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Pyrochemical Extraction of Transition Metals from Pacific Ocean Deep Sea Nodules

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ABSTRACT

Considerable success has been achieved in lixiviation transition metals from Pacific Ocean deep sea nodules. These nodules typically contain ~30 wt% Mn, ~7 wt% Fe, ~1 wt% Ni, ~1 wt% Cu, and ~0.3 wt% Co. Samples of the nodules have been subjected to extraction tests at 450°C using LiCl-KCl eutectic and $MgCl_2$-NaCl-KCl eutectic. The most impressive results came from studies using the Mg, Na, K/Cl eutectic. With this salt, nearly 100% of the Co, Cu, Fe, Mn, and Ni are brought into solution. The dissolution reaction is quite vigorous, with nearly complete extraction occurring in a very short time (minutes) following melting of the eutectic. Quantitative recovery of cobalt is achieved with nodule-to-salt weight ratios as high as 1:3. Electronic absorption spectroscopy (carried out on the molten extract solution at the test temperature) showed that the oxidation states of the dissolved transition metals are Co^{2+}, Cu^{2+}, Fe^{3+}, Mn^{2+}, and Ni^{2+}. At temperatures $\geq$450°C, the Fe^{3+} and Cu^{2+} distill out of the extract solution at a rapid rate and condense as binary halides or halide complexes. Using a combination of distillation followed by electrochemical reduction of the Co^{2+} and Ni^{2+} in the extract salt, it appears possible to recover a fairly high grade of cobalt metal and nickel metal as well as high grade Cu^{2+}, Fe^{3+}, and Mn^{2+} in the form of a halide salt ($CuCl_2$, $FeCl_3$) or an oxide precipitate (Mn_2O_3).

INTRODUCTION

There is considerable long-range incentive to develop practical, economically competitive processes for recovering a number of technologically vital base metals from domestic and off-shore mineral reserves. In particular, the metals cobalt and manganese find many important applications in alloys, catalysts, etc., used in both the military and commercial sectors. The United States is presently dependent on foreign sources for both of these base metals, which are imported in large part from countries with tentative political environments.

This paper reports the latest results of a research effort aimed at exploring the prospects for developing compact pyrochemical processes to recover cobalt and manganese from low- and medium-grade domestic ores, deep sea nodules, and scrap materials. A recent publication (*1*) describes the considerable success achieved with several different types of cobalt and manganese ores from land-based North American mineral reserves. The process methodology that is unfolding from this work is one that appears to be appreciably simpler than conventional metal winning technologies. It has been found that several relatively inexpensive, low-melting (*i.e.*, $\leq 400°C$) alkali and alkaline earth chloride eutectics selectively lixiviate cobalt and manganese from their respective ores, leaving behind in the undissolved residue most of the nontransition metal mineral matter including the heavy metals. The dissolved transition metals can then be recovered by a sequence of process steps involving selective distillation (*e.g.*, of iron and copper chlorides), controlled potential electrodeposition (*e.g.*, of nickel and cobalt), and oxidative precipitation (*e.g.*, of manganese oxides).

EXPERIMENTAL

The deep sea nodules used in this study were obtained from the Bureau of Mines, Avondale, MD. Their chemistry and geology are described in a recent Bureau of Mines Information Circular (*2*). Chemical analyses of the as-received nodules were performed by Inductively Coupled Plasma/Atomic Emission Spectroscopy (ICP/AES). The samples to be analyzed were dissolved in aqua regia and HF, taken to dryness, then redissolved in HCl. Results of a typical ICP/AES assay are given in Table 1 together with assay data supplied by Haynes (*3*) based on analyses carried out by the Bureau of Mines. In order to determine whether there was any segregation of ore constituents during grinding and sieving, ICP/AES analyses were performed on nodule specimens in three particle size ranges: $<50\ \mu m$, $50 \rightarrow 125\ \mu m$, and $>125\ \mu m$. Composition variations of Co, Mn, Ni, Cu, and Fe were small ($<10\%$ case-to-case) and random, probably reflecting more than anything else the slight compositional variability of the nodules. Nodule material in the $50 \rightarrow 125\ \mu m$ range was used in all subsequent experimentation. Prior to use, the size-sorted nodule material was dried at 110°C in a vacuum drying oven for several days and thereafter transferred to a helium atmosphere glovebox.

The molten salt eutectics were high purity grades obtained in sealed glass ampoules from Anderson Physics Laboratories, Inc. The ampoules were opened in a

TABLE 1.

