

BACTERIAL AND CHEMICAL DEPRESSION OF
PYRITE IN FROTH FLOTATION OF COAL

by

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1. INTRODUCTION

In the past few years, air pollution resulting from burning high-sulfur coals has become a growing public concern. Before the passage of the sulfur emission control regulations (Clean Air Act of 1970), the sulfur reduction was merely done to lower the corrosive effects of SO_x on the coal-burning installations.

Early public concern was over the smoke emissions of the coal-burning plants. This concern over the smoke emission led to the passage of regulations as the Air Quality Act of 1967 (Crentz and Deurbrouck, 1971). At that time, efforts were concentrated on a more complete combustion in the coal-burning installations, development of methods for smokeless fuel for domestic use, and reduction of the fly ash from chimneys. More recently, sulfur in coals has become the subject of public scrutiny. Sulfur dioxide emitted from burning coal has been identified as a major cause of air pollution.

The sulfur dioxide emitted by coal-burning installations has increased drastically. In 1963, for example, SO_x emitted into the atmosphere was about 5 million tons annually (Ergun and Bean, 1968). By 1966 sulfur emission into the atmosphere had increased to 26 million tons (Meyers et al., 1972). It is also estimated that by 1990, in the absence of controls, the annual sulfur emission into the atmosphere will be 55 million tons (Meyers et al., 1972). The Clean Air Act of 1970 clearly mandated the SO_x emission controls. This act also stated that "the trace elements present in the raw coal must be identified and traced to the final disposal--be it coal preparation, refuse disposal, clean coal, fly ash, or emission exhaust; environmental effects of the

coal preparation process itself must meet stringent requirements" (Warnke and Deurbrouck, 1977). The emission standards require that no more than two pounds of SO_2 per million Btu be emitted into the atmosphere.

Sulfur in coal is in two forms: organic and inorganic sulfur. The organic sulfur, being an integral part of the coal, can not be removed by conventional coal cleaning methods. The coal molecule would actually have to be disintegrated in order to extract the organic sulfur from the coal. Organic sulfur usually constitutes about 50 percent of the total sulfur in United States coals. The inorganic sulfur consists of sulfate sulfur and pyritic sulfur. The sulfate sulfur constitutes a very small portion of the inorganic sulfur in United States coals, whereas the pyritic sulfur constitutes about 50 percent (Abel et al., 1973).

Separation of pyrite from coal is often a difficult task because the pyrite is disseminated in the coal matrix. In order to liberate the pyrite from the coal, the coal has to be ground to a very small size (minus 200 mesh). The grinding of the coal to such a small size is not economically feasible. Furthermore, there are only a limited number of coal cleaning methods which are able to separate the pyrite from the pulverized coal. These coal cleaning methods are often inefficient and must be operated with some knowledge of their principle of operation (i.e. froth flotation).

The pyrite size distribution in coal can be estimated by microscopic observation of coal samples (McCartney et al., 1969). The microscopic examinations of thin sections or polished sections of coal sam-

ples reveal the degree to which the pyrite is disseminated in the coal matrix. Also, such examinations show the extent to which the coal should be ground to liberate the locked pyrite particles in the coal matrix.

Pyrite is separated from pulverized coal samples (minus 35 mesh in size) by different combinations of gravity methods, such as hydrocyclone cleaning and shaking table cleaning (Weyher and Lovell, 1969). Pyrite is also separated from coal by froth flotation. In the froth flotation process, pyrite particles are depressed by a chemical reagent known as a pyrite depressant (Leonard and Cockrell, 1970). A pyrite depressant must have the ability to change the surface chemistry of pyrite. For example, oxidation of the surfaces of pyrite particles changes pyrite surface properties.

The pyrite particles would be oxidized when in the presence of the bacteria Thiobacillus ferrooxidans. These microorganisms were first discovered in acid mine waters in West Virginia. Later, the pyrite oxidation and acid mine water formation was partially attributed to the activities of the bacteria (Leathen et al., 1953). Hence, the pyritic sulfur can be removed from coal by bacterial oxidation. However, the removal of pyrite by bacterial oxidation requires days of retention time of the coal samples in the presence of the bacteria.

In this investigation coal samples of the Illinois No. 6, the Middle Kittanning, and the Pittsburgh Seams were conditioned in a pregnant "bacterial liquor" containing the iron oxidizing bacteria Thiobacillus ferrooxidans. The surface chemistry of coal pyrite was changed as the result of the bacterial oxidation of the pyrite particle surfaces. The

pyrite was then separated from the coal by froth flotation technique. A number of froth flotation tests were performed using chemical reagents as pyrite depressants. The results of the two series of experiments with the bacteria and the chemical reagents were then compared.

The efficiency of the flotation tests was estimated by microscopic observation of Illinois No. 6 Seam coal samples. Also, washability studies were performed on three coal seams: the Illinois No. 6, the Middle Kittanning, and the Pittsburgh to determine the efficiency of the flotation tests.

2. STATEMENT OF THE PROBLEM

There are two major problems in separating pyritic sulfur from coal. The first problem is that the pyrite is finely disseminated throughout the coal matrix. The second problem is that the coal and mineral pyrite have the same surface characteristics. When separating coal pyrite by froth flotation, the choice of an effective pyrite depressant is highly important.

Oxidation of pyrite in coal flotation by the bacteria Thiobacillus ferrooxidans was suggested by Capes et al., (1973). They, however, used an oil agglomeration technique which does not have industrial application. Froth flotation utilizing the bacteria has the potential for replacing oil agglomeration. The purpose of this work was to examine the effect of the bacterial action on the depression of coal pyrite (by superficial oxidation of pyrite) in the froth flotation process.

3. LITERATURE REVIEW

3.1 Bacterial Oxidation of Pyrite:

3.1.2 Scope:

In contrast to pathogenic bacteria, there are many species of beneficial bacteria which have industrial uses, such as the manufacture of certain chemicals, agricultural products, and antibiotics. Microorganisms are also used in mineral processing. Metal sulfides and sulfates of iron and copper can now be prepared commercially by microbial interaction (Silverman and Ehrlich, 1964; Duncan and Bruynesteyn, 1971; Atkins, 1976). Different leaching techniques are suitable to solubilize sulfide ores in the presence of bacteria (Corrans et al., 1972; Atkins, 1976).

Several investigators have shown that microorganisms are involved in the oxidation of such sulfide minerals as pyrite, marcasite, chalcopyrite, sphalerite, and galena (Silverman et al., 1961; Sutton and Corrick, 1974; Ehrlich, 1961).

Species of genus Thiobacillus can oxidize sulfides and other incompletely oxidized compounds of sulfur (Silverman and Ehrlich, 1964).

Thiobacillus ferrooxidans and Thiobacillus thiooxidans are two members of the genus Thiobacillus which are involved in leaching operations where the pH is below 3.0.

Microorganisms are also involved in the oxidation of sulfur and sulfur compounds in coal (Leathen et al., 1953). Thiobacillus ferrooxidans is often present in coal mines, causing the oxidation of pyrite and other sulfide minerals. The oxidized sulfides, when in contact with water, produce sulfuric acid. The sulfuric acid would then dis-

solve metal cations into solution. Hence the bacterial action lowers the pH, which in turn solubilizes the metals.

The acid mine drainage from the above reaction creates problems of major importance in some mines. The corrosive and environmental effects of acid mine drainage are examples of such problems.

3.1.3 Description of the Species T. Ferrooxidans and T. Thiooxidans:

These bacteria are the members of genus Thiobacillus. They are rod shaped microorganisms .5 by 1 to 3 microns in size, which are often mobile. T. ferrooxidans and T. thiooxidans are chemoautotrophic, aerobic bacilli (Silverman and Lundgren, 1959).

3.1.4 Optimum Physiological Conditions for Bacterial Growth:

The optimum temperature for growth of the organisms may vary among different strains of bacteria. The optimum temperatures are reported to be 20° to 25°C (Leathen et al., 1956), 28°C (Silverman and Lundgren, 1959), and 32°C (Kinel, 1960). These organisms cease to grow at 50°C or higher temperatures (Marchlewitz and Schwartz, 1961).

The pH required for growth is reported to be 2.5 to 4.5 (Beck, 1960; Silverman and Ehrlich, 1964; Razzell and Trussell, 1963a). The organisms do not survive above pH 6.5 (Silverman and Ehrlich, 1964).

The standard nutrients used for optimum conditions were proposed by Silverman and Lundgren in 1959. This combination of salts was conventionally called "9'K salts" by Silverman and Lundgren. Table 3.1 lists the 9'K salts.

Ferrous sulfate is used as the substrate by the bacteria. Other sulfide minerals can also be utilized by Thiobacillus ferrooxidans.

Table 3.1. 9'K Salts Used for Optimum Bacterial Growth.*

<u>Name of Salt</u>	<u>Chemical Formula</u>	<u>Grams/Liter</u>
Ammonium Sulfate	$(\text{NH}_4)_2 \text{SO}_4$	3.0
Potassium Chloride	KCl	0.1
Potassium Hydrogen Phosphate	K_2HPO_4	0.5
Magnesium Sulfate (Hydrated)	$\text{MgSO}_4, 7 \text{H}_2\text{O}$	0.5
Calcium Nitrate	$\text{Ca}(\text{NO}_3)_2$	0.01
Ferrous Sulfate (Hydrated)	$\text{FeSO}_4, 7 \text{H}_2\text{O}$	44.0

* Silverman and Lundgren (1959)

For example pyrite, sphalerite, and chalcopyrite can be used as substrates for Thiobacillus ferrooxidans (Atkins, 1976).

3.1.5 The History of Investigation of Oxidation of Sulfides (Pyrite) in the Presence of Bacteria:

The concept of recovery of naturally leached sulfides of iron and copper is credited to the ancient Romans. The first recovery of leached copper on a large scale is thought to have taken place at the old Rio Tinto mines of Spain (Atkins, 1976). Records show that "by the seventeenth century, copper was being recovered by cementation on scrap iron from ground waters which had percolated through sulfide areas" (Corrans et al., 1972). This percolation sulfide recovery technique is known to be ideal for bacterial activities.

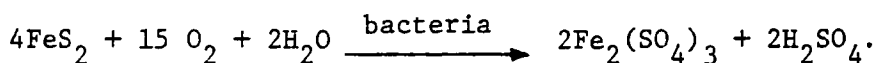
Investigators began questioning bacterial involvement in the oxidation of pyritic coal in the early 1900's. As reported by Atkins (1976); in 1919 Powell and Parr concluded that the bacterial action was partially responsible for the oxidation of coal pyrite. In 1947, Colmer and Hinkle postulated the role of bacteria in the oxidation of sulfur and sulfur compounds in coal. Investigators such as Leathen et al. (1953) and Colmer and Temple (1951) reported that the pure cultures of iron oxidizing bacteria had increased the oxidation of sulfides. In 1951, Colmer and Temple confirmed the presence of Thiobacillus thiooxidans. They also isolated a new species of Thiobacillus, and called it Thiobacillus ferrooxidans. Some investigators who have done major work on sulfide oxidation are Temple and Delchamps (1953), Ashmead (1955), Bryner and Anderson (1957), Bryner and Jameson (1958), Silverman et al. (1963), Silverman (1967), Le Roux et al. (1973), Silver and Torma (1974),

and Atkins (1976).

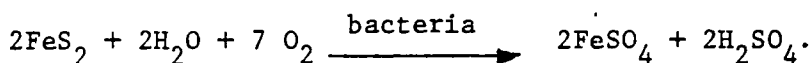
3.1.6 Mechanism of Bacterial Oxidation of Sulfides (Pyrite):

It has been suggested that there are two types of bacterial oxidation of sulfides: a) direct oxidation; and b) indirect oxidation (Silverman, 1967; Duncan and Bruynesteyn, 1971; Atkins, 1976). The direct oxidation process involves the bacterial attack being directed to the surface of the sulfide (i.e. FeS_2), sulfate, or sulfur. Utilization of these inorganic substances provides energy for these microorganisms.

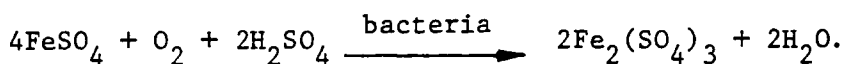
The following reactions postulate the chemical processes of direct bacterial oxidation (after Atkins, 1976):



This reaction may take place in two steps:



The ferrous iron produced is then oxidized to ferric iron,



With indirect oxidation, ferric ions are thought to be the "primary oxidant of metal sulfides" (Atkins, 1976). The ferric ion in this case is reduced to the ferrous state. The bacterial interactions then oxidize the ferrous ions to the ferric state.

3.1.7 Description and Characteristics of Pyrite:

The sulfide mineral pyrite, FeS_2 , has long been known. Generally it is classified as a gangue mineral, occurring with many ore bodies.

Pyrite is found in igneous, metamorphic, and sedimentary rocks. It is the most abundant sulfide mineral. Although pyrite in small percentages has no economic value, its occurrence can be used as a guide for finding other precious and valuable minerals, such as gold and chal-

copyrite.

Pyrites of sedimentary origin are of particular interest. Sedimentary rocks which are formed in a reducing environment (oxygen free environment) often contain minerals which are at a chemically reduced state (FeS_2). Coal is an example of this group of sedimentary rocks which contains pyrite mineralization. Pyrite oxidizes in the presence of oxygen and water, but the rate of this oxidation depends upon the chemical and bacterial activities (Walsh and Mitchell, 1972; Fliermans and Brock, 1972).

The combined chemical and microbial activities are the major causes of acid mine drainage in many coal and metal mines. When the pH drops below 4.5, the bacterial activities increase. Subsequently, the oxidation of pyrite is enhanced. The acidophilic bacilli, Thiobacillus, is the genus which takes an active part in the oxidation of pyrite. The two members of this genus, T. ferrooxidans and T. thiooxidans, are particularly important.

3.1.8 Factors Affecting Bacterial Oxidation of Pyrite:

There are several factors affecting the bacterial oxidation of pyrite. Some of these variables will be discussed.

3.1.8.1 Effect of Pulp Density:

The rate of pyrite oxidation increases with the increase of pulp density, up to a certain point. This increased oxidation rate has a linear relationship with pulp density. The optimum pulp density (pyrite to liquid ratio) has been empirically proven to be 10 percent (Atkins, 1976).

3.1.8.2 Effect of Particle Size:

The rate of bacterial oxidation of pyrite increases as the particle size decreases. Silverman et al. (1961) reported that when the size was reduced from minus 60 mesh to minus 325 mesh the pyrite oxidation rate increased. This indicated that some of the disseminated pyrite particles in coal were not liberated at 60 mesh; at 325 mesh, the percentage of free pyrite particles was very high.

3.1.8.3 Effect of Chemical Properties of Other Minerals Associated with Pyrite:

If the minerals occurring with pyrite raise the pH of the media or interfere with the metabolism of the bacteria, the rate of oxidation of pyrite will drop. Silverman et al. (1961) demonstrated that a significant decrease in pyrite oxidation occurred when a coal sample containing 18.8 percent calcite (CaCO_3) was used. When the same sample was treated with HCl, it became susceptible to oxidation in the presence of T. ferrooxidans.

3.1.8.4 Effect of Other Variables--Temperature, pH Values, Nutrients, Aeration, and Cell Concentration:

The temperature for the optimum oxidation of pyrite is 35°C; however, the optimum temperature for cell growth is 25°C. The optimum pH for oxidation is less than 3.0 (Atkins, 1976),

Thiobacilli are autotrophic bacteria and their autotrophic action provides their energy for their activities (Buchanan and Gibbons, 1974). Therefore, for optimum microbial activities, their media must contain the inorganic salts necessary for their survival. These salts must contain nitrogen, sulfur, phosphorus, metallic elements, and vitamins

(Atkins, 1976). The 9'K salts (Silverman and Lundgren, 1959) include the above elements and are used by the majority of investigators. The proportion of these salts is arranged to maintain optimum metabolic conditions. The ore bodies and gangue minerals contain some of these nutrients required for the metabolism of the bacteria. Therefore, the use of some of the 9'K salts can be eliminated (Duncan and Bruynesteyn, 1971; Atkins, 1976).

Thiobacillus are aerobic bacteria and must have free oxygen dissolved in their aquatic environment. The aeration of the solution containing the bacteria supplies not only oxygen to the bacteria, but also provides carbon dioxide (CO_2) for these microorganisms. Oxygen is thought to be "the ultimate electron acceptor on the oxidation process" and carbon dioxide is the only source of carbon required for cell growth (Atkins, 1976).

3.2 The Properties of, and Impurities in, Coal:

The hydrophobic nature of coal, and subsequently its floatability, are affected by the mineralogy, petrographical makeup, and oxidation of coal. The presence of gangue minerals also affect the floatability of coal.

Coal can be seen in both bright and dull layers. The bright layers are usually called vitrain and clarain (see the classification of lithotypes of coal, Table 3.2). The bright layers usually have a higher floatability and lower specific gravity than the dull layers (Glebotskii et al., 1963).

3.2.1 Petrographic Classification of Coal:

The two major systems of classification which have been developed for the microscopic examination of coal are the "transmitted light" and the "reflected light" systems. In the transmitted light system the light is transmitted through a very thin section of coal (5-10 microns in thickness) and the sample is examined microscopically. In the reflected light system, the light is reflected from the surface of a polished section, and the sample is examined by a reflected light microscope.

The Stopes-Heerlen system (S-H) is a reflected light system in which four major rock types are recognized: vitrain, clarain, durain, and fusain (Stopes, 1935). The coal lithotypes are also referred to as the "macerals" (Harrison and Latimer, 1968). This term was proposed by Stopes in 1935. The macerals are divided further into three groups: vitrinite, exinite, and inertinite. Table 3.2 gives the Stopes-Heerlen (S-H) classification of coal. Vitrain and fusain are composed of a sin-

Table 3.2. Stopes-Heerlen Classification of Coal.

Lithotypes	Group Macerals	Macerals
Vitrain	Vitrinite	Collinite Telinite
Clarain	Vitrinite (dominant)	Collinite, Telinite
	Exinite	Sporinite, Cutinite, Alginate, Waxes & Resins
	Intertinite (less prominent)	Fusinite, Micrinite, Sclerotinite & Semifusinite
Durain	Intertinite (dominant)	Fusinite, Micrinite, Sclerotinite, Semifusinite
	Vitrinite	Collinite, Telinite
	Exinite (less prominent)	Sporinite, Cutinite, Alginate, Waxes & Resinite
Fusain	Inertinite	Fusinite

From: Coal Preparation, "The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.", 1968, p. 1.10.

gle maceral group, whereas clarain and durain are composed of multi-maceral groups in which one maceral group is dominant (Harrison and Latimer, 1968).

3.2.2 Inorganic Mineral Inclusions in Coal:

Inorganic mineral impurities in coal can affect the floatability of coal lithotypes. The impurities can be external (from the roof and floor of the mine), or internal (being a part of the original makeup of the plants and subsequently a part of the coal).

The floatability of the gangue inclusions in coal tend to increase as they become "impregnated" with carbonaceous matter (composed largely of carbon) (Glembotskii et al., 1963).

Mineral impurities in coal are the principal ash forming agents found in both disseminated and segregated forms. These impurities may also be divided into ash forming and sulfur forming minerals (Yancey and Geer, 1968). These inclusions are further classified into disseminated and segregated impurities.

Disseminated mineral impurities (DMI) are the fine mineral inclusions which are impregnated in the structure of the coal. Disseminated mineral impurities can not be separated efficiently from coal by the usual gravity separation techniques; hence they are called the inherent ash content of coal (Yancey and Geer, 1968).

The paleoenvironmental studies of coal formation reveal that disseminated mineral impurities in coal are formed either by sedimentation and deposition, or by being an integral part of the swamp vegetation (Yancey and Geer, 1968). If disseminated mineral impurities are formed by sedimentation and deposition, the minerals are carried into the swamp

from other geological environments (i.e. mineral, garnet, and staurolite which are formed under high temperature and pressure are not formed in the swamp).

Segregated mineral impurities are impurities which are found as discrete particles and can be liberated from coal with relative ease. These mineral impurities can be separated from coal by conventional mechanical separation methods.

3.2.2.1 Ash Forming Minerals (Clays and Shales):

Clays and shales are the principal coal impurities which contaminate the coal, either from the top and the bottom of the mine or from interbedded partings within the coal layers. The weakly bonded clay materials are normally disintegrated in coal cleaning circuits and affect washery-water clarification, dewatering of fine size coal, filtration of froth-flotation concentrates, and disposal of fine refuse (Yancey and Geer, 1968).

The disintegration of shale usually increases as the rank of coal decreases. Shale is usually compacted into slate when associated with anthracite coal, resulting in less disintegration of the clays. Bituminous coal is usually associated with disintegrated clay particles in the form of slimes.

3.2.2.2 Other Ash Forming Minerals in Coal:

In addition to clay and sulfur minerals in coal, there are other minerals in coal which contribute to the ash content. Quartz and gypsum are the most important of these minerals (Aplan, 1976). Table 3.3 presents some of the mineral impurities in coal.

Table 3.3. Minerals Found in Coal.

<u>Shale Group:</u>	<u>Illite</u> , <u>Montmorillonite</u> , <u>Bravaisite</u> , <u>Hydromuscovite</u> , <u>Muscovite</u>
<u>Kaolin Group:</u>	<u>Kaolinite</u> , <u>Levisite</u> , <u>Metahalloysite</u>
<u>Sulfide Group:</u>	<u>Pyrite</u> , <u>Marcasite</u>
<u>Carbonate Group:</u>	<u>Calcite</u> , <u>Siderite</u> , <u>Dolomite</u> , <u>Ankerite</u>
<u>Chloride Group:</u>	<u>Sylvite</u> , <u>Halite</u>
<u>Accessory Minerals Group:</u>	<u>Quartz</u> , <u>Gypsum</u> , <u>Chlorite</u> , <u>Rutile</u> , <u>Hematite</u> , <u>Magnetite</u> , <u>Sphalerite</u> , <u>Feldspar</u> , <u>Garnet</u> , <u>Hornblende</u> , <u>Apatite</u> , <u>Zircon</u> , <u>Epidote</u> , <u>Biotite</u> , <u>Augite</u> , <u>Prochlorite</u> , <u>Diaspore</u> , <u>Lepidocrocite</u> , <u>Barite</u> , <u>Kyanite</u> , <u>Staurolite</u> , <u>Topaz</u> , <u>Tourmaline</u> , <u>Pyrophyllite</u> , <u>Penninite</u>

From: Flotation, American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc., New York, 1976, p. 1241.

3.3 Forms of Sulfur in Coal:

The sulfur content of coal is subdivided into three major forms: sulfate sulfur, organic sulfur, and sulfide sulfur. Elemental sulfur is seldom found in coals. Sulfates are soluble in HCl, whereas sulfides dissolve only in HNO_3 (Aplan, 1976; McMillan, 1975).

3.3.1 Sulfate Sulfur:

Sulfate sulfur is usually found in very insignificant amounts in coal (0.07 percent in Illinois coals and 0.2 percent in British coals) (Gluskoter, 1968). Its presence is usually due to weathering of the sulfides. When occurring in significant quantities in coal, sulfates are in the form of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

3.3.2 Organic Sulfur:

Organic sulfur is a part of the total sulfur in coal whose mode of occurrence is not yet understood. The studies of modern plants show that sulfur is essential for metabolic functions of some plants. The sulfur is often found in protective tissue coverings and proteins (McMillan, 1975).

Organic sulfur can not be removed by any of the physical coal cleaning techniques. However, the sulfur can be removed chemically by breaking the chemical bonds of sulfur and the organic matter. Hence, the percentage of organic sulfur in the coal usually determines the theoretical value of the sulfur which can be removed by sulfur removal methods (Gluskoter, 1968).

3.3.3 Elemental Sulfur:

Native or free sulfur has been reported to occur in coal (McMillan, 1975). It is thought that during coalification and under the reducing

environments, hydrogen sulfide was combined with ferrous sulfate. This reaction produced pyrite and elemental sulfur.

3.3.4 Sulfide Sulfur (Pyrite)

Sulfide sulfur in coal, often in the form of iron disulfide or sulfide, contributes to the contamination of the environment, either in the form of dilute sulfuric acid (acid mine drainage) or as gaseous sulfur dioxide (emitted primarily by power plants). The most abundant sulfide found in United States coals is mineral pyrite (FeS_2) with an isometric crystal structure. Marcasite is another iron sulfide in coal with the same chemical formula as pyrite (FeS_2), but with an orthohombic crystalline structure. The term pyritic sulfur refers to the sulfur in either of the two dimorphs of ferrous disulfide.

Pyrite size distribution in the coal is often an important factor affecting its removal from the coal. Pyrite particle sizes range from fractions of microns to particles several millimeters in diameter. Pyrite particles larger than 100 microns are considered macroscopic, and those smaller than 100 microns are considered microscopic pyrite (McMillan, 1975).

Macroscopic pyrite usually fills fractures and replaces plant tissues. It also can be seen in platy and lens forms along the bedding planes of coal. Macroscopic pyrite is associated with fusain layers (McMillan, 1975).

Microscopic pyrite is more or less evenly disseminated throughout the coal matrix. The microscopic fractions of pyrite are formed at the time of the coal formation in the swampy environment. Hence, this type of disseminated pyrite is referred to as primary pyrite in coal (Caruc-

cio, 1970).

As the percent of microscopic pyrite increases in coal, the removal of pyritic sulfur becomes more difficult. To liberate the microscopic pyrite from coal, the sample must be ground to very fine sizes (depending on the size of the microscopic pyrite). Although it is impossible to completely liberate the pyrite from coal, separating the liberated pyrite particles from such a fine coal matrix is uneconomical and inefficient (McCartney et al., 1969).

3.3.4.1 The Effect of Comminution on Removal of Pyrite from Coal:

Several investigators have studied the effect of comminution on the liberation and removal of pyrite from coal (McCartney et al., 1969). They studied the effect of stage crushing on the liberation and removal of pyrite from the Appalachian coals. They concluded that the required extent of crushing of the coal, in order to liberate and remove pyritic sulfur, depended on characteristics of the individual coal samples. Pyrite can be liberated from some coal samples, while other coal samples show very little liberation at each successive crushing stage. Terchick (1971) reported that, as the top size of a Pittsburgh seam coal was reduced from 1/4 inches to 28 mesh, the sulfur content reduced rapidly. He concluded later that, "the raw coal should be crushed to minus 1/4 inch to achieve economical sulfur reduction."

Cavallaro and Van Eck (1973) studied the Iowa coals. The crushing and size analysis of ten representative samples of Iowa coals indicated that crushing below 3/8 inch top size resulted in some additional sulfur reduction, but not a significant amount. The writer believes that the discrepancy in the results of Cavallaro and Van Eck (1973) and Ter-

chick (1971) is due to the difference in the characteristics and pyrite size distribution in the coal samples; Iowa coal samples used by Cavallo and Van Eck probably contained less microscopic pyrite.

Therefore, it can be concluded that the percent of organic sulfur is not the only factor determining the efficiency of lowering the sulfur content of coal. The quantity of the disseminated microscopic pyrite also affects the sulfur removal efficiencies of coal. McCartney et al. (1969) states that, if the size distribution of the pyrite is known, the probable efficiency of the pyrite removal process can be estimated. Also, as the coal top size decreases, the mean top size of pyrite decreases accordingly. McCartney et al. (1969) indicated that "for minus 14 mesh samples, the mean pyrite particle sizes ranged from 20 to 400 microns."

3.3.4.2 Morphology and Genesis of Pyrite in Coal:

Pyrite particles are identified as reactive grains (framboidal) and inert grains. The reactive pyrite is formed at the time of the formation of the coal (Caruccio, 1970). Framboidal pyrites are fine sized particles which may form clusters of reactive pyrite in the coal matrix. Framboidal pyrite is also referred to as primary pyrite, since it is believed to have formed at the time of the coal formation. Inert pyrites, however, are coarser sized pyrites which do not decompose readily and are often considered secondary mineral deposits. The manner in which these two types of pyrites (framboidal and inert) crystallize within the coal (in the matrix or fissures and cracks in coal) are classified as follows (McMillan, 1975):

Euhedral form: The form of pyrite particles which demonstrate a

distinct crystal form.

Dendritic form: The form of pyrite which demonstrate a branching growth pattern.

Cleat class: This refers to the tabular, vertical or normal to bedding, and joint coating forms of pyrite.

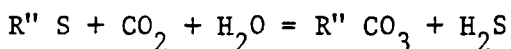
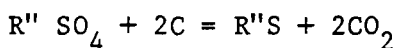
Bleb class: This refers to the spherical forms of pyrite.

Layer class: The grains of pyrite which are elongated to the bedding.

The more common terminology which divides the forms of pyrite into veins, lenses, nodules, and pyritized plant tissues (Gluskoter, 1968) can easily be fitted into the above classifications.

The mineral pyrite can be formed under a variety of conditions. Its presence in such diverse types of environments is the result of the ability of pyrite to form in a wide range of conditions. Pyrite will form at oxidation potentials less than .2 volts in an acidic environment and -.2 volt in a basic environment, with pH ranging from very acidic to moderately alkaline (McMillan, 1975).

The swamp has a reducing environment in which the pyrite forms. It is believed that the conversion of soluble iron salts into the insoluble pyrite is enhanced by the action of the anerobic bacteria, microspira. When organic matter and sulfate are present in oxygen deficient conditions, microspira act as catalysts to form sulfide and H_2S , according to the following formula (McMillan, 1975).



Hence, the genesis of pyrite is traced to its formation in the reducing

environment of the swamp. The study of the present day peat swamps indicates that, insoluble ferric iron (in alkaline solutions) is absorbed on clays and transported into the swamps. Ferric iron is then reduced to a ferrous state and combined with the available sulfide to form pyrite (McMillan, 1975).

3.3.4.3 Occurrence of Sulfur in Coal:

The sulfates and elemental sulfur contained in the coal are insignificant; hence, their occurrence in different parts of the coal seam does not affect the quality of the coal. The organic and pyritic sulfur occur in significant amounts in coal and yield a low or high sulfur coal seam. McCartney et al. (1969) indicated that pyrite was distributed in coal quite irregularly. Coarse pyrites had a very irregular distribution, while microscopic pyrite had a much more uniform distribution throughout the coal seam. Organic sulfur also had a relatively uniform distribution, especially when low sulfur coals were examined. But some coals exhibited irregular organic sulfur distribution in a given mine (McCartney et al., 1969). Gluskoter (1968) agreed with the fact that pyrite sulfur in a given coal seam showed significant vertical and lateral variations. A knowledge of the occurrence of sulfur in coal enables one to selectively mine the coal with a lower sulfur content.

3.4 Froth Flotation of Coal:

3.4.1 Development of the Flotation Process:

The term "Flotation" is applied to the process by which particles heavier than water are lifted to the surface. Flotation processes are used to separate different types of minerals which are less than 28 mesh in size.

Flotation processes can be classified into two groups: froth flotation and oil flotation. Froth flotation involves the separation of minerals in "the form of a froth using gas as a bouyant medium" (Aplan, 1976). The froth flotation process requires a very small amount of reagents. The oil flotation usually requires large quantities of oils. The hydrophobic surfaces of minerals are attached to the oil droplets, and the minerals are levitated to the surface. There are several types of oil flotation of which bulk oil flotation (divided into skin flotation and trent process), spherical agglomeration, emulsion, and oil agglomeration are the most important (Aplan, 1976).

The flotation process has been used primarily in metallic ore concentrations; however, it has gained popularity in coal cleaning plants.

The experimental work of this investigation was concerned with the froth flotation of coal. The term flotation in this report refers to froth flotation, unless otherwise specified.

In recent years, the use of froth flotation in coal has increased. The increased use in coal cleaning plants is due to the increased value of the coal, the increase in the percentages of the fine particles in the run of mine coal, the environmental restrictions on waste water treatment, and the effectiveness of the flotation process in reducing

the amount of the material sent to the refuse disposal.

Historically, it has been reported that the Persians in the fifteenth century used four different oil flotation techniques (Gaudin, 1957). At the turn of the century Bessel, Froment, Delprat, and Potter used gas as a bouyant medium (Gaudin, 1957). The use of an impeller, or beater, for creating air bubbles was first reported by Sulman in 1906 and by T. J. Hoover in 1910 (Gaudin, 1957).

Selective froth flotation was developed when the importance of some organic compounds as collectors was discovered. By the turn of the century, the inorganic salts were recognized as very effective chemical reagents in flotation (Gaudin, 1957). The flotation process was applied to coal at a later time. The work of Yancey and Taylor (1935) is a classic example of the early coal flotation studies. The work of several investigators in this area is mentioned later.

3.4.2 The Scope of Froth Flotation in the Beneficiation of Coal:

Beneficiation engineers have been able to clean and beneficiate coarse sizes of coal (5 inches to 28 mesh) for many years. Gravity separation techniques have been used for many decades and still offer the most efficient and economical way for concentrating clean coal with low ash and sulfur. Approximately half of the coal produced annually in the United States (300 million tons) is cleaned by various coal cleaning techniques (mostly by gravity cleaning methods).

When it comes to the beneficiation of fine sizes of coal (-28 mesh) however, one notes that:

- a) Coal cleaning methods are not diverse.
- b) Often they are not efficient and sometimes they simply fail to

do the job.

Fine coal cleaning is often done by shaking tables, washing cyclones, and flotation.

As coal becomes more valuable, the beneficiation of fine coal is more feasible. Subsequently, fine coal is not discarded or incorporated into coarser sizes anymore. Although a small tonnage of coal is cleaned by the flotation technique in the United States, this process has tremendous capacities. Coal flotation, already popular in Europe, is becoming an acceptable method of fine coal cleaning in the United States. In recent years, froth flotation of coal has been employed as a recovery method in the United States (Milliken, 1978). Coal flotation was practiced in only a few coal cleaning plants in 1950. Within ten years it was employed in 31 preparation plants. This number more than doubled by 1970, and today almost all new preparation plants include flotation circuits in their flow sheets (Aplan, 1976).

3.4.3 Reagents Used in Coal Flotation:

"Flotation agents, or reagents, are substances added to the mineral (coal) pulp prior to, or during flotation in order to make possible or facilitate the process" (Zimmerman, 1968).

Flotation reagents are divided into three general classes: frothers, collectors or promoters, and modifying agents (Zimmerman, 1968). Reagents are also grouped into non-polar reagents (oils) and heteropolar reagents (alcohols) (Glembotskii et al., 1963). The non-polar reagents have collecting properties, while the heteropolar reagents have both collecting and frothing properties.

3.4.3.1 Frothers:

Frothers are chemical reagents which facilitate the formation of "stable froths." In general, frothers are heteropolar organic substances. Frothers have the ability to change the surface tension of water. Their structural formulas have two parts, a non-polar part which is hydrophobic and a polar part which is water avid.

Different frothers have been examined by several investigators of coal flotation. The three most popular frothers used in coal flotation are cresylic acid, pine oil, and methyl isobutyl carbinol (MIBC). Other than the above three frothers, Zimmerman (1968) lists terpeneol, cresols, kerosene, crude oil, and different coal tar products as effective frothers. The choice of a frother is determined by the availability and price of the reagent.

Cresylic acid, which has traditionally been used as a frother, is a low cost coke oven by-product. Cresylic acid adsorbs at the coal surface and subsequently reduces the "residual concentration in solution" necessary for frothing. To maintain this residual concentration in solution, higher dosages of this compound are usually desired to achieve the same frothing effect as pine oil and MIBC (Aplan, 1976). Economically, it is feasible to use varying amounts of cresylic acid to obtain higher yields.

Cresylic acid has been used by several investigators. Crawford (1936) used 0.53 and 0.4 pounds per ton of cresylic acid to treat the washery sludge in rougher float and in the cleaner float, respectively. Davis (1947) lists pine oil, anilin, toludine, synthetic alcohols, and cresylic acid as effective frothers. He indicated that the best results

were obtained when cresylic acid was used.

Pine oil is a common frother whose popularity has decreased in coal flotation. This decrease in the use of pine oil has been due to the fact that it has some collecting properties which tend to concentrate ash and sulfur. It also absorbs on the coal surface. As a result of this absorption, higher dosages of pine oil are required in order to achieve the same recovery as MIBC (Aplan, 1976). Pine oil principally contains terpineol which is a long chain alcohol. Yancey and Taylor (1935) diluted pine oil with methyl alcohol and used it as an effective frother on a Pittsburgh washery sludge. Aplan (1976) used pine oil to float a Lower Kittanning coal sample and compared the recovery of coal with recoveries from MIBC.

Methyl isobutyl carbinol (MIBC) is a short chain alcohol and is the most commonly used frother in coal flotation. The main advantage of this frother is that it is not absorbed on the coal surface. Consequently, it has no collecting properties (Aplan, 1976). Since MIBC is not absorbed on the coal particle surfaces, its dosage can be minimized. Baker and Miller (1971) used MIBC and reported that the recovery of coal and sulfur increased as the dosage of MIBC increased. Lewis (1972) reported that MIBC was a more effective frother than pine oil.

Aplan (1976) indicated that MIBC is not absorbed by the coal, hence it does not have any collecting property. He also compared the dosage of MIBC and pine oil and their effects on the percent of floated yield. A coal sample from the Lower Kittanning Seam of Cambria County, Pennsylvania was used. The test results indicated that lower dosages of MIBC were required to obtain the same yields as the tests with pine oil. The

optimal amount of frother to be used in coal flotation differs for different coals and should be determined by trial and error. The staff of the United States Bureau of Mines (1972) reported that an average of 0.19 pound per ton of frother was used in coal flotation in the United States in 1970.

Inorganic salts are also used as frothers. Sea water is an example of a frother which has been used in the Union of Soviet Socialist Republics (U.S.S.R.). The inorganic salts used as the frothers in coal flotation raise the surface tensions of water and provide a frothing medium (Aplan, 1976).

3.4.3.2 Collectors or Promoters:

Collectors or promoters are non-polar or heteropolar organic reagents which promote contact between coal particles and air bubbles. This is done by selectively coating the emulsified reagent droplets on the coal particles, hence making them hydrophobic. For most coals, the use of a heteropolar frother--which also has collecting ability--is sufficient.

Kerosene or fuel oil is usually used as collectors in coal flotation. Yancey and Taylor (1935) used kerosene in order to create a "non-wetted coal surface." Crawford (1936) used kerosene as a collector, and combined this reagent's effect with cresylic acid to get the optimum results. Davis (1947) combined kerosene and spray oil in a three to one ratio. He indicated that kerosene deadened the froth and broke it down. He also used spray oil and fuel oil as collectors in his experiments.

Horsley (1951-1952) showed that while the rank of coal affected

its floatability, flotation was greatly improved when fuel oil was used as a collector. Generally, higher rank bituminous coals require little or no collector, while lower rank bituminous coals may need from one to three pounds per ton of oil for satisfactory recoveries (Aplan, 1976). Zimmerman (1968) reported that the amount of oily collectors used in the United States was .5 to 2 pounds per ton, while the staff of the United States Bureau of Mines (1972) reported that an average of 1.7 pounds per ton of oil was used in the United States as collector in 1970.

3.4.3.3 Modifying Reagents--Depressing Agents:

The term "modifying reagents" is applied to the reagents whose functions are other than frothing or collecting (Zimmerman, 1968). These reagents change the conditions or medium of the flotation cell, selectively alter the surface charges, selectively oxidize or reduce the coal or mineral surfaces, and coat the selected surfaces in order to prevent their flotation or depression. As is apparent from the above statement, "modifying reagents" is a very loose term. Zimmerman (1968) mentioned the following groups as some of the more important modifying agents: activating agents, pH regulators, dispersing agents, protective colloids, and depressing agents.

Activating agents alter the surface of particular minerals so that they accept the emulsified oil droplets of collectors or the heteropolar charges of the frothers. This action of activating agents facilitates the attachment of minerals to the air bubbles. Sodium sulfide and copper sulfate are examples of activating agents (Zimmerman, 1968).

The pH regulators are reagents used to adjust the pH of the flota-

tion pulp to a desired level. Lime and soda ash are generally used for this purpose (Zimmerman, 1968). In laboratory experiments, sodium and potassium hydroxides are also used.

Dispersing agents are used to deflocculate the flotation pulp and lower the slime absorption on coal particles. Sodium silicate and sulfide wastes are often used for this purpose (Zimmerman, 1968).

Depressing agents either inhibit the flotation of the impurities which are to be removed from coal or they inhibit the flotation of the coal itself while the impurities are floated. Depressing agents should be highly selective in changing the surface characteristics of particular mineral particles. These reagents are used primarily when two or more minerals have similar surface characteristics. In coal flotation, pyrite and coal particles show similar surface characteristics. By selectively depressing one of these two and floating the other, a reasonable separation may be obtained. Depressing action covers three areas in coal flotation: depressing the coal, depressing the gangue material, and depressing the pyrite. Depressing the pyrite has been used in traditional flotation tests where the coal particles have been floated out of the flotation pulp.

The work on the depression of pyrite in coal flotation started in the first half of this century. As the environmental restrictions on burning high sulfur coal increased, the efforts to remove pyritic sulfur from coal were enhanced. Yancey and Taylor (1935) reported their classic work on pyrite depression in coal flotation. They reported that ferric sulfate was a pyrite depressing substance. It was concluded that the depressing action of ferric sulfate was "attributed to the absorp-

tion of either a ferric hydroxide sol or of a basic sulphate slime" (Yancey and Taylor, 1935). They also reported ferrous sulfate and para-aminophenol as good pyrite depressants. Davis (1947) reported his work with ferrous and ferric sulfate as pyrite depressants. He also indicated that sulfites, cyanides, alkali silicates, sulfates, and lime were effective pyrite depressants. Brown (1962) reported that lime was the most commonly used pyrite depressant. He also mentioned that sodium and potassium cyanides, as well as ferric and ferrous sulfates at pH 4.5-6.9 were effective pyrite depressants. In addition to sodium and potassium cyanide, Zimmerman (1968) listed potassium permanganate, sodium sulfite, and potassium chromate as pyrite depressants.

Baker and Miller (1971) worked with ferric chloride (FeCl_3), aluminum chloride (AlCl_3), chromium chloride (CrCl_3), cupric sulfate (CuSO_4), and calcium chloride (CaCl_2), and reported that the most effective pyrite depressant would be 2 parts per million ferric chloride.

Aplan (1976) indicated that lime and sodium cyanide were popular pyrite depressants. He also reported that oxidation products of pyrite (ferrous and ferric sulfates) were effective pyrite depressants.

One of the methods used to depress pyrite was to oxidize the pyrite particle surfaces. This may be achieved by selectively oxidizing the pyrite surfaces with chemical substances or with bacterial action of sulfur oxidizing microorganisms. The bacterial oxidation of pyrite in coal flotation was reported by Capes et al. (1973). They used an oil agglomeration flotation technique. The bacteria Thiobacillus ferrooxidans was used as the pyrite oxidizing agent. Atkins (1976) reported a similar depressing method by bacterial action.

Depressing the gangue material--usually siliceous and seldom calcareous--has been practiced for many years in coal flotation. The gangue material usually forms a wetttable surface and becomes water avid. As the percent of the gangue material (also known as ash content) in a coal sample increases, the depression of the material becomes more difficult. Siliceous matter is often depressed by sodium carbonate and sodium silicate (Brown, 1962; Aplan, 1976).

When a high percentage of slimes is reported in the froth, a slime dispersant can be used. The use of sodium silicate, hexameta-phosphate, lignin and other polymeric sulfonates, quebracho, and tannins is recommended (Aplan, 1976).

The depression of coal in coal flotation has recently been examined. In this new approach the impurities are reported to the froth, while the coal remains in the sink. Coal can be depressed by the addition of "non-electrolytes or wetting agents to the pulp," or by starvation feeding of the collector (Brown, 1962). In their new approach the United States Bureau of Mines reported that Aero Depressant 633 (from American Cyanamid Company) was the strongest coal depressant (Miller, 1973). Other coal depressants are reported to be starches (dextrin), natural hydrocolloids, and inorganic salts such as stannous chloride, hypophosphoric acid, and potassium permanganate (Miller, 1973).

3.4.4 Factors Affecting Coal Flotation:

3.4.4.1 Effect of the Particle Size:

The effect of particle size on the flotation of coal has been studied by several investigators. Crawford (1936) reported that the number of particles in a cubic unit was much more important than the pulp

density. He found that when cleaning minus 200 mesh sizes, the percent plus 48 mesh should be minimized to reduce its detrimental effects on the process. Crawford concluded that when an effort was made to recover plus 48 mesh coal, it resulted in the flotation of the pyrite and gangue material. Davis (1947) explained that as the percent plus 48 mesh increased, the quantity of reagent which was required to float the larger particles increased. Consequently, more ash was reported in the froth. On the other hand, as the percent minus 200 mesh clay particles increased, it became harder to make a sharp separation. Furthermore, Davis indicated that minus 200 mesh pulps required less quantities of reagents. Dilute pulp required more reagents. The optimum pulp density depended more on the percentage of fines in the pulp than on the ash content of the pulp.

Miller et al. (1967) studied the rate of the flotation in relation to the particle size and concluded that the rate of flotation was slower for coarser particle sizes. As a result, in the coarsest size ranges, higher selectivity could be expected. Conversely, the flotation rate increased as the particle size decreased down to 100 mesh in size. They predicted that "the selectivity or contamination of products" would be constant for minus 100 mesh particle sizes. For particle size ranges of 48 to 100 mesh, the selectivity decreased and contamination of products increased as the size decreased. Hence, Miller et al.'s investigations narrowed the optimum flotation size range to 14 x 48 mesh sizes, and indicated that the process becomes inefficient for minus 100 mesh coal.

Miller et al. also made a note of the fact that, for 100 x 325

mesh sizes, the flotation rate and "contamination of products" was constant where product sulfur was very high. The inefficiency of the flotation process for cleaning minus 100 mesh pulps was explained by Miller et al. to be due to the fact that the bubble sizes were too large and would buoy up any particle that had carbon exposed at its surface. They suggested that this inefficiency could be overcome by redesigning the flotation apparatus to produce smaller bubbles.

The effect of slimes on the flotation of coal was studied by Lewis (1972). He concluded that when slimes were removed before flotation, good recoveries would result. Merkley and Cavallaro (1974) worked with fine particle sizes and reported that minus 325 mesh size particles were detrimental to flotation. They indicated that the finest size feeds gave the poorest quality of products, but resulted in higher yields. The flotation of coarse coal (14 x 28 mesh), however, is a function of the rank of the coal, the amount and type of the reagents, the pulp density, the hydrodynamic conditions in the flotation cell, and the flotation time (Aplan, 1976).

3.4.4.2 Effect of the Pulp Density:

The pulp density is the weight percent of solids to liquid ratio of coal-water slurry. In metalliferous ore flotation solid-liquid ratios are as high as 20 to 30 percent, but in coal flotation the pulp density is considerably smaller. Yancey and Taylor (1935) reported that when dilute pulp ratios were used, lower ash yields were obtained. Crawford (1936) indicated that lower pulp densities used in coal flotation are due to the fact that "coal has lower specific gravity and friable tendencies and occupies two to three times more space for the same ton-

nage at the same pulp dilution as heavier minerals." He reported that a ten to twelve percent pulp density was ideal. Poor results were obtained when pulp densities higher than 17 percent were used. Davis (1947) reported good separations at 10 to twelve percent pulp densities. He indicated that more dilute pulps gave more pyrite in the float. He also reported that 18 percent solids was the maximum pulp density used in the coal cleaning industry. Zimmerman (1968) reported a pulp density of 7 to be an optimum ratio. Merkley and Cavallaro (1974) concluded that low pulp densities resulted in the best overall results. The current practice in the United States indicates that pulp densities used in coal flotation circuits are 3-4 percent below the optimum value. This is due to the fact that most of the coal cleaning plants use the flotation process for treatment of the "Black Water" clarification (Aplan, 1976).

3.4.4.3 Effect of the pH Value:

Different values of pH affect the sulfur rejection, the recovery of coal, and the ash rejection in the flotation of coal. The optimum pH value for the flotation of coal is near pH 7 (Aplan, 1976). Zimmerman (1968) showed that the recovery of coal decreased at both ends of the pH scale and it peaked near pH 7.0. The recovery of sulfur in the float decreased steadily as the pH increased, while the recovery of ash in the float increased with the increase in pH.

Yancey and Taylor (1935) observed that pyritic sulfur depression ceased below pH 4.5 when ferric sulfate was used as the pyrite depressant. Davis (1947) indicated that the pH for the removal of ash and sulfur should be slightly acid and alkaline, respectively. The Zeta

potential studies of Baker and Miller (1971) showed that both coal and pyrite have negative surface charges in the distilled water of pH 4 or greater. The difference between the negative Zeta potential increased at pH values higher than 7.75. They concluded that, as the pH increased, the recovery of coal and pyrite increased.

3.4.4.4 Effect of Oxidation and Rank of Coals:

The degree of oxidation of coals is an important factor that affects its flotation. Freshly mined coal generally has better floatability than when it has been exposed to air and its surfaces have become oxidized. The floatability of oxidized coal can be restored by treating the coal by an alkaline solution such as one percent caustic soda or by the addition of benzidine in benzoyl alcohol at 85°C (Brown, 1962).

