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Recovery of Metals from Process Streams of Deep-Sea Ferromanganese Nodules by Adsorptive Bubble Techniques

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Abstract

A method for the separation of Cu, Co, Ni, and Zn with varying degrees of selectivity from chemically treated deep-sea ferromanganese nodules is described. Quantitative removal of these species is achieved primarily by precipitate flotation of insoluble sulfides. Recovery of residual metal values of Cu, Co, Ni, and Zn in process rejects of the nodules is also possible. The quantitative removal of Pb and V, which are the most abundant toxic elements in nodules and tailings, is achieved simultaneously. Cationic and anionic surfactants are employed for collection depending on zeta potentials of the flocs generated upon addition of Na_2S to sample solutions. Separations are more selective and efficient at lower pH than previously reported for flotation of metals from nodules as insoluble hydroxides. Modifications resulting in slight improvements over previously employed high temperature sulfation processes are also described.

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INTRODUCTION

In recent years a great deal of interest has been shown in deep-sea ferromanganese nodules as a potential source of metals such as Cu, Ni, Co, Mo, V, and Mn. Although the total of the minor metal constituents is only 3 to 4%, these deep-sea nodules represent a renewable mineral resource that can be used to supply many of the metals of strategic importance if the technology can be developed for the recovery of these metals at a reasonable profit.

The various methodologies which are currently being considered for the recovery of the valuable metals from nodules include hydrometallurgy, pyrometallurgy, and solvent extractions (*1*). Recent work in our laboratory has shown that a simple and rapid technique called adsorbing colloid flotation (ACF) can successfully remove Co, Cu, Ni, and Mn from acid-digested deep-sea ferromanganese nodules and from leach liquors of sulfated nodules (*2, 3*). Quantitative recoveries of the desired elements were achieved by judicious pH manipulations using ferric hydroxide that is precipitated *in situ* as the collector.

While the application of ACF is a recent development, flotation in the mineral and ore industry dates back to 1911 (*4*). One of the most widely used applications of mineral and ore flotation technology has been in the flotation of sulfide ores (5). Because of the large number and great economic importance of sulfide ores, the literature on sulfide mineral flotation is quite extensive. Unfortunately, the technology employed in mineral and ore flotation cannot be applied directly to the concentration of minor constituents that are present in the nodules due to the extremely short-range order of the mineral phases of interest (*1*).

This communication reports the results of a study which involved the addition of sulfide ion to various chemically treated ferromanganese nodule solutions and the subsequent recovery of Co, Cu, Ni, and Zn by adsorptive bubble techniques. Improvements over previously developed bench-scale processing methods by high temperature sulfation are also described.

EXPERIMENTAL SECTION

Apparatus and Equipment

The experimental apparatus and flow-through gas sampling system used for the high temperature sulfation of nodules were modifications of those previously described by Lee and by Shinn (*6, 7*). The set-up consisted of a

Lindberg Single Zone furnace mounted on a temperature control console with temperature capabilities up to 1200°C. Gas flow rates were measured using Linde Series 150 flowmeters calibrated with the appropriate gases. Electrophoretic mobility measurements were made with a Zeta Meter Corporation Zeta Meter equipped with a Zeiss D/R stereomicroscope and a Type II UVA electrophoresis cell. Flotation studies were carried out using a modification of the cell employed by Kim and Zeitlin (*8*). Cells were constructed so as to hold a maximum sample size of 200 mL. The pH of solutions was determined using an Orion Research Model 801-A Digital Ionanalyzer calibrated daily against Scientific Products Standard Reference Buffers. All absorption measurements employed standard flame methods using a Perkin-Elmer Model 2380 atomic absorption spectrophotometer.

Reagents

All chemicals used were of analytical reagent grade. Aqueous solutions were prepared with water purified in a Millipore Model Milli R/Q reverse osmosis/ion exchange water purifier. Individual surfactant solutions were prepared in ethanol as follows: 2.5 and 5 mg/mL cetyltrimethyl ammonium chloride (CTA); 1 mg/mL lauryl ammonium chloride (LA); 0.5 mg/mL sodium lauryl sulfate (SLS); 15 mg/mL Triton X-100. Concentrated and dilute aqueous solutions of HCl, HNO_3, HF, H_3BO_3, NaOH, and Na_2S were employed throughout the studies as required in the analytical procedure. Atomic absorption standard reference solutions (1000 μg/mL for all elements analyzed) were purchased from Anderson Laboratories, Inc. Standard mixed element solutions for AAS analysis were prepared prior to analysis by dilutions of the individual 1000 μg/mL standards in the appropriate sample matrix.

ANALYTICAL PROCEDURE

High-Temperature Sulfation Procedure

Samples of *SEDCO* 445 nodules were sulfated with a mixture of SO_2 and O_2 at an elevated temperature according to the following procedure. Sample tubes containing 100.0 g of ground (100/150 mesh) nodule were placed in the furnace overnight at 450°C in order to determine the dehydrated weight of the nodules. Dehydrated nodule samples were then equilibrated at 400°C for 30 min before reaction with SO_2 and O_2 was initiated. Gas flow rates through the system were maintained as follows: SO_2, 50 mL/min; O_2, 50 mL/min; N_2, 100 mL/min. After specified time intervals the reagent gas flow was interrupted and the samples purged with N_2 for an additional 15 min to flush the sample of any remaining reagent gases. The sample tubes were capped and cooled to room temperature before weighing to determine the increase in weight from the reaction of the nodules with SO_2 and O_2. The samples were treated repetitively in this manner for a total of 5 h. The temperature of the furnace was then increased to 600°C and the samples equilibrated at this temperature for 30 min. Gas flow was again initiated and the weight gain due to sulfation at 600°C monitored for a total of 4 h in the manner previously described.

