Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Separation of Metals from Sulfated Deep-Sea Ferromanganese Nodules by Adsorbing Colloid Flotation

E. H. De Carlo[a]; B. D. Bleasdell[ab]; H. Zeitlin[a]; Q. Fernando[c]
[a] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF HAWAII, HONOLULU, HAWAII [b] Department of Chemistry, Southern Oregon State College, Ashland, Oregon [c] DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARIZONA, TUCSON, ARIZONA

To cite this Article De Carlo, E. H. , Bleasdell, B. D. , Zeitlin, H. and Fernando, Q.(1982) 'Separation of Metals from Sulfated Deep-Sea Ferromanganese Nodules by Adsorbing Colloid Flotation', Separation Science and Technology, 17: 10, 1205 — 1218

To link to this Article: DOI: 10.1080/01496398208060645

URL: http://dx.doi.org/10.1080/01496398208060645

SEPARATION SCIENCE AND TECHNOLOGY, 17(10), pp. 1205–1218, 1982

Separation of Metals from Sulfated Deep-Sea Ferromanganese Nodules by Adsorbing Colloid Flotation

E. H. DE CARLO, B. D. BLEASDELL,* and H. ZEITLIN

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF HAWAII
HONOLULU, HAWAII 96822

Q. FERNANDO

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF ARIZONA
TUCSON, ARIZONA 85721

Abstract

Adsorbing colloid flotation (ACF) is applied to aqueous leach solutions of sulfated deep-sea ferromanganese nodules and their process tailings. Metal cations of Cu, Co, Ni, Mn, Al, and Zn are separated simultaneously by flotation with hydroxide collectors and cationic surfactants from the leach liquors of sulfated ferromanganese nodules. Applications of ACF to the nodule tailings also makes possible the recovery of residual Cu, Co, Ni, Ti, Zn, Al, Fe, Mn, and the separation of Pb and V, the most abundant toxic species in the nodules and tailings.

INTRODUCTION

In recent years the separation and recovery of valuable metals from deep-sea ferromanganese nodules has become a subject of great interest. The nodules, which are present in vast amounts on the sea floor, constitute a major and strategic resource and reservoir of cobalt, copper, nickel, molybdenum, vanadium, and manganese (*1*). The deposits of greatest

---

*Present address: Department of Chemistry, Southern Oregon State College, Ashland, Oregon 97520.

economic interest are located in the equatorial North Pacific Ocean (*1*). These deposits are valuable because their enrichment in the transition metals Cu, Co, and Ni exceeds many of the presently exploited continental sources. The metals of interest have been found to account for approximately 3% of the nodules on a dry weight basis (*1*). The recovery of these metals has been carried out by smelting, high temperature chlorination, and by extractive hydrometallurgical processes that involve leaching with acids, ammonia, or aqueous solutions of reducing agents such as SO_2 (*2, 3*). It is anticipated that within the next decade, large-scale recovery of metals from deep-sea nodules will become the focus of an emerging industry uniquely concerned with ocean mining and processing. This new industry, however, may face a number of serious socioeconomic, legal, and environmental problems which remain as yet unresolved (*4, 5*).

A well-developed physical separation technique which has been used extensively for many years on a large scale, and applied to silicates as well as to oxide and sulfide minerals, is ore flotation (*6*). Ore flotation technology, however, has not been employed for the preconcentration of elements in deep-sea nodules. The short-range order (20–100 Å) of the mineral phases encountered in nodules is the major drawback to the application of ore flotation which is generally useful for minerals with an ordered structure in particle sizes of about 100 μM (*3*).