It has been proven that higher ranks of coal, when floated under the same test conditions, have a higher degree of floatability than the lower ranks of coal, with the exception of anthracite. The effect of the rank of the coal on its oxidation can be overcome to an extent by adding sufficient amounts of reagents or by changing reagents (Zimmerman, 1968).

3.4.4.5 Other Factors Affecting the Flotation Rate:

Conditioning time, aeration, agitation, maceral separation, high ash content, and flotation reagents affect the flotation rate of coal, while temperature (ranging from 3 to 50°C) has a very small effect on the flotation rate (Aplan, 1976).

Markley and Cavallaro (1974), when defining the quality Q of a flotation test (Q is the ratio of percent ash in feed to percent ash in

product), indicated that when retention time increased, better quality resulted while the yield stayed constant. Conditioning time is important when an oily collector is used, but when using frothers such as alcohols, long conditioning times are unnecessary (Aplan, 1976).

Aeration and agitation are essential for flotation. The flotation rate increases as the aeration rate increases within certain limits (Aplan, 1976). The impeller speed is also important in coal flotation. Lewis (1972) reported that the lack of sufficient impeller speed (600 rpm) during conditioning resulted in low recovery and a poor percent of yield. Markley and Cavallaro (1974) reported that the percent of yield increased after the agitator speed was lowered to 900 rpm. They concluded that high agitation speeds impeded particle bubble attachment.

Maceral separation has been studied by several investigators (Yancey and Geer, 1968; Glembotskii et al., 1963; Gaudin, 1957; Stopes, 1935). The bright vitrinite is more floatable than dull fusinite. Within Stope's classification, the floatability of macerals decreases as one studies them from vitrinite to inertinite.

High ash contents can lower flotation efficiency. Yancey and Taylor (1935) reported that as the ratio of the coal to ash increased, the percent of ash recovered in the froth increased, and vice versa. Davis (1947) explained that the reason for low recoveries of coal with high ash content was that the surfaces of the coal particles were coated "with a gangue or clay coating."

The use of flotation reagents should be optimized for individual coals. Often, when sufficient amounts of reagents are not added to the pulp, lower yields and poorer qualities of flotation result. The man-

ner in which the reagents are added to the flotation pulp is also important. Stage addition and starvation reagent addition are examples of methods of reagent addition to the pulp.

3.5 Methods Used to Remove Sulfur from Coal Before Combustion:

3.5.1 Froth Flotation:

Froth flotation is used in two ways: either the pyrite is depressed and the coal is floated, or the coal is depressed and the pyrite floated (Akhtar et al., 1971; Miller, 1973; Miller, 1975). Froth flotation of coal has been explained in detail in Section 3.4. Some investigators claim pyrite sulfur removals of up to 80 percent from the coal (Capes et al., 1973).

3.5.2 Chemical Reaction Methods:

3.5.2.1 Bacterial Leaching of Pyrite:

The bacteria Thiobacillus ferrooxidans and Thiobacillus thiooxidans are two species of microorganisms which are involved in the oxidation of pyrite. Bacterial leaching of pyrite has been explained in detail in Section 3.1. In this area the work of Silverman et al. (1963) is well known.

3.5.2.2 Leaching of Pyrite by Ferric Sulfate--Meyers Process:

The Meyers process involves a mild aqueous extraction of pyrite sulfur from coal under standard pressure and a temperature of 108°C. The oxidizing reagent in this process is ferric sulfate or ferric chloride (Meyer et al., 1972; Lorenzi et al., 1973; Hamersma et al., 1973a; Hamersma et al., 1973b; Hamersma et al., 1974). The laboratory results indicated that 40 to 75 percent of the total sulfur could be removed from coal samples collected from various regions of the United States.

3.5.2.3 Battelle Process:

This is a hydrothermal leaching process in which sodium and calcium hydroxide are used as lixiviants (to lixiviate is to extract a

soluble constituent from a solid mixture by washing or percolation). The sulfur is removed in the compound form of gaseous hydrogen sulfide at high temperatures (Oder et al., 1977).

3.5.2.4 KVB Process:

This process involves the heating of pulverized coal samples in the presence of nitric oxide and other gases. The pyrite and some of the organic compounds of sulfur are decomposed and turned into oxides of sulfur. Some of the pyritic sulfur is changed to sulfate sulfur, which is soluble in water and is removed by washing. The process claims 50 percent removal of pyritic sulfur and an unspecified amount of organic sulfur (Oder et al., 1977).

3.5.2.5 Removal of Sulfur from Coal by Air Oxidation at 350-450° Centigrade:

In this method pulverized coal is heated to different temperatures in a tube furnace, while a dry air current flows over the coal sample (Sinha and Walker, 1971). It was concluded that the sulfur removal increased in a direct proportion to the increase in temperature, to the increase in the length of exposure time of the sample, to the heated atmosphere, and to the decrease of the particle size. Sinha and Walker claim 64 to 90 percent removal of pyritic sulfur at optimum conditions.

3.5.2.6 Removal of Sulfur from Coal by Treatment with Hydrogen:

In this solvent refining process, pulverized coal is mixed with an organic solvent. The slurry is then agitated at high temperature and pressure under a "hydrogen blanket." The sulfur compounds react with the hydrogen to form hydrogen sulfide. The hydrogen sulfide is then removed. The process claims 70 percent removal of pyritic sulfur from

coal (Gary et al., 1974).

3.5.2.7 Microwave Power to Reduce the Sulfur Content of Coal:

Coal-pyrite mixtures subjected to the microwave radiation are heated differentially so that the pyrite particles are selectively heated. The selectively heated pyrite particles then react with a treatment gas (air or nitrogen) and release a gaseous sulfur compound. The coal particles remain intact (Besson et al., 1975).

3.5.2.8 Ledgemont and BOM/ERDA Processes:

These two processes are oxygenation processes in which pyrite is oxidized in the presence of water and oxygen. The Ledgemont process uses pure oxygen, whereas the BOM/ERDA process uses air at temperatures high enough to remove the organic sulfur (greater than 280°F). The BOM/ERDA process claims up to 40 percent removal of organic sulfur, whereas the Ledgemont process claims 10 percent removal. Both of the processes substantially remove pyritic sulfur (amount unspecified) (Oder et al., 1977).

3.5.3 Electrostatic in Combination with Centrifugal Separation of Pyrite from Coal:

Abel et al. (1973) investigated this dry separation method which removed pyritic sulfur from coal. This method consisted of two stages: a centrifugal separation stage and an electrostatic separation stage. The two stages complemented each other in removing 24.6 percent of the pyritic sulfur from a Pittsburgh coal seam.

3.5.4 Magnetic Separation of Pyrite from Coal:

This method selectively separates the more magnetically susceptible pyrite particles from the coal. Although pyrite has a low magnetic sus-

ceptibility, it could be treated so that it gains a magnetically susceptible surface.

Ergun and Bean (1968), after an extensive study of the magnetic susceptibility of coal pyrite, reported that, in order to efficiently separate pyrite from coal, about 0.1 percent of the pyrite must be converted into a ferromagnetic compound of iron. They concluded that steam treating the coal samples, heat treating the coal samples, weathering the coal samples, and having finer pyrite particles in the coal samples enhanced the magnetic susceptibility of pyrite.

In the Magnex Process the magnetic susceptibility of pyrite is increased by exposing the pulverized coal sample to vapors of iron pentacarbonyl at 40 psia pressure and 380°F temperature. Iron pentacarbonyl selectively decomposes on pyrite and other mineral impurities and, subsequently, their impurities are separated from coal by magnetic separation (Oder et al., 1977).

3.5.5 Electrophoretic Separation of Pyrite from Coal:

Electrophoresis is defined as "the migration of electrokinetically charged particles in a liquid toward an electrode of an opposite charge in a direct current electrical field." Miller and Baker (1974) applied the principle of electrophoresis to separate pyrite and other impurities from coal. They indicated that there was a difference between the migration rate of coal and its impurities toward the anode. The migration rate was enhanced when distilled water was used. They concluded that this method of sulfur separation was uneconomical to be used industrially.

3.5.6 Gravity Separation of Pyrite from Coal:

Gravity separation of plus 35 mesh coal from sulfur and ash has been the most efficient means of cleaning coal in preparation plants for many years (Leonard and Cockrell, 1970). When the cleaning of minus 35 mesh samples of coal is desired, gravity separation loses its efficiency. However, if the gravity separation process is optimized, loss of efficiency could be prevented.

Equipment used for gravity cleaning of fine sized coal is usually Deister tables, hydrocyclones, classifying cyclones, and heavy-medium systems.

It is generally accepted that each of these coal cleaning systems have to be used in combination with another system in order to obtain optimum results. These systems are also used in combination with froth flotation (Weyher and Lovell, 1969).

Blagou et al. (1968) used concentration tables, and concluded that the top size of coal particles for the removal of sulfur was .025 millimeter and that finer sizes had to be treated with froth flotation.

Leonard and Cockrell (1970) indicated that hydrocyclone separation was efficient for 35 x 150 mesh coal. Also, they reported that, in general, hydrocyclones were more efficient for pyritic sulfur reduction (in 35 x 150 mesh) than froth flotation. However, when the two methods were combined they produced better results.

Terchick (1971) reported that tables and heavy-medium systems complement each other, since at low specific gravity separation, heavy-medium systems are most efficient, and high specific gravities, tables are most efficient in removing sulfur.

Miller and Podgursky (1972) reported that hydrocyclones and tables complemented each other when cleaning a .14 mesh x 0 sized coal. This combination increased the overall recovery of coal, provided more flexibility in the fine-coal circuit, and efficiently handled a wide size range of coals with variable sulfur contents.

Sisti (1975) worked with the Elkhorn No. 3 Coal Seam of Kentucky. He reported that an effective removal of pyritic sulfur was achieved when a combination of hydrocyclones, Deister tables, classifying cyclones, and froth flotation was used. He concluded that excellent results could be achieved with just a combination of a hydrocyclone and a Deister table.

3.6 After Combustion, Measures of Removing Coal Sulfur from Stack

Gases:

There are two principal approaches for removing sulfur from stack gases: the "throw-away" process and the catalytic-regeneration process.

3.6.1 "Throw-Away" Process:

The reactants used in this process are not recycled and are used only once. These reactants are usually inexpensive. Some of the methods used in this process are as follows.

3.6.1.1 Dry Limestone Method:

In this method, pulverized dry limestone or dolomite is injected into the combustion chamber where they react with sulfur oxides. The reaction products of sulfur (sulfate and sulfite) are then carried with the rest of the fly ash into the electrostatic precipitators. This method removes 25 to 50 percent of the total sulfur in the untreated stack gases (Creutz and Deurbrouck, 1971).

3.6.1.2 Wet Limestone Method:

This method of collecting sulfur from stack gases is similar to the dry limestone method, but the solids are gathered in a wet scrubber which contains calcined limestone. Sulfur dioxide is converted to calcium sulfate or sulfite during the scrubbing action. The solids are brought to a disposal area as a slurry. This method claims the removal of 90 percent of the stack gas sulfur (Creutz and Deurbrouckm 1971).

3.6.2 Catalytic and Regenerative Processes:

These processes utilize more expensive sorbents, or catalysts, which are regenerated and used in a closed system. The sulfur is collected as gaseous or liquid sulfur compounds. The regenerative proces-

ses are gaining popularity and, in the future, will replace the "throw-away" processes. Some of the methods of sulfur removal in this process are as follows.

3.6.2.1 Catalytic Oxidation:

In this system the fly ash is removed by an electrostatic precipitator. The sulfur dioxide is then converted to sulfur trioxide by passing through a vanadium pentoxide catalyst. The sulfur trioxide reacts with water and is converted into dilute sulfuric acid which can be used commercially. This process claims high efficiencies in removing sulfur from the stack gases (Crentz and Deurbrouck, 1971).

3.6.2.2 Alkaline Scrubbing:

This system utilizes either sodium carbonate or magnesium oxide. Sulfur oxide is converted into sulfites of sodium or magnesium. The soluble sulfites are then removed and crystallized. The sulfite crystals are then taken to a regeneration plant and the alkaline sorbent is recovered and reused in the system (Crentz and Deurbrouck, 1971).

3.6.2.3 Stone and Webster Ionics System:

Stone and Webster Engineering and Ionics, Incorporated developed this system which utilizes sodium hydroxide. The reaction products of sulfur with sodium hydroxide are sodium sulfite and sodium bisulfite which are treated with sulfuric acid to form sulfur dioxide and sodium sulfate. The former is converted to acid and the latter is decomposed electrolytically to form acid and sodium hydroxide. The regenerated sodium hydroxide is then ready to be reused (Crentz and Deurbrouck, 1971).

3.7 Washability Studies in Coal Preparation:

A washability study of coal is used to determine the specific gravity distribution of the materials in the coal. A washability study of coal is made by mixing the coal samples in preselected organic liquids of a known specific gravity. The lighter fraction of coal is floated to the surface and is termed "the float." The heavier fraction is sunk to the bottom of the liquid and is termed "the sink." The float and the sink, collected by the float-sink technique, are then analyzed for ash and sulfur content.

When designing coal preparation plants or studying the efficiency of a certain coal cleaning method, the washability studies of the coal samples provide invaluable data. The assessment of the efficiency of the coal cleaning systems is done by determining the percentage of near gravity material in the coal by washability studies.

In a conventional and systematic washability study, the coal particles of preselected size ranges are mixed in heavy liquids of different specific gravities. Hence, the decrease in particle size can be plotted versus the weight percentages of the float and the sink of different specific gravities.

Washability studies are used to assess the efficiency of the flotation tests (Miller et al., 1967). In spite of the fact that, in the flotation process the surface chemistry of the coal is more important than its specific gravity, the float-sink technique can forecast the efficiency of the flotation process. The degree of success of the separation of sulfur and ash from the coal in the flotation process can be determined by the washability studies of that coal.

There are several methods of presenting float-sink data. A commonly used method of presenting washability data is the arithmetic plot of the data points. Five sets of well known curves are constructed to present the data obtained from the float-sink process.

The specific gravity or yield curve is drawn by plotting the cumulative-percent weight of the float versus the specific gravity fractions used. The cumulative-float ash curve is constructed by plotting the cumulative-percent weight of the float versus the cumulative-percent ash in the float. The cumulative-sink ash is constructed by plotting the cumulative-percent weight of the sink versus cumulative-percent ash in the sink. The ± 0.1 specific gravity distribution curve shows the weight percentages of the coal that lies within ± 0.1 specific gravity units. The elementary-ash curve is used to show the rate of change of the ash content at different yields (Coe, 1938; Schopiro and Clendenin, 1968). In addition to the above mentioned curves, other curves such as cumulative-sulfur float, cumulative-sulfur sink, and cumulative Btu float may also be constructed.

4. MATERIALS AND METHODS

4.1 Procedure Used for Growth and Harvesting of the Bacteria, Thiobacillus ferrooxidans:

4.1.1 Source of the Culture:

The culture of Thiobacillus ferrooxidans was received from the Department of Minerals Exploitation, University of Wales, Cardiff, Wales, United Kingdom.

4.1.2 Adaptations and Abilities of the Culture:

This particular bacterial culture is mutated to stand high concentrations of sulfides. The culture is well adapted to oxidize pyrite. Atkins (1976), who used the same strain of Thiobacillus ferrooxidans, indicates that these bacteria mutate and consequently adapt themselves to use sulfides or any other sulfur based salts. Hence, the oxidation and removal of the pyrite could be enhanced when a well mutated sample of Thiobacillus ferrooxidans is used. The following procedure was used in order to obtain a well adapted culture. Thiobacillus ferrooxidans was grown on a pyrite substrate. The pregnant "bacterial liquor" was then centrifuged at 10000 rpm and viable cells of Thiobacillus ferrooxidans were separated from the liquid. This procedure was repeated four times (in a time period of 20 days) until a strong and well mutated bacterial culture was obtained.

4.1.3 Fermentation Tanks:

The fermentation tanks consisted of two ordinary fish tanks (20 and 80 liter capacity) made of glass with plastic linings. The temperature of the tanks was kept at 33°C. Two fish tank heaters (25 and 100 watt power) were used to maintain the desired temperature. The tanks

were aerated by small fish tank air pumps. Figures 4.1a and 4.1b show the fermentation tank setup before and after the inoculation of Thiobacillus ferrooxidans respectively. Note the pH after inoculation was lowered to 1.6 (the pH before the inoculation was 2.2). Also note the color change of the liquor in the tank.

4.1.4 Inorganic Salts Used for Optimum Cell Growth:

Silverman and Lundgren's 9'K salt solution was prepared by the following method. The pH of two liters of distilled water was lowered (by 5 N sulfuric acid) to 2.0. The water was then heated to 80°C, and the 9'K salts were added to the water in the order given in Table 3.1. The solution was gently stirred. If precipitation occurred, 5 N H₂SO₄ was added to redissolve the precipitate. Hydrated ferrous sulfate was dissolved in 44 grams/liter with 10 liters of distilled water. The solution was then poured into the fermentation tanks. The 9'K salt solution was added to the tanks and the remaining space in the tanks were filled to the desired level with distilled water. The pH was adjusted to 2.0. At this point, the liquid in the tank had a light green color. The temperature was adjusted to 33°C and the solution was aerated. The culture of bacteria was then added to the tanks. After approximately four days (94 hours) the color of the solution turned to a dark reddish brown (see Figures 4.1a and 4.1b).

The reddish brown color of the solution indicated that a sufficient number of bacteria had been produced and had oxidized the ferrous sulfate (light green in solution) to ferric sulfate (reddish brown). A portion of Thiobacillus ferrooxidans had attached themselves to the walls of the tank. The rest of the bacteria were in solution. This

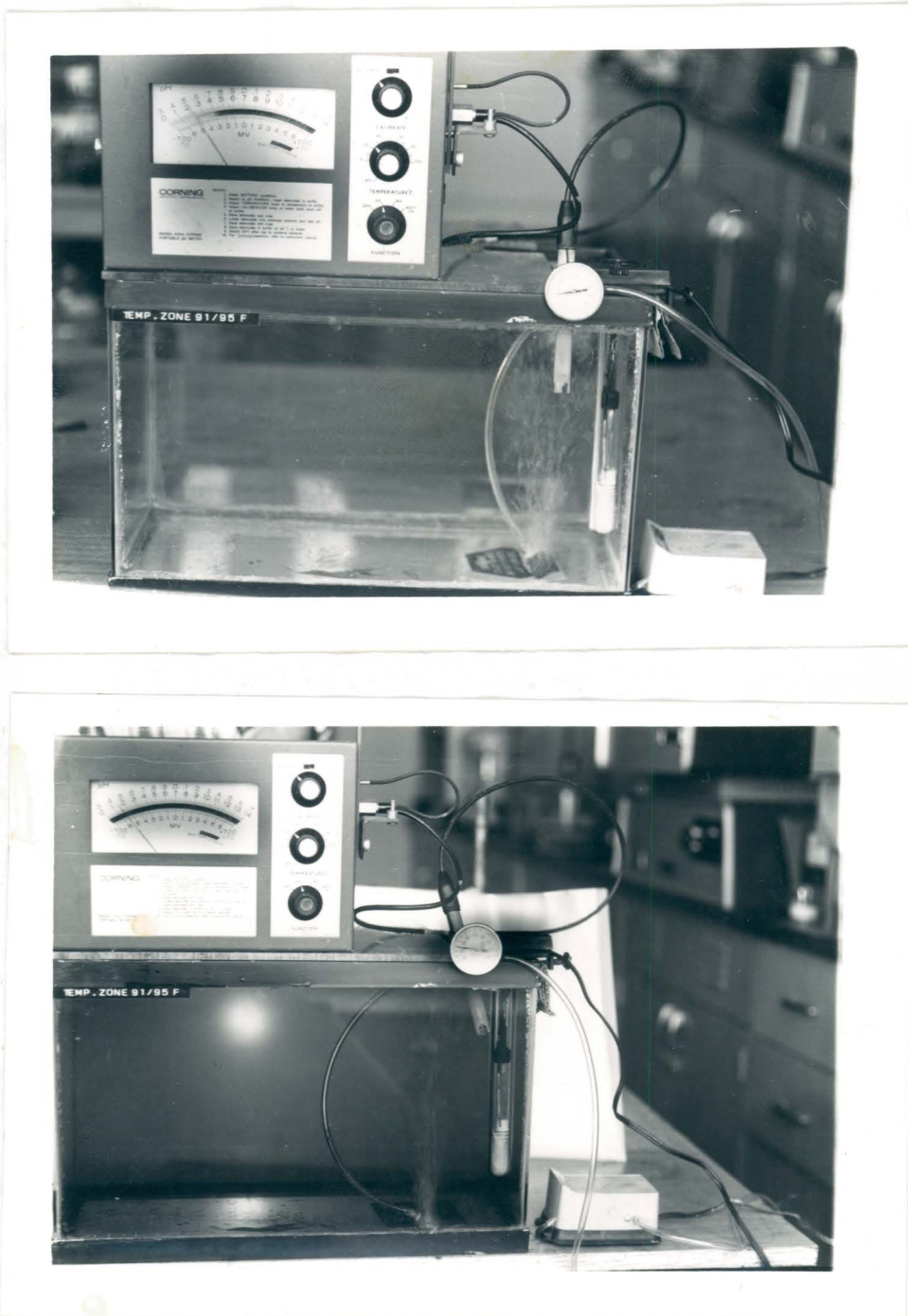


Figure 4.1. Fermentation Tank Set Up. Figure 4.1 (a) Before the Inoculation of T. ferrooxidans. Figure 4.1 (b) After the Inoculation of T. ferrooxidans.

kind of heterogeneous distribution of the bacteria would make the viable count of the bacteria difficult. The regular agar plate colony count technique could not be adapted for this reason. The viable count by the detection of ammonia has been used by several investigators (Silverman, 1964; Atkins, 1976). An accurate measurement of the viable count was beyond the scope of this work.

4.2 Preparation of Illinois No. 6 Coal Samples for Microscopic

Examination:

4.2.1 Scope:

The microscopic examination of Illinois No. 6 coal included the study of coal samples of different size ranges. A sample that was 38 x 100 mesh in size was first examined by a binocular microscope. Next, the samples of minus 100 mesh in size were ground for different time periods. These samples were then studied by a reflected light microscope. For this purpose, polished sections of such samples were prepared. The samples were examined for percentages of binary and free pyrite particles. A float-sink technique was developed which employed the centrifugal separation of pyrite from coal. The floated part of each float-sink test was examined and compared with the feed sample before treatment.

4.2.2 Preparation of Polished Sections of Illinois No. 6 Coal Samples:

A small fraction of a powdered coal sample (about .05 gram) of Illinois No. 6 coal was sprinkled into a small cylindrical plastic container 3 centimeters high and 2 centimeters in diameter. A mixture of epoxy glue was then poured into the cylindrical container. The epoxy glue on the top of the coal powder was left to solidify over night. The samples were then polished in the following manner:

first, the samples, or sections, were polished by a 400 micron carbide grit paper; then the sections were polished by a 600 micron grit paper; and finally the sections were cleaned by an ultrasonic cleaner and were placed on a vibratory polisher over night. Prior to putting the sections in the vibratory polisher, 0.5 micron alumina particles were mixed

with water and poured on the silk cloth of the vibratory polisher. The vibrating action of the polisher polished the sections in a circular pattern over the alumina particles. The polished sections were then removed from the polisher, rinsed, dried, and examined by a Unitron reflected light microscope.

4.2.3 Centrifugal Separation of Pyrite and Ash from Illinois No. 6

Coal Samples:

Pulverized coal, according to Stoke's law, has a low settling velocity in a heavy liquid compound. In order to shorten the particle settling time in the liquid, a centrifugal process was developed as follows: one gram of coal was mixed in heavy liquid and was placed in a specially made test tube (this test tube is described in the following paragraph). The sample was then centrifuged for 30 minutes at 1200 rpm. After a complete separation of float and sink, the tail part of the test tube was cut and broken off from the top part of the tube. The sink material contained in the test tube was placed in a dryer at 105°C and dried to a constant weight.

The test tube was a 10 cm. glass tube with a top diameter of 2.5 cm., a bottom diameter of 0.8 cm., and a gradual contraction of 1.7 cm. in the middle. Masking tape was used to prevent the contact of glass and the metal centrifuge tube holder.

The above centrifugal method was used to separate pyrite from coal and ash. This method was developed for the quantitative analysis of pyrite. Due to the disseminated and unliberated occurrence of pyrite in the coal, only about 50 percent of the pyrite was separated from the coal. The specific gravity (s.g.) of the liquid used for the separation

of pyrite from coal had to be greater than that of the coal (with the maximum s.g. of 1.95) and clays (maximum s.g. of 2.7, according to Grim, 1953). Tetrabromoethane, with a specific gravity of 2.97, fulfilled these requirements. One gram of fine coal was mixed with tetrabromoethane in the centrifugal test tube. The mixture was then centrifuged at 1200 rpm, and the pyrite sink was separated, dried, and weighed. Microscopic examination of the sink showed that only 5 percent of the sink was made of minerals other than pyrite. The quantitative analysis of pyrite by this method showed only 1.17 percent pyrite in the Illinois No. 6 coal sample, whereas the chemical analysis of pyrite indicated that there was 2.99 percent pyrite in the Illinois No. 6 coal head sample. The comparison of the two results showed that the centrifugal method could not be used for the quantitative analysis of pyrite.

The centrifugal process mentioned above was also used to separate impurities other than pyrite from the coal samples. The process was used for washability studies of all of the samples (coals from Illinois, West Virginia, and Pennsylvania). Heavy liquids of different specific gravities were used to separate various fractions of the coal samples.

One gram of coal head sample was mixed with heavy liquids of different specific gravities. The mixtures were centrifuged at 1200 rpm for 30 minutes. The sink was collected, dried, and weighed. The weight of the sink was then subtracted from the weight of the sample in order to find the weight of the float. The percentages of the float and the sink were actually the cumulative percentages of the float and the sink. The samples of the float and the sink were then analyzed for ash and total sulfur content.

4.2.4 Preparation of 38 x 100 Mesh Illinois No. 6 Coal Samples:

A multiple deck sieve assembly consisting of 38, 48, 65, and 100 mesh Tyler sizes was used. Illinois No. 6 coal samples of 1/4 inch by zero in size were put in the sieve assembly and placed in a rotap for 30 minutes. Next, the classified samples were removed from the sieve assembly and each size range (38 x 48, 48 x 65, 65 x 100, and 100 x 0 mesh in size) was sampled by the coning and quartering technique. A fraction of each head sample obtained by coning and quartering (0.5 gram) was then spread on a grit paper and was examined by a binocular microscope (65 x magnification).

4.2.5 Preparation of Minus 100 Mesh Illinois No. 6 Coal Samples:

Twenty gram fractions of the Illinois No. 6 coal head samples were ground by a small ball mill (3.5 centimeters in diameter and 6 centimeters in length) for time periods of 5, 10, 15, 20, 30, 40, 50, and 60 minutes (see the results of size analysis, Table 5.2). In order to study an extreme grinding case, one sample was ground for 53 hours. Five gram fractions of each of the ground samples were mixed with tetrabromoethane and centrifuged at 1200 rpm, using an International Equipment, 38 centimeter diameter centrifuge unit. In order to prevent flocculation and entrapment of free pyrite particles by the coal particles, each of the 5 gram fractions of coal samples were added to the liquid in small fractions of 0.5 grams. The slurry was then centrifuged for 10 minutes. At the end of every 10 minutes the centrifuge was stopped, the crust of the coal on the top of the heavy liquid (the float) was scraped off, and a new 0.5 gram fraction of Illinois No. 6 coal sample was added to the liquid. The float products obtained by the float-sink

process were then dried at 105°C to a constant weight. Polished sections of the float products were prepared as described in Section 4.2.2. These polished sections were examined by a Unitron reflected light microscope at 200 magnification. The free pyrite, pyrite binary particles, and nonpyrite were counted. The particles counted were converted into percentages by dividing the number of particles (i.e. pyrite binary particles) into the total number of particles times 100.

The remaining portions of the 20 gram samples were mixed thoroughly and 10 grams of each sample were weighed and sieved through a 325 mesh Tyler series sieve. This analysis was done parallel to the particle count procedure.

The samples were also studied by a scanning electron microscope (AMR Model 900). Illinois No. 6 coal samples were mounted on small copper plates (0.5 by 0.5 centimeter) and were examined under the electron beam of the electron microscope. Since this technique transmits the anomalies of the rough surfaces, only the relative decrease in size was recorded. Consequently, the liberation of pyrite could not be studied by this system. However, some of the particles were identified by X-ray fluorescence (i.e. pyrite grains locked in the shale particles).

4.3 Procedures and Materials Used for Flotation Tests:

4.3.1 Methodology of the Flotation Tests:

Theoretically, coal is floated while the pyrite and ash are depressed and collected in the sink. For this purpose, different depressants such as potassium ferrocyanide, dextrin, and hydrofluoric acid were used. The results of these tests were compared with the results of the tests with pregnant "bacterial liquor." (The term "bacterial liquor" refers to a liquid containing Silverman and Lundgren's 9'K salts as well as ferric and ferrous sulfates. The liquid is pregnant with the bacteria Thiobacillus ferrooxidans.)

Samples of three well known coal seams were examined: Illinois No. 6, Middle Kittanning, and Pittsburgh seams. One hundred gram fractions of pulverized coal samples were deslimed and conditioned in a 200 ml capacity flotation cell with 2 lb./ton of pyrite depressants (the type of the depressant is given for the individual tests). The coal samples were then conditioned with the pyrite depressants for various lengths of time (the conditioning time is specified for individual flotation tests). A five percent pulp density was maintained in the flotation cell for all the tests. The rpm of the impeller of the flotation cell was kept at 900 for the tests. The pH of the flotation pulp was adjusted to 7.0, unless otherwise specified. The pH was adjusted to the desired levels by use of 5N HCl and 5N NaOH. Distilled water was used in all tests. Two pounds of frother per ton of sample were used for all the tests, except when cresylic acid was used. The cresylic acid was added to the pulp as it was required ("as it was required" means that the cresylic acid was added to the pulp in sufficient amounts so that

the froth no longer would carry anymore particles to the surface of the pulp. However, the amount of the cresylic acid did not exceed 8 lb./ton). The removed float and collected sink were then dried in a dryer at 105°C. A Wemco laboratory scale sub-aeration flotation cell was used for all flotation tests.

4.3.2 Process Developed for the Flotation of Coal Samples Conditioned in "Bacterial Liquor":

When treating the coal samples with "bacterial liquor," a more complicated process was developed. One hundred grams of pulverized coal samples of Illinois No. 6, Pittsburgh seam, or Middle Kittanning were mixed with 2000 ml of "bacterial liquor" to obtain a 51 percent density (unless otherwise specified). The pulp was then conditioned at 33°C for different time intervals while it was gently stirred by a magnetic stirrer. The pulp was then transferred to a vacuum filtration system where the "bacterial liquor" was separated from the solids. Next, the solids were washed and vacuum filtered, in order to remove the remaining ferrous and ferric sulfates, and then vacuum filtered again. The solids were then transferred into the flotation cell, and 2000 ml of distilled water were added to the cell (to make a 5 percent pulp density). The pH of the flotation pulp was raised to a desired level (7.0-8.0 for most tests) while the pulp was being mixed at 900 rpm. Next, a predetermined amount of frother was added to the pulp. The air bubbles were then introduced into the flotation pulp and the froth was formed. The froth was then scraped off the top of the flotation cell, washed, and vacuum filtered. The clean coal was then put in a dryer at 105°C for 24 hours (or enough time to reach a constant weight at 105°C). Figure 4.2 shows

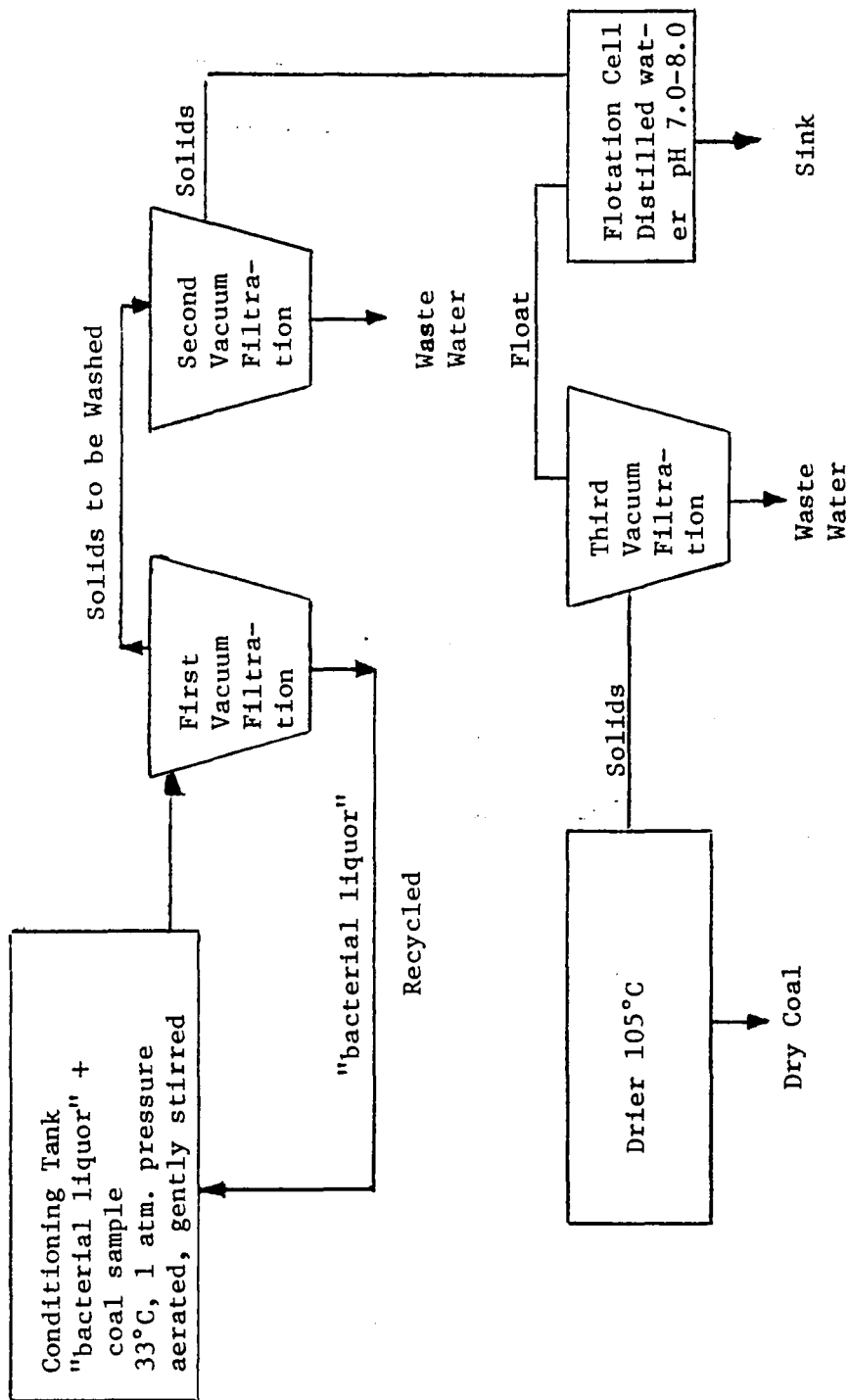


Figure 4.2. Process Diagram of Bacterial Conditioning and Flotation of Coal.

a diagram of the above procedure.

There are three main purposes for the use of two consecutive vacuum filtrations in the above process:

- a) To separate the "bacterial liquor" from the coal to be recycled (for most of the tests fresh "bacterial liquor" was used).
- b) To wash off soluble sulfate salts.
- c) To prevent colloidal coating of the "bacterial liquor" (the colloidal coating of the "bacterial liquor" is explained in the following paragraph).

When the pH of the "bacterial liquor" was raised from 2.0 to above 4.0, the liquor turned into a colloidal pulp, coating the particles in the flotation pulp. Due to this colloidal coating, the formation of froth was inhibited. However, when the pH was lowered to about 2.0, the colloidal liquid turned back to its original fluidity.

4.4 Analytical Procedures Used to Analyze the Flotation Products:

4.4.1 Drying the Coal Samples:

The coal samples were dried in a dryer at 105°C in accordance with the American Society for Testing and Materials (ASTM) Standard, Designation (D.3173-73)26.

4.4.2 Ashing the Coal Samples:

One gram of the moisture free coal sample was weighed, to the nearest 0.1 mg., in a crucible. The crucible containing the sample was then placed in an electric furnace at a low temperature, and gradually heated to redness "at such a rate as to avoid mechanical loss from too rapid explosion of volatile matter" (ASTM Designation [D.3174-73]26). The sample was burned at a final temperature of 725°C to a constant weight (+ .001 g.). The ashed sample was then cooled in a desiccator and weighed as soon as the crucible cooled. The ash which remained in the crucible was then weighed and converted into the percentage value. (See Section 6.2 for calculations of percent ash.)

4.4.3 Determining Total Sulfur:

The coal samples were burned by the oxygen flask combustion method in which the total sulfur content of the samples was put into solution. This solution was then titrated with barium perchlorate (BaClO_4). Percent total sulfur was then calculated by relating the amount of BaClO_4 to the amount of the sulfur required by the BaClO_4 for conversion into barium sulfate.

4.5 Sampling of the Coal Samples:

The purpose of sampling the Illinois, Pittsburgh, and Middle Kittanning coal samples was to collect a representative sample which contained a representative portion of all of the particles in the run of mine samples. This representative sample is called the head sample. The following definitions in sampling were adopted from ASTM Standards Designation (D.2013)26: air drying--a process of partial drying of the coal to bring its moisture near equilibrium with the atmosphere in the room in which further reduction and division of the sample is to take place; representative sample--a sample collected in such a manner that every particle in the lot to be sampled is equally represented in the gross sample; riffle--a hand-feed sample divider device that divides the sample into two parts of approximately the same weights; sample division--the process whereby a sample is reduced in weight change in particle size; sample preparation--the process that may include air drying, crushing, division, and mixing of a gross sample for the purpose of obtaining an unbiased analysis sample; sample reduction--the process whereby a sample is reduced in particle size by crushing or grinding without a change in weight; and size consist--the particle size distribution of a coal.

The manner in which the representative samples of Illinois No. 6, Pittsburgh, and Middle Kittanning coals were prepared is outlined in diagrammatic form in Figure 4.3. Table 4.1 gives the sieve analysis and the percent of total sulfur in the representative samples.

4.5.3 Source of the Coal Samples:

The Illinois No. 6 coal samples were received from Monterey Coal

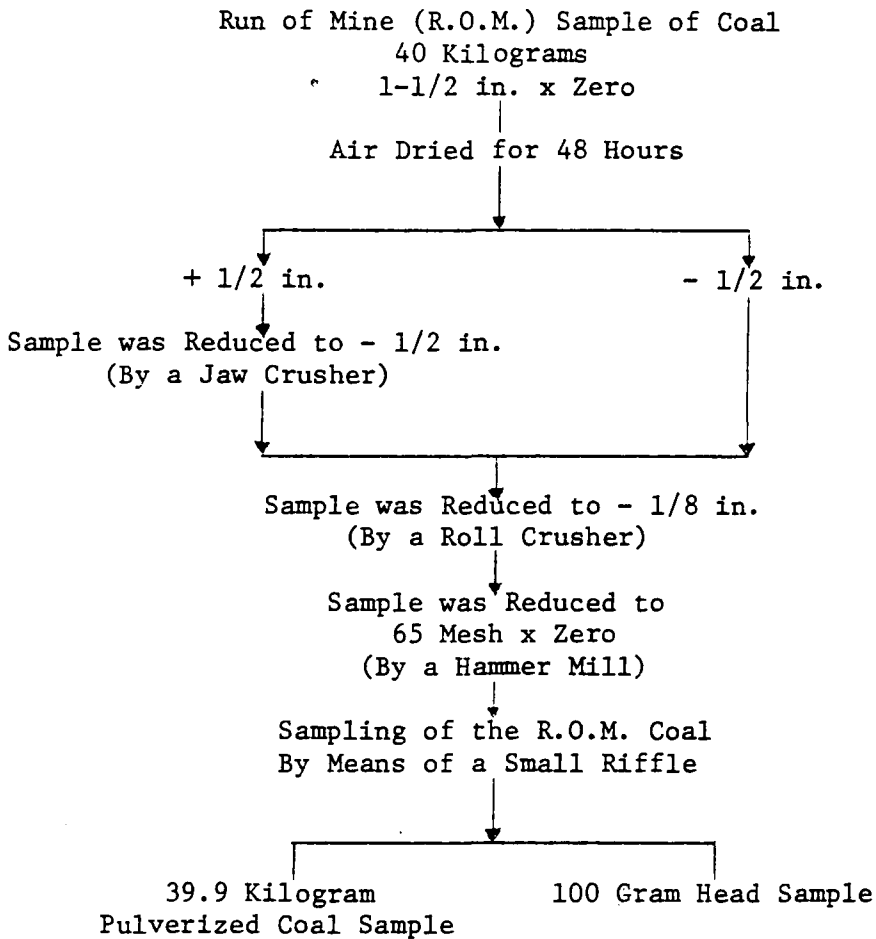


Figure 4.3. Preparation of the Representative Samples from Run of Mine (R.O.M.) Coal Samples of Illinois No. 6, Pittsburgh, and Middle Kittanning Seam Coals.

Table 4.1. Sieve Analysis of the Representative Coal Samples of Illinois No. 6, Pittsburgh, and Middle Kittanning Seams.

	<u>Size Range (mesh)</u>	<u>Weight Percent</u>	<u>Total Sulfur, %</u>
Illinois No. 6 Coal	+ 65	0.0	
	65 x 100	2.0	
	100 x 200	10.8	
	200 x 325	77.8	
	325 x 0	<u>10.2</u>	
	100		5.21
Pittsburgh Coal	+ 65	16.2	
	65 x 100	13.2	
	100 x 200	24.4	
	200 x 325	14.1	
	325 x 0	<u>32.1</u>	
	100		4.31
Middle Kittan- ning Coal	+ 65	0.0	
	65 x 100	1.1	
	100 x 200	8.0	
	200 x 325	76.1	
	325 x 0	<u>14.8</u>	
	100		3.18

Company. The coal samples were collected from the Monterey Number 1 mine, Carlinville, Illinois.

The Pittsburgh coal samples were received from Pittston Coal Company. The coal samples were collected from Compass Number 3 mine, Philip, West Virginia.

The Middle Kittanning coal samples were received from Associated Drilling Company. The coal samples were collected from Kephart mine, Osceola Mills, Pennsylvania.

5. EXPERIMENTAL RESULTS OF THE LIBERATION OF PYRITE FROM THE ILLINOIS
NO. 6 COAL SAMPLES

5.1 Description and Morphology of Pyrite Particles in Illinois No. 6
Coal Samples:

The pyrite particles in the Illinois No. 6 coal were distributed in both disseminated and segregated forms. These particles were found in euhedral, cleat, bleb, and layered forms. The pyrite particles would break into smaller particles under slight pressure.

The segregated pyrite could be seen with the naked eye and mineralized on the surface of coal and shale. These mineralized surfaces of pyrite could be peeled off the nonpyrite surfaces with a sharp blade.

The disseminated pyrite particles were integrated into the coal matrix. These particles were spherical in shape. However, the coarse Illinois No. 6 coal samples contained more angular disseminated pyrite particles than the fine coal samples.

5.2 Examination of 38 x 100 Mesh Illinois No. 6 Coal Samples:

The coal particles 38 x 100 mesh in size were examined by a binocular microscope (see Section 4.2.4 for details). These particles were classified into three groups: pyrite particles, binary particles of pyrite (particles of pyrite locked in other minerals), and nonpyrite particles (coal, shale, and other minerals). The particles were counted and the percent of binary and free pyrite determined. The results of the liberation size studies of pyrite from the Illinois No. 6 coal samples are tabulated in Table 5.1.

It was concluded that the percent of binary particles decreased as the size of the particles decreased. This was due to the fact that the binary particles were broken and the pyrite was liberated from the nonpyrite minerals (coal and shale). Consequently, the number of free pyrite particles was increased as the percent of nonpyrite particles remained relatively unchanged.

Table 5.1. Pyrite Liberation Size Studies of Illinois No. 6 Coal
38 x 100 Mesh in Size.

Mesh Size Range	Particle Specifications	Nature of Particle Occurrence		
		Free Pyrite	Binary Particles	Nonpyrite
38 x 48	% Distribution of Particles	1.7	3.4	94.9
	Particle Count	45	90	2524
48 x 65	% Distribution of Particles	6.2	2.0	91.8
	Particle Count	127	41	1873
65 x 100	% Distribution of Particles	7.0	0.8	92.2
	Particle Count	177	21	2326

5.3 Examination of Minus 100 Mesh Illinois No. 6 Coal Samples:

5.3.1 Scope:

The purpose of the following experiments was to compare the degree of liberation of pyrite from the Illinois No. 6 coal samples, which were ground for different lengths of time. Also, the relationship of the liberation of pyrite to its removal from coal by the float-sink technique was studied. Three sets of experiments were performed to determine the effect of grinding time on sample size reduction and the liberation of pyrite. These tests included the determination of the percent of minus 325 mesh particles, the size comparison of the coal samples by electron microscope, and the feed-float particle count by Uniflex reflected light microscope. Experimental procedures for the above tests have been previously described in Section 4.2.5.

5.3.2 Determination of Percent of Minus 325 Mesh Coal Particles in Minus 100 Mesh Illinois No. 6 Coal Samples:

The first five minutes of grinding the Illinois No. 6 coal samples resulted in an abrupt increase in the percent of particles passing through a 325 mesh sieve (about a 55 percent increase). The percentage of minus 325 mesh particles increased moderately during 5 to 25 minutes of grinding time (about a 13 percent increase). A very slight increase of minus 325 mesh sized particles was observed when grinding continued from 25 to 60 minutes. These results are tabulated in Table 5.2. Figure 5.1 shows the decreasing trend of particle sizes with respect to grinding time. The curve in Figure 5.1 shows that after 30 minutes of grinding time, there was a very small increase in the percentage of the particles passing through a 325 mesh sieve. Optical inves-

Table 5.2. Effect of Ball Mill Grinding Time on Weight Percent of Illinois No. 6 Coal Passing Through 325 Mesh Tyler Sieve.

Grinding Time (min.)	% Passing Through 325 Mesh Tyler Sieve
0.0	10.0
5.0	66.0
10.0	67.5
15.0	72.0
20.0	77.0
30.0	79.03
60.0	82.0

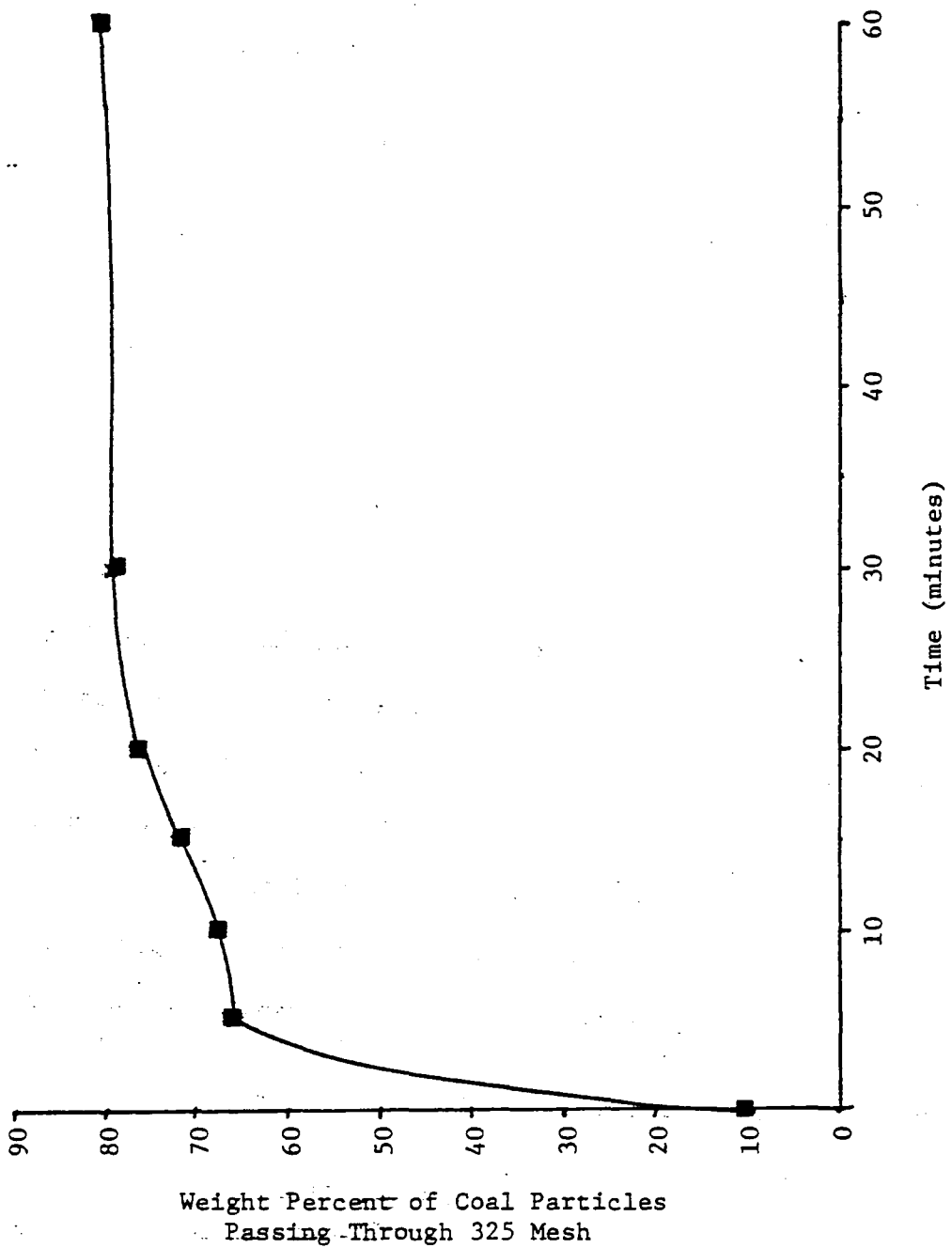


Figure 5.1. Grinding Time versus Weight Percent Passing Through 325 Mesh Size of Illinois No. 6 Coal Samples.

