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Development of Enhanced Sulfur Rejection Processes

by

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**ABSTRACT**

Pyrite becomes hydrophobic upon superficial oxidation and floats without a collector. The flotation begins to occur at potentials above the stable potentials identified by the chronoamperometry experiments conducted with freshly fractured pyrite. This finding suggests that iron polysulfide, formed during the initial stages of oxidation, is responsible for the flotation. The collectorless flotation is suppressed above the potential where the mineral is aggressively oxidized, forming iron hydroxide and soluble sulfoxy species. The collectorless flotation is less significant at pH 9.2 than at pH 4.6, possibly due to the formation of iron hydroxide. At pH 9.2, the collectorless flotation increases in the presence of EDTA and hydrocarbon oil.

The collectorless flotation of pyrite can be suppressed by galvanically coupling the mineral with reactive metals such as aluminum, manganese, and zinc. This effectively prevents the mineral from oxidation. The microflotation tests conducted with mono-sized pyrite samples show that the collectorless flotation can be suppressed effectively in the presence of metal powders. Bench-scale flotation experiments conducted using Denver laboratory flotation cell and a 2-inch diameter Microcel flotation column, also demonstrates that the collectorless flotation can be suppressed in the presence of the reactive metals. It has been established that the most important parameters determining the effectiveness of suppressing pyrite flotation by the galvanic coupling technique are the surface area of the galvanic contractors and the solids concentration of the slurry during conditioning.

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## INTRODUCTION

Pyrite ( $\text{FeS}_2$ ) is one of the most common sulfide minerals, and is a major source of sulfur in coal. Control of its surface chemistry is important in the beneficiation of coal and complex sulfide ores by flotation. Although froth flotation is the most widely used method of cleaning fine coal, it is not efficient in removing pyrite. Part of the reason is that the mineral can be superficially oxidized during flotation, and it acquires considerable hydrophobicity without using a hydrophobizing reagent known as collector.

The collectorless flotation of pyrite has been studied extensively and results are controversial. Chernosky and Lyon [1] report that in the absence of xanthate collectors, mineral-pyrite does not float but coal-pyrite exhibited 20% recovery at pH above 6.5. Rao and Finch [2] report similar results. Kawatra and Eisele [3] show, on the other hand, that mineral pyrite can only be floated in acidic pH, while coal pyrite can be floated over a wide range of pH. Trahar et al. [4] show that mineral pyrite is weakly floatable only in acidic solutions.

According to Finkelstein et al. [5], sulfide minerals are neither strongly hydrophobic nor strongly hydrophilic, implying that they are weakly hydrophobic. This view can be supported by the work of Kocabag et al. [6], who show that pyrite can be floated by oil (isooctane) but not by air. Yoon and his co-workers [7,8] show, however, that pyrite is inherently hydrophilic and becomes hydrophobic upon superficial oxidation. It suggests that iron polysulfides formed during the initial stages of oxidation are responsible for the hydrophobicity of the mineral [7]. Tao et al. [8] studied the incipient oxidation of freshly fractured pyrite, and show that the mineral begins to

oxidize at potentials as low as -0.28 V at pH 9.2 and 0 V at pH 4.6. These potentials are referred to as stable potentials. At potentials above or below these potentials, the mineral becomes oxidized or reduced. These findings suggest that flotation of the pyrite can be suppressed when the mineral is subjected to reducing conditions below the stable potentials of the mineral.

### **OBJECTIVES DURING THIS REPORTING PERIOD**

It is the purpose of the current investigation to conduct microflotation under controlled potential conditions, so that the potential for the onset of pyrite flotation can be determined. These potentials are compared with the stable potentials. It is also the purpose to conduct bench-scale continuous flotation tests on a high-sulfur coal, in which the potential of pyrite can be kept below the stable potential. This is so that pyrite flotation can be minimized. The potential control during flotation is achieved by contacting the mineral with sacrificial anodes such as, zinc and manganese. The work reported pertains to Task 6.

### **EXPERIMENTAL**

#### **Samples**

Mineral pyrite specimens, originally from Huanzala, Peru, were purchased from Ward's Scientific Company. Chunks of Illinois No. 6 coal-pyrite and Pittsburgh No. 8 coal-pyrite were obtained from run-of-mine coal samples. Lumps of high-sulfur, high-ash Lower Kittanning coal



(containing approximately 9% total sulfur, 8% pyritic sulfur and 30% ash) were obtained from the Bradford Coal Company's Manor Mine in Clearfield County, Pennsylvania.

