Role of pH and dissolved mineral species in Pittsburgh No. 8 coal flotation system — I. Separation of pyrite and non-pyritic minerals from coal

D. Liu, P. Somasundaran*, T.V. Vasudevan, C.C. Harris
Henry Krumb School of Mines, Columbia University, New York, NY 10027, USA
(Received 15 May 1992; accepted after revision 21 October 1993)

Abstract

The role of pH and of dissolved mineral species on the separation of pyrite and non-pyritic minerals from Pittsburgh No. 8 coal by flotation was investigated. In the pH range of 4 to 8, enhanced pyrite rejection was obtained at higher pH. However, pH itself had no measurable effect on the separation of non-pyritic minerals from coal in the pH range of 4 to 10. The precipitation/adsorption of the dissolved mineral ions resulted in a measurable decrease in the selectivity for non-pyritic minerals separation. Increased pyrite rejection with pH increase was shown, by induction time measurements, to be mainly due to the decrease of the pyrite hydrophobicity. The adsorption of Ca ions in the coal flotation systems had a positive effect on the pyrite separation, although it did not affect coal recovery to a measurable extent. This could be due to the selective precipitation/adsorption of Ca species on the pyrite surface. The precipitation/adsorption of Fe species had no measurable effect on the selectivity, even though it depressed coal flotation considerably. This is attributed to the non-selective precipitation of Fe species between the surfaces of coal and pyrite.

1. Introduction

Use of high sulfur coals as an environmentally acceptable fuel requires near complete removal of pyritic sulfur. Froth flotation that exploits the surface properties of minerals for separation is a promising technique for efficient and eco-

*To whom correspondence should be addressed.
economic removal of pyrite and other ash forming minerals from coal. However, the flotation process currently used in coal preparation plants is a relatively crude process (Osborne, 1988), not being capable of rejecting pyrite to the desirable levels. The separation efficiency of pyrite from coal by flotation is basically determined by the relative hydrophobicities of the coal and the pyrite. To enhance the separation, the surfaces need to be modified appropriately so that the coal surface is more hydrophobic and/or the pyrite surface more hydrophilic. Extensive research work aimed to improve the efficiency of pyrite separation has been done during the past several decades. A number of organic and inorganic reagents have been reported to be good surface modifiers for either coal or pyrite (Choudhry and Aplan, 1992; Klimek, 1992), but the separation efficiency has not reached to the desirable levels.

pH is a parameter commonly used in the study of the surface characteristics of coal and the relative minerals during flotation. The floatability of coal has been found to depend on both the pH and the precipitation of dissolved inorganic species Celik and Somasundaran, 1986; Liu et al., 1994a). Also, the natural hydrophobicity of pyrite has been shown to be very much dependent on pH Kocabag et al., 1990). Zimmerman's work (1948) has demonstrated the significant effect of pH on the separation of pyrite from coal. However, earlier investigations involved the study of the effect of only added salts, and the effect of inorganic species dissolved from the minerals present in coal was not studied in detail. This effect is important since all the high sulfur coals contain high percentage of ash-forming minerals also. Further, in the earlier studies the mechanism of the effect of pH and of its interaction with dissolved mineral species on the separation was not elucidated.

In the present study, the role of pH and the dissolved mineral species on the flotation separation of pyrite and other ash forming minerals from a bituminous coal sample was investigated. The experimental procedure allowed the effect of pH to be isolated from that of the precipitation of dissolved mineral species. Mechanisms of the effect of interactions between pH and the dissolved mineral species on the separation of pyrite and non-pyritic minerals from coal are discussed.

2. Experimental

Coal used in this study is a Pittsburgh No. 8 sample supplied by R and F Coal Co., Ohio. The 2–4 inch sample supplied was crushed to a nominal 1/4 inch size in a laboratory roll crusher under argon atmosphere and the product was stored under argon. The flotation feed was prepared by wet grinding (either in distilled water or in caustic solution) the 1/4 inch sample to 95% passing 200 mesh in a rod mill. Details of the procedures used for the preparation of feed, batch flotation tests and dissolved species analysis are given in Part I (Liu et al., 1994a). Coal–pyrite was obtained from a sample rejected from Pocahontas No. 3 coal by Deister tables, supplied by Island Creek Coal Company, Oakwood, VA. The coal
refuse supplied has a high content of pyrite and was concentrated further by washing, sieving, shaking, and magnetic separation. The 60 x 100 mesh size fraction of the final concentrate contained about 90% by weight of pyrite. This sample was stored under argon atmosphere in a freezer. Before use, the stored sample was washed three times with triply distilled water (TDW) to remove the suspected oxidation products and was ground in TDW. A desirable size fraction obtained from the ground sample was used as coal–pyrite sample for zeta potential and induction time measurements.

