Role of pH and dissolved mineral species in Pittsburgh No. 8 coal flotation system — I. Floatability of 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 roles of pH and of dissolved mineral species on the floatability of Pittsburgh No. 8 coal was investigated. Isolation of the direct effect of pH from that of the interaction of the dissolved mineral species with OH\(^{-}\) was achieved by the appropriate design of the experimental procedure. The effect of pH on flotation, determined using a washed coal sample, was found to be significant, especially above pH 8, with the floatability falling sharply with pH increase. The effect of interaction of the dissolved mineral species with OH\(^{-}\) depended on the path of approach to the flotation pH. Under the conditions of increasing pH, precipitation/adsorption of Fe, Al, Ca and Mg species occurred, and the effect of interaction was marked with the floatability decreasing with pH increase. This was shown to be mainly due to precipitation/adsorption on the coal surface of dissolved Fe species which were the predominant inorganic species in the supernatant of the coal slurry. Under the conditions of decreasing pH, dissolution of Fe, Ca and Mg species and precipitation of Al species occurred as the pH is lowered, and the effect of the interaction between pH and the dissolved mineral species was marginal.

I. Introduction

Efficient utilization of coals as environmentally acceptable form of fuel requires deep cleaning of coal to removal pyrite and other ash-forming minerals. Froth flotation, which exploits the surface properties of minerals, is recognized as an efficient method for coal cleaning. Deep cleaning of coal by flotation requires enhancing the floatability of coal relative to that of the gangue minerals.

*To whom correspondence should be addressed.

0301-7516/94/$07.00 © 1994 Elsevier Science B.V. All rights reserved
SSDI 0301-7516(93)E0063-Q
The floatability/hydrophobicity of bituminous coal has been shown to be dependent on pH, generally exhibiting a maximum in the neutral pH region (Zimmermann, 1948; Brown, 1962; Celik and Somasundaran, 1986; Ye et al., 1989). Various multivalent cations such as Fe$^{2+}$/Fe$^{3+}$, Al$^{3+}$ and Ca$^{2+}$ have been found to depress coal flotation in the pH region of metal hydroxide precipitation (Ye et al., 1989; Baker and Miller, 1971; Celik and Somasundaran, 1980). Also, adsorption of humic substances on the surfaces of coal and coal-containing minerals was reported to result in a significant decrease in the coal flotation response (Firth and Nicol, 1981; Lai and Wen, 1989). However, the earlier investigations had focussed mainly on the effect of externally added organic and inorganic reagents. The effect of multivalent cations and humic substances dissolved from coal minerals, although very important, has not been adequately understood. Also, the effect of interaction of these species with H$^+$/OH$^-$ from the direct pH effect itself has not been isolated.

In this study, the role of pH and of dissolved mineral species on the floatability of coal was investigated using a sample from Pittsburgh No. 8 seam. Dissolved mineral species analysis and particle zeta potential and solution potential measurements were conducted, and the information obtained was used to explain the mechanism of depression of coal caused by the interaction between pH and the dissolved mineral species.

2. Experimental

2.1. Materials

Coal

Coal used in this study is a Pittsburgh No. 8 seam sample supplied by R and F Coal Co., Ohio. The proximate, ultimate and sulfur forms analyses of this sample are given in Table 1. The 2 to 4 inch sample supplied was crushed to nominal 1/4 inch size in a laboratory roll crushe under argon atmosphere and the product was stored under argon. The flotation feed was prepared by wet grinding (either

<table>
<thead>
<tr>
<th>Ultimate analysis (%)</th>
<th>Proximate analysis and sulfur-forms analysis (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 69.87</td>
<td>Moisture 2.30</td>
</tr>
<tr>
<td>H 5.10</td>
<td>Volatile matter 35.55</td>
</tr>
<tr>
<td>N 1.45</td>
<td>Fixed carbon 51.86</td>
</tr>
<tr>
<td>O 6.40</td>
<td>Ash 12.59</td>
</tr>
<tr>
<td>S 4.58</td>
<td>Sulfatic S 0.28</td>
</tr>
<tr>
<td>Ash 12.60</td>
<td>Pyritic S 2.72</td>
</tr>
<tr>
<td>Heating value, Blt/lb</td>
<td>Organic S 1.64</td>
</tr>
<tr>
<td>12,420</td>
<td>Total sulfur 4.64</td>
</tr>
</tbody>
</table>
in distilled water or in caustic solution) the 1/4 inch sample to 95% passing 200 mesh in a rod mill.