### **Procedure**

#### *Electrochemical Flotation:*

The mineral pyrite specimens are crushed by means of a mortar and pestle and screened to obtain a -65+150 fraction. The monosized sample is used for the microflotation tests, which are carried out in an electrochemical flotation cell as described by Walker et al. [9]. In each test, a 1.0 g sample is used as a working electrode, whose potential is controlled by means of a PAR 273 potentiostat.

#### *Microflotation Tests:*

The -65+150 mesh pyrite sample is also subjected to flotation tests in a Partridge and Smith-type microflotation cell [10]. The tests are conducted in the presence of zinc or manganese powders, which are added as galvanic contactors. The metal powders are cleaned in a dilute HCl solution (0.05 M) for 5 minutes prior to their use for flotation experiments. Pyrite samples are freshly ground just before experiments and conditioned with emulsified kerosene and MIBC for 2 minutes. Buffer solutions are used in both the electrochemical flotation and microflotation tests. Ultrapure nitrogen is used for purging the solution and for flotation.

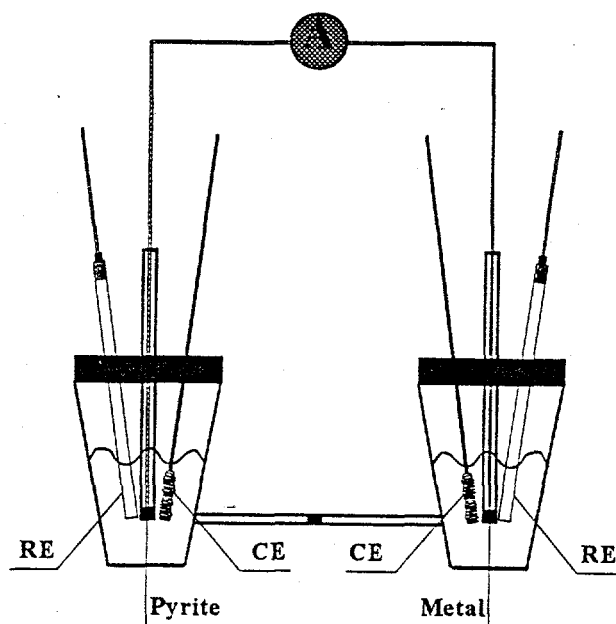


Figure 1. Schematic representation of the apparatus used for measuring galvanic potentials between pyrite and sacrificial anode (metal): RE, reference electrode; CE counter electrode; A, ammeter.

#### Laboratory Flotation Tests on Coal Sample:

The Low Kittaning coal sample is subjected to a series of laboratory flotation tests using a 2" diameter Microcel™ flotation column and a conventional flotation cell. The flotation column is described in detail elsewhere [11]. The operating conditions are set as follows: aeration rate, 1.2 l/min; wash water flow rate, 0.4 l/min; frother dosage, 0.45 kg/ton; froth height, 30 cm; and % solids in feed, 5%. The conventional flotation tests are performed in a 5-liter Denver laboratory cell with a feed of 200 g with 0.23 kg/ton of MIBC.

Galvanic Potential Measurements:

The pyrite specimens are cut into rectangular prisms with dimensions of 10×10×5 mm and galvanically coupled with sacrificial anodes by means of a copper wire. The copper wire is glued onto the 10x10 mm surface of the mineral specimen by means of a conducting silver epoxy cement. All other faces of the specimen are coated with a thick layer of non-conducting epoxy resin to prevent their contact with solution. Metal electrodes are fabricated in a similar way. Galvanic potentials are measured in the electrochemical cell shown in Figure 1. The system consists of two independent electrochemical cells connected by a salt bridge. The potentials are measured against a saturated calomel reference electrode (SCE) and converted to the standard hydrogen electrode (SHE) scale by adding 0.245 V. After a galvanic contact, the pyrite specimen is subjected to voltammetry experiments to determine the effects of the galvanic contact on the changes in surface chemistry of the mineral.

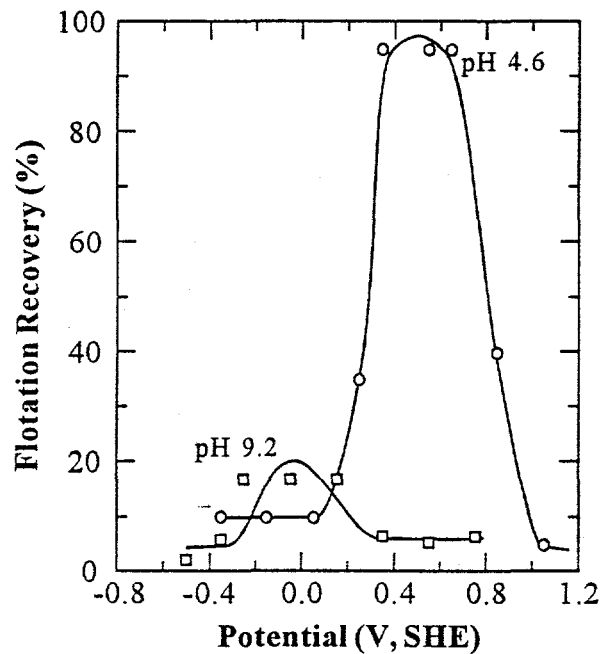


Figure 2: Results of the electrochemical flotation tests conducted on the freshly ground mineral pyrite (-100+200 mesh) sample at pH 4.6 and 9.2.

