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FINAL REPORT

Control of Pyrite Surface Chemistry
in Physical Coal Cleaning

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EXECUTIVE SUMMARY

Recent studies show that the collectorless flotation of pyrite is one of the major problems encountered in the desulfurization of coal by surface-based separation techniques such as froth flotation or oil agglomeration. Collectorless ("self-induced") flotation is believed to be related to the superficial oxidation of pyrite. The oxidation produces a sulfur-rich surface layer that is hydrophobic, making pyrite and coal difficult to separate based on differences in hydrophobicity. This report is the result of a two-part study (i) to obtain a better understanding of the oxidation reactions that lead to self-induced flotation of pyrite and (ii) to utilize this increased understanding to develop effective methods of rejecting pyrite during advanced physical coal cleaning.

In Part I, *Surface Chemistry of Coal Pyrite*, the mechanisms responsible for the inefficient rejection of coal pyrite were investigated using a number of experimental techniques. These included X-ray Photoelectron Spectroscopy (XPS) and electrochemical voltammetry. Microflotation studies and induction time measurements were also conducted during this phase so that the flotation of pyrite could be correlated with the results of fundamental surface chemical measurements. The test results demonstrate that the hydrophobicity of coal pyrite is related to the surface products formed during oxidation in aqueous solutions. During oxidation, a sulfur-rich surface layer is produced in near neutral pH solutions. This surface layer is composed mainly of sulfur species in the form of an iron-polysulfide along with a smaller amount of iron oxide/hydroxides. Low Energy Ion Scattering Spectroscopy (ISS) data show that the surface layer has an overlayer-type structure on the pyrite surface with the hydrophobic sulfur species in the outermost region. In alkaline solutions, oxidation of coal pyrite produces

a surface layer containing only iron and oxygen species, most likely in the form of hydrophilic iron oxide/hydroxides. The floatability of coal pyrite is depressed under these conditions. In contrast, the floatability of coal pyrite increases dramatically in the presence of frothers and hydrocarbon collectors. These reagents are believed to absorb on the weakly hydrophobic pyrite surfaces as a result of hydrophobic interaction forces.

In Part II, *Developing the Best Possible Rejection Schemes*, a number of pyrite depressants were evaluated in column and conventional flotation tests. These included manganese (Mn) metal, chelating agents quinone and diethylenetriamine (DETA), and several commercially-available organic depressants. Of these, the additives which serve as reducing agents were found to be most effective. Reducing agents were used to prevent pyrite oxidation and/or remove oxidation products present on previously oxidized surfaces. These data show that Mn is a significantly stronger depressant for pyrite than quinone or DETA. Important factors in determining the pyrite depression effect of Mn include the slurry solid content during conditioning, the addition of acid (HCl), and the amount of Mn. The acid helps remove the oxide layer from the surface of Mn and promotes the depression of pyrite by Mn. Common commercial depressants (i.e., ORFOM D8 and PRC), which are known to be good depressants for mineral pyrite, have no depression effect on the coal pyrite sample examined in the present work.

In addition to the aforementioned depressants, a novel pyrite depressant, referred to as NB, was synthesized for the selective separation of coal from coal pyrite. This reagent contains no sulfur group in its structure and has a stronger affinity towards pyrite than coal. Due to a pending patent application, the identity of NB will not be disclosed until rights are secured. The

effect of a number of parameters such as pH, reagent concentration, and flotation time on flotation response was investigated in microflotation tests. The reagent demonstrated superior performance at relatively low concentrations when compared to the commercially-available sulfur-based pyrite depressants.

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INTRODUCTION

The primary objectives of the physical cleaning of coal for utility and steam markets traditionally are ash reduction and energy enrichment; however, increasing public concern regarding environmental pollution by acid rain are broadening the scope of coal beneficiation to include sulfur reduction. Recent studies by the U.S. Department of Energy (DOE) and others suggest that the physical cleaning of coal to remove inorganic sulfur can be, under certain conditions, more cost effective than alternative post-combustion technologies such as flue gas scrubbing.

Although physical cleaning methods appear to be more economically attractive, they are effective only if the materials to be separated are sufficiently liberated. Although the liberation size for pyrite in coal varies from seam to seam, most studies indicate that many of the major U.S. coal seams will have to be pulverized to micron sizes to achieve sufficient liberation. For example, according to studies by Consolidation Coal Company (Zitterbart *et al.*, 1985) only approximately 53% of the pyrite in Pittsburgh seam coals is liberated at a grind size of 200 mesh (74 μm), while pyrite liberation reaches up to 70% at 200 mesh with Illinois No. 6 coals. Investigations at Virginia Tech show that for some coal seams, pyrite can be so finely disseminated that it can only be liberated by attrition grinding to below 10 μm .

Most available conventional coal cleaning technologies are not effective in this fine particle range. As a result, DOE has promoted several advanced physical coal cleaning (APCC) technologies, including advanced froth flotation and selective agglomeration, for the upgrading of finely pulverized coal. Several of these technologies are capable of achieving 90% sulfur rejection while operating at Btu recoveries above 90% based on run-of-mine quality coal.

One such APCC technology is the microbubble column flotation (MCF) process developed at Virginia Tech, which was developed under the sponsorship of DOE. This technology was successfully tested at a pilot-scale of 500 lb/hr and an industrial-scale demonstration in conjunction with Kaiser Engineers is underway. Flotation tests on a variety of high- and low-sulfur coals showed that MCF can produce grade-recovery curves close to those determined using flotation release analysis. This demonstrates that MCF is capable of removing impurities from coal with the maximum efficiency attainable for a given degree of liberation and surface chemistry. Pyritic sulfur rejections as high as 90% with high Btu recoveries can be obtained with some coals provided that the surface chemistry of the coal pyrite is properly controlled.

Despite the success of many APCC processes in removing mineral matter from coal, there is evidence that even well-liberated pyrite particles are recovered in the flotation product if surface conditions are not properly controlled. Olson and Aplan (1984) showed, for example, that the addition of hydrocarbon collectors can increase the rate of flotation of liberated pyrite ten-fold, making it difficult to separate from coal. This problem is further complicated since the surface chemistry of coal pyrite differs significantly from one coal to another (Esposito *et al.* (1987). Wheelock *et al.* (1988) showed that the coal pyrite from the Illinois No. 6 coal seam has a much more hydrophobic nature than pyrite from the Pittsburgh and Upper Freeport coal seams. Thus, further improvements in the rejection of pyritic sulfur by APCC processes will require a better understanding of the nature of coal pyrite surface chemistry and methods for its control.

Although liberation is important in pyrite rejection, liberated pyrite is often found to

display some degree of hydrophobicity and, therefore, floats with the coal. It is known that many sulfide minerals, such as chalcopyrite, pyrite, pyrrhotite, and galena, can be floated without a collector (Yoon, 1979, 1981; Luttrell and Yoon, 1984 a,b; Heyes and Trahar, 1977; Gardner and Woods, 1979; Fuerstenau and Sabacky, 1981). This phenomenon, generally known as "collectorless flotation," is observed when the sulfide mineral is superficially oxidized to the extent that elemental sulfur (S^0) or metal-polysulfides ($M-S_x$) are formed. Since these oxidation products are inherently hydrophobic, the mineral becomes floatable with frother alone. Since pyrite is a semiconductor, its oxidation process is controlled by electrochemical mechanisms involving anodic oxidation of the mineral and cathodic reduction of oxygen. Collectorless flotation is possible only at potentials where mineral surfaces begin to oxidize and hydrophobic surface species (such as elemental sulfur (S^0) or metal polysulfides ($M-S_x$)) begin to form. As the potential is further increased, the rate of oxidation becomes fast enough to produce hydrophilic oxidation products such as thiosulfate ($S_2O_3^{2-}$) or sulfate (SO_4^{2-}), which render the mineral hydrophilic and nonfloatable. Thus, the redox conditions which regulate the surface composition play an important role in the flotation and depression of coal pyrite.

The above discussion suggests four possible solutions to the problem of coal pyrite flotation:

- 1) prevent coal pyrite from being exposed to an oxidizing environment so that hydrophobic species cannot form;
- 2) oxidize the coal pyrite to the extent that hydrophilic oxidation products such as $FeSO_4$, FeS_2O_3 and $FeOOH$ are formed;
- 3) add appropriate reagents that render the coal pyrite hydrophobic and coal itself

hydrophilic (reverse flotation); and

- 4) add appropriate reagents that render the coal pyrite hydrophilic but do not affect the hydrophobicity of the coal.

