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Flotation of Metals from Acid-Digested Coal Ash

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Abstract

Adsorptive bubble techniques are used for the simultaneous separation of the metal cations of Cu, Co, Ni, Mn, Fe, Pb, Zn, V, Al, and Cr from acid-digested coal ash. Recovery of the elements is achieved through the addition of sulfide ion and careful adjustment of the solution pH.

INTRODUCTION

Coal is the most abundant nonrenewable energy resource in the world. Therefore, as oil and natural gas have become increasingly expensive and generally less available, more emphasis has been placed on the burning of coal in the generation of electricity. In 1978, coal consumption in power plants in the United States was approximately 481 million tons (*1*), and some estimate that by 1985 as much as 2 billion tons of coal may be burned annually to produce electricity in the United States (*2*). Such large-scale use of coal has resulted in the production of equally staggering amounts of coal wastes: approximately 68.2 million tons in 1978 (*1*) and an estimated 200 million tons by 1985 (*2*).

This continued growth in coal usage presents a unique problem in waste

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disposal. Of the 48.8 million tons of fly ash produced in 1978, only about 15.4% was put to some productive use, mainly in the construction industry or in soil stabilization (*1*). Coal contains practically every naturally occurring element, and elements that have a strong positive effect in one method of disposal, e.g., in use as a fertilizer, may have a deleterious effect if emitted to the atmosphere or used as landfill. In addition to the toxic elements such as chromium, arsenic, barium, and lead, the wastes contain relatively large amounts of aluminum and iron as well as smaller quantities of copper, cobalt, and nickel. Thus coal wastes may also be viewed as a valuable resource and under certain conditions may present a unique opportunity for the recovery of metals. Currently, attempts are being made to recover metals such as aluminum and iron from waste materials. Techniques under investigation include acid digestion or leaching, sintering processes, magnetic separation of iron oxide, and high temperature chlorination (*1*).

During the past decade our research group has successfully applied adsorptive bubble techniques for the concentration and separation of a variety of elements from seawater and chemically treated ferromanganese nodules and their process tailings (*3–5*). Both adsorbing colloid flotation using hydroxy complexes and precipitate flotation of sulfides have been employed to quantitatively remove the elements of interest. As the chemical composition of coal ash is similar to that of ferromanganese nodules, a study was undertaken to determine whether adsorptive bubble techniques could be applied for the simultaneous separation of several metal cations from acid-digested coal ash. This communication reports the results of this investigation.

EXPERIMENTAL

Apparatus and Equipment

The atomic absorption analyses were performed on a Perkin-Elmer Model 2380 Spectrophotometer. The pH of the solutions was measured with an Orion Digital Ionanalyzer Model 801A which was calibrated with standard buffer solutions. The 200-mL flotation cell employed in this study was a modification of a cell previously described by Kim and Zeitlin (*6*).

Reagents

Analytical grade reagents were used throughout the study. The water used in solution preparation and dilution was obtained from a Millipore Model

Milli R/Q ion exchange and reverse osmosis water purifier. A solution of 5.0 mg/mL cetyltrimethylammonium chloride (CTA) was prepared by dissolving 1.0 g of the surfactant (50% in ethanol) in 100 mL of ethanol. Concentrated and dilute solutions of HNO_3, HCl, and NaOH were used as necessary for pH adjustment and dissolution of the floc. Standard solutions of appropriate concentrations for atomic absorption analyses were prepared by dilution of 1000 μg/mL standards.

Procedure

The coal ash was obtained by burning 50.0 g of coal under controlled conditions that minimized the loss of fly ash. The 5 g of coal ash produced was bomb-digested using a modification of the technique described by Bernas (*7*). The bomb-digested solution was diluted with a saturated solution of boric acid to prepare a standard coal ash solution of 25 mg/mL. The boric acid was added to complex the fluoride from the bomb digestion.

Ten milliliter aliquots of the coal ash solution were pipetted into 250-mL beakers and diluted to approximately 150 ml with water. The pH was adjusted to the desired value and then 10 mL of 1.0 *M* sodium sulfide was added. After allowing 2–3 min for the system to reach equilibrium, the pH was again adjusted to the desired value. The solution and the precipitate were then transferred quantitatively to the flotation cell. The flow rate of the air was maintained below 20 mL/min to minimize redistribution of the floc. Four milliliters of surfactant was injected with a hypodermic syringe. At the higher pH values studied, an additional 1–2 mL of surfactant were necessary to clear the solution because of the large amount of precipitate formed. The floc was removed from the top of the cell with a Teflon spatula and dissolved over medium heat with a few milliliters of HNO_3 and HCl. The dissolved floc was diluted to 25.0 mL, filtered to remove any insoluble surfactant, and analyzed by atomic absorption spectrometry.

DISCUSSION AND RESULTS

Table 1 compares the concentration of 10 elements found in our coal sample to the world wide average of all coals. Wide variations in the elemental composition are anticipated, and the values for the coal used in this study were found to be more or less typical for all of the elements except iron which was less than expected.