## RESULTS AND DISCUSSION

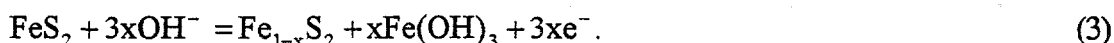
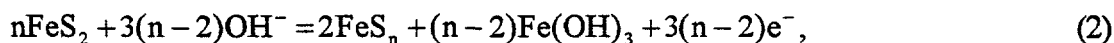
### Collectorless Flotation

Figure 2 shows the results of the electrochemical flotation experiments conducted on the -65+150 mineral pyrite sample. Flotation occurs without the collector at potentials in the range of 0.1 to 0.8 V at pH 4.6 and -0.3 to 0.4 V at pH 9.2. The flotation recovery is considerably higher at pH 4.6 than at pH 9.2. The lower flotation edge corresponds to the stable potential at which the incipient oxidation of pyrite commences, as established by Tao et al. [12] with freshly fractured

pyrite electrodes. Hamilton and Woods [13] and Buckley and Woods [14] suggest that the initial oxidation of pyrite occurs *via* the following reaction (1),

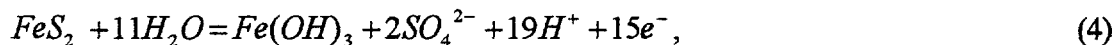


where  $S^0$  is the hydrophobic species responsible for the collector flotation. However, based on the chronoamperometry and voltammetry studies conducted on freshly fractured pyrite electrodes, Tao et al. [8] suggest the following reactions:



for the incipient oxidation of pyrite, which results in the formation of metal-deficient sulfides ( $Fe_{1-x}S_2$ ,  $x < 1$ ) or polysulfides ( $FeS_n$ ,  $n > 2$ ). Both of these sulfur-rich oxidation products represent the hydrophobic species responsible for the collectorless flotation.

Ahlberg et al [15] suggest that the upper flotation edges shown in Figure 2 can be attributed to the oxidation of the sulfur-rich hydrophobic species to hydrophilic sulfoxy species. However, the electrochemical studies of Hamilton and Woods [13] show that the amount of elemental sulfur formed during oxidation increases with increasing potential. Therefore, the reaction occurring at potentials above the upper flotation edge can be represented as follows:



where the ferric hydroxide is likely to be the hydrophilic species responsible for the suppression of pyrite flotation. The decrease in flotation recovery of pyrite at higher potentials can be explained

by the increase in the amount of ferric hydroxide formed by the reaction (4). Yoon et al. [7] observe that there is a good correlation between the floatability of pyrite and the ratio of hydrophilic iron hydroxide to hydrophobic sulfur-rich species. They conclude that the hydrophobicity of pyrite is determined by the relative abundance of iron hydroxide and sulfur oxidation species. The fact that the flotation recovery is lower at pH 9.2 than at pH 4.6 can be explained by the higher concentration of ferric hydroxide on the mineral surface at the higher pH.

Figure 3 shows that the effects of EDTA and kerosene on the floatability of pyrite at pH 9.2. The presence of EDTA significantly increases the flotation recovery of pyrite. Similar results are obtained by Ahlberg et al. [15] and Pang and Chander [16].

