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MASTER

FLOATABILITY OF COAL AND PYRITE

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Date Transmitted: July 1977

PREPARED FOR THE U. S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
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M. S. Thesis Submitted to Iowa State University

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Ames, Iowa 50011

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Floatability of coal and pyrite

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Huu Van Le

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ABSTRACT

An experimental investigation was carried out to improve the froth flotation method of separating coal pyrite. The effect of several surface active agents on the floatability of an Iowa coal and its associated pyrite was studied in both the presence and absence of methyl isobutyl carbinol (MIBC), a commonly used frother. The effectiveness of a special method of chemical pretreatment for depressing pyrite was also investigated. In another phase of the research, the zeta potential of the same coal and pyrite was measured under the same conditions used in the flotation tests (in the absence of frother).

In the absence of MIBC, the floatability of coal and pyrite was low, and appeared to depend on pH. The maximum recovery of pyrite was obtained at a pH of 4.5 with recovery being less at higher or lower pH. The addition of small amounts of sodium cyanide, ferric chloride, Na_2H_2EDTA, and ammonium thiocyanate appeared to reduce the floatability of pyrite somewhat over a wide range of pH.

The addition of a small amount of MIBC significantly increased the recovery of coal and pyrite with the increase in the recovery of coal being much greater than the increase in the recovery of pyrite. Also in the presence of MIBC, the floatability of coal and pyrite seemed to be affected more by pH than in the absence of MIBC. On the other hand, several potential pyrite depressants were found to be ineffective in the presence of MIBC. The special chemical pretreatment reduced the floatability of pyrite markedly while not greatly affecting the floatability of coal.

Measurement of the zeta potential of coal and pyrite suspensions in dilute aqueous solutions of various reagents provided an indication of adsorption phenomena. However, there appeared to be no consistent direct correlation between zeta potential and floatability.

INTRODUCTION

With constantly increasing consumption of fossil fuels and limited supplies of crude oil, the coal industry recognizes the need to make technological advances. The utilization of coal, however, poses a difficult problem because the sulfur in coal upon combustion produces sulfur dioxide, a major air pollutant. Most Iowa coal, which contains a substantial amount of sulfur, cannot be burned directly without violating recent air quality regulations. The necessity for new and improved coal preparation processes, resulting in lower benefication costs and the reduction of sulfur in coal, is becoming more pressing.

There are basically two approaches to the reduction of sulfur in coal. One is aimed at removal of sulfur in the form of sulfur dioxide from the stack gas, while the other approach involves the removal of sulfur from coal prior to combustion. The first approach is fraught with many problems, such as the low concentration of sulfur dioxide in the stack gas and usually requires four to five times the stoichiometric amount of acceptor to secure the desired elimination. The tremendous gas flow rates also create a difficult problem for this approach. Hence, physical and chemical processes to eliminate sulfur from coal prior to combustion appear more economically promising than stack gas desulfurization.

Sulfur in coal generally occurs in three forms: (1) pyritic sulfur, (2) organic sulfur, and (3) sulfate sulfur. The organic sulfur, being molecularly bound to the coal matrix, cannot be directly removed by mechanical preparation procedures. On the other hand, sulfate sulfur which occurs primarily as calcium sulfate or iron sulfate can be removed by most of the mechanical preparation techniques. The major form of sulfur in many coals, pyrite can also be removed by various mechanical benefication methods.

Although there is a large number of potential methods which can be utilized for removing pyritic sulfur from coal, the applicability of various processes is heavily dependent on the particle size of the coal, and the difference in specific gravity between coal and its impurities. They are effective only on relatively coarse coal, i.e., greater than 35 mesh (35). In much coal, however, the pyrite is finely disseminated and can be liberated only by very fine grinding. It follows that two steps can be used for removing pyrite, first liberation by fine grinding, and second removal of inorganic entities in which pyrite occurs. Froth flotation can be used to achieve the second step.

Froth flotation is a surface dependent process in which the separation is based on the difference in surface characteristics of coal and inorganic minerals (27). Thus a better understanding of surface properties of coal and pyrite would lay the foundation for further development and improvement of the froth flotation method of separating coal and pyrite.

One of the most difficult problems in applying froth flotation for separating pyrite from coal is that pyrite tends to float with coal. According to Gaudin (23) pyrite is extremely floatable if its surface is unoxidized or slightly oxidized. The purpose of the present study was to improve the separation of pyrite from coal by applying various surface chemical treatments which held promise of reducing the floatability of pyrite without damaging the floatability of coal. One type of treatment involved adsorption of a chemical agent on the surface of the pyrite which would render the surface hydrophilic and thereby depress the pyrite during the flotation process. Another type of treatment involved oxidizing the surface of the pyrite to make it hydrophilic.

The floatability of an Iowa coal and of pyrite isolated from the coal by hand-picking was determined with a modified Hallimond tube microflotation cell. The floatability of coal or pyrite was determined in the presence of various potential pyrite depressants over a wide range of pH and in both the presence and absence of methyl isobutyl carbinol (MIBC), a commonly used frothing agent. The floatability of coal or pyrite was also determined after applying a special chemical pretreatment which involved treating the materials with a hot oxidizing solution of sodium carbonate through which air was bubbled continuously.

The zeta potential of aqueous suspensions of coal or pyrite was measured to study the effect on the zeta potential of the various possible pyrite depressants and pH regulating agents which were employed in the floatability tests. This was done to gain further insight into the adsorption of the various chemical agents by the solid particles in question. Since most of the agents were ionizable compounds, the selective adsorption of cations or anions by coal or pyrite resulted in a change in surface charge on the particles which was reflected by a change in the zeta potential. In addition the zeta potential was investigated to see if there was any correlation between the zeta potential of particles in suspension and their floatability.

LITERATURE REVIEW

Theoretical Background of Froth Flotation

Native floatability

Froth flotation is a method for separating various types of solid particles from each other based on differences in surface properties. One of the products, known as tailings, contains the worthless substances and is discarded; the other product is known as concentrates and it contains the valuable substances in a more concentrated state (23). Froth flotation processes can be classified into film, oil and froth flotation. The latter is the most widely used process. It, as well as the other flotation processes, is based on utilization of differences in the physicochemical surface properties of particles of various minerals (27).

Arbiter et al. (3) stated that the surface of solid particles usually contains both hydrophobic and hydrophilic areas. The former area contains adsorption sites which are predominantly nonpolar and which hold an adsorbate by means of van der Waals forces. The latter area, in contrast, contains adsorption sites which are predominantly ionic, and can form potential ion-ion or ion-dipole bonds with air adsorbate. Gaudin (23) noted the influence of crystal chemistry and stated that crystals which do not have ions at their surface will have more or less native floatability.

Conversely, crystals which do have ions at their surface will have no native floatability. Chander et al. (12) suggested that floatability is determined primarily by the hydrophobic part of the surface. Coal and other minerals such as graphite, sulfur, and molybdenite show native floatability or natural hydrophobicity (11).

In nature, most coals consist of floatable and nonfloatable chemical constituents which affect the flotation properties in an opposite way. The floatability of coal is governed by the balance between the two groups of components (49). The floatable constituents are considered water-repellent and the nonfloatable constituents water-avid. The surface of a coal which is composed predominantly of floatable components is more floatable than that of another coal whose surface is composed predominantly of nonfloatable components (11).

The extent of particle surface oxidation is of great importance in coal flotation. The surface of coal particles oxidizes quite rapidly, rendering the coal surface fairly water-avid (27). Sun (50) made an extensive study of the effects of oxidation on the flotation properties of coal. He found the following results:

1. The floatability of coals in the presence of a neutral oily collector generally decreases with an increase in the extent of their oxidation.

2. With neutral oil as a collector, the floatability of coals, particularly anthracite and lignite, is little affected and occasionally benefited by superficial oxidation at low temperature.
3. The low floatability of a mildly oxidized coal is caused chiefly by the water-insoluble oxidation products of its oxidized surface.
4. Generally the flotation of unoxidized coals with oily collectors is very little affected by the presence of a small amount of water-soluble oxidation products of the coals.
5. Certain cationic reagents are found to be effective for the flotation of oxidized coals.
6. The floatability of oxidized coals in the presence of oily collectors as well as cationic collectors generally increases with a decrease in pH value.

According to Gaudin (23), pyrite is extremely floatable if its surface is unoxidized. The floatability of pyrite also depends upon the temperature at which it was formed. Weakly oxidized pyrite is readily floated by fatty acid and soap-type collectors, and by all reagents which can be used for sulfide ore flotation. When pyrite is oxidized in the presence of water, a film of ferric hydroxide, $Fe(OH)_3$, forms on its surface, leading to an extremely high level of hydration (27).

Flotation reagents

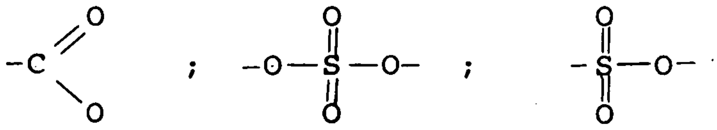
The hydrophobicity of solid particles can be increased or decreased by addition of surfactants to an aqueous suspension of the particles. To be advantageous the surfactant should adsorb selectively on the material to be floated or depressed (47). Surfactants are classified into several categories, depending on their functions, as follows: collectors, frothers, and regulating agents (23).

Collectors

Gaudin (23) described collectors as exerting their action by adhering to the surface of certain mineral particles, either in their natural state or in some altered chemical state, forming a nonpolar coating that repels water but attaches itself readily to gas bubbles. Based on structure, collectors are classified as nonpolar and heteropolar. Collectors which are nonpolar hydrocarbon liquids without a heteropolar structure and which do not associate into ions are little used in flotation practice (27). Typical nonpolar reagents, often termed oils, are kerosene, crude petroleum, fuel oil, and certain coal-tar distillates (11). The nonpolar collectors render the mineral water-repellent by covering its surface with a thin film. The attachment of nonpolar collectors becomes progressively easier as mineral surfaces become less hydrated (27). For this reason, nonpolar collectors can be used only with minerals which are naturally water-repellent such as coal, graphite, sulfur, diamond, etc. They are completely inapplicable to flotation of minerals with anions which contain oxygen (barite, calcite, etc.) or to flotation of oxides (quartz, caprite, etc.) (27).

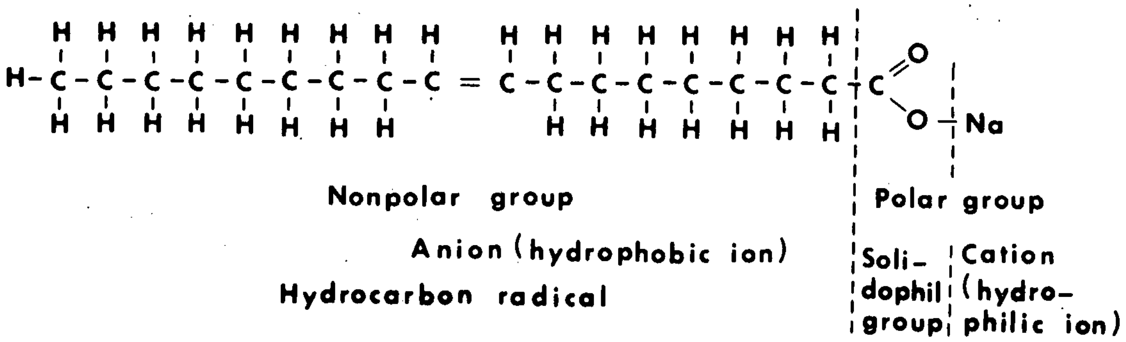
The heteropolar collectors dissociate into ions in aqueous solutions. Depending on the type of ion which gives the water-repelling effect, the ionizing collectors are divided into anionic and cationic collectors (24). The water repellent ion structure always includes a hydrocarbon radical, the presence of which ensures that the mineral is rendered water-repellent, and a group of atoms forming a link between the hydrocarbon radical and the mineral surface. The linking group of atoms is referred to as the "solidophil" group (27). According to DeBruyn (15), the behavior of collectors at the mineral-solution interface is usually referred to as an ionic adsorption process. Through the distribution of collector ions between the solid surface and the co-existing solution phase, the mineral is believed to acquire a water-repellent surface coating.

Anionic collectors Anionic collectors are classified into two basic forms according to their composition and structural properties of their solidophil group (27). The first form utilizes either sulfonic acid or carboxyl groups as the solidophil group.



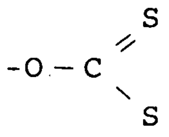
$$-C\begin{matrix}{\diagup\!\!\!\diagup O}\\{\diagdown O}\end{matrix} \quad ; \quad -O-\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O- \quad ; \quad -\overset{O}{\underset{O}{\overset{\|}{\underset{\|}{S}}}}-O-$$

Of these collectors, the most commonly used are organic acids or soaps which are salts of alkali metals and organic acids. A typical example is sodium oleate, the structure of which is shown below (27).

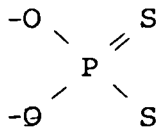


The commonly used collector of this type in coal flotation is sodium dodecylsulfate. The adsorption of this agent on the coal surface was found to be insufficient to make flotation possible in the absence of a nonpolar oil, but the reagent did facilitate the spreading of a nonpolar oil and improve flotation recovery (11).

The second form of anionic collectors is based on a solidophil group containing bivalent sulfur. The xanthogenates and dithiophosphates must be mentioned in this category (27). The soldiophil groups for these substances are:



solidophil group
of
xanthogenates



solidophil group
of
dithiophosphates

The xanthogenates and dithiophosphates are highly selective and effective collectors in sulfide mineral flotation (23).

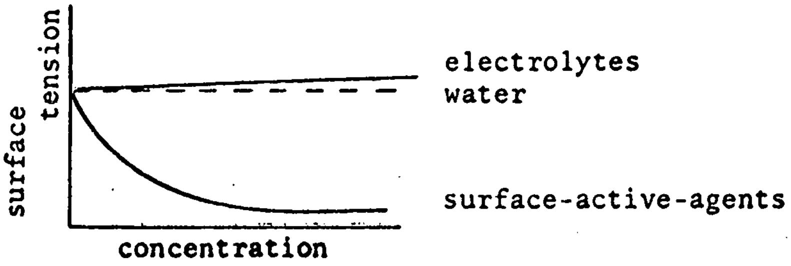
Cationic collectors Cationic collectors are widely used for flotation of silicates and certain oxides, for which anionic collectors are not effective enough (27). Most of the cationic collectors contain a solidophil group with nitrogen as an amino group constituent. Collectors of this type are extensively used to float many nonsulfide and sulfide minerals (11). Glembotskii et al. (27) indicated that cationic collectors are weakly attached to the mineral surface. Sun (49) reported that certain cationic collectors, laurylamine, rosin amine-D acetate, and iso-amyl amine are very effective for floating oxidized coals.

Frothers Frothers are heteropolar surface-active organic substances which are capable of being concentrated at an air-water interface. Their presence in the liquid phase of a flotation pulp increases air bubble strength and helps to keep air bubbles dispersed, thus improving the conditions for mineral particle attachment and increasing froth stability (27).

Pure liquids of nonpolar, polar or heteropolar structure (water, kerosene or alcohol) do not form a stable froth when agitated in the presence of air (27). However, in the presence of a small amount of a heteropolar surface-active reagent, water will form a fairly stable froth. In the water-frother reaction, the water dipoles readily react with the polar groups of a frother and hydrate them, but produce no reaction with the nonpolar hydrocarbon group tending to force it into the air phase. Thus the molecules concentrate in the surface layer with nonpolar groups oriented towards the air phase and the polar groups towards the water phase (27).

In addition to providing froth stability, the frother, according to Somasundaran (47), plays another important role in the flotation mechanism. The frother molecules can migrate from the bubble surface to the particle/bubble interface and co-adsorb on the particle along with the collector ions. Such frother adsorption can be favorable for flotation, because the adsorption of the neutral frother molecules between the collector ions prevents the collector ions from repelling each other and thereby enhances the overall adsorption of the collector.

Addition of an electrolyte to water usually increases its surface tension but the presence of surface-active agents, such as frothers, lowers the surface tension of water as shown below (27).



Alcohols, terpinol, pine oil, cresylic acid, and wash liquids from the recovery of coke by-products have been used as frothers in coal flotation (11).

Regulators   Regulating agents take the form of activators and depressants. They are used to intensify or reduce the water-repellent property of mineral particles. A great number of chemical compounds are used as regulators including salts, acids, alkalis, electrolytes, nondissociating inorganic and organic compounds (27).

Hydrogen ions and hydroxyl ions play an important role in flotation processes. The recovery of alumina, quartz, calcite (47), stilomite, and graphite (3) is found to be dependent on pH. Coal has been found to float well over a wide range of pH, although in one study optimum conditions were obtained near the neutral point (11). Pyrite was also found extremely floatable in acidic solutions but not in an alkaline medium (27). Sun (50) showed that flotation of oxidized coals is not affected by pH, however, recovery of unoxidized anthracite and bituminous coals is pH dependent. He found the optimum pH values for floating these coals in the presence of pine oil to be 7.0 and 7.5 respectively.

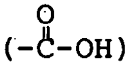
Activators Activators are usually electrolytes, readily soluble in water. Their action leads to changes in the chemical composition of the mineral surface layer which may reduce surface hydration, increase the amount of collector attached to the surface, and improve mineral flotation (27). The water-soluble salts of heavy nonferrous metals are used as activators for flotation of sphalerite, pyrite, quartz and certain nonsulfide minerals. Inorganic electrolytes are capable of dehydrating mineral surfaces, but this ability is not very great and much smaller than that of collectors. Inorganic electrolytes do not render floatable which are not naturally hydrophobic.

Depressants Reagents which prevent the adsorption of collectors on minerals and thereby retard their flotation are known as depressants (42). Like activators, most depressing agents are inorganic electrolytes. They are used to reduce mineral surface hydration to provide a more selective flotation process. There is no specific classification for depressants; however, some of the more important types of depressants are listed below (27).