Recent work in our laboratory has shown the feasibility of using adsorbing colloid flotation (ACF) for the separation of potentially toxic anionic species such as AsO_4^{3-}, SeO_3^{2-}, SbO_4^{3-}, and $Ge(OH)_3O^-$ from acidic solutions containing large amounts of transition metals, and various cations from solutions of acid-digested deep-sea nodules (*7, 8*). The latter work involved the separation of positively charged copper, cobalt, nickel, and manganese species from the bulk of the nodule material using a negatively charged ferric hydroxide collector generated from *in-situ* iron, a cationic surfactant, and air. Preliminary studies in our laboratory have shown that a high temperature sulfation of the nodules followed by an aqueous leach might be a feasible method of separating valuable transition metals from the remaining less desirable nodule constituents (*2, 9*). Since high temperature sulfation and leaching provide a selective means of recovering certain metals of interest, while acid digestion nonselectively solubilizes the entire nodule matrix, it is possible, on the basis of our work, that the former method could be expanded to a large-scale industrial process. A study was initiated to evaluate the recovery of Cu, Co, Ni, and Mn from leach solutions in the sulfation-leach process by ACF. Since Fe is recovered only at trace levels (less than 10 ppm) in the leach solution, it cannot be used as a collector that is generated *in situ*. It has been established, however, that hydrous manganese oxide can act effectively as a scavenger for trace metals both by surface adsorption and by lattice substitution (*10*). A preliminary study by Sedwick has demonstrated the effectiveness of hydrous manganese oxide as a collector in unbuffered leach solutions of sulfated nodules. Upon adjustment of the pH of these solutions with NaOH, the manganese hydroxide phase was found to bear a negative surface change and was able, therefore, to concentrate low levels of copper, nickel, and cobalt that were present in solution (*11*).

An additional and vital aspect of any metallurgical processing scheme is the disposal of the process rejects or tailings. In the high temperature sulfation and leaching process, a large portion of the nodule material remains behind as tailings. These rejects are known to contain an abundance of minor and trace elements, many of which are potentially toxic, as well as the bulk of the iron-bearing phase (*2, 9, 12*). Any processing scheme that will be implemented would have to deal with the environmentally safe disposal of the tailings in accordance with stringent federal regulations. Since several of the toxic elements may be solubilized after sulfation and the leach step, it would be of great importance to effectively separate and remove these undesirable species from the tailings. For this reason a further investigation was initiated to study the removal of various elements found in the tailings by ACF with a negatively charged ferric hydroxide collector generated from *in-situ* iron, a cationic surfactant, and air.

This communication is concerned with the simultaneous separation of the metal cations of Cu, Co, Ni, Fe, Ti, V, Pb, Mn, Al, and Zn on a laboratory bench scale from the leach liquors of sulfated deep-sea ferromanganese nodules and their tailings by ACF employing Mn(II) and Fe(III) hydroxides as collectors. Both collectors lie above their respective pzc (point of zero charge) values in the pH range studied, and consequently concentrate cations and leave the anions behind. The flotation scheme permits the recovery of the valuable metals from the nodules and their tailings as well as the separation of a large portion of Pb and V which are the most abundant toxic species in the nodules and tailings.

EXPERIMENTAL

Apparatus and Equipment

A Perkin-Elmer Model 2380 atomic absorption spectrophotometer was used for all absorbance measurements. The pH of solutions was determined using a Beckman Expand-O-Matic pH meter or an Orion Research Model 801-A Digital Ionalyzer, each calibrated daily against Scientific Products Standard Reference Buffers (pH 4.01, 7.00, and 10.00). All flotations were carried out using a modification of the cell previously described by Kim and Zeitlin (*13*). The cells were constructed so as to hold a maximum sample volume of 200 mL.

Reagents

All chemicals used were of Analytical Reagent grade. Aqueous solutions were prepared with water purified in a Millipore Model Milli R/Q ion exchange and reverse osmosis water purifier. Individual surfactant solutions were prepared in ethanol as follows: 1 mg/mL laurylamine HCl, 15 mg/mL cetyltrimethyl ammonium chloride, 15 mg/mL Triton X-100. Concentrated and dilute solutions of HCl, HNO_3, H_3BO_3, HF, and NaOH were used throughout the studies as required. Atomic absorption standard reference solutions (1000 μg/mL) for all metals analyzed were purchased from Anderson Laboratories Inc. Standard mixed element solutions for AAS analysis were prepared prior to analysis by appropriate dilutions of the individual 1000 μg/mL standards.