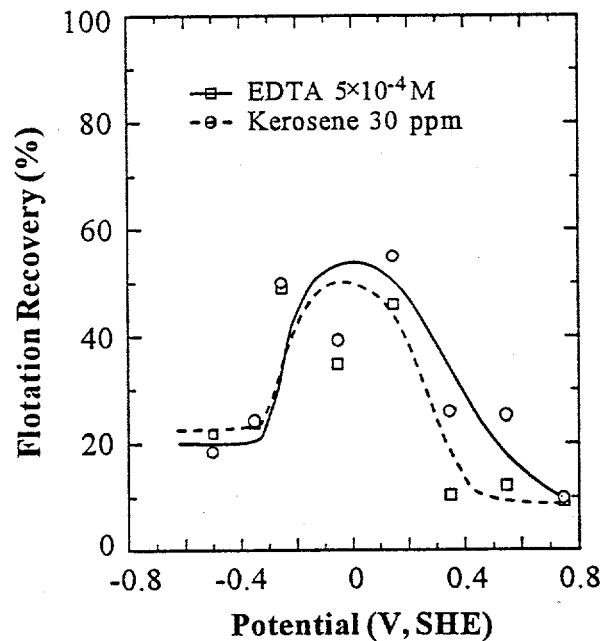


Figure 3. Result of the electrochemical flotation tests conducted on the freshly ground mineral pyrite sample (-100+200 mesh) sample at pH 4.6 and 9.2 in the presence of EDTA or kerosene.

It is believed that EDTA increases the floatability of pyrite by removing iron hydroxide from the mineral surface. The use of kerosene also significantly increases the flotation recovery of pyrite. This is consistent with the results of Olson and Aplan [17], who show that the flotation rate of pyrite increases substantially in the presence of oil. It is interesting that the flotation edges do not change in the presence of EDTA or kerosene. This finding supports the suggestion that the hydrophobicity of pyrite originates from the electrochemical reactions that produce hydrophobic sulfur-rich species. Since neither the EDTA nor kerosene is affecting the electrochemical reactions, their presence should not affect the flotation edge. Therefore, the hydrophobicity of pyrite can be minimized most effectively by preventing the mineral from being oxidized.

Electrochemical flotation tests were also conducted on the coal pyrite sample from the Illinois No. 6 coal. The results are similar to those obtained with mineral pyrite shown in Figure 3, except that its flotation recovery is lower than that of mineral-pyrite. It was shown earlier that the coal pyrite from the Pocahontas No. 3 seam exhibits significantly lower floatability than mineral pyrite [7]. These findings suggest that the ratio between hydrophilic iron hydroxide and hydrophobic sulfur-rich species is higher on the coal pyrite than on the mineral pyrite. In fact, the electrochemical studies of Tao et al. [18] show that the Pittsburgh No. 8 coal pyrite produces a higher concentration of iron hydroxides on the surface of coal-pyrite. Moreover, coal-pyrite can be poorly crystallized, while mineral pyrite possesses more defects on the surface, and is generally of a higher surface area. Consequently, it might oxidize faster than mineral pyrite and its metastable

hydrophobic sulfur-rich species are more readily transformed to soluble sulfate, reducing its hydrophobicity.

In industrial flotation processes, pyrite is expected to show stronger floatability than those shown in Figures 2 and 3. This is because there is only negligible attrition between particles in the microflotation cell as a result of low solids concentration and negligible hydraulic turbulence. Chander et al. [19,20] suggest that vigorous pulp stirring and high solids content in industrial flotation cells might generate particle-particle abrasion that is intense enough to remove the hydrophilic iron hydroxide layer from the pyrite surface. This results in the exposure of the underlying hydrophobic sulfur-rich layer, considerably increasing the floatability of pyrite.

An important conclusion that can be obtained from Figures 2 and 3 is that pyrite can be depressed under reducing or strongly oxidizing conditions. However, strongly oxidizing conditions might not be conducive to improving pyrite rejection in coal flotation for two reasons. First, some of the hydrophobic sulfur oxidation products might still be present on the surface, and even increase with increasing potential [13]. Pyrite might still float once ferric hydroxide is removed by mechanical agitation. Second, coal might also be oxidized under strongly oxidizing conditions, which decreases its hydrophobicity and reduces the selectivity between coal and pyrite. Coal flotation tests conducted in our laboratory (not shown in this communication) show that virtually no improvement in pyrite rejection can be achieved by using oxidizing agents such as potassium permanganate. Therefore, flotation under a reducing environment might be more desirable for improving pyrite rejection. It is unfortunate, however, that most of the common reducing agents



are sulfur-containing agents, and the amount of the reagents that are needed to effect the pyrite rejection is prohibitively high [7]. A more practicable method of creating reducing conditions might be to use the galvanic coupling technique.

### Galvanic Coupling

It is well known that some active metals are fairly strong reducing agents. For example, the standard redox potentials for  $\text{Al}^{3+}/\text{Al}$ ,  $\text{Mn}^{2+}/\text{Mn}$ ,  $\text{Zn}^{2+}/\text{Zn}$ , and  $\text{Fe}^{2+}/\text{Fe}$  are -1.66, -1.18, -0.76, and -0.44 V, respectively. On the other hand, pyrite is the most noble of sulfide minerals whose rest potential are 0.6 V at pH 4.6 and 0.2 V at pH 9.2 [11,25]. When pyrite is galvanically contacted with an active metal, pyrite acts as a cathode on which oxygen is reduced, while the metal acts as a sacrificial anode.