"Washed coal" sample was prepared by washing the wet ground (in distilled water) product three times with distilled water at a solids concentration of 10% by weight.

Coal supernatant used in the tests was obtained from the wet ground (in distilled water) product which was prepared as flotation feed. The coal slurry was centrifuged and filtered to separate the solids and then alkali was added to raise the pH to the desired value.

Reagents
NaOH and HCl were used as pH modifiers and were of ACS Fisher certified grade. Distilled water was used for preparing solutions.

2.2. Methods

Grinding and flotation
A laboratory rod mill was used to prepare minus 200 mesh wet ground feed for flotation. Rod mill dimensions and details of various experimental parameters used are given in Table 2. The ground product from the rod mill was divided into four fractions using a mechanical splitter. Each of these fractions contains about

Table 2
Grinding and flotation experimental conditions

<table>
<thead>
<tr>
<th>Grinding</th>
<th>Flotation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rod mill dimensions</td>
<td>Denver D1</td>
</tr>
<tr>
<td>Rod dimensions</td>
<td>12.5 cm X 12.5 cm X 15 cm</td>
</tr>
<tr>
<td>Number of rods</td>
<td>1200 rpm</td>
</tr>
<tr>
<td>Feed</td>
<td>2 X 2</td>
</tr>
<tr>
<td>Grinding medium</td>
<td>38 rpm</td>
</tr>
<tr>
<td>Mill speed</td>
<td>4 lit./min.</td>
</tr>
<tr>
<td>Grinding time</td>
<td>6.25% wt.</td>
</tr>
<tr>
<td>Product</td>
<td>12 minutes</td>
</tr>
<tr>
<td>Flotation machine</td>
<td>5 minutes</td>
</tr>
<tr>
<td>Flotation cell dimensions</td>
<td>Conditioning time</td>
</tr>
<tr>
<td>Impeller speed</td>
<td>10 minutes</td>
</tr>
<tr>
<td>Number of paddles</td>
<td>Conditioning time</td>
</tr>
<tr>
<td>Paddle speed</td>
<td>15 minutes</td>
</tr>
<tr>
<td>Air flow rate</td>
<td>Conditioning time</td>
</tr>
<tr>
<td>Solid concentration</td>
<td>Conditioning time</td>
</tr>
<tr>
<td>Conditioning time</td>
<td>Conditioning time</td>
</tr>
<tr>
<td>Flotation time</td>
<td>Conditioning time</td>
</tr>
</tbody>
</table>
125 grams of solids and 375 ml of water. This sample was stored/aged in air for about one hour, and thereafter was used as flotation feed.

Flotation tests were conducted in a Denver D-1 flotation machine with a two liter cell and provisions for mechanical froth removal and air flow control. The aged coal slurry was diluted with distilled water into 1800 ml. The slurry was agitated for two minutes prior to the addition of the reagents. Following the preconditioning, a known amount of frother was added and the slurry was agitated for one minute after which a specified amount of collector was added. Conditioning with the reagents will be continued until the total conditioning time, including the preconditioning time, of twelve minutes is reached. Flotation will then be carried out for five minutes. Details of flotation machine parameters and other pertinent variables are also given in Table 2.

**Particle zeta potential and solution potential**

Zeta potential of coal particles was determined by microelectrophoresis technique using a Pen Kern 501 Lazer Zee Meter. $E_h$ of the coal slurry was measured using a Pt electrode with silver/silver chloride as the reference electrode. For comparison purpose, the Eh of coal slurry was also measured by employing standard calomel electrode (SCE) as reference. All potentials quoted are given on the standard hydrogen (SHE) scale.

**Solution potential measurements**

Electrode potential ($E_h$) of the coal slurry was measured under flotation conditions (just after the conditioning stage) using a platinum electrode with a silver/silver chloride electrode as the reference. All potentials quoted are in reference to the standard hydrogen electrode (SHE).

**Dissolved mineral species analysis and pH control**

A Perkin-Elmer ICP/6500 Inductively Coupled Plasma spectrophotometer was used to measure the concentrations of dissolved multivalent cations. For dissolved organic species, a Dohrmann DC-90 Total Organic Carbon Analyzer was used. The desired pH was achieved by adding NaOH solution either in flotation cell during conditioning or adding NaOH solution with dry coal sample in the mill before grinding.