Hydrophobicity of coal and coal–pyrite were determined by measuring their induction times using an APT-100 type induction timer. The important device parameters that could have affected the measured induction time were the voltage which controlled the speed of vertical movement, bubble size (fixed at about 1.5 mm diameter), the distance travelled by the bubble (0.2 to 0.3 mm), and the distance between the bubble and the bed of particles (about 0.1 mm). The “induction time” was taken as the contact time for which fifty percent of the contacts were fruitful. A minimum of fifteen measurements (contacts) for each selected contact time was attempted.

The 100 x 140 mesh fractions of the samples of coal, coal–pyrite were used in the induction time measurements. The samples were first washed three times with TDW and then conditioned for ten minutes in a solution at a solid concentration of 10 %. pH was controlled throughout the conditioning time. The conditioned slurry was transferred to a special sample cell for induction time measurements.

Zeta potential of coal and coal–pyrite particles was determined by microelectrophoresis technique using a Pen Kem 501 Lazer Zee Meter. Wet ground minus 200 mesh coal samples and freshly crushed minus 400 mesh coal–pyrite samples were conditioned for ten minutes in either triply distilled water or coal supernatant at a solid concentration of 6.5 % by weight. pH was adjusted using the same procedure as for flotation tests. A fraction containing about 0.05 % by weight of solids of the conditioned slurry was used for zeta potential measurements. In addition to the zeta potential measurements, the electrolyte conductivity of the slurry was also determined using the same equipment. The latter was used in the evaluation of the effect of ionic strength on zeta potential behavior of particles.

3. Results and discussion

In this paper, the results of the flotation tests are presented in the form of selectivity curves, which are plots of the percent pyrite or non-pyritic minerals rejection versus the percent coal substance recovery. Increase in coal substance recovery along the selectivity curve is obtained by increasing the frother dosage, while maintaining the collector dosage and other parameters, such as the pH, the point of addition of sodium hydroxide and the type of coal (washed or unwashed) the same. Increased selectivity is indicated by the shift of the curve towards the upper right hand corner.
3.1. Effect of pH and dissolved ions on pyrite separation

The effect of pH on the efficiency of separation of pyrite from coal under decreasing pH (non-precipitation) and increasing pH (precipitation) conditions is illustrated in Figs. 1 and 2, respectively. It can be seen that between pH 8 and 10 (or 9.2 under non-precipitation conditions), there is no measurable effect of pH on the selectivity. Between pH 4 and 8, on the other hand, enhanced selectivity is obtained at higher pH values under both the precipitation and the non-precipitation conditions. Comparison of the selectivities obtained under the two conditions suggests that for a given coal recovery a slightly higher pyrite rejection can be obtained under the non-precipitation conditions when alkali is added in to the mill (Fig. 3).

The above results suggest that both pH and the precipitation/adsorption of dissolved ions has an effect on the pyrite separation. The favorable effect of pH increase on the selectivity could, at the moment, be attributed to the chemical effects of hydroxyl ions on the hydrophobicity of coal and pyrite and will be discussed later. The effect of precipitation/adsorption of dissolved ions on the selectivity is quite complex in the natural coal-minerals system, although Fig. 3 shows that the selectivity obtained under the non-precipitation conditions is higher than that obtained under the precipitation conditions. The results presented in this figure suggest that both the precipitation/adsorption of dissolved ions and the different pH conditioning times (10 minutes for precipitation conditions, about 100 minutes for non-precipitation conditions) could have an effect on the selectivity.

![Figure 1: Effect of pH on the separation of pyrite from coal under decreasing pH conditions](image)

Fig. 1. Effect of pH on the separation of pyrite from coal under decreasing pH conditions (addition of sodium hydroxide in the mill).
Fig. 2. Effect of pH on the separation of pyrite from coal under increasing pH conditions (addition of sodium hydroxide in the cell).

Fig. 3. Comparison of pyrite rejections obtained under decreasing pH and increasing pH conditions.
3.2. Effect of pH and dissolved ions on non-pyritic mineral separation

Selectivity curves obtained for the separation of non-pyritic minerals from coal under decreasing pH (non-precipitation) and increasing pH (precipitation) conditions are shown in Figs. 4 and 5, respectively. It can be seen that under the non-precipitation conditions there is no effect of pH on selectivity. However, under the precipitation conditions, selectivity decreases with pH increase in the range of pH 4 to 8. This effect is opposite to that observed for selectivity in terms of pyrite rejection.

These results suggest that pH itself has no measurable effect on the selectivity for non-pyritic minerals separation and that the precipitation/adsorption of dissolved ions has a negative effect on the selectivity (Fig. 5). This was attributed to the decrease in the hydrophobicity of the coal due to both the adsorption of the precipitates of metal-hydroxides and the precipitation of the dissolved ions on the coal surfaces, as discussed in Part I.