1. Sodium sulfide and other water-soluble sulfides are used principally for depression of sulfide minerals.
2. Cyanides are extensively used for selective sulfide or flotation and depression of copper minerals and pyrite.
3. Sulfites, hyposulfites and certain sulfates (i.e., zinc and ferrous sulfates) are used for depression of sphalerite.
4. Sodium silicate (water-glass) is normally used for depression of quartz and gangue minerals.
5. Lime is a specific depressant for ion-bearing sulfides in the flotation of sulfide ores.

This list only includes the most important representatives of the various depressants. Some of the listed agents can be used differently in relation to various minerals. For example, sodium sulfide is an activator for oxidized minerals of nonferrous metals but a depressant for sulfide minerals.

The variables of coal flotation

Froth flotation is widely used for the desulfurization of fine coal. The effectiveness of froth flotation is mainly dependent upon the coal characteristics, particle size, pulp density, pH value, and flotation reagents (11). The native floatability of coal is affected by two basic processes which occur during coalification (27). Firstly, the organic matter becomes carbonized and its crystalline structure increases the natural water-repellent properties of coal. Secondly, the organic matter is oxidized and carbonyl ($>c=O$) and carboxyl  $(-\overset{\overset{O}{\|}}{C}-OH)$ groups are formed. These groups react with water and render the surface water avid.

The floatability of coal is heavily dependent on the size and the specific gravity of the particles. Brown (10) stated the lower the specific gravity of the coal, the greater the maximum size of particle that can be floated. He also reported that the maximum size of bituminous coal particles (sp. gr. 1.35) which floated in a bench scale cell was 3x6 mesh tyler (6.7 x 3.3 mm). Under some conditions, maximum recovery is obtained with coal of an intermediate size, as both coarse and fine coal float poorly (10). The pulp density also plays an important role in coal flotation. It averages from 20 to 30% by weight of solids in pulp (27). However, pulp density varies in practice and depends on the coal rank, type and ash content (10). Brown (10) reported that high pulp density favors the flotation of fine particles rather than coarse.

Coal has been found to float well over a wide range of pH; in some cases the optimum value occurs near the neutral point (10). Near pH 7.0 the coal has a negative charge and as the pulp is made more acidic, hydrogen ions will be adsorbed to reduce the charge to near zero and the hydrophotocity of the surface will be at a maximum. In a more acidic pulp the coal surface will acquire a positive charge and in an alkaline solution hydroxyl ions will be adsorbed to increase the negative charge, with a consequent reduction in hydrophoticity (10).

In coal flotation, surface active agents adsorb on the coal surface and alter the flotation properties of the coal. Nonpolar reagents with low solubility in water, such as oils, are widely used in coal flotation as collectors. When oil is added to the pulp it divides into droplets which adhere to the coal and make it more hydrophobic (10). Heteropolar reagents, having both polar and nonpolar groups are commonly used in coal flotation as collectors and frothing agents (10). The effectiveness of a frothing agent depends on the length of the carbon chain. The effective frothers of monohydric aliphatic alcohol and monocarboxylic acid types are found to have between five and ten carbon atoms in the nonpolar group with an optimum of eight (10). The heteropolar reagents used as frothers not only stabilize the froth but also affect the emulsification and the spreading of nonpolar reagents (27). Addition of inorganic electrolytes also affects the flotability of the coal. In the early days of coal flotation, sea water was suggested as a substitute for cresol as a frother (11). Coal has a considerable capacity to adsorb the electrolytes. The adsorption of ions changes the electrostatic charge at the coal surface and renders the surface more or less hydrophobic. Electrolytes are also able to compress the electrical double layer around the coal particles and so may affect the stability of the hydrated layer at the surface.

It is notable that the reagent-coal contact time should be optimized. With a long contact time, much of the reagent charge is adsorbed by the coal, passing into the particles through their pores, and the effect of the reagent on the coal surface is lost (27).

The presence of impurities and pyrite is frequently troublesome in coal flotation because of their tendency to float with coal. Depression of pyrite may be brought about by adding reagents such as lime, sodium cyanide, ferric chloride, ferric sulfate, etc. Sodium carbonate and sodium silicate are sometimes added to the pulp to disperse clay and shale (10). In the depression process, the pH of the suspension appears to be more important than the choice of reagents. Pyrite was found to be extremely floatable in an acid medium and completely depressed in alkaline solution (27).

Other variables which also affect coal flotation are temperature, feed rate, rate of removal, type of flotation machine and the air flow rate.

Theoretical Background of Electrokinetics

The reaction of water and the ions present in it with minerals may cause changes in the composition and the electrical state of the mineral surface (26). An important feature of this reaction is the formation of a double layer at the mineral-water interface.

Models of double layer

The approach of Helmholtz-Perrin was one of the first attempts to explain the formation of an electrical double layer. They suggested a model in which the double layer is similar to a plate condenser, with its inner layer the charged surface of a solid particle and its outer layer a single plane of ions of opposite charge with the two layers separated from each other by a thin film of water molecules (33). Kruyt (31) stated that this basic idea was later modified by Gouy and Chapman who introduced the concept of a diffuse ionic "atmosphere". According to this concept, the counter ions (ions which have opposite charge from that of the surface) are electrostatically attracted by the charged surface. At the same time; however, these ions have a tendency to diffuse away from the surface towards the bulk of the solution where their concentration is lower. The action of the two competitive tendencies results in an equilibrium concentration of counter ions such that the concentration gradually decreases with increasing distance from the solid surface. The counter-ion "atmosphere" is often referred to as the Gouy layer.

Stern (48), in 1924, introduced a model in which some of the idealizations of the Gouy model are corrected. The corrections resulted in the concept of a double layer that can be regarded as a combination of the compact Helmholtz model and the diffuse layer type model (11). According to Stern (48), the thickness of the layer of counter-ions closest to the charges surface of the solid is limited by the size of these ions. The layer of counter-ions is usually referred to as the stern layer and is considered to be separated from the solid surface by a layer of water having a thickness δ, in which there is no charge (Figure 1). Beyond the stern layer, the counter-ions are distributed as in a diffuse Gouy "atmosphere". The total electrical charge of the counter-ions in this system is divided between the electrical charge at the Stern layer, and the electrical charge of the diffuse Gouy "atmosphere". The sum of these two charges is equal and opposite to the solid surface charge. The potential of the solid-solution interface drops linearly with distance from the solid surface to the Stern layer. Beyond this layer the potential decreases roughly exponentially with distance.

Potential-determining ions and point-of-zero-charge

Potential-determining ions may be defined as those ions which affect the electrical potential at the particle surface (11). These ions include both the ions which attach themselves to the mineral surface and form the double layer and their counter-ions (27). In general, the ions which constitute the crystal lattice are potential-determining ions for ionic solids, and hydrogen and hydroxyl ions are potential-determining ions for oxides (2).

With certain concentrations of potential-determining ions, no double layer exists and the surface of the solid in solution is uncharged. This condition is called the point-of-zero-charge (11).

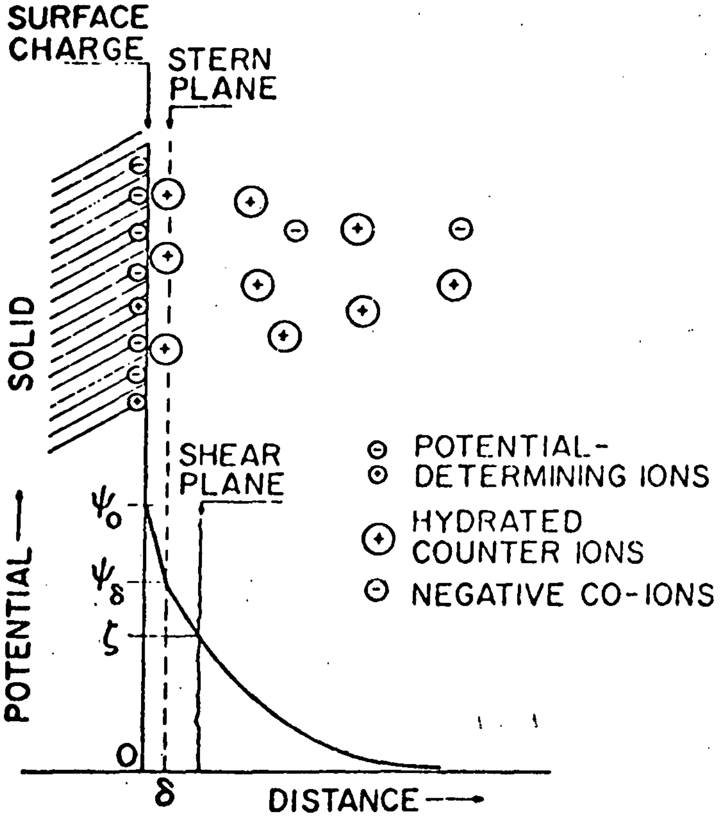


Figure 1. Schematic representation of the double layer according to Stern's model (47)

The point-of-zero-charge (PZC) of oxides depends on the crystal structure, the chemical nature of the metal ions, the presence of impurities, the degree of bulk and surface hydration, and consequently on the past treatment of the oxides (2). Campbell and Sun (11) suggested that the PZC of an oxide may be determined by the pH at which the solid shows a minimum solubility. However, Ahmed (2) stated that the PZC values obtained by slow acid-base titration using hydrated oxide precipitates can also be misleading in practical work. The PZC of such oxide precipitates depends on the impurities present in the precipitates and on the hydrated nature and solubility of such precipitates. At the pH of minimum solubility the concentrations of negative and positive hydroxocomplexes of the cations in solution are found to be equal (11). Under this condition, oxide particles do not move in an electric field. This is called the isoelectric point (IEP). In other words, if hydronium and hydroxide ions are potential-determining ions, then the PZC may be given the special name isoelectric point. Essentially, there is no difference between PZC and IEP (11).

Electrokinetic system

The phenomena referred to collectively as electrokinetic effects pertain to the liquid flow that occurs along a solid/liquid interface as a result of an applied potential gradient, and conversely to the potential developed when a liquid is made to flow along an interface (43).

The electrokinetic effects which have been observed are electrophoresis, electro-osmosis, sedimentation potential or Dorn potential and streaming potential. These phenomena are defined by Van Olphen (52) as follows:

Electrophoresis The suspended charged particles move through a liquid when an electric field is applied.

Electro-osmosis When a potential difference is maintained across a porous medium or a capillary, a flow of liquid occurs from one end to the other.

Sedimentation potential A vertical electrical field is created when charged particles are forced to move through a liquid in response to gravitation or centrifugation.

Streaming potential An electric field is created when a liquid is forced to move through a porous medium or a capillary containing charged particles.

It is evident that all of these electrokinetic phenomena depend on the nature of the double layer, and the potential at the surface of shear between the charged surface and the electrolyte solution (44). This potential is called the electrokinetic or zeta potential (Figure 1). Shaw (44) stated that some difficulty is encountered in both calculation and interpretation of zeta potentials, the latter difficulty arising from uncertainty associated with the term surface of shear. The location of this surface is never precisely known and, in reality, it is a region of rapidly changing viscosity rather than a mathematical plane.

Electrophoresis

Electrophoresis has the greatest practical applicability of the four electrokinetic effects and has received by far the most attention (44). There are two well-known types of electrophoresis, zone electrophoresis and microelectrophoresis (43). Zone electrophoresis involves the migration of charged particles which are supported on a relatively inert and homogeneous solid in order to minimize convectional disturbances (5). It is used mainly as an analytical technique for small scale preparative separation (44). The main applications are biochemical and clinical, particularly for the study of protein mixtures (5). If the material under investigation is in the form of a reasonably stable, dilute suspension or emulsion containing microscopically visible particles or droplets, then electrophoretic mobility can be observed and measured directly by the microelectrophoresis method (43).

The applications of microelectrophoresis measurements fall broadly into three categories (44):

Colloid stability This involves measurement of the zeta potential, and identification of the zeta potential with the Stern potential.

Ion adsorption studies This involves measurement of the zeta potential of solid particles utilizing this property to obtain conditions for adsorption of ions on solid surfaces.

Characterization of particle surfaces Studies of the effects of pH, surface active agents, enzymes, etc. on particle mobilities give valuable information regarding the nature of particle surfaces. This application is the most pertinent to the present study.

The operation relating the electrophoretic mobility and zeta potential is expressed as follows (44):

$$V_E = D\zeta E/4\pi\eta$$

where:

V_E = mobility of particles
D = dielectric constant of the medium
E = the applied electric field
η = viscosity of medium
ζ = zeta potential

This equation is called the Smoluchowski equation. For an aqueous medium at 25°C the equation becomes:

$$\zeta = 12.85\ V_E$$

For the complete derivation of this equation the papers of Shaw (44) and Sennett and Oliver (43) may be consulted.

The assumptions made in deriving the equation are (44):

1. The dielectric constant and viscosity of the medium are assumed to be uniform throughout the mobile part of the double layer,
2. The thickness of the double layer is uniform and small compared to the radius of curvature of the surface,
3. The liquid undergoes laminar flow.

The viscosity η and the dielectric constant D are assumed constant because experimental and theoretical information concerning their variation is lacking at present (43). Laminar flow is not difficult to obtain in practice, but more complicated problems arise when particles are nonspherical resulting in a double layer at nonuniform thickness.

The mobility of suspended particles is observed at so-called "stationary levels". No matter what the cell geometry, the suspension moves rapidly in one direction near the wall, more slowly further from the wall, and in the opposite direction at the center of the cell. At some point in the cell there is no net motion applied to the suspension. This is called the stationary level. The observed velocity of the particles in the system at the stationary level is equal to their electrophoretic velocity. The stationary level is located at a distance equal to 14.8% of the diameter from the wall of a cylindrical cell (31).

The Significance of Zeta Potential

Although not always taken into account, the nature of the electrical double layer has an important influence on many practical systems. A review of the literature shows that many workers have investigated the relation between zeta potential and froth flotation. According to Glembotskii et al. (27) the electrical double layer has an important effect on the mineral surface wetability, since hydration occurs in the outer layer of the double layer. It is notable that the zeta potential is determined principally by the thickness of the diffuse layer. The addition of an electrolyte reduces the zeta potential and also reduces the diffuse layer thickness, therefore, the extent of mineral surface hydration must also be reduced in these circumstances (27). A decrease in the concentration of the electrolyte will have the opposite effect.

Riddick (41) made an extensive study of the significance of zeta potential on many hydrophobic industrial colloids. He related the practical stability of a colloid and zeta potential as shown in Table 1.

Table 1. Relationship of practical colloids to zeta potential (42)

Stability characteristics	Average Z.P., mv
Maximum agglomeration and precipitation	+3 to zero
Excellent agglomeration and precipitation	-1 to -4
Fair agglomeration and precipitation	-5 to -10
Threshold of agglomeration (aggregates of 2 to 10 colloidal particles)	-11 to -20
Plateau of slight stability (substantially no aggregates)	-21 to -30
Moderate stability (no aggregates)	-31 to -40
Good stability	-41 to -50
Very good stability	-51 to -60
Excellent stability	-61 to -80
Maximum stability	-81 to -100

The Surface Adsorption Models

Adsorption involves the adhesion of reagents to the surface of mineral particles (1). The effect of reagents on the flotation process is related to their attachment to the surface of mineral particles. According to Glembotskii et al. (27) the adsorption of reagents on mineral surfaces may involve the following:

1. Physical or chemical interaction between the mineral surface and reagents,
2. Formation of a surface compound in which the reagents participate,
3. Adsorption of reagents on the mineral surface in the form of films.

Physical and chemical adsorption

In physical adsorption the reagents are concentrated in the outer layer of the double layer. Such concentration is unstable and reversible. A simple reduction in bulk solution concentration shifts the adsorption equilibrium and causes the reagent to pass from the mineral double layer into solution (27). Physical adsorption occurs as a result of attraction and repulsion between the solid and the adsorbate due to van der Waals forces. Chemical adsorption involves the incorporation of reagents into the inner layer of the electrical double layer. Adsorption of this type involves the chemical interaction between the adsorbate and the solid resulting in chemical bond formation (1). In chemical adsorption, the adsorbed layer is very stable and cannot be removed even by repeated washings with water (27). Chemical adsorption is comparatively selective, results in less even distribution of reagents on the solid surface, and is much slower than physical adsorption.

Formation of the surface compound

In the formation of a surface compound the atoms or ions forming the mineral crystal lattice combine with ions adsorbed from solution (27). It differs from chemical adsorption because in the formation of a surface compound, not only ions having dimensions similar to those of the mineral lattice ions but also ions which differ greatly in size and even configuration may become attached to the crystal lattice. Another important feature of surface compound formation is that the compound exists only in conjunction with the surface, not as a homogeneous substance having a definite composition.

Formation of films on the mineral surface

The interaction of a reagent and a mineral may result in the formation of a film on the mineral surface. The film is an independent phase which can exist apart from the mineral. The formation of a film on a mineral surface is important in flotation practice because it changes the flotation behavior of that mineral. The rate of the film formation process depends on the reagent concentration in the solution, the concentration of mineral matter, the bulk temperature and the uniformity of the mineral surface.

Campbell and Sun (11) stated that the adsorption of flotation reagents on a solid surface depends upon the behavior of the electrical double layer. It was shown that the double layer is dependent upon the surface potential. Impurities strongly influence the surface potential; therefore, it follows that the adsorption of flotation reagents may be affected by impurities present in the sample. For this reason, among many other factors which influence the flotation process, the past history of the mineral itself is one of the most important factors.

EXPERIMENTAL METHODS

Materials and Equipment Used

The coal samples used in this work were obtained from the Iowa State University Demonstration Mine No. 1 in Mahaska County, Iowa. The coal was crushed and then screened to provide a -20/-40 mesh product. The coal was cleaned by floating it in a 1.3 specific gravity solution of tetrachloroethylene and hexane. The float fraction was recovered and dried, then pulverized to obtain a -60 mesh coal sample. A fraction of the cleaned coal was ground to a size of 5 to 50 μm. Another fraction was screened to provide a -60/+100 mesh sample.