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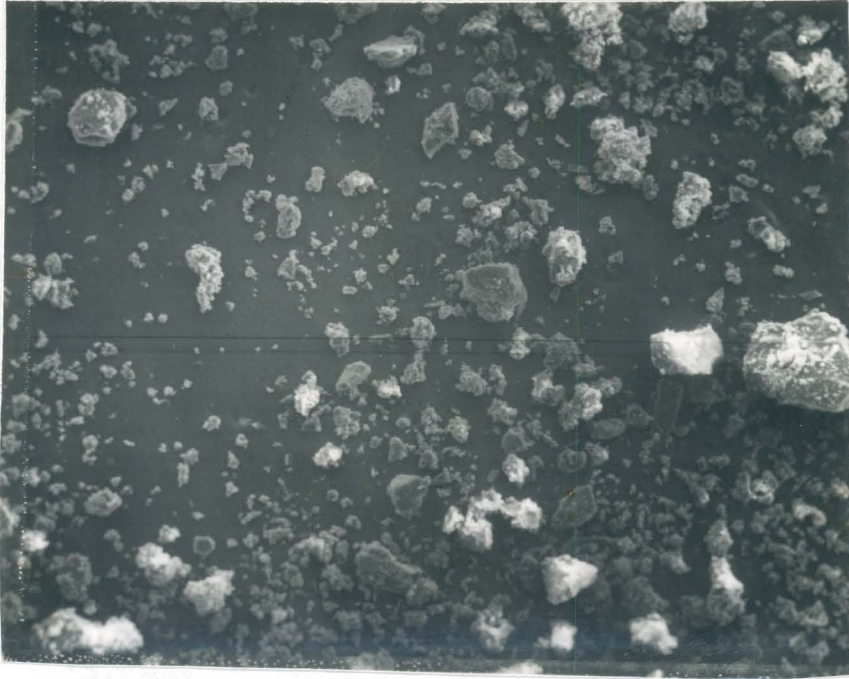
tigation by a scanning electron microscope showed that the particles generally became smaller as the grinding time increased (see Section 5.3.3). When the two results were compared, it was concluded that after 20 minutes of grinding there remained only a small portion of particles which offered more resistance to grinding. These particles were examined optically and were analyzed by X-ray fluorescence technique (using an EDAX unit). See the following section for details.

5.3.3 Size Comparison of Illinois No. 6 Coal Samples Ground for Different Time Intervals:

A size comparison was made between the coal samples which were ground for different time intervals, using a scanning electron microscope. The particles became finer as the grinding time increased. However, the coarser particles became smaller at a slower rate than the matrix they were in. Figures 5.2a and 5.2b are Photomicrographs comparing 5 minute and 60 minute grinding times of the Illinois No. 6 coal samples. The matrix of 60 minute grinding time is very fine and packed, whereas the matrix of the 5 minute grinding time is coarse. When examining the 60 minute ground sample, often no distinction could be made between the coarser particles in the matrix and the matrix itself. Although the scanning electron microscope is an efficient and accurate instrument for comparing the fine particle size of coal samples, the mineralogical make up of the particles could not be identified optically. For size comparison purposes, the photomicrographs of the Illinois No. 6 coal samples which were ground for different time intervals are given in the Appendix.

Analysis of the individual particles in the coal samples by the X-

(a)



(b)



Figure 5.2. Size Comparison of Photomicrographs of Illinois No. 6 Coal Samples Ground for (a) 5 Minutes and (b) 60 Minutes, Magnified 100 Times. Note: AMR Model 900 Scanning Electron Microscope Was Used.

M.L.N./78/VPI&SU

ray fluorescence technique revealed that most of the larger particles in the matrix of the samples were composed of silicon, aluminum, sulfur, and iron. Silicon and aluminum were the major constituents of clay minerals, where sulfur and iron were the elements forming the pyrite and marcasite.

The Energy Dispersive Analysis by X-ray (EDAX) is a unit attached to the electron microscope. It receives the energy dispersed from different elements and gives an analysis of their energy level. The result of the analysis is then translated into different X-ray peaks. These peaks are centered on the lines passing through the points (on the abscissa) representing the atomic numbers of the respective elements. Figures 5.3 and 5.5 show the X-ray analysis by the EDAX unit. A number of the individual particles in the coal matrix were magnified one thousand times by the scanning electron microscope. These particles were then analyzed by the X-ray fluorescence (using the EDAX unit). A representative particle of every five analyzed particles was photographed. (See Figures 5.4 and 5.6.) The representative photomicrographs of the individual particles (a thousand times magnified) and the pictures of the X-ray dispersion analysis of the representative particles are also presented in detail in the Appendix of this report.

Figure 5.4 is the photomicrograph which corresponds to the EDAX X-ray peaks of Figure 5.3. The elements identified in the particle in Figure 5.4 are as follows: silicon, aluminum, sulfur, and iron. Since these elements constitute clay, shale, and pyrite minerals, it was concluded that the pyrite particle was locked in the shale particle (binary pyrite particle). Figure 5.6 is the photomicrograph which corresponds

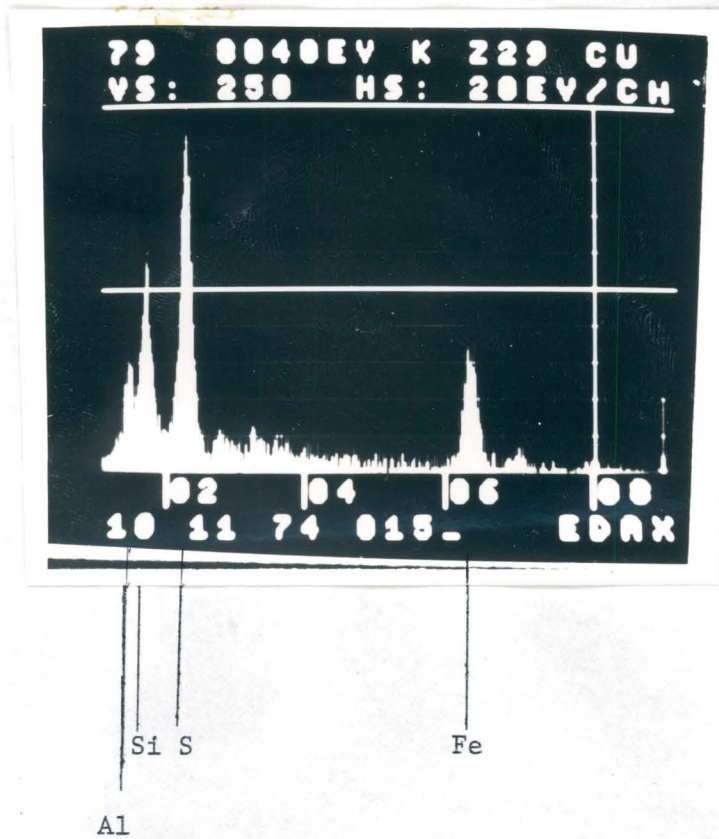


Figure 5.3. X-ray Analysis of a Representative Particle in Illinois No. 6 Coal Sample Ground for 15 Minutes.
Note: The X-ray Analysis was Done by an EDAX Unit Attached to the Scanning Electron Microscope.

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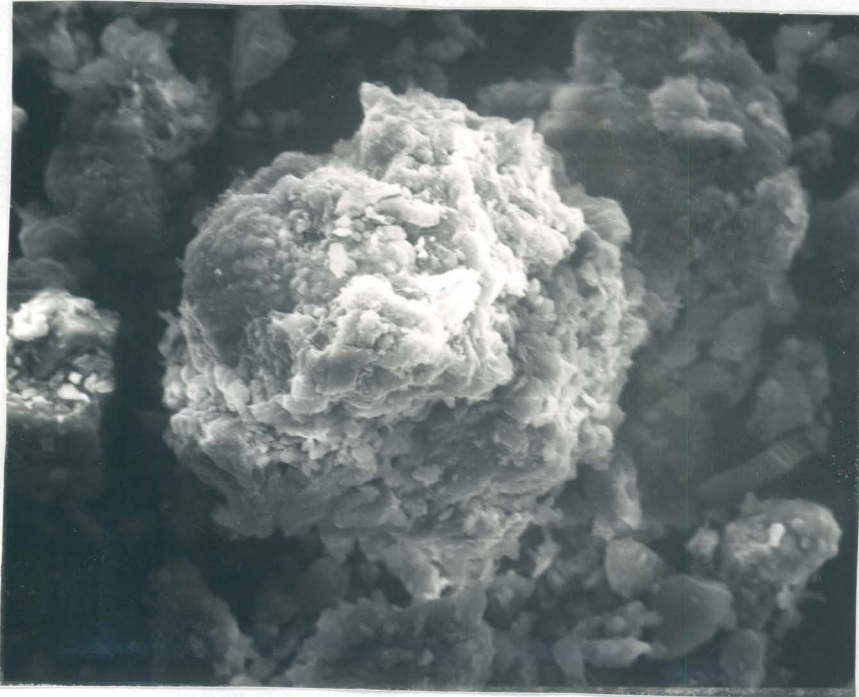


Figure 5.4. Photomicrograph of Illinois No. 6 Coal Sample Ground for 15 Minutes Magnified 1000 Times.

Note: AMR Model 900 Scanning Electron Microscope Was Used.

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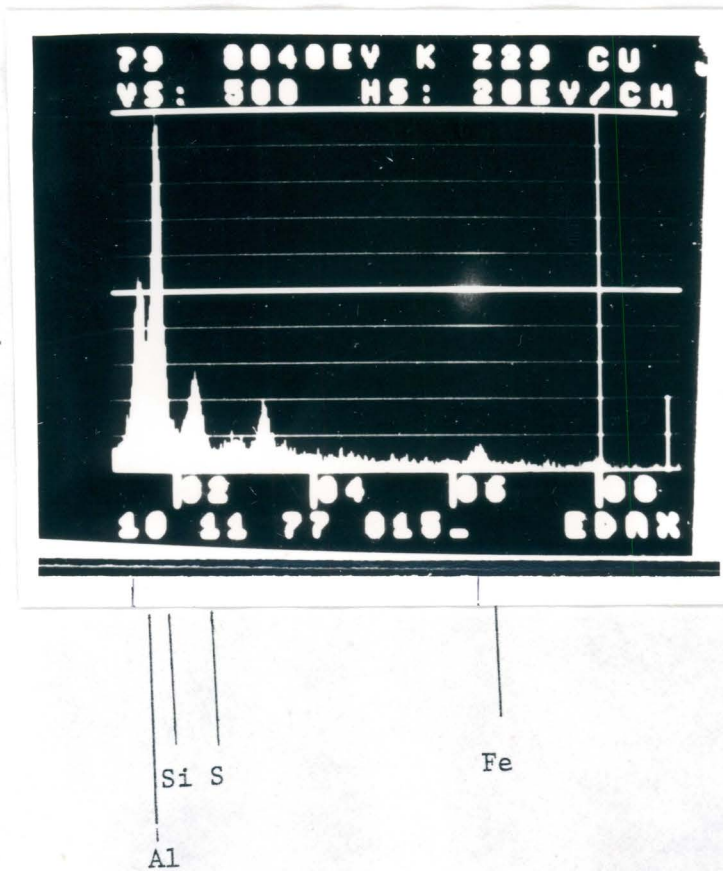


Figure 5.5. X-ray Analysis of a Representative Particle in Illinois No. 6 Coal Sample Ground for 15 Minutes.
Note: The X-ray Analysis was Done by an Edax Unit Attached to the Scanning Electron Microscope.

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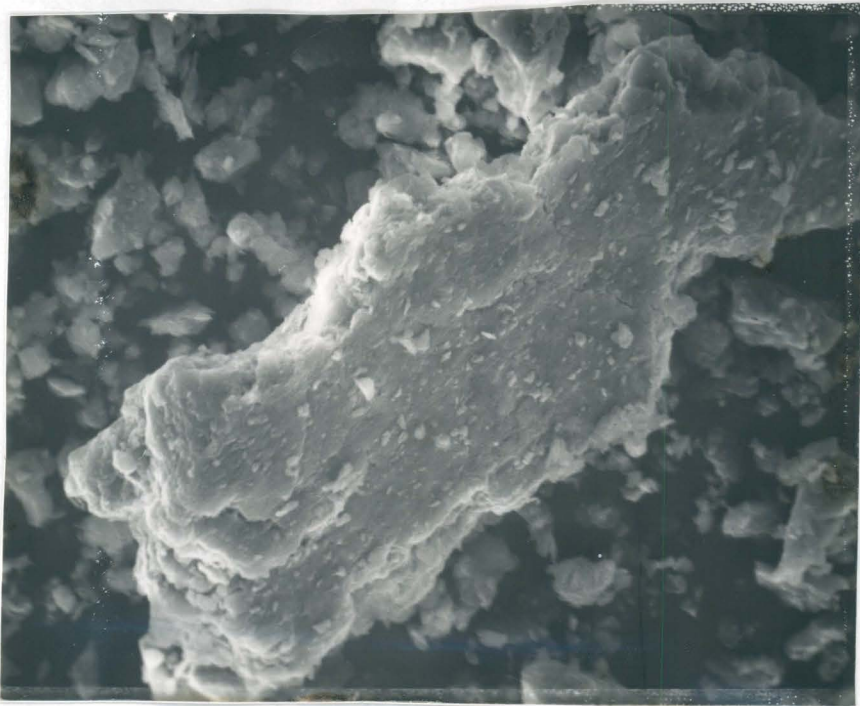


Figure 5.6. Photomicrograph of Illinois No. 6 Coal Sample Ground for 15 Minutes, Magnified 1000 Times.

Note: AMR Model 900 Scanning Electron Microscope was Used.

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to the EDAX X-ray peaks of Figure 5.5. This particle has small amounts of iron and sulfur, as can be seen from the peaks in Figure 5.5.

5.3.4 Examination of Polished Sections of Minus 100 Mesh Illinois No. 6 Coal by the Unitron Reflected Light Microscope:

5.3.4.1 Scope:

The reflected light system of the microscopic examination of polished sections was used to locate and study the luminous pyrite particles in the coal matrix. The easily identified pyrite particles were divided into two groups: free pyrite particles and binary pyrite particles. Furthermore, this study was conducted to observe the degree of dissemination of pyrite in the Illinois No. 6 coal matrix.

The Illinois No. 6 coal samples of different grinding times were floated by a heavy liquid, tetrabromoethane. Polished sections of the float and the feed were then prepared in accordance with the procedure outlined in Section 4.2.2. The polished sections were then examined by a reflected light microscope.

5.3.4.2 Particle Count System:

The particles (free pyrite, binary pyrite, and nonpyrite) were counted by advancing the stage of the microscope back and forth in a rectangular path.

5.3.4.3 Description of the Particles of Illinois No. 6 Coal Samples:

The particles of the Illinois No. 6 coal samples examined were generally angular in shape. The pyrite particles were easily identified as the shiny, metallic luster globules. The nonpyrite particles were primarily shale and coal, which had a top size of 75 microns. As the grinding time increased, the nonpyrite particle sizes moderately

decreased. The pyrite particles had a top size of 30 microns which sharply decreased with the increase of grinding time. The unliberated pyrite particle sizes ranged from 12 microns down to a fraction of a micron. The average size range of pyrite binary particles was between 3 to 1 microns in size. The binary particles in the 53 hour ground sample ranged between 0.9 to 0.5 microns in size.

The polished sections of the Illinois No. 6 coal samples were examined at 200 magnification. Figures 5.7 and 5.8 are the photomicrographs of 40 minute and 53 hour ground samples. Figures 5.7a and 5.8a are the polished sections of the float of 40 minute and 53 hour ground coal samples, respectively. Figures 5.7b and 5.8b are the photomicrographs of the feed of 40 minute and 53 hour ground coal samples. Photomicrographs of the polished sections of 5, 30, and 60 minute ground samples are given in the Appendix.

5.3.4.4 Results and Discussions:

Three sets of particles (free pyrite, binary pyrite, and nonpyrite) were counted in both the float and the feed. Each set of particle count was divided by the total particle count to get an apparent percent distribution of pyrite, binary pyrite, and nonpyrite in both the float and the feed. These results are tabulated in Table 5.3. The ratio of binary pyrite to free pyrite in the float and the feed was calculated and plotted against grinding time (see Figure 5.9).

The graphs in Figure 5.9 show that, as the grinding time increased, the particles became progressively smaller and more locked particles of pyrite were liberated. Hence, the number of binary pyrite particles in the feed decreased, whereas the number of free pyrite particles in the

(a)



(b)

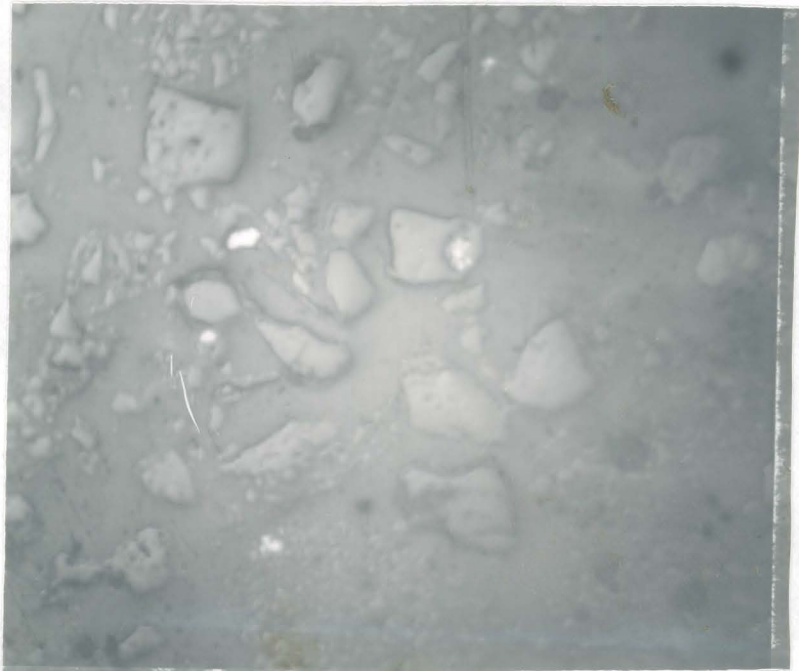
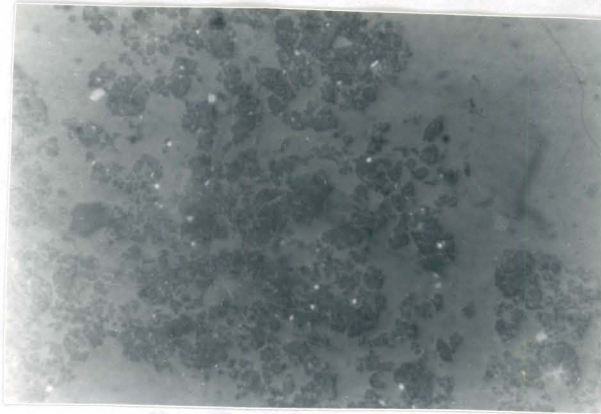


Figure 5.7. Comparison of the Photomicrographs of Illinois No. 6 Coal Samples Before Treatment in Tetrabromoethane (a) and After Treatment with Tetrabromoethane (b) by Float-Sink Technique. Samples Were Ground for 40 Minutes. Particles are Magnified 200 Times.

Note: A Unitron Reflected Light Microscope was Used.

(a)



(b)



Figure 5.8. Comparison of the Photomicrographs of Illinois No. 6 Coal Samples Before Treatment in Tetrabromoethane (a) and After Treatment with Tetrabromoethane (b) by Float-Sink Technique. Samples Were Ground for 53 Hours. Particles are Magnified 200 Times.
Note: A Unitron Reflected Light Microscope was Used.

Table 5.3. Microscopic Examination and Liberation Studies of Pyrite in Illinois No. 6 Coal Samples.

Grinding Time	Particle Specification	Source of Sample	Nature of Particle Occurrence			
			Free Pyrite	Binary Pyrite/Free Pyrite	Binary Pyrite	Non Pyrite Particles
5 min.	% Distribution of Particles	Feed	12.1	.45	5.4	82.5
		Float	5.0	1.0	5.0	90.0
	Particle	Feed	176.0	-	79	1200
	Count	Float	243.0	-	242	4248
30 min.	% Distribution of Particles	Feed	8.7	.16	1.4	89.9
		Float	1.8	1.4	2.5	95.7
	Particle	Feed	464.0	-	75	4800
	Count	Float	70.0	-	94	3655
40 min.	% Distribution of Particles	Feed	5.1	.14	0.7	94.2
		Float	1.8	1.5	2.7	95.5
	Particle	Feed	70.0	-	10	1300
	Count	Float	169.0	-	253	8950
1 hr.	% Distribution of Particles	Feed	8.8	.13	1.2	90.0
		Float	0.8	4.0	3.2	96.0
	Particle	Feed	1132.0	-	155	11650
	Count	Float	48.0	-	193	585
53 hrs.	% Distribution of Particles	Feed	2.1	1.4	3.0	94.9
		Float	0.8	3.1	2.5	96.7
	Particle	Feed	72.0	-	100	3200
	Count	Float	16.0	-	52	2000

Note the Effect of Increased Grinding Time on Pyrite Liberation from the Coal.

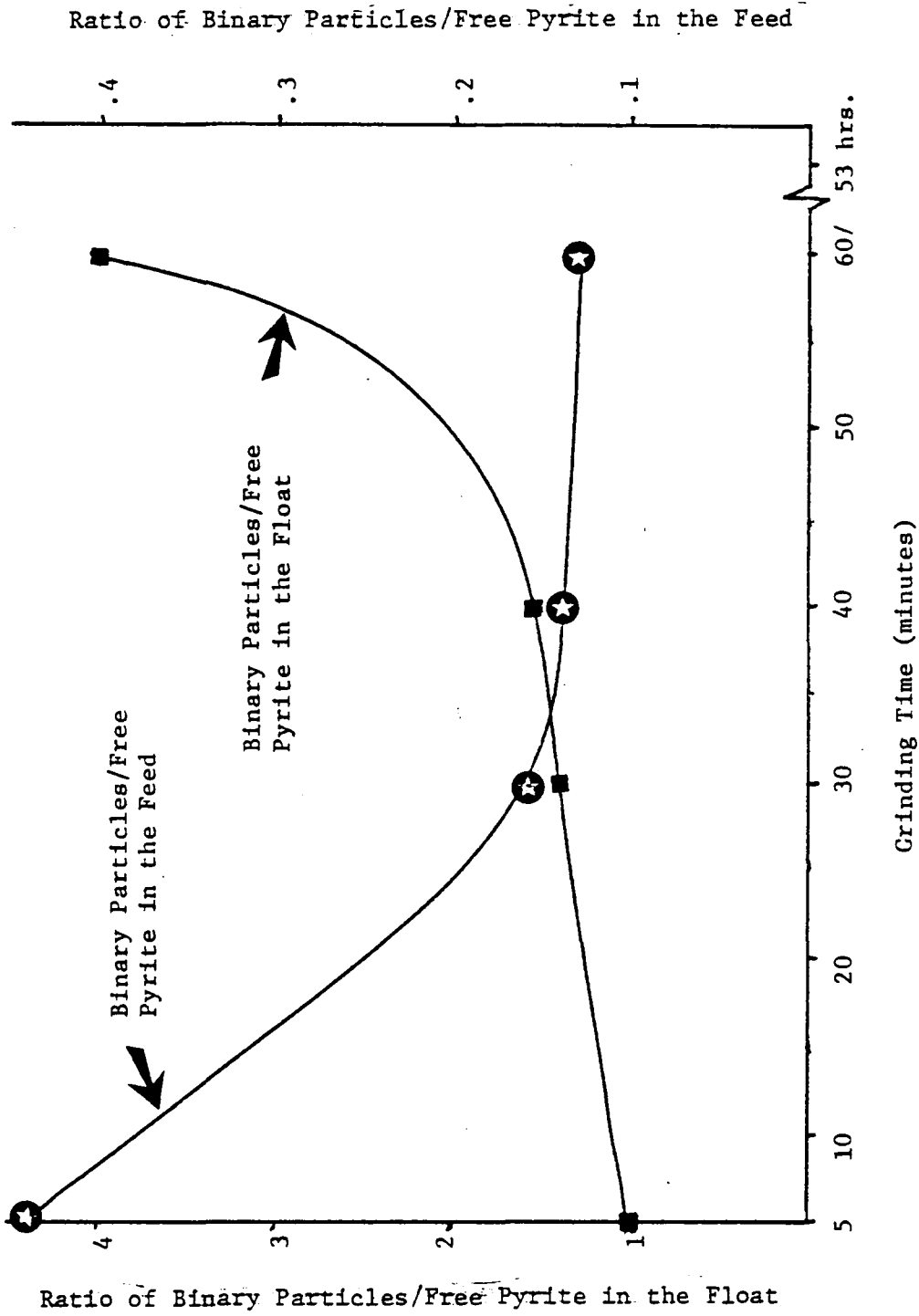


Figure 5.9. Grinding Time versus Ratio of Binary Pyrite Particles/Free Pyrite Particles in the Float and in the Feed of the Illinois No. 6 Coal Samples.

feed increased. Consequently, the ratio of binary pyrite to free pyrite decreased.

In the float portion of the coal samples, the liberated pyrite particles were easily removed from the coal matrix (by the float-sink method). As the grinding time increased, the number of liberated pyrite particles also increased. Consequently, more pyrite particles were removed (by the float-sink method) from the samples ground for longer time periods. As a result of the decrease in the number of free pyrite particles, the ratio of binary pyrite to free pyrite increased (since the denominator was decreased).

The data from the 53 hour ground sample does not follow the same path as the other points on the graph. There is a sharp increase of the binary pyrite/free pyrite ratio in the feed and a moderate decrease in the same ratio in the float.

5.3.5 Conclusion:

The fluctuation of the ratios of apparent percentages of the binary pyrite/free pyrite particle ratio indicated that, at the end of each stage of grinding (38 x 100 mesh and 100 mesh ground for 5 to 60 minutes, and 53 hour ground samples), the actual percentage of binary pyrite was always greater than its apparent percentage. This is especially true for a coal sample which has a high degree of pyrite dissemination.

The writer believes that, as the samples were further ground, more pyrite particles still locked in the nonpyrite matrix were exposed and could be seen by the reflected light system of optical examinations. For example, when the minus 100 mesh samples were ground 5 to 60 min-

utes, the apparent percentage of the binary particles increased. Also, when the sample was ground for 53 hours the apparent percentage of the binary particles and the ratio of binary to free pyrite in the feed increased from 1.2 to 3 and 0.13 to 1.4, respectively.

This indicated that the number of binary pyrite particles had increased. On the other hand, the ratio of the binary pyrite/free pyrite indicated that the number of free pyrite particles was substantially lower than the binary particles. This increase in the binary particles of pyrite could have been from the exposure of the new coal or shale surfaces in which the disseminated pyrite was locked.

6. EXPERIMENTAL RESULTS OF THE FLOTATION TESTS

6.1 Introduction:

The flotation process in coal requires careful selection of reagents and choice of physio-chemical conditions which result in selective separation of pyrite, ash, and other impurities. The objective of this work was to depress pyrite particles so that they could be selectively separated from the coal.

The selective flotation of coal and depression of pyrite was achieved by altering the surface characteristics of pyrite either by the action of the bacteria Thiobacillus ferrooxidans or by chemical reagents such as potassium ferrocyanide, hydrofluoric acid, dextrin, and sodium carbonate. The changes in the physio-chemical conditions within the flotation cell were also studied.

It is a new concept to depress coal pyrite by bacterial action in the flotation process. In fact, only two sources of literature were cited based on this concept (Capes et al., 1973; Atkins, 1976). Only Atkins (1976) reported on some preliminary work with froth flotation of coal conditioned in the "bacterial liquor" (see the Literature Review Section).

6.2 Calculations of Weight Percentages of Flotation Products*:

% Ash is calculated as follows:

$$\% \text{ Ash in analysis sample (D)} = [(A - B)/C] \times 100$$

where:

A = weight of crucible and ash residue (gram)

B = weight of empty crucible (gram)

C = weight of analysis sample used (gram).

% Ash-free coal is then (E) = (100 - D).

Weight Distribution Percentages are calculated as follows:

$$\% \text{ Ash distribution in float } (D_{DF}) = \frac{D_F(F)}{C_{TD}}$$

$$\% \text{ Ash distribution in sink } (D_{DS}) = \frac{D_S(S)}{C_{TD}} = (100 - D_{DF})$$

$$\% \text{ Ash-free Coal distribution in float } (D_{EF}) = \frac{E_F(F)}{C_{TE}}$$

$$\% \text{ Ash-free Coal distribution in sink } (D_{ES}) = \frac{E_S(S)}{C_{TE}}$$

where:

D_F = % ash in the float

F = % of the feed reported to the float (yield)

C_{TD} = % ash in the composite total

D_S = % ash in the sink

S = % of the feed reported to the sink

E_F = % ash-free coal reported to the float

C_{TE} = % ash-free coal in the composite total = 100 - C_{TD}

* All Calculations Were Done on Moisture Free Basis.

E_S = % ash-free coal reported to sink.

$$\% \text{ total sulfur distribution in float } (D_{SUF}) = \frac{SU_F(F)}{C_{TSU}}$$

$$\% \text{ total sulfur distribution in sink } (D_{SUS}) = \frac{SU_S(F)}{C_{TSU}}$$

where:

SU_F = % sulfur in the float

C_{TSU} = % sulfur in the composite total

SU_S = % sulfur in the sink.

% Reduction of Sulfur/Ash-free Coal ratio $R_{(SU/E)}$

$$= \frac{(C_{TSU}/C_{TE}) - (SU_F/E_F)}{(C_{TSU}/C_{TE})} \times 100$$

% Reduction of Sulfur in the float (R_S)

$$= \frac{C_{TSU} - SU_F}{C_{TSU}}$$

% Composite total fractions are C_{TD} , C_{TE} , and C_{TSU} .

$$C_{TD} = (D_F \times F/100) + (D_S \times S/100)$$

$$C_{TE} = (E_F \times F/100) + (E_S \times S/100)$$

$$C_{TSU} = (SU_F \times F/100) + (SU_S \times S/100) = (100 - C_{TE}).$$

6.3 Flotation Tests Conducted by Chemical Reagents:

6.3.1 Variations of pH and its Effect on the Reduction of Sulfur and Ash of the Illinois No. 6 Coal Samples:

Several flotation tests were conducted to determine the effect of pH on the reduction of sulfur and ash of the Illinois No. 6 coal samples. Two sets of experiments were conducted with two different frothers: methyl iso-butyl carbinol (MIBC) and cresylic acid (which also has collecting ability). All of the conditions were kept constant except the pH of the flotation pulp. In order to study the sole effect of pH on the removal of pyritic sulfur, pyrite depressants were not used in these tests.

The first set of results is tabulated in Table 6.1. Only MIBC (2 lb./ton) was used as frother for this set of experiments. The pH was varied from 2 to 9. This variation of pH was plotted versus the percent yield and the weight distribution percentages of the ash, combustibles (ash-free coal), and sulfur in Figure 6.1.

The highest yield, as well as combustible recovery, were obtained at pH 3.0. These results do not agree with the results reported by Zimmerman (1968), in which the highest percent recovery of combustibles was reported at pH 7.0. The recovery of sulfur in the float also had the highest value at pH 3.0. This high recovery of sulfur in the float decreased as the pH value increased (in agreement with Zimmerman's results). The percent ash distribution in the float increased with the increase in pH value.

Figure 6.2 is the graph of variations of pH versus weight percent reduction of sulfur, and weight percent reduction of the sulfur/ash-free coal ratio. The reduction of sulfur increased with the increase of

Table 6.1. Variations of pH and its Effect on Reduction of Sulfur and Ash from Illinois No. 6 Coal (Using MLBC as Frother).

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Variations of pH
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₄₉	Float	45.2	15.8	84.2	6.4	29.0	50.5	41.6			
	Sink	54.8	32.0	68.0	7.4	71.0	49.5	58.4	7.9	17.6	2
	Composite Total	100	24.7	75.3	6.9	100	100	100			
C ₅₀	Float	64.2	17.8	82.2	6.4	42.5	72.1	60.8			
	Sink	35.8	43.1	56.9	7.4	57.5	27.9	39.2	5.2	15.6	3
	Composite Total	100	26.9	73.2	6.7	100	100	100			
C ₅₁	Float	55.5	15.2	84.8	5.8	33.2	63.1	47.0			
	Sink	44.5	38.2	61.8	8.2	66.8	36.9	53.0	15.4	25.5	5
	Composite Total	100	25.4	74.6	6.8	100	100	100			
C ₅₂	Float	44.4	17.8	82.2	5.6	34.1	47.5	62.7			
	Sink	45.6	33.5	66.5	7.3	65.9	52.5	57.3	3.8	10.1	7
	Composite Total	100	23.2	76.8	5.8	100	100	100			
C ₅₃	Float	33.5	33.7	66.3	5.3	36.4	32.2	28.3			
	Sink	66.5	29.6	70.4	6.8	63.6	67.8	71.7	15.5	12.1	8
	Composite Total	100	31.0	69.0	6.3	100	100	100			

Table 6.1. (cont.)

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Dis-tribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Variations of pH
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
	Float	42.0	18.7	81.3	5.5	29.4	46.0	35.8			
C ₅₄	Sink	58.0	30.7	69.3	7.1	70.6	54.0	64.2	14.7	22.0	9
	Composite Total	100	26.7	74.3	6.4	100	100	100			

Remarks:

Size of the coal sample = minus 65 mesh

Flotation cell conditions:

pH = variable, rpm = 900

Pulp density = 5(w/v)

Flotation time = 4 minutes

Frother conditioning time = 1 minute

Reagents used:

Frother: 2 lb./ton MIBC

Collector: none

Pyrite depressant: none

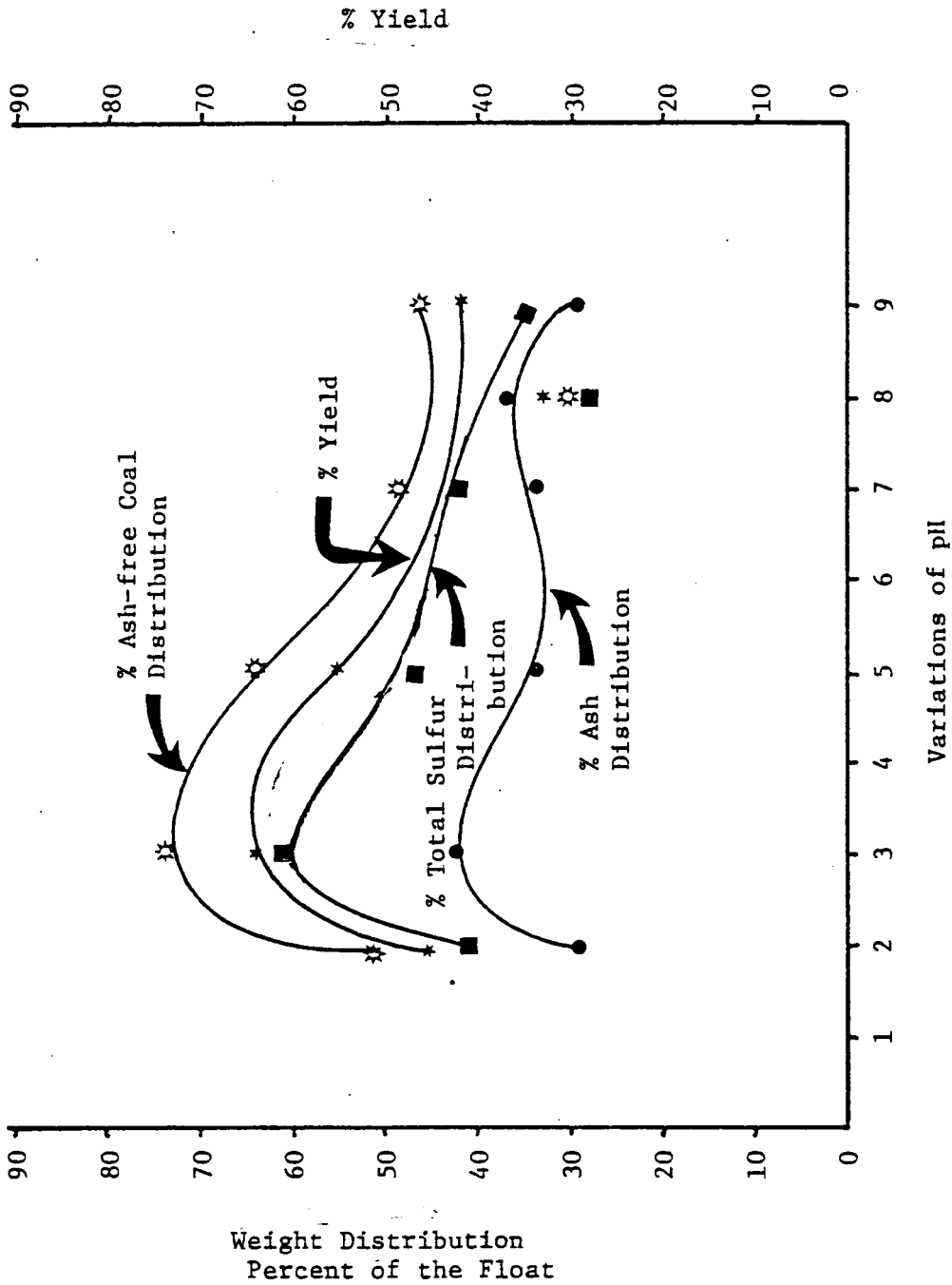


Figure 6.1. Variations of pH versus Weight Distribution Percent of Sulfur, Ash, and Ash-free Coal in the Float Using MIBC as a Frother.

pH. As can be seen in Figure 6.2, the ash-free coal ratio is erratic.

The second set of results was obtained by using a combination of frother and collector reagents. Methyl iso-butyl carbinol (MIBC) as the frother and cresylic acid as the collector were added to the flotation pulp. Four minutes of conditioning time was allowed for the cresylic acid to be mixed with the pulp. The cresylic acid was added to the pulp as required. The results are tabulated in Table 6.2. Figure 6.3 shows the graphs of the percent yield and weight distribution of sulfur, ash, and ash-free coal in the float.

The highest percent yield and combustible (ash-free coal) recovery was at pH 3.0. As the pH increased, percent yield and distribution of ash and ash-free coal in the float decreased. There was a slight decrease in ash distribution in the float. A sudden decrease occurred in the distribution of ash and combustibles in the float and the yield at pH 8.0. The sink portions of this set of flotation tests were not available for analysis. Hence, sulfur and ash analysis for this set of tests could not be performed. The ash content was taken to be 26.6 (the ash content in the head sample).

Graphs in Figures 6.1 and 6.3 show that the two sets of results with cresylic acid and MIBC-cresylic acid followed the same general trends. Both had the highest peaks at pH 3.0 and decreased with the increase of pH. The percent yield and distribution of float materials of both sets of results suddenly dropped at pH 8.0. The combustible recovery of the second set (the frother-collector combination) of results was higher when only a frother was used. The percentages of ash increased with the rise of pH when only a frother was used (disregard-

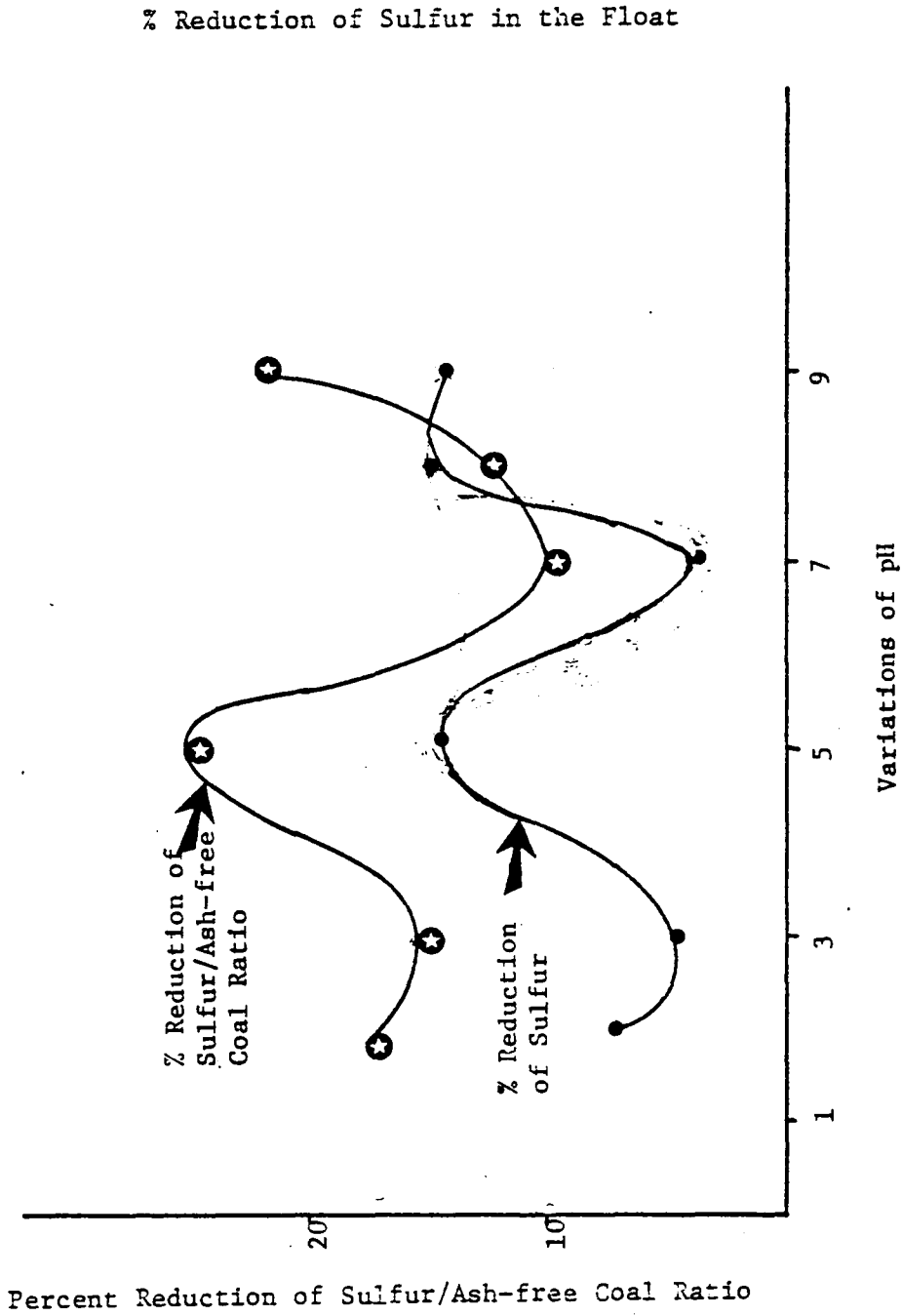


Figure 6.2. Variations of pH versus Percent Reduction of Sulfur and Percent Reduction of Sulfur/Ash-free Coal Ratio of Illinois No. 6 Coal Samples Using MIBC as a Frother.

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Table 6.2. Variations of pH and its Effect on the Recovery of Clean Coal and the Removal of Ash from Illinois No. 6 Coal Samples (Using a Combination of MIBC and Cresylic Acid as Frother and Collector).

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %		% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Variations of pH
			Ash *	Combustibles	Total Sulfur	Ash	Combustibles			
C ₄₀	Float	44.1	16.6	83.4	5.6	27.5	50.1			2
	Sink	55.9	34.5	65.5		72.5	49.9			
	Composite Total	100	26.6	73.4		100	100			
C ₄₁	Float	59.7	13.6	86.4	5.7	30.5	70.3			3
	Sink	40.3	45.9	54.1		69.5	29.7			
	Composite Total	100	26.6	73.4		100	100			
C ₄₂	Float	53.7	14.7	85.3	5.2	29.7	62.4			5
	Sink	46.3	40.4	59.6		70.3	37.6			
	Composite Total	100	26.6	73.4		100	100			
C ₄₃	Float	43.7	17.0	83.0	5.2	27.9	49.4			7
	Sink	56.3	34.0	66.0		72.1	50.6			
	Composite Total	100	26.6	73.4		100	100			
C ₄₄	Float	33.1	11.7	88.3	5.4	14.6	39.9			8
	Sink	66.9	34.0	66.0		85.4	60.1			
	Composite Total	100	26.6	73.4		100	100			
C ₄₅	Float	38.5	18.2	81.8	6.1	26.3	42.9			9
	Sink	61.5	31.9	68.1		73.6	57.1			
	Composite Total	100	26.6	73.4		100	100			

Table 6.2. (cont.)

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Dis-tribution, %		% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Variations of pH
			Ash	Combustibles	Total Sulfur	Ash	Combustibles			
	Float	36.2	15.0	85.0	4.9	20.4	41.9			
C ₄₆	Sink	63.8	33.2	66.8		79.6	58.1			10
	Composite Total	100	26.6	73.4		100	100			

Remarks:

* The sink was not analyzed for ash and sulfur content. Total percent ash in the head sample was used as composite ash (26.6 percent ash).

Sample size = minus 65 mesh

Flotation cell conditions:

pH = variable, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Collector-frother conditioning time = 3 minutes

Reagents used:

Frother: 2 lb./ton MIBC

Collector: < 8 lb./ton cresylic acid

Pyrite depressant: None

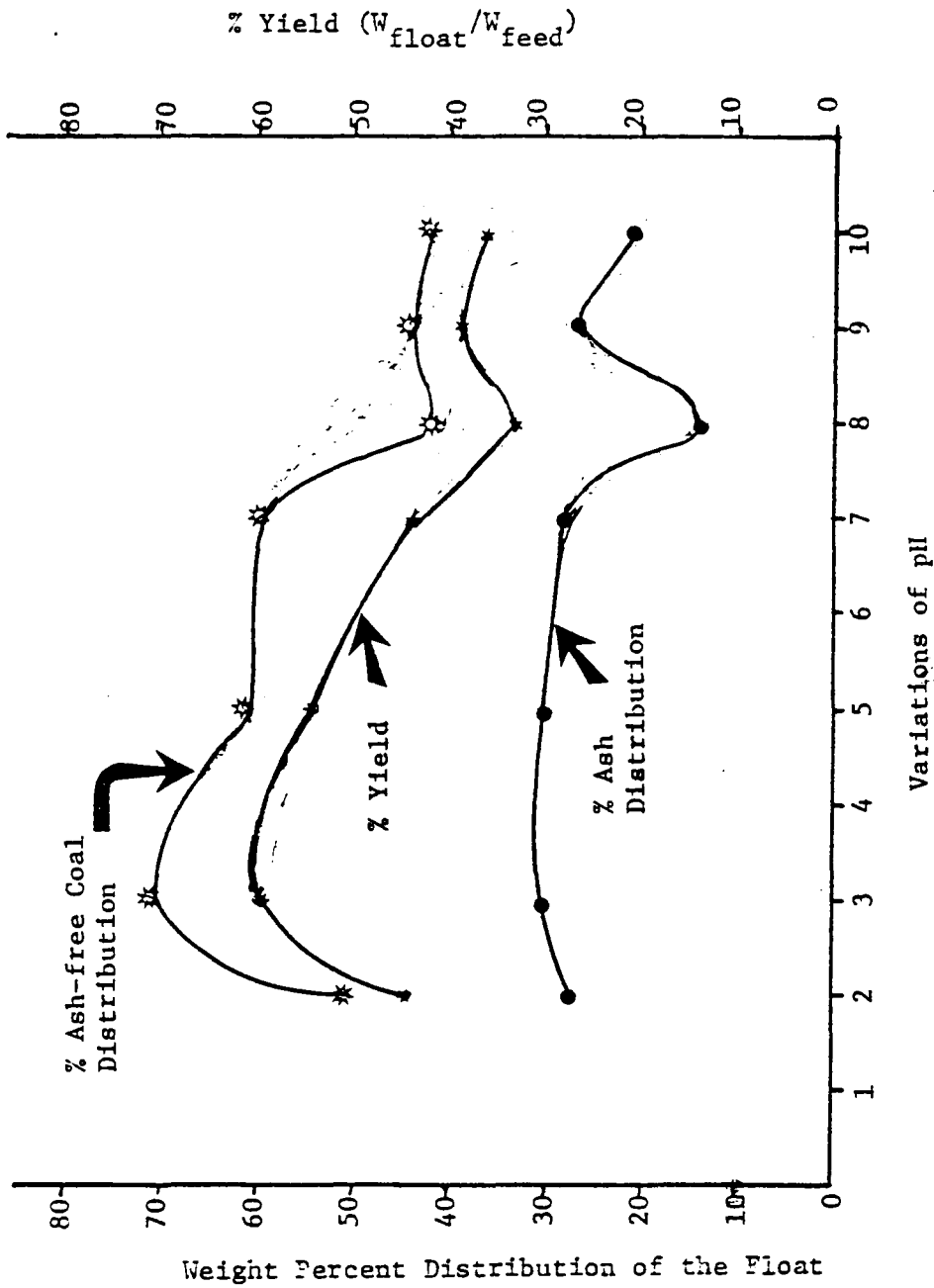


Figure 6.3. Variations of pH versus Percent Yield and Weight Distribution Percent of the Float Products of Illinois No. 6 Coal Sample. A Combination of Frother-Collector (MIBC-Cresylic Acid) was Used.

ing the ash value points at pH 3.0 and 8.0). The ash distribution in the float decreased when the frother-collector combination (MIBC and cresylic acid) was used.

