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Separation of Metals from Sulfated Deep-Sea Ferromanganese Nodules with Organic Precipitating Reagents and Adsorptive Bubble Techniques

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Abstract

Organic precipitating reagents and adsorptive bubble techniques were used to separate copper, cobalt, nickel, and manganese from the leach liquors of sulfated deep-sea ferromanganese nodules. Recoveries of the four elements were examined as a function of pH and the quantity of the organic precipitating reagent added. Three reagents were studied: 8-hydroxyquinoline, ammonium 1-pyrrolidine-dithiocarbamate, and dithizone.

INTRODUCTION

Adsorbing colloid flotation (ACF) is an adsorptive bubble technique which has been used successfully in our laboratory for several years for the separation of a variety of elements from seawater (*1*). In a series of experiments, both cationic and anionic species present in μg/L quantities were concentrated and removed by adsorption on a charged colloidal collector which was then floated with an ionic surfactant.

In the past decade there has been a growing interest in the possible use of deep-sea ferromanganese nodules as a source of the valuable transition metals copper, cobalt, and nickel. Although the composition of nodules from different locations on the ocean floor may vary considerably, high grade nodules contain approximately 3% by weight of these three metals (*2*). In addition, there are large amounts of manganese (15–30%) which may or may not be included in an economically viable recovery scheme (*3*). Suggested methods of processing these nodules include extractive hydrometallurgical technologies such as leaching with acids, ammonia, or aqueous solutions of reducing agents such as SO_2 and pyrometallurgical methods including smelting and chlorination (*4*).

Recent work has demonstrated that ACF can be applied for the recovery of copper, cobalt, nickel, and manganese as well as several other metals from chemically treated ferromanganese nodules and their process tailings. The chemical treatment has included both nonselective acid digestion and high temperature sulfation and leaching processes (*5*, *6*). Quantitative removal of the elements of interest has been achieved both with sulfide and hydroxide collectors through careful adjustment of the pH.

Flotation work involving the use of organic precipitating reagents has recently been reviewed by Grieves (*1*). The majority of the reported experiments have dealt with the selective separation of a single element in the presence of a large excess of a second or third competing element. This communication reports the results of a study in which three organic precipitating reagents, 8-hydroxyquinoline (oxine), ammonium 1-pyrrolidine-dithio-carbamate (APDC), and dithizone, were added to a series of leach solutions from sulfated deep-sea ferromanganese nodules. The resulting colored chelates were then floated to the surface by an adsorptive bubble technique and analyzed by atomic absorption spectrometry for copper, cobalt, nickel, and manganese.

EXPERIMENTAL

Apparatus and Equipment

The 200-mL flotation cell employed was a modification of the cell described previously (*7*). All pH measurements were made with an Orion Digital Ionalyzer Model 801A which was calibrated with standard buffer solutions. The atomic absorption analyses were performed using a Perkin-Elmer Model 2380 Spectrophotometer.

Reagents

All chemicals were analytical grade reagents. The water used in solution preparation and dilutions was obtained from a Millipore Model Milli R/Q ion exchange and reverse osmosis water purifier. A 1-mg/mL solution of surfactant was prepared by dissolving 0.2 g of a 50% solution of stearyltrimethylammonium chloride in 100 mL of ethanol. Standard solutions of the organic precipitating reagents, 2% (w/w) oxine, 2% (w/w) APDC, and 1% (w/w) dithizone, were prepared in ethanol. Dilute and concentrated solutions of NaOH, HCl, and HNO_3 were employed for pH adjustment and dissolution of the floc. Standard solutions of appropriate concentrations for atomic absorption analyses were prepared by dilution of stock 1000 mg/L standards.

Procedure

The leach solutions were obtained from a previous study conducted in our laboratory in which Sedco nodules were sulfated by a mixture of SO_2 and O_2 gases at 400 and 600°C and then leached at 90°C with water to remove the soluble sulfates. A 5.0-mL aliquot of the leach solution was pipetted into a 250-mL beaker and diluted to approximately 160 mL with water. The pH of the solution was adjusted to the desired value, the organic precipitating reagent was pipetted into the solution, and the pH readjusted to the original desired value. The solution and the precipitate were then transferred quantitatively to the flotation cell. The air flow rate was maintained below 10 mL/min to minimize redistribution of the floc due to air turbulence. One milliliter of surfactant injected with a hypodermic syringe was usually sufficient to float all of the precipitate and decolorize the solution; however, at certain pH values, when larger quantities of precipitate were present, it was occasionally necessary to make a second 1-mL injection of surfactant. After all of the floc collected at the surface (typically 3–5 min), it was removed manually with a Teflon spatula and dissolved over medium heat with a few milliliters of HNO_3 and HCl. The dissolved floc was diluted to a final volume of 50 mL, filtered to remove any remaining insoluble surfactant, and analyzed by atomic absorption spectrometry.