Hydrometallurgical Leaching of Sulfated Nodules

Immediately after cooling and weighing, samples from the sulfation experiment were transferred to Nalgene polyethylene containers and thoroughly shaken in order to ensure homogeneous mixing of the reacted nodule material. Three replicates of 10.00 ± 0.01 g of sulfated nodules were weighed, each placed in 500-mL Erlenmeyer flasks, and leached in 250 mL of purified water with constant stirring for a period of 2 h at 90°C. The leached samples were cooled to ambient temperature before filtration. The volume of the leach solutions was permitted to fall slightly below 250 mL in order to permit filtration and dilution to a final volume of exactly 250 mL. Each sample was then filtered through 0.45 μm Millipore filters using a vacuum filtration device designed in our laboratory (*9*). Filtered samples were transferred to Nalgene containers for storage, and the solid residue or tailings were stored in covered glass Petri dishes.

Flotation of Metals from Acid-Digested Nodules

Samples of ground *VALDIVIA* nodules (100-150 mesh) dried at 110°C were acid-digested in a Parr Bomb using a modification of the technique described by Bernas (*10*). The resulting solution was diluted with 0.5 *M* H_3BO_3 to prepare a 5.0 g/L stock nodule solution. Boric acid was used to complex any fluoride remaining from the digestion procedure.

Twenty milliliters aliquots of the stock solution were pipetted into 250-mL beakers and diluted to approximately 175 mL with water. The pH was adjusted to the desired value (±0.05 pH units). Varying quantities of a sodium sulfide solution were added following pH adjustment. The introduction of sulfide ion into the acidic solutions resulted in the formation of SH^- and $H_2S(g)$ and a rapid rise in the pH. The pH was allowed to stabilize, which usually required 2 to 3 min, and then readjusted to the desired value. The solutions were then transferred quantitatively to the flotation cell, and 4 mL of 5 mg/mL CTA surfactant solution was injected with a hypodermic syringe to float the insoluble sulfides. The air flow through the cell was maintained at 17 ± 2 mL/min and the floc was allowed to gather at the top of the cell. In a few of the flotations there was a tendency for the floc to redistribute, and in these instances the air flow rate was reduced slightly. Additional 1-mL injections of the surfactant solution were made until the solution cleared completely; most solutions required a total of 5 mL although as many as 7 mL were used when there was a large amount of floc collected (high pH). Flotations were usually completed within 5 min and always within 10 min. The enriched foam was removed manually with a Teflon spatula and dissolved in 1 to 2 mL each of concentrated HNO_3 and HCl over medium heat. After diluting to exactly 50 mL, the solution was filtered to remove excess insoluble surfactant. Further dilutions were prepared as necessary for atomic absorption (AAS) analyses. The remaining mother liquor (~200 mL) was also collected, filtered through Millipore 0.45 μm filters, and reduced in volume over heat to exactly 100 mL to determine the amount of metals remaining in solution. The Millipore filters were ignited, dissolved in 2 mL of 50% HCl/50% HNO_3, and diluted to 25 mL with water for subsequent AAS analysis.

Flotation of Metals from Acid-Digested Tailings of Sulfated Nodules

A 5.0-g/L stock solution of tailings derived from the two-step sulfation of *SEDCO* 445 nodules carried out in the previous stages of these studies was prepared by the acid-digestion procedure described above. Ten milliliter aliquots of the stock tailings solution were diluted to approximately 160 mL. After the sample pH was adjusted to the desired value with NaOH, 10 mmol of sodium sulfide were added. Within a few minutes the pH of the solution had stabilized and was readjusted to the original value with HCl. The samples were then transferred to the flotation cell and 5 mL of 2.5 mg/mL CTA surfactant solution injected into the cell. The floc was then collected and treated with aqua regia before filtering and diluting to a final volume of 25 mL.

Flotation of Metals from Leach Liquors of Sulfated Nodules

The leach liquors used in this study were derived from the sulfated *SEDCO* 445 nodules as previously described. The leach liquors were rendered 0.4 *M* in H_3BO_3 by the addition of solid boric acid and analyzed by flame AAS to determine their composition. Five milliliter aliquots of the leach solution were diluted to approximately 160 mL and the pH adjusted. After 2 mmol of Na_2S were added to the solution, several minutes were allowed for the pH to stabilize, and the pH was readjusted to the desired value with HCl. Flotation of the precipitates was carried out with 5 mL of 0.5 mg/mL SLS surfactant solution. In cases where the foam stability was poor, an additional 0.5 mL of 15 mg/mL Triton X-100 was injected into the cell. The enriched foam was dissolved in aqua regia and diluted to exactly 100 mL with water. Three sets of replicate flotations were carried out between pH 2 and pH 6. Flotations between pH 2 and pH 4 were also attempted using 5 mL of 2.5 mg/mL CTA surfactant solution. Above pH 4 there appeared to be a change in the charge characteristics of the system which precluded the use of this cationic surfactant.

Since the surface charge characteristics of the precipitates produced from the leach liquors of sulfated nodules were found to vary significantly from those generated in acid-digested samples, experiments were undertaken to investigate the effect of several complex anions on the charge of the flocs.

Flotations were carried out on 5-mL aliquots of the leach liquor after filtration to remove the insoluble $BaSO_4$ precipitated by addition of Ba^{2+} as $BaCl_2$. In this manner flotations were carried out both in the presence and absence of SO_4^{2-}. Flotations were also carried out on aliquots of the leach liquor before and after addition of 150 mg NaF (resultant solution = 0.02 *M* F^-), and the effect of SiF_6^{2-} was evaluated in a similar manner by the addition of 7.5 mL of 0.2 mg/mL Si(IV) as Na_2SiF_6. The amounts of NaF and Na_2SiF_6 added in these studies represented approximately those which would be present in equal-size aliquots of acid-digested samples.

The zeta potentials of the flocs in the presence and absence of SO_4^{2-} and SiF_6^{2-} were measured between pH 2 and pH 6 only.