The first approach could be pursued by floating the mineral as soon as it is liberated from the coal during grinding, grinding the coal under an inert atmosphere, or by creating reducing conditions by adding appropriate reagents such as sodium sulfide, sodium dithionate, etc., during grinding or flotation. Since reagent additions can be costly, the same could be achieved by using appropriate grinding media that can provide reducing conditions. It is well known that the rate of oxidation of sulfide minerals such as pyrite and pyrrhotite is critically affected by galvanic contacts (Nakazawa and Iwasaki, 1985; Adam *et al.*, 1984).

The second approach consists of adding oxidizing agents to induce the formation of hydrophilic oxidation products on the surface of coal pyrite. In practice, this may be difficult to implement because of the danger of oxidizing the coal and making it difficult to float as well. Nevertheless, systematic studies on the rate of coal pyrite oxidation relative to that of coal are warranted.

The third approach was demonstrated by Miller (1973) and was proven effective with some coals. The major disadvantage of this technique is that relatively large amounts of reagents are usually required because of the large amount of coal that must be depressed. This becomes particularly significant, because of the very large surface area, for coals that are micronized to liberate pyrite. Furthermore, this process requires two stages of flotation, which increases the costs compared to conventional single-stage flotation processes.

The fourth approach for improved coal pyrite reaction involves the addition of surface-

modifying reagents that would selectively adsorb on the surface of coal pyrite and render it hydrophilic. There are several commercial pyrite depressants available today, although few are successful in applications related to coal. These include functionalized polymers, sodium hydrosulfide, cyanides, and bifunctional surfactants such as Orform-D8. The polymeric depressants do a very good job of depressing pyrite, but they have a tendency to depress coal flotation as well. Sodium hydrosulfide and cyanide can remove the hydrophobic oxidation products and provide a reducing environment, although the amounts of the reagents required may have to be relatively high depending on the coal. One of the more intriguing reagents is Orform-D8 which has a trithiocarbonate functional group on one end of a hydrocarbon chain and a hydroxyl group on the other. This reagent is believed to anchor itself to the surface of coal pyrite through the trithiocarbonate group, then render the mineral hydrophilic by orienting its hydroxyl groups towards the aqueous phase. This depressant should be more selective than the functionalized polymers, and the amount of the reagent required should be much less than that required for sodium hydrosulfide and sodium cyanide; however, only a limited amount of test work has been conducted using bifunction surfactants such as Orform-D8 for improving coal pyrite depression.

OBJECTIVES

The primary objectives of the research were (i) to obtain fundamental knowledge of the surface properties of coal pyrite and (ii) to use this knowledge to develop or improve advanced physical coal cleaning technologies.

RESEARCH APPROACH

To accomplish the proposed objectives, the work was divided into two parts. In Part I, *The Surface Chemistry of Coal Pyrite*, the chemical mechanisms responsible for the inefficient rejection of coal pyrite were determined using a number of spectroscopic and electrochemical techniques. The techniques included X-ray photoelectron spectroscopy (XPS) for chemical identification of oxidation products and electrochemical voltammetry for *in-situ* studies of the mechanisms and kinetics of pyrite oxidation. Microflotation studies and induction time measurements were also conducted during this phase so that the flotation of pyrite could be correlated with the results of fundamental surface chemical measurements.

In Part II, *Improving Pyrite Rejection*, microbubble column flotation and conventional flotation were used to evaluate and develop new methods for rejecting pyrite from coal. These methods were based on the results of Part I.

The first phase of the work involved characterizing the hydrophobicity of relatively pure samples of pyrite under a variety of experimental conditions. Hydrophobicity was quantified by conducting both microflotation tests and induction time measurements. Experiments were conducted as a function of pH, oxidation time and reagent addition. Tests were carried out on coal pyrite and mineral pyrite from different sources.

To obtain a correlation of the surface chemistry of pyrite with its flotation/hydrophobic

properties, XPS and electrochemical studies were used to characterize the samples used in flotation and induction time measurements. The electrochemical studies had several advantages. First, the degree of oxidation or reduction of minerals could be precisely controlled using electrochemical techniques. Second, the current-voltage behavior of pyrite electrodes under dynamic potential sweep methods provided direct rate and mechanistic information on the electrochemical reactions occurring at pyrite-aqueous solution interfaces. Third, this technique avoided the unknown chemical effects associated with the use of oxidation and reduction reagents; alternatively, a comparison of the flotation response using electrochemical techniques with that using oxidizing and reducing reagents provides information on the chemical, as opposed to electrochemical processes, occurring on pyrite.

EXPERIMENTAL

Electrochemical Measurements

Electrochemical measurements were conducted to define the reduction/oxidation behavior of both coal and mineral pyrite. A PAR 273 potentiostat and a conventional three electrode cell consisting of working (pyrite), counter (platinum), and reference (saturated Calomel or silver-silver chloride) electrodes were employed for these studies. All potentials are reported against the standard hydrogen electrode. The supporting electrolyte for electrochemical studies was 1M KCl, which produced a solution of near neutral pH. Ultra high purity nitrogen was used for purging the solution.

Surface Analysis

In conjunction with the basic electrochemical studies, surface analysis techniques, XPS

and ion scattering spectroscopy (ISS) were used to identify the chemical surface products of reduction/oxidation processes. XPS was also used to identify the chemical species formed on the pyrite powders used in microflotation experiments. For most studies, the XPS spectra were recorded on a Perkin-Elmer PHI 550 spectrometer with $K\alpha$ -excitation from a magnesium anode operated at 10 kV and 10mA. The pressure in the analyzer chamber was nearly 10^{-8} Pa. The measurements were performed with a take-off angle close to 45° . Narrow scan spectra were collected for the oxygen (O1s), carbon (C1s), sulfur (S2p), and iron (Fe2p and Fe3p) lines. The S2p, O1s, Fe3p, and Fe2p lines were fitted with a mixture of Gaussian and Lorentzian peak shapes (maximum of 20% Lorentzian). The binding energies were referenced to the C1s peak at 284.9 eV. For studies on powdered specimens from flotation experiments, a Kratos XSAM-800 spectrometer, equipped with a magnesium anode, was used to record the XPS spectra. Its operating pressure was approximately 10^{-9} torr.

The ISS examination of the sample was performed in conjunction with the XPS measurements. After evacuation to nearly 10^{-9} Pa, the vacuum chamber was backfilled to 2×10^{-5} Pa with pure helium. The primary energy of 1 keV was used with a beam current density of $9\mu\text{A}/\text{cm}^2$. The sputtering process was sufficiently slow to measure a depth profile within ten minutes. The backscattered $^3\text{He}^+$ ions were measured at 123° for analysis of the surface.

Flotation Tests

A Partridge and Smith-type cell was used for microflotation experiments (Partridge and Smith, 1971). A 2-inch diameter by 67-inch height column was used for microbubble column flotation and a 5-liter laboratory Denver cell was used for conventional flotation. Operating parameters for flotation cells are given in the appropriate sections within this report.

Induction Time Measurements

A VPI&SU designed electronic induction timer equipped with a built-in electronic eye for auto-calibration was used for determining the rate of bubble-particle attachment. The utility of induction time measurement for flotation related studies is described elsewhere (Yoon and Yordon, 1988). The induction time measurements were conducted using 1-mm diameter bubbles. At a given contact time, ten bubble-particle contacts were made to determine the probability of attachment. The induction time was determined as the contact time that gave a 50% probability (5 successful attachments per 10 attempts) of bubble-particle attachment.

Materials

A number of different coal- and mineral-pyrite specimens were used in this study. These included coal-pyrite samples from the Pittsburgh No. 8, Pocahontas No. 3, and Lower Kittanning seams, and mineral pyrite from Logrono, Spain, and Huanzala, Peru. Further details and methods of preparing the samples for the various studies are given in the appropriate sections within this report.

PART I: SURFACE CHEMISTRY OF COAL PYRITE

These studies used coal pyrite from the Pittsburgh No. 8 seam and mineral pyrite from Logrono, Spain. Slab electrodes were cut and initially rough-polished using different grades of silicon carbide papers. The final polishing was done using 0.3- and 0.05- μm alumina powder. After polishing, the electrodes were washed successively in an ultrasonic bath in warm ethyl alcohol, in a 10% H_2SO_4 solution for 15 seconds, then in 18 M Ω deionized water. The electrodes were then immediately transferred to the electrochemical cell. Cyclic voltammograms were recorded after the insertion of the electrodes into the cell. For spectroscopic analysis, the electrode potential was stepped from the open-circuit value to the desired potential and held for ten minutes. The electrode was then removed from the cell, quickly rinsed with deionized water, blown dry with nitrogen, and inserted into the spectrometer for analysis. After each spectrum was recorded, the electrode was polished for the next measurement.

