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The Separation of Metals from Treated Deep-Sea Ferromanganese Nodules by Adsorptive Bubble Techniques Using Salicylaldoxime and Sodium Diethyldithiocarbamate as Organic Precipitating Reagents

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Abstract

An adsorptive bubble technique, using two organic precipitating reagents, is applied to separate cobalt, copper, nickel, and manganese from the leach liquors of sulfated deep-sea ferromanganese nodules. Recoveries of the four metal values are studied as a function of pH for each system. The organic precipitating reagents studied are salicylaldoxime and sodium diethyldithiocarbamate.

INTRODUCTION

In recent years, deep-sea ferromanganese nodules have generated considerable interest as a major reservoir of the valuable transition metals cobalt, copper, nickel, and manganese. Nodules are present in vast amounts on the ocean floors, and high-grade siliceous nodules of the equatorial North Pacific area are approximately 3% in cobalt, copper, and nickel, and 20% in manganese, on a dry weight basis (*1*). Suggested processing methods include hydrometallurgical extraction techniques, using acids, ammonia, or aqueous

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solutions of reducing agents such as SO_2, and pyrometallurgical techniques such as smelting and high-temperature chlorination (*2, 3*). Preliminary studies by Lee (*2*) have demonstrated that a high-temperature sulfation of the nodules followed by an aqueous leach may be a feasible means of separating desirable transition metals from less valuable nodule constituents such as iron oxides and aluminosilicates.

Prior to this investigation, studies by DeCarlo (*4*) have shown that various cations may be separated from solutions of acid digested deep-sea nodules and from the aqueous leach liquors of sulfated high-grade nodules by adsorbing colloid flotation (ACF). Specifically, this work involved the separation of positively charged cobalt, copper, nickel, and manganese species from the bulk of the nodule matrix using a negatively charged ferric hydroxide or manganese hydroxide collector (generated from *in situ* iron or manganese), a cationic surfactant, and air. Quantitative recoveries of the metals of interest were obtained by judicious control of the solution pH.

Recent work in our laboratory by Bleasdell (5) has demonstrated that organic precipitating reagents may be used to separate cobalt, copper, nickel, and manganese from the leach liquors of sulfated deep-sea ferro-manganese nodules with adsorptive bubble techniques. Recoveries of the four elements were studied as a function of pH and the quantity of organic precipitating reagent added. Three reagents were studied: 8 hydroxyquinoline, ammonium 1-pyrrolidinedithiocarbamate (APDC), and dithizone. Results showed this to be a useful method of quantitatively removing the four elements when the amount of precipitating reagent and the pH are controlled. This study also suggested that the use of organic precipitating reagents in place of *in-situ* generated metal hydroxide collectors may allow greater selectivity in the metals which are separated from the leach liquor.

This communication reports a study in which two organic precipitating reagents, sodium diethyldithiocarbamate (NaDEDC) and salicylaldoxime, were added to the aqueous leach liquors of sulfated deep-sea ferromanganese nodules. The two precipitating reagents selected for this study have been reported to form chelates which are insoluble in aqueous solution with cobalt, copper, nickel, and manganese cations (*6*). Using the resulting chelates, the separation of cobalt, copper, nickel, and manganese was attempted by an adsorptive bubble technique. Metal recoveries were examined as a function of pH, and the salicylaldoxime was studied on a preliminary basis.

EXPERIMENTAL

Apparatus and Equipment

The 200-mL flotation cell employed was a modification of that previously described by Kim and Zeitlin (*7*). All pH measurements were made with an

Orion Digital Ionanalyzer Model 801A which was calibrated daily against Scientific Products Standard Reference Buffers (pH 4.01, 7.00, and 10.00). The atomic absorption analyses were performed using a Perkin-Elmer Model 2380 spectrophotometer with appropriate hollow cathode lamps.

Reagents

All chemicals used were of analytical reagent grade. Aqueous solutions and dilutions were prepared with water purified in either a Millipore Model Milli R/Q ion exchange and reverse osmosis water purifier, or in Barnstead organic removal and cation removal water purification cartridges. Concentrated and dilute solutions of NaOH, HCl, and HNO_3 were used throughout the study as required for pH adjustment and dissolution of the floc. Individual surfactant solutions were prepared in ethanol as follows: 2 mg/mL stearyltrimethylammonium chloride and 15 mg/mL Triton X-100. Standard mixed element solutions for atomic adsorption analysis were prepared by dilution of stock 1000 mg/L spectrophotometric standards. Standard solutions of the organic precipitation reagents, 20 mg/mL NaDEDC and 50 mg/mL salicylaldoxime, were prepared in water and ethanol, respectively.

Procedure

The leach solutions were obtained from a previous study to our laboratory in which homogenized *RC9-T1* nodules were dehydrated at 450°C, sulfated by a mixture of SO_2 and O_2 gases at 400°C until the weight increase with time (due to sulfation) was asymptotic, and then leached in water (50 g nodule per liter of water) at 90°C for 1 h to remove the soluble sulfates (*8*). Approximately 200 mL of five such leach solutions were combined to create a composite solution.