RESULTS AND DISCUSSION

Two-Stage Sulfation of SEDCO 445 Nodules at 400 and 600°C

The high temperature sulfation of deep-sea ferromanganese nodules has been studied and reported by various workers (*6, 7, 11, 12*). Studies carried out to date in our laboratory have concentrated primarily on a single-stage roasting at elevated temperatures (300–600°C). The efficiency of solubilization of the metals of interest was found to vary significantly as a function of temperature as well as particle size (*6*). The sulfation was found to be a two-

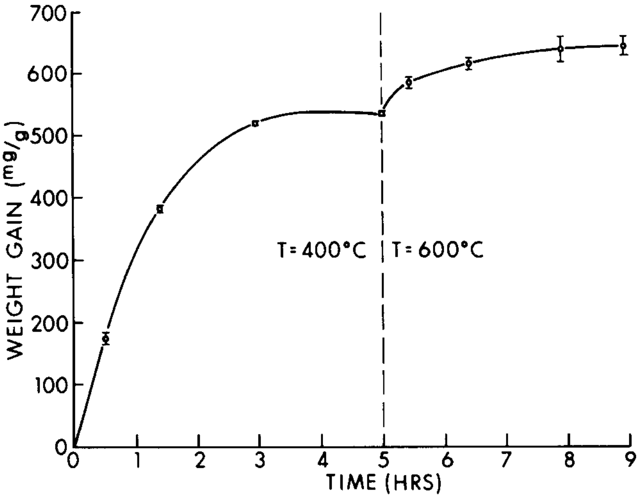

FIG. 1. Relative weight gains of *SEDCO* 445 nodules upon roasting with SO_2 and O_2 at 400 and 600°C.

step process: the first step is controlled by surface chemisorption and the second by pore diffusion. This results in a rapid initial weight increase due to conversion of the metal oxides to sulfates followed by an asymptotic leveling of the weight gain. In general, the relative weight gain caused by sulfation was found to increase up to 425°C and decrease at a higher temperature which has been attributed to the decomposition of $Fe_2(SO_4)_3$ above 400°C (*6*). It has been proposed, therefore, that a two-stage sulfation of the nodules should result in a more efficient conversion of the oxide phases to sulfates. Optimum conditions were believed to be at temperatures slightly below the decomposition temperature of the desired metal sulfates (*13*). A single roasting at elevated temperatures (i.e., >600°C) was not recommended as it would most likely lead to the formation of refractory mixed-metal oxides and inhibit the conversion to sulfates. For these reasons a two-stage sulfation was selected. The first roasting was conducted at 400°C in order to duplicate the optimum sulfation as determined by Shinn and by Lee (*6, 7*); the second stage was carried out at 600°C (temperature at or below the decomposition temperatures of $MnSO_4$, $CuSO_4$, $NiSO_4$, $CoSO_4$, $ZnSO_4$). The first step did not lead to the formation of mixed metal oxides and the partially sulfated oxides were thus not available for the formation of mixed-metal oxides at higher temperatures. The average of relative weight gains for two replicate runs as a function of time are presented in Fig. 1. The first segment (400°C) of the

TABLE 1
Recovery of Elements from *SEDCO* 445 Nodules by High Temperature Sulfation and Aqueous Leaching

Metal	This work[a]	Mass balance,[b] this work	Previous work[c]
Cu	62.0 ± 0.1%	96.8%	61.6 ± 0.6%
Co	99.6 ± 1.2%	99.7%	77.6 ± 1.0%
Ni	64.3 ± 0.5%	96.5%	55.5 ± 1.2%
Mn	99.1 ± 0.4%	99.8%	91.8 ± 1.4%
Fe	1.2 ± 0.1%	91.3%	0.66 ± 0.05%
Al	23.5 ± 0.8%	100.2%	~30% ±[d]
Zn	41.6 ± 0.4%	102.1%	~50% ±[d]

[a] Calculated from mass balance of tailings and leach solutions compositions.
[b] Calculated from concentrations in nodules, tailings, and leach liquors.
[c] After Shinn (*6*).
[d] Approximate values calculated from solution composition—not reported by the author.

curve is identical to that reported by Shinn (*6*). The second stage at 600°C, however, resulted in further weight gains as compared to a single-stage procedure. The additional increase in weight suggests that an increased conversion of the metal oxides to soluble sulfates is occurring, although it is most likely offset partially by a weight loss due to the decomposition of $Fe_2(SO_4)_3(s)$. This partial weight loss probably contributes to the large deviations of the weight gains at 600°C during replicate sulfation runs. A comparison of the metal recoveries for the one- and two-stage sulfation processes are presented in Table 1. It appears from these data that the second sulfation stage resulted in further solubilization of Co, Ni, and Mn, while the recoveries of Fe, Al, and Cu remained essentially unchanged. The Zn recovery appears to have decreased slightly, which may be due to the onset of decomposition of its sulfate (decomposition temperature is 600°C) (*14*). The low recovery of iron, although weight gains indicate partial conversion of Fe_2O_3 to $Fe_2(SO_4)_3$, is probably a result of the hydrolysis of iron in solution and the precipitation of insoluble $Fe(OH)_3 \cdot nH_2O$.

Flotation from Acid-Digested VALDIVIA Nodule Solutions

The location and compositions of *VALDIVIA* and *SEDCO* 445 nodules are given in Tables 2a and 2b. Nodules from two different locations but with similar compositions were used in these studies in order to assess the applicability of the flotation methods to a range of ore grade nodules.

TABLE 2a

Composition of *VALDIVIA* Nodules[a,b] and Acid-Digested Nodule Solutions[c]

	% Composition					
Metal	Fe	Mn	Cu	Co	Ni	H_2O[d]
Nodules	7.5	20.5	0.70	0.21	1.07	27.5
Solutions	375	1025	35	10.5	53.5	—

[a] Expressed as percent by weight on 110°C dry basis.

[b] Latitude 9°00′ N, longitude 148°30′ W, depth 5000 m.

[c] Expressed as mg/L.

[d] Calculated from weight loss upon dehydration at 450°C for 2 h.