Open Circuit Potential

The open circuit potentials of freshly polished coal and mineral pyrite electrodes as a function of solution pH are shown in Figure 1. There appears to be little difference between the open-circuit potentials recorded for the coal and mineral pyrite samples examined in these measurements. It is well known that a thin oxide film forms on pyrite polished in air (Buckley *et al.*, 1988a,b) and that the presence of this film can influence the open-circuit potential measured in the system. The small differences in the open-circuit potentials observed for the coal- and mineral-pyrite samples suggest that the surface products formed on each may be similar.

Figure 1. Open-circuit potentials of mineral pyrite and coal pyrite as a function of pH.

Cyclic Voltammetry

Steady-state cyclic voltammograms of stationary mineral- and coal-pyrite electrodes in 1M KCl solution are shown in Figure 2. The voltammograms for both samples are very similar, showing four anodic and three cathodic peaks. These peaks are numbered I-VII for the ease of reference in the following discussion pertaining to both electrodes. Peaks I-III correspond to the oxidation of iron species. According to Ahlberg (Ahlbert *et al.*, 1990), peak

Figure 2. Cyclic voltammetry of (a) coal pyrite and (b) mineral pyrite in 1M KCl at 25 mV/sec.

I can be attributed to the oxidation of elemental iron. $\text{Fe}(\text{OH})_2$ is typically formed in this region; however, when iron is oxidized in the presence of hydrosulfide ions, iron sulfide (FeS) may be formed. Peaks II and III correspond to the oxidation of $\text{Fe}(\text{OH})_2$ and FeS formed at peak I, respectively. Moreover, elemental sulfur can be formed in this region from the

oxidation of hydrosulfide ions. Pyrite oxidation occurs close to the open-circuit potential and continues at higher potentials as evidenced by the dramatic increase in current for peak IV. Hamilton and Woods (1981) described the oxidation of pyrite in alkaline solution by the following reaction:

in which only monolayer quantities of elemental sulfur are formed, while the majority of the sulfur is oxidized to sulfate with increasing overpotential by reaction,

More recently Buckley *et al.* (1988(a)) reformulated reaction (1) on the basis of more detailed XPS and electrochemical measurements and described the oxidation in terms of the formation of a sulfur-rich or metal-deficient surface:

Mycroft *et al.* (1990) concluded that the electrochemical oxidation of pyrite surfaces in near neutral aqueous solutions produces polysulfides and elemental sulfur as evidenced from Raman spectroscopy of the surface. On the reverse scan, cathodic peak V occurs and is coupled with the anodic processes occurring at peak IV. Mycroft *et al.* postulated that this redox couple is associated with the oxidation and reduction of a sulfur species since iron is already in the ferric state. Moreover, from their Raman and XPS results, this potential region is known to be an active region for the formation of polysulfide and sulfur. Peak VI corresponds to the reduction of oxidic species produced in reactions (1-3) by the following reactions:

The reduction of bulk pyrite, iron sulfide, and Fe(OH)_2 occurs at more negative

potentials in the region of peak VII. In this region, elemental iron forms on the electrode surface while hydrosulfide ions are released to the solution.

Surface Analysis

Surface analysis of a polished coal pyrite electrode by XPS shows that the S2p/Fe3p ratio is 2.9 and the positions of the S2p_{3/2} and Fe2p_{3/2} peaks on the narrow scans are 162.8 and 707.5 eV, respectively. Oxidation at potentials below the region of peak IV (Figure 2) resulted in only minor changes in the XPS spectra. Figure 3 shows the differences in the S2p, Fe2p_{3/2}, and O1s lines for a coal pyrite electrode oxidized for ten minutes at 0.3V (SHE), i.e., at the open-circuit potential, and at 0.7V (SHE). At the open-circuit potential, the S2p, Fe2p_{3/2}, and O1s narrow scans are unchanged from freshly-polished pyrite; however, the S2p/Fe3p ratio is 3.3 which reflects a small change in the relative amount of surface sulfur. A dramatic change in the narrow scans occurs when the electrode is oxidized for ten minutes at 0.7V (SHE). The S2p narrow scan shows a significant broadening to higher binding energies and the S2p/Fe3p ratio increases to 7.5, suggesting that additional sulfur species are present on the electrode surface. The Fe2p_{3/2} narrow scan looks similar to the open-circuit scan except that the intensity is greatly diminished; moreover, additional intensity occurs from 711-712 eV. Since the Fe2p line is more surface sensitive than the Fe3p line the lower overall intensity of the Fe2p line, together with the additional intensity at 711 eV, suggests that an overlayer is present on the electrode surface. This is further supported by the O1s narrow scan showing a significant increase in the

Figure 3. S2p, Fe2p_{3/2}, and O1s XPS spectra for coal pyrite oxidized at (a) open-circuit and (b) 0.7V (SHE) for 10 minutes in 1M KCl.

component attributed to hydroxides at 532 eV.

Figure 4 illustrates the difference in the line shape and binding energy of the S2p narrow scan for the coal-pyrite electrode oxidized at the open-circuit potential and at 0.7V (SHE). The S2p line is a spin-split doublet, in which the 2p_{3/2} and 2p_{1/2} components are separated by 1.2 eV and have an intensity ratio of 2:1. The S2p line at open circuit can be curve fit with one

spin-split doublet, which indicates the presence of only one sulfur species, namely S_2^{2-} , at 162.8 eV; however, the S2p line for the coal-pyrite electrode oxidized at 0.7V (SHE) is more complex. The S2p line is broader towards the higher binding energy side of the spectrum and can be curve fit with at least three spin-split doublets. The lowest binding energy doublet corresponds to pyritic sulfur at 162.7 eV. The highest binding energy doublet occurs close to

Figure 4. S2p spectra for a coal pyrite oxidized at (a) open-circuit and (b) 0.7V (SHE) for 10 minutes in 1M KCl.

that reported for elemental sulfur at 164 eV. The third doublet is intermediate, between those for pyritic sulfur and elemental sulfur, and occurs at 163.4 eV, suggesting a polysulfide may be present on the mineral surface (Mycroft *et al.*, 1990; Buckley *et al.*, 1988(b); Termes *et al.*, 1987).

These XPS results establish that the sulfur environment of the coal pyrite electrode changes upon oxidation. Curve fits of the S2p line reveal additional sulfur species present on the electrode surface. This additional sulfur is at a higher oxidation state than the lattice sulfur. This oxidation layer, which contains the additional sulfur species, is probably several atomic layers thick because of the significant attenuation of the Fe2p signal. The stability of these additional sulfur species was determined by extended exposure to high vacuum. The position and intensity of each component did not change appreciably after four hours exposure to the high vacuum. This indicates that the overlayer is stable and that the elemental sulfur-like species present probably represent the sulfur atoms in a metal polysulfide molecule most remote from the sulfur atoms closest to the metal atom.

Low-energy ion scattering spectroscopy (ISS), using $^3\text{He}^+$ ions of an oxidized coal pyrite electrode, provided the time dependent spectra shown in Figure 5. The scattered ion intensity is plotted as a function of the scattered ion energy ratio (E/E_0). The initial ISS spectrum, at $t=0$ seconds, reveals peaks corresponding to oxygen and sulfur. There is no evidence of iron on the initial spectra for oxidized coal pyrite. The initial ISS spectrum of freshly polished coal pyrite shows iron, in addition to sulfur and oxygen, with a S/Fe ratio of 2:1. The steeply increasing intensity with decreasing E/E_0 (Figure 5) indicates the presence of adventitious carbon. The chief advantage of ISS lies in its high sensitivity for the first atomic layer. With this in mind,

the initial ISS spectrum indicates that the outermost surface of the oxidized coal pyrite electrode is composed of an overlayer containing oxygen and sulfur species, as well as hydrocarbon contamination. This finding supports the interpretation made from the XPS measurements that the oxidation layer contains additional sulfur species.

The ISS spectra were recorded at regular intervals during the low energy sputtering. After about 200 seconds of sputtering, an iron peak is observed in the spectra. The sulfur and iron peaks continue to grow with increased sputtering time and reach a constant level after about ten minutes. This is better seen in the depth profile shown in Figure 6, in which the element

Figure 5. ISS spectra for coal pyrite oxidized at 0.7V (SHE) for 10 minutes in 1M KCl. Elapsed sputter time: (a) 0 sec; (b) 210 sec; (c) 330 sec; (d) 550 sec.

area is plotted as a function of the sputter time. Three distinct regions are seen on the plot with respect to the iron. Below 100 seconds the ISS spectrum is dominated by sulfur, oxygen, and carbon. From 100 to 350 seconds the concentration of iron increases and reaches a plateau, while the amount of sulfur constantly increases with the amount of oxygen slowly decreasing. The slow increase in iron along with the continuous increase in sulfur may represent the penetration of the helium ions through a sulfur-rich layer, which is probably composed of polysulfides and a small amount of iron oxide/hydroxides. After about 350 seconds, the sulfur reaches a plateau, while the iron increases and the oxygen continues to decrease slowly. At

Figure 6. Low energy sputter depth profile of coal pyrite oxidized at 0.7V (SHE) for 10 minutes in 1M KCl at near neutral pH.

close to ten minutes the S/Fe ratio is 2:1, indicating that the underlying pyrite has been reached.