A 5.0-mL aliquot of this composite solution was pipetted into a 250-mL beaker and the volume adjusted to approximately 175 mL with water. The pH of this solution was adjusted to the desired value with NaOH and HNO_3 solutions, 5.0 mL of the organic precipitating reagent was pipetted into the solution, and the pH readjusted to the original desired value. The solution and resultant precipitate were then transferred quantitatively into the flotation cell. Filtered, water-saturated air was passed through the cell at a flow rate of 10 ± 2 mL/min, and 2 mL of stearyltrimethylammonium chloride solution (cationic surfactant) injected with a hypodermic syringe. This was followed by an immediate injection of 0.5 mL of Triton X-100 nonionic surfactant solution in order to stabilize the bed of colloid-enriched foam. The floc was allowed to collect for approximately 10 additional minutes, then scooped into a 150-mL beaker with a Teflon spatula. Approximately 2 mL each of concentrated HCl and HNO_3, followed by water, was used to rinse adhering floc from the spatula into the beaker and subsequently to dissolve the floc over medium heat. The dissolved floc was quantitatively transferred to a 50-mL volumetric flask, diluted to volume with water, and transferred to a Nalgene container for storage. Triplicate flotations were performed at unit pH-intervals between pH 3 and pH 7 with NaDEDC. The same pH range was studied with salicylaldoxime; however, only a single trial was conducted for each pH value. This is then a preliminary study with respect to salicylaldoxime. Appropriate dilutions of the stored samples and the composite mother solution were analyzed by atomic absorption spectrophotometry (AAS) for Co, Cu, Ni, and Mn, and the percent recovery of each metal calculated. Standards and sample dilutions for AAS analysis were prepared with a matrix-matched solution containing an appropriate amount of acid and surfactant to compensate for the lower surface tension of the analyte solutions.

DISCUSSION AND RESULTS

The *RC9-T1* deep-sea ferromanganese nodules used in this study are characterized by a high manganese-to-iron content ratio (*2*), and contain around 1½% on a combined dry-weight basis of the metals cobalt, copper, and nickel. They were dredged at latitude 42°17′S, longitude 135°43′E, and at a depth of 4750 m. The Co, Cu, Ni, and Mn content of the leach solution composite used in this investigation is presented in Table 1 along with the composition of the untreated nodules as determined by Shinn (*8*).

TABLE 1

Cobalt, Copper, Nickel, and Manganese Content of Leach Solution Composite and Untreated Nodules

	Concentration	
Metal	Composite solution[a]	RC9-T1 nodule[b]
Co	34.5	0.166
Cu	48.6	0.361
Ni	100	0.847
Mn	3800	20.0
Fe	Not determined	9.18

[a] Expressed as mg/L.

[b] Expressed as % dry weight.

The aforementioned investigation by Bleasdell (*5*), performed with similar leach solutions, examined the recovery of metals as a function of the amount of organic precipitating reagent added (oxine, APDC, and dithizone solutions). Following the results of Bleasdell's study, 5 mL of the precipitating reagent solution of interest (20 mg/L NaDEDC or 50 mg/L salicylaldoxime) was chosen as an initial volume for addition to the diluted leach liquor after pH adjustment. Metal recoveries were evaluated as a function of pH at unit pH intervals between pH 3 and pH 7. The diluted leach solution composites had an initial pH of approximately 3.4, so pH 3 was chosen as a convenient lower limit for the pH range studied. Above pH 7, the formation and flotation of the hydroxides of manganese and copper occur to an appreciable extent (*9*); pH 7 was thus chosen as an upper pH limit. Also following the results of Bleasdell's investigation, 2 mL of stearyltrimethylammonium chloride cationic surfactant solution was used to float or support the insoluble metal chelates. An additional 0.5 mL of Triton X-100 nonionic surfactant solution provided a clean foam bed beneath the enriched foam, preventing redispersion of precipitate into the bulk solution.

The addition of NaDEDC to the diluted leach liquor resulted in the formation of dark-brown hydrophobic colloidal particles. The floc exhibited a natural floatability without surfactant, so the technique can accurately be termed precipitate flotation of the second kind (*10*). The addition of surfactants prevented redistribution of the precipitate into the mother liquor during manual collection. Table 2 presents the recoveries of Co, Cu, Ni, and Mn from the leach solution composite as a function of pH using NaDEDC. For the entire pH range studied, copper and nickel recoveries are nearly quantitative while cobalt recovery is high (>80%). Manganese recovery, however, increases slowly from 33% at pH 3 to 48% at pH 7; this increase may be partly attributed to the simultaneous flotation of manganese hydroxide at the higher pH values. The increased recoveries of Cu and Ni

TABLE 2

Relative (%) Recoveries of Co, Cu, Ni, and Mn from Nodule Leach Liquor Composite with NaDEDC

	pH				
Metal	3	4	5	6	7
Co	84.9	85.3	83.7	84.3	83.6
Cu	96.7	95.1	91.7	97.6	98.1
Ni	97.9	98.6	96.7	97.3	96.6
Mn[a]	33	34	39	38	48

[a] All relative standard deviations in the replicate set at each pH are ≤3%.

are probably due to preferential chelation by NaDEDC of Cu and Ni over Co and Mn.