TABLE 2b

Composition of *SEDCO* 445 Nodules,[a] Tailings, and Leach Solutions

	Concentration		
Metal	Nodules[b]	Tailings[b]	Leach[c]
Cu	0.92	0.92	220
Co	0.20	0.08	61.1
Ni	1.14	1.28	258
Fe	5.73	19.0	22.8
Mn	23.0	1.92	7630
Al	2.46	6.33	197
Zn	0.12	0.24	17.4
Pb	0.036	0.12	nd[d]
V	0.036	0.12	nd
H_2O[e]	25.6	—	—

[a] Latitude 9°24′N, longitude 151°21′ W, depth 5200 m. 0.298 g of tailings result from 1.000 g of dry untreated nodules.

[b] Expressed as percent by weight on 110°C dry basis.

[c] Expressed as mg/L.

[d] nd: none detected.

[e] Calculated from weight loss upon dehydration at 450°C for 2 h.

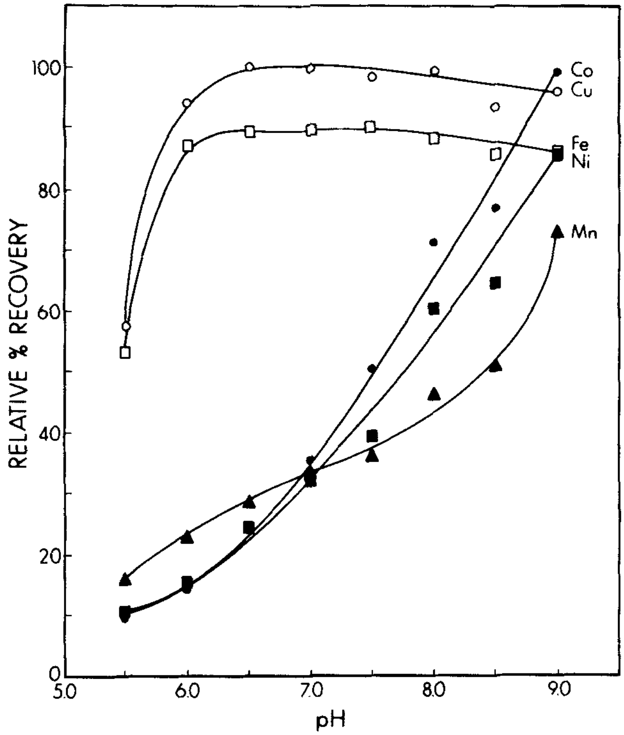

FIG. 2. Relative recovery of elements floated as insoluble hydroxides as a function of pH: Cu (○), Co (●), Ni (■), Fe (□), Mn (▲) (*2*).

Previous studies have examined the recovery of Cu, Co, Ni, and Mn as insoluble hydroxide from *VALDIVIA* nodules using ACF (*2*). Some of the results of this previous work are presented in Fig. 2. In ACF, ions in solution are absorbed onto the surface of oppositely charged colloidal species and then floated with the aid of a surfactant. Because a relatively large amount of iron (~6%) was present in the *VALDIVIA* nodules, colloidal iron hydroxide was used as an *in-situ* collector. The iron hydroxide formation was controlled by adjustment of the pH of digested nodules with NaOH. At pH values higher than about 5.5, which appears to be the point of zero charge (pzc) for the iron hydroxide in this system, the surface bears a negative charge, and therefore is floated by a cationic surfactant such as laurylamine hydrochloride. As can be readily seen in Fig. 2, Cu recoveries of 95 to 100% were obtained above pH 6 while the removal of Co, Ni, and Mn did not become quantitative until pH 9 or above. Thus, ACF was found to be an effective method of recovering the four metals only at relatively high pH values. In addition, the removal of large amounts of iron in this system is undesirable from an economical or industrial standpoint where only the Cu, Co, Ni, and possibly Mn are of interest. A system in which only the metals of importance are removed by the flotation procedure would be of much greater value. An examination of solubilities of various metal sulfides indicated that flotation of insoluble sulfides may well meet this criterion.

To determine the effect of sulfide addition on the recovery of Co, Cu, Ni, Mn, and Fe, a study of the relative recoveries of these metals as a function of the concentration of sulfide added was undertaken at pH 3. The averages of triplicate flotations are presented in Fig. 3; relative deviations were generally less than 3% but reached 10% for low recovery levels. At a given concentration of sodium sulfide added, the order of relative recoveries is Cu > Co > Ni > Fe > Mn. This behavior is expected as the pK_{sp} values of the metal sulfides follow the same pattern. At pH 3 there is no colloidal iron hydroxide present to act as a collector for ACF. Under these circumstances

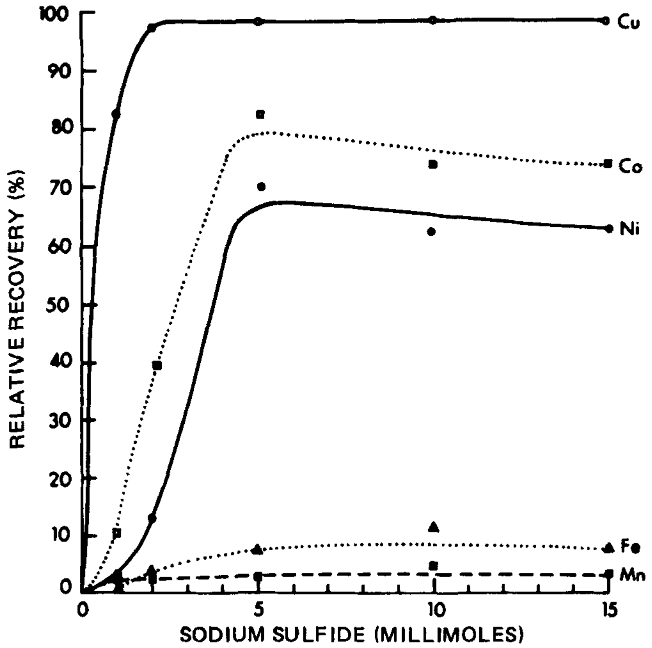

FIG. 3. Relative recovery of elements floated at pH 3 as a function of millimoles of sodium sulfide added: Cu (○), Co (□), Ni (●), Fe (▲), Mn (■).

