The Effect of Multivalent Ions on the Flotation of Coal

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Abstract

Flotation of coal generally exhibits a maximum around neutral pH. This maximum, despite the marked mineralogical heterogeneity, has been attributed to the isoelectric point of the coal in this pH region. The results obtained in this study demonstrate the important role of multivalent ions in determining the pH dependence of flotation. Ca, Fe, and Al electrolytes are found to depress coal in the pH region of metal hydroxide precipitation. Adsorption tests as a function of pH show coal to adsorb the multivalent ions in a manner similar to oxides. The data obtained here are examined in terms of possible surface and bulk precipitation of metal hydroxide species on coal surfaces.

INTRODUCTION

Flotation mechanisms of coal have not been properly elucidated, mainly because of the complex heterogenous nature of coal and its tendency to undergo surface modifications when exposed to various environments. Variation of pH is a commonly used technique to study the surface characteristics of coal during its flotation. Flotation of coal has been shown to exhibit a maximum in the neutral pH region (1), and this behavior has been attributed in the past to variations in the electrokinetic characteristics of coal (2-4). The point of zero charge was proposed to correspond to the pH of maximum flotation. This view, on the other hand, has been criticized by others (5, 6). Multivalent species of Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Al^{3+}, etc. are often present in coal supernatants, and since the nature of the species can be strongly dependent on pH, the role of these ions in determining the flotation behavior of coal was

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investigated by conducting coal flotation as a function of pH in various electrolytes.

EXPERIMENTAL

Flotation of 50 × 100 U.S. Mesh bituminous coal (Pittsburgh coal, 16.4% ash content, see Table 1), was determined using a 120-cm³ column cell (2.2 cm × 8 cm) with perforated bottom for passage of gas and a magnetic stirrer. The taller design helped minimize levitation due to mechanical entrapment of the coal particles.

The coal prepared using a roll crusher was sieved to obtain the required size fraction and then kept in a sealed plastic bag. One gram samples of coal were conditioned in 120 cm³ of solution containing the desired chemicals for 20 min and floated with methylisobutylcarbinol (MIBC) till completion using nitrogen at a flow rate of 39 cm³/min. Use of MIBC at low concentrations at both low and high pH values produced inadequate froth. Thus a high concentration of MIBC, 80 mg/L, was employed throughout the pH region studied.

In most cases flotation was complete in less than a minute. It is to be noted that the samples were not deslimed prior to flotation in these tests to avoid loss of released ions during such an operation. Coal of −400 mesh was prepared in an agate mortar to minimize contamination problems in adsorption tests. The specific surface area of this sample as measured by N_2 adsorption was found to be 5.1 m²/g.

The residual concentration of calcium after adsorption was followed by using labeled Ca-45 compound in conjunction with a Beckman

TABLE 1
Analysis of the Coal Sample

Constituent	Ultimate analysis (%)		Proximate analysis (%)	
	As received	Dry basis		
C	69.37			
H	4.64		Moisture	1.34
N	1.29		Volatile matter	33.67
O	—			
S	2.61		Fixed C	48.82
Ash	16.19		Ash	16.17
Heating values, Btu/lb	12,393			

scintillation counter. While the released iron was measured by atomic absorption, the released and adsorbed aluminum were measured by colorimetry using aluminon at 535 nm. All chemicals used in this study were of ACS Fisher certified grade, and solutions were prepared using triple distilled water.

RESULTS AND DISCUSSION

The amount of iron and aluminum released from coal as a function of pH is given in Fig. 1. As expected, the amount of released iron is found to increase substantially with a decrease in pH below about pH 6. The concentration of iron remained at a level of less than 1 ppm above pH 6. It should be noted, however, that our chemical analysis does not distinguish between various dissolved forms of iron though they can be easily calculated from the chemical equilibria. Interestingly, the release of aluminum, though not at a comparable level, showed a minimum around the neutral pH region. As much as 8 and 7 ppm aluminum were measured at pH 1 and pH 13, respectively.

The results obtained for the adsorption of aluminum and calcium as a function of pH are given in Fig. 2. Uptake of calcium increases slightly with pH up to about pH 8 and then sharply above that value. Uptake of aluminum, on the other hand, exhibits a sharp increase over a narrow pH range of 3 to 5. This adsorption behavior is similar to that observed for the uptake by oxides in general (7-9) and appears to be governed by the formation of $CaOH^+$ or $AlOH^{2+}$. The similarity in adsorption could be the result of the oxidized nature of the coal surface. Since these, as well as the presence of various oxide and silicate minerals, constitute more than 16% of the coal in the present case, calcium adsorption can be significantly influenced by the uptake of minerals present on the surface of the coal particle. Oxidation, which increases the hydrophilicity of coal, can further increase the adsorption of multivalent ions on coal.