6.3.2 Variations of Temperature and its Effect on the Distribution of Ash, Sulfur, and Ash-free Coal in the Float:

The effect of different temperatures of the flotation pulp on the distribution of float material (ash, sulfur, and ash-free coal) was investigated. The mean temperature (\bar{T}) was recorded as the temperature of the flotation pulp. The mean temperature was calculated as:

$$\left[\begin{array}{l} \text{Temperature at the start of the flotation} + \\ \text{Temperature at the end of the flotation} \end{array} \right] / 2$$

Cresylic acid was used as the frother-collector reagent. The cresylic acid was added to the pulp as was required. The pulp was mixed with the cresylic acid for four minutes. The flotation time was four minutes.

The only variable in these experiments was the mean temperature. The results are tabulated in Table 6.3. In Figure 6.4 the mean temperature is plotted versus percent yield and weight distributions of ash, sulfur, and ash-free coal in the float.

It was noted that the weight distribution of ash, ash-free coal, and sulfur in the float varied within ten percent throughout the experiments. The distribution of sulfur in the float at different temperatures remained about the same.

The variations of temperature were plotted against the percent reduction of sulfur and percent reduction of sulfur/ash-free coal ratio, Figure 6.5. The reduction of sulfur steadily increased to its highest level at 55°C (mean temperature). The lowest sulfur reduction was

Table 6.3. Effect of Variations of Temperature on the Recovery of Ash-free Coal and Removal of Ash and Sulfur from Illinois No. 6 Coal Samples.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Cell Temperature °C
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₅₂	Float	44.4	17.8	82.2	5.6	34.1	54.6	42.8			
	Sink	45.6	33.5	66.5	7.3	65.9	45.4	57.2	3.6	21.7	20
	Composite Total	100	23.2	66.8	5.8	100	100	100			
C ₆₄	Float	43.3	17.7	82.3	5.8	26.2	50.3	40.4			
	Sink	56.7	38.0	62.0	7.0	73.8	49.7	59.6	6.6	19.7	40
	Composite Total	100	29.2	70.8	6.2	100	100	100			
C ₆₃	Float	47.6	17.6	82.4	6.0	32.0	53.1	43.9			
	Sink	52.4	34.0	66.0	7.0	68.0	47.0	56.1	7.8	17.4	45
	Composite Total	100	26.2	73.8	6.5	100	100	100			
C ₆₂	Float	50.4	18.9	81.1	5.4	35.9	55.6	41.0			
	Sink	49.6	34.3	65.7	7.8	64.1	44.4	59.0	18.7	26.3	55
	Composite Total	100	26.5	73.5	6.6	100	100	100			
C ₆₁	Float	45.4	17.8	82.2	5.4	31.1	50.4	39.0			
	Sink	54.6	32.8	67.2	7.0	68.9	49.6	61.0	14.1	22.7	65
	Composite Total	100	26.0	74.0	6.2	100	100	100			

Table 6.3. (cont.)

Sample No.	Flotation Products	Weight, %	Analysis, %				Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Cell Temperature, °C
			Ash	Combustibles	Total Sulfur	5.8	Ash	Combustibles	Total Sulfur			
	Float	40.1	18.7	81.3	5.8	30.0	43.5	38.8				
C ₆₀	Sink	59.9	29.2	70.8	6.1	70.0	56.5	61.2	3.2	10.7	75	
	Composite Total	100	25.0	75.0	6.0	100	100	100				

Remarks:

Size of the coal sample = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Frother conditioning time = 3 minutes

Reagents used:

Frother: Cresylic acid was added as required

Collector: same as frother

Pyrite depressant: none

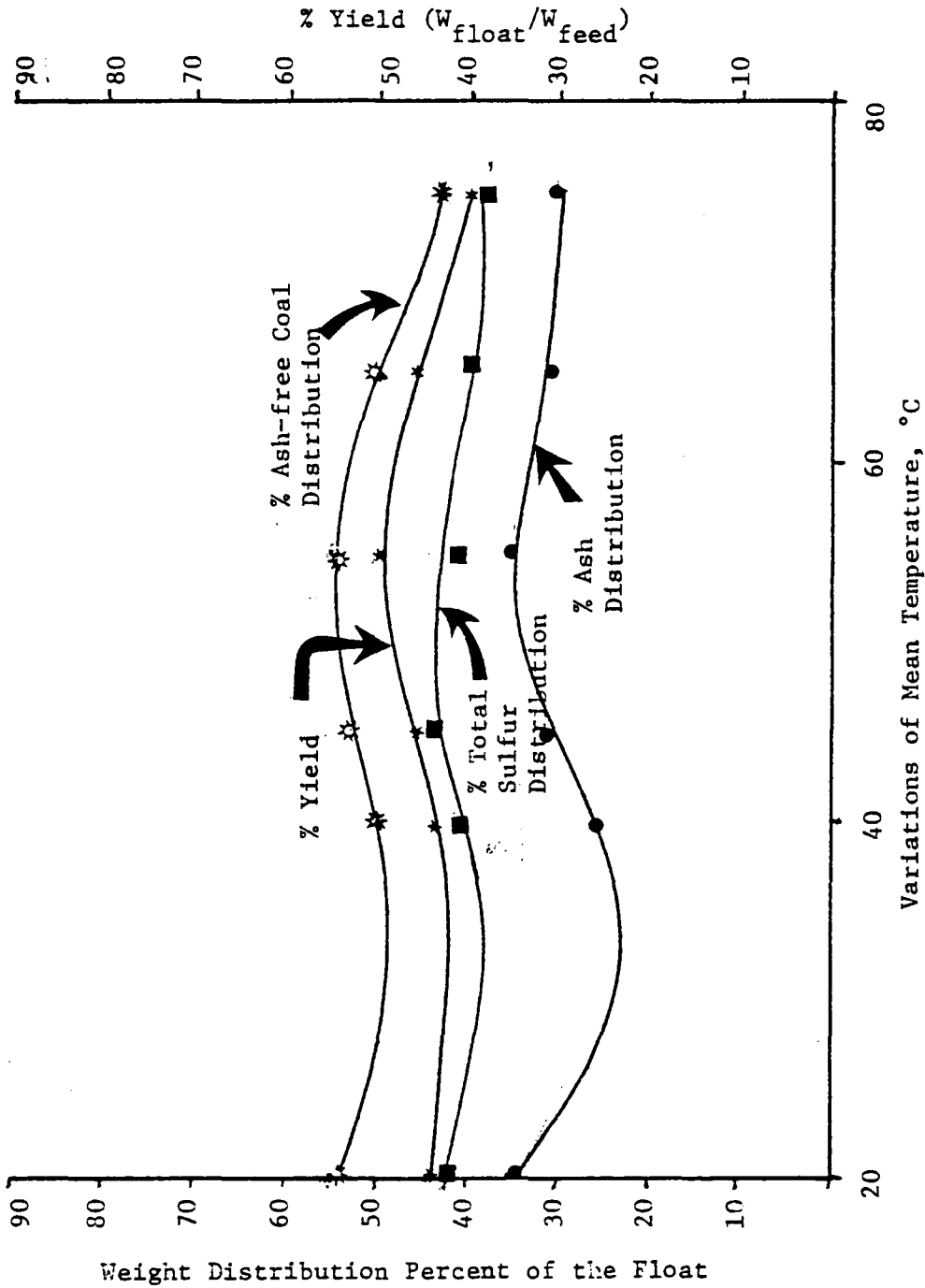


Figure 6.4. Variations of Mean Temperature versus Percent Yield and Weight Distribution Percent of Sulfur, Ash, and Ash-free Coal in the Float of Illinois No. 6 Coal.

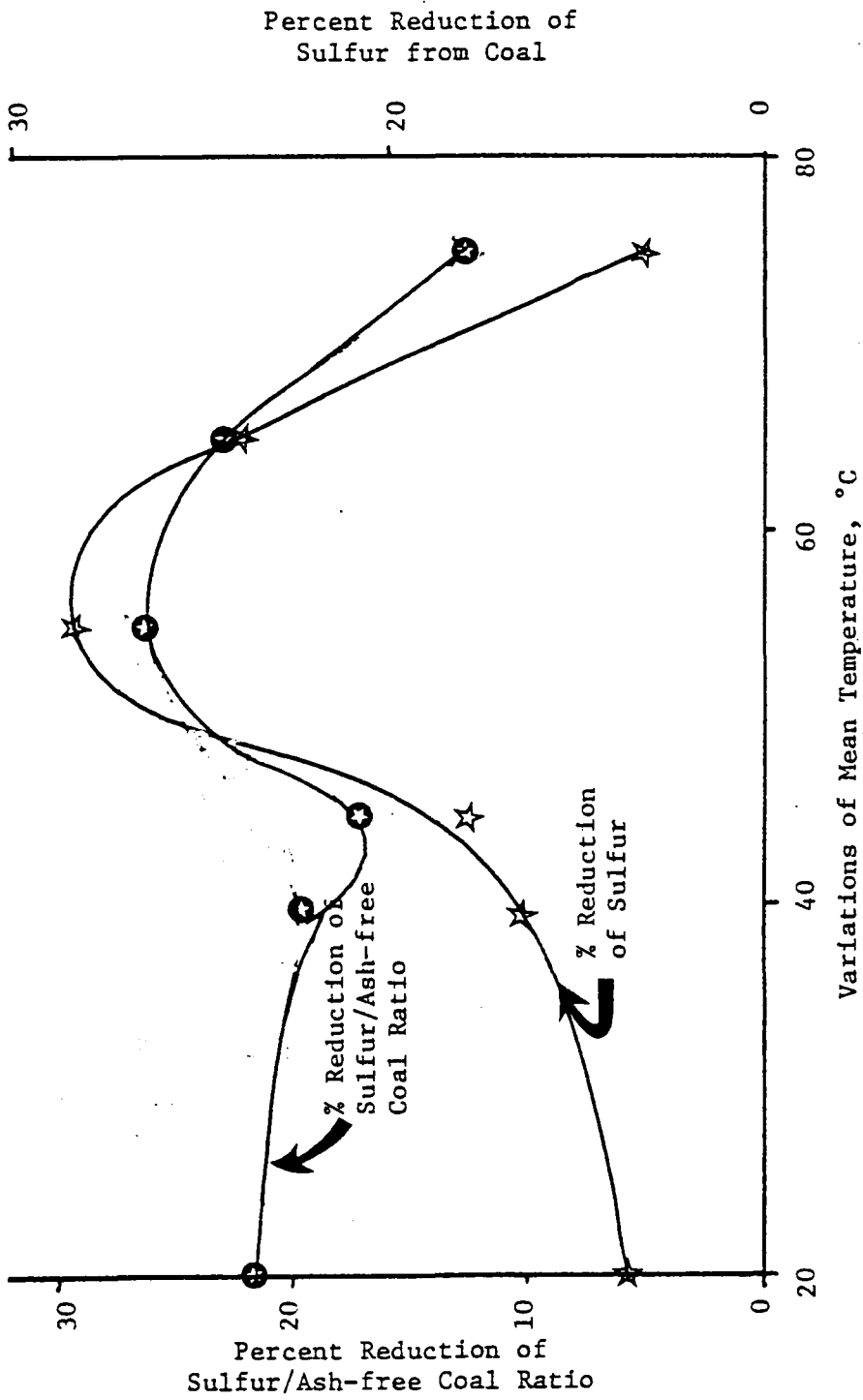


Figure 6.5. Variations of Mean Temperature versus Percent Reduction of Sulfur and Percent Reduction of Sulfur/Ash-free Coal Ratio. Illinois No. 6 Coal was Used.

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reached at 75°C. - The reduction ratio of sulfur/ash-free coal steadily decreased when the temperature increased from 20°C to 45°C and then reached its highest point at 55°C. This ratio then decreased from 26.3 to 10.7 when the temperature increased from 55 to 75°C. One should note that these results could be different if a different frother was used.

6.3.3 Comparison of the Effect of Different Combinations of Depressants and Frothers on Illinois No. 6 Coal Samples:

In this section of the report, the effect of frothers and depressants on the separation of ash and sulfur from Illinois No. 6 coal samples were studied. The pulverized Illinois No. 6 coal samples were tested with different reagents. The results of these tests are presented in Table 6.4 and in proportionally drawn bar graphs in Figure 6.6.

Selectively depressing pyrite by chemical reagents was the principal objective of these tests. Some of the pyrite depressants were examined and their results were compared. Later in this report, the results of depressing action of chemical reagents and the effect of the bacteria Thiobacillus ferrooxidans on depressing pyrite are compared. A systematic approach for examining such depressants was not followed in this work since such studies were beyond the scope of this work. Similar sets of studies were conducted on Pittsburgh and Middle Kittanning coal samples.

Potassium ferrocyanide, dextrin, and hydrofluoric acid were used as the pyrite depressants. Cresylic acid and terpineol were used as frothers. The flotation test procedures outlined in Section 4.3.1 were followed. The results of these tests are tabulated in Table 6.4. Figure 6.6 illustrates the weight percent distributions of sulfur, ash,

Table 6.4. Comparison of the Effect of Different Combinations of Depressants and Frothers on the Removal of Sulfur from Illinois No. 6 Coal Samples.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Dis-tribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Reagent Set
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
1	Float	77.1	11.9	88.1	3.6	31.5	95.8	63.1	18.2	34.2	a
	Sink	22.9	87.0	13.0	7.0	68.5	4.2	36.9			
	Composite Total	100	29.1	70.9	4.4	100	100	100			
2	Float	27.7	24.8	75.2	3.5	24.0	29.2	16.4	40.7	43.7	b
	Sink	72.3	30.0	70.0	6.1	76.0	70.8	83.6			
	Composite Total	100	28.6	71.4	5.9	100	100	100			
3	Float	48.5	17.4	82.6	3.6	26.9	58.4	35.6	26.7	39.1	c
	Sink	51.5	44.6	55.4	6.1	73.1	41.6	64.4			
	Composite Total	100	31.4	68.6	4.9	100	100	100			
21	Float	55.7	14.1	85.9	4.0	29.2	65.5	41.9	24.7	35.9	d
	Sink	44.3	43.0	57.0	6.9	70.8	34.5	58.1			
	Composite Total	100	26.9	73.1	5.3	100	100	100			

Remarks:

Size of the coal sample = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Frother conditioning time = 3 minutes

Table 6.4. (cont.)

Reagents used (reagent sets are as follows):

- a = pyrite depressant: 2 lb./ton potassium ferrocyanide
frother: cresylic acid added as required
- b = pyrite depressant: 2 lb./ton dextrin~~W~~
frother: 2 lb./ton terpeneol
- c = pyrite depressant: 2 lb./ton potassium ferrocyanide
frother: 2 lb./ton terpeneol
- d = pyrite depressant: 2 lb./ton hydrofluoric acid
frother: cresylic acid added as required

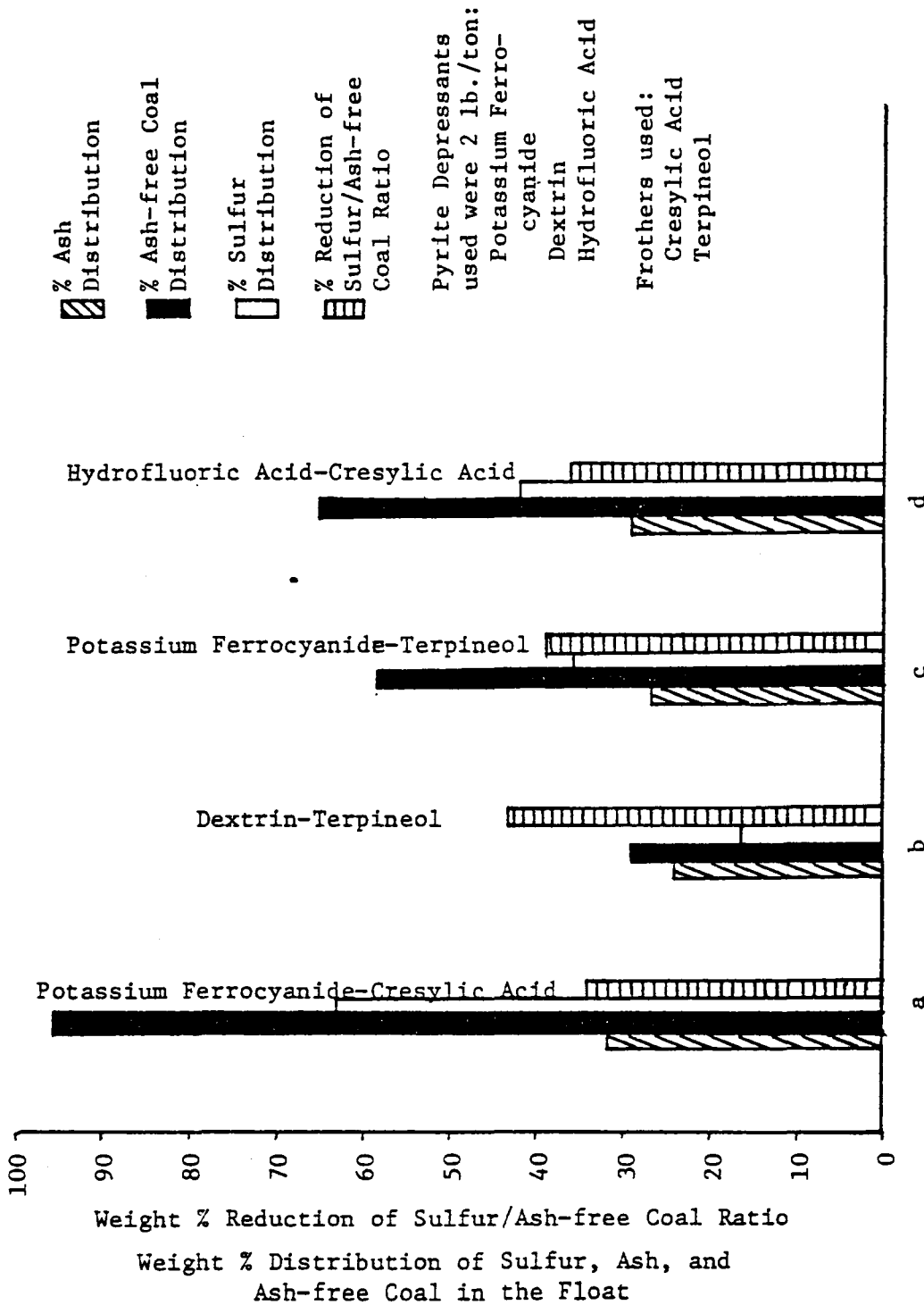


Figure 6.6. Bar Graphs Comparing the Effect of Different Combinations of Pyrite Depressant-Frother on Sulfur, Ash, and Ash-free Coal Distribution in the Float of Illinois No. 6 Coal.

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and ash-free coal in the float. Bar graph Set "a" in Figure 6.6 can be compared with Set "c." Potassium ferrocyanide was used for both tests, but terpeneol was used for Set "c" and cresylic acid was used for Set "a." Cresylic acid, having collecting ability, collected a higher weight distribution of combustibles (or ash-free coal) in the float. Cresylic acid also collected more sulfur in the float than when terpeneol was used. The use of the cresylic acid also gave a lower reduction ratio of sulfur/ash-free coal in this test (Set "a"). The use of terpeneol resulted in lower ash distributions in the float.

Terpeneol was used in Sets "b" and "c" in combination with dextrin and potassium ferrocyanide (as pyrite depressants). Since dextrin is a starch, it coated most of the particle surfaces; as a result, less ash-free coal and sulfur were distributed in the float. The distribution of ash in the float was relatively the same as in previous tests (since clays have a wettable surface under both conditions). The sulfur/ash-free coal reduction ratio was higher with dextrin than with all the other sets (43.5 percent).

Hydrofluoric acid was used in Set "d." The results of this test can be compared with Set "a," since cresylic acid was used as frother in both tests. It was noted that the collecting ability of cresylic acid was inhibited by hydrofluoric acid, since there was a lower distribution of sulfur, ash, and ash-free coal in the float. The use of hydrofluoric acid resulted in a slightly higher sulfur/ash-free coal reduction ratio than when sodium carbonate or potassium ferrocyanide was used as a pyrite depressant.

6.3.4 Comparison of the Effect of Different Pyrite Depressants on the Removal of Sulfur from the Pittsburgh Coal Samples:

In this series of flotation experiments, 2 lb./ton of four different types of pyrite depressants were used: potassium ferrocyanide, sodium carbonate, hydrofluoric acid, and the "bacterial liquor." The Pittsburgh coal samples were conditioned with the above chemical reagents for fifteen minutes and for four hours with the "bacterial liquor." The flotation pulp pH was raised to 8.0, and then cresylic acid was added to the pulp as frother. The standard flotation procedure, previously mentioned in Section 4.3.1 was followed. The results of these tests are tabulated in Table 6.5 and are illustrated in Figure 6.7. The bar graphs in Figure 6.7 indicate that the sulfur/ash-free coal reduction ratio continually increased from Sets "a" to "d." The "bacterial liquor" was the most effective depressant of pyrite. The next best pyrite depressant was hydrofluoric acid for this coal. The results of all of the tests indicated that high distributions of ash, sulfur, and ash-free coal were reported to the float. Consequently, a small sulfur reduction resulted.

6.3.5 Comparison of the Effects of Different Pyrite Depressants on the Removal of Sulfur and Ash from the Middle Kittanning Coal Samples:

Pulverized Middle Kittanning coal samples were conditioned in dextrin, potassium ferrocyanide, and "bacterial liquor." The coal was conditioned with 2 lb./ton of depressants for thirty minutes and with "bacterial liquor" for five minutes. No frother was used, yet almost one hundred percent recovery of combustibles was achieved. Only dextrin was able to coat some of the ash and pyrite and resulted in a lower ash

Table 6.5. Comparison of the Effect of Different Pyrite Depressants on the Removal of Sulfur from the Pittsburgh Seam Coal Samples.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Depressant Sets
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
B ₂	Float	93.8	8.9	91.9	5.3	68.9	97.2	91.3			
	Sink	6.2	60.9	39.1	7.6	31.3	2.8	8.7	2.4	6.0	a
	Composite Total	100.	12.1	87.9	5.4	100.	100.	100.			
B ₃	Float	95.6	8.4	91.6	5.8	75.4	98.0	92.6			
	Sink	4.4	59.5	40.5	10.3	24.6	2.0	7.4	3.3	5.9	a
	Composite Total	100.	10.6	89.4	6.0	100.	100.	100.			
B ₄	Float	93.4	8.6	91.4	4.2	70.1	96.4	87.3			
	Sink	6.6	52.0	48.0	8.7	29.9	3.6	12.7	6.4	9.4	b
	Composite Total	100.	11.5	88.5	4.5	100.	100.	100.			
B ₅	Float	94.3	8.9	91.1	6.4	72.1	97.2	90.3			
	Sink	5.7	57.0	43.0	11.4	27.9	2.8	9.7	4.2	7.0	b
	Composite Total	100.	11.6	88.4	6.7	100.	100.	100.			
B ₆	Float	94.0	8.7	91.3	4.6	69.1	97.3	87.5			
	Sink	6.0	61.0	39.0	10.2	30.9	2.7	12.5	6.8	9.9	c
	Composite Total	100.	11.8	88.2	4.9	100.	100.	100.			
B ₁	Float	91.9	7.8	92.2	3.4	67.1	94.9	82.9			
	Sink	8.1	43.3	56.7	7.9	32.9	5.1	17.1	9.8	12.7	d
	Composite Total	100.	10.7	89.3	3.8	100.	100.	100.			

Table 6.5. (cont.)

Remarks:

Size of the coal sample = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Frother conditioning time = 3 minutes

Pyrite conditioning time = 15 minutes

Bacterial Liquor conditioning time = 4 hours

Reagents used (pyrite depressant sets are as follows):

a = potassium ferrocyanide 2 lb./ton

b = sodium carbonate 2 lb./ton

c = hydrofluoric acid 2 lb./ton

d = bacterial liquor

Frother used:

Cresylic acid added as required

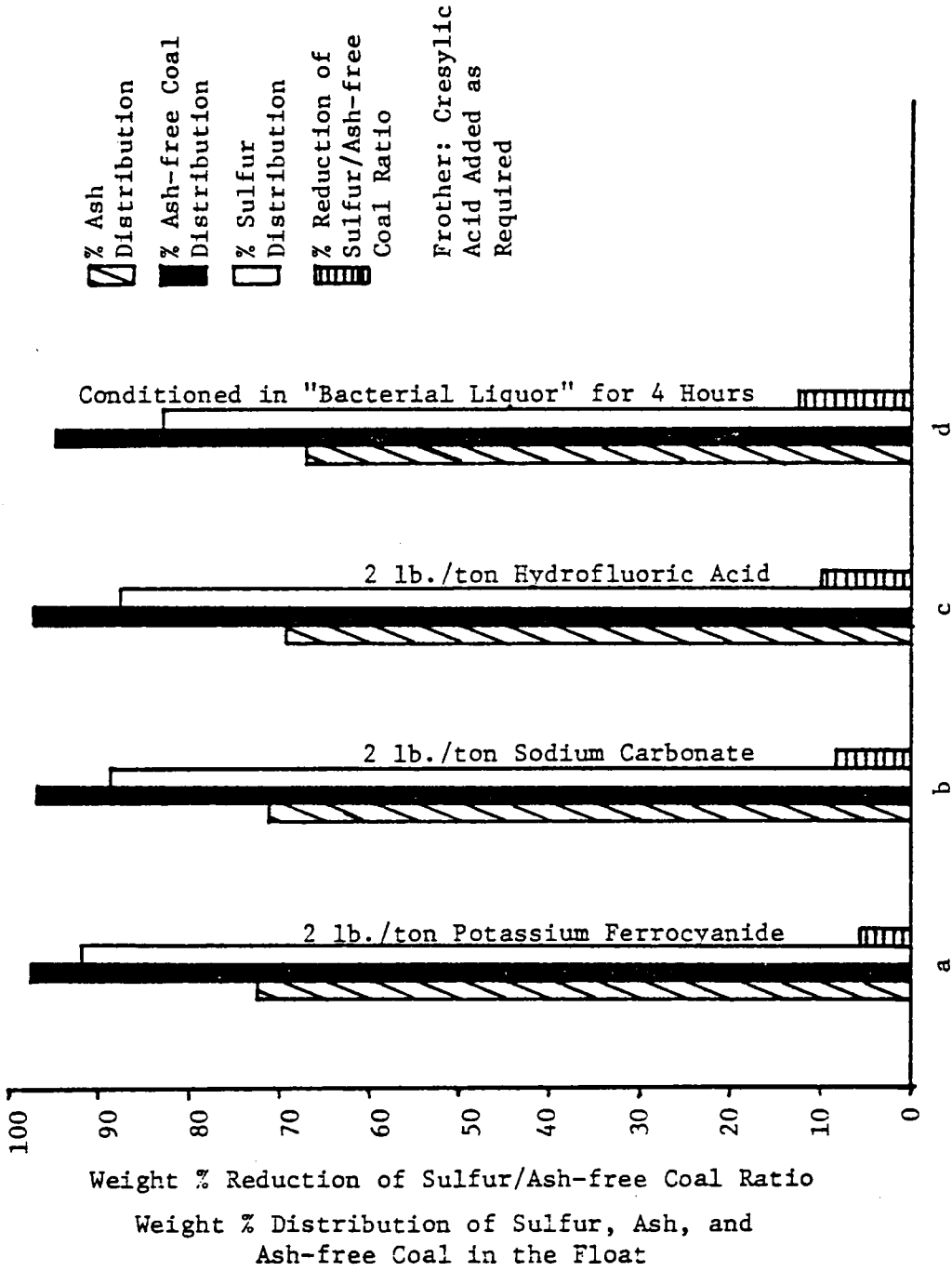


Figure 6.7. Bar Graphs Comparing the Effect of Different Pyrite Depressants on the Reduction of Sulfur/Ash-free Coal Ratio and Distribution of Sulfur, Ash, and Ash-free Coals in the Float of the Pittsburgh Seam Coal. M.I.N./78/VPI&SU

and sulfur distribution in the float than when other pyrite depressants were used. Consequently, the use of dextrin resulted in a higher sulfur/ash-free coal ratio (see Table 6.6 and Figure 6.8).

It was observed that the coal slurry had a coating of oily carbonaceous matter that covered most of the particles. This observation was made by preliminary visual examination of the froth.

6.3.6 Comparison of the Effect of Different Frothers on Percent Yield and Distribution of Ash, Sulfur, and Ash-free Coal in the Float of the Illinois No. 6 Coal Samples:

The following flotation tests were performed to investigate the distribution of sulfur, ash, and ash-free coal (or combustibles) in the float. The effectiveness of 1 lb./ton of potassium ferrocyanide, which was used in combination with different frothers, was studied. The pH of the flotation pulp was adjusted to 7.0. The standard flotation test method was used for all the tests (in accordance with the procedure outlined in Section 4.3.1). The results of these experiments are tabulated in Table 6.7. Figure 6.9 illustrates the bar graphs proportionally drawn to compare these results.

The highest combustible and sulfur distributions in the float resulted when terpineol was used (Set "g"). The use of aerofroth 65 and 2-Octanol, Sets "d" and "e," also resulted in high sulfur and combustible distribution in the float. The highest sulfur/ash-free coal reduction ratio was obtained when aerofroth 77 was used (Set "b"). However, less combustibles were recovered when aerofroth 77 was used. The use of MIBC in Set "a" gave an average set of results (50 percent combustible distribution and 45 percent sulfur distribution in the float).

Table 6.6. Comparison of the Effects of Different Pyrite Depressants on the Removal of Sulfur and Ash from the Middle Kittanning Coal Samples.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Depressant Sets
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
A ₁	Float	96.1	6.8	93.2	3.4	77.0	97.9	93.4	2.8	4.6	a
	Sink	3.9	51.6	48.4	6.12	23.0	2.1	6.6			
	Composite Total	100	8.5	91.5	3.5	100	100	100			
A ₂	Float	90.9	8.4	91.6	2.6	68.2	93.8	76.6	15.7	18.2	a
	Sink	9.1	39.3	60.7	8.1	31.8	6.2	23.4			
	Composite Total	100	11.2	88.8	3.1	100	100	100			
A ₆	Float	98.7	9.3	90.7	3.2	91.8	99.5	94.2	4.5	5.3	b
	Sink	1.3	63.1	36.9	14.9	8.2	0.5	5.8			
	Composite Total	100	10.0	90.0	3.3	100	100	100			
A ₃	Float	99.1	11.3	88.7	3.0	95.7	99.5	89.8	9.4	9.8	c
	Sink	.9	55.7	44.3	37.4	4.3	0.5	10.2			
	Composite Total	100	11.7	88.3	3.3	100	100	100			

Remarks:

Size of the coal sample = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 2 minutes

Pyrite depressant conditioning time = 30 minutes

Bacterial Liquor conditioning time = 5 minutes

Table 6.6. (cont.)

Reagents used:

Frother: none

Pyrite depressant:

a = dextrin 2 lb./ton

b = potassium ferrocyanide 2 lb./ton

c = bacterial liquor

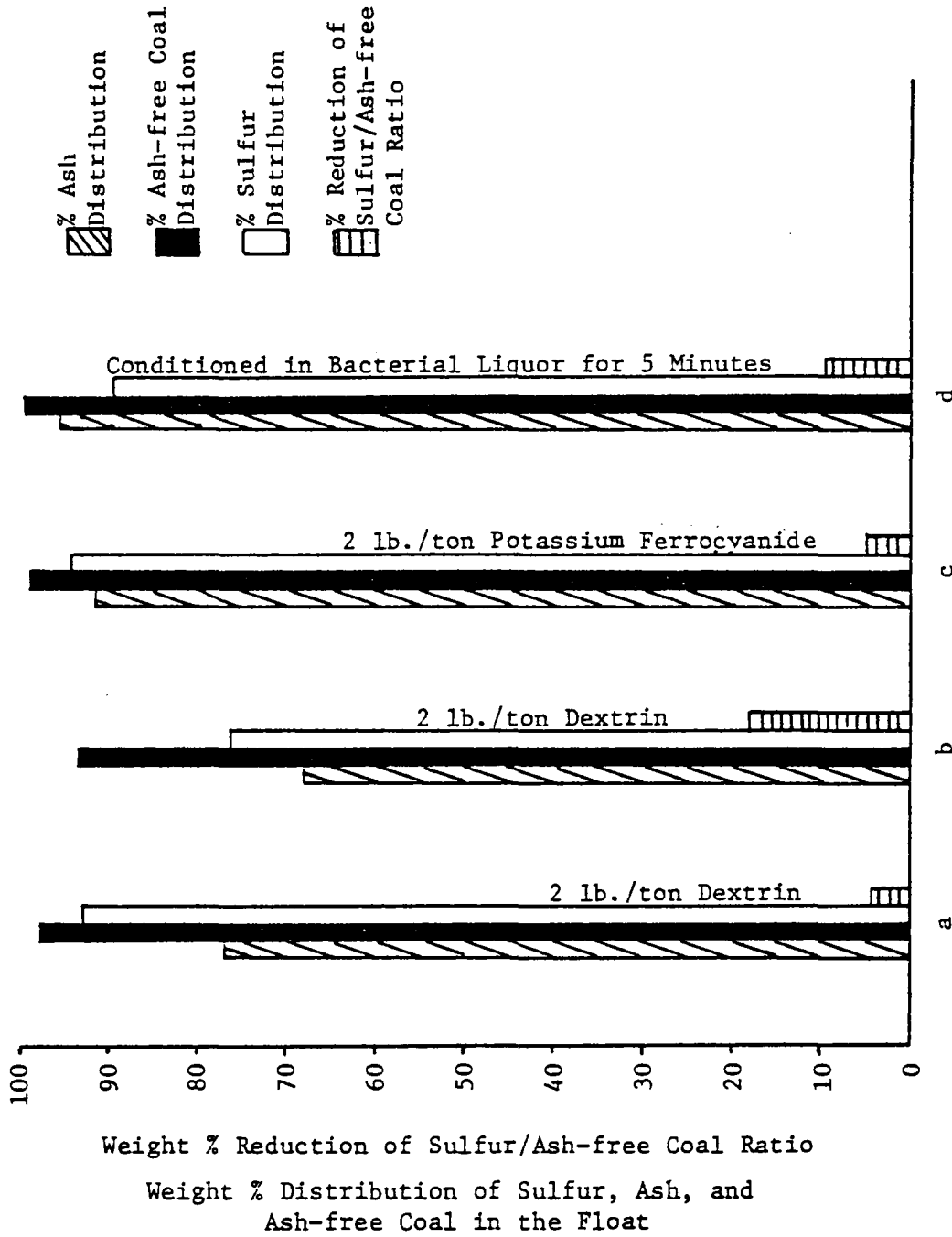


Figure 6.8. Bar Graphs Comparing the Effect of Different Pyrite Depressants on Reduction of Sulfur/Ash-free Coal Ratio and Sulfur, Ash, and Ash-free Coal Distribution of Middle Kittanning Coal Samples. M.L.N./78/VPI&SU

Table 6.7. Comparison of the Effect of Different Frothers on Flotation of Illinois No. 6 Coal Samples.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Frothers Sets
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₈₁	Float	52.3	20.6	79.4	5.2	42.3	55.7	45.1	13.8	19.2	a
	Sink	47.7	30.8	69.2	7.0	57.7	44.3	54.9			
	Composite Total	100	25.5	74.5	6.1	100	100	100			
C ₈₂	Float	58.2	20.3	79.7	5.7	48.6	61.3	46.2	20.5	24.5	a
	Sink	41.2	30.2	69.7	9.4	51.4	38.7	53.0			
	Composite Total	100	24.3	75.7	7.2	100	100	100			
C ₈₃	Float	63.3	18.1	81.9	5.8	45.8	69.1	54.4	14.1	21.3	b
	Sink	36.7	36.9	63.1	8.4	54.2	30.9	45.6			
	Composite Total	100	25.0	75.0	6.7	100	100	100			
C ₈₄	Float	43.4	18.8	81.2	5.3	39.3	44.5	29.0	14.1	34.9	b
	Sink	56.6	22.3	77.7	10.0	60.7	55.5	71.0			
	Composite Total	100	20.8	79.2	8.0	100	100	100			
C ₈₅	Float	53.8	16.4	83.6	6.8	33.4	61.1	49.1	8.7	19.7	c
	Sink	46.2	38.0	62.0	8.2	66.6	38.9	50.9			
	Composite Total	100	26.4	73.6	7.4	100	100	100			
C ₈₆	Float	62.7	15.5	84.5	5.0	36.7	72.1	53.8	14.1	25.3	c
	Sink	37.3	45.1	54.9	7.2	63.3	27.9	46.2			
	Composite Total	100	26.5	73.5	5.8	100	100	100			

Table 6.7. (cont.)

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Dis-tribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Frothers Sets
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₈₇	Float	78.1	18.8	81.2	6.6	53.8	87.2	78.6	0.0	9.8	d
	Sink	21.9	57.4	42.6	6.4	46.2	12.8	21.4			
	Composite Total	100	27.2	72.8	6.6	100	100	100			
C ₈₈	Float	74.5	22.9	77.1	6.4	78.7	73.3	75.5	0.0	0.0	d
	Sink	25.5	18.1	81.9	6.0	21.3	26.7	24.5			
	Composite Total	100	21.7	78.3	6.3	100	100	100			
C ₉₀	Float	76.5	18.1	81.9	5.5	52.6	85.4	71.7	6.2	16.0	e
	Sink	23.5	54.5	45.5	7.0	48.0	14.6	28.3			
	Composite Total	100	26.7	73.3	5.8	100	100	100			
C ₉₁	Float	70.7	16.9	83.1	5.8	46.9	78.9	69.0	2.3	12.4	e
	Sink	29.3	46.4	53.6	7.6	53.1	21.1	31.0			
	Composite Total	100	25.5	74.5	6.0	100	100	100			
C ₉₂	Float	62.4	19.8	80.2	6.9	48.1	67.4	61.2	1.6	8.8	f
	Sink	37.6	35.4	64.6	7.2	51.9	32.6	38.8			
	Composite Total	100	25.7	74.3	7.0	100	100	100			
C ₉₃	Float	62.0	18.3	81.7	5.7	45.1	67.7	57.1	7.9	15.7	f
	Sink	38.0	36.4	63.6	7.0	54.9	32.3	42.9			
	Composite Total	100	25.2	74.8	6.2	100	100	100			

Table 6.7. (cont.)

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Dis-tribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Frothers Sets
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₉₄	Float	81.0	16.0	84.0	6.4	51.7	90.8	82.0			
	Sink	19.0	63.6	36.4	5.9	48.3	9.2	18.0	0.0	9.7	g
	Composite Total	100	25.1	74.9	6.3	100	100	100			
C ₉₅	Float	79.7	17.6	82.4	7.1	52.8	89.4				
	Sink	20.3	61.7	38.8		47.2	10.6				g
	Composite Total	100	26.6	73.4		100	100				
C ₉₆	Float	42.9	22.3	77.7	7.6	37.4	44.8	45.6			
	Sink	57.1	28.1	71.9	6.8	62.6	55.2	54.4	0.0	0.0	h
	Composite Total	100	25.6	74.4	7.2	100	100	100			
C ₉₇	Float	35.9	21.1	78.9	6.6	30.0	37.9	32.2			
	Sink	64.1	27.6	72.4	7.8	70.0	67.1	67.8	10.3	15.1	h
	Composite Total	100	25.3	74.7	7.4	100	100	100			

Remarks:

Size of the coal samples = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Pyrite depressant conditioning time = 15 minutes

Frother conditioning time = 3 minutes

Table 6.7. (cont.)

Reagents used:

Pyrite depressant: 2 lb./ton potassium ferricyanide

Frother: amount of frother used = 1 lb./ton

a = MIBC

b = Aerofroth 77

c = Aerofroth 71

d = Aerofroth 65

e = 2-Octanol

f = Pine oil

g = Terpineol

h = Cresylic acid

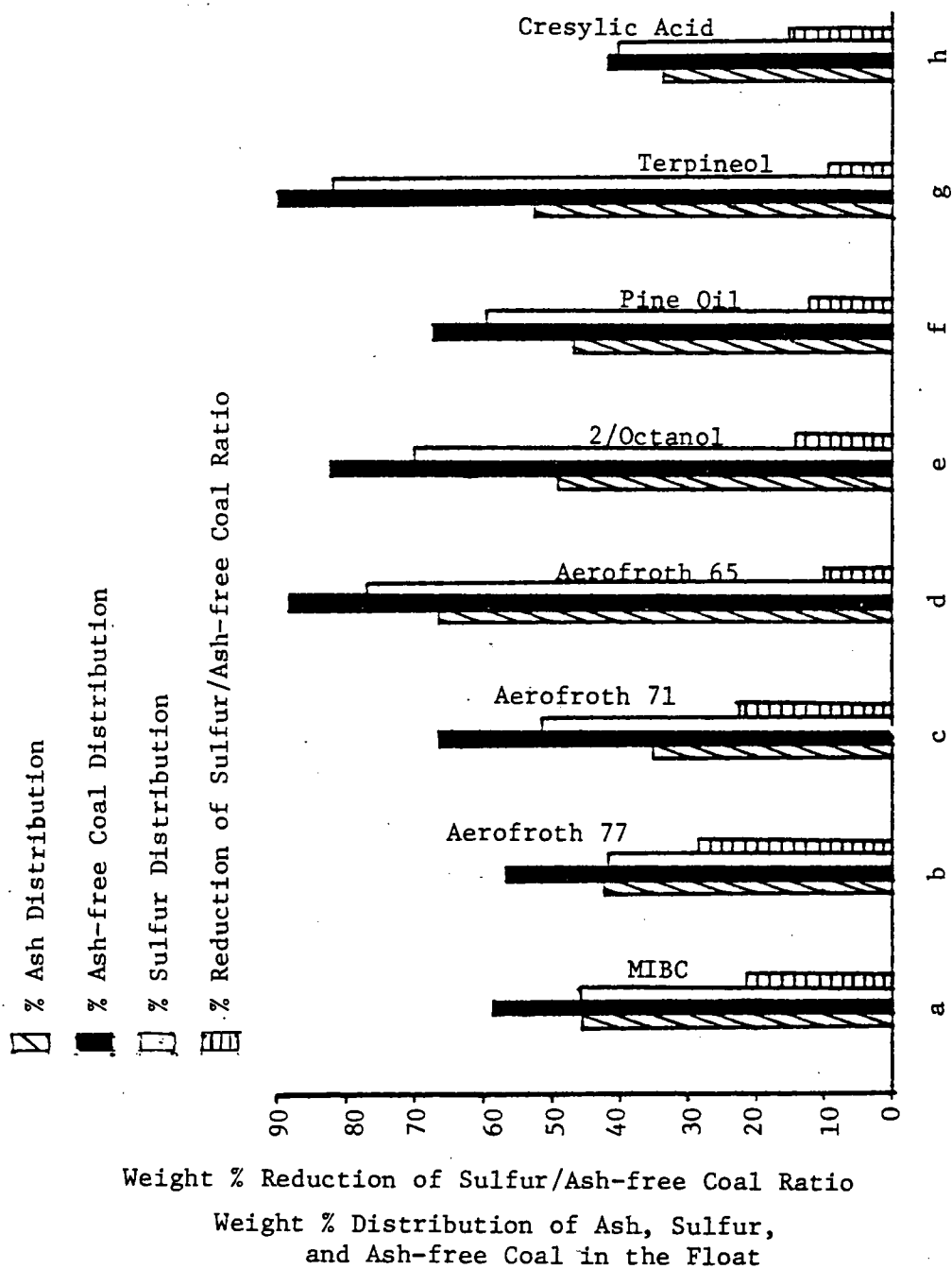


Figure 6.9. Bar Graphs Comparing the Effect of Different Frothers on Reduction of Sulfur/Ash-free Coal Ratio, and Ash, Ash-free Coal, and Sulfur Distribution in the Float.

The ash distribution in the float was lowest when aerofroth 71 was used (Set "c"). In Set "h," 1 lb./ton of cresylic acid was used, which gave the poorest results. The previous results with cresylic acid as frother were much better since greater amounts of cresylic acid were used. The test results in the graph in Figure 6.9 are the average of the two tests.

6.3.7 Comparison of the Effect of Different Chain Length Alcohols on the Sulfur/Ash-free Coal Reduction Ratio and Distribution of the Float Materials:

These tests were performed to study the effect of different alcohols on the distribution of sulfur, ash, and ash-free coal in the float. No pyrite depressant or collector was used. The standard procedure of flotation tests, as described in Section 4.3.1, was followed. A pH of 7.0 was maintained in the flotation cell. The results of these tests are tabulated in Table 6.8 and illustrated in Figure 6.10.

The highest combustible distribution in the float was obtained when aerofroth 77 was used in Set "c." The highest sulfur/ash-free coal reduction ratio was obtained when aerofroth 65 was used, but the lowest combustible recovery was also obtained in this test (Set "d"). The use of MIBC gave an average set of results for sulfur and combustible recovery in the float and the lowest ash distribution in the float.

6.3.8 Variations of the Length of the Frothing Time and its Effect on Recovery of Ash, Sulfur, and Ash-free Coal in the Float, Using Illinois No. 6 Coal Samples (Examination of Grab and Run Theory):

This experiment was performed to study the manner in which sulfur, ash, and combustibles were distributed in the float with respect to

Table 6.8. Effect of Different Chain Length Alcohols on the Distribution of Ash, Sulfur, and Ash-free Coal in the Float.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Reagent Sets
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
	Float	46.0	14.0	86.0	4.5	24.8	53.4	38.9			
22	Sink	54.0	36.2	63.8	6.0	75.2	46.6	61.1	15.5	27.3	a
	Composite Total	100	26.0	74.0	5.3	100	100	100			
	Float	53.5	15.4	84.6	4.4	33.5	60.0	49.2			
23	Sink	46.5	35.1	64.9	5.2	66.5	40.0	50.8	8.0	18.0	b
	Composite Total	100	24.5	75.4	4.8	100	100	100			
	Float	57.1	14.4	85.6	3.0	31.9	65.8	51.5			
26	Sink	42.9	40.9	59.1	6.3	68.1	34.2	48.5	9.7	21.7	c
	Composite Total	100	25.7	74.2	5.6	100	100	100			
	Float	38.8	19.0	81.0	3.8	28.4	42.4	27.9			
28	Sink	61.2	30.3	69.7	6.2	71.6	57.6	72.1	28.0	34.0	d
	Composite Total	100	25.9	74.1	5.3	100	100	100			

Remarks:

Size of the coal sample = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Frother conditioning time = 5 minutes

Table 6.8. (cont.)

