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Control of Pyrite Surface Chemistry in Physical Coal Cleaning

by

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ABSTRACT

Several pyrite depressants have been evaluated for their effectiveness in depressing coal pyrite. A novel reagent, NVT, has been synthesized and shown to be selective for the separation of coal from coal pyrite by froth flotation. This organic reagent contains no sulfur group in its structure and exhibits a stronger affinity toward pyrite than toward coal. The effects of a number of parameters such as pH, reagent concentration and flotation time on flotation response were investigated in a microflotation cell and a bench-scale Denver flotation cell. The reagent has demonstrated good performance at relatively low concentrations when compared to the commercially available sulfur-based pyrite depressants.

INTRODUCTION

The primary objective of this research is to obtain fundamental knowledge concerning the surface properties of coal pyrite as they relate to advanced physical coal cleaning (APCC) processes. This goal will be met by: (1) investigating the mechanisms responsible for the inefficient rejection of coal pyrite and (2) developing schemes for improving the rejection of coal pyrite based on information gathered from part (1).

Studies aimed at defining the mechanism of the inherent or natural hydrophobicity of mineral and coal pyrite are continuing as planned. However, due to equipment problems the data are not complete at this point. Therefore, in this reporting period studies on the effects of various depressants on the floatability of coal and mineral pyrite have been undertaken. Studies have also been carried out to determine whether these reagents would adversely impact the floatability of the pure coal.

EXPERIMENTAL

Mineral pyrite from Huanzala, Peru, was dry ground using an agate mortar and pestle, sieved to obtain the 65x100 mesh size fraction, then used immediately. A sample of coal pyrite from the Pocahontas No. 3 seam was obtained from a Deister table reject stream. It was received in slurry form which was subsequently wet sieved and vacuum dried to obtain the 65x100 mesh size fraction. This product was passed through a dry magnetic separator to remove any magnetic particles. The cleaned product, which assayed 2.5% combustible material, was stored in a freezer to minimize oxidation. A sample of Pocahontas No. 3 seam coal was received in lump form and was prepared by crushing in a jaw crusher followed by a roll crusher to obtain the 65x100 mesh size fraction. The coal product assayed 8.9% ash and 0.9% sulfur and was stored in a freezer until use.

Floatabilities of 65x100 mesh mineral pyrite, coal pyrite, and raw coal were determined using a 120 ml column-microflotation cell with a fine-glass frit. In each microflotation test, either 0.8 gm of mineral or coal pyrite or 0.5 gm of raw coal were used. The samples were conditioned in 120 ml of solution containing the desired reagents for 5 minutes then floated with 4-methyl 2-pentanol (MIBC, 99% purity purchased from Aldrich Chemicals) as frother for 2 minutes using nitrogen gas at a flow rate of 40 cc/min. The effect of cleaning the pyrite surface was determined by conditioning the mineral in an ultrasonic bath for 1 minute. The pH level in the flotation tests was maintained by addition of HCl and NaOH.

Larger-scale flotation tests were conducted using a bench-scale Denver flotation cell. A slurry of either coal or pyrite was prepared by combining 10 gm of 100x140 mesh sample and distilled water in a 2-liter cell. The slurry was conditioned for 10 minutes in the absence of depressant followed by

a 1 minute conditioning with 50 mg/l of MIBC. The sample was then floated. For those tests during which depressant performance was evaluated, the depressant was added immediately following the 10 minute conditioning period and the flotation pulp was conditioned for one additional minute prior to adding the frother.

The performance of several depressants during flotation of coal pyrite and coal was evaluated. The depressants examined were sodium sulfide (Na_2S - reagent grade Fisher chemical); ORFOM D8 (Phillips Chemicals) a commercially available sulfide mineral depressant; MAC, a proprietary reagent of American Cyanamid Company; and NVT, a novel organic depressant synthesized in our laboratory.