A different situation occurs when the coal pyrite is oxidized in an alkaline solution. The depth profile for oxidized coal pyrite from low energy sputtering is shown in Figure 7. Only oxygen and iron are detected over a ten minute sputter time. The XPS spectrum of this sample reveals an overlayer of iron oxide/hydroxide that completely attenuates the sulfur signal. A sulfur signal can be detected only after medium energy sputtering with argon gas at 3 keV. The oxidation layer produced on coal pyrite in alkaline solution differs from the oxidation layer produced in near-neutral solution, where additional sulfur species are incorporated in the

Figure 7. Low energy sputter depth profile of coal pyrite oxidized at 0.4V (SHE) for 10 minutes in 1M KCl at pH 10.

overlayer along with small amounts of iron oxide/hydroxides. In alkaline solution, a thick overlayer composed solely of iron oxide/hydroxides results from oxidation.

Flotation and Induction Time Measurements

Materials and Procedure

Microflotation studies were carried out on the same Pittsburgh No. 8 coal pyrite that was used in the electrochemical and spectroscopic studies. To minimize oxidation, the sample was crushed, ground, and wet-screened to obtain the -100+150 mesh (U.S.) fraction just prior to each flotation experiment. In some experiments, Dowfroth M-150, a polypropylene glycol methyl ether with a molecular weight of approximately 400, was used as frother. Industrial-grade kerosene was used as a collector. The solution pH was controlled by the addition of either acid (HCl) or base (KOH) to a 1M KCl solution.

In the microflotation experiments, approximately three grams of -100+150 mesh coal pyrite was conditioned for five minutes in a beaker containing 120 ml of pH adjusted electrolyte solution. The sample and solution were then transferred to a Partridge and Smith (1971) - type cell and floated for two minutes using nitrogen as the carrier gas. The percentage floatability was determined from the oven-dried weight of the flotation product.

In order to correlate the flotation response and wettability properties of pyrite with its surface chemistry, additional microflotation tests and induction-time measurements were carried out on superficially-oxidized samples of coal pyrite and mineral pyrite. The induction time refers to the minimum time required for bubble-particle adhesion, and varies as a function of particle hydrophobicity. The test samples were then subjected to XPS analysis to identify the

species responsible for the hydrophobicity acquired during oxidation.

Large specimens of Peruvian mineral pyrite, obtained through Ward's Scientific Company, were used for the XPS and induction time studies. To minimize oxidation, the pyrite was crushed, ground, and wet-screened to obtain the -100+150 mesh fraction just before each flotation experiment. The coal-pyrite sample used in the present work was taken from the reject stream of a Deister table processing Pocahontas No. 3 coal. Pure grains of pyrite were hand-picked and stored in a freezer. Prior to each experiment, a small lot (<5 grams) of the sample was pulverized and wet-screened to obtain the -100+150 mesh fraction. Approximately 3 grams of the mineral- or coal-pyrite samples were conditioned in a beaker containing 120 ml of buffer solution for a designated period of time, then split into three equal portions for induction time, flotation, and XPS measurements. A two-minute flotation time was employed in all the flotation experiments.

Most flotation tests and all induction-time measurements were conducted in reagent-grade buffer solutions with the following compositions:

pH 4.6; 0.5M CH_3COOH and 0.5M CH_3COONa ,

pH 6.8; 0.025M K_2PO_4 and 0.025 M Na_2HPO_4 , and

pH 9.2; 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$.

Most flotation experiments were conducted without frothers or collectors; however, the effects of Dowfroth M-150 and kerosene were examined in a few of the experiments. Reagent-grade potassium permanganate (KMnO_4) and hydrazine (NH_2NH_2) were used to control the electrochemical potentials of the pyrite suspensions.

For XPS measurements, the conditioned pyrite sample was filtered using a Buchner

funnel, rinsed with distilled water to remove the buffer solution, then dried in a vacuum desiccator. The dried sample was quickly mounted on a sample probe using double-sided adhesive tape, and inserted into the spectrometer chamber. The spectra were collected for the oxygen (O1s), carbon (C1s), sulfur (S2p), and iron (Fe2p, Fe3p) lines. The binding energies were referenced to the C1s peak at 284.9 eV.

Experimental Results

Microflotation Tests

The hydrophobicity of coal-pyrite particles was observed during microflotation measurements. The results of microflotation floatability as a function of solution pH for coal pyrite are shown in Figure 8. Freshly-ground coal pyrite in the presence of frother alone exhibits the lowest level of hydrophobicity (curve A). When collector is added to the system the floatability increases significantly over the examined pH range (curve B). Maximum floatability is obtained between pH 8-9, with the floatability decreasing above and below this region.

When the coal-pyrite sample is conditioned for 30 minutes prior to flotation, the resulting floatability in the presence of frother alone is significantly higher than for the freshly-ground sample (curve C). This is expected since the surface analysis measurements described above revealed that a sulfur-rich overlayer is formed on oxidized coal pyrite in near-neutral solution. The hydrophobicity of the oxidized coal pyrite decreases rapidly with increasing solution pH.

The flotation response of coal pyrite in alkaline solutions can be explained in light of the XPS and ISS data shown previously, i.e., the deterioration in hydrophobicity can be related to

Figure 8. Floatability of coal pyrite at 0.25 lb/ton Dowfroth M-150. A - fresh ground; B - fresh ground, 0.25 lb/ton kerosene; C - oxidized 30 minutes; D - coal contaminated pyrite, 0.25 lb/ton kerosene.

the production of an overlayer containing mostly hydrophilic iron oxide/hydroxides.

The overall level of floatability for the oxidized coal pyrite is comparable to that observed for the freshly-ground sample in the presence of flotation reagents; however, the freshly-ground

sample in the presence of Dowfroth M-150 and kerosene exhibits higher floatability in the alkaline pH region. This is believed to be due to the adsorption of these reagents on the coal pyrite, which is weakly hydrophobic for the reasons given above, by means of the hydrophobic interaction force. Although its origin is still uncertain, this force was measured directly (Pashley and Israelachvili, 1981), and was recognized as the major force for the attraction between hydrophobic substances (Xu and Yoon, 1989, 1990).

The largest difference in hydrophobicity is observed when coal pyrite that has been contaminated with coal inclusions is floated in the presence of frother and collector (Figure 8, curve D). The contaminated coal pyrite exhibits the highest floatability across the entire pH range. This behavior illustrates the difficulty in separating composite particles (or middlings) from completely-liberated coal particles. Even a small inclusion of coal in a pyrite/coal composite particle can readily induce bubble-particle attachment, causing the pyrite to report to the clean coal product. The inclusions may also impact the oxidation behavior of coal pyrite.

Effect of pH

Figure 9A shows the results of flotation and induction time measurements conducted with the -100+150 mesh mineral-pyrite sample. Prior to these experiments, the sample was conditioned for different lengths of time, i.e., 20 minutes, 1.5 hours and 5 hours, as a means of controlling the oxidation. In general, a decrease in pH increased the floatability and decreased the induction time, both of which indicate an increase in coal-pyrite hydrophobicity. Induction time is a good measure of bubble-particle adhesion kinetics. Luttrell and Yoon (1988) also showed that the probability of bubble-particle adhesion (P_a) can be predicted from induction time.

The results obtained with coal pyrite are shown in Figure 9B. As shown, the floatability of coal pyrite also increased with decreasing pH. Compared with mineral pyrite, however, the induction times were higher by an order of magnitude. The slightly higher floatability at pH 9.2 compared to pH 6.8 can be partly attributed to the smaller bubble sizes generated at the higher pH (due to increased electrostatic repulsion). It is well known that flotation recovery can be improved using smaller bubbles (Yoon and Luttrell; 1986, 1989).