Galvanic interactions occur during grinding and flotation processes. Adam et al. [21] report that galvanic coupling between pyrrhotite and active metals such as mild steel, stainless steel, zinc, and magnesium reduce the floatability of pyrrhotite in the presence of thiol collectors. Similarly, the floatability of iron sulfides (pyrite and pyrrhotite) is seriously affected by the galvanic interactions with a grinding media [22]. It is shown that galvanic coupling between nickel arsenide and pyrrhotite improve the floatability of nickel arsenide, which acts as anode; however, it adversely affects the floatability of pyrrhotite which serves as the cathode [23].

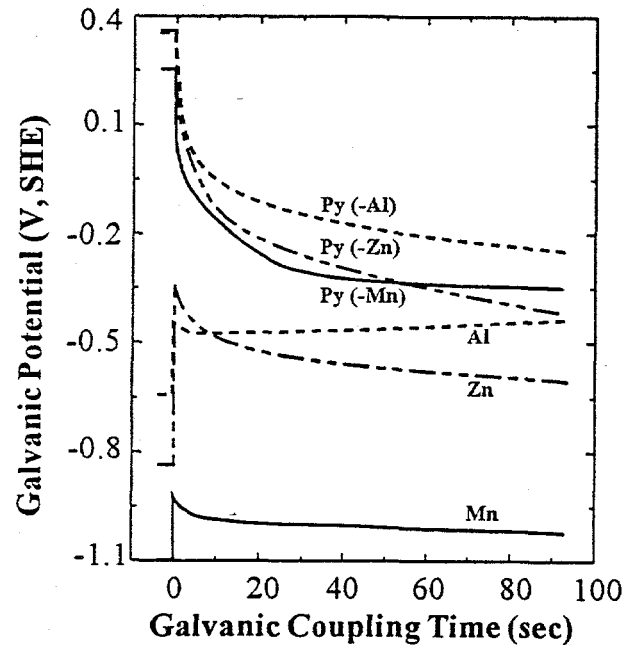
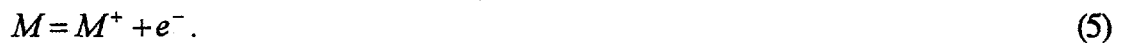


Figure 4. Potentials of the coal pyrite (from Pittsburgh No. 8 seam) and the metal electrodes galvanically coupled with each other at pH 4.6.

Figure 4 shows the potentials of the pyrite (from Pittsburgh No. 8 seam) and metal electrodes (Al, Mn, and Zn) galvanically coupled with each at pH 4.6. The potential of the pyrite decayed from its rest potential (0.3 V) to very low values, while the potentials of the metal electrodes increased sharply upon galvanic contact and decayed to lower potentials. The results obtained at pH 9.2 showed similar results. These results demonstrate that galvanic coupling is an effective technique for keeping pyrite under reducing conditions.

During galvanic contact, the sacrificial anodes might undergo the following reaction,



When the potential is low enough and no oxygen is present in the system, the oxidation products on the surface of pyrite might be reduced as follows:



and/or



In acidic pH, the following reaction might also occur,



In the presence of oxygen, the cathodic reaction might be the following:



in which case, the galvanic potential is lower than the rest potential of pyrite by only approximately 0.2 V.

In nitrogenated solutions, the potentials of pyrite galvanically coupled with the sacrificial anodes used in the present work are lower than the stable potentials of pyrite, i.e., 0 V at pH 4.6 and -0.28 V at pH 9.2, determined by Tao et al. [12]. Therefore, the oxidation of pyrite can be prevented, which helps the mineral acquiring hydrophobicity. Although the galvanic potential determined in the presence of oxygen is not below the stable potentials, pyrite oxidation can be prevented, because the sacrificial anode is oxidized in preference to the mineral. In essence, pyrite is simply offering a site for oxygen reduction and passage for the electrons.