The pyrite was carefully hand-picked from the university preparation plant tailings produced in treating similar coal. The pyrite was crushed to 1/4 in. The material was then split into two batches, pyrite I and pyrite II.

Pyrite I was pulverized and then screened to provide -80/+100 mesh material. A fraction of this material was ground to 5-50 μm size and was used for both electrokinetic and flotation studies.

Pyrite II was only used to conduct flotation tests involving methyl isobutyl carbinol. Pyrite II having a particle size of about 1/4 in. was stored and was freshly ground to provide -80/+100 mesh sample prior to the tests.

The proximate analysis and sulfur distribution of the coal and pyrite samples are given in Table 2.

Throughout this investigation, deionized water was used for all the experiments. Deionized water was obtained by running Iowa State University tap water through a demineralizing column, Catalog No. D8901, hose nipple cartridge (Barnstead Corp.).

For size reduction, drying, weighing and pH measurement the following equipment was used:

1. A Bench-Scale Double Roll Crusher (Smith Engineering Works, Milwaukee, Wis.). Coal was crushed to 1/4 in. top size with this machine.
2. A Mickro-Samplmill (Pulverizing Machinery Division, American-Marietta Co., Summit, N.J.). Coal was pulverized to -60 mesh size with this device.
3. An Analytical Mill (Tekma Company, Cincinnati, Ohio), Model A-10 was used for reducing particles to micron size.
4. A Drying Oven (Labline Inc., Chicago, Illinois) was used for drying samples.
5. A Mettler H31 analytical balance (Mettler Instrument Corp.) was used for weighing samples.
6. A Beckman pH meter (Beckman Instrument Inc.), Model 76 was used for measuring pH.

Table 2. Chemical analysis of the coal and pyrite

Material	Proximate analysis, wt. %				Sulfur distribution, wt. %			
	Moisture	Ash	Volatile matter	Fixed carbon	Pyritic	Organic	Sulfate	Total
Untreated coal	8.26	14.31	34.52	42.91	3.64	4.00	0.59	8.23
Float fraction	1.72	3.51	44.92	49.85	0.55	3.96	0.16	4.35
Pyrite I					45.77		0.89	49.55
Pyrite II					48.31		0.66	49.39

Chemicals

The chemicals, their source, purity and stock solution concentration are listed in Table 3. Basically the stock solutions were prepared by weighing out a predetermined amount of chemical and diluting it with deionized water. Fresh solutions were prepared as needed for those that change with age.

Zeta Potential Measurement and Apparatus

For zeta potential measurement, aqueous suspensions of coal or pyrite having pH values from 3 to 10 were prepared with deionized water and different chemical reagents. The suspensions were prepared by weighing out 0.05 g. of coal or 0.10 g. of pyrite and then mixing the solids with 500 ml. of deionized water. Mixing was carried out in a 1000 ml. beaker using a magnetic stirrer with a polyethylene coated stirring bar. An appropriate amount of chemical solution taken from the stock materials was added to the beaker and the pH was adjusted by adding a small amount of 0.1N hydrochloric acid or 0.1N sodium hydroxide solution. Three zeta potential determinations were made on each suspension using a fresh portion of the suspension for each measurement.

The apparatus used for measurement of the zeta potential in this investigation was a Model 400 Laser Zee Meter

Table 3. Chemicals used for the zeta potential and flotation tests

Reagent	Purity	Source	Stock soln. concentration
HCl	Reagent grade	Fisher Scientific Co.	0.1 M
H_2SO_4	"	"	0.1 M
NaOH	"	"	0.1 M
$Ca(OH)_2$	"	"	0.1 M
NaCl	"	Baker Chemical Co.	0.1 M
NaCN	"	Fisher Scientific Co.	0.1 M
Na_2CO_3	"	"	0.1 M
Na_2SO_3	"	"	0.1 M
Na_2SiO_3	"	Matheson Coleman & Bell	0.1 M
Na_3PO_4	"	Baker Chemical Co.	0.1 M
$FeCl_3$	"	Fisher Scientific Co.	0.1 M
Aero 633 Depressant	As received	American Cyamid Co.	5% wt.
EDTA disodium	Reagent grade	Eastman Organic Chem.	0.1 M
NH_4SCN	"	Matheson Coleman & Bell	0.1 M
$(NH_4)_2HC_6H_5O_7$	"	Baker Chemical Co.	0.1 M
MIBC	As received	Union Carbide Corp.	

(Pen Kem Company). The Zee Meter measures the zeta potential of colloidal particles by applying a micro-electrophoresis technique to determine the rate of movement of these particles. The colloid to be measured is placed in an electrophoresis cell consisting of two electrode chambers and a connecting chamber for viewing the particles. A voltage is applied between two electrodes, one located in each chamber. The applied voltage produces a uniform electric field in the viewing chamber and the charged particles respond by moving toward one or the other electrode. The positively charged particles move toward the cathode (negative electrode) and the negatively charged particles migrate towards the anode (positive electrode). The speed of the particles is directly proportional to the magnitude of the particle charge or zeta potential. When the voltage is applied to the cell, the particles move with respect to the fluid and the fluid also moves with respect to the cell. This second effect is referred to as electroosmosis and is characterized by a movement of the fluid in one direction near the surface of the viewing chamber walls, accompanied by a return flow in the opposite direction in the center of the viewing chamber. Obviously there must be a plane where there is no net motion applied to the fluid. This plane is called the stationary level, which is located at a distance equal to

14.8% of the diameter from the viewing wall. All the measurements must be made at this stationary level to avoid errors due to the fluid movement.

In order to obtain accurate results, samples used for zeta potential measurement should have certain characteristics which are described in Table 4.

Table 4. Input sample constraints in using the Model 400 Zee Meter

Parameter	Range
Particle size	0.1 to 50 μm
Number of particles/ml.	10^6 to 10^9
Typical concentration for 2 μm particles	1 to 10^3 ppm
Specific conductance	1 to 10^5 mhos/cm
pH	3 to 10
Minimum sample size	25 ml. using syringe

Froth Flotation Apparatus and Operation

Two series of froth flotation tests were conducted using two different particle size fractions of coal and pyrite. The fractions used in the tests without methyl isobutyl carbinol (MIBC) were taken from the same stock materials as those used in the electrokinetic tests (5 to

50 μm). For the series of experiments with MIBC, the size fractions of material used were -60/+100 and -80/+100 mesh for coal and pyrite respectively.

Apparatus

A modified Hallimond tube microflotation cell similar to that described by Fuerstenau (21) was used to measure the recovery of coal and pyrite. The equipment consisted of a nitrogen tank fitted with a pressure control valve, a rotameter, a 3-way stopcock, and a modified Hallimond tube microflotation cell. A magnetic stirrer with a polyethylene coated stirring bar was used for agitating the suspensions. Copper tubing was used to connect the nitrogen tank and the pressure control valve, and tygon tubing was used for connecting the other equipment.

The microflotation cell (Figure 2) consisted of a lower part, which was a specially designed vessel (Figure 3), and an upper part. The two parts were connected by a 28/42 ground glass joint.

Operation

Compressed nitrogen in the tank was passed through the pressure control valve, the rotameter, and the 3-way stopcock. The gas was first vented to the atmosphere establish a constant flowrate. To conduct a flotation test,

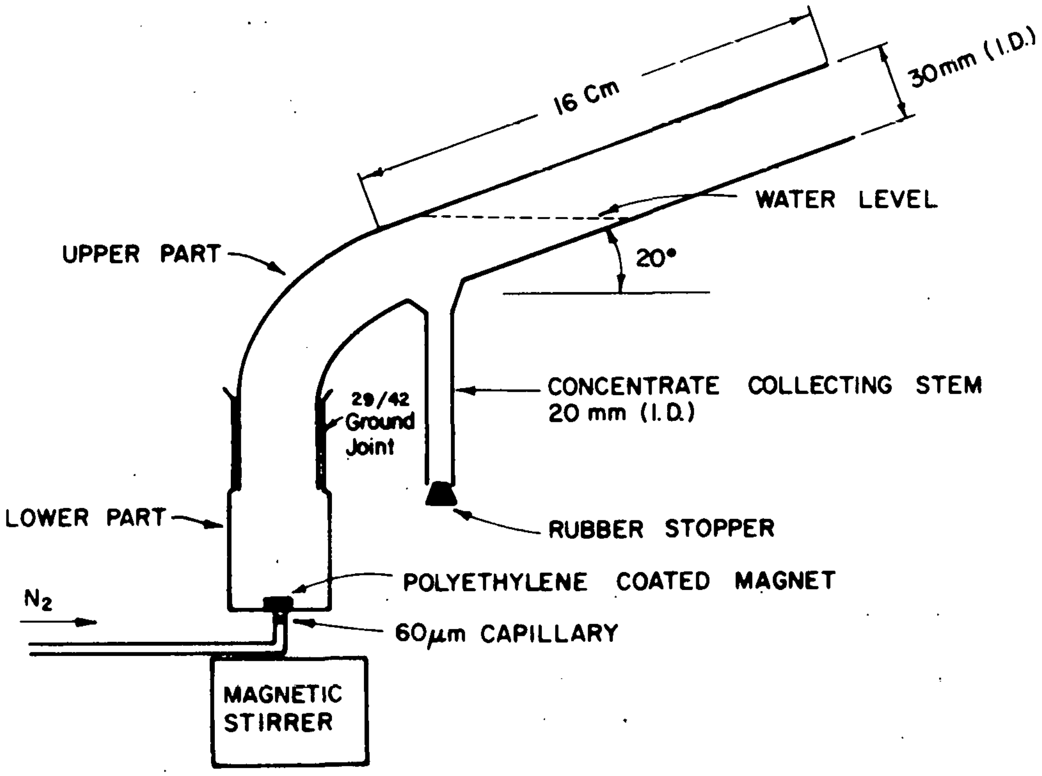


Figure 2. Modified Hallimond tube microflotation cell

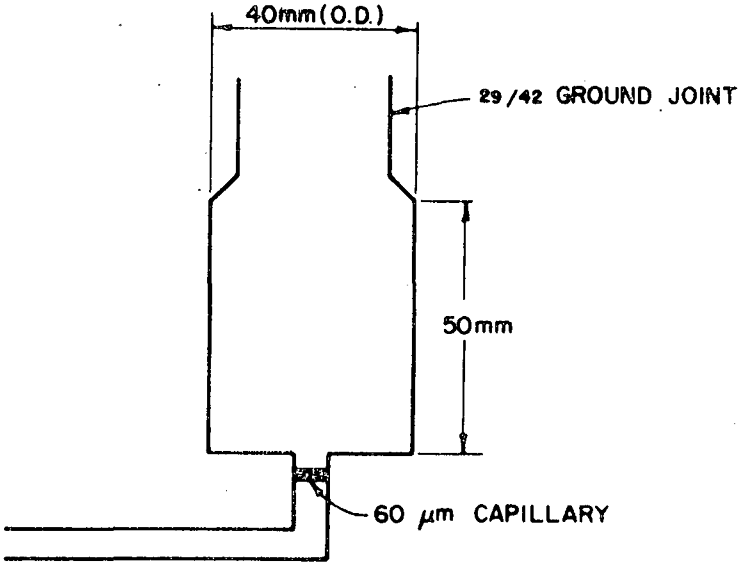


Figure 3. Lower part of Hallimond cell

100 ml. of deionized water or of a reagent solution of predetermined concentration was prepared in a 250 ml. beaker and 25 ml. of the liquid was then placed in the lower part of the microflotation cell. The magnetic stirrer was turned on and operated at a predetermined speed. Nitrogen was allowed to pass through the lower part of the cell. One gram of coal or pyrite was then added to the cell. The pH of the suspension was adjusted next by adding a small amount of 0.1 N hydrochloric acid or 0.1 N sodium hydroxide solutions. For the runs with methyl isobutyl carbinol, 0.01 ml. of this reagent was added after pH adjustment. The suspension was then conditioned for 10 min. with agitation and nitrogen flowing. After the conditioning period the upper part of the Hallimond cell was connected to the lower part and 75 ml. of the remaining liquid was added. The floatability test was carried out in a 4 min. at a nitrogen flowrate of 27 ml./min. The float fraction was collected in a 140 ml. beaker by carefully removing the rubber stopper from the concentrate collecting stem. Deionized water was used to wash off the solid particles sticking to the wall of the concentrate collecting stem. The remaining suspension was collected in a 250 ml. beaker and the pH of the tailings was measured. This pH value was recorded as the flotation pH. The lower part of the cell was then carefully washed to

collect all the particles remaining therein. The concentrate and the tailings were then filtered using a 30 ml. medium porosity Buchner funnel, dried in the oven for 3 hr. at 100°C, and weighed. The relative recovery percentage of solids was calculated as follows:

$$\text{Relative Recovery Percentage} = \frac{\text{wt. of concentrate}}{\text{wt. of concentrate + wt. of tailing}} \times 100$$

The Hallimond tube microflotation cell was used for the floatability test of coal and pyrite because it offers several advantages (21). First the results can be reproduced with small samples (1-3 g.). Second, operating conditions can be controlled accurately. Third, the amount of liquid in the cell and the reagent concentration remain constant during the test.

RESULTS AND DISCUSSION

Zeta Potential of Coal and Pyrite

The zeta potential versus pH of coal and pyrite was determined and the results are shown in Figure 4. In general, the electrokinetic properties of Iowa coal were found to be similar to those found for bituminous coal during previous investigation by Campbell and Sun (11), and Baker and Miller (4). The curves strongly suggest that hydronium and hydroxyl ions behave as potential determining ions for coal. As the pH of the solution is decreased hydronium ions are adsorbed, causing the surface of the coal to become positively charged. As the pH is increased, hydronium ions are replaced by hydroxyl ions and the surface of the coal becomes negatively charged.

The zeta potential of pyrite is rather erratic. Apparently, it behaves similarly to the zeta potential of coal at high pH, when sodium hydroxide is used to regulate the pH, but at pH less than 4.5 the pyrite surface becomes more negatively charged, which is hard to explain. Campbell and Sun (11) also reported that hydronium ions and hydroxyl ions are potential determining ions for coal but not for gangue.

In an attempt to study the effect of different pH regulators on the solid surface charge, hydrochloric acid, sulfuric acid, sodium hydroxide and calcium hydroxide were used to adjust the pH of the suspensions. The results shown in Figure 4 indicate that the presence of multivalent ions causes a slight change in the zeta potential of coal but the effect is more pronounced for pyrite. When calcium hydroxide is used to regulate the pH, the zeta potential of pyrite reverses from negative to positive. The results suggest the adsorption of positively charged calcium ions on the pyrite surface. Glembotskii et al. (27) noted that calcium ions strongly attach themselves to the pyrite surface. They also suggested that calcium ions form insoluble compounds with the products of sulfide oxidation and a film of calcium sulfate may be formed on the pyrite surface.

A series of measurements was conducted to investigate the effects of various electrolytes on the zeta potential of coal and pyrite. For these measurements, the pH of the suspensions was regulated by either 0.1 N hydrochloric acid or 0.1 N sodium hydroxide.

The addition of sodium chloride had little effect on the zeta potential of coal or pyrite. The results shown in Figure 5 indicate that the zeta potential of coal and pyrite at various pH is nearly independent of sodium chloride concentration. Campbell and Sun (11) reported that the zeta potential of bituminous coal at its natural pH is independent of sodium chloride concentration.