At constant pH, calcium adsorption increases with an increase in temperature. This can be attributed to the enhanced solubility of coal which in turn gives rise to a larger number of hydroxyl ions for reaction at the surface. The adsorption of octylhydroxamate on hematite has been reported to exhibit a similar temperature effect (10).

Results obtained for the flotation of coal in different electrolytes are given in Fig. 3 as a function of pH. In the absence of any added salt, the maximum hydrophobicity is found to occur around the neutral pH region. Note that the solid line passes through the points representing the absence of any salt. While there is a slight change in flotation in the pH
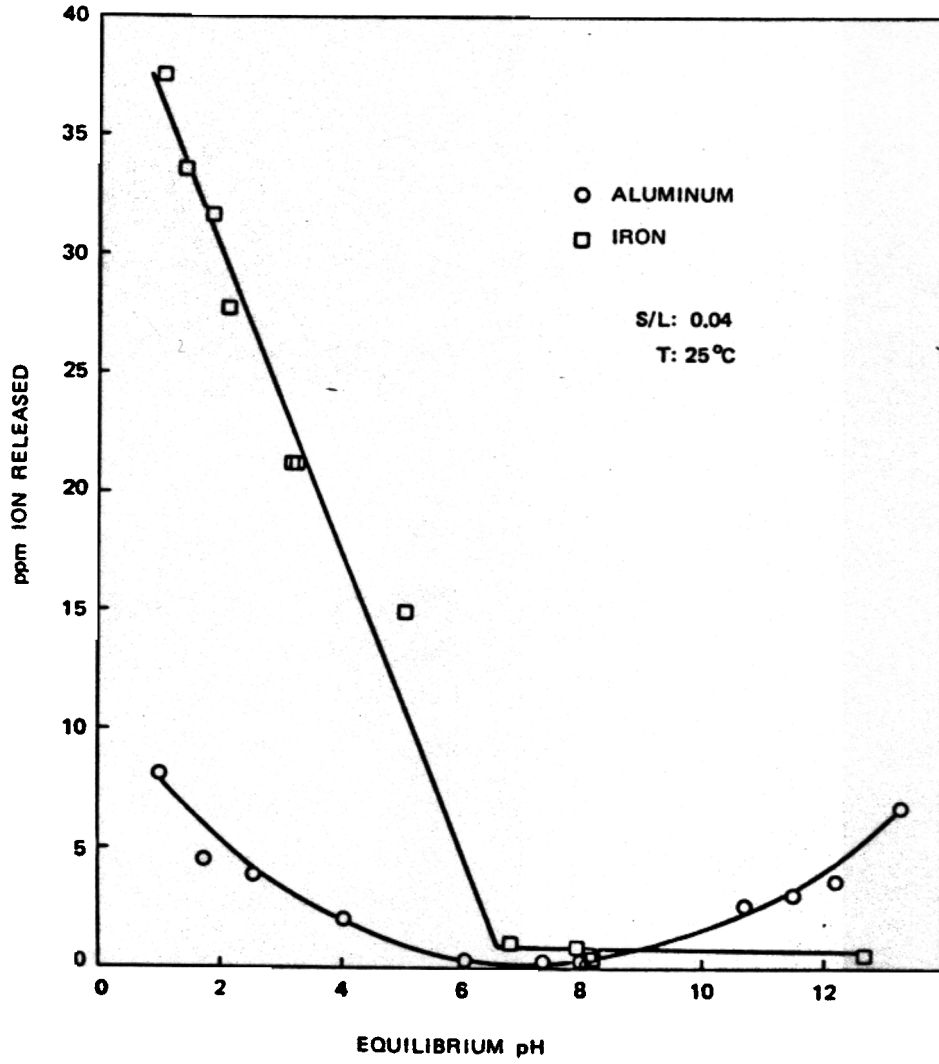
FIG. 1. The amount of iron and aluminum released upon conditioning coal in varying pH
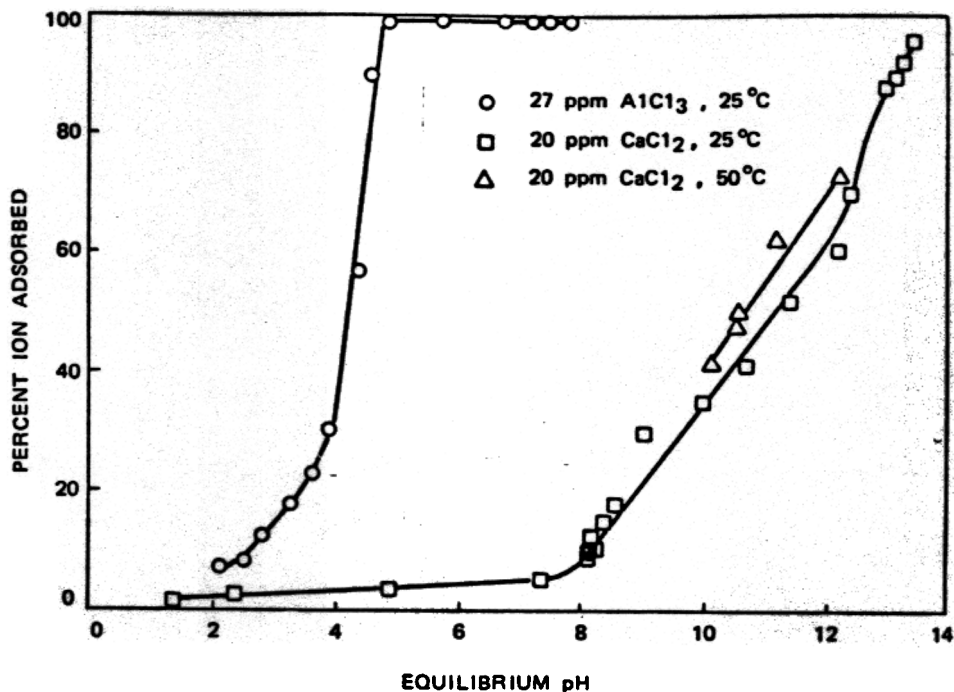solutions.