Effect of Flotation Reagents

Figures 10A and B show the effect of typical flotation reagents on the floatability and induction time of the freshly-ground mineral- and coal-pyrite samples. The mineral pyrite

Figure 9. Effect of pH on the floatability (solid lines) and induction time (dashed lines) of mineral pyrite (A) and coal pyrite (B) samples wet-oxidized for different times at ambient temperature.

floated well in the absence of any reagent, particularly at lower pHs. When a frother and a collector were added, the induction time decreased and the floatability increased considerably. In contrast, the freshly-ground coal pyrite did not float significantly, with induction times in the range of 100 msec in the neutral and alkaline pH ranges. The conclusion is that the coal-pyrite sample was marginally hydrophobic; however, when flotation reagents were added, the floatabilities were increased by more than 60% and the induction times were reduced to 10-15 msec, close to the sensitivity limit of the induction timer.

Effect of Potentials

Figure 11 shows the effect of controlling the electrochemical potential or the floatability

Figure 10. Effect of reagents on the floatability (solid lines) and induction time (dashed lines) of mineral pyrite (A) and coal pyrite (B) samples at different pH values.

of mineral and coal pyrite. The potentials were controlled by adding either oxidizing (KMnO_4) or reducing (NH_2NH_2) agents. A bright platinum wire and saturated calomel electrode pair were used to monitor the open-circuit potentials. All potentials are reported relative to the standard hydrogen electrode (SHE). In general, both mineral pyrite and coal pyrite became floatable when the potential was raised above approximately -100 mV SHE. This finding suggests that hydrophobic species are formed during oxidation, and that in the absence of frothers and hydrocarbon collectors, pyrite can be prevented from floating by keeping the mineral from oxidizing. Figure 11 also shows that at higher potentials coal-pyrite flotation was suppressed significantly, while the mineral-pyrite flotation was not. It is possible that the coal pyrite

Figure 11. Effect of electrochemical potential on the floatability of mineral and coal pyrite.

oxidized faster, producing increased amounts of hydrophilic oxidation products.

XPS Measurements

Figure 12 shows the S2p spectrum of the coal-pyrite sample oxidized at pH 4.6 for 20 minutes. The spectrum was curve-fitted with Gaussian peaks using a least-square fitting technique. If the sulfur (S_2^{-2}) on the pyrite surface had been unoxidized, each spectrum would have been fitted with only one spin-split doublet, i.e., $S2p_{3/2}$ and $S2p_{1/2}$, which are split by 1.2 eV with a 2:1 intensity ratio. It was necessary, however, to include an additional doublet to adequately fit the spectrum. As shown, this additional doublet showed higher binding energies

Figure 12. S2p spectra of coal pyrite oxidized at pH 4.6 for 20 minutes.

than the unoxidized S_2^{-2} species, indicating that some of the sulfur in the surface region was oxidized to a higher oxidation state. Note that the XPS results on polished slab electrodes, which were more extensively oxidized at -0.7V (SHE), required three doublets to obtain a fit with the spectra.

Table I shows the results of the curve fits for both mineral- and coal-pyrite samples treated under different conditions. There was no significant difference in the binding energies for the unoxidized coal- and mineral-pyrite samples, which were in the range of 162.2-162.4 eV. These values agree well with the reported literature values for pyrite (Buckley and Woods, 1987; Brion, 1980) and with the value of approximately 162.7 eV obtained on the slab electrodes. The most significant information given in Table I is that the binding energies of the oxidized sulfur

Table I. Changes in the $S2p_{3/2}$ lines for the mineral pyrite and coal pyrite with superficial oxidation.

Oxidation Condition		Mineral Pyrite			Coal Pyrite		
		S2p _{3/2}		% Oxidized Sulfur	S2p _{3/2}		% Oxidized Sulfur
		Binding Energy (eV)			Binding Energy (eV)		
		Unoxidized	Oxidized		Unoxidized	Oxidized	
pH	Time (hr)						
4.6	0.33	162.3	163.7	14.0	162.3	163.6	16.0
	1.5	162.3	163.8	12.0	162.2	163.8	16.0
	5.0	162.4	163.9	11.0	162.3	163.6	14.0
6.8	0.33	162.4	164.0	15.0	162.3	163.7	10.0
	1.5	162.4	164.2	14.0	162.4	164.0	11.0
	5.0	162.3	163.9	14.0	162.3	163.8	11.0
9.2	0.33	162.3	163.9	9.0	162.2	163.7	9.0
	1.5	-	-	-	162.3	164.0	8.0
	5.0	162.3	163.9	9.0	162.2	163.9	4.0

species were close to those of elemental sulfur (S^0). The binding energy of elemental sulfur was reported in the range of 163.5-164.3 (Buckley and Woods; Brion, 1980; Hyland and Bancroft, 1989). Since elemental sulfur is a well-known hydrophobic substance, it may be reasonable to consider that the S^0 -like species was responsible for rendering the oxidized pyrite surface hydrophobic. Under the conditions employed in the present work, no evidence of sulfates or other sulfoxy species being formed on the surface was found. These hydrophilic sulfoxy species have binding energies in the 165-169 eV range (Brion, 1980). It is unlikely that the S^0 -like species formed during the initial stages of oxidation was actually in the form of bulk elemental sulfur (S_8). If it was, the intensity of the $S2p$ line characteristic of the S^0 -like species would have decreased during XPS measurement. It is possible that at this early stage of oxidation, the oxidized sulfur stays in the original crystallographic sites, creating a metal-deficient surface. Alternatively, it can be viewed as a sulfur-rich surface, consisting of iron polysulfides, with the S^0 -like species forming a part of the polysulfide chain (S_n^{2-}). Note that the percent of oxidized sulfur decreased with increasing pH, particularly with coal pyrite, suggesting that coal flotation in alkaline pH should give a higher sulfur rejection.

Figures 13A and B show the $Fe2p$ spectra of coal-pyrite samples oxidized at pH 4.6 and 9.2 for different lengths of time. The sharp peaks at 707.5 eV and 722 eV represent unoxidized iron (Fe^{2+}) on the pyrite surface, while the broad shoulder in the 710-715 eV range represents the oxidized iron. This shoulder is attributed to several different oxides/hydroxides of iron such as $Fe(OH)_3$, $FeO(OH)$, Fe_2O_3 , Fe_3O_4 , etc. (Baltrus and Proctor, 1990; Harvey and Linton, 1981). As the oxidation time and pH were increased, these oxidation products increased. Mineral pyrite showed similar $Fe2p$ spectra (not shown in Figure 13), although the amount of

Figure 13. FeS₂p spectra of coal pyrite oxidized at pH 4.6 (A) and pH 9.2 (B) for different times compared to dry ground coal pyrite and mineral pyrite (C).

oxidized iron was considerably less.

Figure 13C compares the Fe2p spectra of the dry-ground coal- and mineral-pyrite samples. Interestingly, the coal-pyrite spectrum showed a significant shoulder indicating the presence of iron oxide/hydroxides, while the surface of the dry-ground mineral-pyrite sample was relatively clean. This finding suggests that either the coal-pyrite sample already contained some oxides/hydroxides before oxidation, or that it oxidized faster than the mineral pyrite.

An important finding made in this investigation is that both coal pyrite and mineral pyrite become floatable when they are superficially oxidized. One can speculate, therefore, that some of the oxidation products must be responsible for the acquired hydrophobicity of the minerals. According to the XPS data, the oxidized sulfur species showed binding energies close to that of elemental sulfur (S^0). It is unlikely, however, that the S^0 -like species formed during the initial stages of oxidation is in the form of bulk S_8 , a well-known hydrophobic substance. Rather, the oxidized sulfur species may stay more or less in the original crystallographic sites when the S_2^{2-} ion of the unoxidized pyrite loses an electron during the initial stages of oxidation. Such was the conclusion drawn by Buckley and Woods (1984), who examined superficially-oxidized sulfide minerals such as galena and chalcopyrite using XPS. If S_8 was present on the surface, the intensity of the S2p line characteristic of the S^0 -like species would have diminished with time during the measurement. The S^0 -like species observed in the present work was also stable during the XPS measurements, indicating that it was not S_8 .

Alternatively, it may be viewed that the S^0 -like species becomes part of the polysulfide chains (S_n^{2-}), which are still bound to the surface. When the oxidation progresses further, S_n^{2-} eventually becomes S_8 . Buckley and Woods (1984) showed, however, that S_8 does not form on

sulfide minerals unless they are subjected to severe oxidation conditions. It may be suggested, therefore, that the hydrophobic species responsible for the flotation of both mineral pyrite and coal pyrite are the iron polysulfides formed on their surfaces during the initial stages of oxidation. Luttrell and Yoon (1984b) proposed a similar mechanism to explain the hydrophobicity of superficially-oxidized chalcopyrite.