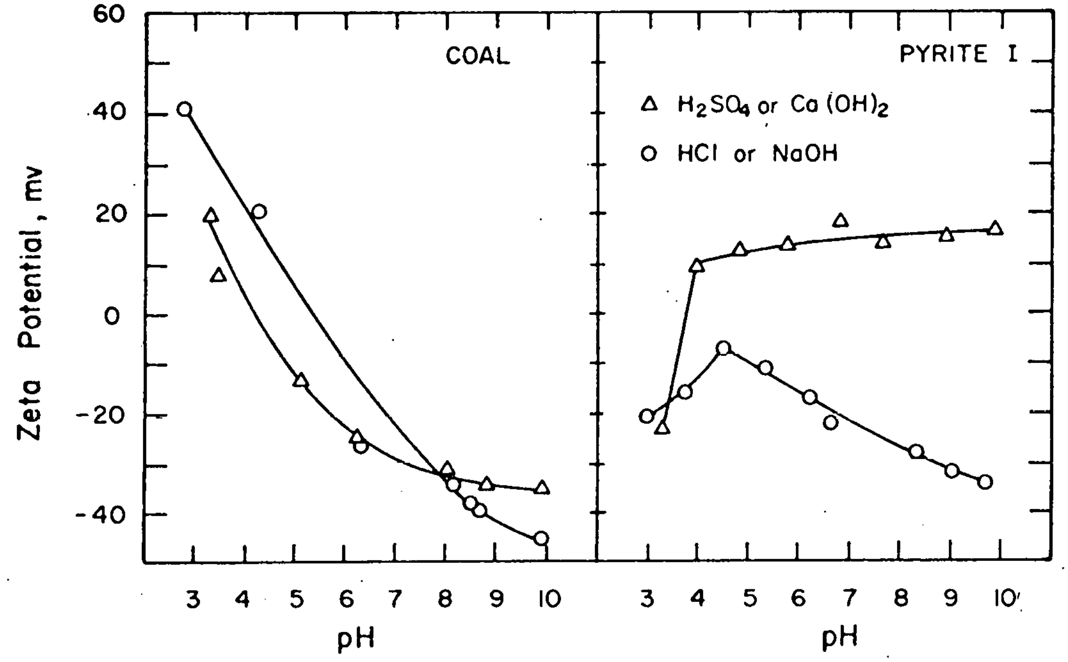


Figure 4. Variation of zeta potential of coal and pyrite with various modifiers

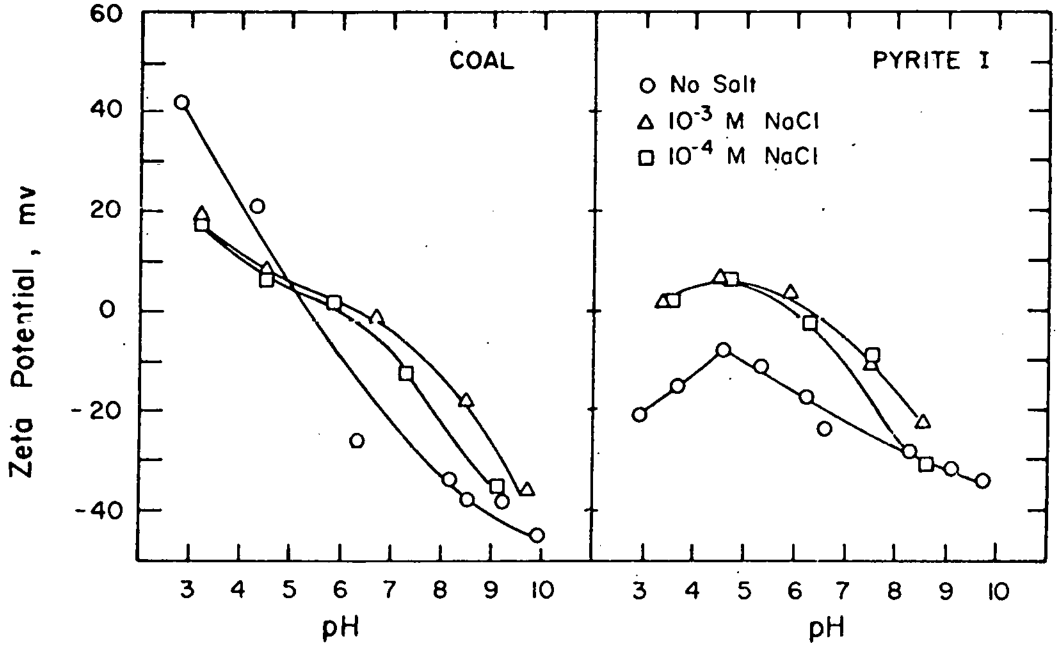


Figure 5. Effect of sodium chloride on zeta potential of coal and pyrite at various pH

Cyanides, which contain the flotation-active anion CN^-, are widely used as pyrite depressants in the selective flotation of sulfide minerals where anionic collectors such as xanthates are used to recover other sulfide minerals (19). The addition of small amounts of sodium cyanide shows a significant effect on the zeta potential of pyrite (Figure 6). At a concentration of 10^{-5} mole/l. of sodium cyanide, and pH below 7.5, the zeta potential of pyrite shows a charge reversal from negative to positive indicating the possible adsorption of positively charged species. According to Glembotskii et al. (27) cyanide reacts with metal cations in two stages. Precipitates of relatively insoluble cyanide salts are formed first, then these salts dissolve due to the action of excess cyanide, and complex cyanide compounds are formed.

1st stage - $Fe^{+++} + 3CN^- \rightleftarrows Fe(CN)_3$

2nd stage - $Fe(CN)_3 + 3CN^- \rightleftarrows Fe(CN)_6^{---}$

At a concentration of 10^{-5} mole/l., the solution probably does not have enough excess cyanide to proceed to the second stage, therefore, the major product at this concentration is $Fe(CN)_3$. Thus the positive charge of the pyrite may be due to the adsorption of the positively charged species $Fe(CN)_3$. As the concentration of sodium cyanide is

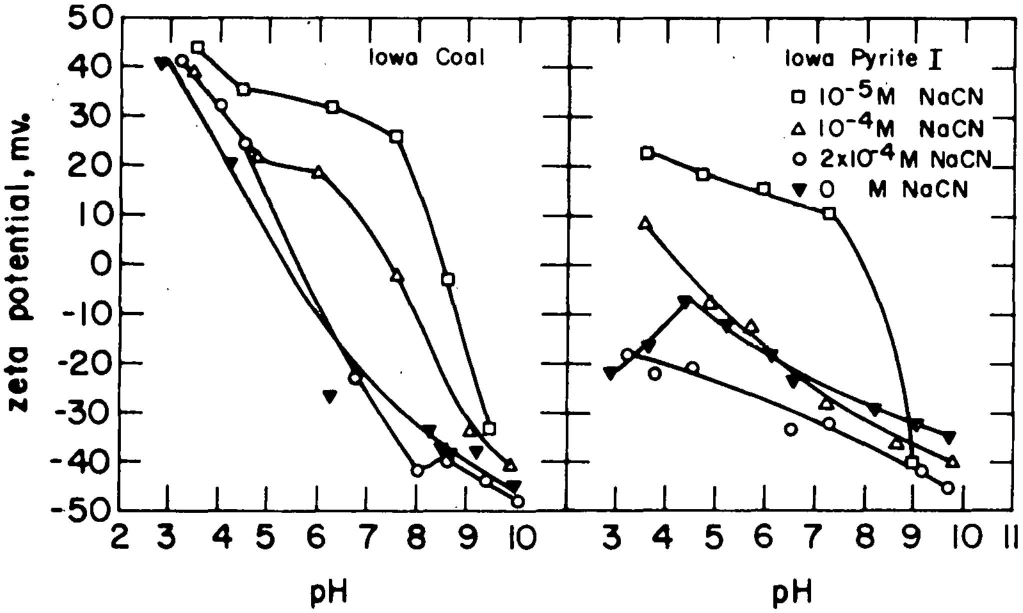


Figure 6. Effect of sodium cyanide on zeta potential of coal and pyrite at various pH

increased, excess cyanide anions are available to cause the second stage reaction to proceed further which provides the negatively charged species $Fe(CN)_6^{-3}$. Thus the negative charge of the pyrite surface at higher concentrations of sodium cyanide may be due to the adsorption of the negatively charged species $Fe(CN)_6^{-3}$ and CN^{--}. Similar results were obtained for coal, which suggests the adsorption of similar species in both cases. Since both pyrite and coal contain some acid soluble iron compounds (19), it seems possible that enough iron was leached out of coal and pyrite to react with cyanide to produce charged species which are absorbed by the coal or pyrite surface. The similar effect which sodium cyanide displays on coal and pyrite does not offer much promise for sodium cyanide as a selective depressant for pyrite in coal flotation.

The addition of sodium carbonate produces a major change in the zeta potential of pyrite (Figure 7). At a concentration of 10^{-4} mole/l., the zeta potential of pyrite undergoes a charge reversal from negative to positive for a pH smaller than 8. The results may be attributed to the adsorption of positively charged species. Since sodium chloride has little effect on the zeta potential of pyrite, it seems doubtful that sodium ions play an important role. Another possibility is the adsorption of a positively charged

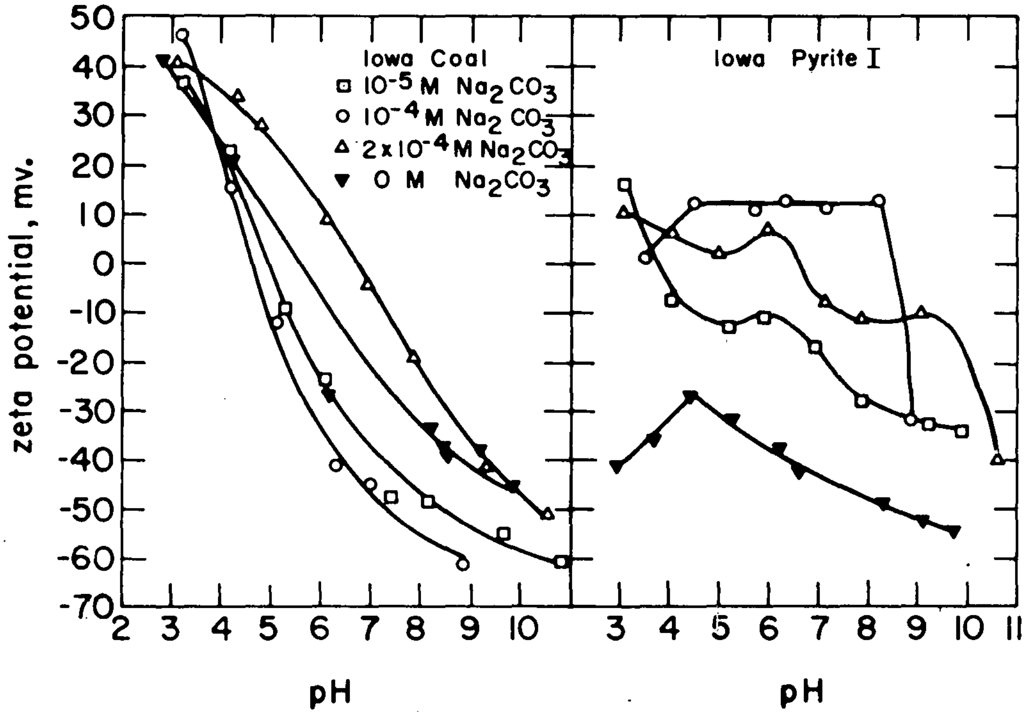


Figure 7. Effect of sodium carbonate on zeta potential of coal and pyrite at various pH

film of iron carbonate. The reduction in the zeta potential of pyrite at a concentration of 2 x 10^{-4} mole/l. indicates the possible adsorption of the negatively charged species CO_3^{--} or HCO_3^-. The effect of sodium carbonate on the zeta potential of coal seems to be different. It appears that the zeta potential of coal decreases as the concentration of sodium carbonate is increased. However, when the concentration of sodium carbonate was increased from 10^{-4} mole/l. to 2 x 10^{-4} mole/l. the zeta potential of coal also increased. It suggests that at this concentration, the coal surface absorbs some kinds of positively charged species causing the increase in the zeta potential. Since sodium carbonate affects the zeta potential of coal and pyrite differently, it might serve as a selective depressant, especially at a concentration of 10^{-4} mole/l. where coal and pyrite show opposite surface charges for a pH between 5.0 and 8.0. Glembotskii et al. (27) reported that sodium carbonate can serve as a pyrite depressant if the pyrite surface is unoxidized or oxidized very little. However, if the pyrite surface is highly oxidized then soda ash will serve as an activator for pyrite. The depressive action of sodium carbonate on pyrite is due to the presence of hydroxyl ions resulting from the hydrolysis of sodium carbonate. However, the hydroxide ions may become carbonate ions due to the reverse reaction

$$2Na_2CO_3 + 3H_2O \rightleftarrows 3NaOH + NaHCO_3 + H_2CO_3$$

Under such conditions, carbonate ions dominate the ions present in the suspension making them more available to react with ferrous ions leached from pyrite to form positively charged iron carbonate. Thus the increase in the zeta potential of pyrite at sodium carbonate concentrations of 10^{-5} and 10^{-4} mole/l. may be attributed to the adsorption of iron carbonate. However, the decrease in the zeta potential of pyrite as the concentration of sodium carbonate was increased from 10^{-4} to 2×10^{-4} mole/l. may be due to the adsorption of excess negatively charged ions CO_3^{--} and HCO_3^-.

Ferric chloride shows a pronounced effect on the zeta potential of pyrite, Figure 8. The results indicate that the zeta potential of pyrite increases as the concentration of ferric chloride is increased. The results obtained generally agree with those reported by Baker and Miller (4). The positive values of the zeta potential of pyrite in acidic solutions suggest the adsorption of positively charged species. According to Mackenzie (32), for a pH lower than 5.0, the positive ferric ions $Fe_2(CH)_2^{+4}$, Fe^{+3}, $Fe(OH)^{+2}$ and $Fe(OH)_2^+$ are present in the solution. Thus the positive zeta potential of pyrite in ferric chloride solutions

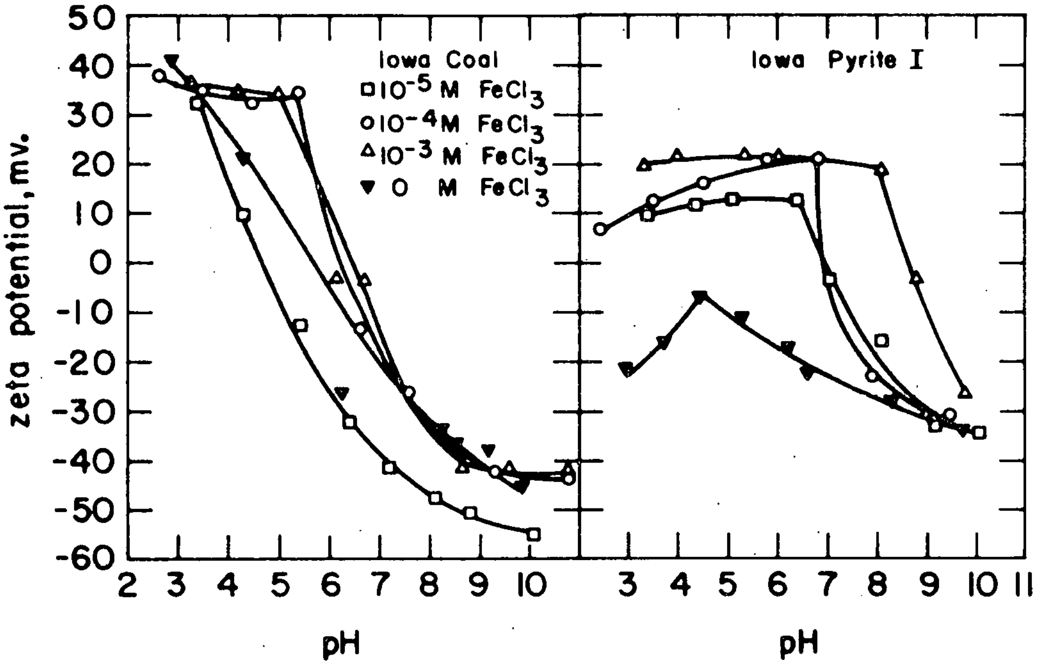


Figure 8. Effect of ferric chloride on zeta potential of coal and pyrite at various pH

for pH smaller than 5.0 may be attributed to the adsorption of these positively charged complex ions. The existence of a positive zeta potential for pyrite in the pH range of 6.0 to 8.0 cannot be explained by the adsorption of the positively charged ferric ions mentioned above, since in this range of pH, the concentration of these ions is negligible (32). However, in this pH range the presence of positively charged $Fe(OH)_3$ colloids may account for the results obtained. The presence of ferric chloride does not appear to have the same effect on the zeta potential of coal. The results shown in Figure 8 indicate that the zeta potential of coal at three different concentrations of ferric chloride is just slightly different than the zeta potential without any ferric chloride. Apparently, ferric chloride provides a very different effect on the zeta potential of pyrite and of coal; thus it may serve as a selective depressant for pyrite. In the pH ranges of 4.5 to 7.0, 6.0 to 7.0 and 6.5 to 8.0 for 10^{-5}, 10^{-4} and 10^{-3} mole/l. respectively, coal and pyrite show opposite surface charges. The negative charge of the coal surface in these ranges of pH may produce a selective adsorption of cationic collectors due to better electrostatic attraction between the coal surface and the cationic collectors.

The effect of the disodium salt of ethylenediaminetetracetic acid (Na_2H_2EDTA) on the zeta potential of coal and of pyrite was also studied. The results shown in Figure 9 indicate that the zeta potential of pyrite in the presence of Na_2H_2 EDTA is independent of pH and decreases as the concentration of this salt is increased. The disodium salt of EDTA is known to form stable complexes with iron. Thus, the increasing negative charge of the pyrite surface may be due to the adsorption of negatively charged iron complexes.

The zeta potential of coal, on the other hand, was not affected in the same manner. Apparently, it is dependent of pH and decreases as the concentration of Na_2H_2 EDTA is increased. The effect of the salt on the zeta potential of coal is more pronounced at high pH.

The results shown in Figure 9 indicate that for a pH smaller than 5.0, the zeta potential of coal and of pyrite are of opposite sign. Under these conditions the positively charged coal surface should selectively adsorb an anionic collector making it possible to separate coal from pyrite.