Analytical Procedure

All leach liquor and tailings of sulfated deep-sea ferromanganese nodules were obtained from a previous investigation in our laboratory (*9*). The aqueous leach liquors were diluted to provide solutions approximately 20, 40, 60, and 80% of the original sample concentration in 0.4 M H_3BO_3. A 20-mL aliquot of the diluted leach liquor was pipetted into a 250-mL beaker and the volume adjusted to approximately 160 mL with water. The pH was adjusted to the desired value with NaOH. The solution containing the colloidal precipitate was transferred quantitatively to the flotation cell, purified air passed through the cell at a flow rate of 17 ± 2 mL/min, and 4 mL of cationic surfactant solution (laurylamine HCl) injected by means of a hypodermic syringe. After several minutes of gas flow (or until the cell had almost completely cleared), 0.5 mL of Triton X-100 nonionic surfactant solution was injected in order to stablize the enriched foam bed. The foam was allowed to collect for an additional 3–4 min and manually scooped into a beaker with a Teflon spatula. A few drops of concentrated HCl and water were used to rinse adhering floc from the spatula into the beaker. Several milliliters of concentrated HCl were added to break up the foam and dissolve the floc over medium heat. The resulting solutions were quantitatively transferred to 50- or 100-mL volumetric flasks, diluted to the mark with water, and transferred to Nalgene containers for storage. Replicate flotations were carried out at pH 8, 9, and 10 in order to evaluate the reproducibility of recovery of the metal cations of interest. The samples, or appropriate dilutions thereof, were then analyzed by AAS. Whenever undiluted samples were analyzed, it was found necessary to add surfactant and NaCl to the standards to compensate for the slight signal enhancement observed in the presence of sodium and surfactants in the samples.

A solution of sulfated nodule tailings was prepared by dissolving a 3.398-g portion of the tailings using a modification of the bomb-digestion procedure described by Bernas (*14*). A dilution to 400 mL with 0.5 *M* H_3BO_3 provided a stock 8.5 mg/mL tailings solution. Ten milliliter aliquots of the stock tailings solution were then treated in a manner similar to the leach liquors except that 5 mL of the cationic surfactant cetyltrimethylammonium chloride solution were injected. Concentrated HCl and HNO_3 were used to dissolve the floc and foam over medium heat. The solutions were transferred to 25-mL volumetric flasks and diluted to the mark with water. Due to the high surfactant concentration used, all samples were filtered before storage and analysis to remove any suspended surfactant. Replicate flotations were performed at 1 pH unit intervals between pH 5 and 10. The concentrations of metals in the leach liquors and tailings before flotation were determined by AAS and used to calculate relative recoveries of the metals.

RESULTS AND DISCUSSION

The nodules used in this investigation were obtained from the *SEDCO* cruise, at station 445 which is located at latitude 9°24′ N, longitude 151°21′ W, at a depth of 5200 m. Generally, nodules found in this area of the North Equatorial Pacific Ocean are a high ore grade, contain up to 3% on a dry weight basis of the metals copper, cobalt, and nickel, and are characterized by a high manganese and low iron content. The elemental analysis of the leach solutions and the tailings employed in these studies is presented in Table 1 together with the composition of the untreated nodules as determined by Shinn (*9*). It is noteworthy that the leach liquors have high manganese concentrations and practically no iron, whereas in the tailings the iron content is twice that of the manganese. The nodules and tailings cannot be compared directly as a given mass of tailings is not derived from the same mass of untreated nodules (*9*). It will be noted later, however, that similarities do exist in the flotation behavior of untreated nodules and tailings.

Recovery of Metals

The recoveries of metals from the leach solutions by ACF are given in Table 2. These data show the relative recovery as a function of sample loading as well as a function of pH. The total ionic strength of solutions is known to affect the efficiency of flotation and must be carefully controlled in

TABLE 1

Elemental Composition of Tailings and Leach Liquors

Metal	Concentration					
	Leach 1[a]	Leach 2	Leach 3	Leach 4	Tailings[b]	Nodules[b]
Cu	27.3	53.8	81.8	118	0.82	1.04
Co	6.3	12.4	19.8	27.4	0.12	0.18
Ni	29.2	56.5	84.8	121	1.40	1.18
Mn	850	1660	2660	3860	5.08	22.6
Fe	2	ND[c]	ND	ND	11.5	5.48
Al	ND	ND	ND	92	6.08	ND
Ti	ND	ND	ND	n.d.[d]	1.55	ND
V	ND	ND	ND	n.d.	0.11	ND
Zn	ND	ND	ND	8.6	0.11	ND
Pb	ND	ND	ND	n.d.	0.09	ND

