SEPARATION OF ULTRAFINE PYRITE FROM COAL BY SELECTIVE DISPERSION AND FLOCCULATION

Yosry A. Attia

The Ohio State University
Division of Mining Engineering
140 W. 19th Avenue
Columbus, Ohio 43210

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ABSTRACT

A novel technique for separating ultrafine pyrite particles (minus 40 microns) from coal fines has been conceptually developed and tested. The technique involves the use of a selective polymeric dispersant for pyrite, while flocculating coal particles with a general polymeric flocculant. The suspended pyrite can be then removed from the flocculated coal fines which settle preferentially by gravity.

The key to this separation was the design and preparation of the selective dispersant for pyrite (PAAX). This was achieved by incorporating xanthate groups into the structure of a low molecular weight acrylic acid polymer (PAA). Testing this reagent on individual suspensions of coal and pyrite confirmed its selective dispersion action towards pyrite, while it had no dispersion action on coal suspension when using Purifloc-A22 flocculant. Preliminary tests on high sulfur coal from Kentucky No. 9 seam, also confirmed this selectivity. Further process development is needed however before this promising technique can be commercially feasible.

Introduction

Most of the Eastern U.S. coals, suffer from high sulfur content, which on burning emit sulfur dioxide in excess of EPA limit of 1.2 lb SO_2/million Btu. Specifically, there are three broad regions that suffer from severe sulfur problems. These are: Northern Appalachia (Pennsylvania, Ohio, West Virginia) with average sulfur content of about 3%; Midwest region (Indiana, Illinois, Kentucky) with average sulfur of 3.9%; and Central Midwest (Iowa, Missouri, Kansas, Oklahoma) with average sulfur of 5.25%.

The presence of sulfur in coal is generally attributed to two forms, organic sulfur and pyritic sulfur. The proportion of pyritic sulfur to organic sulfur varies significantly from one coal seam to another, but it appears that pyritic sulfur generally represents about 70 percent or more of the total sulfur (1). The pyrite is found in coal in a wide size distribution, with a significant proportion in the very fine size fraction (less than 25 microns). For example the mean particle size of pyrite in the Midwest region is about 37u (400 mesh) and for Central to Western Midwest region is about 107u (150 mesh), and in the Appalachian regions is about 68-100u. This can only mean that a significant amount of the pyrite is in the very fine to colloidal fractions. In fact, there are coal seams, such as Kentucky No. 9 where all the pyrite particles are often smaller than about ten microns (2).

It is believed therefore, that the separation-removal of pyrite from coal prior to its combustion would greatly reduce the sulfur dioxide emission and render many coal deposits within the EPA limits.

For separation of coal from relatively coarse shale and pyrite, gravity-based techniques have been effectively utilized. For sizes below 300 microns to about 100 microns, froth flotation has been used satisfactorily for separating coal from shales (3). Even separation of pyrite from coal has been achieved by flotation (4). However, most of these processes become less effective when the particle size of the coal suspension is significantly below 100 microns.

One of the promising new technologies for separation of very fine particles is selective flocculation. The selective flocculation process has been used effectively to separate very finely disseminated minerals from mixed ore suspension (5). The process is based on the preferential adsorption of an organic flocculant on the wanted minerals, thereby flocculating them, while leaving the remainder of the suspension particles dispersed. The dispersion of certain components in the suspension such as pyrite, can be enhanced by using more selective or powerful dispersants. Methods for achieving selective flocculation and dispersion have been recently described by Attia (6).

The objective of this research was to investigate the feasibility of separating coal fines from mixed suspensions with pyrite by selective flocculation. In this work, the separation of pyrite from coal was based on the distinct differences in their surface chemical properties. Pyrite being a sulfide mineral has an affinity for xanthate containing reagents, while coal does not have such an affinity towards xanthates. Therefore, if xanthate groups could be incorporated into the structure of long-chain polymers, selective polyxanthate flocculants or dispersants for pyrite might thus be achieved. The use of polyxanthates for selective flocculation of sulfide minerals, particularly for copper, was first reported by Attia and Kitchener (7). The separation of pyrite from coal using polyxanthate dispersants was demonstrated recently by Attia and Fuerstenau (8).

This article describes the progress made to achieve selective flocculation of coal from pyrite from a coal sample containing about 2.9% total sulfur.