Three different chemicals, sodium silicate, sodium sulfite and sodium phosphate, were tested separately to determine the effect of each agent on the zeta potential of coal and pyrite. The results are shown in Figure 10. According to Glembotskii et al. (27) aqueous solutions of water-glass produce an alkaline reaction, due to the hydrolytic decomposition of sodium silicates which are salts of a

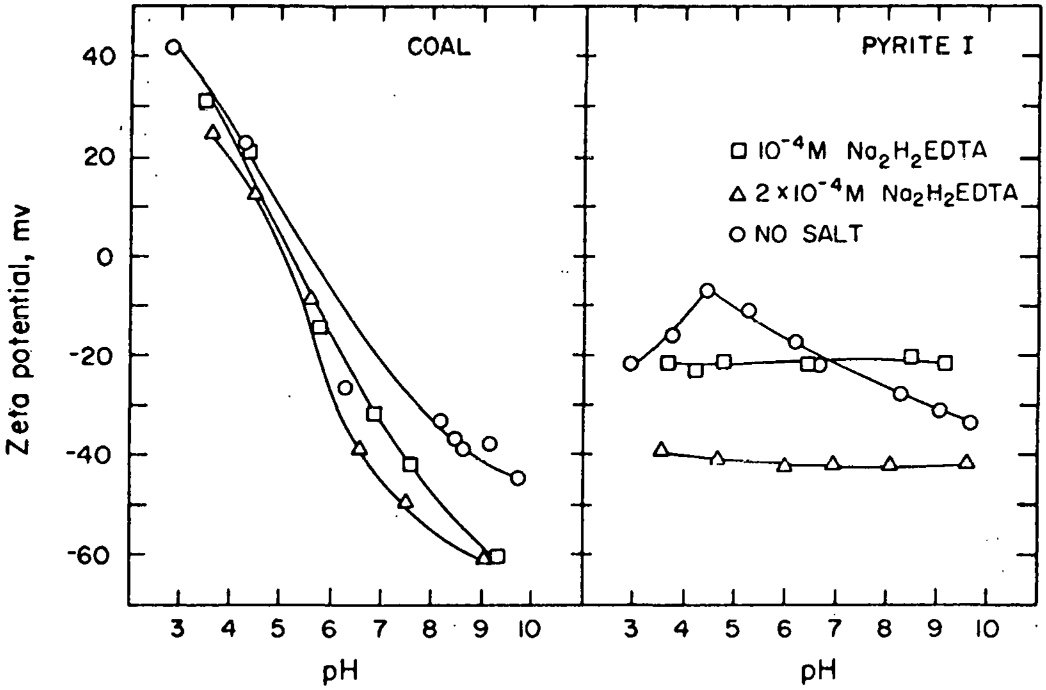


Figure 9. Effect of the disodium salt of EDTA on zeta potential of coal and pyrite

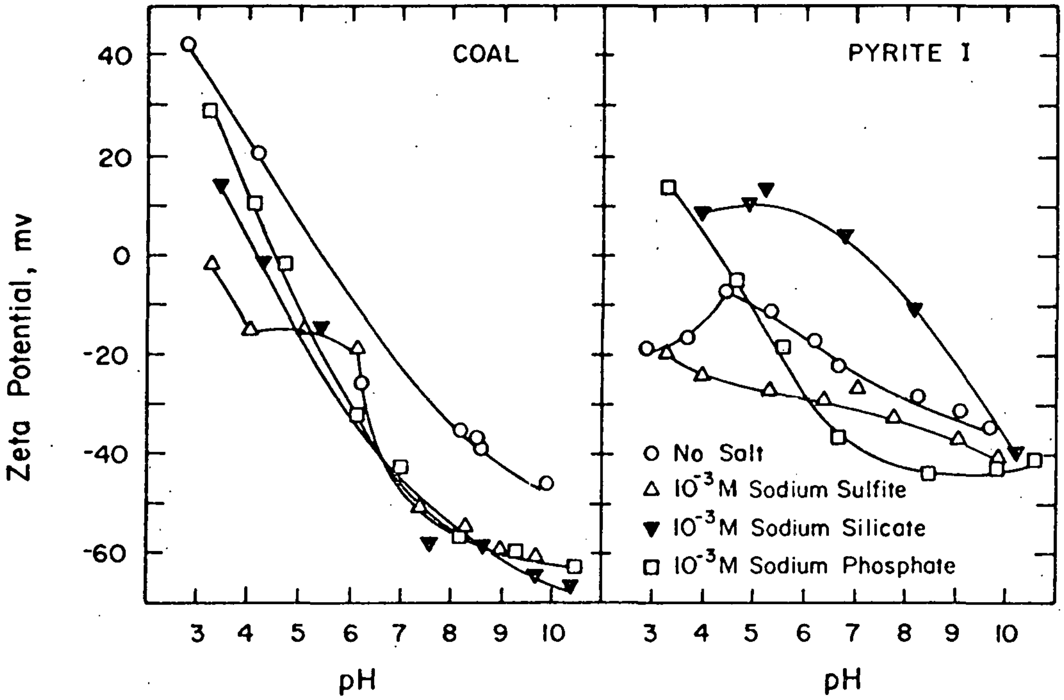


Figure 10. Effect of sodium sulfite, sodium silicate, and sodium phosphate on zeta potential of coal and pyrite at various pH

strong base and a weak acid

$$Na_2SiO_3 + 2H_2O \rightleftarrows H_2SiO_3 + 2NaOH$$

Wark (53) suggested that silicic acid molecules tend to polymerize with silicate ions to give large ionic micelles of variable composition. These are surrounded by an ionic atmosphere of sodium or hydrogen ions which are attracted by the negative charges of the micelles. Thus the increasingly negative charge of the coal surface in the presence of sodium silicate may be due to the adsorption of negatively charged ions or micelles of silicic acid. Gelmbotskii et al. (27) noted that the absorption of sodium silicate by the double layer next to a mineral surface is not stable because it is easily removed by washing. The positive charge of the pyrite surface in acidified solutions of sodium silicate may be due to the adsorption of positively charged species. It seems possible that ferric ions leached from the pyrite react with hydroxyl ions, the product of hydrolytic decomposition of sodium silicate, to form positively charged iron complexes or ferric hydroxide colloids. Sodium silicate displays a different effect on the zeta potential of coal and pyrite. In the pH range of 4.0 to 7.0 the coal surface has a negative charge while the pyrite surface is positively charged. The results suggest that cationic collectors may be used for coal flotation because they should be selectively absorbed by the coal surface.

The zeta potential of both coal and pyrite appears to be reduced by sodium sulfite (Figure 10). Taggart (51) stated that in sulfide minerals flotation, sodium sulfite can be used to depress pyrite. In depressing pyrite, the mineral surface is covered by a coating of ferric sulfate in the pH rage 6.4 to 8.2 and by basic ferric sulfite at higher pH. These ions, within their respective pH ranges, prevent bubble attachment to a pyrite surface originally xanthate coated (51). Glembotskii et al. (27) noted that sodium cyanide, sodium silicate and sodium sulfite are similarly depressing on gangue minerals. The results shown in Figure 10 suggest that sodium sulfite depresses both coal and pyrite. The coal and pyrite with similar negative surface charges are unlikely to selectively adsorb either anionic or cationic collectors.

Sodium phosphate similarly affects the zeta potential of both coal and pyrite (Figure 10). As in the case of sodium sulfite, sodium phosphate does not appear to have a selectively depressive action on pyrite.

Two organic agents which might serve as pyrite depressants were tested for their effects on the zeta potential of coal and of pyrite, Figure 11. In the presence of ammonium thiocyanate, the negative charge of the coal surface increases while the pyrite surface undergoes a charge reversal from negative to positive at pH below 6. Ammonium thiocyanate hydrolyzes in aqueous solution as follows:

$$NH_4CNS \rightleftarrows NH_4^+ + CNS^-$$

In the presence of ferric ions, complex ferric ions can be formed (17).

$$CNS^- + Fe^{+++} \rightleftarrows FeCNS^{++}$$

The presence of positively charged complexes may account for the positive charge of the pyrite surface. The different effects which ammonium thiocyanate produces on coal and pyrite surfaces may provide a selective depressive action on pyrite.

Diammonium citrate appears to have the same effect on the zeta potential of both coal and pyrite. Both coal and pyrite surfaces show an increase in negative charge, Figure 11. The results indicate that this agent is unlikely to serve as a selective depressant for pyrite.

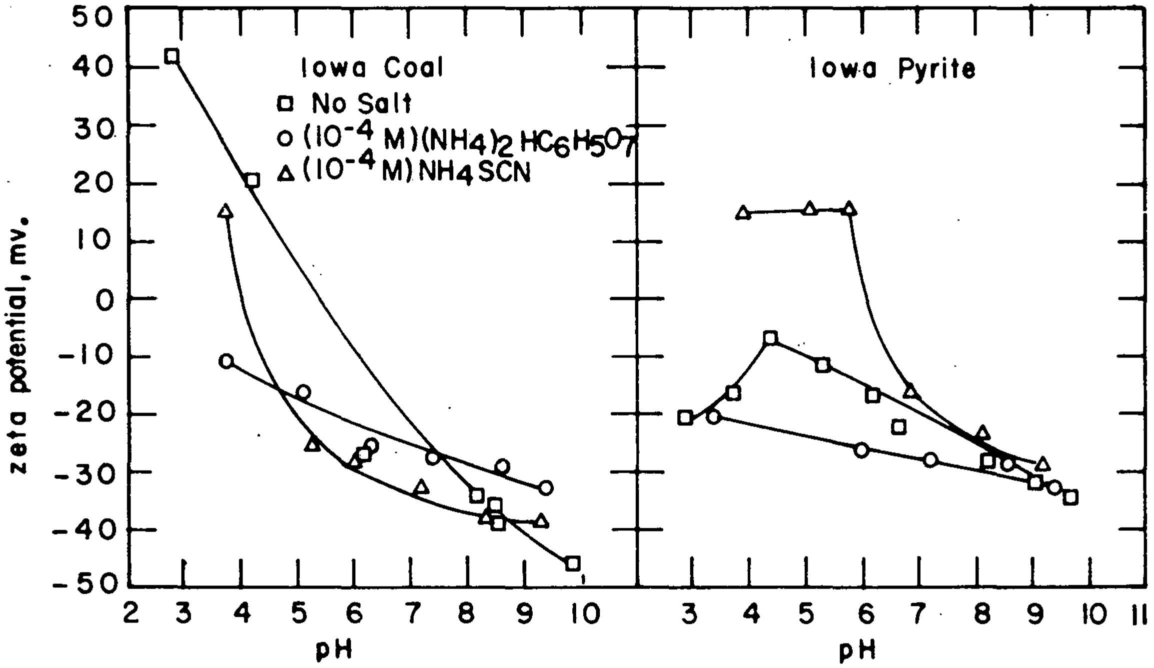


Figure 11. Effect of ammonium citrate, and ammonium thiocyanate on zeta potential of coal and pyrite

Flotation of Coal and Pyrite

Flotation without frothers

An attempt was made to discover some of the basic mechanisms involved in froth flotation by correlating the zeta potential and the floatability of coal and pyrite. A modified Hallimond tube microflotation cell was used for conducting the flotation tests.

In the following series of experiments only the floatability of pyrite I was tested. The pyrite was taken from the same stock of materials prepared for zeta potential measurements (5 to 50 μm). In this series of floatability tests no frothing agent was used, only several potential pyrite depressants were tested.

The floatability of pyrite was tested at different pH without any flotation reagents other than pH regulators. Figure 12 shows relative per cent recovery of pyrite versus pH along with the previously measured zeta potential. The results indicate that the maximum recovery is obtained at a pH of 5.0 with the relative recovery of pyrite decreasing as the pH of the suspensions is increased or decreased. The depression of pyrite in an alkaline medium is in agreement with the behavior reported by Glembotskii et al. (27). The behavior of pyrite is closely connected with its tendency to oxidize rapidly. According to

Glembotskii et al. (27) the water-avidity of pyrite increases sharply after 20 min. in water or 30 min. in air. Since sodium cations are indifferent ions, their adsorption on the pyrite surface, a reversible process, has no significant effect on the water hydration of pyrite. Thus the depressive action of sodium hydroxide on pyrite is due to the effect of hydroxyl ions, the presence of which forms ferric hydroxide with ferric ions. Taggart (51) reported that the existence of hydroxyl ions in a pyrite suspension results in the formation of ferric hydroxide which plays a primary role in the depression of pyrite. Because of its low solubility, ferric hydroxide has a strong tendency to form colloidal sols in which both water molecular and hydroxyl ions are associated. A coating of these colloidal sols on pyrite particles forms a water-avid surface.

The water-repellent properties of a mineral surface, which determine its floatability, are partially due to the hydrating effect of ions present in the suspension. Thus the absorption of hydrogen ions by the double electrical layer may change the electrical state of the mineral surface, and affect the attachment of particles to air bubbles (27). This may account for the reduction in pyrite recovery at low pH The similar trend between pyrite recovery and zeta potential at various pH as shown in Figure 12 seems to indicate a correlation between floatability and zeta potential.

The results of the pyrite floatability tests in the presence of sodium cyanide are shown in Figure 13. These indicate that sodium cyanide has a tendency to depress pyrite over a wide range of pH. Also the degree of pyrite depression increases as the concentration of sodium cyanide is increased. Since the zeta potential also is reduced (made more negative) by increases in sodium cyanide concentration (Figure 6) it appears that the zeta potential and floatability of pyrite in dilute sodium cyanide solutions are correlated. Riddick (42) reported that mineral particles with a more negative charge are more stable and less floatable. Glembotskii et al. (27) stated that cyanide is a powerful pyrite depressant. Its depressive effect is stronger than that of caustic soda, and is due to the action on pyrite of (1) hydroxyl ions formed by hydrolysis of sodium cyanide and (2) cyanide ions CN^- which forms complex compounds with ferric ions. The hydrolysis of sodium cyanide can be represented as follows:

$$Na^+ + CN^- + H_2O \rightleftarrows Na^+ + OH^- + HCN$$

Since the presence of hydrogen cyanide is highly dangerous, cyanides must be used in an alkaline medium. The presence of free alkali in solution shifts the reaction to the left. Thus the effect of cyanide on pyrite in an alkaline solution

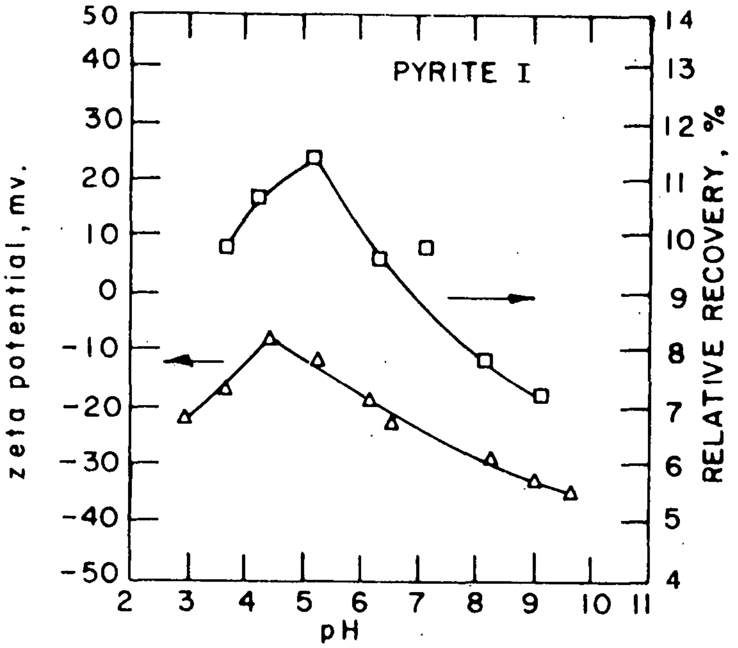


Figure 12. Relation between floatability and zeta potential of pyrite at various pH

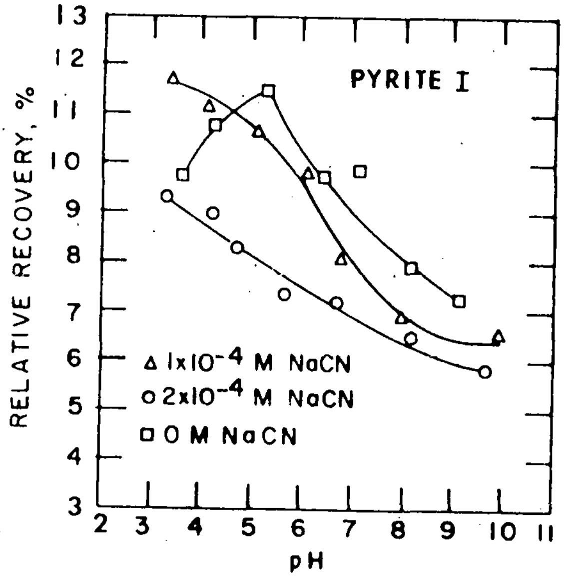


Figure 13. Effect of sodium cyanide on floatability of pyrite at various pH

is primarily due to the action of cyanide ions. Taggart (51) stated that the mechanism of cyanide action with the iron minerals has to be inferred from a variety of facts dealing with the chemistry of cyanide and hydroxyl ions and their interrelations, the amount of ferric and ferrous ions present, and the relative solubilities of the reaction products of the iron ions with the above anions and with collector ions. He found that the depressive effect of cyanide on pyrite in sodium oleate solutions is unstable but that cyanide strongly depresses pyrite in ethyl xanthate solutions. Glembotskii et al. (27) reported that the depressive effect of cyanide depends on its concentration, the composition of the minerals to be separated, the ionic composition of the minerals to be separated, the ionic composition of the pulp and the length of the carbon chain of the collector.

Ferric chloride has a significant effect on the floatability of pyrite. The results shown in Figure 14 indicate that the floatability of pyrite was reduced over a pH range of 4.2 to 10.0. A suspension containing ferric chloride is naturally acidic due to the presence of hydrochloric acid, a product of ferric chloride hydrolysis. The presence of hydrogen ions may activate the pyrite surface making it more floatable. This may account for the increase in recovery of pyrite at lower pH (below 4.0) for the suspensions containing 10^{-5} mole/l. of ferric chloride. As the pH is increased, ferric ions form complexes with hydroxyl ions. The adsorption of these complexes increases the surface hydration of pyrite, and thus reduces the floatability of pyrite. The nature and composition of these complexes vary with the suspension pH. For the suspensions with a pH of 6.0 or smaller, all the ferric complexes present have a positive charge. Between pH 6.0 and 8.0 the primary complexes are various ferric hydroxides and above 8.0 the major complex present is $Fe(OH)_4^-$ (32). Therefore, in coal flotation the type of collector used in combination with ferric chloride should be chosen according to the range of pH.

The previous measurements of the zeta potential of pyrite indicate that ferric complexes are adsorbed on the pyrite surface. However, an agreement between the zeta potential and floatability of pyrite was not obtained. The zeta potential of pyrite in solutions containing 10^{-5} and 10^{-3} mole/l. of ferric chloride approaches zero at a pH of 7.0 and 8.6 respectively. Riddick (42) indicated that the maximum floatability of minerals (without collector) occurs at a zeta potential near zero. The results shown in Figure 14 do not offer such agreement.