Reagents used:

pyrite depressant: none

frother: amount of frother = 2 lb./ton

a = MIBC

b = Octinol

c = Aerofroth 77

d = Aerofroth 65

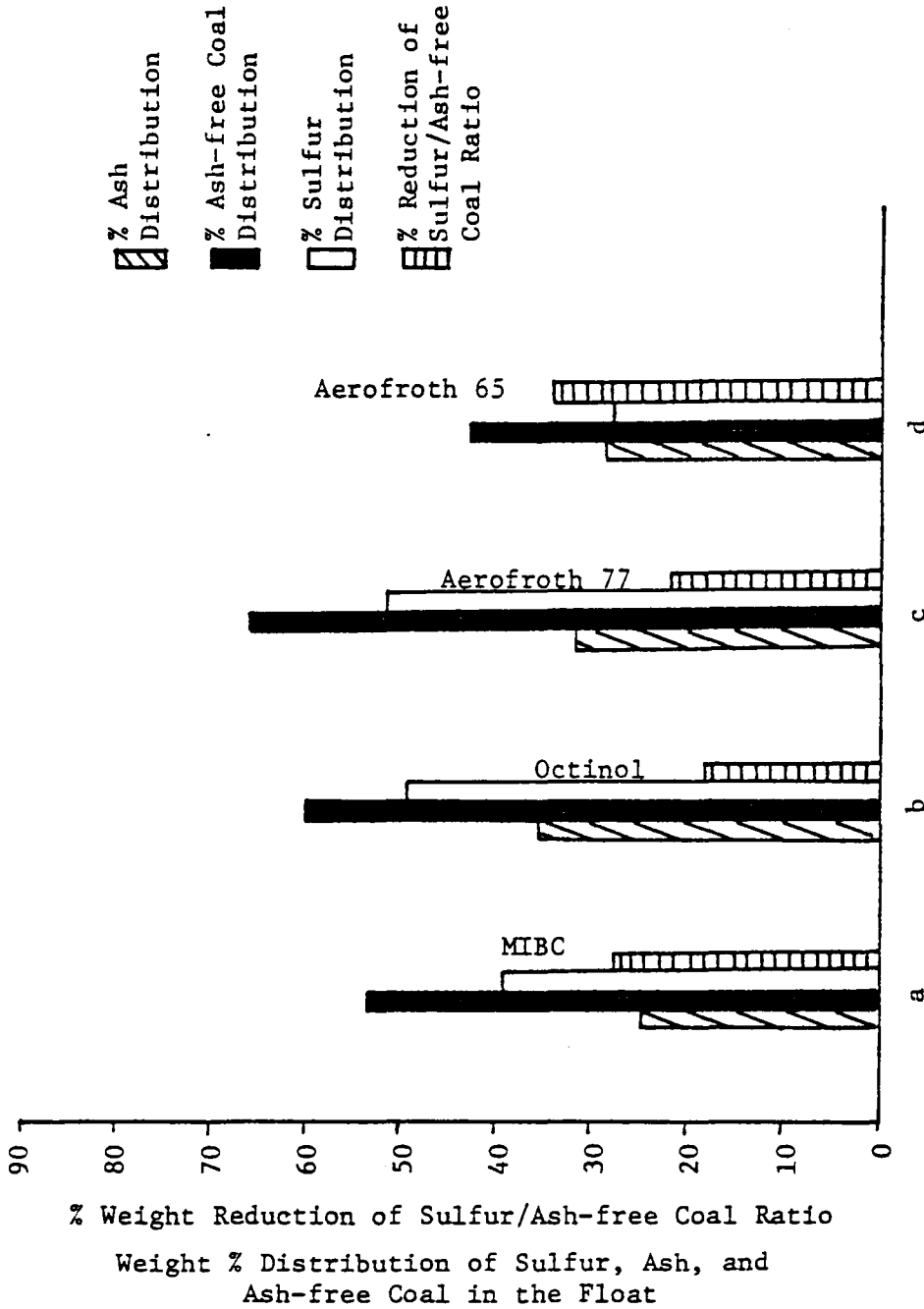


Figure 6.10. Bar Graphs Comparing the Effect of Different Chain Length Alcohols on the Distribution of Sulfur, Ash, and Ash-free Coal in the Float of Illinois No. 6 Coal Samples.
 Note: No Pyrite Depressant was Added.

flotation time. Grab and Run Theory is based on the fact that the best separation occurs during early parts of the frothing time. Hence, in flotation of coal, the highest separation of sulfur and ash from the ash-free coal should occur at the beginning of the frothing time and before the frothing time is half over.

In this test, the froth was continuously scraped off the top of the cell and pushed into a pan. The pan was changed at exactly one minute intervals for nine minutes. At the end of the ninth minute the froth had turned white and no more particles were coming up to the surface. The fractions of the froth in different pans were analyzed for sulfur and ash content. Distribution of sulfur, ash, and ash-free coal were calculated, and a cumulative percent of each component of the float was found with respect to increased frothing time. Cresylic acid was used as a frother. The pH was adjusted to 7.0 at the start of the test. The rest of the test procedures were followed according to the standard procedures of flotation, previously described in Section 4.3.1. The results of these tests are tabulated in Table 6.9. Figure 6.11 shows the cumulative percent distributions of the float components and the yield.

The results showed that at the first minute of the frothing time the highest percent yield was collected in the froth. The distribution of ash, sulfur, and combustibles in the float were the highest during the first minute.

The analysis percent of the individual float fractions indicated that there was an increasing trend of ash content where combustible recovery decreased with respect to time. The sulfur content of the individual float fraction fluctuated and there was no definite decreasing

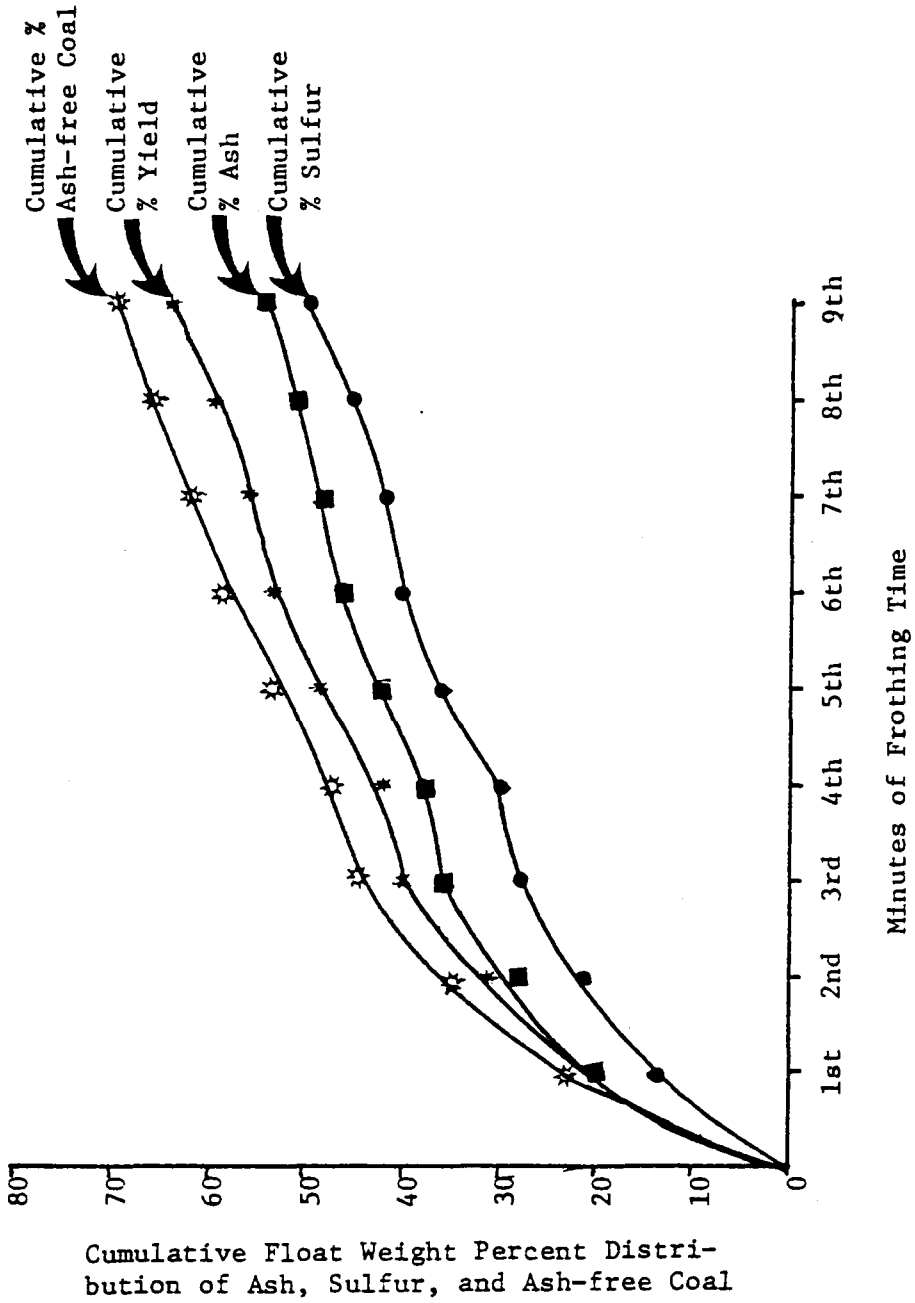


Figure 6.11. Variations of Frothing Time versus Cumulative-Float Weight Percent Distribution of Ash, Sulfur, and Ash-free Coal Distribution (Examination of Grab and Run Theory).

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or increasing pattern.

6.3.9 Double Stage Flotation of Middle Kittanning Coal Samples and its Effect on Removal of Ash and Sulfur:

It was previously mentioned that Middle Kittanning coal samples had a coating of oily carbonaceous matter over most of the particles. A single stage flotation lifted about one hundred percent of sulfur, ash, and ash-free coal to the surface. Therefore a second stage of flotation was added to the process.

The coal was conditioned with potassium ferrocyanide (2 lb./ton) for fifteen minutes. The pulp was then floated. The float was put into a second flotation stage. The results of the two tests are tabulated in Table 6.10. Ninety percent of the ash, ninety-seven percent of the combustibles (ash-free coal), and ninety-three percent of the sulfur were distributed in the float. These results show that even with the addition of a second stage to the flotation process, there was no significant separation of sulfur from the Middle Kittanning coal samples.

Table 6.10. Double Stage Flotation of Middle Kittanning Coal Samples and its Effect on the Removal of Ash and Sulfur.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur		
A ₁₇	Float	96.4	9.6	90.4	4.0	90.4	97.1	92.6	4.0	4.6
	Sink ₁	3.3	25.4	74.6	8.7	8.2	2.7	6.8		
	Sink ₂	.3	48.8	51.2	8.2	1.4	.2	.6		
	Composite Total	100	10.2	89.8	4.2	100	100	100		
A ₁₈	Float	97.2	8.4	91.6	4.1	86.0	98.4	93.3	4.0	5.2
	Sink ₁	1.4	52.8	47.2	11.2	7.8	0.7	3.7		
	Sink ₂	1.4	41.9	58.1	9.0	6.2	0.9	3.0		
	Composite Total	100	9.5	90.5	4.2	100	100	100		

Remarks:

Size of the coal sample = minus 65 mesh

Flotation cell conditions:

pH = 8.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 2 minutes

Pyrite depressant conditioning time = 15 minutes

The froth from the first stage was floated again in the second stage.

Reagents used:

Frother: none

Pyrite depressant: 2 lb./ton potassium ferrocyanide

6.4 Flotation of the Coals Conditioned with the Bacteria Thiobacillus ferrooxidans:

The following tests were performed to determine the effect of the bacteria Thiobacillus ferrooxidans on altering (oxidizing) the surface of coal pyrite. The pyrite would then be depressed in the flotation process as a result of its surface alteration. In the past, bacterial leaching techniques were used to completely oxidize the pyrite by Thiobacillus ferrooxidans. The removal of pyrite from coal by complete leaching methods required days of retention time. But in this work, the superficial bacterial oxidation of coal pyrite and its depression in the flotation process was achieved in a short period of time (2 to 5 hours for optimum results). This new technique of using bacterial action to depress coal pyrite resulted in the removal of about 20 percent of the total sulfur from the samples of Illinois No. 6 coal in a five hour retention time period. This 20 percent reduction of total sulfur corresponds to removal of about 40 percent of pyritic sulfur from the Illinois No. 6 coal samples.

6.4.1 Definition of Old and New "Bacterial Liquors":

The term "new bacterial liquor" refers to a 9'K-ferrous-ferric salt combination in which the bacteria Thiobacillus ferrooxidans is constantly converting the ferrous sulfate to ferric sulfate. During this period the viable count of the bacteria increases to its highest level. The color of the "bacterial liquor" at this time period (1-4 days) turns steadily darker. Due to the increase of the viable count and decrease of substrate (ferrous sulfate), the organisms start to die off. The excretion of the dead cells is detrimental to the rest of the living

organisms. Therefore, the best time period for the use of "bacterial liquor" runs between 4 to 7 days after the inoculation of the 9'K salts with Thiobacillus ferrooxidans. In this report the "bacterial liquor" used during this period is referred to as "new bacterial liquor." The "bacterial liquor" used after this time period is referred to as "old bacterial liquor." Due to the heterogeneous distribution of Thiobacillus ferrooxidans in the liquid, the conventional viable count by the agar plate technique could not be used. A successful indirect count of the organisms by measuring the concentration of ammonia (converted from cellular nitrogen components) was used by Atkins (1976). However, such a systematic approach to this problem was beyond the scope of this work.

6.4.2 Retention Time Studies of Illinois No. 6 Coal in the Freshly Made "Bacterial Liquor" Using Cresylic Acid as Frother:

Samples of Illinois No. 6 coal were conditioned in new "bacterial liquor" for different time intervals. The previously outlined flotation process (Section 4.3.1) was used for all of the tests. The pH of the flotation pulp was raised to 8.0 and cresylic acid was added to the pulp as required. The samples were conditioned in the "bacterial liquor" for various time intervals (between 20 minutes to five hours). The results of these tests are tabulated in Table 6.11. Figure 6.12 illustrates the distribution percentages of sulfur, ash, and ash-free coal in the float.

The distribution of sulfur, ash, and ash-free coal in the float increased as the retention time increased. The distribution of sulfur in the float decreased from 78 percent to 54 percent when the retention

Table 6.11. Retention Time Studies of Illinois No. 6 Coal in "Bacterial Liquor". Effect of Increased Retention Time on Removal of Sulfur and Ash.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Time
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₁₈	Float	82.8	16.0	84.0	4.5	51.4	93.7	78.0	5.8	16.8	10 min.
	Sink	17.2	72.9	37.1	6.1	48.6	6.3	22.0			
	Composite Total	100	25.8	74.2	4.8	100	100	100			
C ₂₀	Float	76.5	17.3	82.7	4.6	48.0	87.4	64.4	15.0	26.3	20 min.
	Sink	23.5	61.0	39.0	8.3	52.0	12.6	36.5			
	Composite Total	100	27.6	72.4	5.5	100	100	100			
C ₁₄	Float	78.5	15.3	84.7	4.4	46.0	90.0	73.8	6.0	17.9	30 min.
	Sink	21.5	65.6	34.4	5.7	54.0	10.0	26.6			
	Composite Total	100	26.1	73.9	4.7	100	100	100			
C ₁₃	Float	75.6	13.9	86.1	5.4	40.9	87.6	72.9	3.6	16.8	1 hr.
	Sink	24.4	62.3	37.7	6.2	59.1	12.4	27.1			
	Composite Total	100	25.7	74.3	5.6	100	100	100			
C ₁₅	Float	76.6	15.0	85.0	4.5	44.0	88.0	68.7	10.3	22.0	2 hrs.
	Sink	23.4	62.3	37.7	6.5	56.0	11.9	31.3			
	Composite Total	100	26.1	73.9	5.0	100	100	100			
C ₈	Float	78.0	12.0	88.0	5.1	37.6	91.4	73.3	5.9	19.7	3 hrs.
	Sink	22.0	70.5	29.5	6.6	62.4	8.6	26.8			
	Composite Total	100	24.9	75.1	5.4	100	100	100			

Table 6.11. (cont.)

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Dis-tribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Time
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₁₇	Float	66.8	15.7	84.3	4.6	39.7	76.5	56.4	5.6	26.3	4 hrs.
	Sink	33.2	48.0	52.0	7.2	60.3	23.5	43.6			
	Composite Total	100	26.4	73.6	5.4	100	100	100			
C ₁₉	Float	65.5	23.7	76.3	4.3	47.3	74.4	54.7	16.5	26.4	5 hrs.
	Sink	34.5	50.1	49.9	6.7	52.7	25.6	45.3			
	Composite Total	100	32.8	67.2	5.1	100	100	100			

Remarks:

Size of the coal sample = minus 65 mesh

Flotation cell conditions:

pH = 8.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Conditioning time of the coal in the "bacterial liquor" = variable

Frother conditioning time = 3 minutes

Reagents used:

Frother: cresylic acid was added as required

Pyrite depressant: "bacterial liquor", pulp density = 5 (w/v)

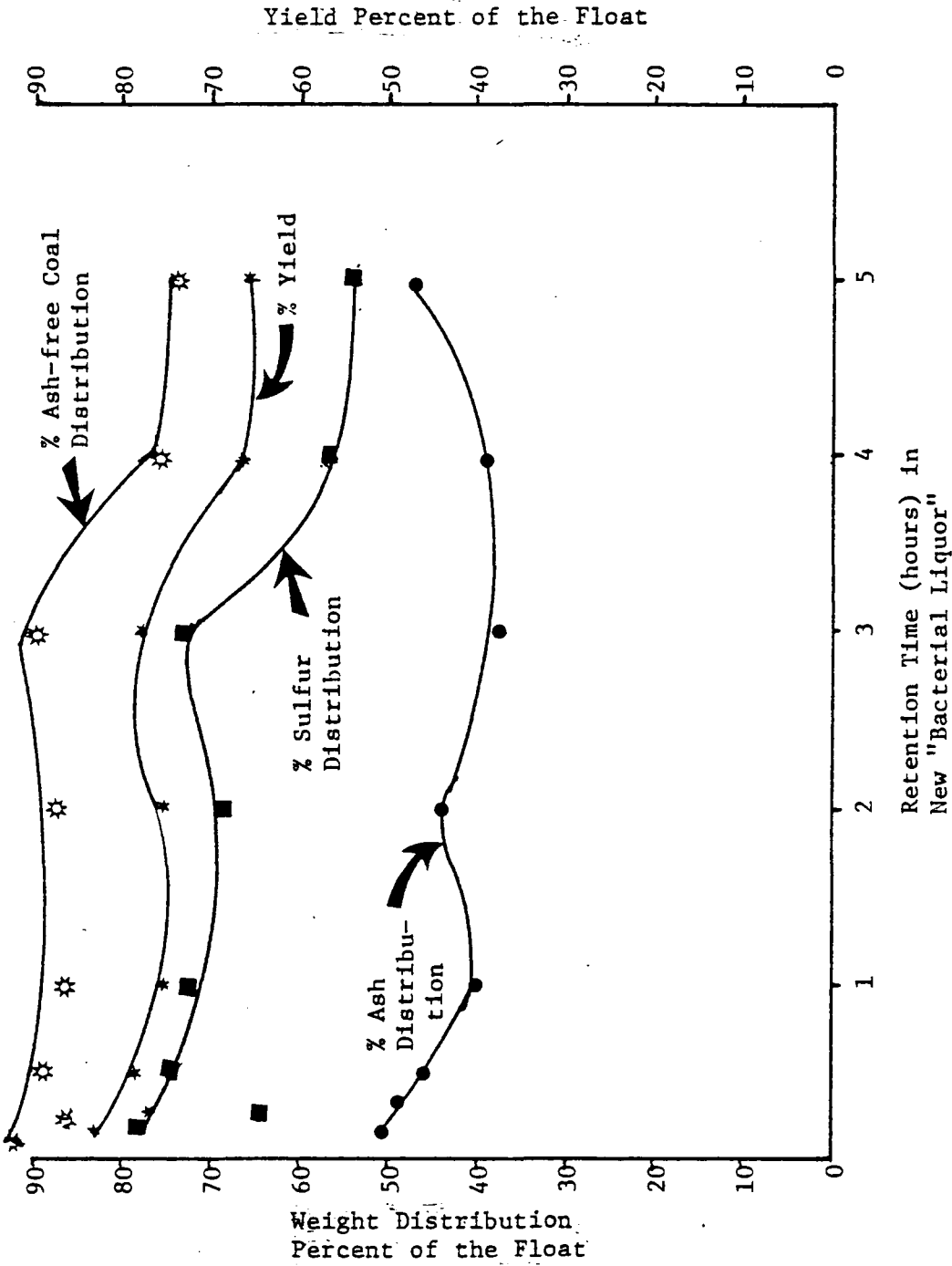


Figure 6.12. Retention Time of Illinois No. 6 Coal Samples in the New "Bacterial Liquor" versus Weight Distribution of Sulfur, Ash, and Ash-free Coal Using Cresylic Acid.

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time was increased from 10 minutes to 5 hours. After three hours of retention time, the distribution of ash-free coal was relatively unchanged. However, the distribution of ash-free coal in the float decreased from 91 to 75 percent after three hours of retention. The distribution of ash in the float varied within 5 percent at different retention time intervals. The yield also varied within five percent but, after three hours of retention time, the percent yield decreased from 78 percent to 65 percent.

Figure 6.13 shows the effect of increased retention time on the reduction of sulfur/ash-free coal ratio and the reduction of sulfur. The reduction of sulfur/ash-free coal ratio was increased from 5 to 26.4 percent when the retention time was increased from zero to five hours. The total sulfur reduction was increased from 2.5 to 16.5 percent when the retention time increased from 1 to 5 hours. There was a sudden decrease of both sulfur/ash-free coal reduction ratio and percent sulfur reduction at the three hour retention time. At retention times from 10 minutes to 30 minutes, high reductions of sulfur from the Illinois No. 6 coal samples resulted. The high reduction of sulfur at 10-30 minute retention times could be credited to the effect of the salts in the "bacterial liquor" and not to the bacterial action.

6.4.3 Retention Time Studies of Illinois No. 6 Coal Samples in the Old "Bacterial Liquor," Using Cresylic Acid as Frother:

Retention time studies were performed using old "bacterial liquor." Retention time intervals of two to twelve hours were examined. The same conditions as were used for coal retention of Illinois No. 6 coal samples in "new bacterial liquor" were used in these tests. The results

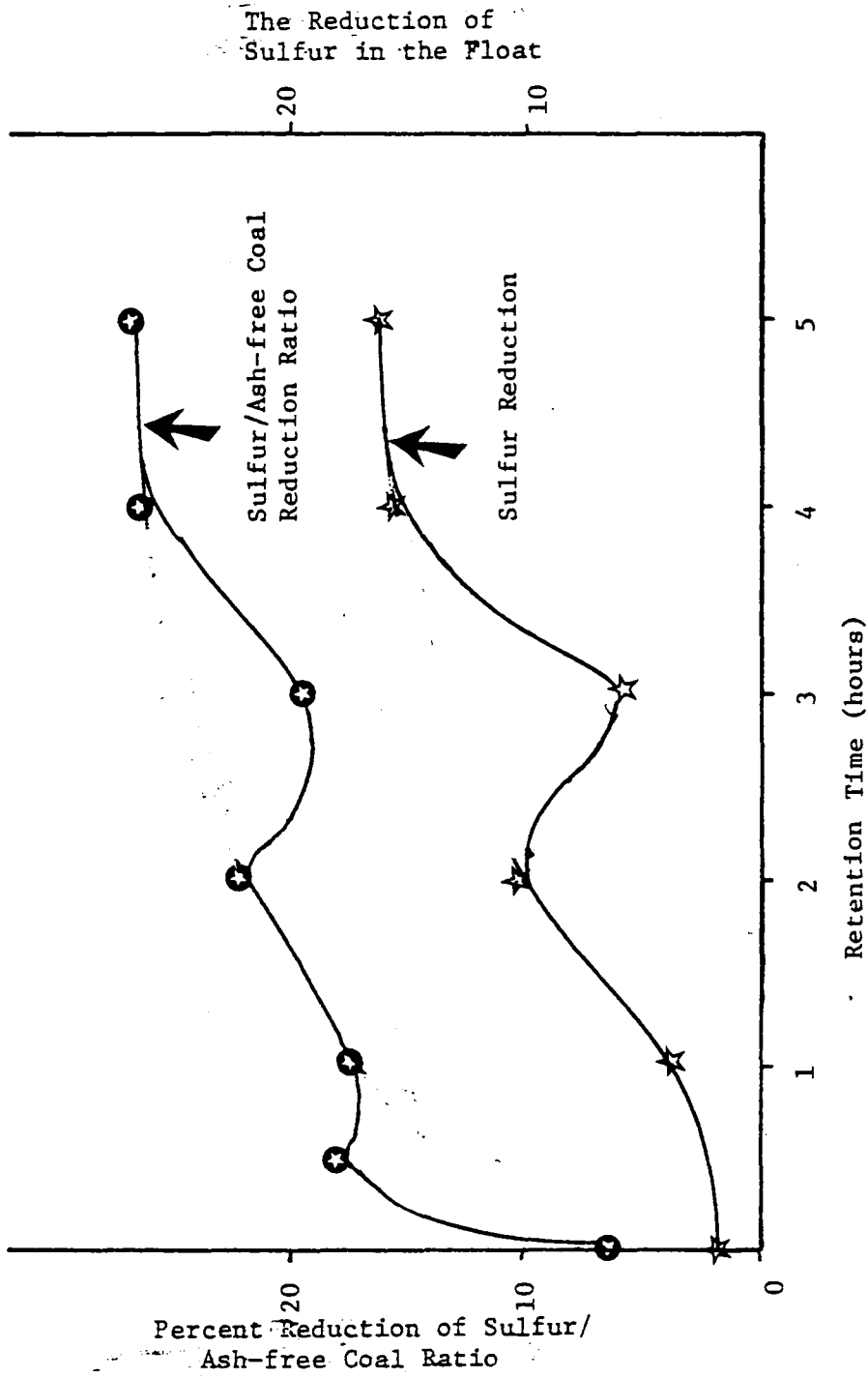


Figure 6.13. Retention Time of Illinois No. 6 Coal in the "Bacterial Liquor" versus Reduction of Sulfur and Sulfur/Ash-free Coal Reduction Ratio. M.L.N./78/VPI&SU

are tabulated in Table 6.12. The distribution of sulfur, ash, and ash-free coal, as well as the percent yield of the float, are shown in Figure 6.14.

The distributions of float components (sulfur, ash, and ash-free coal) were quite erratic. The sulfur distribution increased in the float when the retention time was increased. Distribution of combustibles in the float increased with respect to an increase in retention time. The ash distribution in the float decreased at three hours retention time (30.5 percent), but it reached a maximum level at four hours of retention time (54.1 percent).

6.4.4 Comparison of the Effects of Old and New "Bacterial Liquors" on the Removal of Sulfur:

The yields and combustible recoveries were higher when the new "bacterial liquor" (nbl) was used than when old "bacterial liquor" (obl) was used. The yields and combustible recoveries at two and three hour retention times were substantially higher when new "bacterial liquor" was used. It was noted that the combustible recovery increased at four and five hour retention times when old "bacterial liquor" was used. The recovery of sulfur in the float was highest at four and five hour retention times with old "bacterial liquor" and lowest with new "bacterial liquor." The ash distribution in the float was quite erratic. It was concluded that when old "bacterial liquor" was used, more sulfur was reported in the float.

6.4.5 Retention Time Studies of Illinois No. 6 Coal Samples in Recycled Old "Bacterial Liquor" Using Cresylic Acid as Frother:

The following tests were performed, using recycled old "bacterial

Table 6.12. Retention Time Studies of Illinois No. 6 Coal Samples in the Old "Bacterial Liquor."

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Time
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₆₆	Float	48.3	22.1	77.9	6.6	43.0	50.0	36.8	23.7	26.3	2 hrs.
	Sink	51.7	27.3	72.7	10.5	57.0	50.0	63.2			
	Composite Total	100	24.8	75.2	8.6	100	100	100			
C ₆₇	Float	38.6	19.8	80.2	7.4	30.5	42.0	37.9	2.4	9.0	3 hrs.
	Sink	61.2	29.0	71.0	7.7	70.5	58.0	62.1			
	Composite Total	100	25.2	74.8	7.5	100	100	100			
C ₆₈	Float	70.7	19.7	80.3	7.0	54.1	76.4	67.2	4.9	12.0	4 hrs.
	Sink	29.3	40.3	59.7	8.1	45.9	23.6	32.8			
	Composite Total	100	25.7	74.3	7.3	100	100	100			
C ₇₄	Float	70.2	17.2	82.8	7.8	47.9	77.7	69.0	1.6	11.1	5 hrs.
	Sink	29.8	44.0	56.0	8.3	52.1	22.3	31.0			
	Composite Total	100	25.2	74.8	8.0	100	100	100			
C ₇₂	Float	46.8	19.0	81.0	6.7	35.0	50.8	41.2	11.9	18.9	12 hrs.
	Sink	53.2	31.0	69.0	8.5	65.0	49.2	58.8			
	Composite Total	100	25.4	74.6	7.7	100	100	100			

Remarks:

Size of the coal sample = minus 65 mesh

Table 6.12. (cont.)

Flotation cell conditions:

pH = 8.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Conditioning time of the coal samples in the old bacterial liquor =
variable

Frother conditioning time = 3 minutes

Reagents used:

Frother: cresylic acid added as required

Pyrite depressant: old bacterial liquor, pulp density = 5 (w/v)

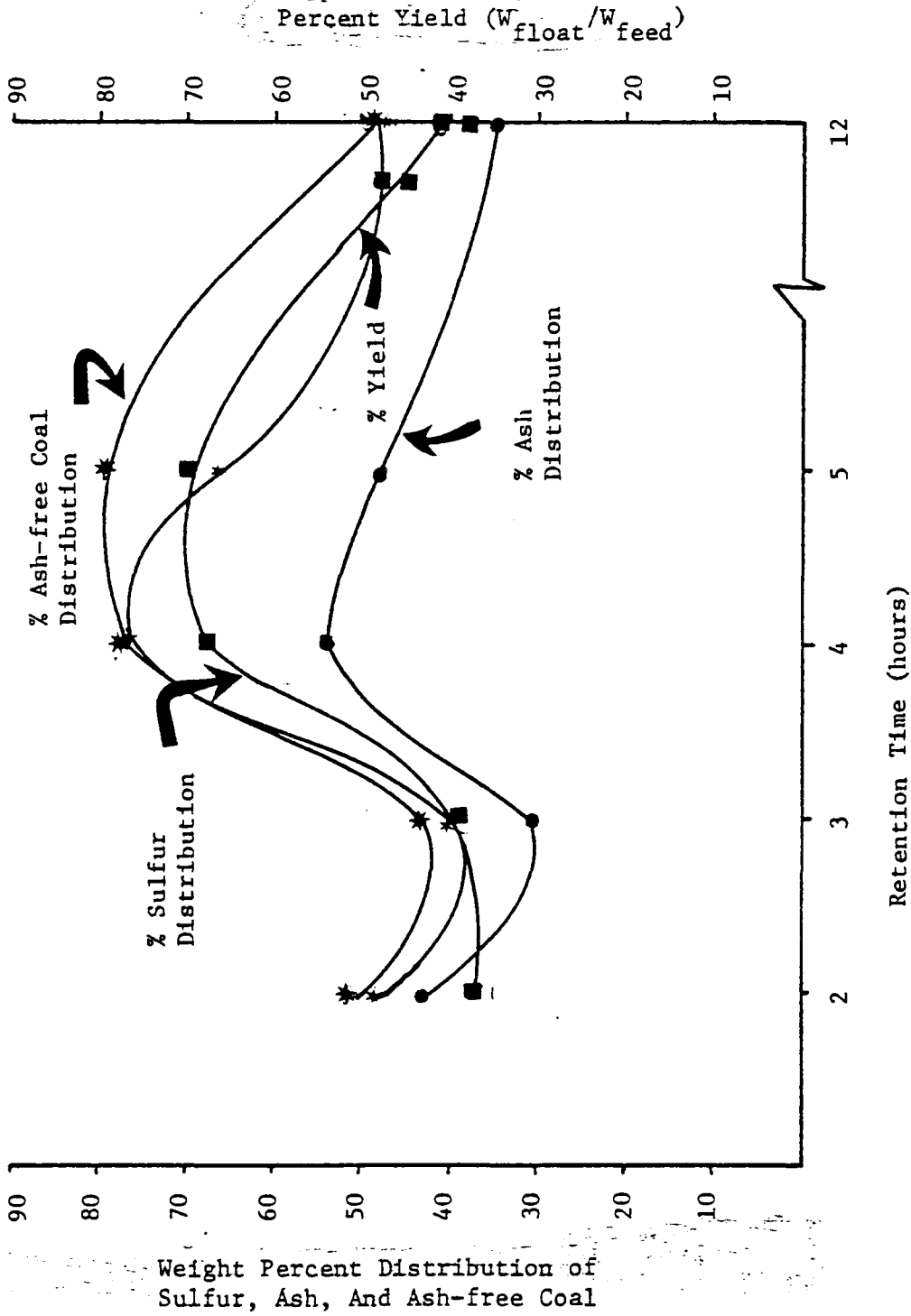


Figure 6.14. Retention Time versus Weight Percent Distribution of Sulfur, Ash, and Ash-free Coal, Using Illinois No. 6 Coal, Cresylic Acid, and Old "Bacterial Liquor."

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liquor" in order to assess its effectiveness on removal of sulfur at different retention times. The procedures and conditions for these tests were the same as the procedure described in Section 4.3.2. The results are tabulated in Table 6.13. Figure 6.15 shows the graphs of percent weight distributions of sulfur, ash, and ash-free coal versus retention time.

The distribution of ash, ash-free coal, and percent yield of the float varied within five percent with an increase in retention time. The distribution of sulfur in the float varied within ten percent when the retention time was increased. It was concluded that the distribution of the materials in the float is unchanged with respect to the increase in retention time.

The curves of the two reduction ratios of sulfur/ash-free coal resulted from the use of old and recycled old "bacterial liquor" are shown in Figure 6.16. The results of these two sets of tests are compared as follows.

The recycled old "bacterial liquor" produced a more linear curve than the recycled "bacterial liquor" itself. This was due to the fact that the combustible distribution in the float remained the same for the recycled liquor, while its sulfur distribution decreased with respect to the increase in retention time.

6.4.6 Retention Time Studies of Illinois No. 6 Coal Samples in Freshly Made "Bacterial Liquor" Using MIBC as Frother:

The object of the following tests was to study the effect of a frother, MIBC, on the flotation of coal samples conditioned in the new "bacterial liquor" and recycled new "bacterial liquor." The test con-

Table 6.13. Retention Time Studies of Illinois No. 6 Coal Samples in Recycled Old "Bacterial Liquor."

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Dis-tribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Time
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₆₉	Float	65.2	19.8	80.2	7.5	49.7	70.7	59.4	8.8	15.9	2 hrs.
	Sink	34.8	37.6	62.4	9.6	50.3	29.3	40.6			
	Composite Total	100	26.0	74.0	8.3	100	100	100			
C ₇₀	Float	71.5	18.3	81.7	7.2	49.6	79.4	66.0	7.7	16.9	3 hrs.
	Sink	28.5	46.6	53.4	9.3	50.4	20.6	44.0			
	Composite Total	100	26.4	73.6	7.8	100	100	100			
C ₇₁	Float	62.2	19.6	80.4	7.2	45.5	68.3	48.9	21.4	28.4	5-1/2 hrs.
	Sink	37.8	38.7	61.3	12.3	54.5	31.7	51.1			
	Composite Total	100	26.8	73.2	9.1	100	100	100			
C ₇₃	Float	66.6	19.5	80.5	7.1	51.6	71.7	54.7	17.8	23.6	12 hrs.
	Sink	33.4	36.5	63.5	11.6	48.4	28.4	45.3			
	Composite Total	100	25.2	74.8	8.6	100	100	100			

Remarks:

Size of the coal samples = minus 65 mesh

Flotation cell conditions:

pH = 8.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Conditioning time in the frother = 3 minutes

Conditioning time of the coal samples in the Recycled Old Bacterial Liquor* = variable

Frother conditioning time = 3 minutes

Table 6.13. (cont.)

Reagents used:

Frother: Cresylic acid was added as required

Pyrite depressant: Recycled old "bacterial liquor," pulp
density = 5 (w/v)

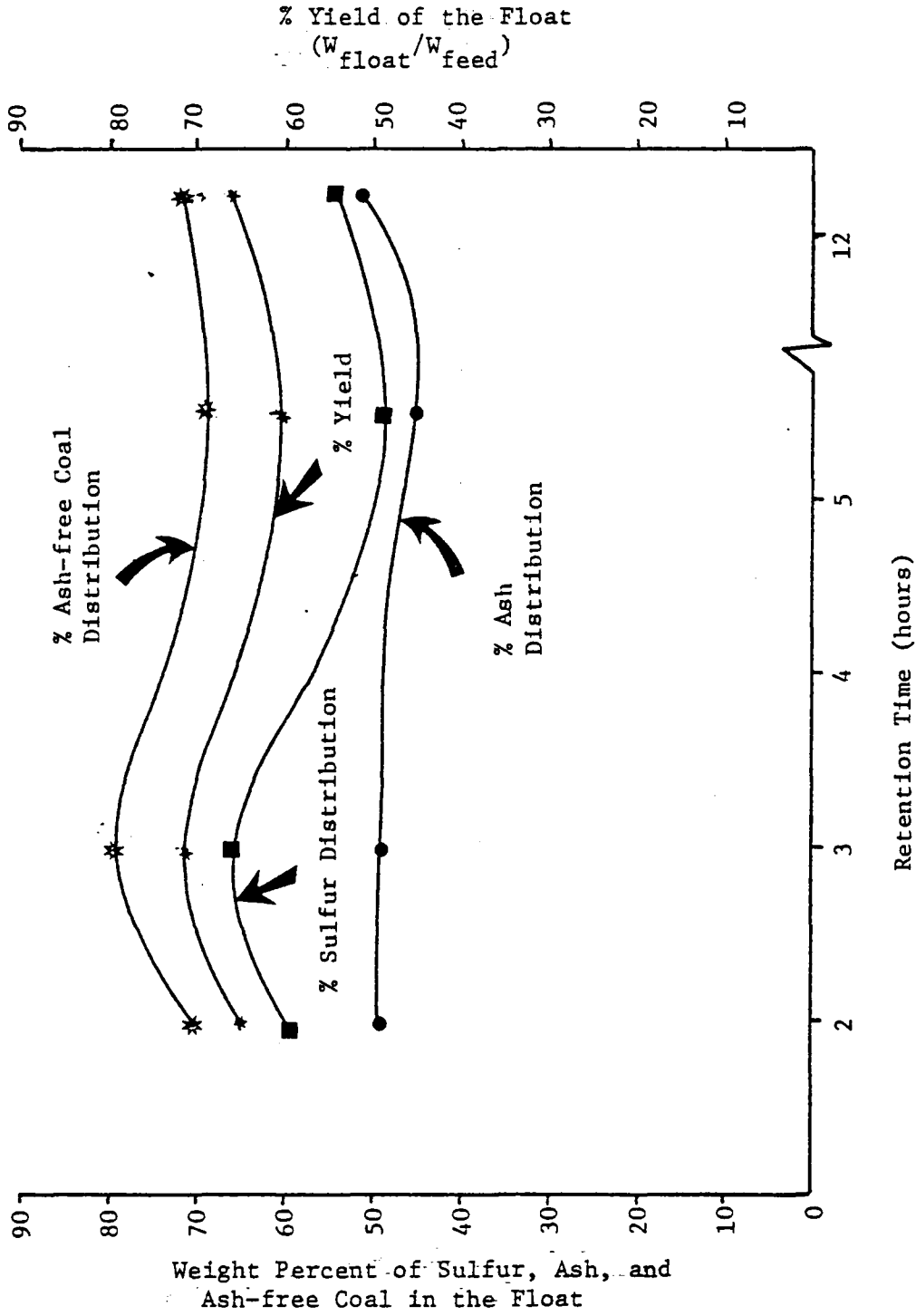


Figure 6.15. Retention Time versus Weight Distribution of Sulfur, Ash, and Ash-free Coal in the Float of Illinois No. 6 Coal Samples Using Recycled Old "Bacterial Liquor."

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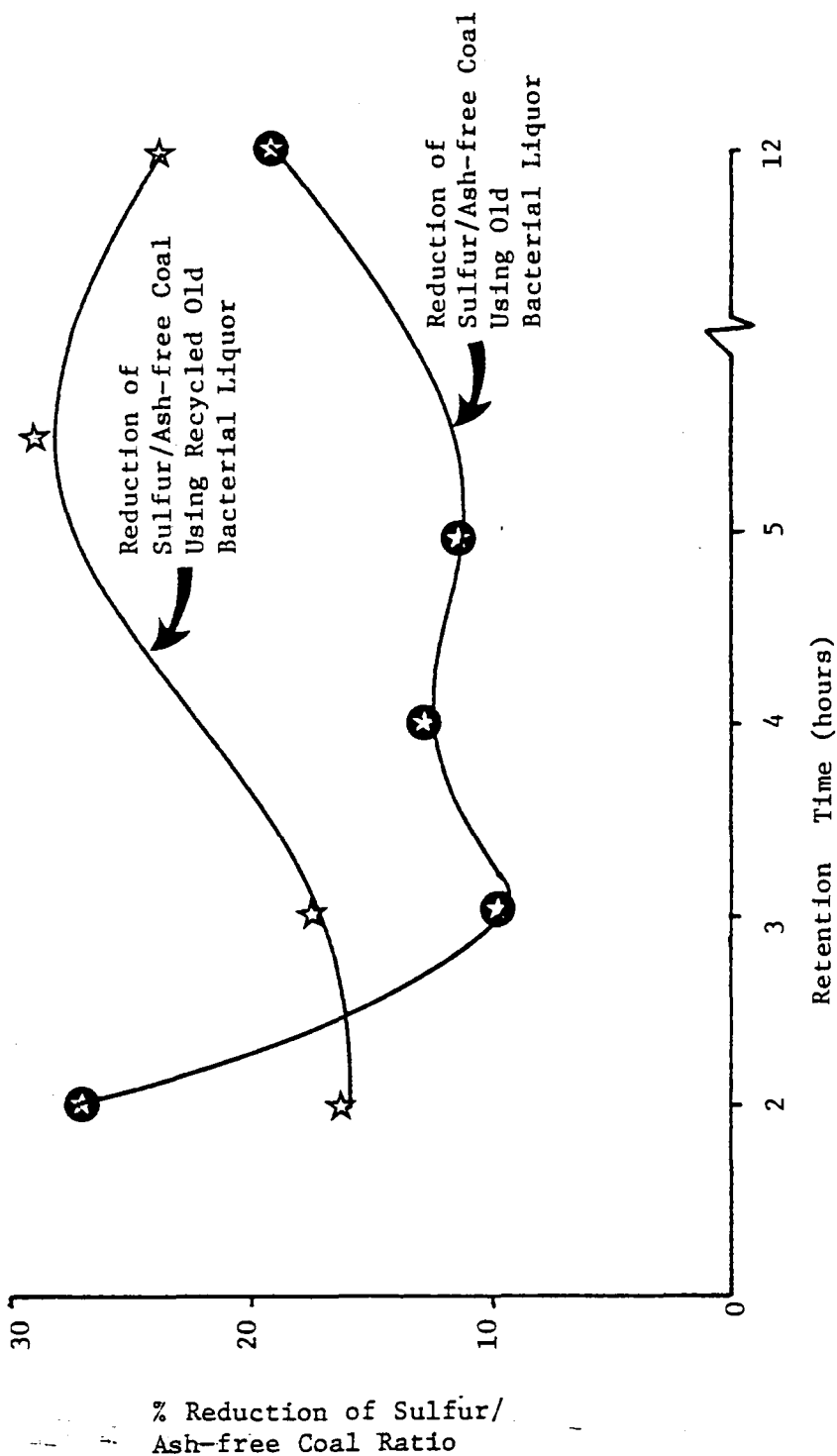


Figure 6.16. Retention Time versus Percent Reduction of Sulfur/Ash-free Coal Ratio of Illinois No. 6 Coal Samples Using Old "Bacterial Liquor" and Recycled Old "Bacterial Liquor."

M.L.N./78/VPI&SU

ditions were the same as before (Section 4.3.2). Two pounds per ton of methyl iso-butyl carbinol (MIBC) was used as frother. This alcohol has no collecting ability, whereas cresylic acid, used in the previous section, has some collecting ability. The results of these tests using new "bacterial liquor" and recycled new "bacterial liquor" are tabulated in Tables 6.14 and 6.15. Figures 6.17 and 6.18 show the distribution of sulfur, ash, and ash-free coal in the float of Illinois No. 6 coal samples. The test results are discussed here. Also, a comparison is made between the test results with "bacterial liquor" and recycled "bacterial liquor." Finally, the test results with MIBC and cresylic acid are compared.

The distribution of float material increased with the increase of retention time of the Illinois No. 6 coal samples in the "bacterial liquor." The three hour retention time test gave the lowest yield with lowest sulfur, ash, and ash-free coal distribution in the float (see Table 6.14 and Figure 6.17).

When recycled "bacterial liquor" was used to condition the Illinois No. 6 coal samples, higher yields were obtained at longer retention times. Also, the distribution of ash-free coal increased with the increase in retention time. The distribution of ash decreased from 41 percent at two hours to 34 percent at four hours retention time. The distribution of sulfur in the float increased with an increase in retention time. The highest sulfur distribution in the float was observed at three hours of retention time (see Table 6.15 and Figure 6.18).

In comparing the two sets of test results with recycled and original "bacterial liquor" (original "bacterial liquor" is the liquor which

Table 6.14. Retention Time Studies of Illinois No. 6 Coal in the Freshly Made "Bacterial Liquor" Using MIBC as Frother.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Dis-tribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Time
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₃₀	Float	53.7	18.6	81.4	5.6	41.1	57.7	51.1	5.0	11.6	2 hrs.
	Sink	46.3	30.9	69.1	6.2	58.9	42.3	48.9			
	Composite Total	100	24.3	75.7	5.9	100	100	100			
C ₂₄	Float	72.7	12.7	87.3	5.8	37.2	84.4	69.4	4.0	17.7	3 hrs.
	Sink	27.3	57.0	43.0	6.8	62.8	15.6	30.6			
	Composite Total	100	24.8	75.2	6.0	100	100	100			
C ₂₇	Float	67.9	15.0	85.0	5.6	34.6	81.7	48.0	12.0	26.7	4 hrs.
	Sink	32.1	59.8	40.2	7.9	65.4	18.3	52.0			
	Composite Total	100	29.4	70.6	6.3	100	100	100			
C ₃₃	Float	74.9	16.0	84.0	3.9	47.4	84.2	56.5	25.0	33.0	5 hrs.
	Sink	25.1	53.1	46.9	9.0	52.6	15.8	43.5			
	Composite Total	100	25.3	74.7	5.2	100	100	100			

Remarks:

Size of the coal samples = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Conditioning time in the frother = 1 minutes

Conditioning time of the coal samples in the "bacterial liquor" = variable

Table 6.14. (cont.)

Reagents Used:

Frother: 2 lb./ton MIBC

Pyrite depressant: "Bacterial liquor," pulp density = 5 (w/v)

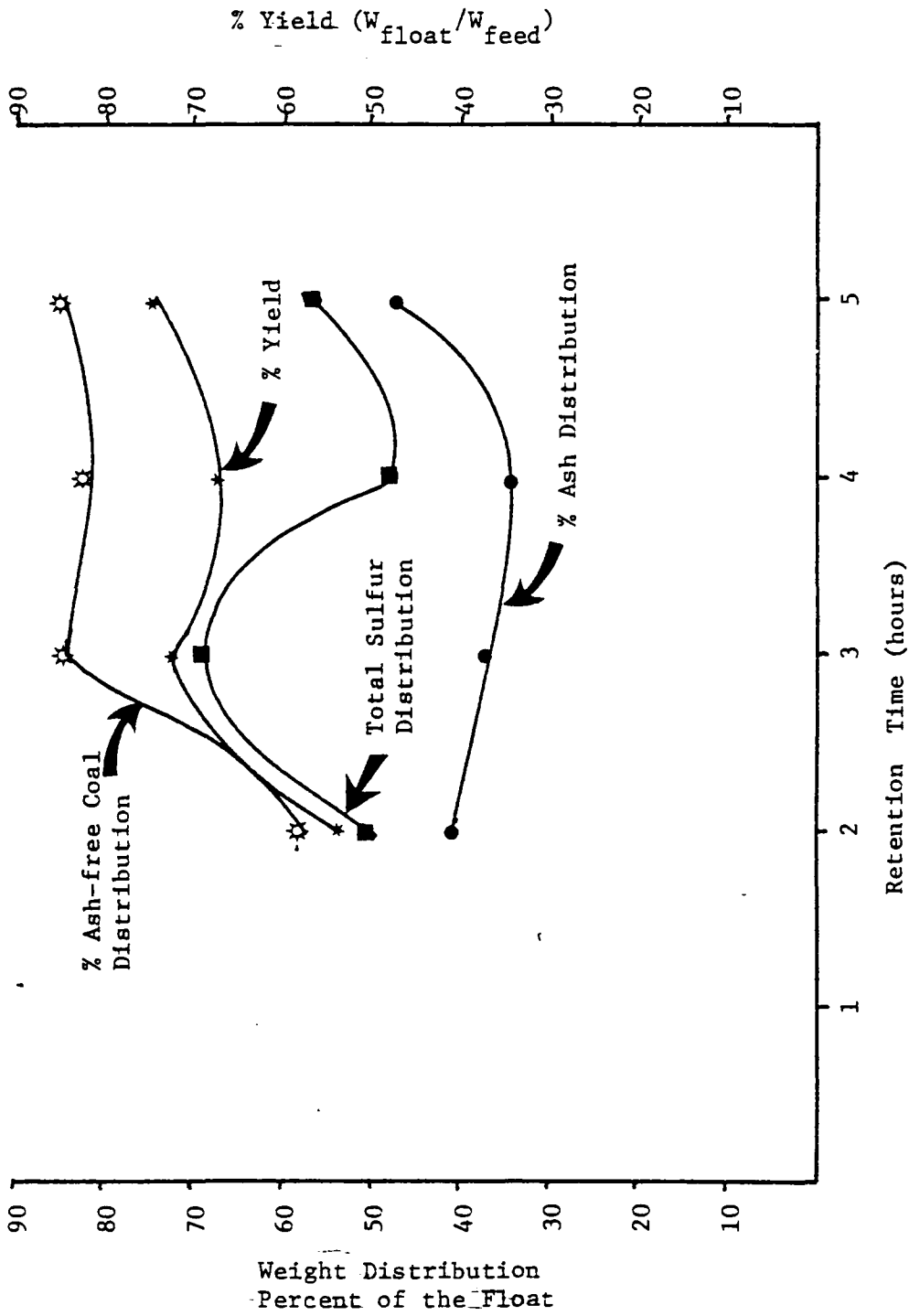


Figure 6.17. Retention Time of Illinois No. 6 Coal Samples in "Bacterial Liquor" versus Weight Distribution of Sulfur, Ash, Ash-free Coal, and Yield, Using MIBC as Frother. M.L.N./78/VPI&SU

Table 6.15. Retention Time Studies of Illinois No. 6 Coal in Recycled "Bacterial Liquor" Using MIBC as Frother.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Time
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₃₁	Float	54.8	33.0	67.0	4.8	58.0	53.4	49.1	10.0	8.0	2 hrs.
	Sink	45.2	29.0	71.0	6.0	42.0	46.6	50.9			
	Composite Total	100	31.2	68.8	5.4	100	100	100			
C ₂₅	Float	39.5	18.6	81.4	4.7	28.7	43.2	35.1	11.0	18.8	3 hrs.
	Sink	60.6	30.2	69.8	5.7	71.3	56.8	64.9			
	Composite Total	100	25.6	74.4	5.3	100	100	100			
C ₂₉	Float	66.9	15.3	84.7	4.6	38.6	77.1	53.7	20.0	30.3	4 hrs.
	Sink	33.1	49.3	50.7	8.1	61.4	22.9	46.3			
	Composite Total	100	26.5	73.5	5.8	100	100	100			
C ₃₄	Float	72.6	30.1	69.9	4.5	59.4	80.3	59.7	18.0	25.7	5 hrs.
	Sink	27.4	54.6	45.4	8.1	40.6	19.7	40.3			
	Composite Total	100	36.8	63.2	5.5	100	100	100			

Remarks:

Size of the coal samples = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Conditioning time in the frother = 1 minute

Conditioning time of the coal samples in the recycled "bacterial liquor" = variable

Table 6.15. (cont.)

