PYRITE SURFACE CHARACTERIZATION AND
CONTROL FOR ADVANCED FINE COAL
DESULFURIZATION TECHNOLOGIES

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SUMMARY

This report briefly summarizes the major accomplishments for the project entitled "Pyrite surface characterization and control for advanced fine coal desulfurization technologies", DE-FG22-90PC90295, performed during the period from March 1, 1992 to March 31, 1992.

The objective of this project is to conduct extensive studies on the surface reactivity and surface hydrophobicity of coal-pyrites using various surface characterization techniques and to correlate the alteration of the coal-pyrite surface with the efficiency of pyrite rejection in coal flotation. During this reporting period, the flotation characteristics of coal-pyrites under various conditions was studied and compared with ore-pyrite and coal to determine the causes of pyrite rejection difficulties in coal flotation. Both the native and induced floatabilities of pyrites were investigated. It was found that both coal- and ore-pyrites, if prepared by dry-grinding, show little or no floatability in the absence of any chemical reagents. After ultrasonic pretreatment, ore-pyrite floats effectively in the acidic to neutral pH range. Kentucky no.9 coal-pyrite (KYPY) shows significant flotation in the pH range 7-10. With ethyl xanthate as collector, ore-pyrite floats well up to pH=10; while coal-pyrite reveals no flotation above pH=6. For the first time, the effect of coal collector on the floatability of coal-pyrite has been studied. It was shown that in the presence of fuel oil--a widely used collector for promoting coal flotation, coal-pyrite, particularly for the fine sizes, shows good flotation below pH=11, whereas ore-pyrite has no or little floatability. These studies demonstrate that one of the main causes of the coal-pyrite flotation in coal separation is the oil-induced floatability due to adsorption/attachment of oil droplets on the coal-pyrite surfaces, the "native" or "self-induced" floatability of pyrite is no as profound as the oil-induced flotation.

INTRODUCTION

Surface-based physical separation techniques such as froth flotation and agglomeration have shown the potential for removing pyritic sulfur from coal. However, the efficiency of these techniques in rejecting pyrite from coal decreases significantly with ultrafine coal. The causes of the difficulties of pyrite separation from coal are complex and have not been systematically investigated. In addition to the superficial changes of pyrite surfaces, there are several other possible factors such as particle size, crystallinity, contamination, etc, that all can change the surface properties of pyrite. Therefore, it is of great significance to determine the role of each of the factors in coal-pyrite flotation.

EXPERIMENTAL

Materials:

Large lumps of hand-picked massive coal- and ore-pyrite were used to prepare flotation samples. Pyrite lumps were first manually crushed. Only those with invisible coal contamination were collected. Then the pyrite samples were dry ground in a porcelain mill to prepare the size fractions of 100x150, 150x200, 200x325 and -325 meshes. The source and chemical composition of the samples were presented in a previous report (Wang et al, March, 1992).

Techniques:

The flotation tests were conducted with a micro-column, courtesy of Dr. Yoon at VPI. One or two grams of the prepared pyrite/coal sample was first conditioned in a beaker, in most cases for about five minutes. It was observed that when the desired slurry pH was far apart from the natural pH, it was difficult to stabilize the pH. In such cases, the condition time was longer than five minutes. The slurry was then transferred into the column. The total volume of slurry was about 150 ml. Flotation was allowed for five minutes using nitrogen gas. After flotation, the pH of tailing was measured and reported as "flotation pH". The concentrate and tailing were then dried and weighted, and flotation

recovery was calculated.

The contact angle measurements have been described in detail in previous reports [2,3].

RESULTS

1. Self-Induced Floatability of Pyrites.

The native floatability of unaltered sulfide surfaces is fundamentally very interesting. The question dates back to 1930s and is still debatable despite numerous studies on this elusive problem. During the last decade, major interest has been directed at understanding the effects of various processing variables such as grinding, ageing, etc on the floatability of sulfides. A new term, "self-induced floatability" was created to describe the flotation of sulfides in the absence of any hydrophobicizing chemicals (e.g., collectors) and to distinguish the native floatability of sulfides as well as other chemical induced flotation. It was shown that most of the other metal sulfide minerals display significant flotation when the surfaces are subject to moderate oxidation. Some previous investigators have attributed the coal-pyrite flotation to the "self-induced" floatability of pyrite due to surface oxidation. Thus, it is important to study the self-induced floatability of coal-pyrite.

Our flotation tests showed that in the absence of any chemicals, both coal- and ore-pyrite displayed no flotation. This indicates that the surfaces of pyrite prepared by dry-grinding are hydrophilic. Previous studies showed that this is due the formation of hydrophilic iron hydroxide layers on pyrite during grinding, and the hydrophilic hydroxide layers can be removed by reacting with EDTA [4] or ultrasonic pretreatment. Figure 1 presents the flotation recovery as function of pH for ore- and coal-pyrite after ultrasonic treatment. After ultrasonic pretreatment, the ore-pyrite (PUPY) exhibits good flotation up to pH = 10. However, the coal-pyrite (KYPY) remains poorly floatable. For comparison, the floatability of coal without any pretreatment is shown in Fig.1. It can be seen that coal floats effectively only in acidic solutions. Above pH 7, no significant flotation occurs.

II. Flotation with Xanthate:

Xanthate has been used as a pyrite collector in ore flotation for more than sixty years. Recently, there has been an increasing interest in promoting pyrite rejection from coal through reverse flotation, i.e., floating pyrite with xanthate while depressing coal. The major motivation of our studies here is to compare the surface reactivity of coal- and ore-pyrite by examining their flotation behavior in the presence of xanthate as collector.