The addition of the disodium salt of ethylenediaminetetraacetic acid (Na_2H_2EDTA) did tend to depress pyrite over the pH range of 3.0 to 7.0 (Figure 15). Apparently, the depressive action of Na_2H_2EDTA on pyrite varies with its concentration. For a pH smaller than 4.3, the recovery of pyrite is higher for the lower concentration. The opposite result was obtained for a pH greater than 4.3. These results are different from those obtained for the zeta potential of pyrite which is independent of pH (Figure 9). Ahmed (2) stated that the adsorption of surfactants with chelating functional groups on oxide surfaces is favored in the neutral region where the surface hydroxyl groups are not fully dissociated and the specific adsorption of cations and anions is at a minimum. Such surfactants can form soluble complexes with metal ions, hydrophilic precipitates or hydrophobic precipitates depending on the character of the functional group.

The addition of ammonium thiocyanate also shows a depressive effect on the floatability of pyrite (Figure 16). The depressive action of ammonium thiocyanate may be due to the adsorption of ferric thiocyanate complexes. According to Durrant (17), ammonium thiocyanate can serve as a pyrite depressant. It forms a ferric thiocyanate complex with ferric ions as follows:

$$CNS^- + Fe^{+++} \rightleftarrows Fe(CNS)^{++}$$

Since the pyrite surface is naturally negative in deionized water, it strongly adsorbs the positively charged ferric thiocyanate complex due to electrostatic attraction. This action increases the surface hydration of pyrite. An attempt was made to correlate the zeta potential and floatability of pyrite in the presence of ammonium thiocyanate. It was found that the correlation between the two properties is very poor. At a pH of 6.0, the zeta potential approaches zero where the floatability would be expected to be a maximum in the absence of a collector. However, the recovery of pyrite (Figure 16) simply increases as the pH decrease with no apparent maximum in the recovery curve.

The effect of MIBC

In the following flotation tests, a constant amount of methyl isobutyl carbinol (MICB), a frother which is widely used in coal flotation practice, was added to determine its effect on the floatability of coal and pyrite at various pH and in the presence of different potential depressants. Scott coal (-60/+100 mesh) and two batches of -80/+100 pyrite (I and II) were used in this series of flotation tests. The coal and pyrite I were prepared at the same time and were used in the previous zeta potential and flotation studies. Pyrite II was freshly ground, just prior to the flotation tests with MIBC. A Hallimond tube microflotation

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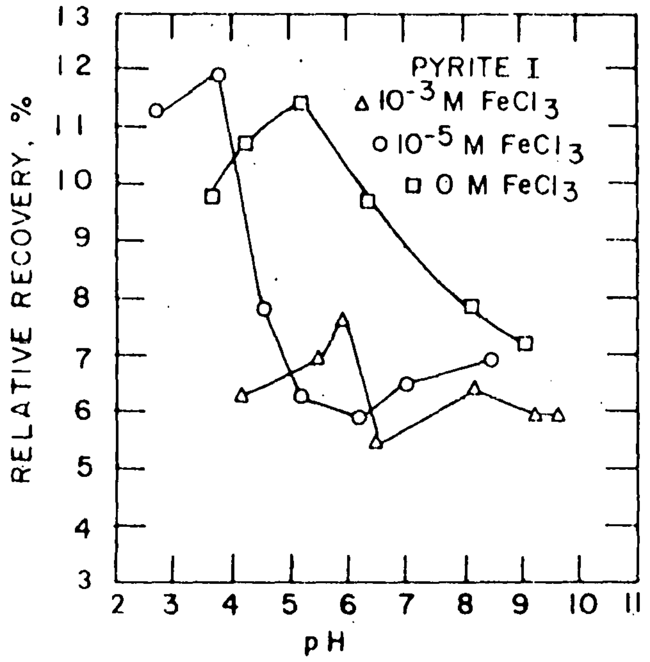
Figure 14. Effect of ferric chloride on floatability of pyrite at various pH

Figure 15. Effect of the disodium salt of EDTA on floatability of pyrite at various pH

Figure 16. Effect of ammonium thiocyanate on floatability of pyrite at various pH


PYRITE I
△ 10^{-3} M $FeCl_3$
○ 10^{-5} M $FeCl_3$
□ 0 M $FeCl_3$
RELATIVE RECOVERY, %
3
4
5
6
7
8
9
10
11
12
13
pH
2
3
4
5
6
7
8
9
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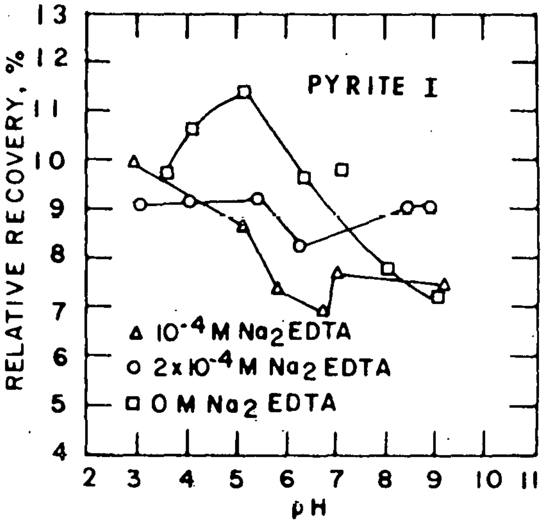
PYRITE I
△ 10^{-4} M Na_2 EDTA
○ 2×10^{-4} M Na_2 EDTA
□ 0 M Na_2 EDTA
RELATIVE RECOVERY, %
4
5
6
7
8
9
10
11
12
13
pH
2
3
4
5
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8
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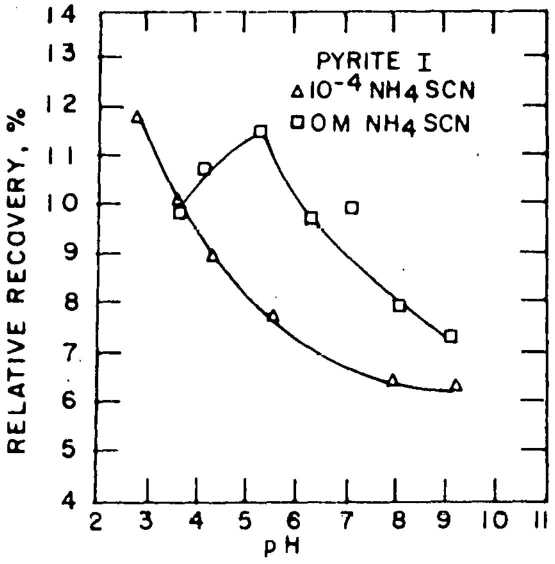
PYRITE I
△ 10^{-4} NH_4SCN
□ 0 M NH_4SCN
RELATIVE RECOVERY, %
4
5
6
7
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10
11
12
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14
pH
2
3
4
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6
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10
11

cell was used to conduct the tests. The procedure used was similar to the one previously used. However, in this series of tests, 2.0 g. of coal or pyrite was used for each run instead of 1.0 g., and 0.01 ml. of MIBC was added to the suspension right after the pH adjustment. The nitrogen flow rate was increased to 35 ml./min. because of the larger size of the solid particles.

The results shown in Figure 17 indicate that the floatability of both coal and pyrite was significantly increased by the addition of MIBC with the effect on the floatability of the coal being much greater than the effect on the floatability of the pyrite. The results also show that MIBC is more effective for both coal and pyrite in an acidic medium. A decrease in the floatability of pyrite as the pH increases was expected because previous studies of the zeta potential and flotation of pyrite in the absence of MIBC indicated that the flotation of pyrite was suppressed by an alkaline medium. Min (35) obtained similar results for untreated Scott coal. He conducted flotation tests of untreated Scott coal using 100 g. of coal (-35 mesh) with 0.4 ml. of kerosene and 0.05 ml. of MIBC, and found that the coal floated better in an acidic medium, with the lower the pH, the higher the recovery. He also reported that the total sulfur reduction was lower at the higher recovery which indicated that the pyrite also floated better in an acidic

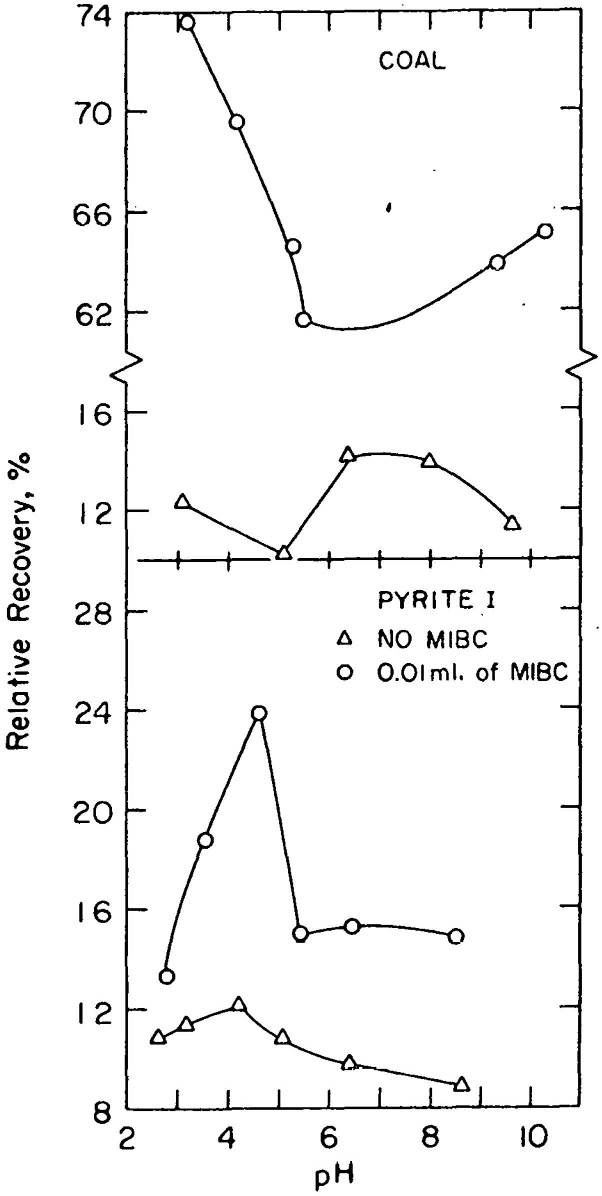

Figure 17. Effect of MIBC on the floatability of coal and pyrite at various pH

medium.

In the presence of MIBC, the floatability of coal and pyrite I depends on the types of acids or bases used for pH regulation. The results obtained when sulfuric acid or calcium hydroxide was used to adjust the pH are shown in Figure 18 along with those obtained using hydrochloric acid or sodium hydroxide. Apparently, the floatability of coal and pyrite I did not depend on the type of acid but did depend on the type of base. The results did not agree with those reported by Glembotskii et al. (27) which indicated that calcium hydroxide is a stronger pyrite depressant than sodium hydroxide.

The use of MIBC for the flotation of coal and pyrite appears to alter the effect of several potential depressing agents for pyrite. The results obtained when ferric chloride was tested as a pyrite depressant are shown in Figure 19. These indicate that ferric chloride tended to depress the flotation of coal but not the flotation of pyrite. In fact it seemed to activate the pyrite and improve its floatability. The results were not expected because the earlier experiments dealing with the flotation of pyrite in the absence of MIBC indicated that ferric chloride tended to depress pyrite in the pH range of 4 to 9.

Other surface active agents such as sodium carbonate,

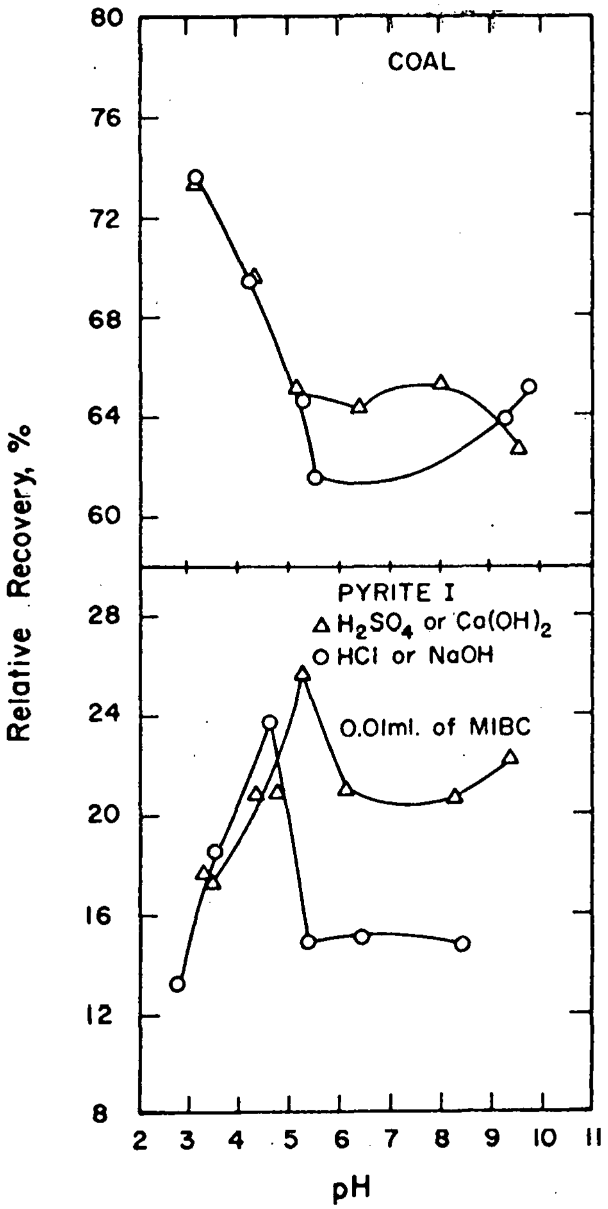

Figure 18. Effect of MIBC on the floatability of coal and pyrite with different pH regulators

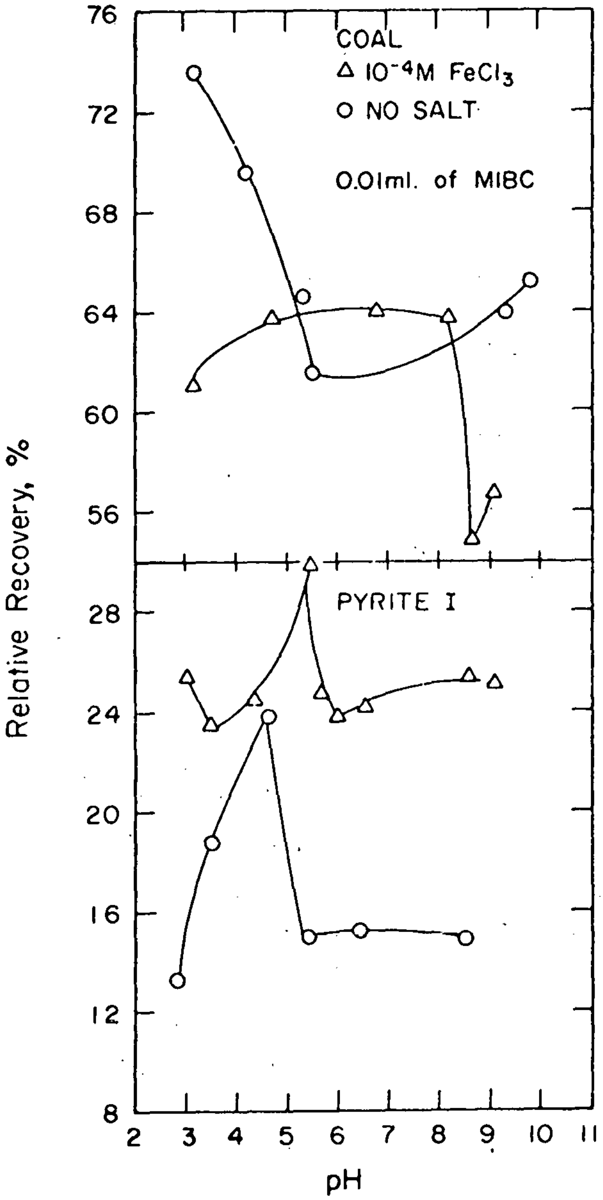

Figure 19. Effect of MIBC on the floatability of coal and pyrite in the ferric chloride solution

Na_2H_2EDTA, sodium silicate, and ammonium thiocyanate appeared to increase the floatability of coal and pyrite I (Figure 20-23). Apparently, these agents served as coal and pyrite activators because they enhanced the recovery. The results were unexpected because previous studies (27, 52) dealing with the flotation of sulfide minerals indicated that these agents are pyrite depressants. Fisher and Wheelock (19) reported that the addition of aluminum nitrate, a reputed pyrite depressant, had the effect of increasing the recovery of Scott coal over a wide range of MIBC concentration. The use of aluminum nitrate also resulted in a slight reduction in ash and sulfur contents of the float product which indicated that aluminum nitrate served as a pyrite depressant. The results were most pronounced at low concentrations of MIBC. Thus the increase in recovery of pyrite I when Na_2H_2EDTA, sodium silicate, and ammonium thiocyanate were added may have been due to the use of excessive amount of MIBC. In general, the use of excess frother reduces the selectivity of froth flotation (19).