Preparation and Testing of Polyxanthate Dispersants.

In a preceeding article (8) Attia and Fuerstaneu prepared polyxanthate dispersants by reacting low molecular weight polyacrylic acid solutions with sodium hydroxide and carbon disulfide. The presence of the xanthate groups (Dithio-carbonate) in the polymeric dispersant was ascertained from the UV - Spectra of the solution, where the absorption peak at 305 to 307 mμ was observed. This is very close to the UV-absorption peak of lower xanthate compounds of 303 mμ.

Selective flocculation of coal from pyrite was investigated using the newly developed polyxanthate dispersant in conjunction with a polystyrene sulfonate (purifloc A22) flocculant. The flocculation results on the individual mineral suspensions are shown in Figure 1 (A & B). These graphs show the effect of polyacrylic acid dispersant before (PAA) and after xanthation (PAAX) on the flocculation-dispersion behavior of individual suspensions of coal and pyrite with Purifloc-A22 flocculant.

From Figure 1(A), it appeared that PAA inhibited or restrained the flocculation action of Purifloc-A22 on both coal and pyrite suspensions at PAA concentrations of 100 mg/l and above. The dispersive action of PAA in this case was therefore unselective. However, the PAAX crude reaction product in Figure 1(B) only dispersed the pyrite suspension to the same level as PAA, while the coal suspension was totally flocculated even at high PAAX concentrations. The polyxanthate dispersant rather than improving the dispersion of pyrite, simply did not adsorb on the coal particles, thereby creating a selective dispersion action for the pyrite. These observations in Figure 1(B) were repeated and noted several times even with purified PAAX solutions. Selective dispersion of pyrite or selective flocculation of coal from pyrite using PAAX reagent appeared, therefore, possible.

Effect of Pyrite Particle Size on Dispersion: It was suspected that a lot of the non-dispersed pyrite particles, shown in Figure 1, was due to the settling of "coarse" particles between 10 and 37 microns. Pyrite has a specific gravity of about 5.4, while that of coal is around 1.6 to 1.8. Therefore, a pyrite suspensions of coal and pyrite of minus 37 microns size were also tested simultaneously. The results showed that the coal was almost totally flocculated as before, while the minus 10 micron pyrite suspension remained very stable, with only 10 - 20% weight of the particle, settled or flocculated. The minus 37 micron pyrite behaved in the same manner as in Figure 1. From these observations, it is believed that the se-

lective dispersion of pyrite will be more effective at the smaller particle sizes.

Selective Flocculation of High Sulfur Coal

Preliminary testing of the polyxanthate dispersant mentioned earlier, during the selective flocculation of high sulfur coal was conducted and described here. A sample of bituminous coal from Kentucky No. 9 seam was kindly supplied by the Occidental Research Corporation. The coal sample was wet ground in a steel ball mill and screened to obtain the minus 400 mesh (-37u) fraction for testing.

Single-step selective flocculation tests were conducted on dilute suspensions (about 3% wt) of the minus 37u coal particles, using 2 mg/l, F1029-D flocculant (a partially hydrophobic polymer prepared by Dai-Ichi Kogyo Sieyako, Japan), at pH 10. The test procedure was as follows: The coal suspension was dispersed at a moderate shear for 10 minutes, during which the required amounts of PAAX solution were added and the pH was adjusted to 10. The flocculant was then administered while the suspension was stirred at high shear for 10 seconds. The suspension was thereafter stirred at a low shear for one minute, followed by gentle rotation in an inclined cylinder for 5 minutes. At the end of this step the suspension was decanted off and the flocculated fraction was recovered. Both fractions were dried, weighed and analyzed for total sulfur. The results of this brief study is shown in Table 1 below.

Table 1: Material Balance for One-Step Selective Flocculation of High Sulfur Coal using PAAX Dispersant and F1029-D Flocculant.