DISCUSSION AND RESULTS

Three common organic precipitating reagents were studied: oxine, APDC, and dithizone. These three were chosen because they are nonselective and are widely accepted as precipitants in gravimetric analysis as they all form chelates which are insoluble in aqueous solution.

The addition of the organic precipitating reagents to the leach solutions resulted in the formation of particulates having hydrophobic surfaces. The chelates could be floated successfully without the addition of a surfactant, and the technique can properly be called precipitate flotation of the second kind (*1*). In the absence of a supporting foam the precipitate tended to redisperse as it was being collected. To minimize this redispersion, a small amount of the cationic surfactant stearyltrimethylammonium chloride was added as a frother in all of the experiments described below. The surfactant not only stabilized the foam but also enhanced the recovery of the metal ions at the higher pH values. Undoubtedly this is due to the occurrence of a simultaneous adsorbing colloid flotation involving the hydroxides of

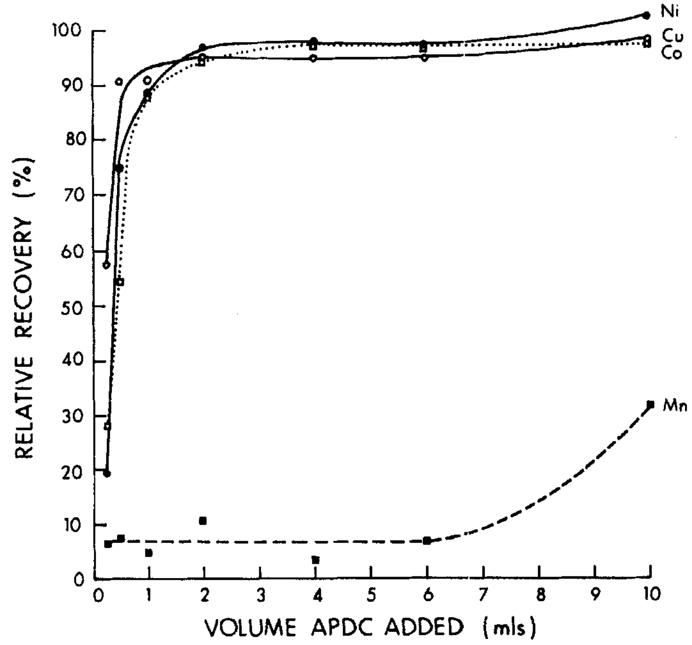

FIG. 1. Relative recovery of elements floated at pH 3 as a function of milliliters of 2% APDC added.

elements such as iron and manganese which are present in the leach solution. At pH values above 5.5, it has been shown that metal cations adsorb on the negatively charged surfaces of colloidal iron hydroxide particulates which are then floated with a cationic surfactant (5). The behavior of several nonionic, amphoteric, anionic, and cationic surfactants was examined. A subjective evaluation determined that the flotation behavior of the stearyltrimethylammonium chloride was superior.

The leach solution of the sulfated Sedco nodule was analyzed and found to contain the following: 140 μg/mL copper, 37.4 μg/mL cobalt, 161 μg/mL nickel, and 4630 μg/mL manganese. The relative recoveries of these four elements were examined both as a function of pH and the quantity of the organic precipitating reagent added.

Figure 1 shows the effect of the quantity of APDC added on the recoveries of the four metals at pH 3. Nickel, cobalt, and copper behave similarly and can be separated quantitatively while the manganese remains in solution. Further studies at pH 8 using 2 mL of APDC showed that the nickel, cobalt, and copper recoveries remained above 95% while the manganese recovery was constant at about 10%.

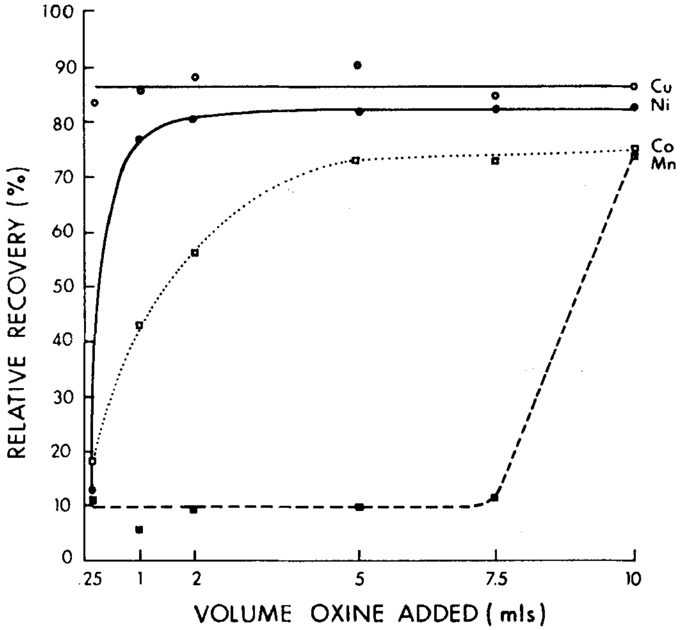

FIG. 2. Relative recovery of elements floated at pH 5 as a function of milliliters of 2% oxine added.