RESULTS AND DISCUSSION

The floatability of mineral pyrite, coal pyrite, and coal as a function of pH in the absence of frother is illustrated in Figure 1. The mineral pyrite sample exhibits the lowest overall floatability followed by the coal pyrite, with the coal sample having the highest floatability over the examined pH range. The floatability of both the coal and mineral pyrite samples is substantially different from that reported in previous quarterly reports, in fact, the response is opposite. The reason for the differences can be explained by the manner in which the samples were prepared for the measurements. The high degree of floatability of the coal pyrite sample reported here is due to the fact that there are large amounts of locked particles containing both coal and pyrite. In the data previously reported, the coal pyrite examined was a hand-picked sample of 10x28 mesh Deister table particles which were then dry ground and wet sieved to obtain the 100x150 mesh size fraction. The sample examined and described in this report is a concentrated split from a Deister table reject stream, as discussed in the

Figure 1. Floatability of Pocahontas No. 3 seam coal and coal pyrite and Huanzala, Peru mineral pyrite in the absence of frother as a function of pH.

experimental section, which was found to contain locked particles. The difference in the floatability of the mineral pyrite can be attributed to the presence of fine particles, or slimes, because the sample shown in Figure 1 was only dry ground and sieved prior to flotation.

The effect of frother addition on the floatability of the mineral pyrite can be seen in Figure 2. Like the previously reported results, the floatability of mineral pyrite is enhanced in the presence of frother over the entire pH range. This effect may be due to either modification of the bubble size or adsorption of frother on the pyrite surface. A combination of both mechanisms seems plausible. The bubble-particle induction time has been observed to decrease with the addition of frother implying the latter mechanism, while the observations on the enhancing effect of reduced bubble size supports the combined approach. The effect of cleaning the surface of the mineral pyrite by sonication is also seen in Figure 2. Surface cleaning, by sonication for only one minute, improved the floatability indicating that clean surfaces are indeed more hydrophobic. In fact, samples aged over a period of several months could be fully floated under acidic conditions after one minute of sonication.

Several depressants were tested for their ability to depress freshly ground mineral pyrite samples and the results are shown in Figure 3. Mineral pyrite conditioned in a 1% Na_2S solution for 15 minutes, then repeatedly rinsed to remove residual sulfide ions became completely floatable regardless of the solution pH. This is believed to be due to enrichment of the surface by elemental sulfur which is naturally hydrophobic. ORFOM D8 is effective in depressing mineral pyrite only in the alkaline pH range as it begins to lose its activity below pH 7. On the other hand, MAC was relatively insensitive to pH with depressant action being greater than ORFOM D8 at the same reagent

Figure 2. The effect of frother and sonication on the floatability of mineral pyrite as a function of pH. Frother dosage: 50 mg/l MIBC.

Figure 3. The effect of various depressants on the floatability of mineral pyrite in the presence of frother as a function of pH. Depressant dosage: $8 \times 10^{-4} M$, except Na_2S - 1%. Frother dosage: 50 mg/l MIBC.

dosage. The novel reagent synthesized in our laboratory, NVT, is effective in depressing pyrite in the acidic pH and displays a slightly greater effectiveness than MAC in this region. These findings suggest that NVT, MAC, and ORFOM D8 all have potential for being effective coal pyrite depressants.

The floatability of Pocahontas No. 3 coal and coal pyrite, in the absence and presence of the depressants with frother, is shown in Figure 4. In the absence of a depressant, both coal and coal pyrite exhibit complete flotation over the entire range of pH. The sulfur-based organic depressants, ORFOM D8 and MAC, though excellent depressants for mineral pyrite, show little depression effect on the Pocahontas No. 3 seam coal pyrite. On the other hand, the addition of NVT depresses the coal pyrite very effectively, but only below pH 6. However, in order for a depressant to be effective, it should not only depress the pyrite, but equally it should not cause any loss in the combustible recovery. The effect of NVT addition on the floatability of coal is also shown in Figure 4. The coal recovery began decreasing gradually with decreasing pH and remained somewhat constant at about 80% even under the conditions where maximum pyrite depression was achieved.