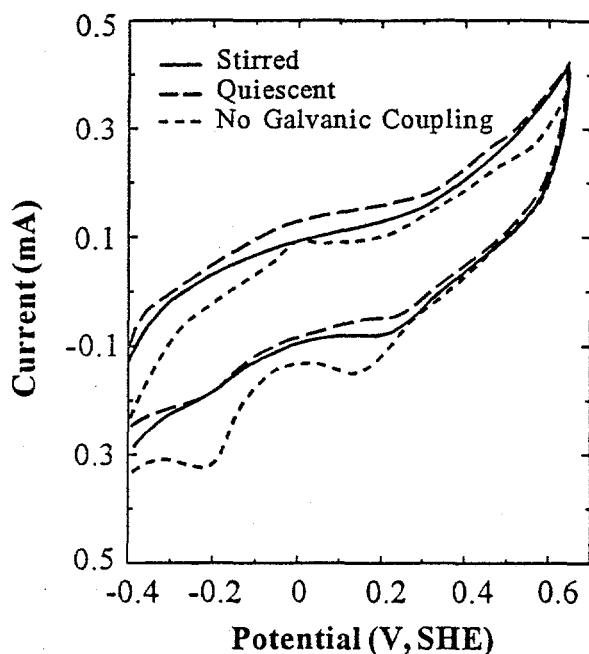


Figure 5. Voltammograms of the coal pyrite (from the Illinois No. 6 seam) electrode that had been galvanically coupled with a manganese at pH 4.6.

Figure 5 shows the first-cycle voltammograms of the pyrite sample from the Illinois No. 6 seam that have been galvanically coupled with manganese. The results are compared with the voltammogram obtained without galvanic coupling. The galvanic coupling greatly reduces the anodic peak at 0 V and the cathodic peak at -0.2 V. According to Hamilton and Woods [13] and Tao et al. [18], the two peaks correspond to the  $S^0/HS^-$  redox couple. It appears, therefore, that the galvanic coupling can reduce the hydrophobic oxidation product such as polysulfides. (It is noted here that polysulfides contain  $S^0$ -like species as part of the chain structure.) Stirring accelerates the diffusion of the  $HS^-$  ions, causing a further decrease in the peak heights.

Voltammetric studies are also conducted with the pyrite electrodes preoxidized at 0.65 V for 5 minutes at pH 4.6. The pyrite sample that is oxidized under this condition has a larger amount of  $S^0$ -like species; nevertheless, galvanic coupling with manganese removes essentially all the sulfur oxidation product, particularly under stirred solutions.

### Depression of Pyrite in the Presence of Sacrificial Anodes

Figure 6 shows the results of the microflotation tests conducted with the pyrite sample in the presence of Mn or Zn powders. The pyrite sample is from the Illinois No. 6 coal seam, and the pH is 4.6. In the absence of metal powders, the coal-pyrite exhibits a flotation recovery of 73%. The use of metal powders results in a substantial decrease in pyrite recovery. The pyrite depression becomes more effective with the increasing amount of metal powders, might be attributed to the increased collision frequency between pyrite and sacrificial anodes.

The depression of pyrite in the presence of metal powders might be explained by galvanic coupling. Galvanic coupling prevents oxidation of the mineral. Another important mechanism for pyrite depression might be the formation of metal hydroxides on pyrite. This is related to cathodic reduction processes such as reactions (6), (8), and (9) which might increase the local pH near the cathode (pyrite). Metal ions, produced by the oxidation of sacrificial anodes, would migrate to the cathode and produce hydroxides. The formation of hydroxides on the surface of other sulfide minerals during galvanic coupling has been observed by other investigators [21,24,25].

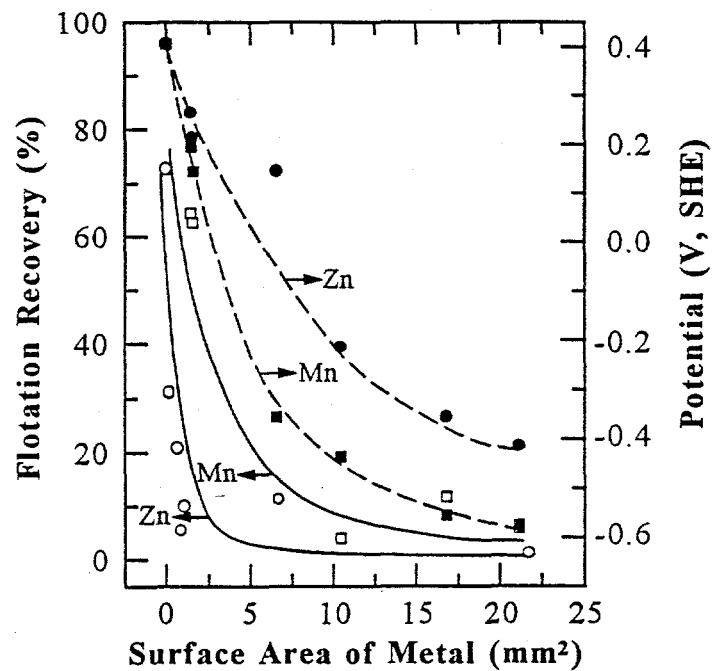


Figure 6. Results of the microflotation tests conducted on the freshly ground coal pyrite (from the Illinois No. 6 seam) sample at pH 4.6 as a function of the surface area of the manganese or zinc powders used as galvanic contactors.