the floc is brought to the surface via precipitate flotation, a different, although related, mechanism. In precipitate flotation of the first kind, an ionic species in solution is precipitated by a nonsurface active reagent and then floated with the addition of a surfactant (*15*). In this study, an excess of negatively charged species present in solution such as HS^-, S^{2-}, or SiF_6^{2-} adsorb on the surface of the precipitate imparting a negative charge. Consequently, a cationic surfactant is necessary to effect the flotation. The hydrogen ion concentration controls the free anion concentration in solutions of salts of weak acids. In solutions saturated with H_2S, a weak diprotic acid, the sulfide ion concentration, and therefore the solubility of metal sulfides, is controlled by the solution pH. In a solution at room temperature saturated with H_2S(gas) at 1 atm pressure: $[H^+]^2[S^{2-}] = 1.1 \times 10^{-22}$ (*16*). Using the values for the total metal concentrations in all forms in the solution given in Table 1 and $[H^+] = 10^{-3}$ M, mass action calculations ($[M^{2+}][S^{2-}] = K_{sp}$) reveal that the solubility product constants for Cu, Co, and Ni sulfide are all exceeded while those for Fe and Mn sulfide are not. In light of this, several observations about Fig. 3 can be made.

(1) For copper, cobalt, and nickel there is a region where each metal shows an increase in recovery before reaching a plateau. In this region it is felt that an insufficient amount of sodium sulfide has been added to produce a solution saturated with H_2S gas. Therefore, $[H^+]^2[S^{2-}] < 1.1 \times 10^{-22}$ and the solubility product constants for the three metals have not been exceeded to a degree so as to allow quantitative precipitation of the three metals. However, as the amount of sodium sulfide added to the solution increases, the recovery increases correspondingly. Once the plateau is reached, the solution has become saturated with H_2S(g) and further addition of sodium sulfide has no effect.

(2) In the plateau region, copper is removed quantitatively (~95%), as expected, while cobalt and nickel recoveries are approximately 80 and 70% respectively. The incomplete, although constant recoveries of cobalt and nickel, may be attributed to one or more of the following: first, the metal concentrations reported in Table 1 represent all forms of the metals in the solution. As many different complex ions of cobalt and nickel are possible in solution, the incomplete recoveries suggest that portions of the cobalt and nickel may exist in an inappropriate form and are not available for precipitation. Second, solubility products are equilibrium values and it is well known that some sulfides form supersaturated solutions and precipitate slowly (*16*). Third, attempts to make detailed equilibrium calculations in a highly complex system such as this necessarily involve concentrations and not activities. In the concentrated acid-digested nodule solutions, the activity of any given ion will be substantially lower than its molar concentration.

Fourth, it was observed during the course of the studies that although the solution is completely cleared of precipitate by flotation with the surfactant, the mother liquor maintained a slightly milky appearance after flotation. The milkiness, which was not observed in hydroxy systems, is due to the presence of colloidal sulfur resulting from a redox reaction in solution. Iron(III) is well known to oxidize S^{2-} and HS^- to S° (*17*) and it was felt that a portion of the cobalt and nickel may be adsorbed by the colloidal sulfur and thus not be removed by flotation. However, a mass balance experiment carried out at pH 3 with 10 mmol Na_2S added showed that within experimental error all the cobalt and nickel were present in the floated and the mother liquor fractions, and essentially no Co or Ni was found on the colloidal sulfur fraction. Thus the incomplete recovery by flotation is not a result of surface adsorption onto colloidal sulfur.

(3) At pH 3, the solubility product constants for iron and manganese have not been exceeded; however, the recoveries of these metals are not zero because of a limited degree of adsorption of these ions on the surface of the CuS, CoS, and NiS precipitates.

Additional studies were undertaken to examine the effect of pH on the recoveries of the five metals. In the first study, the results of which are presented in Fig. 4, a solution of 5.6×10^{-3} F Na_2S (1 mmol) was used which corresponds to a point on the rising portion of the curve in Fig. 3. Depending on the pH, either precipitate flotation, ACF, or both are occurring. Colloidal iron hydroxide at a pH above its pzc is necessary for flotation by a cationic surfactant in ACF. This has been determined to occur between pH 5 and pH 6 as can be seen in Figs 2 and 4; thus, below pH 5 only precipitate flotation should exist. Copper recoveries are near the 80% level until pH 7–8 where they increase to quantitative levels. Using this quantity of sodium sulfide, cobalt, nickel, iron, and manganese recoveries are <10% below pH 4. Cobalt and nickel recoveries increase after pH 4 and became quantitative by pH 9. At pH 9, cobalt recoveries both with and without sulfide are in the 95 to 100% range while nickel recoveries are 85 to 95%. By comparing Figs. 2 and 4 it can be seen that the recoveries of cobalt and nickel are enhanced by the addition of sulfide ions in the range pH 5–8 and are probably due to a combination of ACF and precipitate flotation. The solubility product of iron sulfide is not exceeded below pH 5 and the recovery is near zero. Above pH 5 in Fig. 4 iron demonstrates a recovery curve which is indistinguishable from the one shown in Fig. 2 which is due entirely to the flotation of colloidal iron hydroxide. Manganese, unlike copper, cobalt, and nickel, shows a suppression in relative recovery in the presence of sulfide. Manganese sulfide has the smallest pK_{sp} of the five metals studied and would be expected to precipitate only at high sulfide ion