The effect of NVT reagent concentration is illustrated in Figure 5. At a constant pH of 5.3, the reagent is effective in depressing coal pyrite at concentrations as low as $10^{-4}M$. The effect of depressant dosage on coal depression is also presented in Figure 5 at pH 5.3. Even at the highest reagent concentration tested, the recovery did not fall below 80%, indicating that the reagent has a lower affinity toward coal than toward pyrite. This selectivity provides a window of opportunity for the potential industrial use of this reagent.

It should be noted that the flotation time in Figures 4 and 5 was kept constant at two minutes. As shown in Figure 6, the coal recovery could be

Figure 4. Floatability of Pocahontas No. 3 seam coal and coal pyrite in the absence and presence of various depressants as a function of pH. Frother dosage: 50 mg/l MIBC.

Figure 5. The effect of NVT concentration on the floatability of Pocahontas No. 3 seam coal and coal pyrite in the presence of frother. Frother dosage: 50 mg/l MIBC.

Figure 6. Flotation kinetics of Pocahontas No. 3 seam coal and coal pyrite in the presence of NVT and frother. Frother dosage: 50 mg/l MIBC.

substantially improved with longer flotation times without a significant change in pyrite depression. Addition of a collector, such as kerosene, was found to improve the kinetics of coal recovery at the expense of sulfur recovery.

The equilibrium time for NVT to interact with the solid surface was also studied to determine the reaction kinetics for the depressant. Figure 7 reveals that the majority of the interaction takes place in the first minute and the equilibrium is achieved in less than five minutes. Such rapid kinetic response is again a factor favorable for commercial utilization of this reagent.

The microflotation tests were further corroborated by tests conducted in a Denver flotation cell. Ten grams of 100x140 mesh Pocahontas No. 3 coal and coal pyrite were individually floated in a bench-scale Denver cell. The solids were conditioned for 10 minutes in 2 liters of distilled water followed by one minute of conditioning with 50 mg/l of MIBC.. The slurry was then conditioned for one minute in the presence of $8 \times 10^{-6} \text{M}$ NVT. The data shown in Figure 8 indicate that the flotation rate of coal is not significantly affected in the presence of NVT, while that of pyrite is significantly decreased. The flotation rate constant of coal with and without the depressant is 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 it. Such an effect confirms the results obtained from the microflotation measurements discussed earlier.

CONCLUSIONS AND FUTURE WORK

A novel reagent, NVT, has been developed for coal pyrite depression. The reagent shows good selectivity for the separation of Pocahontas No. 3 seam

Figure 7. The effect of conditioning time with NVT on the floatability of Pocahontas No. 3 seam coal and coal pyrite in the presence of frother. Frother dosage: 50 mg/l MIBC.

Figure 8. Floatability of Pocahontas No. 3 seam coal and coal pyrite in the absence and presence of NVT in a bench-scale Denver flotation cell. Frother dosage: 50 mg/l MIBC.

coal and coal pyrite as compared to the sulfur-based depressants, ORFOM D8 and MAC, which have been shown to be ineffective in depressing coal pyrite. The recovery of coal after treatment with NVT was substantially improved at longer flotation time without a significant change in pyrite depression. Denver cell flotation tests reveal that the rate constant for coal is approximately the same with and without NVT, while those for coal pyrite are significantly lower in the presence of NVT, indicating the considerable commercial potential of this reagent and the need for further investigation. Realization of the commercial potential of this reagent will be determined through pilot-plant microbubble-column flotation testwork. Future studies will include the testing of additional compounds for depression effectiveness, as well as, other run-of-mine coal samples which have been targeted as problem coals with respect to sulfur rejection (i.e., Illinois No. 6, Upper Freeport, and Pittsburgh seam coals).

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