[a] Expressed as mg/L for all leach solutions.
[b] Expressed as % dry weight for tailings and nodules.
[c] ND = not determined.
[d] n.d. = none detected.

any investigation (*15*). In this study the overall ionic strength of the leach solutions of different loadings was essentially independent of the load because of the high boric acid concentration in the matrix. A boric acid matrix was used in these studies in order to complex any fluoride ions remaining in solution after the bomb digestion of the tailings with hydrofluoric acid. Boric acid was also used in the leach solutions as it was found to act as a buffer between pH 8 and 10 and greatly facilitate pH control during flotations. Preliminary work in our laboratory by Sedwick had shown that the pH of unbuffered leach solutions varied considerably during the course of flotations and led to large fluctuations in metal recoveries. From the data in Table 2 it can be seen that the recovery of the various metals did not differ appreciably as a function of loading over the range studied. The only significant variation was found in the slight increase in cobalt and nickel recoveries with increasing load at pH 8. This behavior may be attributed in part to the increased formation of the hydroxides of these metals. Manganese also seemed to exhibit this behavior at pH 8 and 9 although to a somewhat smaller extent. It should be noted that the fourth set of leach solutions showed signs of reaching the upper limit at which flotation was still effective with the amount of cationic surfactant used. This matter is discussed in greater detail below. The recoveries of copper and iron were essentially quantitative throughout the pH range studied, although copper recovery may

TABLE 2

Relative (%) Recovery of Metals from Nodule Leach Liquors by ACF

Metal	Leach solution	pH 8.0	pH 9.0	pH 10.0
Cu	1	87.9	95.9	97.6
	2	91.1	94.9	95.6
	3	90.8	87.0	88.3
	4	85.4	98.1	90.6
Co	1	18.2	83.8	94.6
	2	21.7	95.6	98.6
	3	29.1	84.8	90.3
	4	30.6	102.1	97.3
Ni	1	15.4	77.8	93.8
	2	16.9	89.6	95.3
	3	22.3	84.6	87.7
	4	24.8	99.4	93.1
Mn	1	8.9	44.6	98.9
	2	8.6	44.8	93.7
	3	10.4	49.1	87.7
	4	10.0	62.6	92.8
Zn	4	86.4	99.3	92.5
Al	4	87.7	87.8	75.4

be optimal at pH 9. The behavior of the metals cobalt and nickel seemed to parallel one another; the recoveries increased between pH 8 and 9, and were quantitative at pH 9 and above. In all cases the cobalt recovery slightly exceeded that of nickel. The manganese behavior, however, appeared to be entirely pH dependent with the recovery increasing steadily as a function of pH.

The results of the flotation studies on solutions of acid-digested tailings are presented in Figs. 1 and 2 for 10 metals. The recoveries of some of these metals from the fourth set of leach solutions are presented in Fig. 3. The flotation behavior of iron, lead, copper, and zinc from the tailings seemed to parallel one another. Removal of lead, iron, and zinc increased rapidly between pH 5 and 6, and leveled off at quantitative recoveries above pH 6; the copper recovery was found to be nearly quantitative over the entire pH range studied. This observation suggests that a mechanism other than simple electrostatic attraction and adsorption onto an oppositely charged collector may govern the removal of copper from solution. Wilson and co-workers have developed complicated theoretical treatments regarding the collection of inorganic ions from solution by ACF (*15, 16*). The cobalt, nickel, and