The XPS data show that the amount of oxidized sulfur did not exceed 16% of the total sulfur in the surface region, which might be considered within the margin of error associated with the measurements. Nevertheless, the amount of the S^0 -like species did increase with decreasing pH, which correlates well with the flotation and induction-time data. In this regard alone, the quantitative analysis of the sulfur species by XPS should be given credence. The reason that the amount of the S^0 -like species was relatively small was because the pyrite samples were oxidized at open circuit potentials. As shown earlier, the slab electrodes oxidized at higher potentials showed significantly larger amounts of S^0 -like species than observed on the powder samples that were oxidized at open-circuit.

Other important oxidation products of pyrite are iron oxides and hydroxides. The XPS spectra (given in Figure 13) show clear evidence for the presence of these hydrophilic species on oxidized pyrite surfaces. In general, the amount of iron oxides/hydroxides formed on pyrite increased with increasing pH and with increasing oxidation time. Note, however, that the XPS data showed no significant increase in the amount of S^0 -like species with increasing oxidation time (see Table I); in fact, in some cases, it tended to decrease. Since sulfoxy-compounds were not detected on the surface of the pyrite oxidized at open-circuit potentials, one possible explanation for the discrepancy in the amounts of the sulfur and iron oxidation products, as

determined by XPS, is to assume that some of the S^0 -like species continued to oxidize and became water-soluble oxidation products such as $Fe_2(SO_4)_3$ and $Fe_2(S_2O_3)$. It is also possible that the iron oxides formed an overlayer on top of the S^0 -like species, thereby weakening the signals from the latter.

Figure 14 shows the relationship between the floatability and the percentage of oxidized sulfur (S^0 -like) species for both mineral pyrite and coal pyrite. In general, mineral pyrite floated much more readily than coal pyrite in the absence of a frother or a collector. This finding may be due to coal pyrite showing consistently larger amounts of oxides/hydroxides than mineral pyrite under identical oxidation conditions. Nonetheless, the floatability of coal pyrite increased with increasing percent oxidized sulfur species, as expected. For mineral pyrite, a small increase in percent oxidized sulfur sharply raised the floatability initially, then decreased it with a further increase in percent oxidized sulfur. These variations in the floatability of mineral pyrite are closely related to the amount of oxides/hydroxides present on the surface, which in turn varies significantly with pH. Figure 14 shows that the maximum floatability of the mineral pyrite was observed when the samples were oxidized at pH 4.6, where relatively little hydroxides were detected by XPS. Thus, the floatability of pyrite can be related to the relative amounts of oxides/hydroxides and oxidized sulfur.

In Figure 15, the floatability of both mineral pyrite and coal pyrite is plotted against the atomic ratio between oxygen and oxidized sulfur on the surface. This ratio was determined from the peak areas of the O1s and the S2p spectra. Only the S2p component characteristic of the S^0 -like species was considered. Since oxygen and S^0 -like species represent the hydrophilic and the hydrophobic species respectively, this ratio may be used for approximating the hydrophilic-

Figure 14. Floatability versus percent sulfur species for mineral pyrite and coal pyrite.

Figure 15. Floatability versus oxygen to oxidized sulfur ratio for mineral and coal pyrite.

hydrophobic balance at a given mineral surface. As shown, the floatability of both mineral pyrite and coal pyrite decreased with increasing O/S^0 ratio. The mineral pyrite was more sensitive than the coal pyrite to this ratio, probably because the latter contained significant amounts of oxygen-containing groups before it oxidized. As shown in Figure 13, even the dry-ground coal pyrite showed a considerable amount of iron oxides/hydroxides, while the mineral pyrite did not. It should also be noted that the two different pyrite samples gave two different lines (Figure 15), suggesting that there may be factors other than the O/S^0 ratio determining the floatability (or hydrophobicity) of the pyrite samples.

In view of the above discussions, the following mechanism may be proposed for the oxidation of pyrite:

in which $n > 2$ and FeS_n represents the iron polysulfides formed on the surface. The S^0 -like

PART II: DEVELOPING THE BEST POSSIBLE REJECTION SCHEMES

Pyrite Depression Studies

The above studies addressed only a few of the problems associated with removing pyrite from coal by froth flotation or oil agglomeration processes. An equally-important problem arises from the difficulty in separating the composite particles (or middlings) from fully liberated coal particles. Even a small inclusion of coal in a pyrite-coal composite particle can readily induce bubble-particle attachment, causing the pyrite to report to the clean coal product. Possible solutions to these problems may include: keeping the coal pyrite from oxidizing, preventing it from acquiring hydrophobicity, or if superficial oxidation is unavoidable, keeping the solution pH high enough so that sufficient iron oxides and hydroxide form on the pyrite surface. To keep the composite particles from floating, the grab-and-run technique advocated by Aplan (1977) may also be a viable alternative.

The objective of this part of the study was to address these problems by utilizing laboratory-scale columns and conventional flotation tests to evaluate a variety of chemical reagents as pyrite depressants in flotation. Three reducing agents, viz., metal manganese (Mn) and the organic chelating agents quinone and DETA (diethylenetriamine), were tested. In addition, several commercially-available organic depressants and a novel depressant, NB, developed at VPI&SU were tested.

Materials and Procedures

Lumps of high-sulfur, high-ash, Lower Kittanning coal (containing approximately 9% total sulfur, 7.5% pyritic sulfur, and 30% ash) obtained from the Bradford Coal Company's Manor

species produced during oxidation constitutes part of the polysulfide chain, and renders the surface hydrophobic. In general, the longer the chain, the larger the hydrophobicity will become. On the other hand, some of the Fe^{2+} ions may be further oxidized to Fe^{3+} ions, and become hydrophilic iron oxides and/or hydroxides in alkaline pH.

Although the S^0 -like species in the polysulfide chain is regarded as rendering the surface hydrophobic, the surface may not be as strongly hydrophobic as expected of S_8 because of the polar character of the S_2^{2-} ions at the ends of each S_n^{2-} chain. If $n = 4$, for example, effectively only two of the four sulfurs in the chain may approximate the property of S^0 and contribute to rendering the surface hydrophobic. The hydrophobicity may be further reduced when large amounts of iron hydroxides are formed at a higher pH. These considerations may provide an explanation for the relatively low floatability of oxidized pyrite. As shown in Figure 11B, the floatability of coal pyrite was in the range of 17-30% with no reagent; however, in the presence of Dowfroth M-150 and kerosene, the floatability was increased to 75-95%. It is believed that these reagents adsorb on coal pyrite, which is weakly hydrophobic, for reasons given in the previous paragraph, by means of the hydrophobic interaction force. Although its origin is still uncertain, this force was measured directly (Pashley and Israelachvili, 1981), and was recognized as the major force for the attraction between hydrophobic substances (Xu and Yoon; 1989, 1990).

Mine in Clearfield County, Pennsylvania, were used as feedstock for this series of tests. These lumps were crushed to 1/4-inch, then split into 1-kg lots, sealed in plastic bags, and stored in a freezer.

Column flotation tests were carried out in the two-inch (51mm) diameter column using the base operating conditions: aeration rate of 1200 ml/min, wash water flow rate of 400 ml/min, frother dosage of 1 lb/ton, froth height of 12 inches (305mm), and feed solids content of 5%.

Conventional flotation tests were carried out in a five-liter laboratory Denver cell. The basic operating conditions were: impeller speed of 1700 rpm, air inlet fully open, frother dosage of 0.5 lb/ton, automatic froth scraping, sampling times of 0.25, 0.5, 1.0, 2.0, and 4.0 minutes; and feed sample weight of 200 gms. A representative sample of the feed coal was first conditioned (wetted) with water in the cell for ten minutes. Appropriate amounts of frother and, when necessary, depressants were added to the slurry and conditioned for one minute, during which flotation was initiated.

Experimental Results

Effect of Reductant Additions in Column Flotation

Quinone: Two series of tests were conducted to examine the effects of quinone (a chemical reductant) on the relationship between combustible recovery and sulfur rejection for -30 mesh Lower Kittanning coal. In the first series, no quinone was added to the feed coal. The baseline results obtained under these conditions are shown as solid lines in Figure 16. In the second series, three sets of tests were performed by adding quinone at different dosages and in different forms, i.e., as a solid or in solution. Conditioning times of 10, 20, and 30 minutes were

employed in each set of tests. When quinone was added to the slurry in solution form (achieved by dissolving the powder in hot (50°C) distilled water), it reacted with the pyrite and produced a small drop in the measured potential of the slurry, from 568 mV to 525 mV (SHE). This

Figure 16. Effect of quinone on sulfur rejection from -30 mesh Lower Kittanning coal.

implied that the quinone was reducing the pyrite as follows:

As shown in Figure 16, sulfur rejection increased by approximately 5% by adding 2 lb/ton of quinone, while the combustible recovery remained relatively constant. However, when quinone levels were further increased to 10 lb/ton, sulfur rejection fell back to original levels.