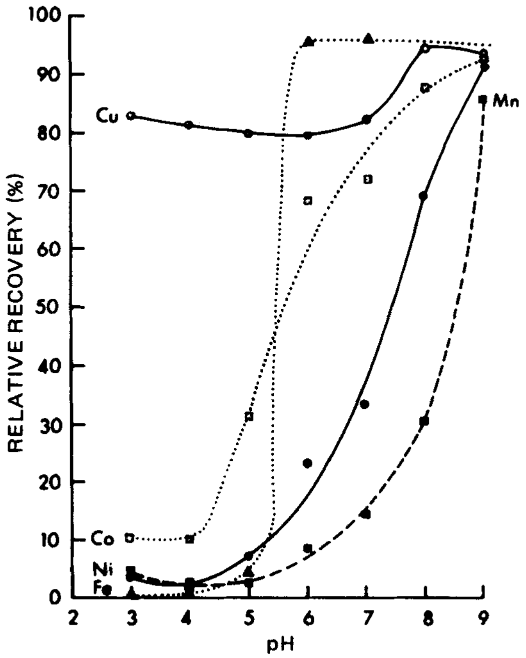

FIG. 4. Relative recovery of elements floated as a function of pH with 1 mmol sodium sulfide added: Cu (○), Co (□), Ni (●), Fe (▲), Mn (■).

concentrations (high pH). Manganese approaches 90% recovery at pH 9 which is approximately where one would calculate that manganese sulfide should be precipitated quantitatively.

An additional study was made where the recoveries of the five metals were examined as a function of pH using a solution of 5.6×10^{-2} F Na_2S (10 mmol). This concentration of Na_2S corresponds to a region in the middle of the plateau in Fig. 3. At this point an excess of Na_2S has been added and the solution has become saturated with $H_2S(g)$. These results are presented in Fig. 5. Here it can be clearly seen that the order of recovery follows the pK_{sp} of the metal sulfides. Although simple mass action calculations suggest that copper, cobalt, and nickel should be removed quantitatively at all pH values studied, this is only true for copper. Possible explanations for this behavior have been discussed previously. The recovery of iron is dependent upon precipitate flotation as the sulfide in the pH range 3–5 and flotation as the colloidal iron hydroxide above pH 5. Note the more gradual increase exhibited by iron in Fig. 5 compared to the abrupt rise shown in Fig. 4. The recovery of manganese remains negligible throughout the pH range studied as its solubility product has not been exceeded.

Flotation from Acid-Digested Tailings of Sulfated SEDCO 445 Nodules

After completion of the leaching process, approximately 25% of the sulfated nodules remain as solid process tailings. We have recently reported on the flotation of the remaining valuable metals and several of the more abundant toxic elements as hydroxides from acid-digested tailings (*3*). Studies described above examined the removal of some of the same elements from acid-digested ferromanganese nodules as insoluble sulfides. In both previous studies the cationic surfactant, CTA, was employed to float the negatively charged colloidal precipitate formed. In the current investigation it was found that the addition of sodium sulfide and subsequent adjustment of

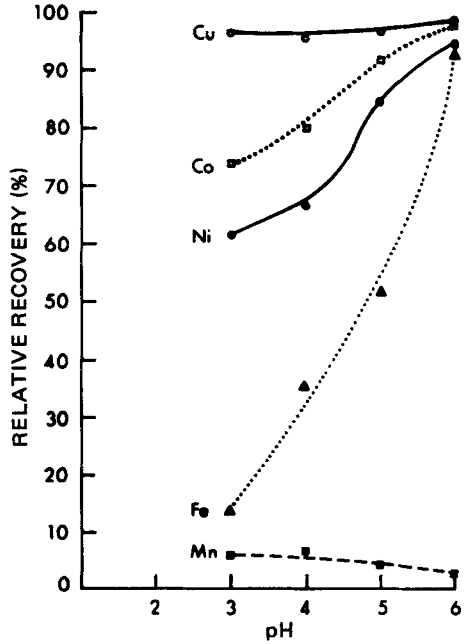

FIG. 5. Relative recovery of elements floated as a function of pH with 10 mmol sodium sulfide added: Cu (○), Co (□), Ni (●), Fe (▲), Mn (■).

the pH also produced a floc with a negative surface charge. This is not surprising because the matrix of the tailings is similar to that of the original nodules, although a large portion of the metals which form soluble sulfates have been removed.

The quantity of sodium sulfide required to provide an excess in solution was chosen from Fig. 3. The recovery of nine metals present in the tailings was determined as a function of pH when the solution was approximately 5.6×10^{-2} *F* in sodium sulfide; the results are shown in Fig. 6. The copper, cobalt, and nickel not removed in the leaching process are separated quantitatively from the tailings solution when the pH has increased to a value of 5. Zinc and aluminum are removed quantitatively at pH 3 and 5, respectively; zinc as a sulfide and aluminum as the hydroxide. The iron recovery follows a pattern similar to that exhibited for the leach solutions: the removal between pH 2 and 4 is due to the adsorption of ions on the surface of the sulfide precipitates of the other elements and the recovery becomes quantitative at the higher pH values as colloidal ferric hydroxide is produced and floated. Manganese is not floated in the pH range studied because the solubility products of its hydroxide and sulfide have not been exceeded. The two most abundant toxic elements in the tailings, lead and vanadium, are removed quantitatively from the tailings at pH 5. Lead forms an insoluble sulfide and vanadium appears to be removed by surface adsorption.

Two general observations about the behavior of the sulfide system compared to the hydroxide system can be made. First, use of sodium sulfide in the flotation scheme resulted in an improved recovery of copper, cobalt, nickel, zinc, lead, and vanadium as compared to the hydroxide system. Second, the pH at which a particular metal is optimally floated is lower in the sulfide system than in the hydroxide system.

Adsorptive Bubble Separation of Metals from Leach Solutions of Sulfated SEDCO 445 Nodules

The floc generated by addition of Na_2S to leach liquors, after pH adjustment with NaOH, was found to have a significantly different surface charge and was effectively floated by the addition of an anionic surfactant, SLS. The enriched foam generated in the cell upon addition of the SLS was generally unstable and gelatinous. In order to facilitate the manual removal of the enriched foam and prevent undesirable redistribution of floc into the underlying solution, a small amount of the nonionic surfactant Triton X-100 was added as a frother. This resulted in the formation of a stable clean foam layer which supported the enriched layer—a procedure which had been previously used in our laboratory (*2*).