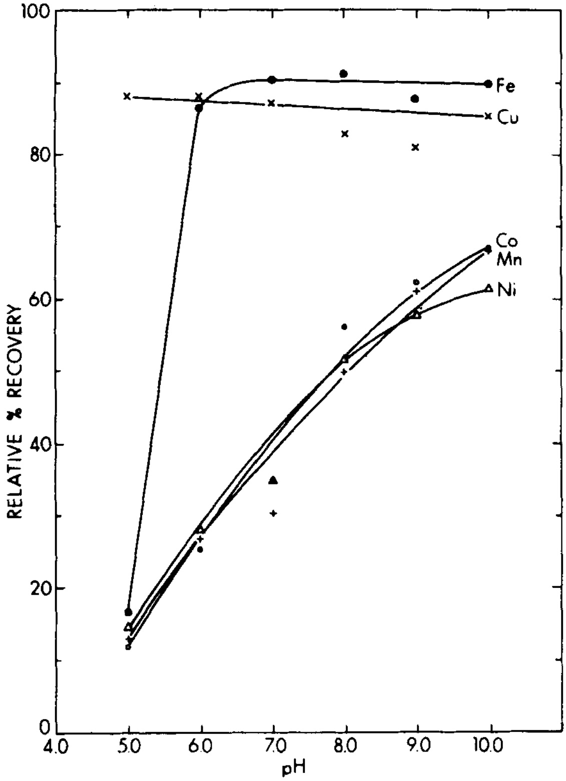

FIG. 1. Recovery of Fe (●), Mn (+), Cu (X), Co(O), and Ni(△) from nodule tailings solutions as a function of pH by ACF.

manganese recoveries from the tailings appear to be pH dependent and increase steadily from approximately 15% at pH 5 to near 65% at pH 10; this behavior was found to be very similar to that observed in solutions of acid-digested untreated nodules (*8*). Titanium and vanadium were not removed totally from the tailings solution with maximum recoveries of about 60% that are reached at pH 10. Aluminum, with its amphoteric nature, exhibited the greatest variability in recovery as a function of pH. Removal was quantitative at pH 6–7, and then decreased as the pH was further increased. This pattern was also observed in the removal of aluminum from leach solutions although it was shifted toward higher pH, with the decrease in recovery at high pH not as pronounced as in the tailings. No lead, titanium, or vanadium were found in the leach solutions; consequently these metals were not available for flotation. Zinc and aluminum, however, were found to be present in the leach solutions along with copper, cobalt, nickel, manganese, and traces of iron, and were easily removed by ACF.

Surfactants

The colloidal precipitates generated upon pH adjustment with NaOH bear a negative surface charge and therefore require cationic surfactants in ACF. Long-chained alkylamines such as laurylamine hydrochloride (LA) and cetyltrimethylammonium chloride (CTA) have been used previously to float both iron and manganese hydroxides (*17*). A preliminary subjective evaluation of foam formation and stability indicated that LA was well suited for the flotation of the leach liquors while CTA was found to float the colloidal precipitates from the tailings solution more readily. Further studies conducted in our laboratory indicated there was no appreciable difference in the recoveries of metals from acid-digested nodules by ACF using either surfactant when aliquots of the same sample at the same pH were floated. A relatively high concentration of CTA was required for the optimum flotation from tailings solution; this can be attributed to the presence of large amounts of aluminosilicates and other interfering anions which can tie up surfactant and decrease its effective concentration. Wilson has shown that polyvalent anions such as silicates and phosphate interfere with the removal of heavy metals from wastewater by ACF (*18*). The presence of sulfate in samples has also been found to affect flotation in our laboratory.

In order to facilitate foam formation and handling, it was sometimes helpful to interrupt the air flow through the cell for short periods of time. Continuous air flow often resulted in wet voluminous unstable foams which had to be permitted to collapse partially before manual collection could be carried out, while occasional interruption of the air flow generally resulted in more dense and stable foams which could be separated easily from the mother liquor. Similarly, small multiple injections of surfactant, rather than a larger single injection of the same total volume, were found to enhance the rising of the floc although the efficiency of recovery was not affected. These modifications to the procedure were most useful at the higher pH values, especially in the fourth set of leach liquors at pH 10. It is anticipated that if leach liquors of higher loadings were to be floated, the 4 mL of cationic surfactant used in this study would not be sufficient to bring up all the colloidal precipitate from the mother liquor. Complete flotation of aliquots of the fourth load leach solutions often required 10 to 20 min, while those for lower loadings and lower pH required only 3 to 5 min if the gas flow was left on continuously. It appears that the heavily loaded surfactant in the former case could not readily reach the surface or remain there due to the turbulence

