heavily oxidized, the pH of the plant slurry dropped to as low as pH=3 due to the action of these organisms.

Polyacrylate flocculants: The plant added two of these flocculants, one cationic and the other anionic, in order to flocculate the suspended solids in the thickener. These act as bridging polymers to hold particles together in loose flocs and thus to increase their settling rate. The use of both cationic and anionic flocculant ensured that all particles would be well-flocculated regardless of their surface charge in solution. The presence of these flocculants in the flotation column may have caused gangue minerals to flocculate to some extent with floatable coal, and thus to be carried into the froth to some extent in spite of froth washing. These flocculants were most plentiful in the coal taken from the filter press for off-line flotation experiments.

Nalco 89DA038 Dewatering Aid: This is a chemical to reduce the affinity of mineral and coal particles for water, and thus to make them easier to dewater and reduce the moisture content of the coal produced by the plant. It is a surface-active agent which unselectively coats hydrophobic and hydrophilic particles alike, forming a thin film on their surface which facilitates water drainage. Unfortunately, it had the side effects of making flotation froth excessively voluminous, decreasing the floatability of the coal, and increasing the floatability of gangue minerals such as pyrite and clays. As a result, addition of this reagent at a sufficient rate to have any benefit made flotation of the coal completely impractical. Luckily, the dewatering aid was not added until the onset of cold weather, after most experiments had been completed, and so it was not a serious problem in most experiments.

Soda Ash, Na_2CO_3: While powdered lime was the primary pH modifier used in the plant, from time to time soda ash was added as a supplement. This was added as briquettes along with the plant feed, in order to make the pH of the recirculating plant water more uniform. These briquettes were mainly added as a stopgap measure when the lime feeder could not handle the acidity of the coal, and were used simply because they were conveniently available, as their main use was for lining the drainage ditches leading to the tailings ponds.

4.4 References

Dow Chemical Co., Midland, MI, materials safety data sheets, 1990
Formulabs, Inc., Escondido, CA, product literature, 1989
Merck Index, 10th ed., Merck and Co., Rahway, NJ 1983
Schmidt, P.F. Fuel Oil Manual, 3rd ed., Industrial Press, New York, 1969

APPENDIX 5: COAL AND PYRITE SAMPLES

Several different coal and pyrite samples were used in the course of this project. Their characteristics, as far as is known, are given below.

1. Meigs Creek coal: 18% ash, 2.0% pyritic sulfur, 4.8% total sulfur, 11406 BTU/lb. This sample was collected from the Muskingum mine, in Ohio, and is from the Meigs Creek (or #9) seam.

2. Middle Kittaning coal: 7.9% ash, 1.1% pyritic sulfur, 2.2% total sulfur, 12734 BTU/lb. This sample was collected from the Crooksville mine, in Ohio, and is from the Middle Kittaning (or #6) seam.

3. Quarto-4 coal: 29.1% ash, 2.8% pyritic sulfur, 4.3% total sulfur, 10059 BTU/lb. This sample was collected from the Quarto-4 mine, in Ohio, and is from the Pittsburgh (or #8) seam.

4. AEP-Pittsburgh coal: 37.2% ash, 2.2% pyritic sulfur, 2.9% total sulfur. This coal was provided by American Electric Power, through the Institute of Material Processing.

5. AMAX coal: This was a super-clean coal provided by AMAX corporation, and was certified to contain less than 1% ash.

6. Rico pyrite: This was a mineral pyrite, provided as rocky lumps by Ward's Natural Science Establishment. It was uniform in color, good grade, and contained very little in the way of non-pyrite inclusions. Purity was greater than 95% pyrite.

7. Custer pyrite: This was also provided as rocky lumps by Ward's. It was less uniform than the Rico pyrite, and showed considerable iron staining on the surface. The Custer pyrite was purchased in two lots:

Lot #1 (Custer-1): Good grade and purity, >95% pyrite
Lot #2 (Custer-2): 48.8% pyrite (insoluble in HCl, soluble in HNO_3)
27.5% soluble in HCl (mostly carbonates and metal salts)
23.7% insoluble in HNO_3 (mostly silicates)

8. Panther Valley pyrite: This was a single sulfur ball, which had been collected from the Panther Valley anthracite mine. It contained a considerable amount of coal (approximately 10% by weight) and had ample opportunity to oxidize, as it had been used as a display specimen for several years.