A series of similar experiments was conducted using pyrite II to compare the floatability of pyrite I and II. The results shown in Figure 24 indicate that in the absence of MIBC, the recovery of pyrite I and II was similar in an alkaline medium. In acidic solutions, the recovery of pyrite

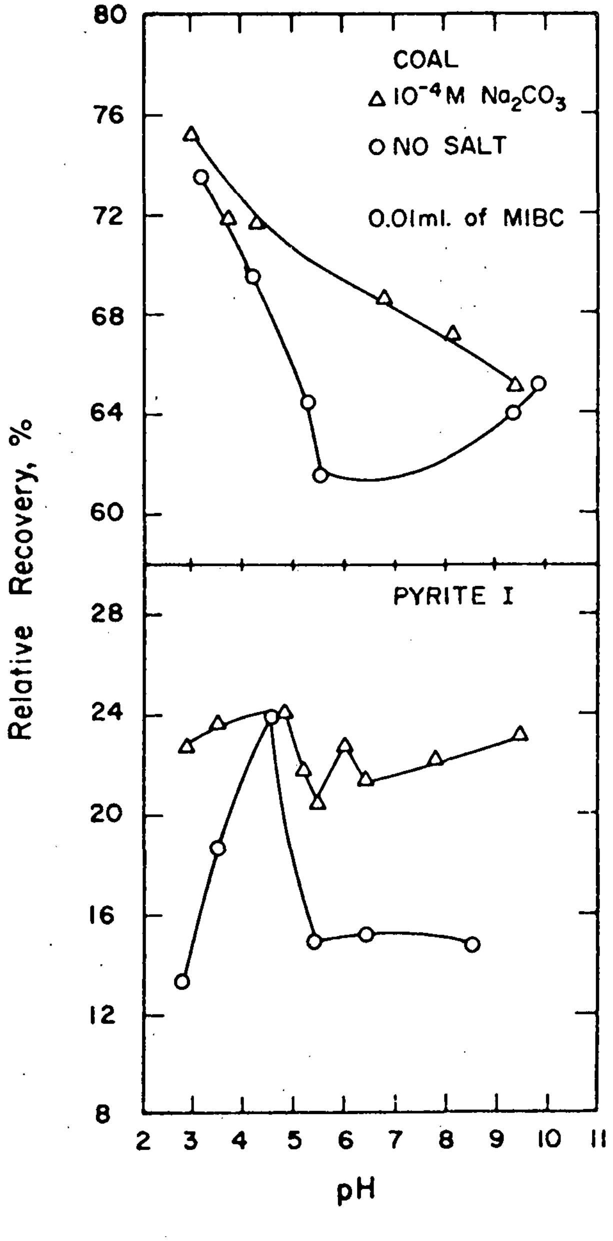

Figure 20. Effect of MIBC on the floatability of coal and pyrite in the sodium carbonate solution

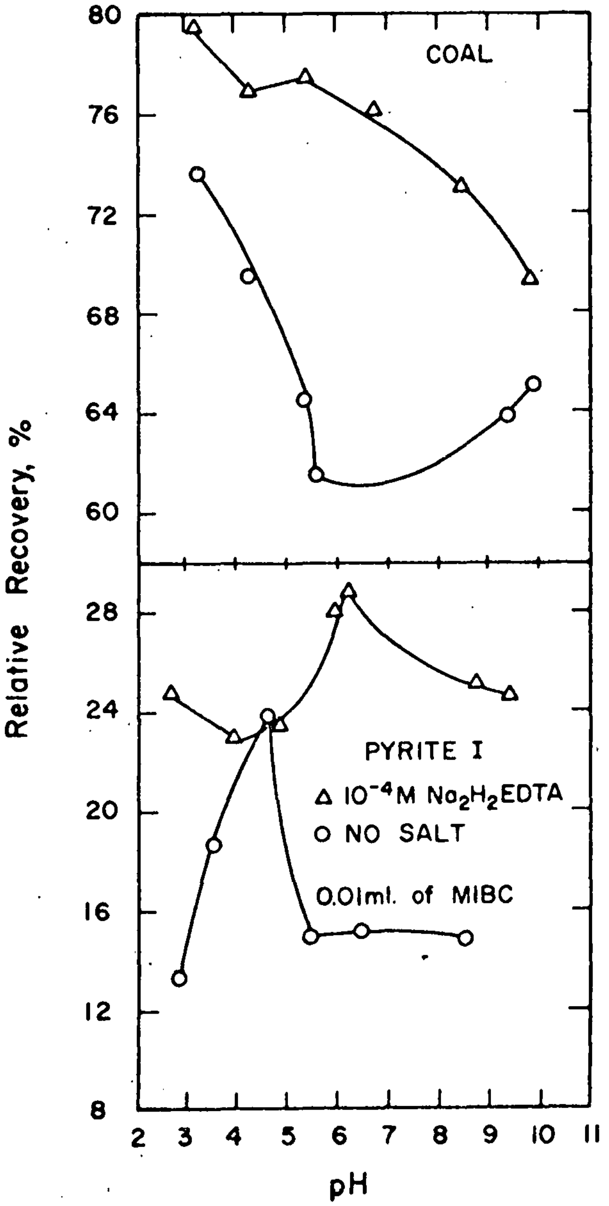

Figure 21. Effect of MIBC on the floatability of coal and pyrite in the disodium salt of EDTA solution

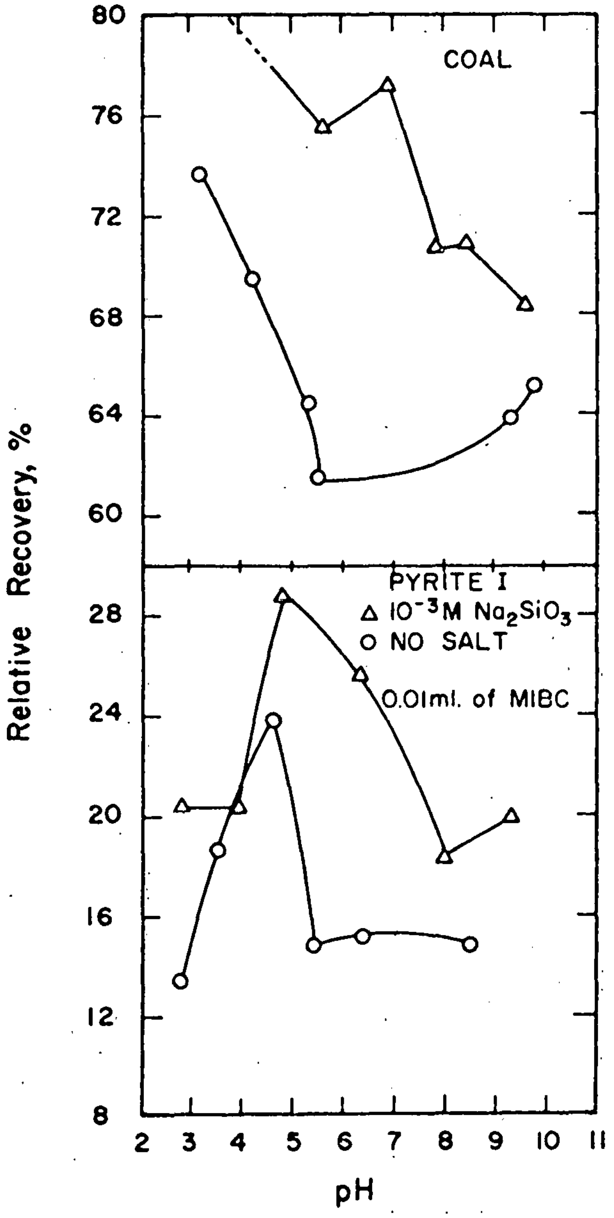

Figure 22. Effect of MIBC on the feasibility of coal and pyrite in the sodium silicate solution

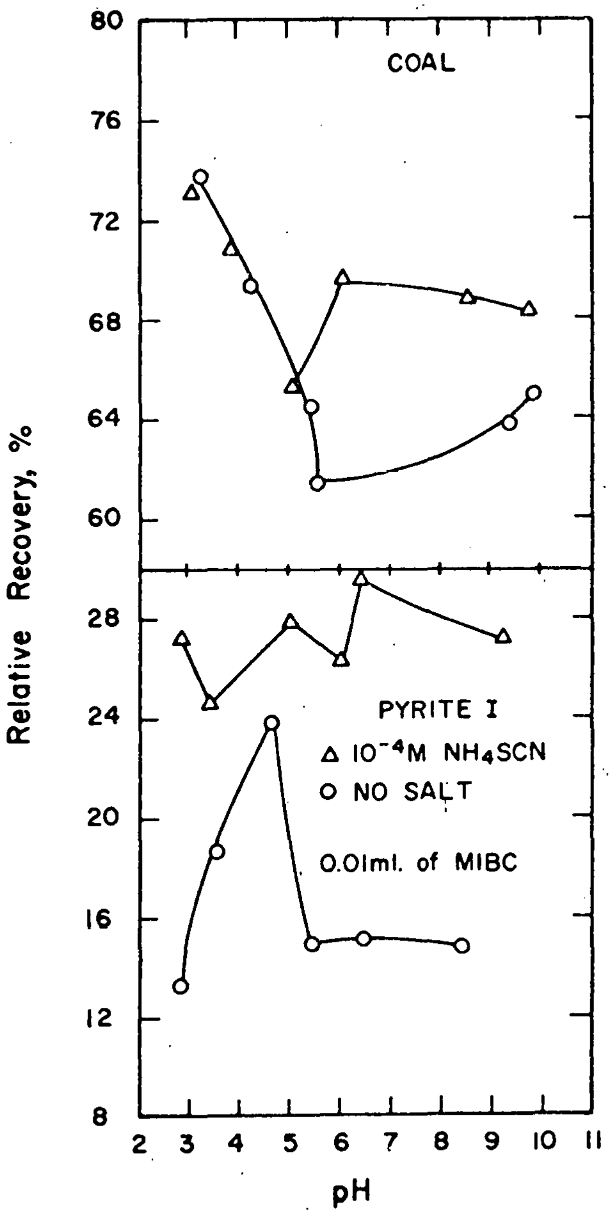

Figure 23. Effect of MIBC on the floatability of coal and pyrite in the ammonium thiocyanate solution

II did not change with pH while the recovery of pyrite I reached a peak at a pH of 4.2.

The addition of MIBC significantly increased the recovery of both pyrite I and II over the whole range of pH (Figure 24). MIBC had the most pronounced effect on pyrite II at low pH while it had little effect on pyrite I at pH below 3. The recovery of pyrite II simply decreased as the pH was increased; on the other hand, the recovery of pyrite I reached a maximum at a pH of 4.6.

An attempt was made to compare the effects of different pH regulators on the floatability of the two pyrites in the presence of MIBC. The results shown in Figure 25 indicate that the use of sulfuric acid slightly increased the recovery of pyrite II but had little effect on the recovery of pyrite I. On the other hand, the use of calcium hydroxide increased the floatability of pyrite I but not the floatability of pyrite II.

As mentioned previously, in the presence of MIBC, the reputed pyrite depressing agents such as ferric chloride, sodium carbonate, Na_2H_2EDTA and sodium silicate served as activators for pyrite I. However, under the same conditions, these agents did not activate the surface of pyrite II but tended in some cases to depress it for pH smaller than 8.

The results shown in Figures 24 to 30 clearly indicate that the effect of a frother on the floatability of a mineral is complicated and dependent on many factors. In general, the primary function of a frother is to extend the froth stability. However, the specific functions and the selectivity of a frother depend on its concentration, impurities, particle size, solid lattice structure, the pH etc., and vary from material to material and even from sample to sample of the same material.

Booth and Freyberger (7) found that the presence of a frother tends to maintain sphericity and smoothness in the shape of air bubbles. A frother also slows the rise of bubbles in a flotation cell, and usually generates small bubbles and closely knit froths which are capable of supporting heavy mineral loads without fallout of mineral grains. The use of a frother provides high recovery but sometimes does not yield high grade concentrates.

The influence of a frother in froth flotation depends on many variables which affect the flotation process. The efficiency of a frother is primarily judged by the grade of concentrate obtained. The effect of a frother on a flotation process not only depends on its chemical and physical properties but also on the type of collector used, the flotation machine, the air flowrate, the type of coal, the presence of impurities, and the previous preparation and pretreatment steps. Booth and Freyberger (7) stated that it is difficult to create a froth in the treatment of coarsely ground ores which essentially have no slimes. However, excessive quantities of slimes make it difficult to break down the froth in the concentrates. The effect of a frother is also influenced by the presence of inorganic salts and organic matter, and the pH of the pulp. Thus, selection of a frother for any particular flotation process depends upon many factors which influence its efficiency. Methyl isobutyl carbinol (MIBC) is widely used in the selective flotation of complex ores, and is of major importance in coal flotation (11). Min (35) found that MIBC did not yield as high a recovery as certain Dowfroth agents but it provided a much better ash reduction.

Flotation after chemical treatment

Chemical pretreatment with a hot sodium carbonate solution containing dissolved oxygen appears to be one of the most effective ways to reduce the floatability of pyrite (19). An experiment was carried out to determine the effect of chemical pretreatment on the floatability of coal and pyrite. The experimental procedure used is as follows: 50 g. of Scott coal (-60/+100) or pyrite II (-80/+100) taken from the same stock of materials used for previous zeta potential and flotation studies was mixed with 500 ml. of a 10% by weight solution of sodium carbonate in a stirred

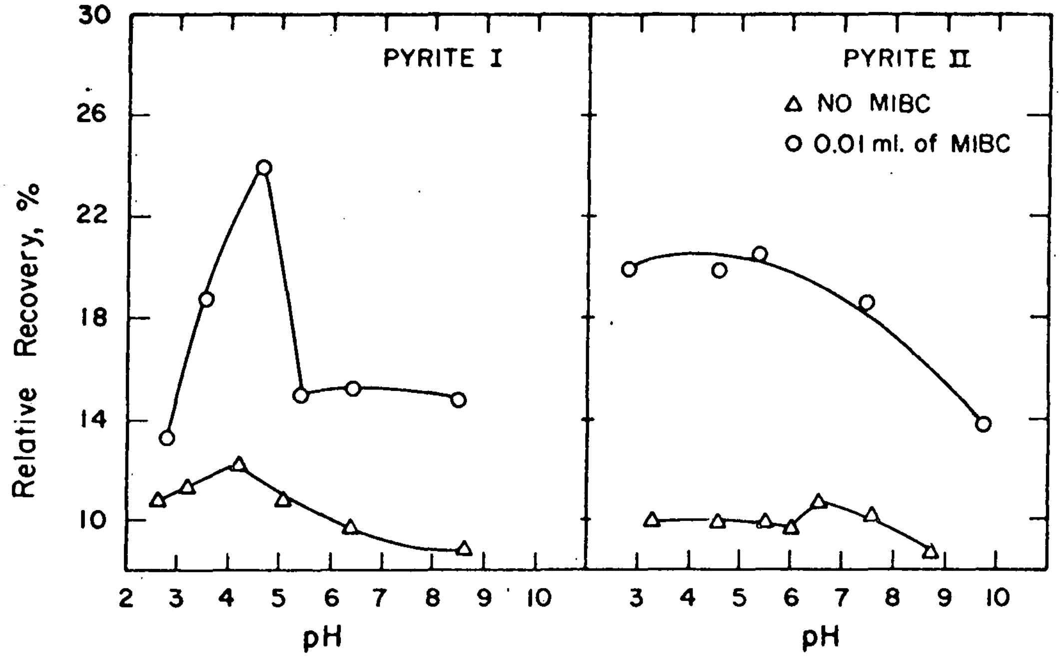

Figure 24. Effect of MIBC on the floatability of pyrite I and II

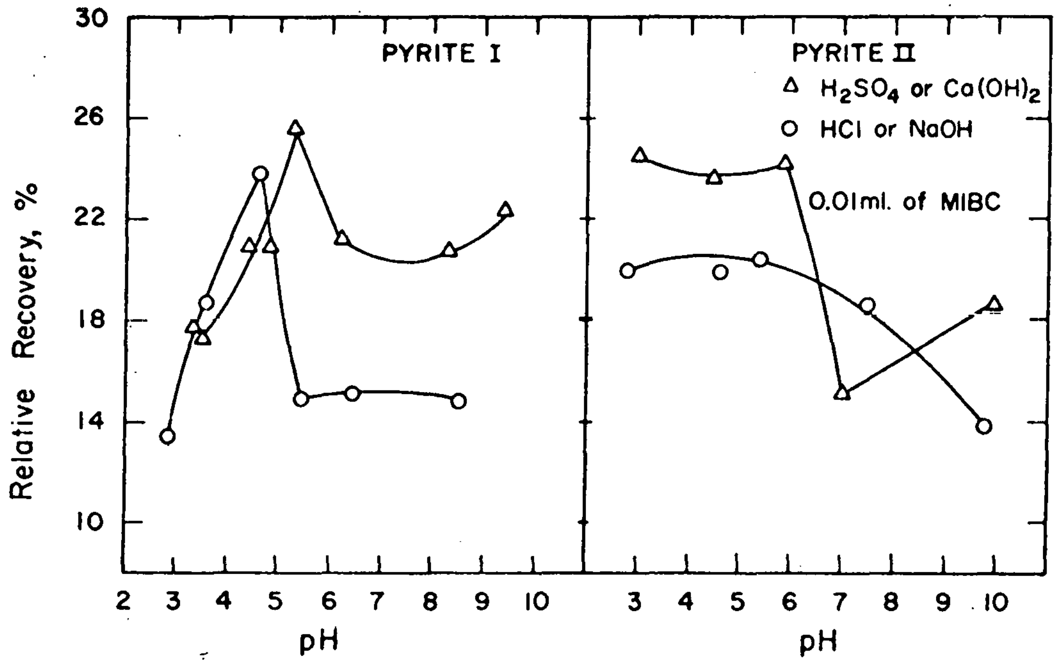

Figure 25. Effect of MIBC on the floatability of pyrite I and II with different pH regulators