Figure 2 shows the relative recoveries at pH 5 as the quantity of oxine added is varied. The degree of separation is based on the relative insolubility of the metal chelates formed which in turn is dependent on the magnitude of the formation constant and the analytical concentration of the metal cation in solutions as well as the concentration of oxine. Because iron and manganese hydroxide flocs are absent at this pH, the separation is due entirely to precipitate flotation of the insoluble oxinates. Figure 3 shows the relative recoveries as a function of pH when 5 mL of oxine were added. This quantity of oxine corresponds to the plateau region in Fig. 2 where an excess of oxine is present for the separation of copper, cobalt, and nickel. In addition to precipitate flotation, it is likely that at pH values above 5.5 there is adsorbing colloid flotation of cobalt and manganese on copper hydroxide flocs. At pH values greater than 8 the improved manganese recovery suggests the formation and flotation of colloidal manganese hydroxide.

Figure 4 shows the relative recoveries as a function of pH when an excess of the precipitating reagent, dithizone, was added. It is not yet clear what the predominant mechanism of separation is using this chelating agent. The recoveries of copper, cobalt, and nickel are probably a combination of precipitate flotation and adsorbing colloid flotation on colloidal cupric

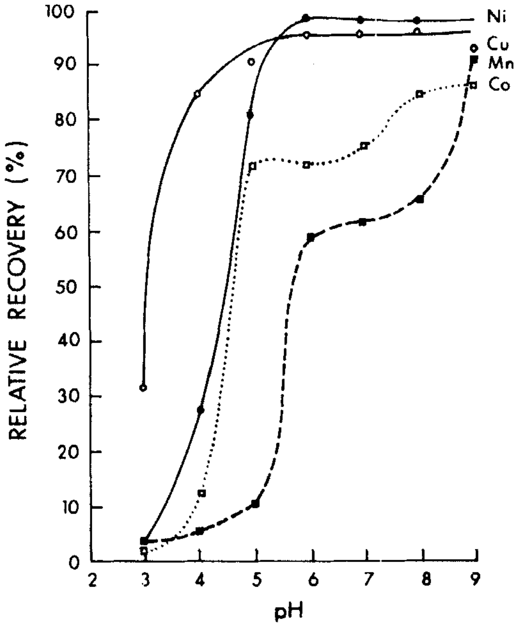

Fig. 3. Relative recovery of elements floated with 5 mL of 2% oxine as a function of pH.

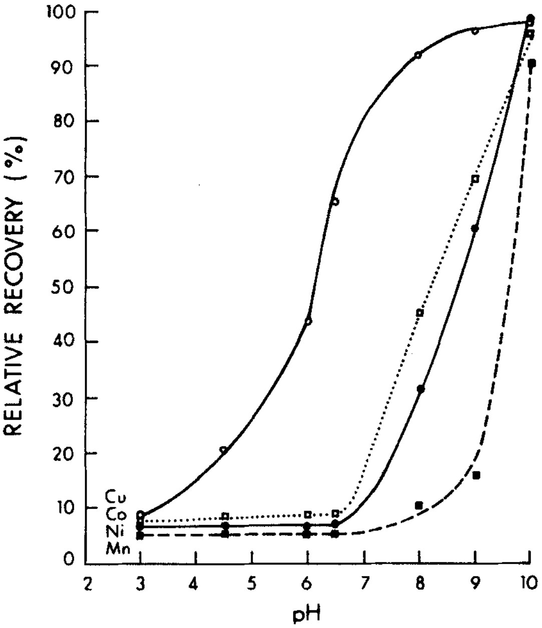

FIG. 4. Relative recovery of elements floated with 5 mL of 1% dithizone as a function of pH.

($K_{sp} \sim 10^{-19}$) hydroxide while the manganese recovery is due to the flotation of colloidal manganeses hydroxide.

Our results show that adsorptive bubble techniques with organic precipitating reagents can provide a useful method of quantitatively removing the four elements of interest when the amount of precipitating reagent and the pH are controlled. Further investigations are currently underway to determine whether these three organic reagents or others can be employed to provide a stepwise separation of the elements.

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