Figure 6 shows that manganese is less effective than zinc in depressing pyrite, despite the fact that the potential of the pulp is lower with the former. There are several possible reasons for this observation. First, hydroxide might be more readily formed on pyrite in the presence of zinc powder than in the presence of manganese powder. The solubility product ( $K_{sp}$ ) of  $Zn(OH)_2$  is  $7.86 \times 10^{-17}$ , while that of  $Mn(OH)_2$  is  $2.04 \times 10^{-13}$ . Second, the manganese used in the flotation tests appears to have been oxidized to a higher extent than the zinc powders. The use of dilute acid

might not completely remove oxides on the surface. The presence of oxides on the metal powders might retard galvanic interaction with pyrite. Third, manganese has a higher specific density than zinc (Mn 7.43; Zn 7.13), which leads to less surface area than zinc at the same dosage by weight.

Figure 7 shows the results of the microbubble column flotation tests conducted on the Lower Kittanning coal samples. The flotation tests are carried out using tap water at the natural pH ( $\approx 6.5$ ). A sample of 200 g coal is conditioned with 10 g Mn powders at 20% solids concentration. The use of manganese shifts the combustible recovery vs. pyritic sulfur rejection curve toward the upper right-hand corner, indicating that the separation efficiency has been achieved. In the absence of metal powders, the pyritic sulfur rejection is about 45% at a combustible recovery of 90%. In the presence of manganese, the sulfur rejection is increased to 75% at 95% combustible recovery.

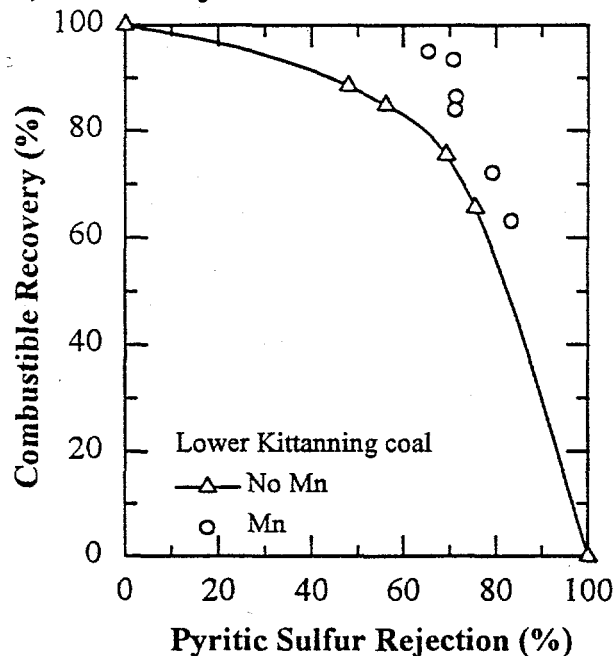


Figure 7. Results of the flotation tests conducted on the Lower Kittanning coal (-100 mesh) sample using a 2 inch-diameter Microcel™ column at natural pH: without manganese ( $\Delta$ ), with 10 g manganese powder ( $\circ$ ) added to 200 g coal sample at 20% solids.

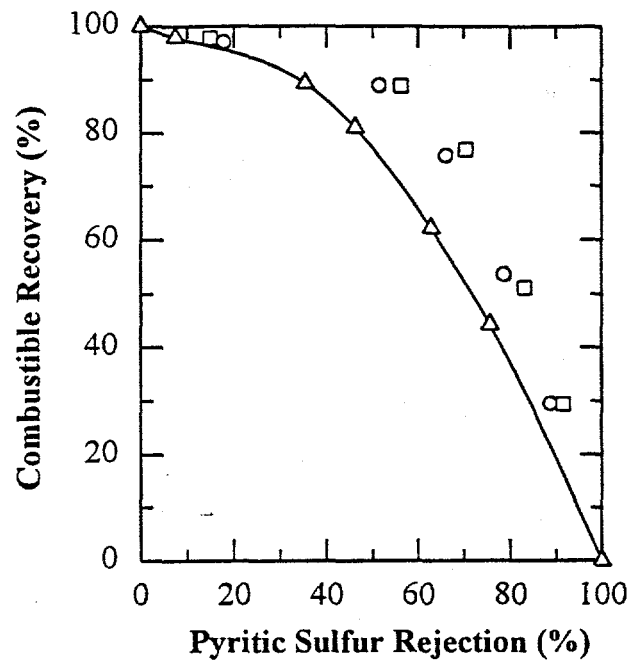


Figure 8. Results of the flotation tests conducted on the Lower Kittanning coal sample (-100 mesh) using a Denver laboratory flotation machine at natural pH; without manganese ( $\Delta$ ), with 2 g ( $\circ$ ) and 10 g ( $\square$ ) manganese added to 200 g coal sample at 20% solids.