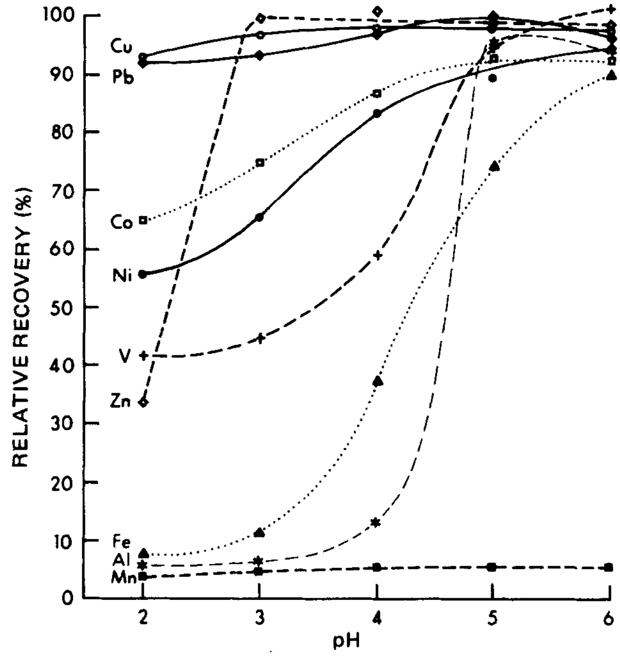

FIG. 6. Relative recoveries of elements floated with cetyltrimethylammonium chloride from acid-digested tailings as a function of pH: Cu (○), Pb (♦), Co (□), Ni (●), V (+), Zn (◊), Fe (▲), Al (*), Mn (■).

Table 2 shows the elemental composition of untreated *SEDCO* 445 nodules, nodule tailings, and leach liquors from the sulfation process. As a check for procedures, a mass balance calculation was performed on both the tailings and the leach liquors and compared to previously determined nodule compositions. The results of this calculation showed that within experimental error no sample loss occurred during treatment. Digestion of the tailings necessarily involved dissolution of the filter as well as the tailings material. A blank determination showed no contamination from the filter. The recovery of metals present in the leach solutions was evaluated in solutions of approximately 1.1×10^{-2} F Na_2S and the results are presented in Fig. 7. The recovery of Cu, Co, and Ni as sulfides was achieved at low pH values, and generally required little pH adjustment prior to precipitation of the metal sulfides. The recovery of the metals of interest at low pH is carried out in a much more efficient manner with the sulfide system than with the previously reported hydroxy system where alkaline pH values (ca. pH 9) were

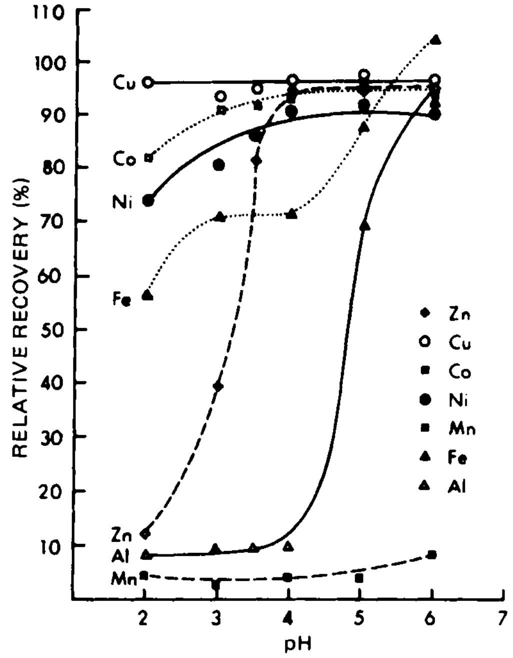

FIG. 7. Relative recoveries of elements floated with sodium laurylsulfate from leach solutions as a function of pH.

necessary for quantitative recoveries. At pH 2 recovery of the Cu was quantitative with that of Co near 83% and Ni near 75%. At this pH value negligible amounts of the Mn and Al were recovered and approximately 13% of the Zn was removed from solution. The recovery of manganese always remained below 4% except at pH 6 where it rose to nearly 9%. At pH 5 and below, the manganese recovery may be attributed partly to the occlusion of Mn^{2+} in the other metal sulfide precipitates or to the ion flotation of Mn^{2+} with SLS. Since the flocs in this portion of the study were found to bear very little surface charge, it is unlikely that manganese ion would be electrostatically adsorbed. Calculations based on activities of ions in solution and solubility limits indicate that some crystalline MnS may begin to form near pH 6 and contribute to the observed increase in recovery. If present as amorphous MnS, however, it would not be expected to precipitate below pH 7. The recoveries of Cu, Co, Ni, and Zn seem to follow the order of general solubility considerations through this study. The shape of the recovery curves for these four metals is nearly identical to that presented in Fig. 6 for the tailings as well as to that for acid-digested nodules (Fig. 5).

Since the systems are quite different in composition as well as in their surface charge characteristics, the similarities in the shapes of the three sets of curves indicate that precipitate flotation is the likely mechanism of removal of the metal sulfides from solution. ACF probably also occurs in this system, and iron is possibly removed by this mechanism below pH 5. The recoveries of 50 to 70% for iron between pH 4 and pH 7 are unusual in that neither the K_{sp} of FeS nor that of $Fe(OH)_3$ should have been exceeded in this range. Fuerstenau and co-workers have shown that hydroxy complexes have such a strong surface activity that they can specifically adsorb even onto positively charged surfaces (*18*). These researchers found that extensive adsorption of the monohydroxy complex of trivalent iron occurred above pH 2 on a positively charged alumina surface. This parallels the specific adsorption behavior of iron in this sulfide system. Since the floc bears little surface charge, a force other than that due only to electrostatic attraction is probably responsible for the surface adsorption of iron. The minimal removal of Al below pH 5 is also believed to be due to the same type of attractive forces because in this pH range up to 10% of the total Al is present as mono- and dihydroxy complexes (*19*). In the ferric hydroxy complex system, however, a much larger portion is present as the monohydroxy complex even as low as pH 2 (*20*). Above pH 4 both Al and Fe are expected to be removed via precipitate flotation of their insoluble hydroxides. This is reflected by a sudden rise in their recovery curves above pH 4 both in the tailings and leach liquors.