Reagents used:

Frother: 2 lb./ton MIBC

Pyrite depressant: Recycled "bacterial liquor," pulp density =
5 (w/v)

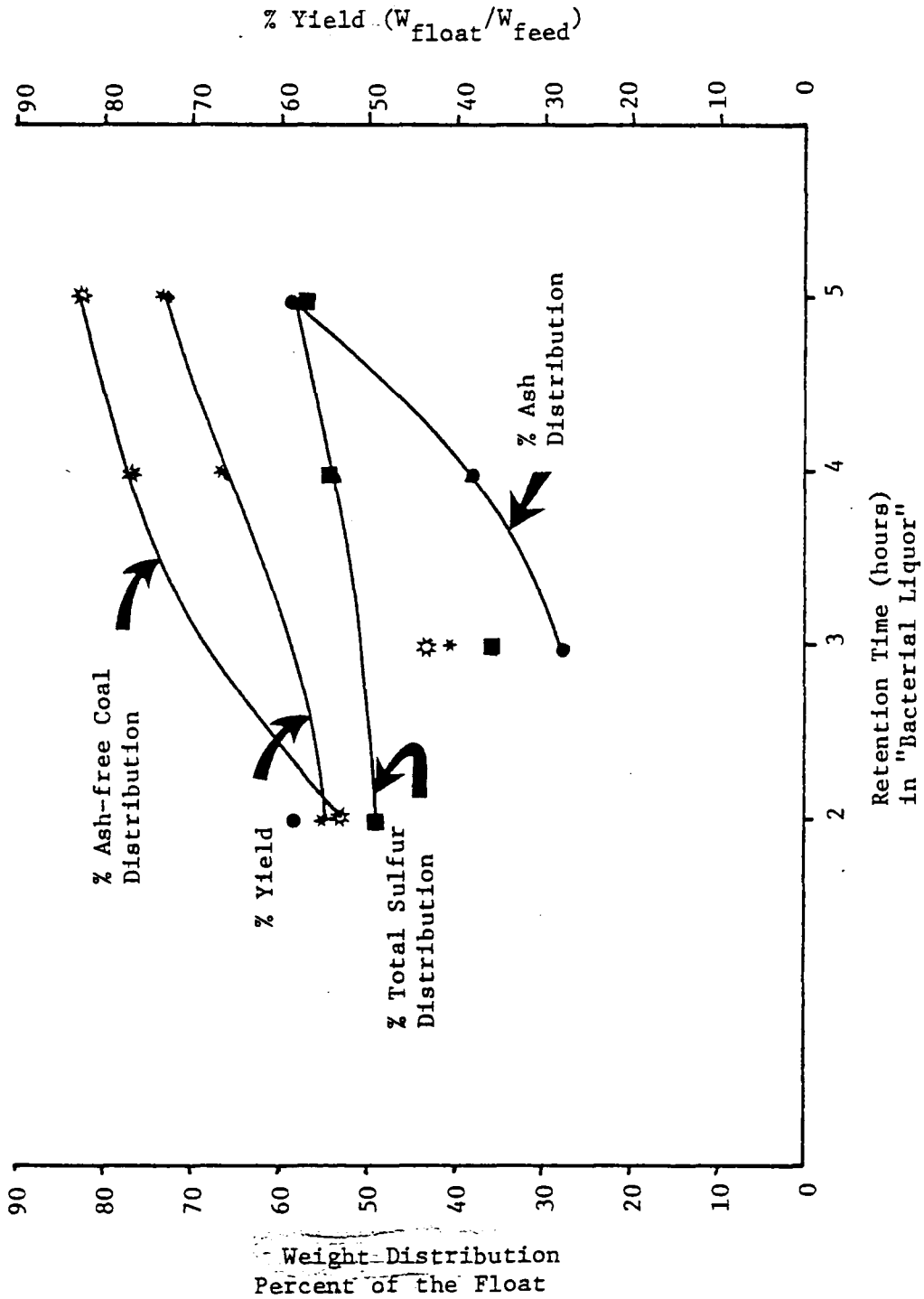


Figure 6.18. Retention Time of Illinois No. 6 Coal Samples in Recycled "Bacterial Liquor" versus Weight Distribution of Sulfur, Ash, Ash-free Coal, and Yield, Using MIBC as Frother.
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is taken directly from the fermentation tank) it was noted that both recycled and original "bacterial liquors" have an increasing effect on the recovery of sulfur, ash, and ash-free coal. The three hour retention time was where the basic difference of the two sets of results occurred. For the recycled "bacterial liquor," the three hour retention time gave the lowest sulfur distribution in the float, whereas the original "bacterial liquor" at this retention time gave the highest sulfur distribution in the float.

Figure 6.19 shows the effect of retention time on the reduction of the sulfur/ash-free coal ratio of both the original and the recycled "bacterial liquors." The results of the tests with original and recycled "bacterial liquors" showed that in both sets of tests the sulfur/ash-free coal reduction ratio had increased with respect to the retention time. Also, it was noted that in both cases the sulfur/ash-free coal reduction ratio curves were generally the same. The results of the tests with the original "bacterial liquor" showed that it was slightly more efficient than the recycled "bacterial liquor."

The comparison of the two series of tests using cresylic acid and MIBC as frothers revealed that the increase in retention time resulted in completely opposite effects on the two sets of tests (see Figures 6.12 and 6.17). When cresylic acid was used as a frother, the percent yield of the float decreased as well as the combustible and sulfur distributions in the float. When MIBC was used, the increased retention time resulted in an increase in the percent of yield and the weight percent distribution of the combustibles (ash-free coal) in the float. The ash distribution in the float decreased with the increase of retention

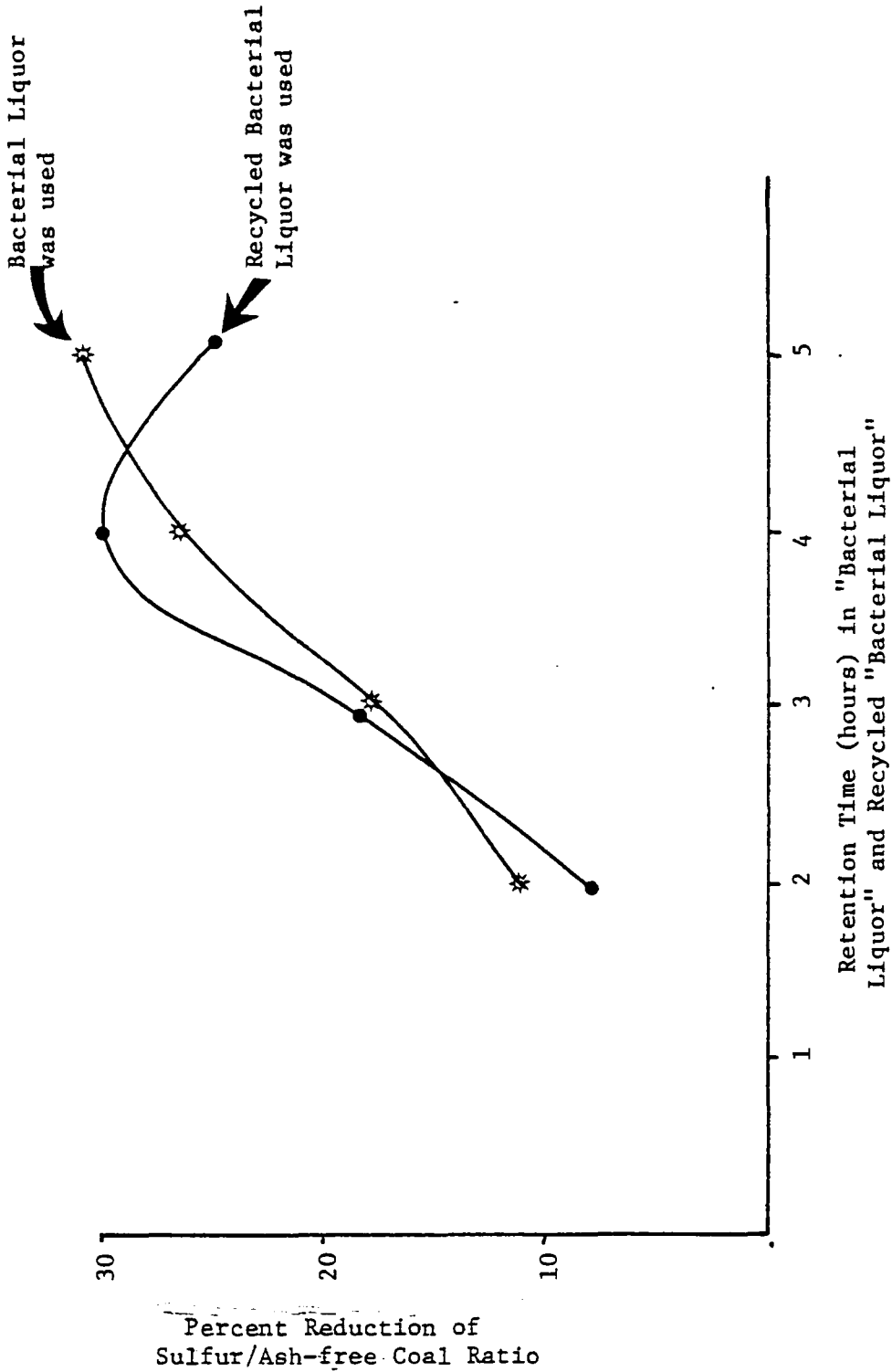


Figure 6.19. Retention Time of Illinois No. 6 Coal Samples in the "Bacterial Liquor" versus Reduction of Sulfur/Ash-free Coal Ratio.
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times up to four hours. It then increased at five hours of retention time. It was noted that at three hours of retention time, the recovery of ash-free coal in the float and the recovery of sulfur in the float had the highest values. A comparison of the two tests at the two hour retention times indicated that the lowest yields and recoveries of ash, sulfur, and combustibles in the float resulted when MIBC was used. When cresylic acid was used, numerical values of yield and percent recoveries of the float components were relatively high.

The distribution of sulfur in the floats of the two series of tests at three hours of retention time were relatively the same. At two, four, and five hours of retention time, the sulfur distributions in the float of the two tests with MIBC were lower than when cresylic acid was used.

The ash distribution in both sets of tests was relatively unchanged with increasing retention times (it varied within ± 5 percent).

6.4.7 Retention Time Studies of Pittsburgh and Middle Kittanning Coal Samples in the "Bacterial Liquor":

The following tests were performed to study the effect of "bacterial liquor" on the removal of ash and sulfur from Pittsburgh and Middle Kittanning coal samples. For this purpose the coal samples were conditioned in "bacterial liquor" for different time intervals. The test conditions and procedures were the same as before (Section 4.3.2). The pH of the flotation pulp was adjusted to 7.0. No frother was used to float the Middle Kittanning coal, but cresylic acid was used to float the Pittsburgh coal samples. The results of the tests with the Pittsburgh and Middle Kittanning coal samples are tabulated in Tables 6.16 and

Table 6.16. Retention Time Studies of the Pittsburgh Coal Samples in "Bacterial Liquor" and its Effect on the Removal of Ash and Sulfur.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Time (hrs.)
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
B ₁₀	Float	85.1	7.8	92.2	4.3	60.9	88.1	76.0			
	Sink	14.9	28.6	71.4	7.7	39.1	11.9	24.0	11.0	13.7	2
	Composite Total	100	10.9	89.1	4.8	100	100	100			
B ₁₂	Float	89.5	7.9	92.1	4.6	71.8	91.4	78.2			
	Sink	10.5	26.5	73.5	10.9	28.2	8.5	21.8	12.0	14.4	2
	Composite Total	100	9.9	90.1	5.2	100	100	100			
B ₁₃	Float	80.3	8.6	91.4	7.2	56.9	83.5	80.0			
	Sink	19.7	26.5	73.5	7.5	43.1	16.5	20.3	1.0	4.4	3
	Composite Total	100	12.1	87.9	7.2	100	100	100			
B ₁	Float	91.9	7.8	92.2	3.4	67.1	94.9	82.9			
	Sink	8.1	43.3	56.7	7.9	32.9	5.1	17.1	10.0	12.4	4
	Composite Total	100	10.7	89.3	3.8	100	100	100			
B ₇	Float	83.2	8.7	91.3	4.5	83.0	83.2	73.9			
	Sink	16.8	8.8	91.2	8.2	17.0	16.8	27.1	12.0	12.2	5-1/4
	Composite Total	100	8.7	91.3	5.1	100	100	100			
B ₈	Float	83.4	8.7	91.3	4.3	61.8	86.3	71.5			
	Sink	16.6	27.0	73.0	8.5	38.2	13.7	28.5	14.0	17.0	5-1/4
	Composite Total	100	11.7	88.3	4.9	100	100	100			

Table 6.16. (cont.)

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Time (hrs.)
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
B ₉	Float	86.3	10.0	90.0	4.7	70.5	88.5	79.9			
	Sink	13.7	26.3	73.7	7.5	29.5	11.5	20.1	7.0	9.7	6
	Composite Total	100	12.2	87.8	5.1	100	100	100			
B ₁₄	Float	88.4	7.8	92.2	5.4	66.6	90.9	81.4			
	Sink	11.6	29.8	70.2	9.3	33.4	9.1	18.6	8.0	10.5	6
	Composite Total	100	10.4	81.6	5.8	100	100	100			
B ₁₆	Float	67.7	10.0	90.0	4.6	47.6	71.0	58.4			
	Sink	32.3	23.1	76.9	6.8	52.4	29.0	41.6	14.0	17.7	10
	Composite Total	100	14.2	85.8	5.3	100	100	100			
B ₁₅	Float	71.6	8.4	91.6	4.4	51.1	74.3	66.1			
	Sink	28.4	20.3	79.7	5.8	48.9	25.7	33.9	8.0	11.1	10
	Composite Total	100	11.8	88.2	4.8	100	100	100			

Remarks:

Size of the coal samples = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 3 minutes

Conditioning time in the frother = 3 minutes

Conditioning time of the coal samples in the "bacterial liquor" = variable

Table 6.16. (cont.)

Reagents used:

Frother: Cresylic acid added as required

Pyrite depressant: "Bacterial liquor," pulp density = 5 (w/v)

6.17, respectively. The percent yield and the distribution of the float products of Pittsburgh and Middle Kittanning coal samples are shown in Figures 6.20 and 6.22, respectively.

The Pittsburgh seam coal, when conditioned in "bacterial liquor" and floated with cresylic acid, gave high percentages of yields and high values of sulfur, ash, and ash-free coal distributions in the float. The high values of sulfur, ash, and ash-free coal distribution in the float varied within five to ten percent. The yield and distribution of the float material decreased at the ten hour retention time. The distribution of ash and sulfur was very high in the float of both the Pittsburgh and the Middle Kittanning coal samples.

The comparison of the test results of the Pittsburgh and Illinois No. 6 coal samples indicated that these two sets of tests had the same decreasing trends of yield and float component distributions with increasing retention times. The Pittsburgh seam coal samples gave the highest yield and recovery of combustibles at four hours of retention time, whereas the Illinois No. 6 coal samples had the highest yield and recovery of combustibles at three hours of retention time. The reduction of the sulfur/ash-free coal ratio of the Pittsburgh coal was quite low (Figure 6.21) and very erratic.

The Middle Kittanning seam coal samples, when conditioned in "bacterial liquor," gave the highest values of yields and distributions of float components. The separation of sulfur and ash from this coal sample was impossible by flotation tests. This coal has previously been described in this report as being oily and highly floatable. This floatability was enhanced when the coal was conditioned in "bacterial liquor."

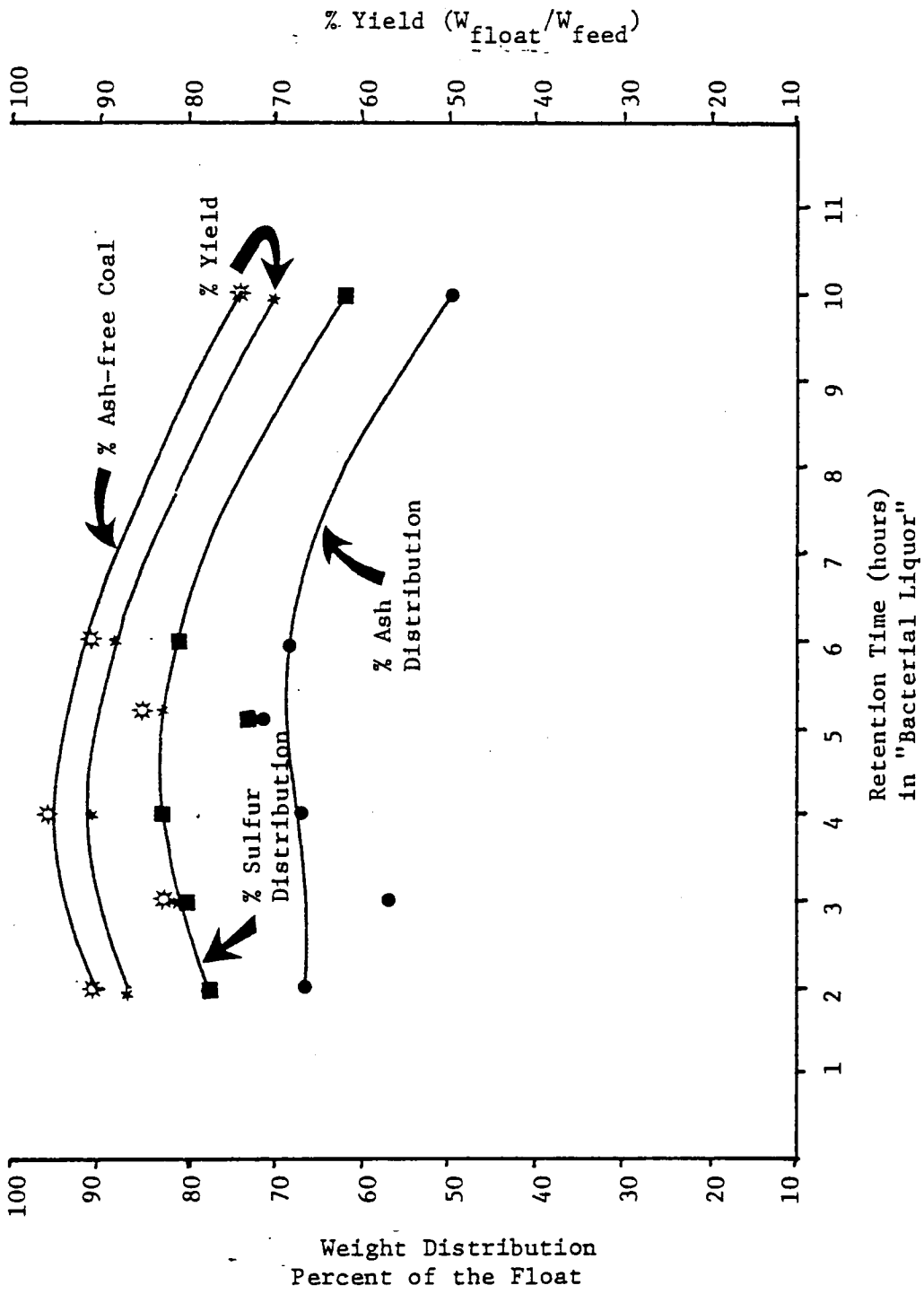


Figure 6.20. Retention Time of the Pittsburgh Seam Coal Samples in the "Bacterial Liquor" versus Yield and versus the Weight Distribution of Sulfur, Ash, and Ash-free Coal.

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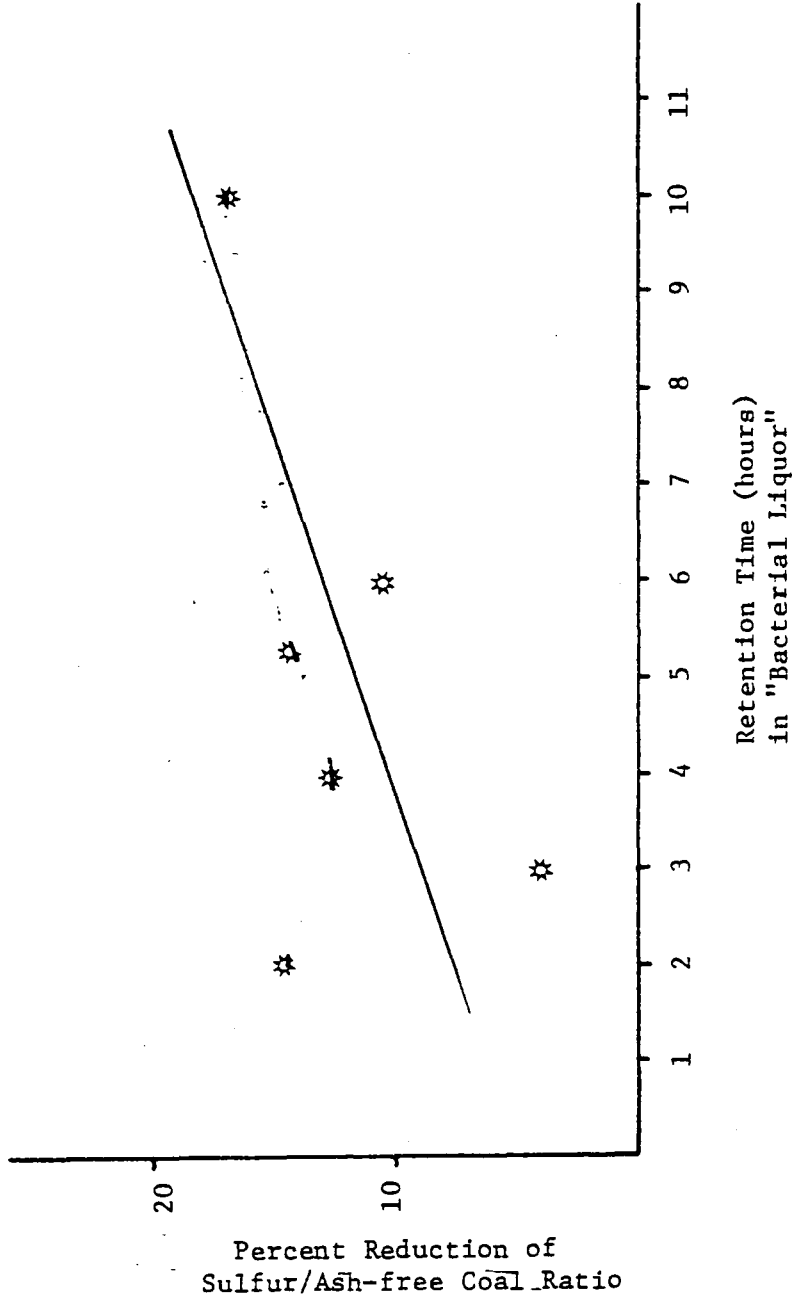


Figure 6.21. Retention Time of Pittsburgh Seam Coal Samples in the "Bacterial Liquor" versus Reduction of Sulfur/Ash-free Coal Ratio.
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Table 6.17. Retention Time Studies of Middle Kittanning Coal in "Bacterial Liquor" and its Effect on Removal of Ash and Sulfur.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Time (hrs.)
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
A ₅	Float	97.6	9.8	90.2	3.2	90.2	98.5	94.1			
	Sink	2.4	43.1	56.9	8.3	9.8	15.0	5.9	4.0	4.5	2
	Composite Total	100	10.6	89.4	3.3	100	100	100			
A ₉	Float	94.7	9.9	90.1	4.5	88.4	95.4	90.3			
	Sink	5.3	22.6	77.4	8.8	11.6	0.6	0.7	5.0	5.4	3
	Composite Total	100	10.6	89.4	4.7	100	100	100			
A ₁₅	Float	98.0	8.9	91.2	4.1	90.9	98.9	92.8			
	Sink	2.0	49.6	50.4	15.7	9.1	0.1	7.2	5.0	6.2	3
	Composite Total	100	9.6	90.4	4.3	100	100	100			
A ₁₆	Float	98.8	8.6	91.4	4.5	95.0	99.2	96.4			
	Sink	1.2	38.3	61.7	14.1	5.0	0.8	3.6	2.0	2.8	4
	Composite Total	100	9.0	91.0	4.6	100	100	100			
A ₁₀	Float	98.6	10.1	89.9	3.7	95.7	98.9	96.3			
	Sink	1.4	32.8	67.2	10.5	4.3	1.1	3.7	2.0	2.7	4
	Composite Total	100	10.4	89.6	3.8	100	100	100			
A ₁₁	Float	98.4	10.0	90.0	3.2	91.6	99.2	91.0			
	Sink	1.6	56.5	43.5	19.5	8.4	0.8	8.9	7.0	8.2	5
	Composite Total	100	10.7	89.3	3.5	100	100	100			

Table 6.17. (cont.)

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Time (hrs.)
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
A ₁₂	Float	98.0	10.3	89.7	4.0	90.1	94.4	94.4			
	Sink	2.0	57.2	42.8	11.6	9.9	5.6	5.6	4.0	4.6	5
	Composite Total	100	11.2	88.8	4.1	100	100	100			
A ₁₃	Float	98.5	9.6	90.4	4.9	95.7	98.8	94.5			
	Sink	1.5	28.2	71.8	19.1	4.3	1.2	5.5	4.0	4.4	10
	Composite Total	100	9.9	90.1	5.1	100	100	100			
A ₁₄	Float	98.5	9.1	90.9	4.9	91.5	99.3	94.6			
	Sink	1.5	57.0	43.0	11.9	8.5	0.7	5.4	2.0	2.9	10
	Composite Total	100	9.8	90.2	5.0	100	100	100			
A ₇	Float	94.3	10.8	89.2	2.9	80.2	96.4	82.0			
	Sink	5.7	43.6	56.4	10.6	19.2	3.6	18.0	13.0	14.9	7 days
	Composite Total	100	12.7	87.3	3.3	100	100	100			

Remarks:

Size of the coal samples = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 2 minutes

Conditioning time of the coal samples in the "bacterial liquor" = variable

Table 6.17. (cont.)

Reagents used:

Frother: none

Pyrite depressant: "bacterial liquor," pulp density = 5 (w/v)

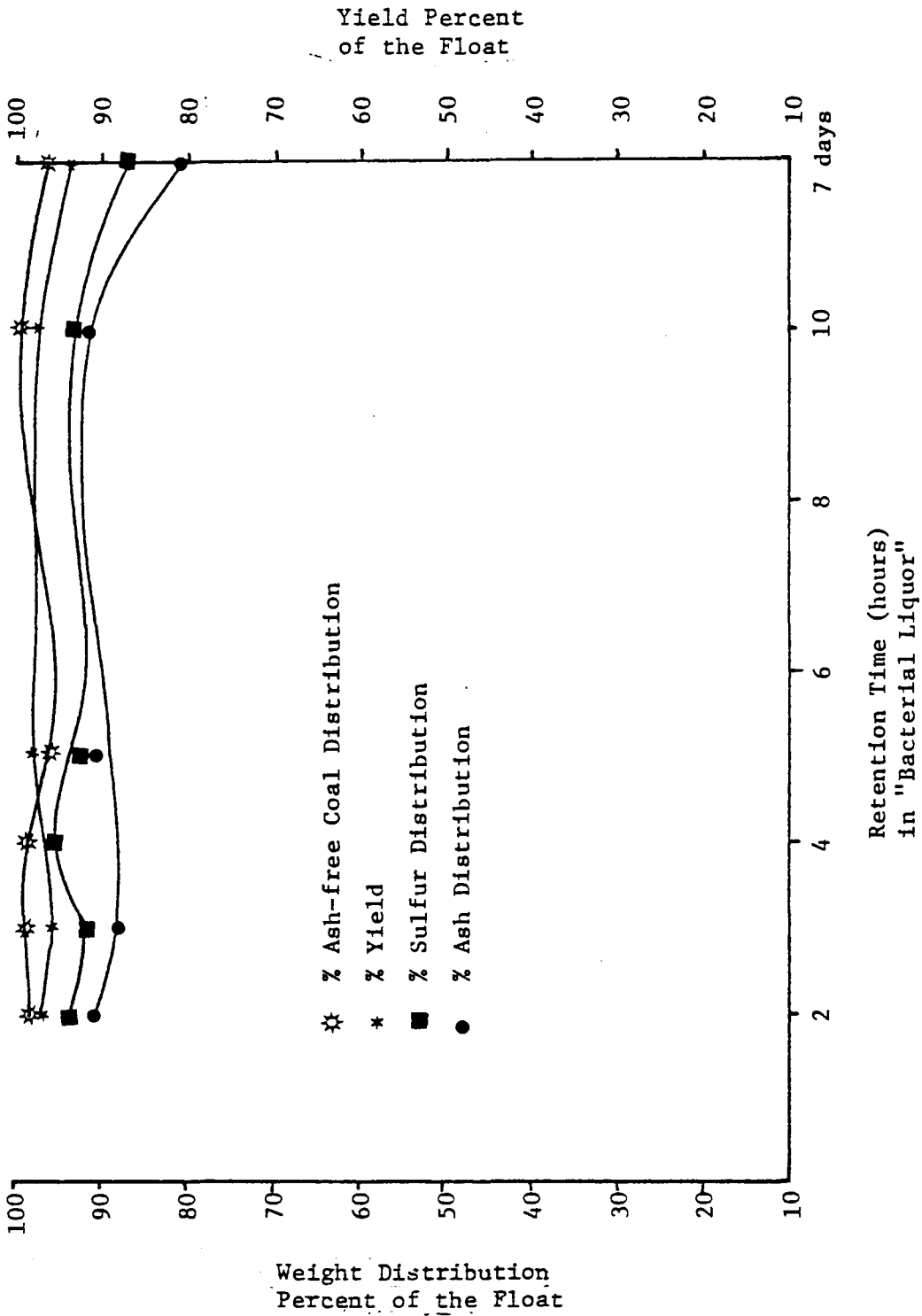


Figure 6.22. Retention Time of Middle-Kittanning Coal Samples in the "Bacterial Liquor" versus Weight Distribution of Sulfur, Ash, Ash-free Coal, and Yield.

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Even after seven days of conditioning time, the coal conditioned in the "bacterial liquor" showed that the distribution of ash and sulfur in the float would still be very high. The reduction of the sulfur/ash-free ratio was very small. After seven days of conditioning time, the reduction ratio was increased to 14.9 percent (see Figure 6.23).

6.4.8 Variations of the Conditioning Tank Pulp Density and its Effect on Sulfur and Ash Reduction in Illinois No. 6 Coal Samples:

The following experiments were performed to investigate the effect of increased pulp density (grams of coal/liters of "bacterial liquor") of the conditioning tank on reducing sulfur and ash in Illinois No. 6 coal samples. The increased pulp would, in turn, increase the capacity of the process (i.e., when the pulp density of the conditioning tank was increased from five to thirty percent (w/u) the capacity was increased six times).

Two sets of experiments were performed. In the first set of tests, cresylic acid, with frothing abilities, was used as a frother. In the second set MIBC was used as a frother. This frother has no collecting abilities. The results of the two sets of tests were then compared.

6.4.8.1 Experiments with Cresylic Acid:

Illinois No. 6 coal samples were conditioned in the "bacterial liquor" for three hours and floated at pH 7.0 in the flotation cell. Cresylic acid was added to the pulp as it was required. The only variable was the pulp density of the conditioning tank, which was changed from five to thirty percent. The results of these experiments are tabulated in Table 6.18. The average of the two tests results are shown in Figure 6.24.

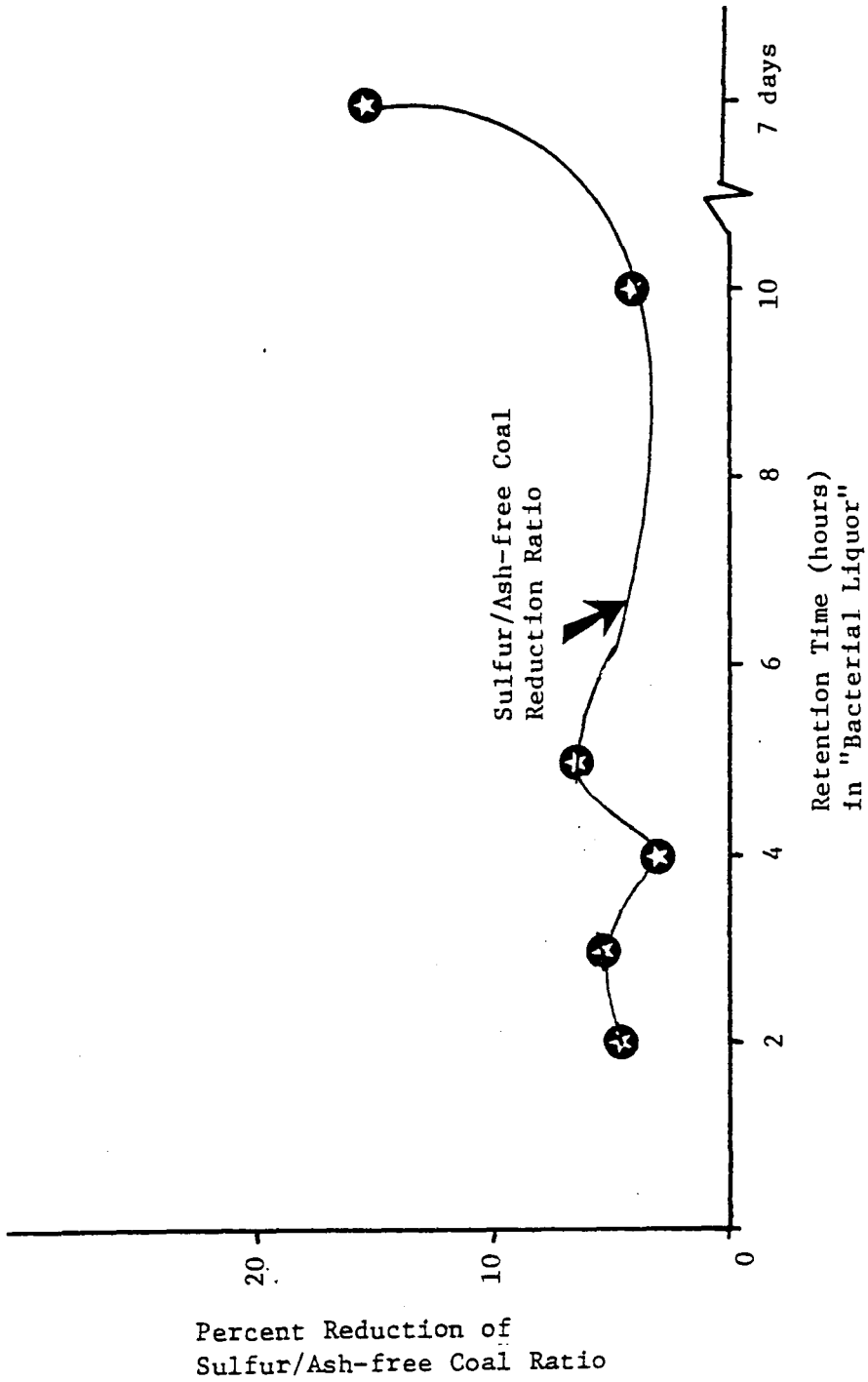


Figure 6.23. Retention Time of the Middle Kittanning Coal Samples in the "Bacterial Liquor" versus Reduction of Sulfur/Ash-free Coal Ratio. M.L.N./78/VPI&SU

Table 6.18. Variations of the Pulp Density of the Conditioning Tank of "Bacterial Liquor" and its Effects on Illinois No. 6 Coal Samples Using Cresylic Acid as Frother.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Tank Pulp Density
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₂₄	Float	72.7	12.7	87.3	5.8	37.2	84.4	69.4			
	Sink	27.3	57.0	43.0	6.8	62.8	15.6	30.6	4.4	17.7	5
	Composite Total	100	24.8	75.2	6.6	100	100	100			
C ₇₀	Float	71.5	18.3	81.7	7.2	49.6	79.4	66.0			
	Sink	28.5	46.6	53.4	9.3	50.4	20.6	34.0	7.7	16.9	5
	Composite Total	100	26.5	73.6	7.8	100	100	100			
C ₇₆	Float	67.9	13.6	86.4	5.3	37.1	78.9	58.3			
	Sink	32.1	48.6	51.4	8.1	62.9	22.0	41.7	14.0	25.3	10
	Composite Total	100	24.8	75.2	6.2	100	100	100			
C ₅₅	Float	63.2	12.8	87.2	5.6	31.4	74.3	53.8			
	Sink	36.8	48.0	52.0	8.2	68.6	25.7	46.2	14.9	27.6	10
	Composite Total	100	25.8	74.2	6.6	100	100	100			
C ₇₇	Float	78.2	16.7	83.3	5.8	54.6	85.6	71.1			
	Sink	21.8	49.7	50.4	8.4	45.4	14.4	28.9	9.1	17.0	15
	Composite Total	100	23.9	76.1	6.4	100	100	100			
C ₅₆	Float	50.8	15.2	84.8	6.2	28.8	58.9	43.4			
	Sink	49.2	38.8	61.2	8.4	71.2	41.1	56.6	14.5	26.2	15
	Composite Total	100	26.8	73.2	7.3	100	100	100			

Table 6.18. (cont.)

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Tank Pulp Density
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₇₈	Float	53.1	18.3	81.7	5.0	33.4	61.2	42.1	20.7	31.2	20
	Sink	46.9	41.3	58.7	7.8	66.6	38.8	57.9			
	Composite Total	100	29.1	70.9	6.3	100	100	100			
C ₅₇	Float	57.0	12.6	87.4	5.2	27.7	67.2	48.4	15.1	28.0	20
	Sink	43.0	43.6	56.4	7.4	72.3	32.8	51.6			
	Composite Total	100	25.9	74.1	6.2	100	100	100			
C ₅₈	Float	68.2	13.2	86.8	6.5	34.8	79.9	63.6	6.8	20.4	25
	Sink	31.8	53.0	47.0	8.0	65.2	20.1	34.4			
	Composite Total	100	25.9	74.1	6.9	100	100	100			
C ₇₉	Float	46.4	18.6	81.4	4.2	33.0	51.0	30.9	34.0	40.0	25
	Sink	53.6	32.5	67.5	8.4	67.0	49.0	69.6			
	Composite Total	100	26.0	74.0	6.4	100	100	100			
C ₈₀	Float	61.4	17.4	82.6	5.1	40.9	68.6	54.8	10.6	20.2	30
	Sink	38.6	40.0	60.0	6.7	59.1	31.4	45.2			
	Composite Total	100	26.1	73.9	5.7	100	100	100			

Table 6.18. (cont.)

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Tank Pulp Density
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
	Float	57.0	15.1	84.9	6.4	35.1	64.1	49.3			
C ₅₉	Sink	43.0	36.9	63.1	8.7	64.9	35.9	50.7	13.5	23.1	
	Composite Total	100	24.5	75.5	7.3	100	100	100		30	

Remarks:

Size of the coal samples = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Conditioning time in the frother = 3 minutes

Conditioning time in the "bacterial liquor" = 3 hours

Pulp density of the conditioning tank = variable

Reagents used:

Frother: Cresylic acid added as required

Pyrite depressant: "Bacterial liquor" added to obtain various pulp densities

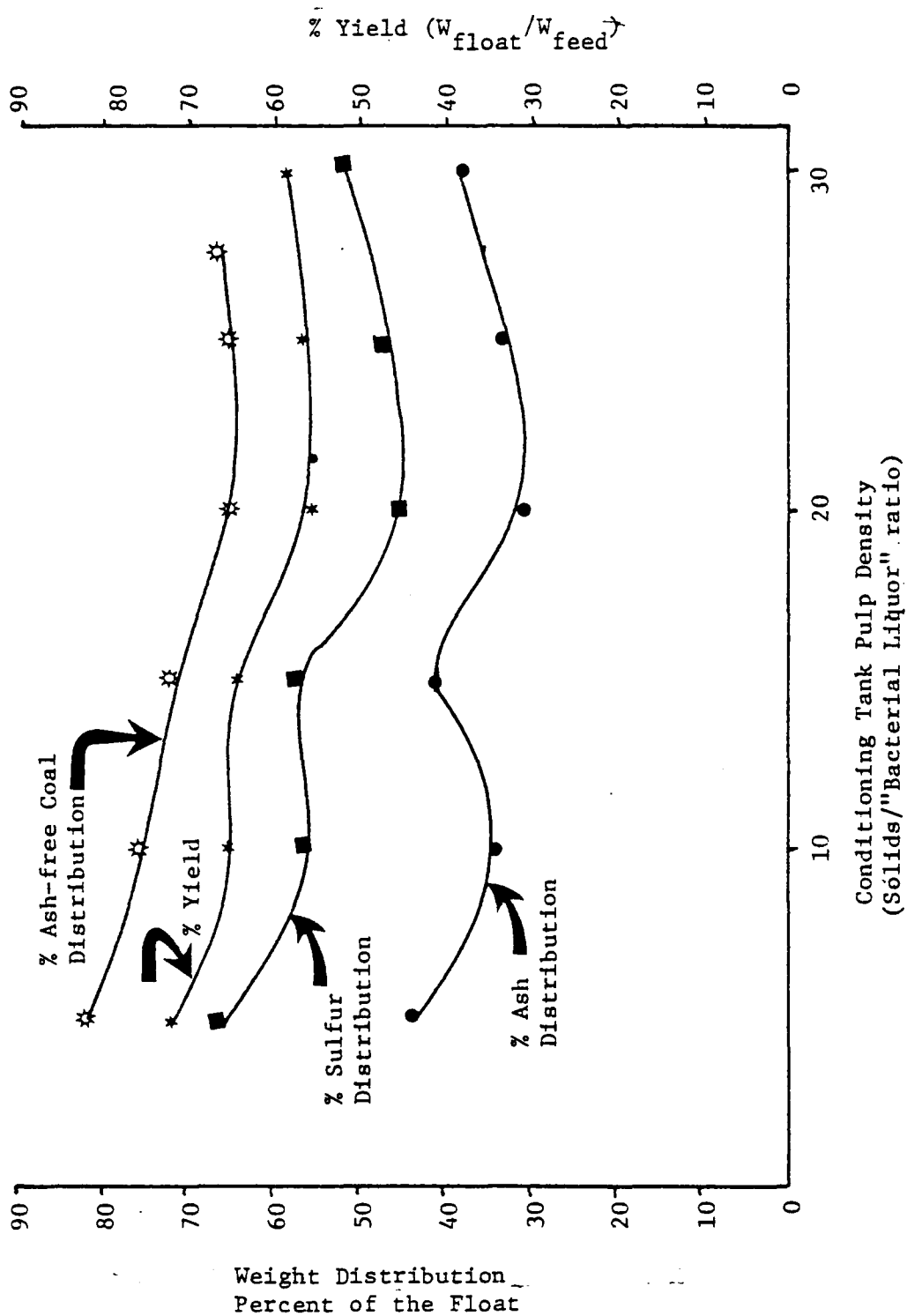


Figure 6.24. Variations of the Pulp Density in the Conditioning Tank versus Weight Distribution of Sulfur, Ash, Ash-free Coal, and Yield, Using the Illinois No. 6 Coal Samples and Cresylic Acid as Frother.

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Generally, the percent distribution of sulfur and ash-free coal in the float and the percent yield decreased as the pulp density was increased. The percent ash distribution, however, remained relatively unchanged.

When a pulp density of 20 percent was used, the lowest yields and distributions of ash, sulfur, and combustibles in the float resulted. The highest yield, as well as percent distribution of ash, combustibles, and sulfur was reported to the float at a five percent pulp density. The variations of sulfur, ash, and combustible distribution in the float with respect to the increased values of the pulp density were small (varied within five percent).

The reduction of sulfur (percent) and the sulfur/ash-free coal reduction ratio were increased as the pulp density increased. The highest reductions of sulfur resulted at pulp densities of 20 and 30 percent. A pulp density of five percent gave the lowest percent sulfur reduction. This would indicate that the percent distributions of float components (ash, sulfur, and combustibles) were small. The percent reduction of sulfur was substantially increased as the pulp density increased. Hence, it could be concluded that, when the pulp density was increased, the sulfur removal was also increased. Figure 6.25 shows the variations of percent sulfur reductions with respect to the pulp density of the conditioning tank.

6.4.8.2 Experiments with MIBC:

For the second set of experiments two pounds per ton of MIBC was used as a frother to float the Illinois No. 6 coal samples. The only variable in these tests was the pulp density of the conditioning tank.

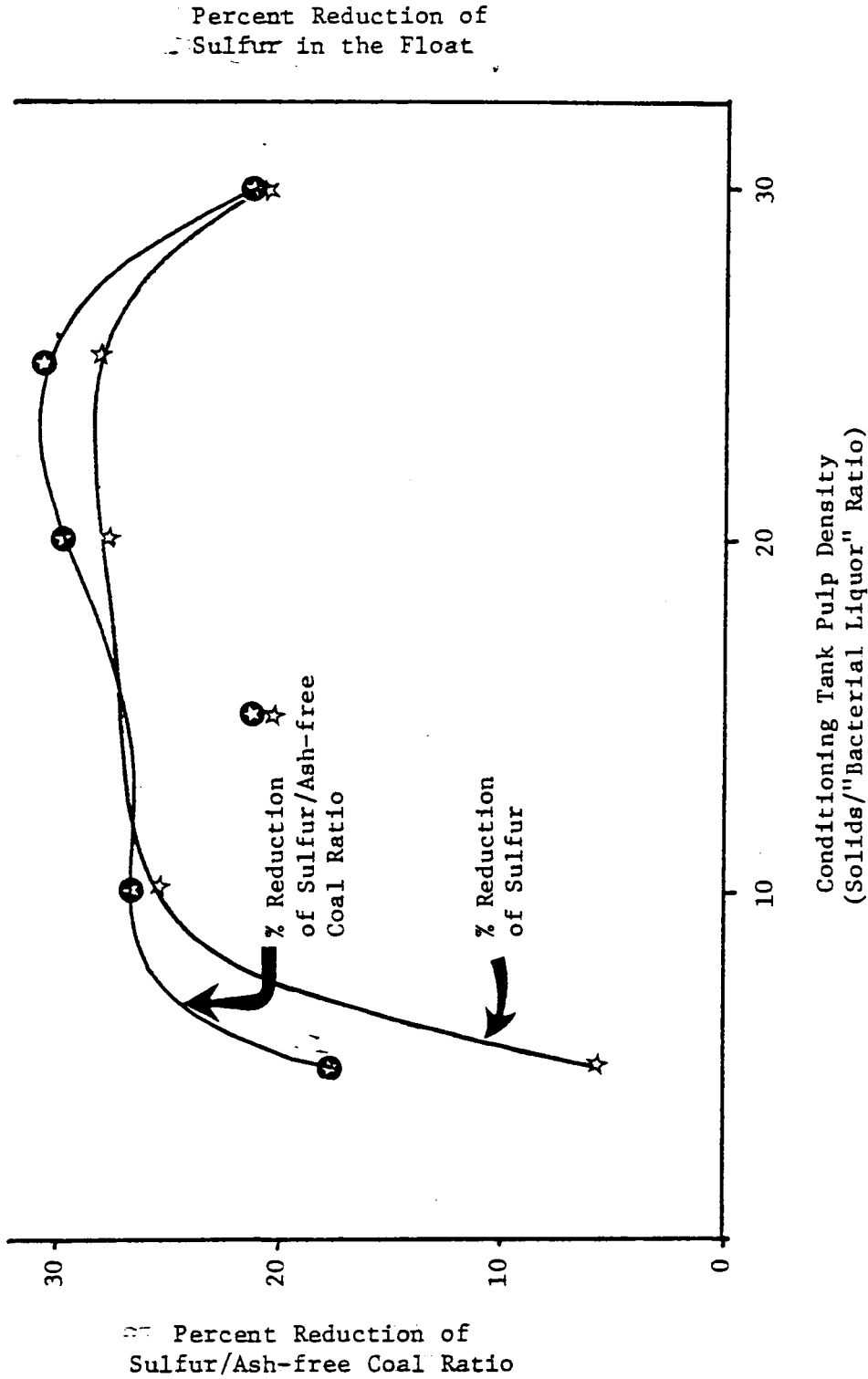


Figure 6.25. Variations of the Pulp Density in the Conditioning Tank versus Reduction of Sulfur and Sulfur/Ash-free Coal Ratio, Using the Illinois No. 6 Coal Samples and Cresylic Acid as a Frother.
M.L.N./78/VPI&SU

The pH was adjusted to 7.0, and the coal samples were conditioned in the "bacterial liquor" for three hours. MIBC was used as the frother because, unlike cresylic acid, it has no collecting ability. The results of these tests are presented in Table 6.19. These results are also graphed in Figure 6.26.