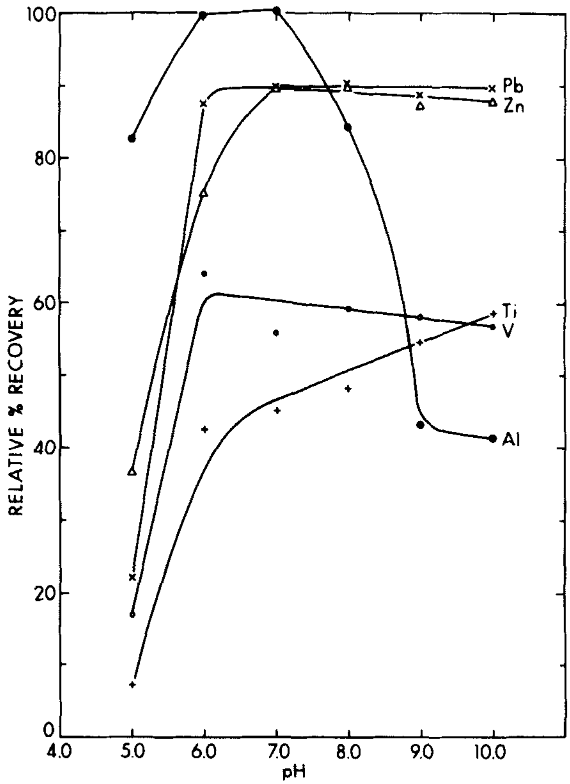

FIG. 2. Recovery of Al(●), Pb(X), Ti(+), V(O), and Zn(△) from nodule tailings solutions as a function of pH by ACF.

created by the air flow through the cell. The lighter surfactant–floc entities of the latter situation, however, could rise easily with the air bubbles and concentrate at the air–water interface.

In all cases involving flotations of the leach solutions, except for the fourth set at pH 10, a small amount of Triton X-100 (nonionic surfactant) was used to generate a clean supporting layer of foam below the sometimes unstable enriched foams. The Triton X-100 foam minimized floc redistribution into the mother liquor which sometimes resulted from disturbances created at the gas–liquid interface during manual collection of the enriched foam. In the fourth set of leach solutions at pH 10, however, the enriched foam was so heavy that the Trition X-100 foam rose through it, causing a general disturbance and redistribution of the floc; consequently, Triton X-100 could not be used in this case.

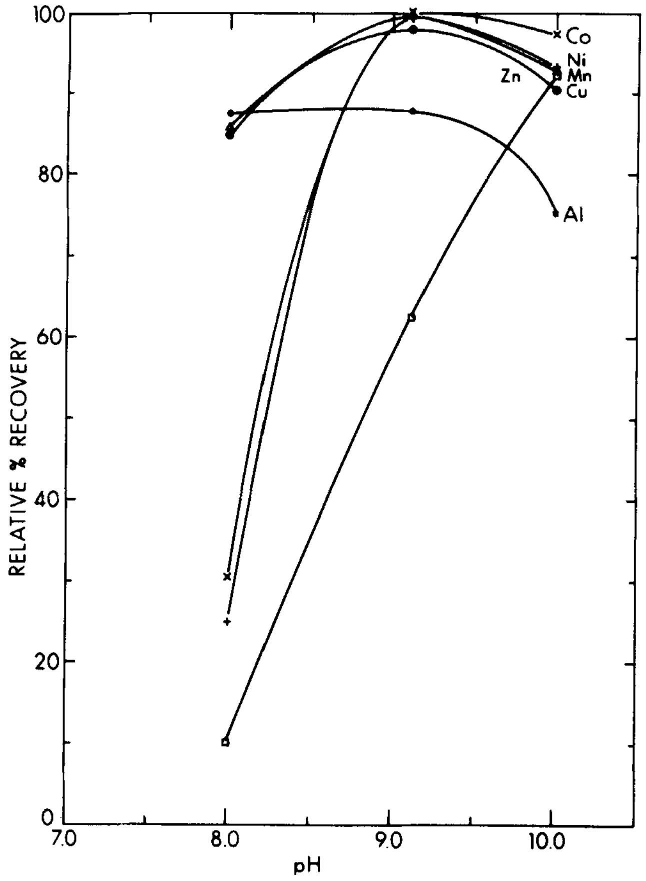

FIG. 3. Recovery of Al(○), Mn(□), Cu(●), Co(×), Ni(+), and Zn(△) from leach liquors of sulfated manganese nodules as a function of pH by ACF.