3. Results and discussion

It is found, during the preliminary tests of this study, that the coal slurry prepared as flotation feed has an equilibrium pH of about 4, and contains a considerable amount of dissolved ions. These dissolved ions can undergo reactions when pH is subjected to any change. In order to identify the direct effect of pH from that of the interaction of pH with the dissolved ions, two different pH controlling methods, *increasing pH* method (NaOH addition in cell) and *decreasing pH* method (NaOH addition in mill), were used in this study.
Effect of pH and the point of sodium hydroxide addition on coal flotation

Floatability of natural coal

The effect of pH on coal flotation recovery, under conditions of sodium hydroxide additions in mill and in cell, is shown in Fig. 1. The sodium hydroxide consumptions for each pH under both the NaOH addition conditions are given in Table 3. When sodium hydroxide is added in the mill, there is a marginal increase of flotation recovery with pH in the acidic pH range (pH 4 to 7) and

![Graph](image)

Fig. 1. Comparison of effects of sodium hydroxide addition to the mill and to the cell on coal flotation recovery.

Table 3
NaOH consumption as a function of pH under various conditions (grams of NaOH per 100 grams coal, or equivalent to that)

<table>
<thead>
<tr>
<th>Unwashed coal NaOH in cell</th>
<th>Unwashed coal NaOH in mill</th>
<th>Washed coal NaOH in cell</th>
<th>Coal supernatant NaOH in cell</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>g NaOH</td>
<td>pH</td>
<td>g NaOH</td>
</tr>
<tr>
<td>4.0</td>
<td>0.00</td>
<td>4.0</td>
<td>0.00</td>
</tr>
<tr>
<td>5.0</td>
<td>0.18</td>
<td>4.8</td>
<td>0.30</td>
</tr>
<tr>
<td>6.0</td>
<td>0.47</td>
<td>5.2</td>
<td>0.50</td>
</tr>
<tr>
<td>7.0</td>
<td>0.58</td>
<td>6.3</td>
<td>0.65</td>
</tr>
<tr>
<td>8.0</td>
<td>0.69</td>
<td>7.5</td>
<td>0.70</td>
</tr>
<tr>
<td>8.0</td>
<td>0.70</td>
<td>8.0</td>
<td>0.75</td>
</tr>
<tr>
<td>10.0</td>
<td>0.84</td>
<td>9.2</td>
<td>0.80</td>
</tr>
</tbody>
</table>

[10.0 | 0.90]
relatively sharp decrease between pH 8 and 10. However, it was discovered during this study that the flotation behavior changes drastically when the point of addition of sodium hydroxide was changed from the mill to the cell. When sodium hydroxide is added into the cell, the flotation recovery decreases with pH increase throughout the entire pH range tested. Thus, in this case the coal surface is rendered more hydrophilic with pH increase than when alkali was added into the mill. This suggests that a factor, possibly related to the presence of dissolved mineral species in the flotation systems, could be responsible for the differences between the two reagent addition schemes: sodium hydroxide addition into the cell, and into the mill.

**Floatability of washed coal**

In this case, a washed coal sample was used as flotation feed to eliminate the effect of dissolved mineral species. The concentrations of Fe, Al, Mg and Ca ions in the flotation system, determined by ICP analysis, were all less than $10^{-4}$ g atoms/liter in the whole pH range investigated. The effect of pH on the flotation recovery of washed coal under the conditions of NaOH additions in cell is given in Fig. 2; the sodium hydroxide consumptions for each pH are given in Table 3. For comparison purposes, the coal flotation recovery obtained for unwashed coal under similar conditions is also presented in Fig. 2. It can be seen that the coal recovery versus pH curve obtained for washed coal differs significantly from that for the natural coal obtained under similar conditions (addition of the alkali in cell). Interestingly, it was found that the recovery curve obtained by adding the alkali into cell for washed coal is similar to the curve obtained by adding the alkali

![Fig. 2. Effect of pH on the floatability of washed and unwashed coals for sodium hydroxide addition in the cell.](image-url)
into mill for natural coal (Fig. 1); these effects will be discussed later. It should be mentioned that the observed flotation behavior of washed coal agrees with the results (Zimmermann, 1948; Brown, 1962; Celik and Somasundaran, 1986) obtained earlier for the pH effect on coal floatability. The decrease in coal flotation recovery with pH increase in the alkaline pH range is mainly attributed to the ionization of surface carboxylic groups (Baker and Miller, 1968; Campbell and Sun, 1970; Wen and Sun, 1977; Jessop and Stretton, 1969; Hamieh and Siffert, 1991). The flotation behavior of natural coal observed in this study has not been reported before, and hence it deserves to be studied further.