Product	Weight %	Total Sulfur%	Total Sulfur Distribution %	Remarks
Dispersed	3.7	13.74	20.3	500 mg/l
Flocculated	96.3	2.08	79.7	PAAX
Feed	100.0	2.52	100.0	
Dispersed	2.7	9.96	9.7	300 mg/l
Flocculated	97.3	2.56	90.3	PAAX
Feed	100.0	2.76	100.0	

These results show that the sulfur content of the dispersed (reject) products was significantly higher than the feed or the flocculated fractions. This was specially evident at the higher PAAX dispersant concentration (500 mg/l) where the sulfur content in the dispersed fraction was 13.74% compared with 2.08% in the flocculated fraction. While these results present a definite evidence for the selectivity of flocculating coal and dispersing pyrite with the reagents mentioned above, the total sulfur removal was very low. The low sulfur removal could be due to the fact that pyrite is known to be very finely disseminated (~10 microns) in Kentucky No. 9 seams from which this sample was obtained. In the brief tests mentioned here no attention was paid to the liberation characteristics of pyrite from coal. It was hoped that grinding to minus 400 mesh (37 microns) would liberate a significant amount of pyrite. Another possible reason for the low sulfur removal was the presence of "coarse" pyrite or pyrite-containing coal particles which would settle at a similar rate as the pure coal flocs, thus, interferring in their separation. As mentioned earlier in this article, the process is expected to be more effective for the 10 microns size pyrite than for 37 microns size pyrite particles, if gravitational settling was used for separation of flocs from suspension. Other floc separation methods such as flotation might extend the effectiveness of this selective flocculation method to coarser sizes. Alternatively, the coarser pyrite particles (greater than 25 microns for example) could be separated by other technique prior to

applying selective flocculation.

Conclusions

From the foregoing discussion, it can be concluded that the addition of the polyxanthate dispersant (PAAX) during the selective flocculation of coal with F1029-D or Purifloc-A22, presents a promising approach for the removal of ultrafine pyrite particles from coal suspensions. This would specially be true however if future investigations could improve the overall pyrite removal, while still obtaining high coal (Btu) recovery. It is believed that by applying multi-stage selective flocculation (i.e., the flocs from the first separation step are re-dispersed and re-flocculated several times) more of the liberated pyrite particles would be removed.

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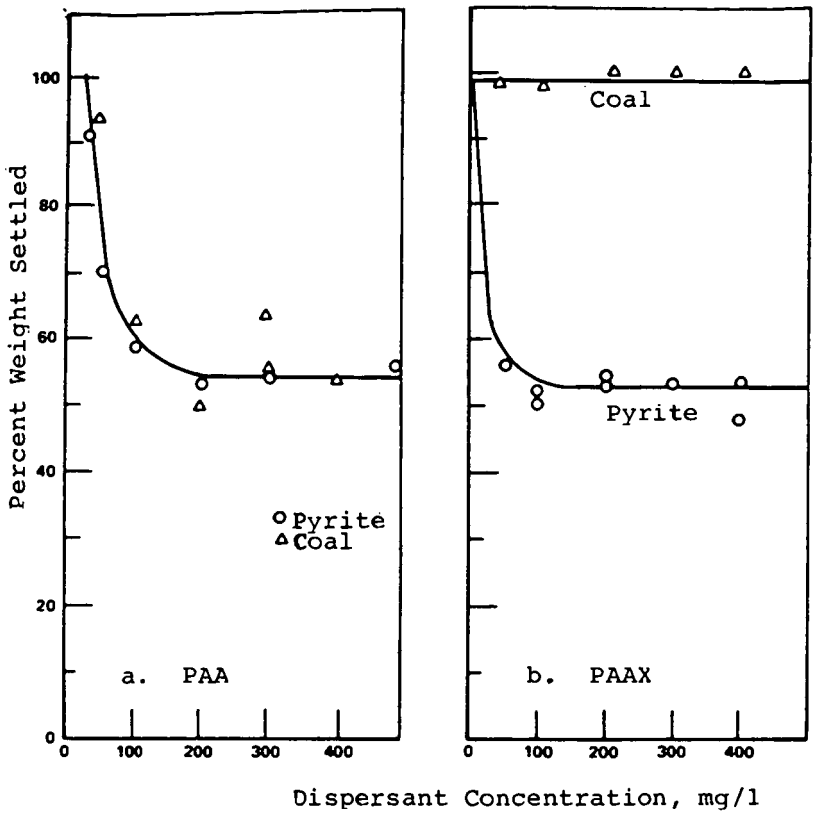

FIGURE 1. EFFECT OF PAA AND PAAX DISPERSANTS ON THE FLOCCULATION OF COAL AND PYRITE WITH PURIFLOC-A22 (4 mg/l) at pH10, AND 2% SOLIDS CONTENT IN SUSPENSIONS.