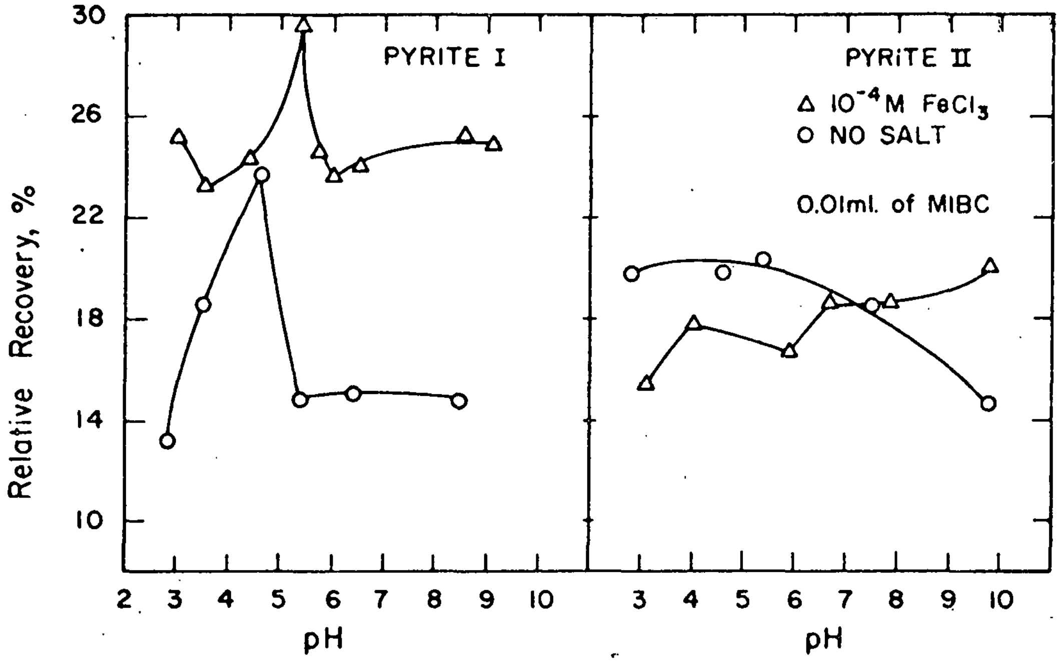

Figure 26. Effect of MIBC on the floatability of pyrite I and II in ferric chloride solution

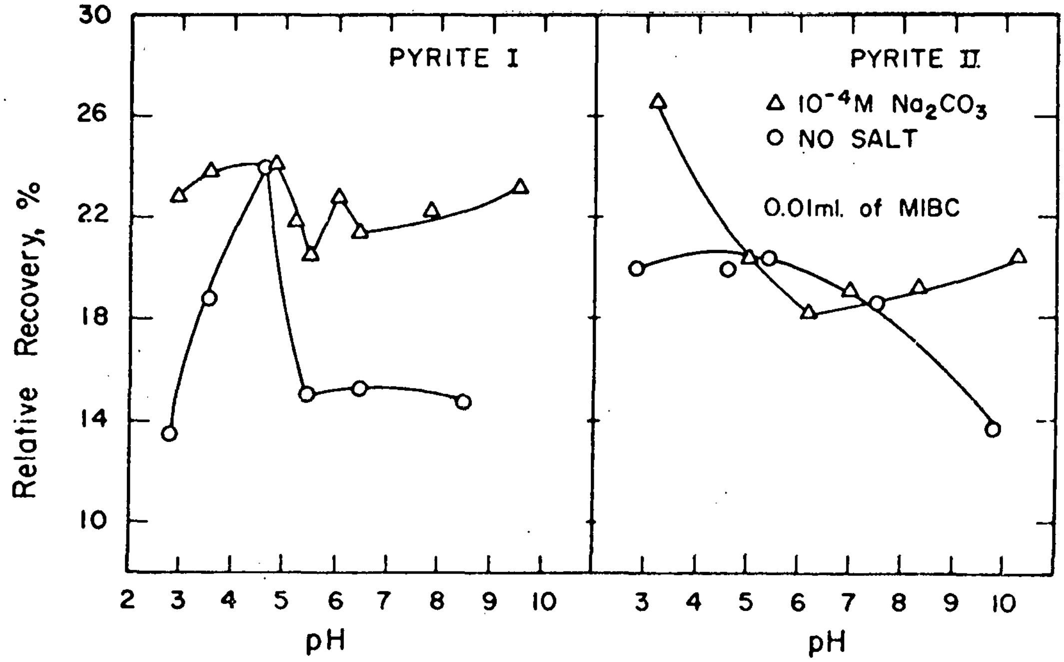

Figure 27. Effect of MIBC on the floatability of pyrite I and II in sodium carbonate solution

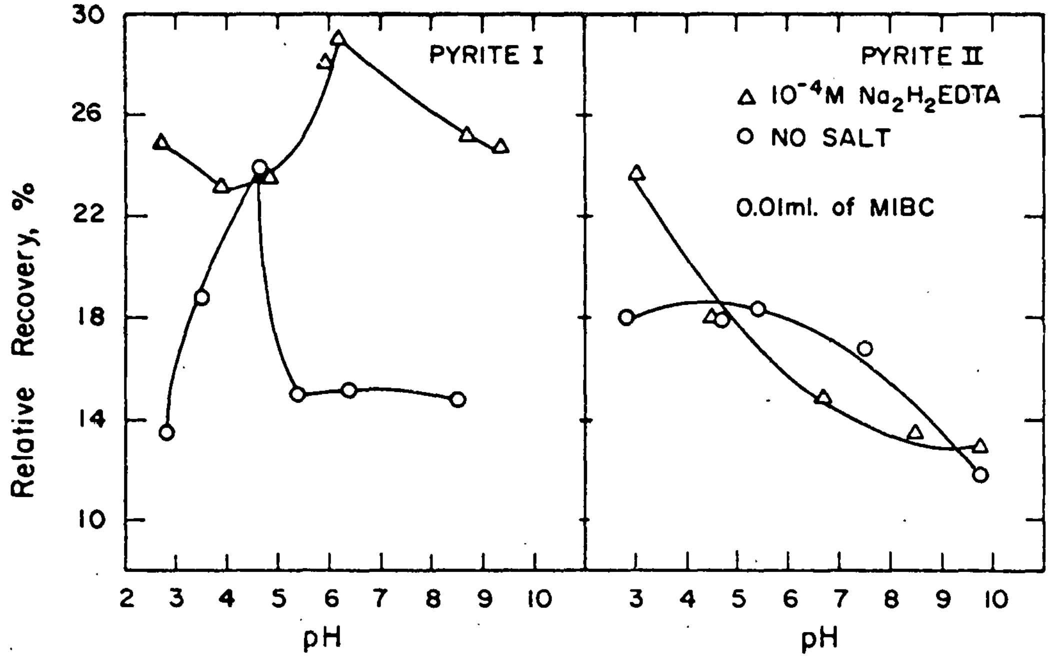

Figure 28. Effect of MIBC on the floatability of pyrite I and II in disodium EDTA solution

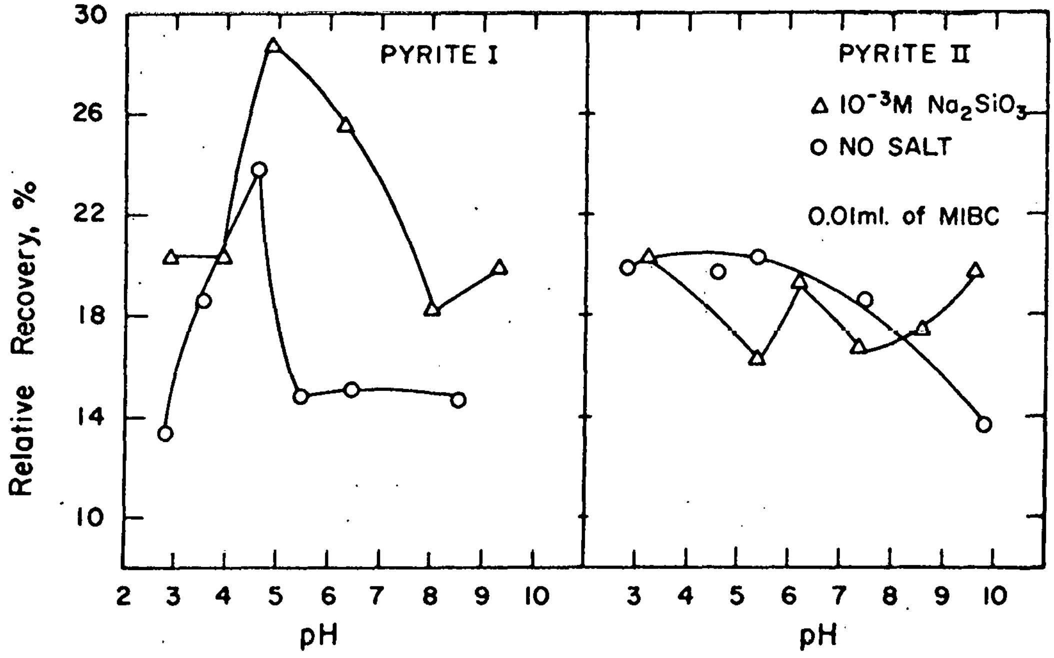

Figure 29. Effect of MIBC on the floatability of pyrite I and II in sodium silicate solution

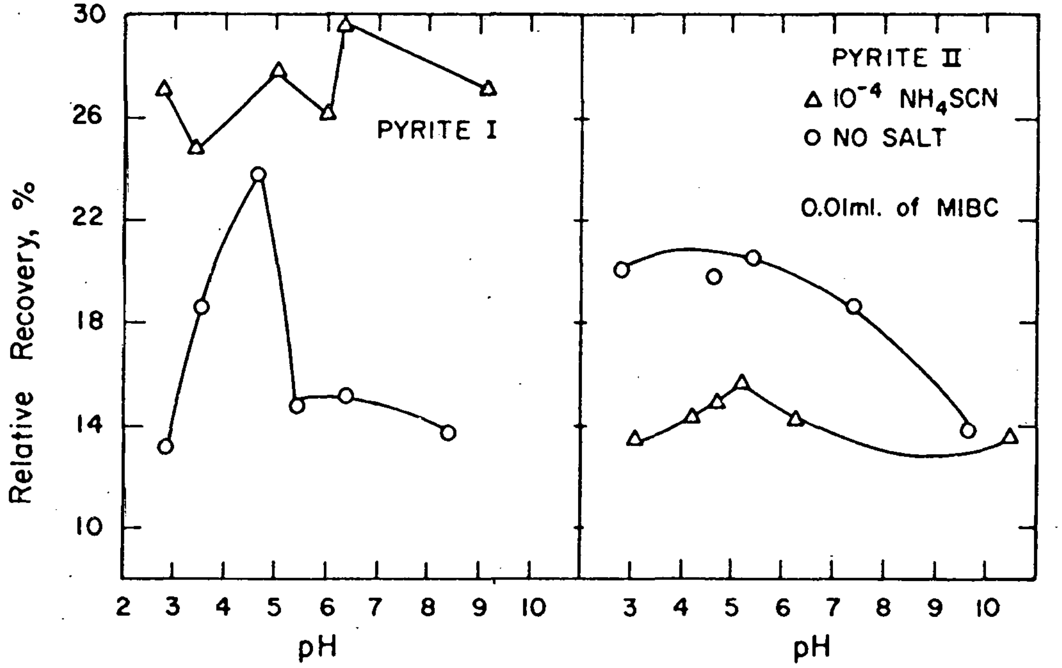

Figure 30. Effect of MIBC on the floatability of pyrite I and II in ammonium thiocyanate solution

laboratory flask. During the mixing period, the flask was heated and the stirrer was set at a predetermined speed. When the temperature of the mixture reached 80°C, air was introduced continuously into the suspension through a diffuser. The treatment was carried out under atmosphere pressure for 30 min. The air supply was disconnected; the flask was removed from the heater, and cooled to room temperature. The suspension was then filtered, and the solids were collected and dried in the oven at 100°C for 3 hr. During filtration, no water was used to wash the filter cake except a very small amount of deionized water was used to remove the solid particles sticking on the wall of the flask. The flotation tests were conducted using pretreated coal or pyrite with deionized water at various pH. The Hallimond tube microflotation cell was used to conduct the flotation tests. The procedure used was similar to the one previously used with 0.01 ml. of MIBC. The results are summarized in Table 5 for coal and pyrite respectively.

The results shown in Table 5 compared to those shown in Figure 17 indicate that chemical treatment prior to flotation reduced the floatability of pyrite greatly while only reducing the floatability of coal slightly.

Min (35) reported that chemically pretreated Scott coal experienced greater total sulfur and ash reduction during

Table 5. Floatability of chemically pretreated coal and pyrite

Coal		Pyrite	
pH	Relative recovery, %	pH	Relative recovery, %
3.2	60.02	3.3	2.65
4.4	60.25	4.8	3.17
6.5	64.67	6.4	3.54
7.5	58.02	7.8	3.32
9.7	63.70	9.0	4.39

froth flotation than Scott coal which had not been treated. Thus when untreated Scott coal was floated in a 0.05 weight percent solution of sodium carbonate it experienced a reduction of 27.2% in ash content and 28.1% in total sulfur content. On the other hand, when Scott coal was pretreated with a 0.05 weight percent solution of sodium carbonate containing dissolved air at 80°C for 30 min. after which the reaction mixture was diluted with deionized water and floated, the coal experienced a reduction of 33.1% in both ash and total sulfur. However, the yield was 92.3% for the untreated coal and 83.0% for the chemically pretreated coal. The process seems to promise a better separation of coal and pyrite by froth flotation. The overall process may be optimized by investigating the parameters which affect both the pretreatments and flotation steps. The pretreatment conditions which should be investigated are time, temperature, type of alkali and its concentration. The flotation conditions which should be investigated are slurry concentration, flotation time, pH, type of frother and its concentration.

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Floatability without MIBC

An investigation of the floatability of an Iowa coal and pyrite in the absence of MIBC led to the following conclusions:

1. In the absence of MIBC, the relative recovery of either coal or pyrite was low and about the same order of magnitude for both components under most conditions tested.
2. The relative recovery of coal or pyrite was somewhat dependent on pH. In the case of pyrite I, the maximum relative recovery was obtained at a pH of 4-5 with the recovery being less at higher or lower pH. In the case of pyrite II, the relative recovery was almost independent of pH.
3. The addition of small amounts of sodium cyanide, ferric chloride, Na_2H_2EDTA, and ammonium thiocyanate exerted a slight depressing action on pyrite I over a rather wide range of pH.

Floatability with MIBC

An investigation of the floatability of an Iowa coal and pyrite in the presence of MIBC led to the following conclusions.

1. The relative recovery of coal or pyrite was increased significantly by the presence of MIBC with the increase in the recovery of coal being much greater than the increase in the recovery of pyrite.
2. The relative recovery of coal or pyrite appeared to be affected more by pH in the presence of MIBC than it was without MIBC. For both materials, acidic pulps resulted in higher recoveries than basic pulps. Also higher recoveries were obtained when calcium hydroxide was used to increase pH rather than sodium hydroxide. This was an unexpected result since calcium hydroxide is reputed to be a better pyrite depressant than sodium hydroxide.
3. Chemical pretreatment of coal and pyrite with a 10% sodium carbonate solution containing dissolved air at 80°C and atmospheric pressure reduced the floatability of pyrite I remarkably while only slightly reducing the floatability of coal.

4. The floatability of pyrite II which had been ground and then stored for some time before being utilized was somewhat different than the floatability of pyrite II which was utilized after being freshly ground. This difference may have been due to a difference in the surface oxidation of the pyrite.
5. The addition of small amounts of ferric chloride, sodium carbonate, Na_2H_2EDTA, sodium silicate, and ammonium thiocyanate appeared to increase the recovery of pyrite I and hence, seemed to serve as activators rather than depressants. On the other hand, these reagents except for ammonium thiocyanate had little effect on the floatability of pyrite II. Ammonium thiocyanate did seem to depress pyrite II somewhat.

Zeta potential of coal and pyrite

1. In coal flotation research, the measurement of the zeta potential appears to be useful mainly as a means for studying the adsorption of various reagents by coal or pyrite rather than as a means for predicting the floatability of either component.

2. No consistent relationship between the zeta potential and the floatability of coal or pyrite was found. The lack of correlation between these two factors may have been due to the anisotropic nature of the solid surface.
3. The zeta potential of Iowa coal was found to be similar to results found for Pittsburgh coal during previous studies by Campbell and Sun (11), and Baker and Miller (4).
4. Hydronium and hydroxyl ions are potential-determining ions for coal. The results agree with those found previously (4, 11). The zeta potential of pyrite behaves similarly to that of coal at high pH suggesting hydroxyl ions are also potential-determining ions for pyrite.
5. Measurements of the zeta potential indicate that the electrical charge on pyrite particles in an aqueous suspension is changed from negative to positive in neutral or basic solution when appropriate concentrations of the following substances are used: calcium hydroxide, ferric chloride, sodium cyanide, and sodium carbonate. Among these substances, only sodium cyanide appears to produce the same sort of charge reversal in the case of coal.

6. The zeta potentials of coal and pyrite are of opposite sign when these materials are suspended in solutions of the following reagents at the indicated pH:

Reagent	pH	Zeta potential Coal	Zeta potential Pyrite
$Ca(OH)_2$	6-10	-	+
$FeCl_3$	7-8	-	+
Na_2CO_3	7-8	-	+
NH_4SCN	5-6	-	+
Na_2H_2EDTA	3-5	+	-

These results show that cationic collectors might be used advantageously for the selective flotation of coal under the conditions indicated above where the coal particles bear a negative charge or anionic collectors where the coal particles bear a positive charge.

RECOMMENDATIONS

1. The use of cationic and anionic collectors in conjunction with other reagents which cause coal and pyrite particles to become oppositely charged in aqueous suspension should be investigated as a means for improving the selectively of coal flotation.
2. A better understanding of the basic structure of coal and pyrite and the physical and chemical changes which these substances undergo due to size reduction is of major importance to the development of the flotation process.
3. Since the addition of MIBC strongly influences the floatability of coal and pyrite, it would be of interest to investigate the interaction among collectors, frothers, depressing agents and the solid surfaces, particularly the adsorption of collectors and frothers by the solid surfaces in various chemical solutions and at different pH.
4. A comprehensive understanding of the chemical pretreatment step would also be helpful in separating coal and pyrite.

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