3.3. Electrokinetic behavior of pyrite

Zeta potential behavior of the coal–pyrite in triply distilled water and in coal supernatant under both increasing pH and decreasing pH conditions is shown as a function of pH in Fig. 6. In the pH range of 5 to 10, the zeta potential of coal–pyrite measured in triply distilled water is the most negative followed by that in the coal supernatant under decreasing pH conditions. The zeta potential of pyrite measured in the coal supernatant under increasing pH conditions is the least negative. Zeta potential of the precipitate of the coal supernatant (obtained in the
Fig. 5. Effect of pH and precipitation on the separation of non-pyritic minerals from coal under increasing pH conditions.

Fig. 6. Zeta potential of coal-pyrite as a function of pH under various conditions.

absence of solids), which is positive at all pH values studied, is also shown in the same figure. Similar to the zeta potential behavior of coal (Fig. 5 in Part 1), the less negative surface of pyrite under the increasing pH conditions can be attributed to the precipitation/adsorption of the species of Fe, Ca and Mg.
The results of zeta potential measurements for pyrite and coal (shown in Fig. 9 and Fig. 5 in Part I, respectively) indicate that coating of the negatively charged particle surfaces with the positively charged precipitates and/or the metal ions or their related ion hydroxide complexes which are expected to occur under the precipitation conditions is not selective between the surface of coal and that of pyrite. Therefore, the reduction of the selectivity for pyrite separation obtained under precipitation conditions in comparison to that for non-precipitation conditions (Fig. 3) can be attributed to the effect of pH conditioning time, and not to the selective precipitation/adsorption of the dissolved ions on the surfaces of coal over those of pyrite. This hypothesis is examined below.

3.4. Isolation of effects of pH and different ions on the separation of pyrite and non-pyritic minerals from coal

Flotation tests to determine the effects of pH and the pH conditioning time on pyrite separation were conducted using washed coal samples to eliminate the effect of dissolved ions, and the results are shown in Fig. 7. As expected, both pH and the pH conditioning time show an effect on the selectivity. Increasing the pH from 4 to 8 results in a substantial increase in pyrite rejection while increase in the pH conditioning time from 10 minutes to 60 minutes increases the effectiveness of the pH modification on pyrite separation. This time effect will be further discussed later. Fig. 8 shows the results of the effects of dissolved Fe$^{2+}$ and Ca$^{2+}$ ions on pyrite separation for washed coal under increasing pH conditions (at pH 8). It can be seen that calcium chloride addition or Ca$^{2+}$ ion adsorption results
in a positive effect on the selectivity, although it does not affect coal recovery to a measurable extent in the Ca\(^{2+}\) concentration range tested. Addition of ferrous chloride, or precipitation/adsorption of dissolved Fe ions, does not affect the selectivity, even though it does depress coal flotation significantly.

3.5. Effect of pH on the hydrophobicity of coal and pyrite

Induction time measurements were carried out to determine the effect of pH on coal and pyrite hydrophobicities\(^*\) and the results are shown in Fig. 9. In the case of coal, the induction time (which is inversely related to hydrophobicity) decreases slightly with pH increase in the pH range of 4 to 7. Above pH 8, the trend is reversed with the induction time increasing measurably with pH increase. Decrease in coal hydrophobicity above pH 8 can be attributed to the ionization of its surface carboxylic groups (Hamieh and Siffert, 1991).

In the case of pyrite, the induction time increases with pH throughout the entire pH range tested (4 to 10) with the steepest increase occurring between pH 6 and 8. Thus, the results of induction time measurements (Fig. 9) suggest that the decrease in pyrite hydrophobicity with pH increase can contribute significantly to the improved pyrite rejection with such pH increase, in the pH range of 4 to 8. The sharp increase in the hydrophobicity of pyrite around pH 6 is attributed to

\(^*\)Pyrite hydrophobicity was measured in the supernatant of the flotation feed to attempt to maintain similar solution conditions.
4. Conclusions

Both pH and precipitation/adsorption of the dissolved mineral ions were found to have an effect on the pyrite separation.

2. Increase of the pH, from 4 to 8, resulted in enhanced pyrite rejection. This was shown, by induction time measurements, to be mainly due to a decrease of pyrite hydrophobicity with pH increase.

3. The adsorption of Ca ions in the coal flotation systems showed a positive effect on the pyrite separation, although it did not affect coal recovery to a measurable extent. This could be due to the selective precipitation/adsorption of Ca species on the pyrite surface. The precipitation/adsorption of Fe species had no measurable effect on the selectivity, even though it depressed coal flotation considerably. This is attributed to the non-selective precipitation of Fe species between the surfaces of coal and pyrite.

4. pH itself has no measurable effect on the separation of non-pyritic minerals from Pittsburgh No. 8 coal in the pH range of 4 to 10. The precipitation/adsorption of the dissolved mineral ions results in a measurable decrease in the selectivity for non-pyritic minerals separation.
Acknowledgement

The authors acknowledge the United States Department of Energy for the financial support (DE-AC22-88PC88878) and Prof. D. W. Fuerstenau of University of California at Berkeley for his helpful suggestions.

References