The surface charge on the flocs generated from leach liquors was measured as a function of pH and the data are presented in Table 3. Although above pH 2 the flocs do bear a slight negative charge, they were much more readily floated with SLS, an anionic surfactant, than with LA or CTA, both cationic surfactants. This behavior may be partly attributed to the natural floatability of freshly precipitated sulfides. It has been previously reported in the literature that the presence of SiF_6^{2-} in solution can readily cause decreases in the surface charge of hydroxide flocs by exchange with the surface hydroxyl groups (*21*). Since acid-digested solutions contain F^- from the mineral acids used in dissolution of the sample and Si(IV) from the silicate phase of the nodules, it is believed that SiF_6^{2-} present in these solutions causes the flocs to carry a significantly more negative surface charge by a related mechanism. This is confirmed by the data presented in Table 3 as the addition of Si(IV) as SiF_6^{2-} to the leach liquors permitted flotation with cationic surfactants and resulted in a marked decrease in the surface charge on the flocs. Flotations with the anionic surfactant, SLS, were no longer

TABLE 3

Zeta Potential of Mixed Sulfides Precipitated from Leach Liquors of Sulfated Nodules[a]

	Zeta potential (in mV)		
pH	No SO_4^{2-} or SiF_6^{2-}	SO_4^{2-}, no SiF_6^{2-}	$SO_4^{2-} + SiF_6^{2-}$
2.0	—	No colloid mobility	−30
2.5	—	−14	−29
3.0	−14.5	−14	−32
4.0	−16	−21	−37
5.0	−18	−19	−47
6.0	−16	−25	−48

[a] Sample conductance: 7.3×10^3 to 2.4×10^3 μU/cm. Applied potential: 50 to 100 V.

possible at pH values where SLS was highly effective in the absence of SiF_6^{2-}. The presence or absence of SO_4^{2-}, however, did not have any effect on the flotation behavior of the precipitates although at pH 4 and above the surface charge of the flocs seems to be altered slightly. Since the pzc (point of zero charge) of many transition metal sulfides is between pH 2 and pH 6, the charge on the flocs generated from the leach liquors is not altogether unexpected. Healy and Moignard have noted that hydroxide formation on the surface of sulfide minerals can lead to reversals in zeta potential from negative to positive in the pH region where hydroxide formation is favored (*22*). At higher pH values the zeta potential again returns to the expected larger negative values. Specific adsorption of cations is also believed to contribute to the alteration of the zeta potential at lower pH and may occur in our system. Another factor which may contribute to the changes in surface charge in the current study is the occurrence of surface oxidation reactions such as

$$\mathrm{MS(surface)} + 2\mathrm{H^+(aq)} + \tfrac{1}{2}\mathrm{O_2(aq)} \rightarrow \mathrm{M^{2+}(surface)} + \mathrm{S^0(s)} + \mathrm{H_2O}$$

Overall, the electrokinetic behavior of most sulfides has been found to depend on several factors, the more predominant of which include surface oxidation, sample pretreatment procedures, and mineral composition (*22*). In light of the above, the behavior exhibited by the leach liquor system is not entirely unusual. Thus, the presence of SiF_6^{2-} does indeed contribute to the more negative zeta potential of acid-digested samples, but the effects mentioned above, rather than the absence of SiF_6^{2-}, lead to the zeta potential changes on the flocs generated from the leach liquors. This is particularly true when one considers the presence of elemental sulfur found in the mother liquors after completion of the flotation procedures, which is indicative of the redox reaction. The behavior exhibited by the various nodule-derived solutions is highly complex and studies to further elucidate mechanisms of flotation are currently underway.

CONCLUSIONS

The two-step high-temperature sulfation procedure described was found to further enhance the recovery of Co, Ni, and Mn as compared to a single-stage sulfation. The increase in recoveries, however, may not be large enough to warrant the second stage in a large-scale operation.

It has been shown that through the addition of sodium sulfide and pH adjustment, quantitative removal of the economically valuable metals Cu, Co, and Ni from an acid-digested ferromanganese nodule solution can be achieved. The separation occurs by means of precipitate and adsorbing colloid flotation depending upon the pH of flotation. Although the precipitation behavior follows the general pattern predicted solely on the basis of solubility product constants, the recovery obviously depends on other factors present in this highly complex system.

The flotation methods described were found to effectively remove residual metals such as Cu, Co, and Ni as well as the bulk of the potentially toxic species Pb and V from tailings of sulfated deep-sea ferromanganese nodules while leaving behind the manganese and silicate phase of the matrix. A more selective recovery of the metals is obtained at lower pH values than by carrying out the flotation of insoluble hydroxides. The flotation of metal sulfides from leach liquors is also more selective than that achievable with hydroxides. At pH 4 excellent recoveries of Cu, Co, Ni, and Zn can be achieved resulting in a clean separation from Mn and Al. Traces of Fe^{3+} are co-floated primarily as a result of the specific adsorption of $Fe(OH)^{2+}$. The principal mechanism of removal is believed to be via precipitate flotation of the insoluble metal sulfides for all three systems investigated.

This dual purpose flotation of leach liquors and tailings solutions may prove valuable in that the extra cost incurred during cleanup of the tailings by flotation may be offset by the increase in valuable metal recovery. This obviously is dependent upon the initial efficiency of removal of valuable metals during nodule pretreatment. Further studies employing sulfhydryl reagent surfactants and other nodule processing methods are currently underway, and may result in further selectivity in the recovery of valuable metals.

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