Diethylenetriamine (DETA): Figure 17 illustrates the effects of DETA on sulfur rejection at conditioning times of 10, 20, 30, 40, 50, and 60 minutes. During these tests, the measured potential of the slurry dropped from 568 to 424 mv when 2 lb/ton DETA was added, confirming that DETA acts as a reducing agent. Increasing the DETA dosage rate from 2 to 10 lb/ton further decreased the measured potential of the slurry to 220 mV; however, as illustrated in Figure 18, higher dosages of DETA (i.e., lower potentials) did not greatly increase pyrite depression.

Manganese: Tests were conducted to determine the effects of Mn addition on sulfur rejection.

Mn is a strong reducing agent whose standard redox potential is -1185 mV for the reaction:

and -1560 mV for the reaction

Thus, Mn may reduce the oxidized surface species back to fresh sulfide, which is believed to be nonfloatable.

Two series of flotation tests were performed to determine the effectiveness of the Mn pyrite depression scheme. In the first series, 50 ml of 2M HCl acid (to activate the passivated,

oxidized surface of the Mn) and 50 gm of Mn (5% of the weight of coal used in the tests) were added to the slurry. The feed slurries were conditioned for 20, 40, and 60 minutes. As shown in Figure 19, this first series of tests produced sulfur rejections that were superior to those obtained in tests carried out at the same combustible recovery in which the depressant was absent.

In the second series, the same quantities of Mn and HCl were used as in the first series; however, instead of air, inert nitrogen was used as the carrier gas for flotation. Also, specially prepared water with a mixed potential of -406 mV was used for wash water. These steps were undertaken in an attempt to maintain a reducing environment inside the column. Slurries were conditioned for 20, 30, and 40 minutes, giving measured potentials ranging from -105 to -220 mv. Figure 19 shows that for this second series, there was only a marginal increase in sulfur rejection over tests carried out at the same combustible recovery in which depressant was absent. This second set of results was unexpected and a full explanation for this behavior can not be given at this time. One possibility is that the results are unreliable due to the low sulfur content of some of the feed samples used in this series of tests (possibly attributable to poor sample splitting procedures).

It is interesting to note that the slurries conditioned with Mn gave higher pH values (8.90 maximum) as compared to 6.03 and 4.52 for slurries conditioned with quinone and DETA, respectively, and more negative measured potentials (-220 mv maximum) as compared to +194 mV and +437 mV for slurries conditioned with quinone and DETA, respectively. This finding shows that Mn produces stronger reducing conditions than DETA and quinone. The manganese hydroxide/oxide species formed during the reaction could have played an important role in the depression of pyrite. It is well documented that metal hydroxides/oxides are hydrophilic species

Figure 17. Effect of DETA (2.0 lb/ton) on sulfur rejection for Lower Kittanning coal (-30 mesh) at different conditioning times.

capable of coating surfaces and rendering them unfloatable.

Figure 20 is a summary of the data presented in the previous figures. It can be concluded from this figure that Mn is the most effective depressant for pyrite. In some cases, the sulfur

Figure 18. The effect of DETA on sulfur rejection for Lower Kittanning coal (-30 mesh) at different dosages for a 30 minute conditioning time.

rejection improves by more than 20 percentage points after the addition of Mn. Quinone and DETA have (at best) only a marginal effect on pyrite depression. This is true even at relatively high dosages of these reagents.

In a third series of tests, a sample of Lower Kittanning was finely pulverized (i.e., -100

Figure 19. Effect of Mn on sulfur rejection for Lower Kittanning coal (-30 mesh) under various test conditions.

mesh) to determine whether particle size would influence the effectiveness of the Mn depression scheme. As shown in Figure 21, the finely-pulverized coal did not respond as well as the coarser grind to the Mn treatment. Also, the use of HCl did not appear to improve the sulfur rejection. As shown in Figure 22, however, the effectiveness of the Mn depressant can be enhanced by

conditioning at higher solids concentrations. This allows the coal pyrite to be exposed to higher reducing potentials. As shown, a significant improvement in sulfur rejection can be made by conditioning the slurry at 20% solids instead of 5% solids. Flotation at 5% and 20% solids gave essentially identical results. The lowest measured potential during conditioning was found to be -310 mV. These data demonstrate that conditioning at higher solid contents improves the sulfur rejection.

Other Depressants: The effects of several other depressants on pyrite floatability were also examined in the present work. In these tests, mineral pyrite from Huanzala, Peru, was ground using an agate mortar and pestle, sieved to a 65x100 mesh size and used immediately. A sample of coal pyrite from the Pocahontas No. 3 seam was taken from a Deister table and also examined in these tests. This sample was received in slurry form and was wet sieved and vacuum dried to obtain a 65x100 mesh size fraction. The product was then passed through a dry magnetic separator to remove the non-magnetic particles. The sample assayed 2.5% combustible material and was kept in a freezer at -10°C for subsequent use. Lumps of Pocahontas No. 3 coal were prepared by crushing in a jaw crusher followed by a roll crusher to obtain the 65x100 mesh size fraction. The coal assayed at 8.9% ash and 0.9% sulfur, and was stored in a freezer to minimize oxidation.

Floatabilities of 65x100 mesh mineral pyrite, coal pyrite, and raw coal were determined using a 120-ml column cell (23x220 mm) with a fine frit and magnetic stirrer. In each test, 0.8 gram of coal pyrite samples and 0.5 gram of coal samples were used in the microflotation tests. The samples were conditioned in 120 ml of solution containing the desired chemical for five minutes and floated with 2-methyl-2-pentanol (MIBC, 99%+ purity purchased from Aldrich

Figure 20. Effect of depressants on sulfur rejection for Lower Kittanning coal (-30 mesh).

Chemicals) for two minutes using nitrogen at a flow rate of 50 cm³/min. The pH of the flotation pulp was adjusted using either HCl and NaOH.

ORFOM D8, a product of Phillips Chemicals, is a water soluble sulfide depressant. The active component is disodium carboxymethyl trithiocarbonate. Because of its unique structure it was considered as a potential coal-pyrite depressant. PRC is a sulfur-containing proprietary

Figure 21. Effect of Mn on sulfur rejection for Lower Kittanning (-100 mesh) coal conditioned for 1 hour.

Figure 22. Effect of Mn on sulfur rejection for Lower Kittanning (-100 mesh) coal conditioned for 1 hour.

reagent of American Cyanamid Company. Its purified form was obtained from Aldrich Chemicals. NB, a novel proprietary depressant developed at VPI&SU, was synthesized in our laboratories. The resulting complex mixture was found to contain various oxidation products and polymeric species.

The microflotation data for Pocahontas No. 3 coal, coal pyrite, and mineral pyrite in the absence of frother are presented in Figure 23. Unlike mineral pyrite, coal pyrite displays a maximum recovery around pH 8. This suggests that coal pyrite exhibits features which are more similar to typical coal flotation data rather than mineral pyrite (Celik and Somasundaran, 1986). The floatability of this coal is, however, practically unaffected over a broad range of pH with recoveries about 90%. Such behavior is commonly found with coals of high hydrophobicity (Celik and Somasundaran, 1980).

The floatability of Pocahontas No. 3 coal and coal pyrite in the absence and presence of the reagents using MIBC as frother is shown in Figure 24. In the absence of reagents, both coal and coal pyrite exhibit complete flotation in a wide range of pH. The sulfur-based organic depressants (ORFOM D8 and PRC), though excellent depressants for mineral pyrite, have no depression effect on coal-sulfur compounds, which were the object of previous research efforts for depressing coal pyrite (Perry and Aplan, 1985).

Interestingly, the addition of NB can effectively depress coal pyrite as illustrated in Figure 24. The pyrite depression improves upon decreasing the pH and increasing the reagent concentration. At a constant pH of 5.3, this reagent is effective in depressing coal pyrite at concentrations as low as 10^{-4}M .

It has been asserted that almost all effective pyrite depressants are also coal depressants

at the same or higher depressant concentrations (Im and Aplan, 1981; Perry and Aplan, 1985). This assertion for NB was tested at the same reagent levels as a function of pH as shown in Figure 24. The coal recoveries decreased gradually with pH and remained approximately constant at about 80% even under the conditions where maximum pyrite depression was achieved. Even at the highest reagent concentration tested, the reagent has less affinity towards coal than pyrite. This selectivity provides a window of opportunity for the potential industrial use of this reagent.

Note that the flotation time used to obtain the data shown in Figure 24 was kept at two

Figure 23. Floatability of various minerals in the absence of frother.