Collectors

The basic mechanism in ACF involves the adsorption of charged particles onto the surface of an oppositely charged colloidal precipitate (*19*). This simple model fails to explain the recovery behavior of several elements in these studies. From the elemental composition of the samples investigated, it is expected that manganese and iron act as the primary collectors in the leach and tailings solutions, respectively. In the leach solutions none of the other metal species are present in sufficient quantities to affect the surface charge of the collector significantly or act as co-collectors (see Table 1). In the tailings, however, there is sufficient aluminum and manganese (6.08 and

5.08% by weight, respectively) to actively participate in the collection of the other metal cations. In all of the above cases the collectors must exhibit an overall negative surface charge to be floated with cationic surfactants. The presence of large quantities of sulfate and borates in the leach solutions, and chloride, nitrate, fluoride, and borates in the digested tailings solutions is believed to affect the surface charge characteristics of the colloidal precipitates. This may contribute in part to the lowering of the pzc of iron and manganese hydroxides from their expected values of pH 6.0–8.5 and 4.5–7.0, respectively, to the much lower pH values encountered in this study (*20, 21*). In previous studies with acid-digested nodules, the surface charge of the colloidal precipitates was found to be negative as low as pH 3.5–4.0, the pH at which the precipitates first appeared; in tailings, effective flotations carried out at pH 5 with CTA indicate a negative surface charge on the collector (*8*). This lowering of the pzc encountered in these samples may explain the anomalous behavior of copper which is recovered nearly quantitatively when other species, including the primary collector, are not floated. Parks reports the pzc of natural hydrous copper hydroxide to be near pH 7.6 (*20*). This indicates that $Cu(OH)_2$ could float directly with LA or CTA if its pzc is exceeded. In the leach solutions there is little doubt as the studies begin at pH 8, a value higher than the pzc reported by Parks; in the tailings, however, the previously mentioned lowering of the pzc may occur which results in the direct flotation of the copper as its hydroxide. The recovery of titanium from the tailings is also anomalous in view of its very small solubility product ($K_{sp} \approx 10^{-40}$) (*22*). The recovery is sufficiently low so as to eliminate this element as a potential collector. The low recovery may be explained in part by slow kinetics of hydrolysis in these solutions even though the reaction is thermodynamically favored. Another factor which may prevent the efficient removal of titanium would be its presence as a complex ion or in some other inappropriate form in solution which cannot be collected by the Fe–Mn–Al mixed collector. The high initial removal of aluminum both in the leach and tailings solutions may also explain in part the atypical behavior exhibited by copper. If aluminum were to act as a collector, it could readily adsorb the Cu^{2+} from solution or enhance the coprecipitation of $Cu(OH)_2$, thus contributing to its recovery. In the tailings the Al/Cu ratio is sufficiently high for the aluminum to act as a collector, but in the leach solutions where the Al/Cu ratio is near unity it is doubtful that the aluminum can contribute to the removal of copper from solution. It must be noted, however, that the ratio of aluminum plus manganese, which is precipitated at pH 8, to copper is approximately four, a value which may be high enough to enhance the coprecipitation of copper hydroxide. Copper is well known for its inherent ability to come out of solution readily, both by adsorption on to surfaces or by coprecipitation with other metals.

The ACF method described has been found to effectively and rapidly remove a variety of elements present as cations from leach liquors and process rejects of sulfated deep-sea ferromanganese nodules. These elements are present in the concentration range of less than 10 ppm to approximately 10% by weight. Some of the economically valuable metals such as Cu, Co, and Ni are concentrated by the leaching process and are then removed in varying degrees of effectiveness by ACF. These elements can, however, be removed quantitatively from the leach liquors by judicious pH manipulations.

A significant portion of the Cu, Co, and Ni, which was also found to be carried over into the process rejects, is further collected by ACF, thus increasing the overall recovery of those metals from nodules to approximately 90, 95, and 80%, respectively. These recoveries compare favorably to the 60, 80, and 55%, respectively, reported by Shinn using only the aqueous leach extraction step. Manganese, which has limited economic value, is recovered at the 90% level by the two flotations, although the majority is recovered in the initial flotation of the aqueous leach liquors. Virtually all of the potentially harmful lead and vanadium in the nodules is passed on to the tailings in the sulfation leaching process. These two metals are the most abundant toxic metals in the nodules and tailings, and represent approximately 0.2% of the tailings weight, a value significantly higher than that of all the other toxic metals present in the tailings combined. The lead and vanadium in the tailings are recovered at the 90 and 60% level, respectively, by flotation. This removal of potentially toxic elements from the tailings is of vital importance as the matrix disruption resulting from the sulfation may enhance the release of these elements to the environment during disposal of the process rejects. This study demonstrates that nearly three-fourths of the combined weight of the two metals is removed by flotation, thus significantly decreasing the amount of toxic elements left behind to be disposed of.