Figure 8 shows flotation results obtained with a conventional Denver flotation cell. In comparison with Figure 7, the conventional flotation exhibited inferior performance due to the nonselective recovery of particles by hydraulic entrainment. Nevertheless, the use of manganese powders shows a significant improvement in pyritic sulfur rejection. At the combustible recovery of 90%, pyritic sulfur rejection increases from 35% to 57% by the use of manganese powders. The amount of the metal powders used for the flotation experiments is 5% of the weight of the feed coal.



The results obtained in the present study show that the dosage of metal powders and the solids concentration in the slurry during conditioning are the most important operating parameters in depressing pyrite. The effect of the dosage of metal powders is shown in Figure 8. The effects of solids concentration are shown in Figure 9. For flotation, the conditioned pulp is diluted to 5% solids. When the coal slurry is conditioned by manganese powder at 5% solids concentration, pyritic sulfur rejection is not significantly enhanced. When the solids concentration is raised to 20%, the pyritic sulfur rejection is significantly improved. In a well stirred conditioning tank, the collision probability between metal powders and pyrite particles is proportional to the product of their concentrations. Therefore, the increase in solids concentration from 5 to 20% represents a 16-fold increase of the collision probability, which might account for the improved sulfur rejection.

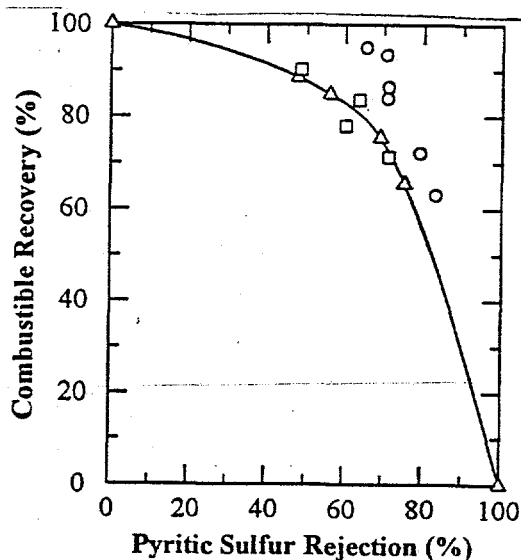


Figure 9. Results of the flotation tests conducted on the Lower Kittanning coal (-100 mesh) sample using a 2 inch-diameter Microcel™ column at natural pH: without manganese (Δ), with 10 g manganese powder (○) added to 200 g coal sample at 5% (□) and 20% (○) solids.

The amount of metal powders used in the present work is excessive for practical application. Nevertheless, the present investigation demonstrates a new concept of using the galvanic coupling technique for improved pyrite rejection. It is possible, in the future, to find a method of using scrap irons as galvanic contactors. It is also possible that conditioning tanks can be made with alloys or metals that can provide reducing conditions, or serve as effective galvanic contactors.

### CONCLUSIONS

1. Incipient oxidation of pyrite produces hydrophobic polysulfides, which renders the mineral hydrophobic and causes the mineral to be floatable without a collector.
2. The floatability of pyrite without a collector is determined by the relative abundance of the polysulfides and iron hydroxides on the surface, which in turn varies with pH and  $E_h$ . The floatability is higher at pH 4.6 than it is at pH 9.2. The difference in floatability is probably due to the higher polysulfide to iron hydroxide ratio on the surface.
3. The potential at which collectorless flotation of pyrite begins to occur is determined by the electrochemical reaction involving incipient oxidation of the mineral. Its upper flotation edge is determined by the electrochemical reactions involving the production of hydrophilic iron hydroxide and sulfoxy species on the surface.

4. At pH 9.2, the collectorless flotation of pyrite increases in the presence of EDTA or kerosene; however, both the lower and upper flotation edges are not affected appreciably by these reagents.
5. Galvanic coupling of pyrite with active metals such as zinc, manganese and aluminum can effectively lower the potential of pyrite to values that are negative enough to prevent the oxidation of pyrite, and to reduce the hydrophobic oxidation products that are already present on surface.
6. Galvanic coupling can effectively depress pyrite without adversely affecting the flotation of coal, thereby significantly improving the pyrite rejection.
7. The most important parameters that determine the effectiveness of galvanic coupling for pyrite depression are the surface area of the galvanic contactors and the solids concentration of slurry during conditioning.

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