Table 2 shows the formal concentrations of sodium sulfide, surfactant, and the 10 elements from the coal ash sample present in the flotation cell. A

TABLE 1
Chemical Composition of Coal (ppm)

Element	Al	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn
This study	9,400	9.2	15	4.7	1,500	12	16	33	16	18
Estimated worldwide average (*8*)	10,000	5	10	15	10,000	50	15	25	25	50

TABLE 2
Formal Concentrations in the Flotation Cell ($\times 10^6$)[a]

Al	Co	Cr	Cu	Fe	Mn	Ni	Pb	V	Zn	Na_2S	CTA[b]
4,800	2.2	4.0	1.0	370	3.0	3.8	2.2	4.4	3.8	56,000	350

[a] All concentrations based on a total volume of solution of 180 mL in the flotation cell.
[b] Calculated for the addition of 4 mL of surfactant.

previous study involving a solution of acid-digested ferromanganese nodules with a composition similar to the coal ash solution used in this study indicated that the efficiency of the flotation was maximized with an excess of sodium sulfide present (*9*). The addition of sodium sulfide to the coal ash solution results in the formation of insoluble metal sulfides; the degree of precipitation of an individual cation being dependent upon the pK_{sp} value of its sulfide and the pH. The precipitate itself bears no formal charge; however, the surface is rendered negative by the adsorption of anions such as sulfide ion, fluoride ion, and silicates (*9*). Therefore, the cationic surfactant, cetyltrimethylammonium chloride, was used in the flotation.

The relative recoveries of the 10 metals as a function of pH are shown in Fig. 1. Several patterns of behavior are exhibited. Cobalt, copper, lead, and zinc recoveries show a rapid increase between pH 2 and 4 and then level off at values above 80%. These four elements form the least soluble sulfides, and the recovery pattern appears to be based primarily on the value of the solubility product constant.

Chromium, nickel, vanadium, and iron recoveries show a continued rise between pH 2 and 6. There is a rapid increase in the nickel recovery from pH 2 to 4 with a slight levelling off in the pH 3 to 4 range. This behavior is analogous to that of cobalt and zinc which have similar pKsp values. However, beyond pH 4 the nickel recovery follows the pattern exhibited by chromium, vanadium, and iron. This behavior is thought to be due to the simultaneous occurrence of precipitate flotation of the sulfides and adsorbing colloid flotation (ACF). In ACF, ions in solution are adsorbed on the surface

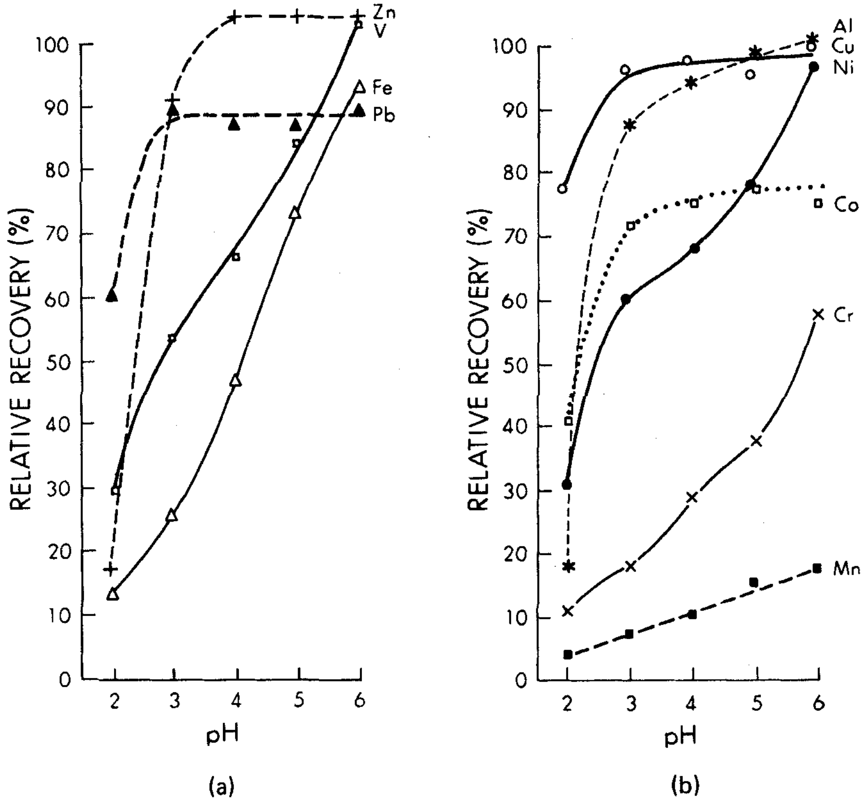

FIG. 1. Relative recovery of elements floated as a function of pH: (a) Zn (+), V (□), Fe (△), Pb (▲); (b) Al (*), Cu (○), Ni (●), Co (□), Cr (×), Mn (■).

of a colloidal species and then floated with the aid of a surfactant. In this case, colloidal ferric hydroxide is acting as a collector and enhancing the recovery of the chromium, nickel, and vanadium. Similarly, colloidal aluminum hydroxide may also be functioning as a collector and improving the relative recoveries of the other elements through an ACF mechanism (*5*).

The relative recovery of manganese remains less than 20% throughout the pH range examined. This is not surprising as the solubility product constant of its sulfide is not exceeded by pH 6. Also, previous studies have indicated there is little adsorption of manganese ion on colloidal ferric hydroxide. Thus manganese remains in solution until much higher pH values (*4, 9*).

Under the experimental conditions employed in this study, it appears that several different metals can be separated quantitatively from coal ash using flotation techniques. Although this work has examined the simultaneous separation of the 10 elements, it may be possible to introduce some selectivity in the process through a more careful adjustment of the solution pH and the quantity of sodium sulfide added.

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