The flotation of elements from leach liquors and tailings may prove to be an economically feasible process because it improves the overall recovery of Cu, Co, and Ni and also removes a large part of the potentially toxic elements from the process rejects. The cost incurred in the processing of the tailings for toxic metal removal may very well be offset by the increase in the valuable metal recovery.

Acknowledgments

We thank D. W. Shinn for graciously providing samples from his studies to be used in our investigations and valuable discussions. The technical assistance of P. N. Sedwick is gratefully appreciated.

Hydrometallurgical Separations of Metals from Deep-Sea Ferromanganese Nodules (MR/R-4) is a research project sponsored by the University of Hawaii Sea Grant College Program under Institutional Grant Nos. NA79AA-D-00085 and NA81AA-D-0070, from NOAA, Office of Sea Grant, U.S. Department of Commerce. This is Sea Grant publication UNIHI-SEAGRANT-JC-83-04.

REFERENCES

1. D. S. Cronan, in *Marine Manganese Deposits* (G. P. Glasby, ed.), Elsevier, Amsterdam, 1977, pp. 11–44.
2. J. H. Lee, PhD Thesis, University of Hawaii, Honolulu, Hawaii, 1979, 162 pp.
3. D. W. Fuerstenau and K. N. Han, in *Marine Manganese Deposits* (G. P. Glasby, ed.), Elsevier, Amsterdam, 1977, pp. 357–390.
4. F. M. Auburn, in *Marine Manganese Deposits* (G. P. Glasby, ed.), Elsevier, Amsterdam, 1977, pp. 439–459.
5. A. F. Amos, O. A. Roels, C. Garside, T. C. Malone, and A. Z. Paul, in *Marine Manganese Deposits* (G. P. Glasby, ed.), Elsevier, Amsterdam, 1977, pp. 391–437.
6. C. Rampacek, *Bureau of Mines Information Circular 8818/1980 Proceedings of Symposium*, April 1978, College Park, Maryland.
7. E. H. DeCarlo, H. Zeitlin, and Q. Fernando, *Anal. Chem.*, *53*, 1104 (1981).
8. E. H. DeCarlo, H. Zeitlin, and Q. Fernando, *Ibid.*, In Press.
9. D. W. Shinn, MS Thesis, University of Hawaii, Honolulu, Hawaii, 1981, 97 pp.
10. J. P. Riley, in *Chemical Oceanography*, Vol. II (J. P. Riley and G. Skirrow, eds.), Academic, New York, 1965, pp. 295–424.
11. P. N. Sedwick, Unpublished Work, University of Hawaii, Honolulu, Hawaii, 1981.
12. J. M. Iskowitz, MS Thesis, University of Hawaii, Honolulu, Hawaii, 1979, 65 pp.
13. Y. S. Kim and H. Zeitlin, *Sep. Sci.*, *7*, 1–12 (1972).
14. B. Bernas, *Anal. Chem.*, *40*, 1682–1686 (1968).
15. B. L. Currin, R. M. Kennedy, A. N. Clarke, and D. J. Wilson, *Sep. Sci. Technol.*, *14*, 669–687 (1979).
16. A. N. Clarke, D. J. Wilson, and J. H. Clarke, *Ibid.*, *13*, 285 (1978).
17. C. Matsuzaki and H. Zeitlin, *Sep. Sci.*, *8*, 185–192 (1973).
18. E. L. Thackston and D. J. Wilson, *EPA Report 600/2-80-138*, U.S. Environmental Protection Agency, Cincinnati, Ohio, June 1980.
19. R. Lemlich (ed.), *Adsorptive Bubble Separation Techniques*, Academic, New York, 1972.
20. G. A. Parks, *Chem. Rev.*, *65*, 177–198 (1965).
21. G. A. Parks, *Adv. Chem.*, No. 67 (1967).
22. D. G. Peters, J. M. Hayes, and G. M. Heftje, *Chemical Separations and Measurements*, Saunders, Philadelphia, 1974.

Received by editor February 22, 1982