FIG. 2. Abstraction of calcium and aluminum from coal (S/L: 0.04).

range of 2 to 10, there is a marked decrease in flotation beyond both extremes. This behavior is in agreement with the reported literature data (11, 12).

Addition of NaCl was found to produce no appreciable change except possibly in the acidic region where flotation increased slightly. This is in accord with the literature data where much higher NaCl concentrations were found to be required for improved salt flotation (13). The effect of CaCl₂ is similar to that of NaCl in the alkaline region where calcium forms hydroxy complexes. However, since flotation decreases sharply between pH values of 9 to 10, changes in percent recovery become highly insensitive, and thus the effect of calcium is largely masked.

The effect of other hydrolyzable multivalent ions present in coal was next tested to examine further the role of hydroxy complexes in the region of flotation maximum. Results obtained in the presence of FeCl₃ and AlCl₃ are shown in Fig. 4 in which % floated is plotted versus the
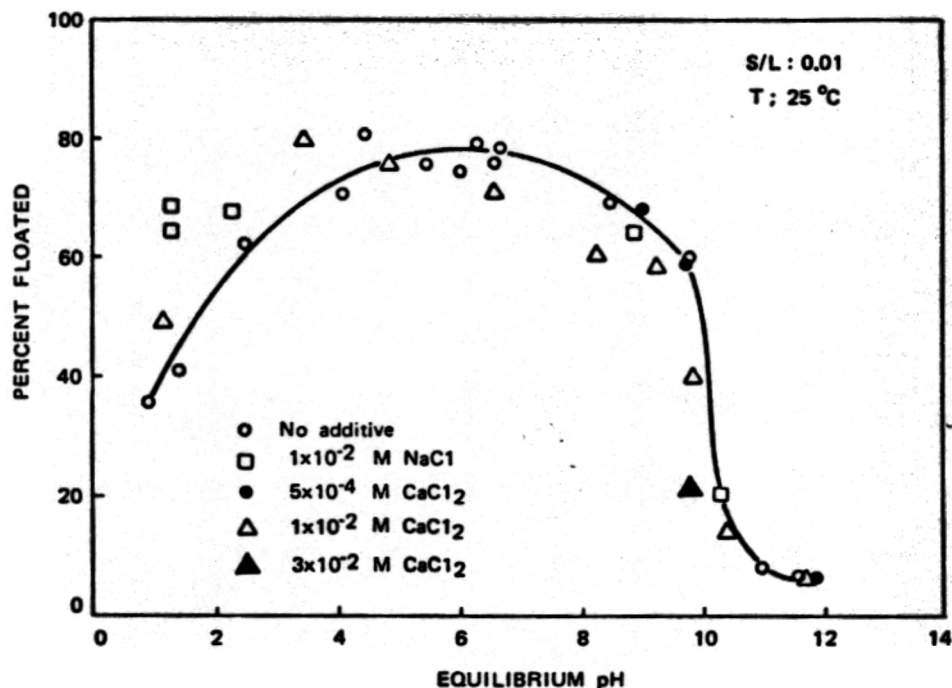
FIG. 3. Flotation of coal versus equilibrium pH under various conditions (MIBC concentration: 80 mg/L).

equilibrium pH. Interestingly, flotation in the presence of $FeCl_3$ goes through a minimum at about pH 2.5 where maximum amounts of $FeOH^{2+}$ and $Fe(OH)_2^+$ are expected to form (14). At higher pH values the flotation dependence on pH was similar to that obtained in NaCl solutions.