Conditioning tank pulp densities of 10, 20, 25, and 30 percent were prepared. The lowest yields and distributions of sulfur, ash, and ash-free coal were obtained when the conditioning pulp density was 10 percent. The highest distribution of ash, sulfur, and ash-free coal was obtained in the float when the conditioning tank pulp density was 15 percent. The distribution of ash in the float stayed relatively constant when pulp densities higher than 15 percent were used.

The percent reduction, or removal, of sulfur had the lowest values at pulp densities of 15 and 20 percent. Also, the reduction of the sulfur/ash-free coal ratio had the lowest value at a 20 percent pulp density. The highest sulfur reduction values were obtained when pulp densities of 25 and 30 percent were used. It was noted that when the highest yields and combustible recoveries were obtained, the lowest sulfur reductions also resulted. Figure 6.27 is a graph of pulp densities versus the percent reductions of sulfur and sulfur/ash-free coal ratios.

A comparison of the two sets of results with cresylic acid and MIBC indicated that the increased pulp density resulted in a decrease in the percent yield and distribution of the float material (sulfur, ash, and ash-free coal) in both sets of tests. The distribution of ash in the float stayed relatively unchanged in both sets of tests. The

Table 6.19. Variations of the Pulp Density of the Conditioning Tank of "Bacterial Liquor" and its Effects on Illinois No. 6 Coal Samples Using MBC as Frother.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Conditioning Tank Pulp Density
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₃₆	Float	48.1	15.1	84.9	4.8	29.2	54.4	41.7			
	Sink	51.9	33.9	66.1	6.2	70.8		58.3	13.4	23.4	10
	Composite Total	100	24.9	75.1	5.5	100	45.6	100			
C ₃₇	Float	65.7	24.9	75.1	5.9	44.1	78.4	61.8			
	Sink	34.3	60.5	39.5	7.0	55.9	21.6	38.2	6.0	21.2	15
	Composite Total	100	37.1	62.9	6.3	100	100	100			
C ₃₅	Float	66.7	15.6	84.4	5.6	40.8	75.6	62.0			
	Sink	33.3	45.4	54.6	6.8	59.2	24.4	38.0	7.0	17.9	20
	Composite Total	100	25.5	74.5	6.0	100	100	100			
C ₃₈	Float	56.4	17.5	82.5	3.9	42.9	60.4	44.6			
	Sink	43.6	30.0	70.0	6.2	57.1	39.6	55.5	20.9	26.1	25
	Composite Total	100	23.0	77.0	4.9	100	100	100			
C ₃₉	Float	58.7	15.4	84.6	4.5	34.8	67.1	47.4			
	Sink	41.3	41.1	58.9	7.0	65.2	32.9	52.6	19.2	29.3	30
	Composite Total	100	26.0	74.0	5.5	100	100	100			

Remarks:

Size of the coal sample = minus 65 mesh

Table 6.19. (cont.)

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Conditioning time in the frother = 1 minute

Conditioning time in the "bacterial liquor" = 3 hours

Pulp density of the conditioning tank = variable

Reagents used:

Frother: 2 lb./ton MIBC

Pyrite depressant: "Bacterial liquor" added to obtain various pulp densities

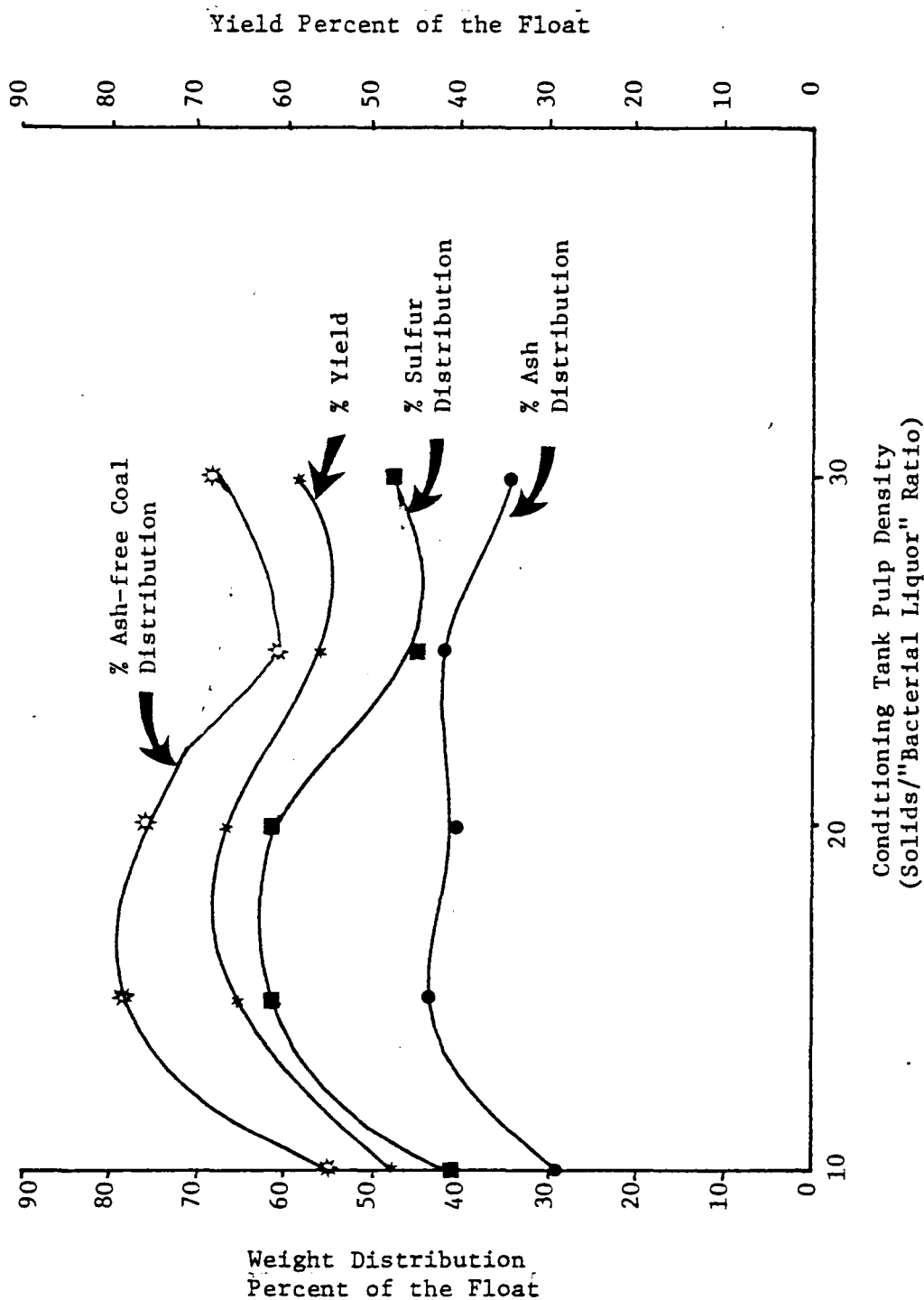


Figure 6.26. Variations of the Pulp Density in the Conditioning Tank versus Weight Distribution of Sulfur, Ash, Ash-free Coal, and Yield of the Illinois No. 6 Coal Samples, Using MIRC as Frother. M.L.N./78/VPI&SU

Percent Reduction of Sulfur in the Float

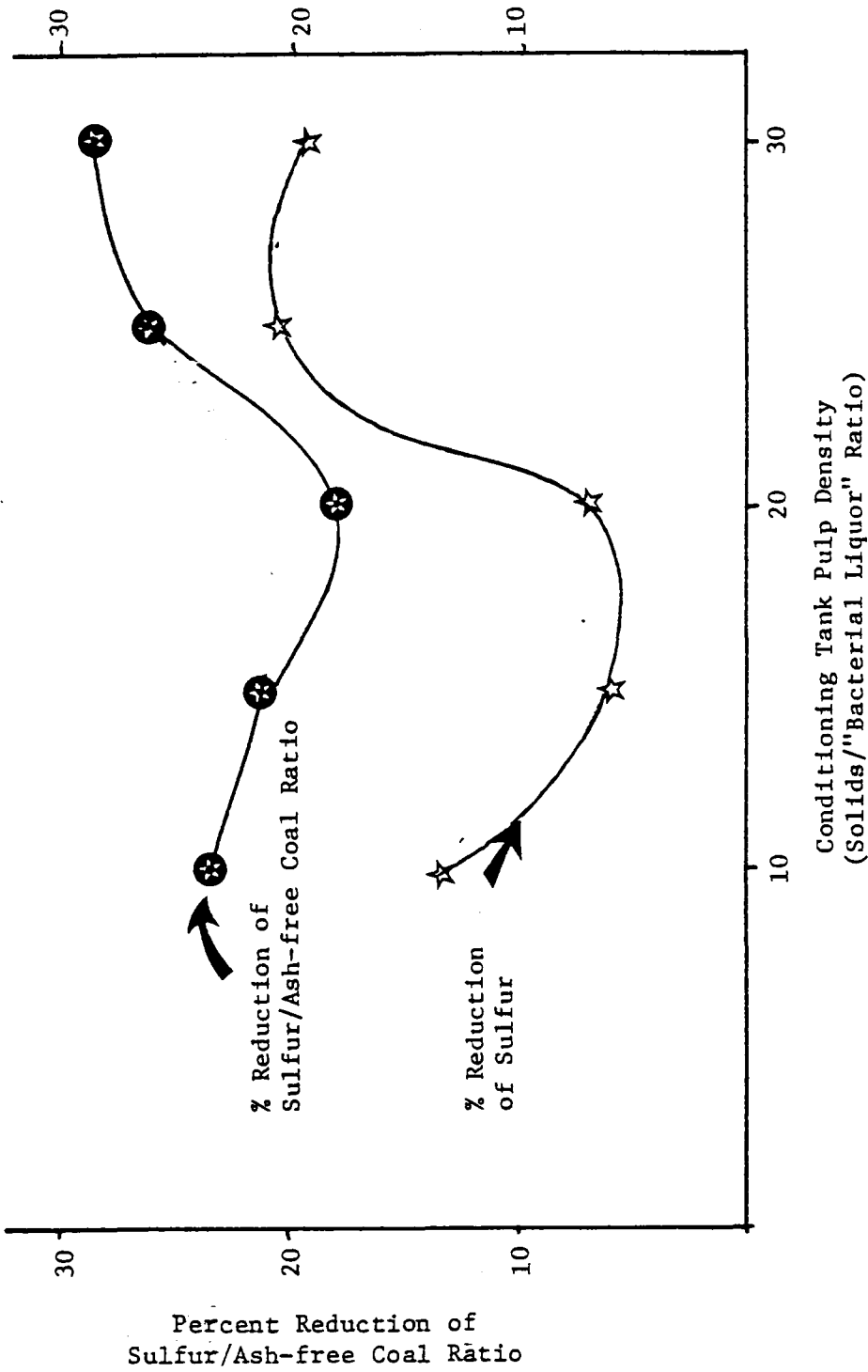


Figure 6.27. Variations of the Pulp Density in the Conditioning Tank versus Reduction of Sulfur and Reduction of Sulfur/Ash-free Coal Ratio in Illinois No. 6 Coal Samples, Using MIBC as Frother. M.L.N./78/VPI&SU

ash-free coal distributed in the float of the flotation products of the tests with cresylic acid was slightly higher than when MIBC was used. The yields were more or less the same in both sets of tests. When cresylic acid was used, the distribution of sulfur in the float decreased as the pulp density increased. When MIBC was used, the sulfur distribution in the float increased with an increase of pulp density from 10 to 20 percent. The distribution of sulfur in the float then decreased from 62 to 45 percent when the pulp density of the conditioning tank increased from 20 to 25 percent.

6.4.9 The Variations of pH of the Flotation Pulp and its Effects on the Coal Samples Preconditioned in the "Bacterial Liquor":

Pulverized Illinois No. 6 coal samples were first conditioned in the "bacterial liquor" for one hour and were then floated according to the procedures outlined in Section 4.3.2. The only variable in these tests was the pH of the flotation pulp, which had values of 3.0, 7.0, and 8.0. The effect of the pH value of the flotation pulp on the reduction of sulfur and ash was previously investigated in Section 6.3.1. In this section, the effect of "bacterial liquor" on the reduction of sulfur and ash at three different values of flotation pulp pH was investigated. The results of these experiments are tabulated in Table 6.20. Figure 6.28 shows the effect of variation of pH on the percent yield and weight distribution percentages of ash, sulfur, and ash-free coal.

The lowest percent values of yield and distributions of sulfur, ash, and ash-free coal in the float were obtained at pH 3.0. At pH 7.0 the percent yield was increased to about 50 percent. The ash-free coal and sulfur distributions were also increased to 66 and 48 percent, res-

Table 6.20. Variations of pH of the Flotation Pulp and its Effects on the Coal Samples Preconditioned in the "Bacterial Liquor."

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio	Variations of pH
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur			
C ₉	Float	49.6	14.4	85.6	5.7	25.0	59.5	43.2			
	Sink	50.4	42.6	57.4	7.3	75.0	40.5	56.8	12.8	27.3	3
	Composite Total	100	28.6	71.4	6.5	100	100	100			
C ₁₀	Float	58.6	17.1	82.9	4.8	37.8	66.1	48.1			
	Sink	41.4	39.9	60.1	7.3	62.2	33.9	51.9	17.9	27.2	7
	Composite Total	100	26.5	73.5	5.8	100	100	100			
C ₇	Float	64.2	12.5	87.5	3.9	31.5	75.4	50.3			
	Sink	35.8	48.9	51.1	6.9	68.5	24.6	49.7	21.7	33.3	8
	Composite Total										

Remarks:

Size of the coal samples = minus 65 mesh

Flotation cell conditions:

pH = variable, rpm = 900

Pulp density = 5 (w/v)

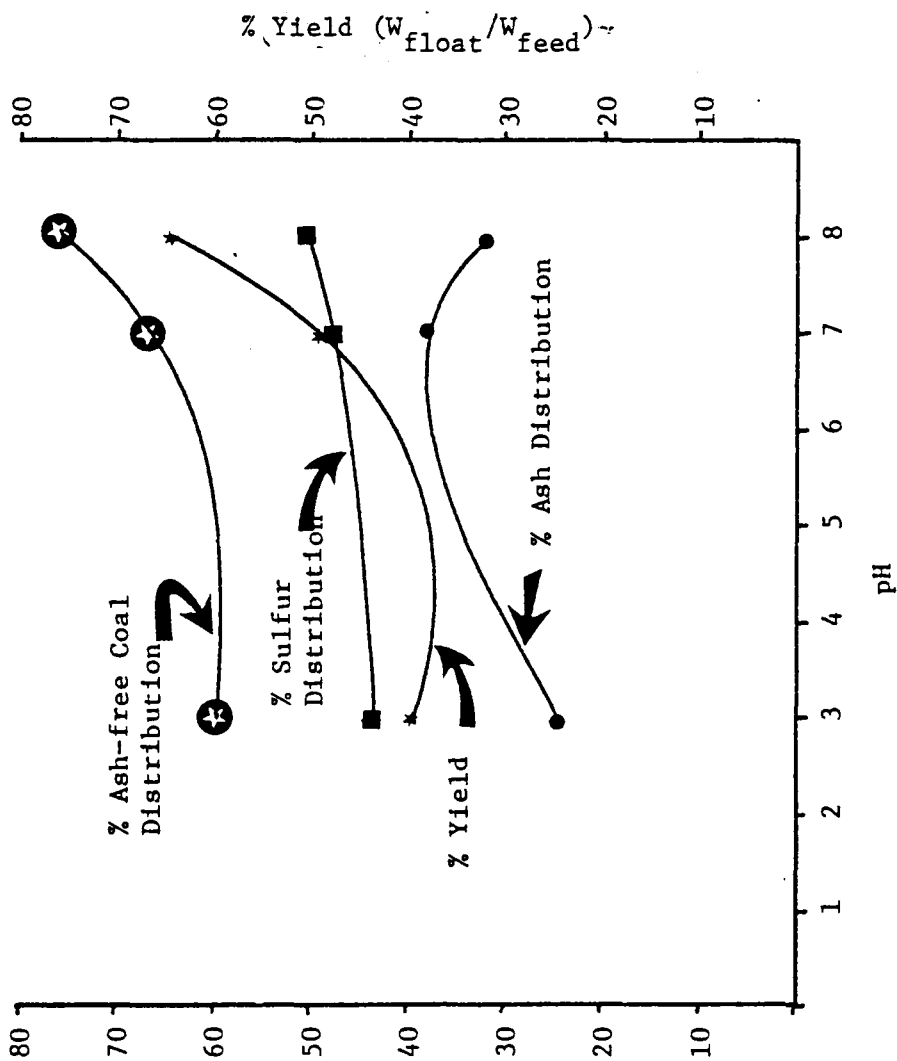
Flotation time = 4 minutes

Conditioning time in the frother = 1 minute

Conditioning time in the "bacterial liquor" = 3 hours

Reagents used:

Frother: Cresylic acid added as required



Weight Percent Distribution of Sulfur, Ash, and Ash-free COal in the Float

Figure 6.28. Variations of pH versus Weight Percent Distribution of Sulfur, Ash, and Ash-free Coal in the Float of the Illinois No. 6 Coal Samples.

M.L.N./78/VPI&SU

pectively. The percent ash distribution in the float was raised to its maximum level of 38 percent at pH 3.0. At pH 8.0 percentages of yield and distributions of ash-free coal and sulfur in the float were increased to 64, 75, and 50 percent, respectively. While the distribution of ash in the float was lower at pH 8.0 than pH 7.0, the percent of sulfur reduction increased from 12.8 percent at pH 3.0 to 21.7 percent at pH 8.0. The sulfur/ash-free coal-reduction ratio also increased from 27 percent at pH 3.0 to 33 percent at pH 8.0.

A comparison of the results of Section 6.3.1 with the results of this section indicates that the highest values of yield and ash-free coal were obtained at pH 3.0 when the coal samples were not conditioned in the "bacterial liquor." When "bacterial liquor" was used, the lowest values of yield and ash-free coal were obtained at pH 3.0. Also, at pH 8.0 the lowest values of yield and ash-free coal were obtained when "bacterial liquor" was not used. These values were highest when "bacterial liquor" was used.

6.4.10 Comparison of the Effects of the Double and Single Stage Flotation Tests on the Removal of Sulfur and Ash from Illinois No. 6 Coal Samples:

The purpose of this experiment was to investigate the effect of the addition of a second flotation stage for the removal of sulfur from the Illinois No. 6 coal sample. The results of this test were then compared with the results of a single stage flotation test with an Illinois No. 6 coal sample.

One hundred grams of pulverized Illinois No. 6 coal sample were first conditioned with two pounds per ton of sodium carbonate (Na_2CO_3)

for 10 minutes and then floated. Next, the float portion was conditioned in "bacterial liquor" for one hour and then floated. Cresylic acid was added to the pulp as frother (cresylic acid was added as required). The rest of the test conditions and procedures were as previously described in Section 4.3.

The results of the double stage flotation test are given in Table 6.21 (sample number C₅). The distribution percent of ash in the float was 9.7 percent. This was very low in comparison with the previous flotation test results with Illinois No. 6 coal samples. The distribution percent of the ash-free coal and sulfur in the float were also low in comparison with the previous test results with Illinois No. 6 coal (66.5 percent ash-free coal and 37.3 percent sulfur distribution in the float). The percent reduction ratio of sulfur/ash-free coal was significantly high: 43.8 percent. The percent of the removal of total sulfur from the Illinois No. 6 coal sample was 29.4 percent. This corresponded to about 60 percent pyritic sulfur removal. (It was previously estimated that 50 percent of the total sulfur in Illinois No. 6 coal samples was pyritic sulfur.)

A single stage flotation test was compared with the double stage flotation test. The test procedures used for the single stage flotation of an Illinois No. 6 coal sample, after conditioning in "bacterial liquor," were as follows. One hundred grams of pulverized Illinois No. 6 coal samples were conditioned in "bacterial liquor" for one hour and then the coal sample was floated with cresylic acid. Cresylic acid was added to the pulp as required. The details of the test procedure are outlined in Section 4.3.2. The test results are given in Table 6.20

Table 6.21. Comparison of the Effects of Double and Single Stage Flotation Tests on Removal of Sulfur and Ash from Illinois No. 6 Coal Samples.

Sample No.	Flotation Products	Weight, %	Analysis, %			Weight Distribution, %			% Reduction of Sulfur	% Reduction of Sulfur/Ash-free coal ratio
			Ash	Combustibles	Total Sulfur	Ash	Combustibles	Total Sulfur		
C ₅	Float	52.9	4.4	95.6	3.4	9.7	66.5	37.3	29.3	43.8
	Sink ₁	21.1	18.9	81.1	6.3	16.7	22.5	27.8		
	Sink ₂	26.0	67.8	32.2	6.4	73.6	11.0	34.9		
	Composite Total	100	23.9	76.1	4.8	100	100	100		
C ₁₃	Float	75.6	13.9	86.1	5.4	40.9	87.6	72.9	3.6	16.8
	Sink	24.4	62.3	37.7	6.2	59.1	12.4	27.1		
	Composite Total	100	25.7	74.3	5.6	100	100	100		

Remarks:

Size of the coal samples = minus 65 mesh

Flotation cell conditions:

pH = 7.0, rpm = 900

Pulp density = 5 (w/v)

Flotation time = 4 minutes

Conditioning time in the frother = 1 minute

(a) Double stage flotation tests:

At the first stage, coal samples were conditioned with 2 lb./ton of Na₂CO₃.

At the second stage, the float from the first stage was conditioned in "bacterial liquor" for 1 hour.

(b) Single stage flotation tests:

Sample was conditioned in "bacterial liquor" for 1 hour.

Reagents used:

Frother: Cresylic acid was added as required

(sample number C₁₃).

The yield of the material in the single stage flotation test was higher than the yield in the double stage flotation test (75.6 percent yield). The percent distribution of ash, ash-free coal, and sulfur in the float were also substantially higher than the double stage flotation test results. The percent reduction of sulfur in the float of the single stage test was quite lower (3.6 percent) than that of the double stage test (29.3 percent). The sulfur/ash-free coal reduction ratio was 2.5 times smaller than that of the double stage flotation test. It was concluded that the addition of a second stage of flotation to the process substantially lowered the sulfur content of the Illinois No. 6 coal sample, but at the cost of a low recovery of combustibles and a small yield. •

6.5 Determination of the Efficiency of the Flotation Tests by Washability Studies of the Illinois No. 6, Middle Kittanning, and Pittsburgh Seam Coals:

6.5.1 Washability Studies of Illinois No. 6 Seam Coal Samples:

Pulverized samples of Illinois No. 6 coal were floated at different specific gravities. The test procedure used was outlined in Section 4.2.3. The data obtained by the float-sink method are tabulated in Table 6.22. Figure 6.29 shows the cumulative-ash float curve, cumulative-ash sink curve, specific gravity or yield curve, ± 0.1 specific gravity curve, and cumulative-sulfur float curve.

The yield curve shows the theoretical yield of the washed coal from the raw coal for any given specific gravity of separation. For example, at 1.4 specific gravity only 42 percent yield resulted, whereas at 1.7 specific gravity 84 percent yield resulted.

The cumulative-ash float curve shows the theoretical percent of ash in the float at any given yield of washed product. For example, when 20 percent of the total material was floated, it contained only two percent ash, whereas when 90 percent of the material was floated, it contained 16 percent ash.

The cumulative-ash sink curve shows the theoretical percent of ash content of the sink at any yield of the washed product. For example, at 30 percent yield or 70 percent sink, there was 36 percent ash in the sink, whereas at 90 percent yield there was 90 percent ash in the sink.

The plus or minus 0.1 specific gravity curve presented in Figure 6.29 shows that 45 percent of the near gravity materials collected in 1.48 ± 0.1 specific gravity interval. The percentage of the near

Table 6.22. Washability Studies of the Illinois No. 6 Coal Samples.

Specific Gravity	Direct Percentages			Cumulative Float			Cumulative Sink									
	% Weight	Ash Product	% Ash	Sulfur Product	% Ash	% Sulfur	Ash Product	% Ash	Sulfur Product							
-	1.28	1.5	1.7	1.1	1.5	1.7	1.1	100.0	2660.0	26.6	521.0	5.2				
1.28	1.38	30.8	76.6	2.5	32.3	116.4	3.6	113.4	3.5	98.5	2620.0	26.6				
1.38	1.62	44.9	618.7	13.8	77.2	735.0	9.5	277.9	3.6	67.7	2543.7	37.6	407.6	6.0		
1.62	1.88	11.2	863.9	77.3	85.4	7.6	88.4	1599.0	18.1	363.3	4.1	22.8	1925.0	84.5	243.1	10.7
1.88	-	11.6	1061.	91.4	157.7	13.6	100.0	2660.0	26.6	521.0	5.2	11.6	1061.0	91.4	157.7	13.6

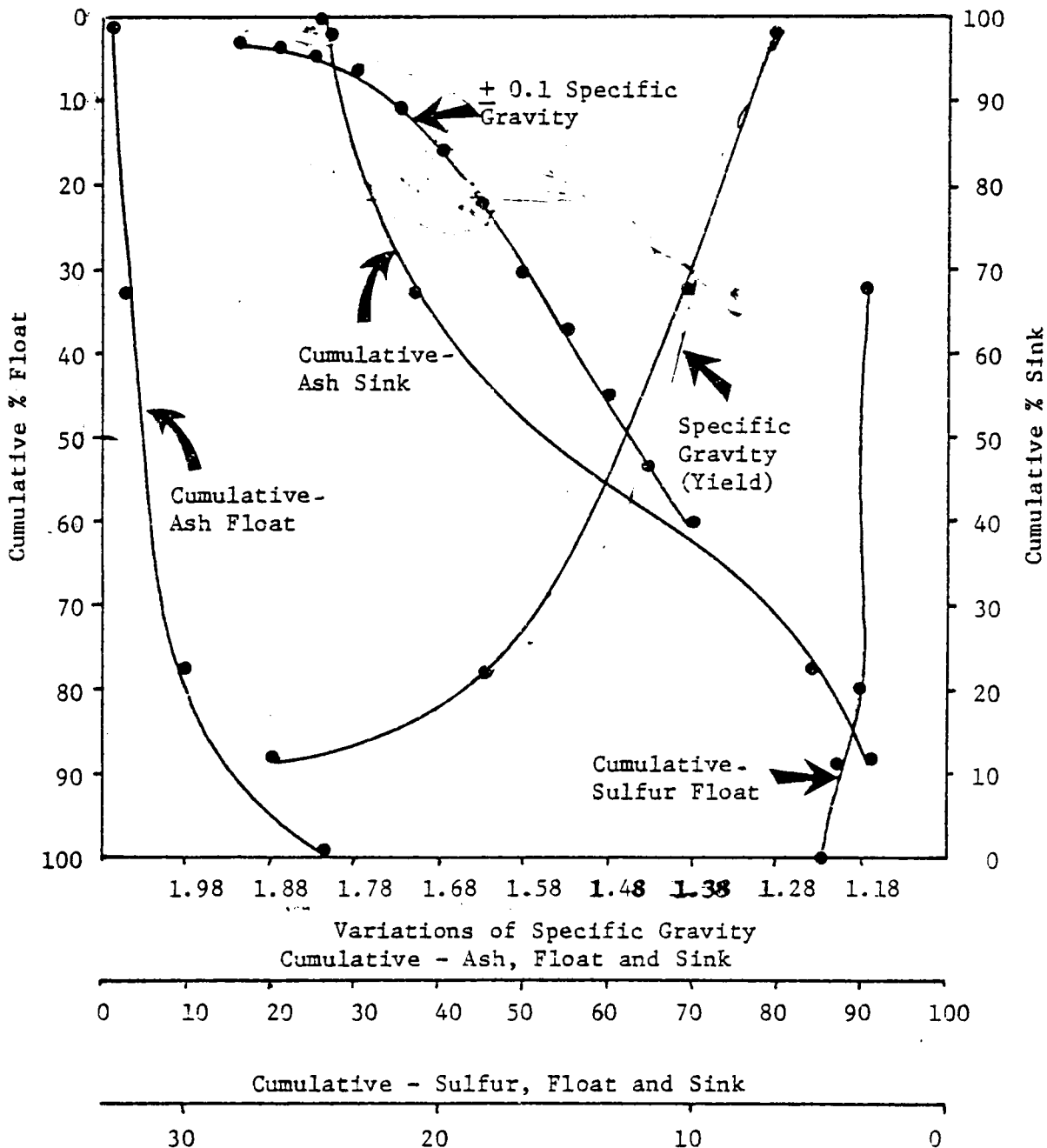


Figure 6.29. Washability Curves of Illinois No. 6 Coal Samples.

gravity materials decreased for specific gravities higher than 1.58.

The cumulative-sulfur float curve indicated that the sulfur content of the Illinois No. 6 coal sample stayed constant between 32 to 80 percent cumulative yields. The float-sink results indicated that the percent sulfur in the Illinois No. 6 coal sample was lowered from 5.21 percent in the feed to 3.51 percent in the float at 1.38 specific gravity (a sulfur reduction of 32.62 percent). The sulfur reduction results of various flotation tests should therefore be compared with the theoretical results of the float-sink studies.

6.5.2 Washability Studies of Pittsburgh Seam Coal Samples:

Coal samples of the Pittsburgh seam were washed according to the procedures outlined in Section 4.2.3. The washability data are tabulated in Table 6.23. Figure 6.30 shows the curves of the cumulative-ash float, cumulative-ash sink, specific gravity or yield, ± 0.1 specific gravity, cumulative-sulfur float, and cumulative-sulfur sink.

The specific gravity curve indicated that the theoretical yield of the floated coal sharply increased to 74 percent when a 1.38 specific gravity was used. This indicated that 74 percent of the material in this coal had a specific gravity lower than 1.38. The specific gravity curve started to level off at specific gravities higher than 1.6, which resulted in a 90 percent yield.

The cumulative-ash float curve showed that, when the cumulative percent of the yield was increased to 74 percent, the cumulative-ash was slightly increased. The increase in the cumulative-ash content of the float started at about a 74 percent yield. When the yield increased

Table 6.23. Washability Studies of the Pittsburgh Seam Coal Samples.

Specific Gravity	Direct Percentages			Cumulative Float			Cumulative Sink									
	% Weight	% Ash Product	% Ash	Sulfur Product	% Sulfur	% Weight	Ash Product	% Ash	Sulfur Product	% Sulfur						
-	1.28	1.6	3.1	2.0	2.9	1.9	1.6	3.1	2.0	2.9	1.9	100.0	1162.0	11.6	431.0	4.3
1.28	1.38	72.3	262.7	3.6	140.3	1.9	73.8	265.8	3.6	143.3	1.9	98.4	1158.9	11.8	428.0	4.4
1.38	1.62	15.4	162.7	10.5	35.3	2.3	89.3	428.5	4.8	178.6	2.0	26.2	896.2	34.3	287.7	11.0
1.62	1.88	1.5	46.0	31.5	8.4	5.7	90.7	474.6	5.2	186.9	2.1	10.7	733.5	68.4	252.4	23.5
1.88	-	9.3	687.4	74.2	244.0	26.35	100.0	1162.0	11.6	431.0	4.3	9.3	687.4	74.2	244.0	26.4

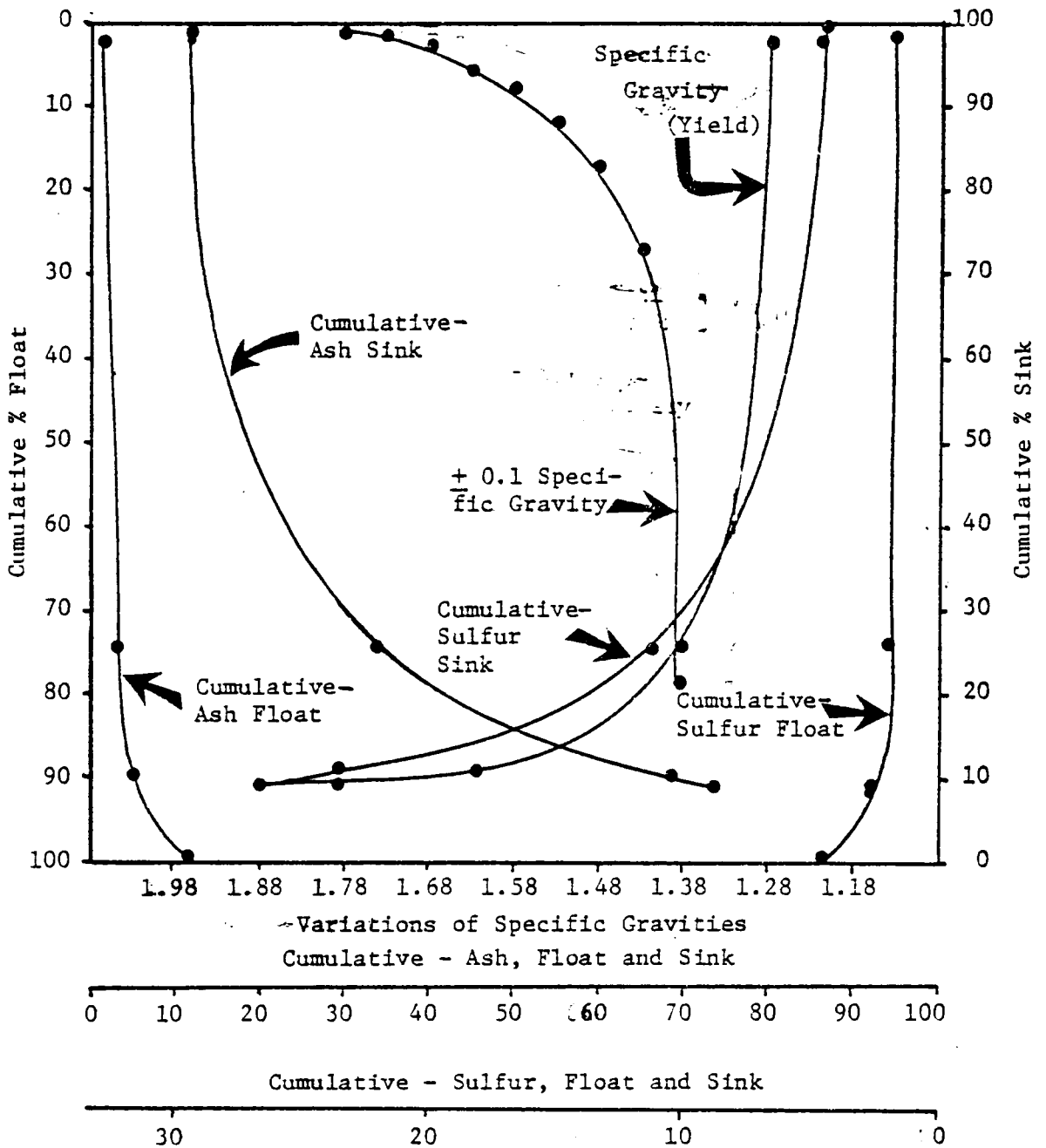


Figure 6.30. Washability Curves of the Pittsburgh Seam Coal Samples.

from 74 to 100 percent, the ash increased from 3.5 percent to 12 percent.

The cumulative-ash sink curve showed that the percent ash reported to the sink moderately increased when the cumulative yield increased from 30 percent to 74 percent. There was an abrupt increase in the cumulative-ash content of the sink when the yield of the float increased from 74 percent to 91 percent.

The cumulative-sulfur float curve showed that the theoretical percentage of sulfur increased from 1.86 percent to 2.06 when the cumulative percent float increased from 1.6 to 90.7. This slight increase in the sulfur content of the float in such a large yield interval (1.6 to 90.7 percent yield) indicated that about 40 percent of the total sulfur could be separated from this coal by gravity separation at specific gravities as low as 1.28. When the theoretical yield was increased from 90 to 100 percent, the sulfur content of the float increased from 2.06 to 4.31 percent by weight.

The cumulative-sulfur sink curve showed that the percent of cumulative-sulfur which reported to the sink was moderately increased when the percent yield was increased from 30 to 60 percent. The percent cumulative-sulfur in the sink sharply increased from 8 percent to 26.6 percent when the percent yield of the cumulative-float was increased from 60 to 90 percent.

The plus or minus 0.1 specific gravity curve presented in Figure 6.30 showed that 22 percent of the near gravity materials collected in 1.48 ± 0.1 specific gravity interval. The percentage of the near gravity materials decreased for specific gravities higher than 1.58.

6.5.3 Washability Studies of Middle Kittanning Seam Coal Samples:

Coal samples of the Middle Kittanning seam were washed according to the procedure outlined in Section 4.2.3. The float-sink data of these tests are tabulated in Table 6.24. Figure 6.31 shows the cumulative-ash float curve, cumulative-ash sink curve, specific gravity or yield curve, ± 0.1 specific gravity curve, cumulative-sulfur float curve, and cumulative-sulfur sink curve.

The specific gravity or yield curve showed that the theoretical yield percent of the washed coal from the raw coal (feed) increased sharply when the specific gravity was raised from 1.28 to 1.58. The increase in yield started to level off at about specific gravity 1.58.

The cumulative-ash float curve showed that the theoretical percent ash in the float was increased only 4 percent where the yield (cumulative-float) increased 89 percent. There was a sudden increase from 4 percent to 11 percent ash in the float when the yield was increased from 89 percent to 100 percent. Hence, it could be concluded that, theoretically, the increase in yield up to about 85 percent introduces only 3.5 percent ash in the float.

The cumulative-ash sink curve showed that the theoretical percent ash content of the sink increased moderately from 10 percent to 23 percent when the cumulative-float (yield) increased from zero to 60 percent. However, when the yield increased from 60 to 92 percent, the cumulative-ash in the sink sharply increased from 22 percent to 76 percent.

The cumulative-sulfur float curve shows that the theoretical percentages of sulfur collected in the float increased from 0.89 percent

Table 6.24. Washability Studies of Middle Kittanning Coal Samples.

Specific Gravity	Direct Percentages				Cumulative Float				Cumulative Sink							
	% Weight	Ash Product	% Ash	Sulfur Product	% Sulfur	Sulfur Product	% Ash	Ash Product	% Weight	% Sulfur	Sulfur Product	% Ash	Ash Product			
-	1.28	0.5	0.8	1.5	0.5	0.9	0.5	0.8	1.5	0.5	0.9	100.0	1047.0	10.5	318.0	3.2
1.28	1.38	37.6	95.3	2.5	34.6	0.9	38.1	96.0	2.5	35.0	0.9	99.5	1046.2	10.5	317.5	3.2
1.38	1.62	50.8	287.1	5.7	53.9	1.1	68.9	383.1	4.3	88.9	1.0	61.9	951.0	15.4	282.9	4.6
1.62	1.88	2.7	28.1	10.5	2.7	1.0	91.6	411.2	4.5	91.6	1.0	11.1	663.9	59.8	229.1	20.6
1.88	-	8.4	635.9	75.4	226.4	26.9	100.0	1047.0	10.5	318.0	3.2	8.4	635.9	75.4	226.4	26.9

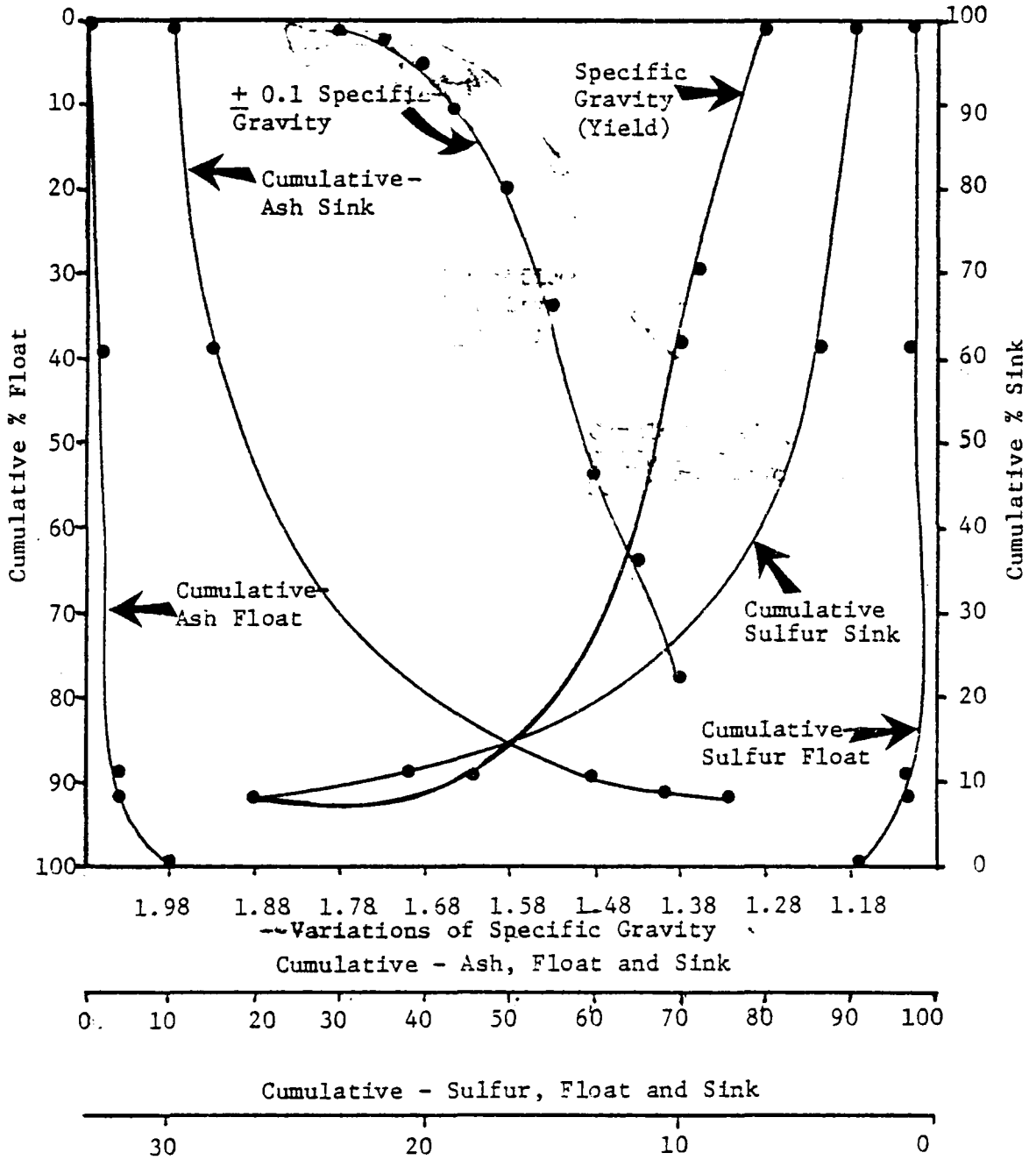


Figure 6.31. Washability Curves of Middle Kittanning Coal Samples.

to 1.0 percent sulfur where the cumulative weight percent of the yield increased from 0.53 to 91.57 percent. The sulfur content of the float sharply increased from 1.0 percent to 3.18 percent when the yield increased from 91.6 percent to 100 percent. The results of the washability studies showed that both sulfur and ash have excellent washability potentials. For example, at a 90 percent theoretical yield, the ash content would be 3 percent and the sulfur content would be 1 percent.

The theoretical sulfur reported to the sink could be forecast by the cumulative-sulfur sink curve. The percent sulfur in the sink slightly increased when the cumulative weight percent of the yield increased to 60. The sulfur in the sink increased from 3.3 to 23.3 percent when the yield increased from 60 to 92 percent.

The plus or minus 0.1 specific gravity curve presented in Figure 6.31 indicated that 55 percent of the near gravity materials collected in 1.48 ± 0.1 specific gravity interval. The percentage of the near gravity materials decreased for specific gravities higher than 1.58.

7. SUMMARY AND CONCLUSIONS

The experimental results are summarized as follows:

7.1 Pyrite Liberation Size Studies:

Microscopic examination of coal pyrite indicated that, the more the samples were ground, the more pyrite particles locked in the non-pyrite matrix were exposed to the surface. In the 5 to 60 minute grinding time range, the ratio of binary pyrite particles/free pyrite particles decreased (from .45 to .13) with an increase in grinding time. When the sample was ground for 53 hours the binary pyrite particle/free pyrite particle ratio increased to 1.4. This large increase in the ratio was due to the further grinding and exposing of the binary particles of pyrite.

7.2 Development of a New Float and Sink Technique:

A new float and sink technique was developed and used for washability studies of pulverized coals. This method separated the lighter fractions of coal from the heavier fractions in a heavy liquid by centrifugal force, but was not effective for analytical pyrite separations.

7.3 Effect of Chemical Reagents, pH Values, and Variations of Temperature:

The effect of chemical reagents and variables such as pH and temperature on the removal of pyritic sulfur were examined. The following conclusions were made.

At a pH value of 3.0, using the Illinois No. 6 coal samples, the values of the distributions of ash, sulfur, and combustibles were highest. However, the increase in pH values resulted in an increase in the

reduction of sulfur from Illinois No. 6 coal samples.

When the temperature of the flotation pulp of the Illinois No. 6 coal was increased from 20 degrees centigrade ($^{\circ}\text{C}$) to 55°C the sulfur reduction increased from 3.6 percent to 18.7 percent. But then the sulfur reduction decreased from 18.7 percent to 3.2 percent when the temperature was increased from 55 to 75°C .

The effect of different depressants on the removal of pyrite from Illinois No. 6, Pittsburgh, and Middle Kittanning coals were studied. It was concluded that dextrin in combination with Terpeneol, and "bacterial liquor" in combination with cresylic acid, were most effective in the removal of sulfur from Illinois No. 6 coal samples (40.7 and 24.7 percent sulfur reduction, respectively). "Bacterial liquor" was most effective in the removal of sulfur from the Pittsburgh coal samples (14.0 percent sulfur reduction), and dextrin was most effective in the removal of sulfur from Middle Kittanning coal samples (15.7 percent sulfur reduction).

7.4 Application of Grab and Run Theory:

Grab and run theory was examined. When 50 percent of the sulfur was distributed in the float, 45 percent of ash and 65 percent of the combustibles were also distributed in the float. The yield at this point was only 55 percent.

7.5 Flotation of Coal Samples Preconditioned in "Bacterial Liquor":

Coal samples of Illinois No. 6, Pittsburgh, and Middle Kittanning seams were conditioned in "bacterial liquor" for various time intervals. The effect of increased retention time on the suppression of coal pyrite was then studied.

In order to facilitate future feasibility studies of bacterial oxidation of pyrite in coal, the effect of recycled "bacterial liquor," old and freshly made "bacterial liquor," and maximum percent of solids in the "bacterial liquor" were studied. The following were concluded.

When the retention time of Illinois No. 6 coal in the "bacterial liquor" was increased from 10 minutes to 5 hours, the sulfur reduction increased from 5.8 to 16.5 percent. The reduction ratio of sulfur/ash-free coal in this time interval increased from 16.8 to 26.4 percent. The sulfur reductions from both Pittsburgh and Middle Kittanning coal were small.

The effect of recycled "bacterial liquor" was relatively the same as the original "bacterial liquor."

Old "bacterial liquor," on the other hand, had lost its effectiveness and resulted in lower reductions of sulfur.

7.6 Effect of Double Stage Flotation on Illinois No. 6 Coal Samples:

A comparison of the effect of the double and single stage flotation tests showed that, when using a single stage flotation test, only 3.6 percent of the total sulfur was removed from Illinois No. 6 coal samples. When a double stage flotation test was used 29.3 percent of the total sulfur was removed from the coal. This figure (29.3 percent) corresponds to a reduction of about 60 percent pyritic sulfur.

7.7 Washability Studies of the Coal Samples:

Washability studies of the coal samples of Illinois No. 6, Pittsburgh, and Middle Kittanning seams indicated that the total sulfur in Illinois No. 6 was reduced from 5.21 to 3.51 percent, the total sulfur in Pittsburgh coal was reduced from 4.31 to 1.86 percent, and the total

sulfur in Middle Kittanning coal was reduced from 3.18 to 0.89 percent. The above results show that Illinois No. 6 coal was desulfurized more efficiently than Pittsburgh and Middle Kittanning coals by the flotation tests presented in this report.