3.2. Interaction between pH and dissolved mineral ions

Release of mineral species as a function of pH and point of NaOH addition

To investigate whether the dissolved mineral species present in the systems play a role in determining the floatability of natural coal, the relationship between pH and dissolved mineral species in the supernatant of the coal slurry was investigated. It was found that the pH of the natural coal slurry reached an equilibrium at pH about 4, and that a significant amount of dissolved multivalent metal ions were present in the natural coal slurry. Fig. 3 shows that the concentrations of the predominant dissolved mineral species in the ground slurry prepared as flotation feed under the two different schemes of alkali addition are function of pH. It can be seen that the concentrations of dissolved Fe, Al, Mg and Ca species are very much dependent on equilibrium pH, but not much on the point

![Fig. 3. Concentration of dissolved mineral species as a function of pH for sodium hydroxide addition in mill and cell.](image-url)
of addition of sodium hydroxide. Also, the concentrations of dissolved Fe, Ca, and Mg species, which are predominant in the supernatant, do decrease with pH increase. This suggests that in the pH range of 4 to 10, if the pH is adjusted to increase there will be precipitation of metal ion species whereas if the pH is adjusted to decrease there will be dissolution of mineral species. It should be mentioned that the amount of dissolved organic species, especially humic substance which has been reported to be released from oxidized coals (Firth and Nicol, 1981; Lai and Wen, 1989), is found to be negligible under the experimental conditions used for this study.

Point of sodium hydroxide addition on pH–time curve

The changes in pH of the coal slurry, under conditions of sodium hydroxide addition in the mill and in the cell, during the sequence of grinding, aging of the ground slurry, conditioning (with alkali and reagents) and flotation are shown as a function of time in Fig. 4. This figure shows the pH versus time curve for a specific case in which the flotation pH was 8, but the trend was the same for all pH values. It can be seen from this figure that the path of approach towards the flotation pH strongly depends on the point of sodium hydroxide addition (mill or cell).

When sodium hydroxide is added in the mill, the pH of the slurry decreases during grinding and remains constant during aging of the slurry, conditioning (with reagents) and flotation. By varying the amount of sodium hydroxide added, different final pH's were achieved. In this case, the slurry is subjected to pH change only in the decreasing pH direction. On the other hand, when grinding is carried out in distilled water the pH of the slurry drops from 6.2 to about 4 which is the lowest value in the pH range tested in this study (pH 4 to 10). Therefore, when
sodium hydroxide is added in the cell the slurry will be subjected to a pH change in the increasing pH direction which, as explained earlier, can cause precipitation to occur, and this can affect mineral surface properties and their flotation behavior.

3.3. Electrokinetic behavior of coal

Flotation results obtained under increasing pH and decreasing pH conditions, and also those with washed coal, suggested that reduction in the floatability of coal under precipitation conditions is due to precipitation/adsorption of the metal ions and/or their hydroxides on the coal surface. To investigate this further, zeta potential studies of coal were conducted under different conditions.

Zeta potential behavior of washed coal and, of unwashed coals under both increasing pH and decreasing pH conditions, is shown as a function of pH in Fig. 5. The isoelectric point is around pH 4.5 for both the natural and the washed coal. In the pH range of 5 to 10, the zeta potential of washed coal under increasing pH conditions is the most negative followed by that of unwashed coal under decreasing pH conditions. The zeta potential of unwashed coal under increasing pH conditions is the least negative. Zeta potential of the precipitate, obtained by raising the pH of the coal supernatant from the natural pH value of about 4 to the desired value, is found to be positive throughout the entire pH range tested (Fig. 5). Coating of negative coal surface with the positively charged precipitates and/or with the metal ions or their relative ion complexes accounts for the less negative zeta potential obtained with unwashed coals compared to that of the washed coal. The less negative surface of coal under increasing pH conditions is attributed to the precipitation of Fe, Ca and Mg species.