Flotation of coal in $AlCl_3$, as shown in Fig. 4, also exhibits an interesting behavior. Above the descending branch of the curve in the alkaline region, the % coal floated shifted to lower pH values with the addition of $AlCl_3$. It is to be noted that this decrease in flotation correlates with the formation of hydroxy complexes of aluminum (14). Even though the concentration of these species is negligible above pH 10, since the flotation in the absence of any $AlCl_3$ is also nil, any effect of $AlCl_3$ in this region is masked.

Flotation results along with adsorption data clearly suggest that adsorption of multivalent species can affect the hydrophobicity of coal
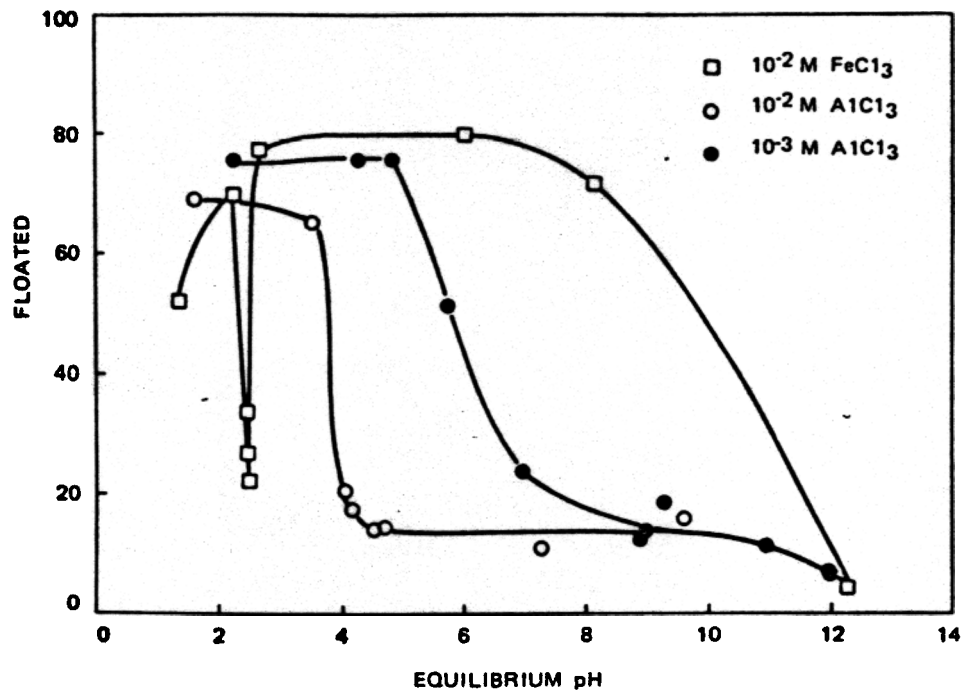
FIG. 4. Flotation of coal as a function of equilibrium pH in the presence of $FeCl_3$ and $AlCl_3$ (S/L: 0.01, T: 25°C).

significantly and, in turn, its flotation. A remarkable correlation obtained in this study is between the flotation of coal and the precipitation of metal hydroxy complexes. It is suggested, however, that as the precipitate can first nucleate on the surface, depression of flotation is possibly caused by surface modifications due to such surface precipitation.

Free Energy of Adsorption of CaOH⁺ on Coal

James and Healy (15) considered the surface precipitate, which is more soluble than the bulk precipitate, to occur at pH values below bulk precipitate formation. The possibility of such surface precipitation, considering free energy changes involved in the adsorption process, is examined below using adsorption of $CaOH^+$ on coal as an example. The reason for the choice of calcium is due to the formation of simple

hydrolysis products in the pH region of approximately 10 to 12. The contribution of each free energy change involved in the above system is calculated with the aim of identifying the mechanism responsible in the adsorption process.