8. RECOMMENDATIONS FOR FUTURE STUDY

Future work in the area of superficial oxidation of pyrite by T. ferrooxidans should include the zeta potential measurements of the pyrite and nonpyrite matter before and after conditioning in "bacterial liquor." The future investigator should expand the range of the retention times and pulp densities of the conditioning tank used by this author. Also, a systematic viable count of the bacteria should be used and the optimum number of bacteria per unit weight of the coal samples should be determined. Multistage flotation should be used and optimized. Also, an accurate analytical procedure for the analysis of pyritic sulfur must be developed. The X-ray diffraction method certainly has future potential for quantitative analysis of pyrite.

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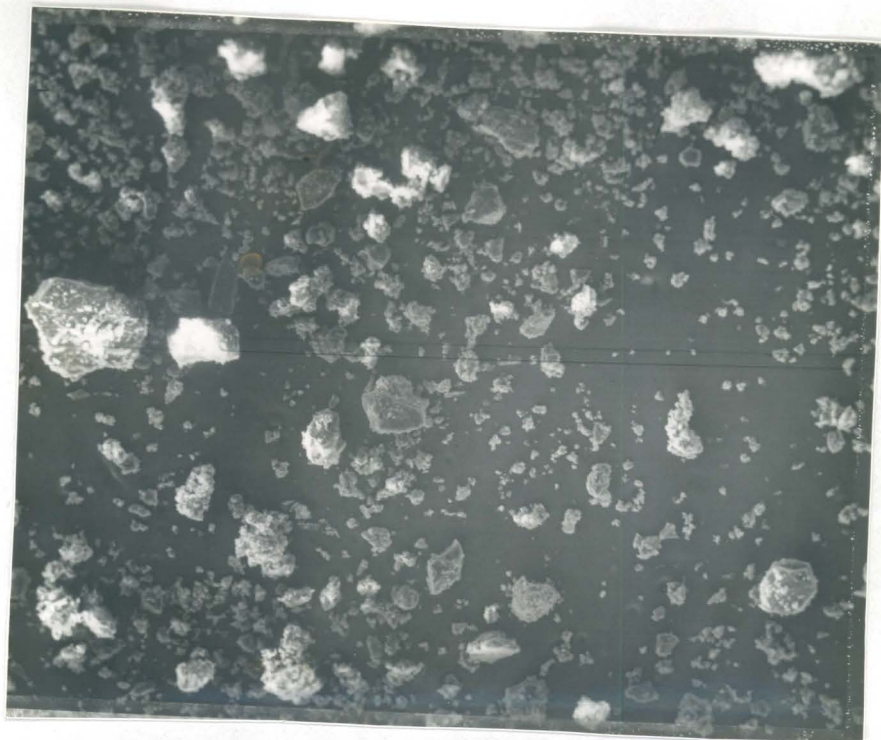
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APPENDIX
PHOTOMICROGRAPHS OF ILLINOIS
NO. 6 SEAM COAL SAMPLES

(a)



(b)

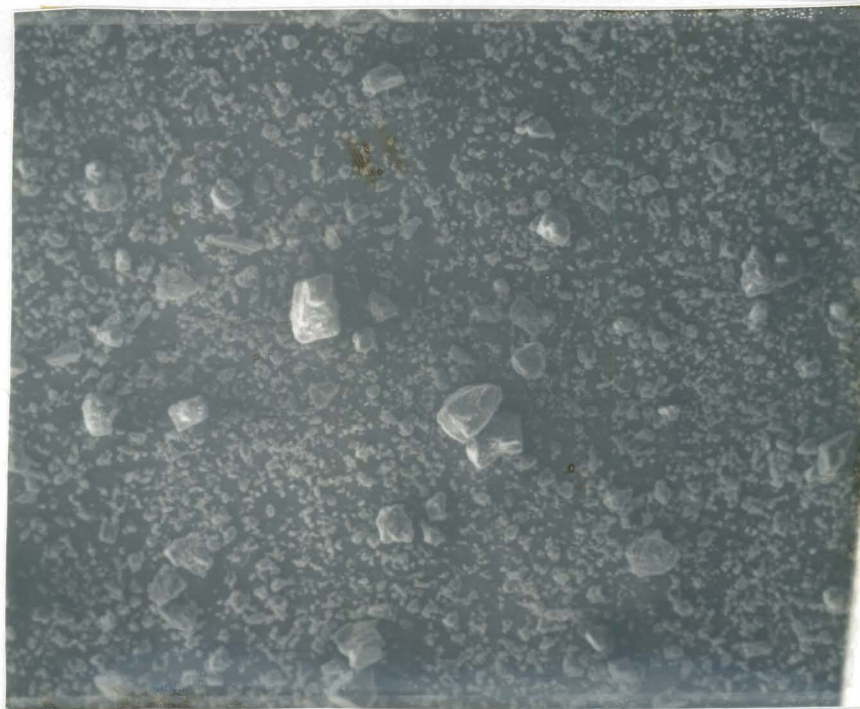
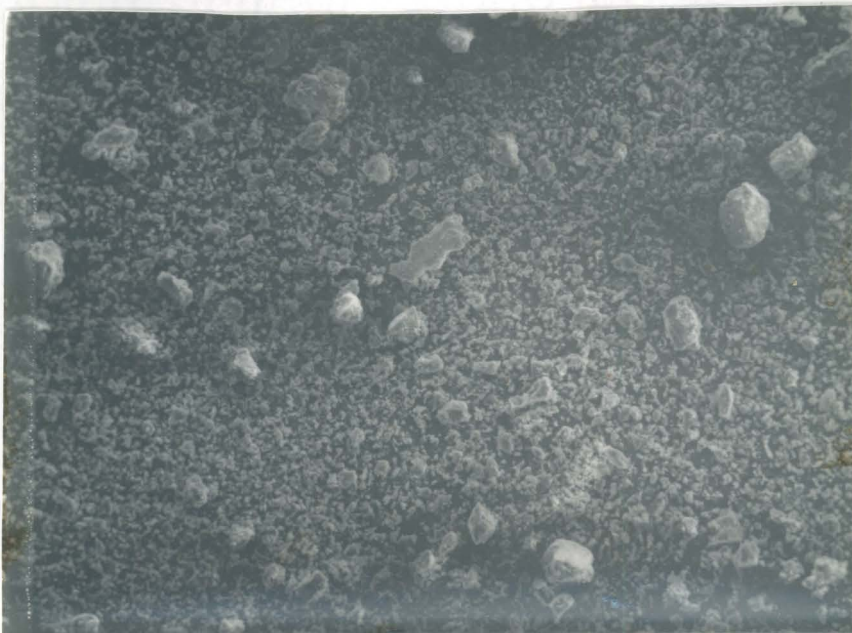


Figure A-1. Size Comparison of Photomicrographs of Illinois No. 6 Coal Samples Ground for (a) 5 Minutes and (b) 10 Minutes, Magnified 100 Times. Note: AMR Model 900 Scanning Electron Microscope was Used.

(a)



(b)



Figure A-2. Size Comparison of Photomicrographs of Illinois No. 6 Coal Samples Ground for (a) 15 Minutes and (b) 20 Minutes, Magnified 100 Times. Note: AMR Model 900 Scanning Electron Microscope was Used.

(a)

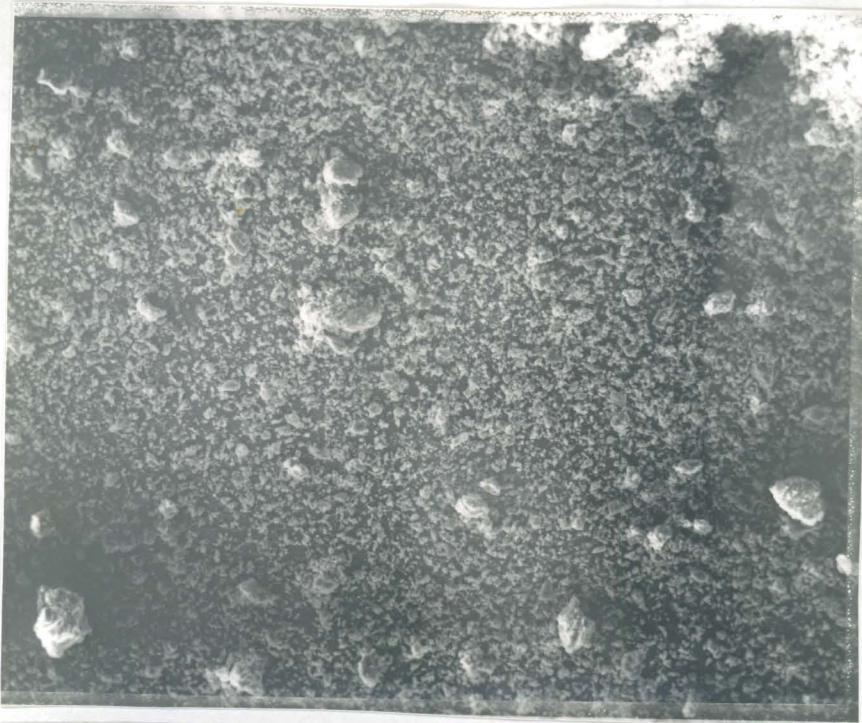


(b)



Figure A-3. Size Comparison of Photomicrographs of Illinois No. 6 Coal Samples Ground for (a) 30 Minutes and (b) 40 Minutes Magnified 100 Times. Note: AMR Model 900 Scanning Electron Microscope was Used.

(a)



(b)



Figure A-4. Size Comparison of Photomicrographs of Illinois No. 6 Coal Samples Ground for (a) 50 Minutes and (b) 60 Minutes Magnified 100 Times. Note: AMR Model 900 Scanning Electron Microscope was Used.

M.L.N./78/VPI&SU

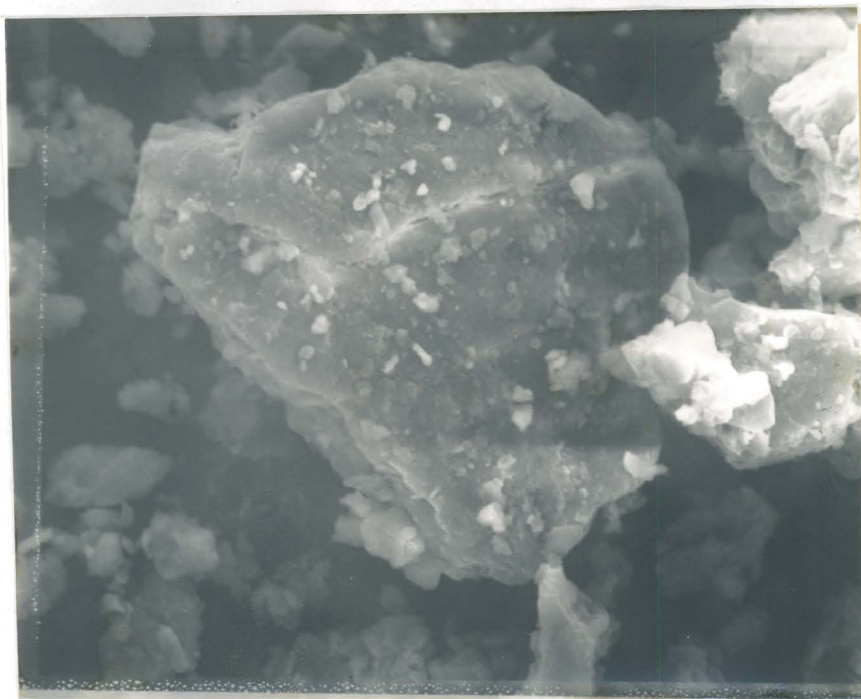


Figure A-5. Photomicrograph of Illinois No. 6 Coal Sample Ground for 5 Minutes, Magnified 1000 Times.
Note: AMR Model 900 Scanning Electron Microscope was Used.

M.L.N./78/VPI&SU

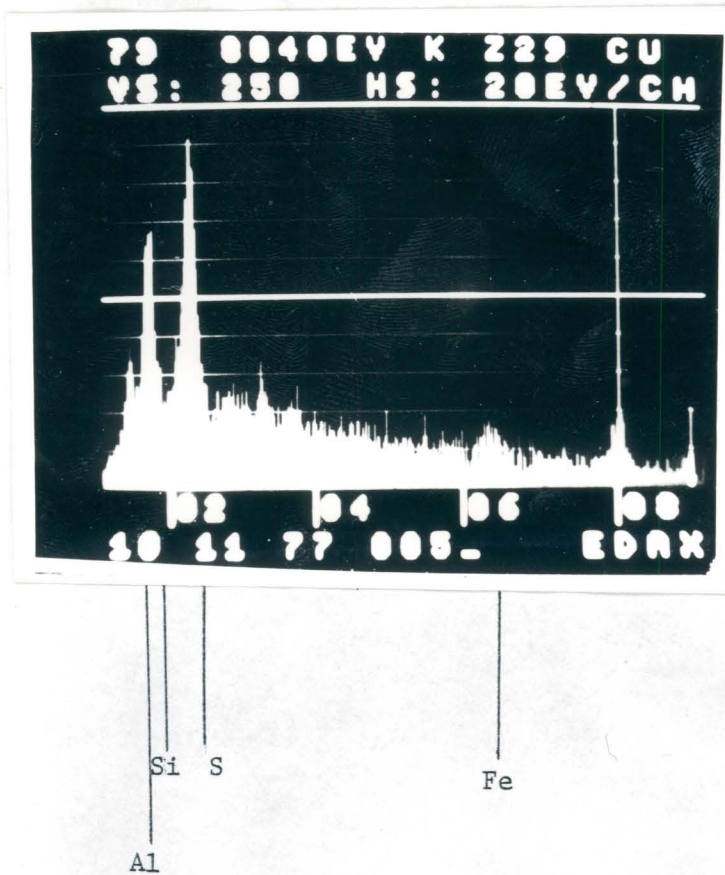


Figure A-6. X-ray Analysis of a Representative Particle in Illinois No. 6 Coal Sample Ground for 5 Minutes.

Note: The X-ray Analysis was Done by an EDAX Unit Attached to the Scanning Electron Microscope.

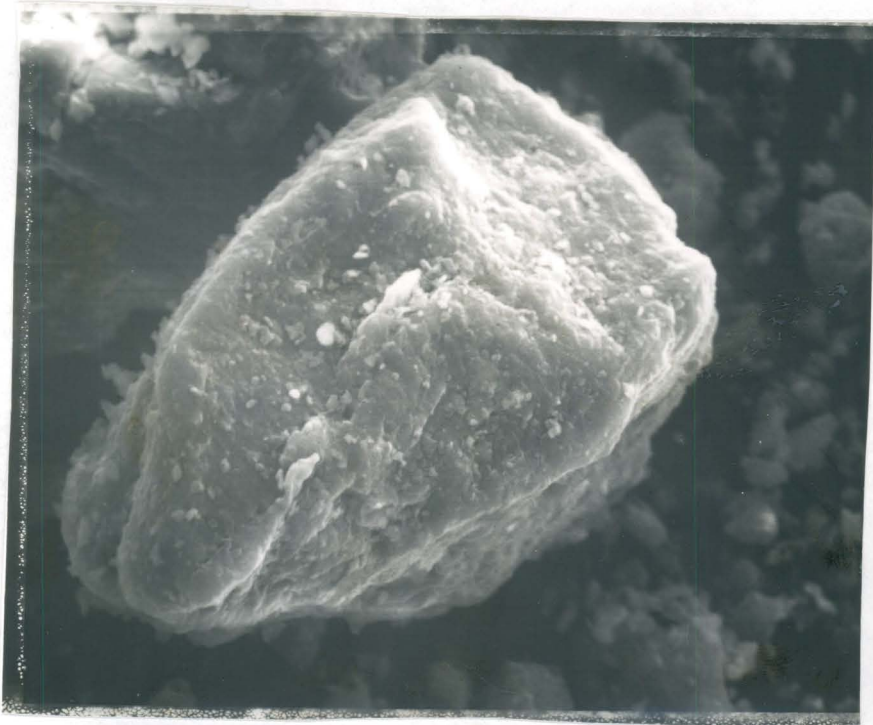


Figure A-7. Photomicrograph of Illinois No. 6 Coal Sample Ground for 10 Minutes Magnified 1000 Times.

Note: AMR Model 900 Scanning Electron Microscope was Used.

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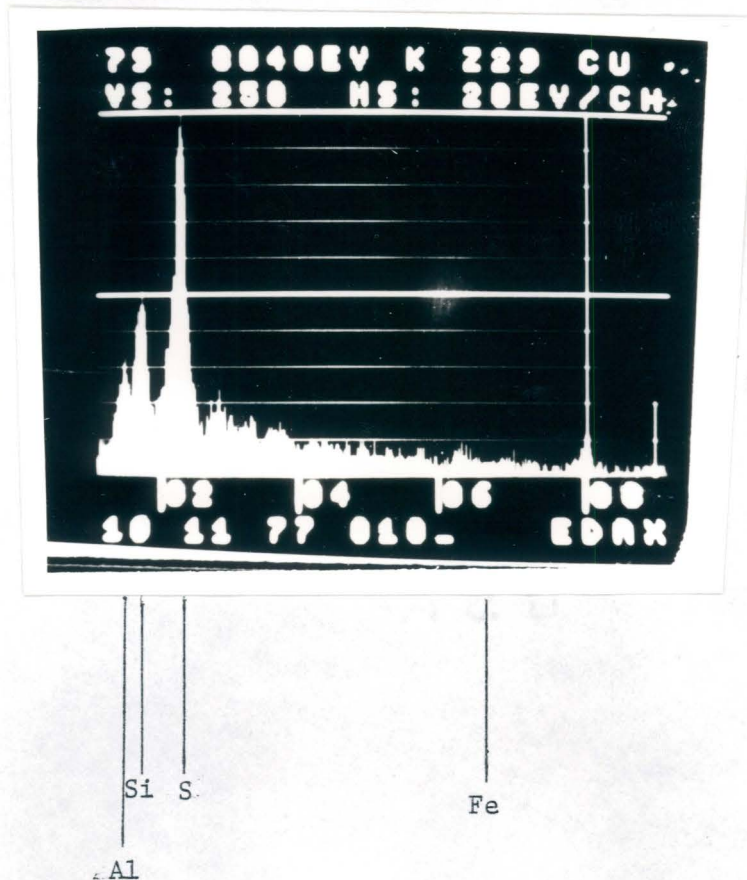


Figure A-8. X-ray Analysis of a Representative Particle in Illinois No. 6 Coal Sample Ground for 10 Minutes.

Note: The X-ray Analysis was Done by an EDAX Unit Attached to the Scanning Electron Microscope.

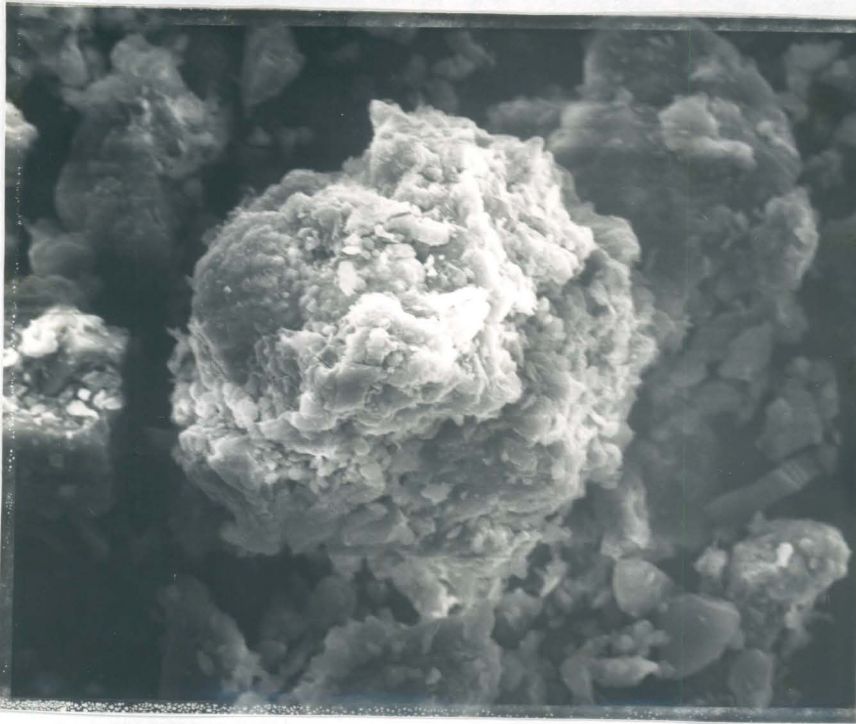


Figure A-9. Photomicrograph of Illinois No. 6 Coal Sample Ground for 15 Minutes Magnified 1000 Times.

Note: AMR Model 900 Scanning Electron Microscope was Used.

M.L.N./78/VPI&SU

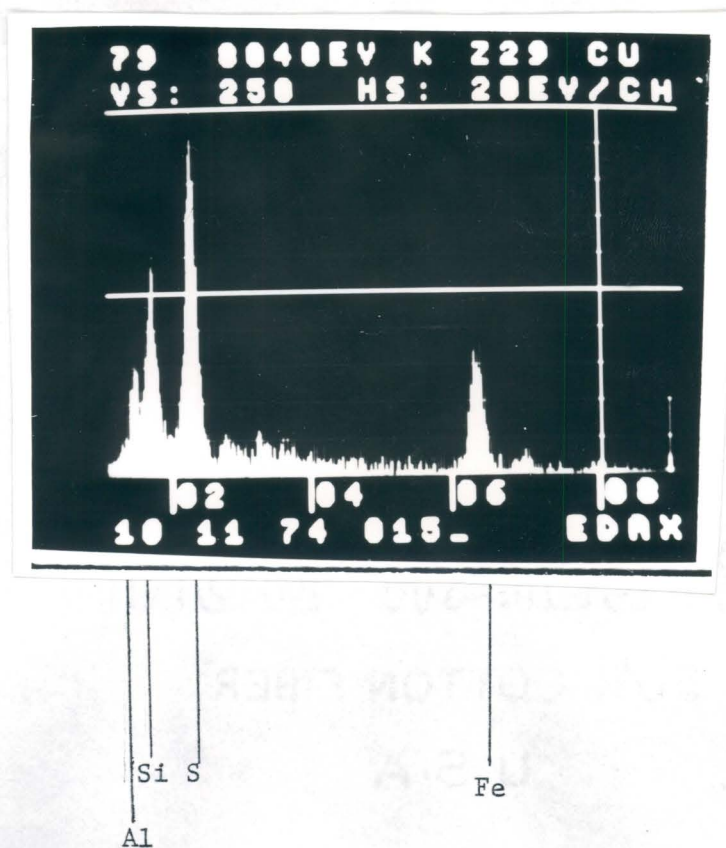


Figure A-10. X-ray Analysis of a Representative Particle in Illinois No. 6 Coal Sample Ground for 15 Minutes.

Note: The X-ray Analysis was Done by an Edax Unit Attached to the Scanning Electron Microscope.



Figure A-11. Photomicrograph of Illinois No. 6 Coal Sample Ground for 20 Minutes Magnified 1000 Times.

Note: AMR Model 900 Scanning Electron Microscope was Used.

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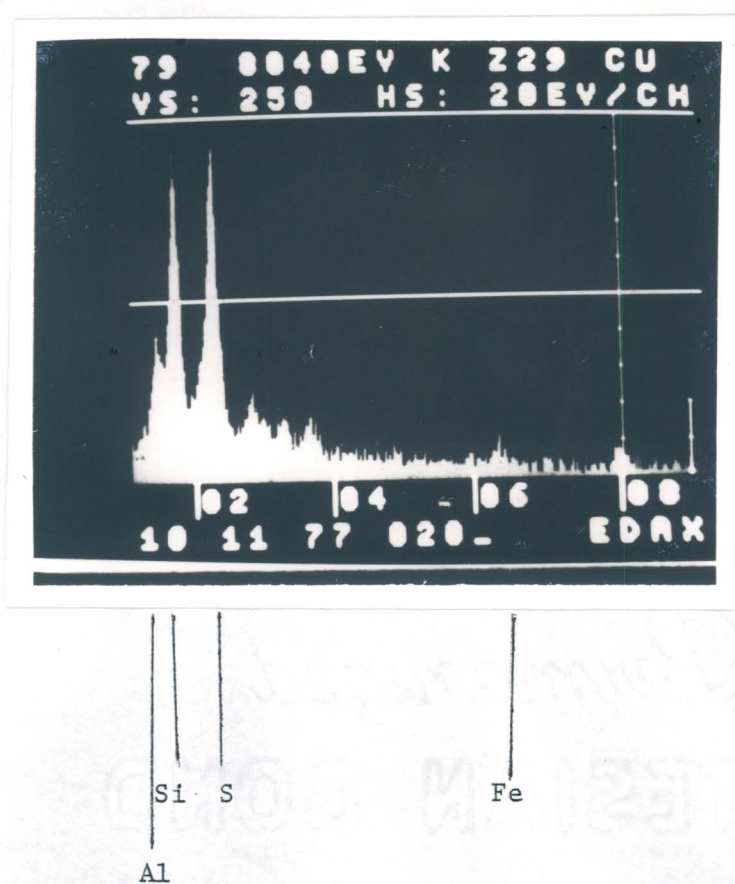


Figure A-12. X-ray Analysis of a Representative Particle in Illinois No. 6 Coal Sample Ground for 20 Minutes.

Note: The X-ray Analysis was Done by an EDAX Unit Attached to the Scanning Electron Microscope.

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Figure A-13. Photomicrograph of Illinois No. 6 Coal Sample Ground for 30 Minutes Magnified 1000 Times.

Note: AMR Model 900 Scanning Electron Microscope was Used.

M.L.N./78/VPI&SU

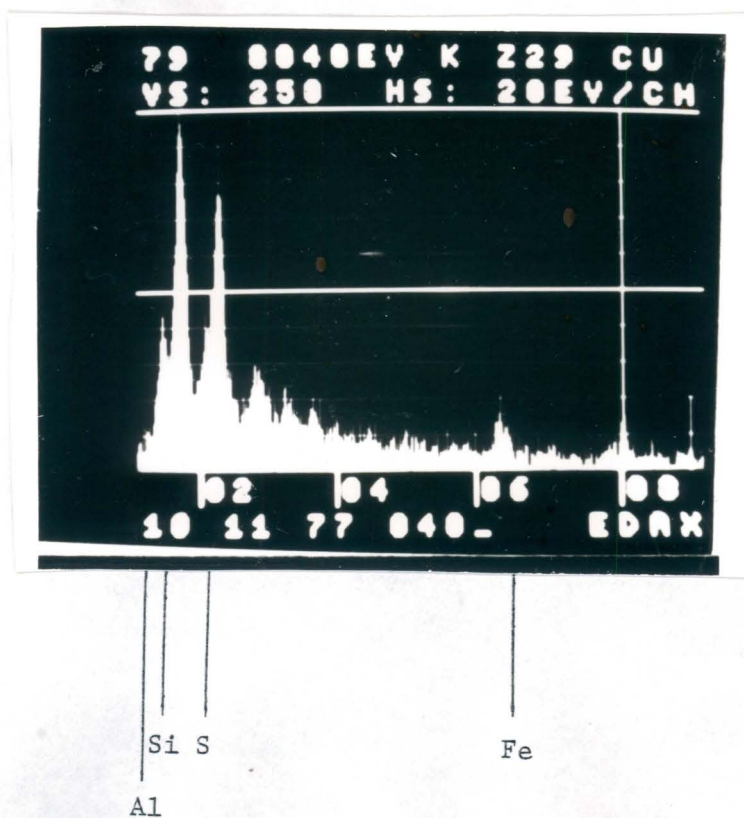


Figure A-14. X-ray Analysis of a Representative Particle in Illinois No. 6 Coal Sample Ground for 30 Minutes.
Note: The X-ray Analysis was Done by an EDAX Unit Attached to the Scanning Electron Microscope.

M.L.N./78/VPI&SU

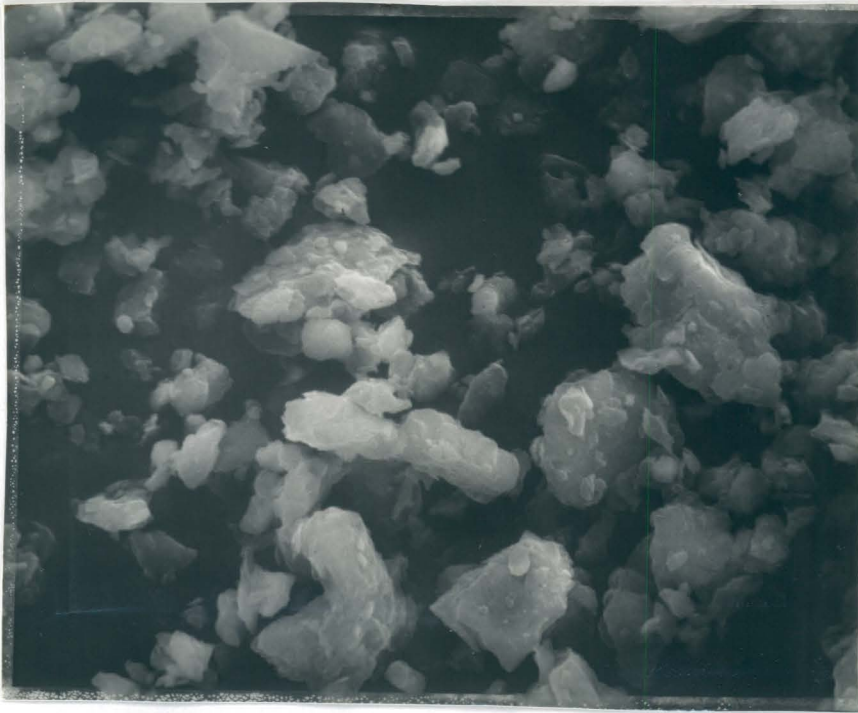


Figure A-15. Photomicrograph of Illinois No. 6 Coal Sample Ground for 40 Minutes Magnified 1000 Times.
Note: AMR Model 900 Scanning Electron Microscope was Used.

M.L.N./78/VPI&SU

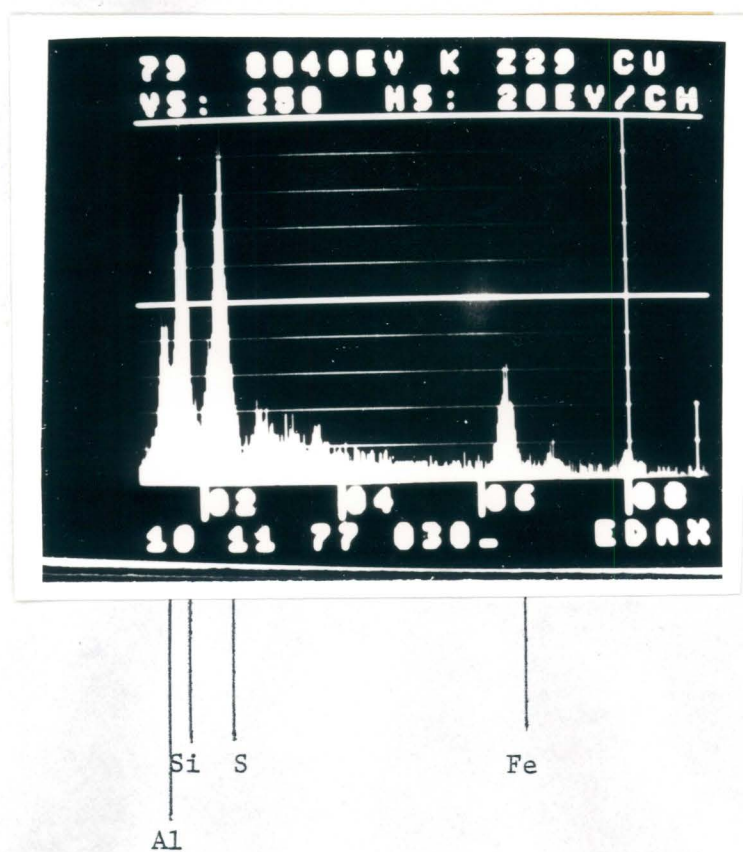


Figure A-16. X-ray Analysis of a Representative Particle in Illinois No. 6 Coal Sample Ground for 40 Minutes.
Note: The X-ray Analysis was Done by an EDAX Unit Attached to the Scanning Electron Microscope.

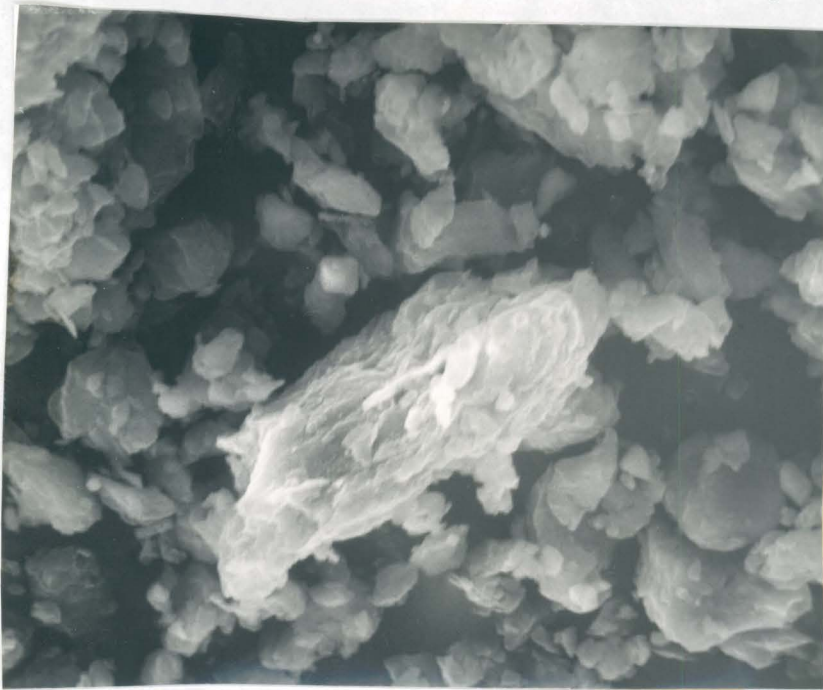


Figure A-17. Photomicrograph of Illinois No. 6 Coal Sample Ground for 50 Minutes Magnified 1000 Times.

Note: AMR Model 900 Scanning Electron Microscope was Used.

M.L.N./78/VPI&SU

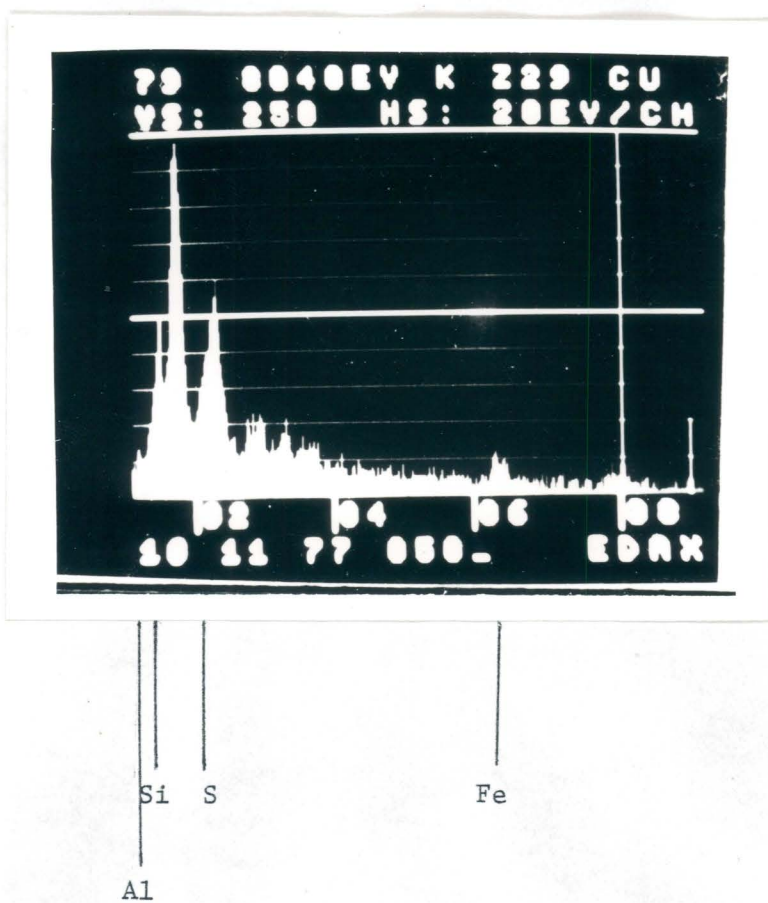
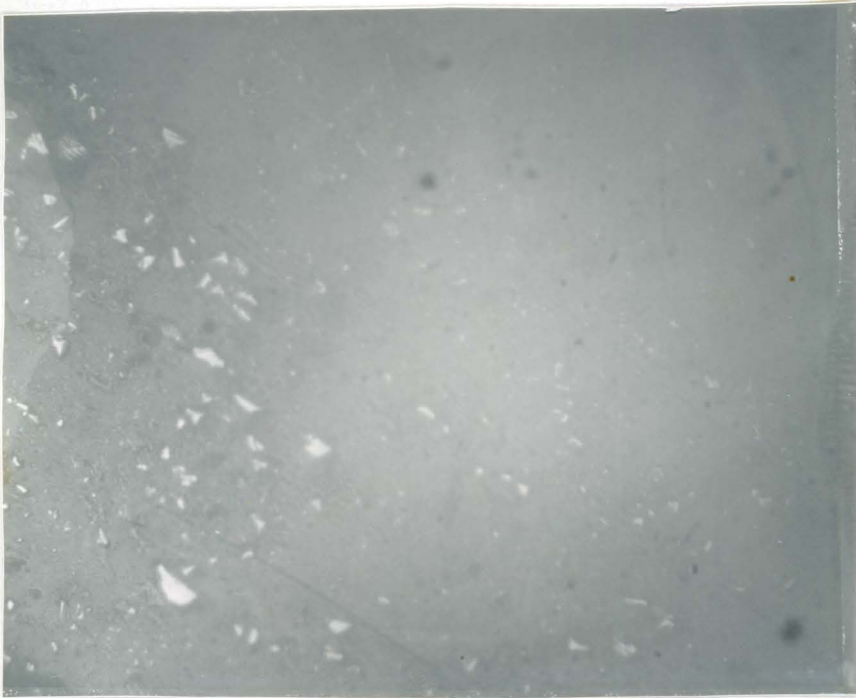


Figure A-18. X-ray Analysis of a Representative Particle of Illinois No. 6 Coal Sample Ground for 50 Minutes.

Note: The X-ray Analysis was Done by an EDAX Unit Attached to the Scanning Electron Microscope.

M.L.N./78/VPI&SU

(a)



(b)

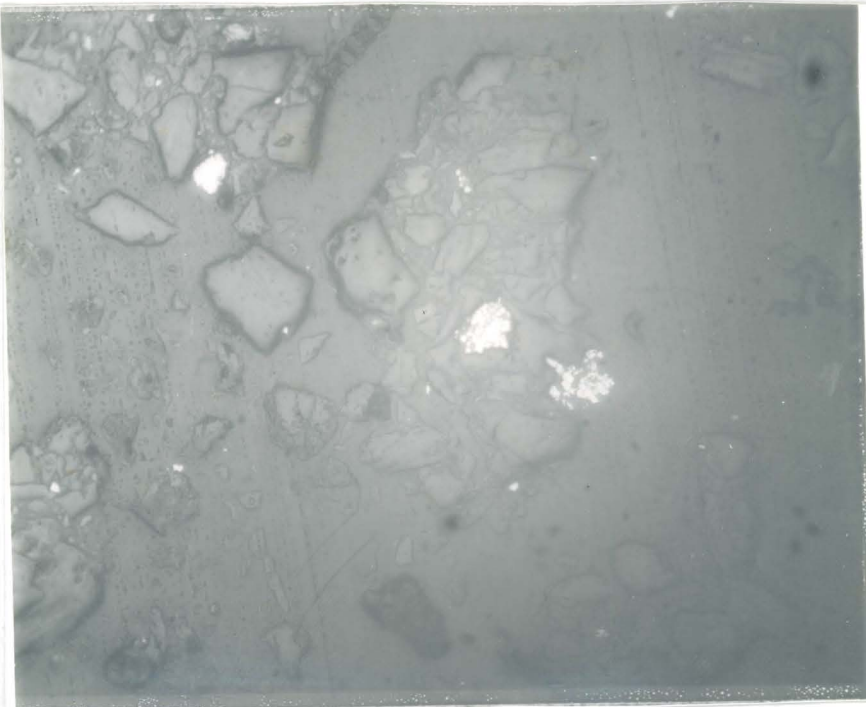
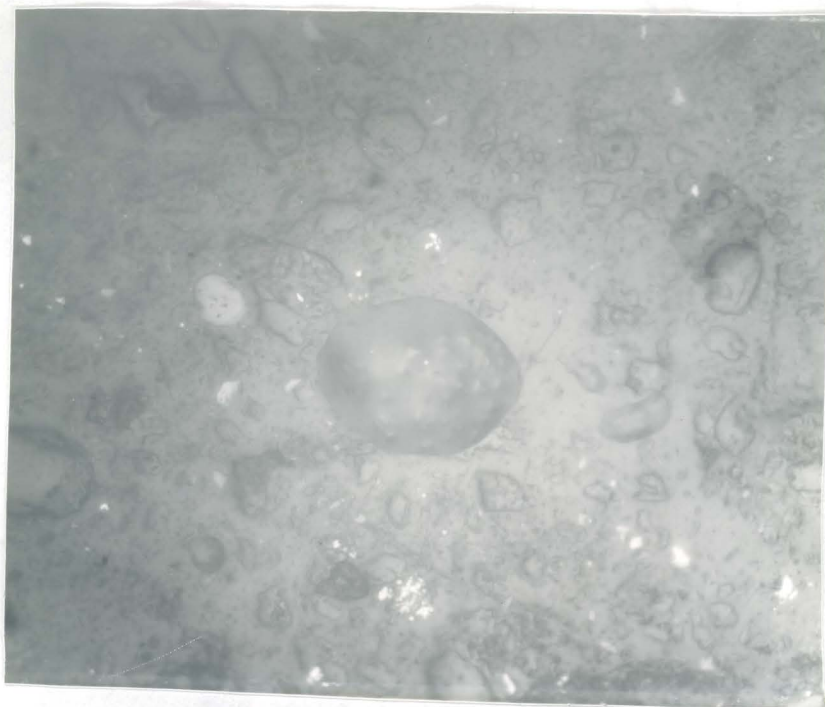


Figure A-19. Comparison of the Photomicrographs of Illinois No. 6 Coal Samples Before Treatment in Tetrabromoethane (a) and After Treatment with Tetrabromoethane (b) by Float-Sink Technique. Samples Were Ground for 5 Minutes. Particles are Magnified 200 Times. Note: A Unitron Reflected Light Microscope was Used.

M.L.N./78/VPI&SU

(a)



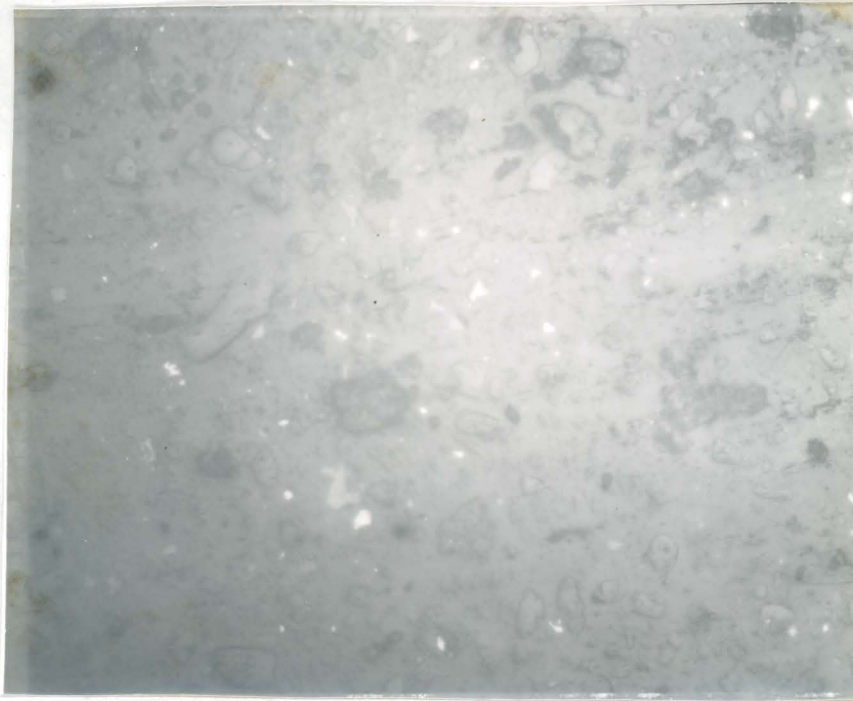
(b)



Figure A-20. Comparison of the Photomicrographs of Illinois No. 6 Coal Samples Before Treatment in Tetrabromoethane (a) and After Treatment with Tetrabromoethane (b) by Float-Sink Technique. Samples Were Ground for 30 Minutes. Particles are Magnified 200 Times. Note: A Unitron Reflected Light Microscope was Used.

M.L.N./78/VPI&SU

(a)



(b)

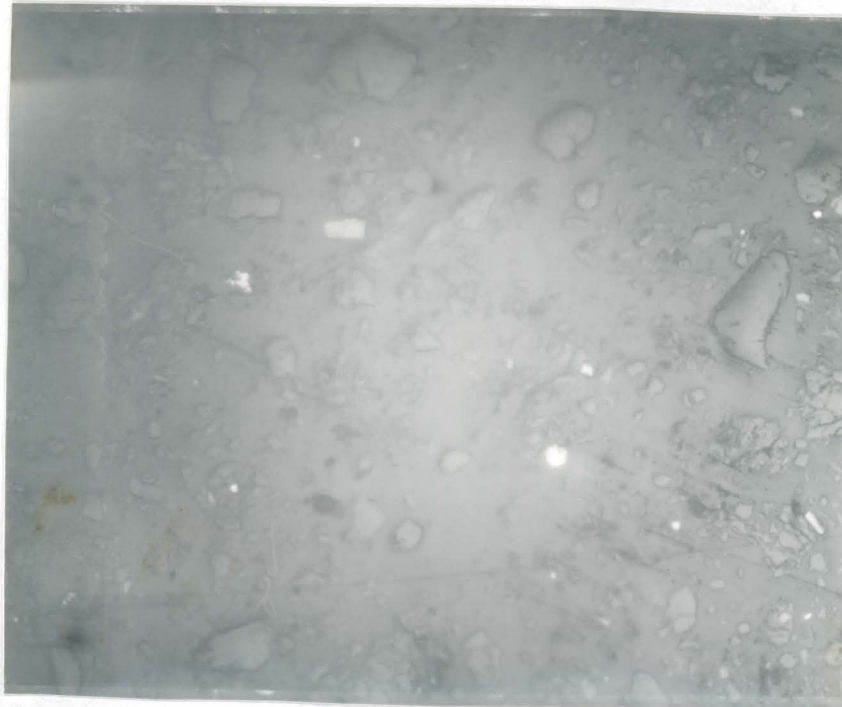


Figure A-21. Comparison of the Photomicrographs of Illinois No. 6 Coal Samples Before Treatment in Tetrabromoethane (a) and After Treatment with Tetrabromoethane (b) by Float-Sink Technique. Samples Were Ground for 60 Minutes. Particles are Magnified 200 Times. Note: A Unitron Reflected Light Microscope was Used.

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"Bacterial and Chemical Depression of
Pyrite in Froth Flotation of Coal"

by

Mehran Lotfi Najafabadi

(ABSTRACT)

Froth flotation was used to separate the pyrite sulfur and ash from pulverized coal samples of Illinois No. 6, Pittsburgh, and Middle Kittanning seams. In order to depress the coal pyrite in the flotation process, the coal samples were conditioned in "bacterial liquor." Iron oxidizing bacteria Thiobacillus ferrooxidans was used to cause the superficial oxidation of the coal pyrite. A number of chemical substances known as pyrite depressants were used to suppress pyrite in the flotation process. The results of the tests with the bacteria and the pyrite depressants were then compared.

The effects of flotation reagents, variations of flotation pulp pH, and mean temperature of the flotation pulp were studied. Also the effectiveness of the freshly made "bacterial liquor," recycled "bacterial liquor," and old "bacterial liquor" was tested. The retention time studies of coal in "bacterial liquor" showed that for a five hour retention time, the maximum sulfur removal from Illinois No. 6 coal seam was accomplished. The effect of increasing the ratio of coal to "bacterial liquor" in the conditioning tank was studied. It was concluded that the sulfur removal increases as the pulp density increased.

Illinois No. 6 coal seam samples were examined optically by binocular, reflected light, and scanning electron microscopes. The degree

of dissemination of pyrite in the coal matrix was observed.

Washability studies of Illinois No. 6, Pittsburgh, and Middle Kittanning coal seam samples were performed. The washability curves of these coals are presented.