It is worth noting that the pH of the precipitate solution was observed to slowly increase after readjustment to the original desired pH. This is probably a result of hydrolysis, because NaDEDC is the water-soluble salt of a weak acid. Although not investigated further, this effect may cause a slight increase in solution pH during the course of flotations.

The addition of salicylaldoxime to the diluted leach liquor resulted in the formation of a very fine greenish-brown precipitate. The particles did not float in the absence of a surfactant. However, upon injection of stearyltrimethylammonium chloride and Triton X-100, the solution cleared considerably as the particles were floated. This technique is then properly termed a precipitate flotation of the first kind (*10*). Figure 1 shows

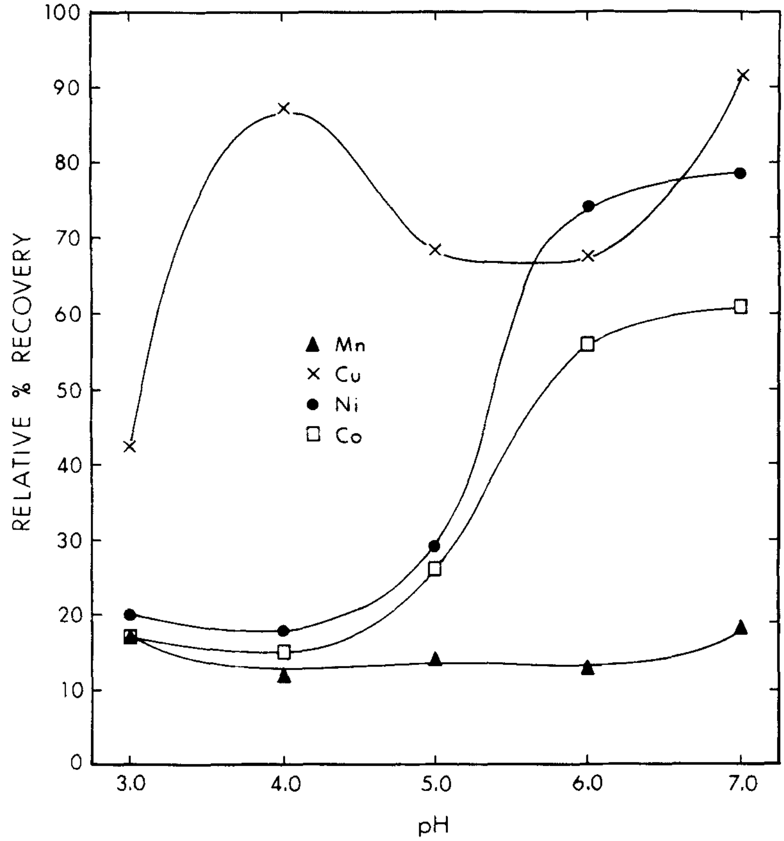

FIG. 1. Relative percentage recovery of metals from nodule leach liquors using foam flotation with salicylaldoxime as a function of pH.

graphically the relative (%) recoveries of Co, Cu, Ni, and Mn as a function of pH between pH 3 and pH 7. The recovery of manganese is low (<20%) for the entire pH range studied; this suggests that the simultaneous flotation of manganese hydroxide at higher pH values does not occur to an appreciable extent in this case. Cobalt recovery is also low, increasing from less than 20% at pH 3 and pH 4 to a maximum of 61% at pH 7. The recovery of nickel parallels that of cobalt, but is consistently greater, and increases to 78.7% at pH 7. Most noteworthy is the behavior of copper, which displays two distinct recovery maxima: 87.1% recovery at pH 4 and 91.9% recovery at pH 7. A possible explanation for this phenomenon is that at pH 4 conditions for chelation of the copper species may be optimum in this system, while the high recovery at pH 7 may be due to the precipitate flotation of $Cu(OH)_2$ by the cationic surfactant (*4*).

In conclusion, it has been demonstrated that a foam flotation technique using NaDEDC can remove Cu and Ni almost quantitatively from the leach liquors of sulfated ferromanganese nodules, with metal recoveries nearly pH-independent between pH 3 and pH 7. The preliminary investigation of salicylaldoxime as a chelating agent, using the above-mentioned foam flotation technique, suggests that around 90% of the nodule leach liquor Cu may be separated from the bulk of the Co, Ni, and Mn species through careful pH manipulation. Additional investigations may reveal that various other organic precipitating reagents are capable of selectively and economically separating individual elements from treated nodules.

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