The driving force for adsorption, ΔG°_{ads}, in this system can be considered to be the sum of a number of contributing forces and can be expressed as

$$\Delta G^{\circ}_{ads} = \Delta G^{\circ}_{coul} + \Delta G^{\circ}_{solv} + \Delta G^{\circ}_{chem} \tag{1}$$

where ΔG°_{coul} is the free energy change due to the coulombic forces, ΔG°_{solv} is the free energy change in desolvating an ion and displacing the interfacial water and ΔG°_{chem} is the specific chemical interaction term. It should be noted that specific adsorption of ions into the inner Helmholtz plane (IHP) can take place only if the net free energy for the process is negative. The free energy change of adsorption (ΔG°_{ads}) for $CaOH^+$ on coal can be calculated by means of Grahame equation

$$\Delta G^{\circ}_{ads} = -RT \ln \frac{\Gamma_{CaOH^+}}{2r_{CaOH^+}c_{b_{CaOH^+}}} \tag{2}$$

$$r_{CaOH^+} = r_{Ca} + 2r_{H_2O} = 3.7 \times 10^{-10} \text{ m} \tag{3}$$

where Γ_{CaOH^+} is the adsorption density of $CaOH^+$ in terms of unit area, r_{CaOH^+} is the thickness of the hydrated adsorbed layer, c_b is the bulk concentration of the adsorbate, and R and T are the gas constant and the absolute temperature, respectively. At pH 12 and $5 \times 10^{-4} M$ added $CaCl_2$ concentration (see Fig. 2), the ΔG°_{ads} is found to be -19.3 kJ/mol. The free energy of adsorption for the dextrose monomer/coal system, which involves hydrophobic bonding, has been reported to be -23 kJ/mol (16).

The coulombic interaction term given by

$$\Delta G^{\circ}_{coul} = zF\Delta\psi_x \tag{4}$$

can be either positive or negative depending on the sign of $\Delta\psi_x$ which is the difference between the bulk and IHP of the double layer. The formulas required to solve Eq. (4) are

$$\Delta\psi_x = \frac{2RT}{zF} \ln \left[\frac{(u+1) + (u-1)e^{-kx}}{(u+1) - (u-1)e^{-kx}} \right] \tag{5}$$

$$u = e^{[zFv_0/2RT]} \qquad (6)$$

$$\psi_0 = \frac{2.3RT}{zF}(pH_{zpc} - pH) \qquad (7)$$

$$k = 0.328 \times 10^{10} \, (I)^{0.5} \, m^{-1} \qquad (8)$$

$$x = (r_{ion} + 2r_{H_2O}) \, m \qquad (9)$$

$$z = 1 \qquad \text{(for 1:1 electrolyte)}$$

ΔG°_{coul} as calculated from Eq. (4) is -16.8 kJ/mol.

James and Healy (8) gave evidence supporting the assumption that there is at least one layer of water molecules between solid and ion. These authors proposed a model for desolvation where removal of the secondary hydration sheath of the ion is considered; this is because the complete stripping of an ion is energetically prohibitive. The equation used by the authors is a modified form of the Born equation:

$$\Delta G^{\circ}_{solv} = \left[\frac{z^2 e^2 N^2}{16\pi\varepsilon_0}\right]\left[\frac{1}{r_{ion} + 2r_{H_2O}} - \frac{r_{ion}}{2(r_{ion} + 2r_{H_2O})^2}\right]\left[\frac{1}{\varepsilon_{int}} - \frac{1}{\varepsilon_b}\right]$$

$$+ \left[\frac{z^2 e^2 N}{32\pi\varepsilon_0} \frac{1}{r_{ion} + r_{H_2O}}\right]\left[\frac{1}{\varepsilon_s} - \frac{1}{\varepsilon_{int}}\right] \qquad (10)$$

where $\varepsilon_{int} = 6$ when $\psi \neq 0$, $\varepsilon_b = 78.5$, and $\varepsilon_s = 4.3$. Using Eq. (10), ΔG°_{solv} is calculated to be 15.4 kJ/mol.

The only unknown in Eq. (1) is the ΔG°_{chem} term which can be calculated as

$$\Delta G^{\circ}_{chem} = -19.3 + 16.8 - 15.4 = -17.9 \, kJ/mol$$

The magnitude of ΔG°_{chem} obtained in this study is similar to the results reported by Dugger et al. (17). The calculated value of -17.9 kJ/mol seems to be higher than the magnitude required for hydrogen bonding. This leads to the conclusion that depression of coal is probably not achieved through the specific adsorption of $CaOH^+$ alone. In fact, it may be interesting to consider a combination of mechanisms including surface precipitation of hydroxy complexes.

Implications of the effects of multivalents and their precipitation in flotation is to be noted since coal pulp water can contain significant

amounts of such dissolved species. Adsorption or precipitation of these multivalent ions, particularly when in the form of hydroxy complexes, can apparently render the surface of the coal hydrophilic and consequently depress its flotation.

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