Figure 24. Floatability of Pocahontas No.3 coal and coal pyrite vs. pH in the presence and absence of various depressants.

minutes. As shown in Figure 25, the coal recoveries could be substantially improved at longer flotation times without a significant change in pyrite depression. Adding kerosene was found to further improve the kinetics at the expense of sulfur recovery. Tests conducted in Denver flotation cell revealed a similar behavior.

The equilibrium time for NB to interact with the solid surface was also studied to determine the reaction kinetics for the reagent. The results revealed that the majority of the interaction takes place in the first minute and equilibrium is achieved in less than five minutes. Such fast kinetics is, again, a favorable factor for commercial utilization of this reagent.

Microflotation tests were further corroborated by tests conducted in a Denver flotation

Figure 25. Flotation kinetics of coal and coal pyrite with 8×10^{-4} M NB.

Figure 26. Floatability coal and pyrite at pH 5 in Denver cell.

cell. Ten grams of 100x140 mesh Pocahontas No. 3 coal and Pocahontas No. 3 coal pyrite were individually floated in a bench scale Denver flotation cell. The solids were conditioned for ten minutes in two liters of distilled water followed by one minute of conditioning with 50 mg/liter of MIBC. The slurry was then conditioned for one minute in the presence of 8×10^{-6} M NB. The data shown in Figure 26 indicate that the flotation rate of coal is not significantly affected in the presence of NB, while that of pyrite flotation is significantly decreased. The flotation rate constant of coal with and without the depressant was approximately 16 min^{-1} . The coal pyrite, on the other hand, exhibited a rate constant of 13 min^{-1} in the absence of the depressant and 1 min^{-1} in the presence of the depressant. These findings confirm the data obtained in the microflotation tests discussed earlier.

The results of zeta-potential measurements for coal and coal pyrite are presented in Figure 27. In the absence of NB the coal and coal pyrite yielded isoelectric points (*iep*) of approximately 4.8 and 3.9, respectively, which fall within the isoelectric point (*iep*) values reported in the literature for coal and mineral pyrite (Fuerstenau *et al.*, 1983; Miller *et al.*, 1983; Healy and Moignard, 1976). Note that the presence of hydrocarbon contamination on coal pyrite appears to lower the *iep* of coal pyrite.

The addition of NB produced negative zeta potentials in the entire pH range with the potentials being constant between about pH 2 to 8. Above pH 8, the zeta potentials progressively approach those in the absence of NB. Modification of the zeta potential of coal and coal pyrite is similar to that found with anionic surfactants which mostly adsorb through their hydrocarbon chain onto coal (Celik, 1989). Sulfide minerals such as pyrite are also not receptive to electrostatic attraction of oppositely-charged species. The only alternative explanation is that the

hydrophobic portion of the NB molecule adsorbs onto the hydrophobic sites of coal (most probably in a flat conformation). In addition, the coal pyrite used in this study, though mostly pyrite, is dominated with the hydrocarbon contamination. The similarity found between the zeta potentials of coal and coal pyrite, as shown in Figure 27, further supports this contention.

Examination of the preceding data on coal pyrite reveals an important factor that was neglected in the past: that mineral pyrite and coal pyrite exhibit significant differences in their responses to flotation. Differences in the electrochemical (Briceno and Chander, 1988) and physical properties (Esposito *et al.*, 1987) were noted not only between mineral pyrite and coal pyrite but also among different coal pyrites. This can be attributed to the complex surface chemistry of coal pyrite itself.

Scanning electron microscopy (SEM) and energy dispersive X-ray analysis of coal pyrite was used to develop a better understanding as to why coal pyrite exhibits different hydrophobic properties. These studies, along with the electrochemical and XPS results, suggest that three factors are involved in the variable flotation behavior of coal pyrite. First, although this coal pyrite assayed 2.5% hydrocarbon, SEM analysis indicated a considerable proportion was present on the surface. Systematic scanning of the coal pyrite particles showed that more than 90% of the surface was covered with a thin layer of hydrocarbon. Second, EDAX determination of the S/Fe stoichiometry of different pyrites showed that some had high sulfur contents, i.e., 2.3:1 for Pocahontas No. 3 and 2:1 for mineral pyrite. Sulfur enrichment probably imparts additional hydrophobicity to coal pyrite. Third, the degree and state of oxidation of coal pyrite has a pronounced effect on its floatability. As observed by others (Esposito *et al.*, 1987), a number of coal pyrites are highly hydrophilic, even after ultrasonic cleaning, indicating a heavily-oxidized

Figure 27. Zeta potential of coal and coal pyrite in the absence and presence of NB.

surface. In many cases, the floatability of superficially oxidized sulfide minerals and coal can be easily restored by mild ultrasonic cleaning (Celik, 1989); however, the flotation response of Pocahontas No. 3 coal pyrite, after about two months of aging under normal atmospheric conditions, could not be brought back to its original floatability upon sonication. Such behavior indicates that the oxidation mechanism of coal pyrite is different from that of mineral pyrite and coal.

On the basis of the above considerations, it can be shown that fresh coal and coal pyrite, particularly of bituminous origin, exhibit similarities in their response to flotation, i.e. both can be highly hydrophobic. On the other hand, coal pyrite is more susceptible to oxidation. Coal pyrite kept under ambient conditions for one week showed very little flotation, whereas coal was

practically unaffected by such mild oxidation. The difficulty in floating coal pyrite, particularly as noted by Esposito *et al.* (1987), can be readily attributed to the oxidized nature of the coal-pyrite samples used in their investigation.

The reagent, NB, exploits the significant differences between the hydrophobicity of coal and coal pyrite. Since coal pyrite is less hydrophobic than coal, coal pyrite is depressed at an incipient concentration of NB while coal still remains hydrophobic. NB seems to have remarkable selectivity over most macromolecular depressants tested for the depression of sulfide minerals reviewed by Pugh (Pugh, 1989). The reagent (NB) developed in this study is expected to open new avenues in the design of new surface active formulations for the coal industry.

CONCLUSIONS

1. Data obtained using a variety of surface analytical techniques, including X-ray photoelectron spectroscopy (XPS), low energy ion scattering spectroscopy (ISS) and cyclic voltammetry, indicate that a sulfur-rich surface layer is produced during the oxidation of pyrite in near neutral pH solutions. This surface layer is mainly composed of sulfur species in the form of elemental sulfur and/or iron polysulfides along with smaller amounts of iron and oxygen species. In alkaline solutions, the oxidation of pyrite produces a surface layer composed predominantly of iron and oxygen species, most probably in the form of hydrophilic iron oxides/hydroxides.
2. XPS and ISS data indicate that the surface layer formed during the oxidation of pyrite has an overlayer-type structure with the sulfur species in the outermost region. The surface layer formed in alkaline solutions is thicker than the layer produced at near neutral pH since the sulfur signal is completely attenuated at the higher pH values.
3. The hydrophobicity of coal pyrite decreases with increasing pH and oxidation time. This decrease is found to correspond to a decrease in the atomic ratio of S⁰-like species to oxygen in the surface layer. This suggests that the balance between iron polysulfide and iron oxide/hydroxide species formed on the pyrite surface controls the hydrophobicity of pyrite.
4. The floatability of coal pyrite is considerably lower than that of mineral pyrite. XPS data show that this difference can be attributed to the larger amount of oxides/hydroxides present on the surface of coal pyrite, probably due to the faster oxidation kinetics of coal pyrite.

5. The floatability of coal pyrite increases dramatically in the presence of frothers and hydrocarbon collectors. The adsorption of these reagents can be explained (i) by the hydrophobic interaction force between the weakly-hydrophobic pyrite and the polar hydrocarbon and (ii) by the presence of hydrophobic coal inclusions in the pyrite.
6. Test data obtained in the present work indicate that manganese metal is a significantly stronger depressant for pyrite than other reducing agents such as quinone and DETA. The test data indicate that (i) higher pulp densities during conditioning intensify the reaction between Mn and pyrite and (ii) the addition of HCl helps remove the oxide layer from the surface of Mn which, in turn, promotes pyrite depression.
7. Common sulfur-based depressants, such as Orfom D8, caused no depression of coal pyrite from the Pocahontas No. 3 and Lower Kittanning seams despite the fact that these reagents are excellent depressants for mineral pyrite.
8. The novel reagent (NB) developed specifically for improving coal pyrite rejection shows superior performance for the selective separation of coal and coal pyrite. Data obtained from bench-scale flotation tests revealed that the rate constants for coal are approximately the same with and without NB, while those for coal pyrite are reduced by nearly 85-90% after the addition of NB.
9. Electrokinetic data suggest that the adsorption mechanism of NB onto coal and coal pyrite is physical in nature. The most plausible mechanism appears to be the hydrophobic bonding of NB molecules onto the hydrophobic sites of the solid surface.

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