Fig. 5. Zeta potential of coal as a function of pH measured under various conditions
3.4. Nature of precipitation/adsorption of the dissolved mineral ions

Precipitation in the presence of and the absence of solids

Precipitation studies were conducted both in the presence and in the absence of solids. In the latter case, the slurry from the rod mill was centrifuged and filtered to separate the solids and then alkali was added to raise the pH to the desired value. Fig. 6 shows the concentration of dissolved species as a function of pH in the presence and absence of solids under increasing pH conditions (sodium hydroxide added in cell). It can be seen that the presence of solids has no detectable effect on the concentration of Fe, Mg and Al species, whereas there is a significant decrease in calcium concentration above pH 6. This suggests that, in addition to surface precipitation/adsorption, adsorption of bulk precipitates occurs in the case of Fe, Mg and Al species, while in the case of Ca species surface precipitation is the mechanism by which the solids are coated.

Precipitation/adsorption of Fe species

The results obtained from measurements of the potential of coal slurry under the precipitation conditions are shown in an Eh-pH equilibrium diagram for Fe-H₂O system (Fig. 7). Since the precipitation of dissolved Fe ions is recognized as a bulk precipitation, the $E_0$-pH diagram for Fe-H₂O system, established based on thermodynamic calculations (Stumm and Morgan, 1981), is used to determine the states of dissolved Fe ions as well as their precipitates present in coal flotation systems. As shown in Fig. 7, the potential of coal slurry decreased dramatically with pH increase in the pH range of 5 to 8, which is just the precipita-
tation pH range for Fe$^{2+}$ species. Therefore, this decrease in potential could be explained as a result of oxidation of Fe$^{2+}$ to Fe$^{3+}$ during the precipitation, which took charges from the liquid phase. The reaction involved in Fe species precipitation is given as following:

$$\text{Fe}^{2+} + 3\text{OH}^- = \text{Fe(OH)}_3 + e^-$$

Therefore, it is concluded that the dissolved Fe species in coal slurry are mainly in the form of Fe$^{2+}$ and the precipitate from the Fe$^{2+}$ is in the form of Fe(OH)$_3$. It should be mentioned that although the precipitation of Fe species could be characterized as bulk precipitation, surface precipitation/adsorption of the species on the surface of coal is also expected to occur under the coal flotation conditions. In addition to surface precipitation, the bulk precipitate of Fe(OH)$_3$ can adsorb on the surface of coal, and render coal particles hydrophilic.

### 3.5. Effects of various dissolved mineral species on coal flotation

**Effect of different mineral species on the floatability of coal**

The relative change in the floatability* of coal as a function of pH (Fig. 8A) is compared with the extent of overall precipitation as well as those of different species (Fig. 8B). It can be seen that Fe species is the predominant component

---

*Relative change in floatability due to precipitation = floatability of washed coal (precip. conditions) - floatability of unwashed coal (precip. conditions).
Fig. 8. Effect of different dissolved mineral ions on the floatability of coal

The role of Fe$^{2+}$ ions precipitation on coal flotation is examined further by testing the effect of added FeCl$_2$ on the floatability of washed coal under precipitation conditions (at a flotation pH of 8). As shown in Fig. 9, coal floatability decreased significantly with Fe$^{2+}$ addition/precipitation. The addition of $5 \times 10^{-3}$ M Fe$^{2+}$ (concentration in the natural coal slurry) resulted in a decrease in coal recovery from about 82% to 42%. Comparison of this result with those of the effect of the precipitation of dissolved mineral species (Fig. 2) suggests the precipitation of dissolved Fe$^{2+}$ species to be a major reason for the drastic depression of coal flotation.
4. Conclusions

By conducting studies with unwashed and washed coals, the direct effect of pH was isolated from that of the OH\textsuperscript{-} interaction with dissolved mineral species.

2. The effect of pH, determined using a washed coal sample, was found to be not very significant between pH 4 and 8, increasing only marginally with pH increase. Above pH 8, the floatability decreased significantly.

3. The effect of interaction of OH\textsuperscript{-} with the dissolved mineral species was found to be dependent on the path of approach to the flotation pH. Under decreasing pH conditions the effect of the interaction, which resulted in precipitation of Al hydroxides and dissolution of Fe, Ca and Mg species, caused only a marginal decrease in floatability. Under increasing pH conditions, the effect of interaction was found to be substantial in the pH region of 4 to 10 which corresponded to precipitation/adsorption of Fe, Ca, Mg and Al species with the effect of Fe species being predominant.

4. Zeta potential studies suggested that metal hydroxide precipitates can coat the surface of coal and thereby reduce its hydrophobicity. Analysis of dissolved species carried out in the presence and absence of solids showed that in the case of Fe species the mechanisms of coating were not only the surface precipitation, but also the adsorption of bulk precipitates, whereas in the case of Ca species it was surface precipitation.
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 helpful suggestions.

References