9. Empire pyrite: This was from a number of sulfur balls hand-collected from the coarse refuse belt at the Empire Coal processing plant. The assay of this pyrite was as follows:

68.5% pyrite (soluble in HNO_3 , insoluble in HCl)
10.0% soluble in HCl (mainly organic and inorganic salts)
21.5% insoluble in HNO_3 (mostly coal, some clays)

It was also very reactive. When specimens were allowed to sit exposed to air at room temperature, they crumbled within a few months, forming crusts which were probably mostly sulfates.

10 Empire coal: This was actually a mixture of three seams (the #5, #6, and #7 seams) which were mined and processed by the Empire Coal Co, in Ohio. The #5 and #6 seams (Lower and Middle Kittanning, respectively) are mined on Empire Coal property, while the #7 seam coal (Upper Freeport) is purchased from a neighboring mine which has no preparation plant. These seams are blended in order to meet the total sulfur and calorific value requirements of the plant's primary customer, with the #7 coal used as the low-sulfur blend component. Control of the blend was done manually, based on periodic sampling of the plant product to measure the sulfur content. The two primary seams are quite different from each other, as shown in Table 5.1, and so the composition of the coal streams in the plant varied quite widely over a very short time. The variability of the coal feed was increased by the fact that three different mining methods were in use: conventional surface mining, hillside augering, and highwall mining. The conventional mining produced primarily coarse lump coal, while the highwall miner performed very much like an underground continuous miner, producing finer coal with a considerable amount of clay gouged out of the ceiling and floor of the seam. Augered coal was intermediate between these two extremes. Finally, the coal was sometimes stockpiled for weeks before it entered the plant, and sometimes fed directly with no delay, and so the degree to which the coal was oxidized was also quite variable.

Table A.1: Analyses of the #5 (Lower Kittanning) and #6 (Upper Kittanning) seam coals mined by conventional strip mining and hillside augering at Empire coal. Analyses of the highwall miner product were not available, but it is finer and higher in ash than the augered products.

	#6 Auger				#6 Strip			
Size	% wt	% Ash	%S	BTU/lb	% wt	% Ash	%S	BTU/lb
4" x 2"	9.37	14.85	4.88	12399	9.43	6.81	4.73	13860
2" x 0.5"	23.40	15.33	5.12	12302	41.33	4.80	3.80	14036
0.5" x 0.25"	18.57	19.64	4.70	11596	18.12	5.19	3.07	13755
0.25" x 6m	17.22	17.78	4.30	11274	9.38	6.49	2.79	13155
6m x 28m	19.66	18.79	4.03	11081	13.15	7.53	2.84	12922
28m x 100m	6.06	19.10	4.06	10878	4.01	10.52	3.14	12384
100m x 200m	1.48	18.37	4.81	11465	1.02	12.42	3.79	12080
200m x 325m	0.68	18.38	6.16	11641	0.63	14.23	3.86	12051
325m x 500m	0.49	17.83	5.84	11690	0.46	12.51	3.36	12320
-500m	3.07	53.06	2.21	6024	2.47	45.79	2.19	6842
Total:	100.00	18.65	4.52	11464	100.00	7.71	3.47	13455

	#5 Auger				#5 Strip			
Size	% wt	% Ash	%S	BTU/lb	% wt	% Ash	%S	BTU/lb
4" x 2"	14.30	21.93	10.84	11140	20.02	21.96	11.21	10944
2" x 0.5"	31.30	16.00	7.88	12272	44.88	10.49	5.89	13094
0.5" x 0.25"	19.63	16.93	8.09	12065	13.61	8.87	5.21	13310
0.25" x 6m	15.47	14.33	7.35	12222	6.13	9.02	4.93	13104
6m x 28m	14.09	16.32	7.32	11789	9.01	10.01	4.80	12882
28m x 100m	3.13	17.64	6.59	11378	2.99	13.56	4.72	11823
100m x 200m	0.77	20.54	7.70	9538	0.89	18.54	5.39	11247
200m x 325m	0.27	20.04	8.50	11052	0.33	19.53	5.28	11352
325m x 500m	0.14	26.27	11.24	10055	0.28	20.69	4.92	11326
-500m	0.90	58.38	7.09	4813	1.86	56.45	2.46	5236
Total:	100.00	17.31	8.14	11871	100.00	12.13	6.14	12669

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