Figure 2 shows the flotation recovery as a function of pH for ore-pyrite. It can be seen that for coarser particles, pyrite floats completely up to pH 11. However, For very fine particle sizes, the flotation strongly depends on the xanthate concentration and solution pH. At a moderate concentration, fine pyrite particles do not float effectively at $\text{pH} > 7$. The results are similar to that reported previously [4]. The flotation response of coal-pyrite differs considerably from that of ore-pyrite. As shown in Fig.3, even for coarse coal-pyrite particles, little or no flotation can be obtained above $\text{pH} = 6$. Unlike ore-pyrite, the flotation behavior of coal-pyrite is almost independent of the particle size.

Figures 4 and 5 compare the flotation recovery vs pH for ore- and coal-pyrite of the same size. It can be seen that for coarse particles, the floatabilities of coal- and ore-pyrite with xanthate as collector differ considerably in neutral to alkaline solutions. However, for ultrafine particles, the flotation behavior of coal- and ore-pyrite becomes almost identical (Fig.5). These results demonstrate that it is not appropriate to draw conclusions such as "coal-pyrite is more reactive than ore-pyrite", or "ore-pyrite is more floatable than coal-pyrite", without given the experimental conditions.

III. Flotation with Fuel Oil.

Nonpolar oily chemicals (such as fuel oil) have been widely used as collectors in coal flotation to improve the hydrophobicity of coal surfaces. It has been assumed that the oily collectors would be adsorbed only on coal particles. Our recent literature survey showed that there has been no study of the effects of the oily collectors on the floatability

of pyrite. Hence, it is necessary to examine the flotation behavior of pyrite in the presence of oily collectors. Fuel oil is one of the most widely coal collector in coal flotation, and thus has been used in this study.

Figure 6 shows the recovery of coal-pyrite (KYPY) and ore-pyrite (PUPY) as a function of solution pH in the presence of fuel oil. The ore-pyrite which floats effectively with xanthate does not display any significant floatability in the presence of fuel oil at pH above 5. However, with fuel oil, the coal-pyrite shows good flotation below pH=10, particularly for the fine particle size. The flotation recovery of coal-pyrite increases with increasing the concentration of fuel oil. These results demonstrate that fuel oil is adsorbed on the coal-pyrite surfaces and increase the floatability of coal-pyrite. Therefore, oily collectors used in coal flotation are adsorbed non-selectively on both coal and pyrite surfaces. This results in greater difficulty in rejecting pyrite from coal by flotation. In order to improve the efficiency of pyrite removal from coal, either selective coal collectors or pyrite depressants are needed. The subjects are being investigated.

IV. Relationship between Surface Properties and Bulk Composition

One of the interesting aspects of coal-pyrite surface chemistry is to determine whether there is any relationship, either qualitative or quantitative, between the surface properties (hydrophobicity, PZC, oxidation rate, etc.) of pyrite and the bulk physical/chemical composition (stoichiometry, impurity content, semiconducting type, crystallinity, etc.). However, this is a very formidable task, since it requires systematic investigations of the surface properties under carefully controlled experimental conditions and accurate characterization of the bulk parameters. In this project, we have examined the relationship between the surface parameters and bulk composition from several aspects. A good qualitative relationship was found between the rate of surface oxidation in air, as measured by the decrease of contact angle, and the S/Fe ratio, as shown in Fig.7. For coal-pyrite in acidic solutions, the decreasing rate of contact angle, i.e., oxidation rate, decreases as the S/Fe increases. This means that highly sulfur-enriched coal-pyrite tends to be oxidized more slowly than purer coal-pyrite having stoichiometry

close to FeS_2 . However, in the neutral pH range, there is no distinct difference between the different coal-pyrites. The oxidation rate also seems to be influenced by the coal/carbon content in the sample, Fig.8. Nevertheless, the ore-pyrites are completely distinct from the coal-pyrites.

FUTURE WORK

The effects of various pretreatment including the grinding media and environment, surface cleaning, etc on the flotation behavior of coal-pyrite are being investigated. It is planned to use advanced surface analytical techniques like ESCA and STM to identify the surface chemicals formed on the pyrite surfaces under different chemical and electrochemical conditions.

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Fig.1 Flotation recovery as a function of solution pH for coal-pyrite (KYPY) and ore-pyrite (PUPY) after surface cleaning by ultrasonication. The floatability of coal (Upper Freeport) is also presented for comparison.

Fig.2 Flotation recovery of PUPY as a function of solution pH and particle size in the presence of ethyl xanthate as collector.

Fig.3 Flotation recovery of KYPY as a function of solution pH and particle size in the presence of ethyl xanthate as collector.

Fig.4 Comparison of floatability of coarse coal- and ore-pyrite particles as a function of pH in the presence of xanthate as collector.

Fig.5 Comparison of floatability of ultrafine coal- and ore-pyrite particles as a function of solution pH in the presence of xanthate as collector.

Fig.6 Comparison of flotation recovery of fine coal- and ore-pyrite particles as function of solution pH in the presence of fuel oil.

Fig.7 Oxidation rate, measured by the reduction rate of contact angle of water droplet on pyrite surfaces in air as function of S/Fe ratio of pyrite.

Fig.8 Oxidation rate of pyrite as function of total coal/carbon content of the pyrite and coal sample.

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