Results of Inductively Coupled Plasma/Atomic Emission Spectrographic (ICP/AES) Analysis of Deep Sea Nodules[a]

Element	ICP/AES Result (Assay in wt. %[b])	Bu. Mines Result (Assay in wt. %[a])
Aluminum	2.46	2.4
Barium	0.29	0.3
Calcium	1.52	1.2
Chromium	nil	–
Cobalt	0.24	0.2
Copper	1.08	1.2
Iron	6.69	6.4
Lead	0.04	0.04
Magnesium	1.75	1.8
Manganese	29.6	31.0
Molybdenum	0.06	0.1
Nickel	1.25	1.3
Silver	<0.01	–
Strontium	0.06	–
Thallium	–	0.02
Titanium	0.33	0.5
Vanadium	0.05	0.04
Zinc	0.15	0.2
Zirconium	<0.04	–

[a] B. W. Haynes, US Bureau of Mines, Avondale, MD.
[b] E. A. Huff, ANL. Estimated accuracy is 5→10% .

helium atmosphere glovebox and stored there. All subsequent handling (weighing, mixing, loading, etc.) was carried out in the glovebox. All extraction, electrochemical, and spectroscopic experiments involving the use of these salts in the molten state were carried out in quartz tubes or quartz optical cells. Typically, the extraction tube, electrochemical cell, etc., was loaded and capped off in the glove box, then removed from the box, placed in a furnace and connected to a glass vacuum line. Several large scale extraction tests, involving ~250 g of salt and ~50 g of nodule material, were carried out in 50-mm OD quartz vessels having built-in sparge tubes and side ports that permitted the gases evolved during lixiviation to be swept out of the vessel and through a series of chemical traps. Other details of the extraction and filtration procedures used during the course of this work were much the same as those described in previous publications (*1,4,5*).

Electronic absorption spectra were obtained using a Cary 17H Spectrophotometer equipped for high temperature studies on molten salts. Both 1-mm and 10-mm path length UV-grade quartz cuvettes were used to contain the samples. The cell assemblies and procedures were the same as those described in previous papers (*1,4,5*).

The pyroelectrolysis and cyclic voltammetry studies were carried out in a specially designed glass apparatus. This apparatus consisted of a 400-mm long, 50-mm-OD quartz tube with a 60/40 male ground joint and a Pyrex 60/40 female cap having four O-ring-type sliding feed-throughs to accommodate the electrodes. The cell was also fitted with a sparge tube which ran to the bottom of the cell, and a side port for evacuation or venting of sparge gas. The working electrode was a glassy carbon rod (3.2 mm diameter) sealed in a Pyrex sheath and polished to give a smooth working surface having an area of 8.3 mm^2. The counter electrode and deposition electrode were 6.4-mm-diameter carbon rods (Spectrographic grade); the counter electrode was sheathed in a fritted quartz tube while the deposition electrode was used unsheathed. The reference electrode was the Ag/AgCl couple, *i.e.*, 1.0 wt.% AgCl in $MgCl_2$-NaCl-KCl eutectic, contained in a frit-tipped quartz tube and contacted electrically through an immersed silver wire. Standard cyclic voltammetry instruments and procedures were employed.

RESULTS

Guided by the findings for domestic land-based minerals reported in a previous paper (*1*), solvolysis studies were initiated on Pacific Ocean deep sea nodules with composition as indicated in Table 1. Initially, two salt eutectics—LiCl-KCl (60-40 mol%, m.p. ~350°C) and $MgCl_2$-NaCl-KCl (50-30-20 mol%, m.p. ~400°C)—were tested as solvolysis media. Extraction tests were carried out in sealed evacuated quartz tubes at 450°C and for nodule:salt mixtures having a 1:15 weight ratio. After a period of a day or so at 450°C, the tube was opened and its contents were loaded into a filter tube. The filter tube was placed in a furnace and heated under vacuum at 450°C until the salt melted. The fused salt was then filtered under helium pressure, leaving a dark residue behind on the frit. The residue was homogenized by grinding to a coarse powder and portions were submitted for chemical (ICP/AES) and X-ray powder diffraction analysis. The filtrate was also homogenized; one portion was submitted for chemical (ICP/AES) analysis and a second was placed in a spectrophotometer tube and used to obtain the electronic absorption spectrum of the dissolved transition metals in the fused filtrate at 450°C. During the absorption spectral measurements, a solid condensate appeared in the upper portion of the spectrophotometer tube which extended outside the heated zone. Spectra of the filtrate were recorded as a function of time until there was no longer any visual evidence of condensate formation. The results of such a treatment are shown in Fig. 1. Curve 1 in Fig. 1 is the initial scan of the filtrate obtained just after fusion; curve 2 was taken several hours later and curve 3 a day later.

A precise interpretation of the results in Fig. 1 required that standardized absorption spectra of the individual 3d transition metals be obtained in the $MgCl_2$-NaCl-KCl eutectic. Standardized spectra of Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}, the stable oxidation states most likely to be present (*6,7*) in the filtrates were recorded and are shown in Fig. 2. Using the data in Fig. 2, the results in Fig. 1 can be interpreted as follows: Curve 1 of Fig. 1 shows the presence of Cu^{2+} (8000→9000 cm^{-1}), Co^{2+} (14,000→18,000 cm^{-1}), and considerable amounts of Fe^{3+} but no Fe^{2+} (compare Figs. 1 and 2). After most of the condensable material had left the salt (several hours), curve 2 was obtained, which indicates the presence of only traces of the original Cu^{2+}, as well as Co^{2+}, Ni^{2+} (~20,000 cm^{-1}), and Mn^{2+} (~23,000 cm^{-1}). Clearly at this point, most of the Cu^{2+} and Fe^{3+} have volatilized out of the melt. Curve 3 in Fig. 1, taken a day later, simply reflects

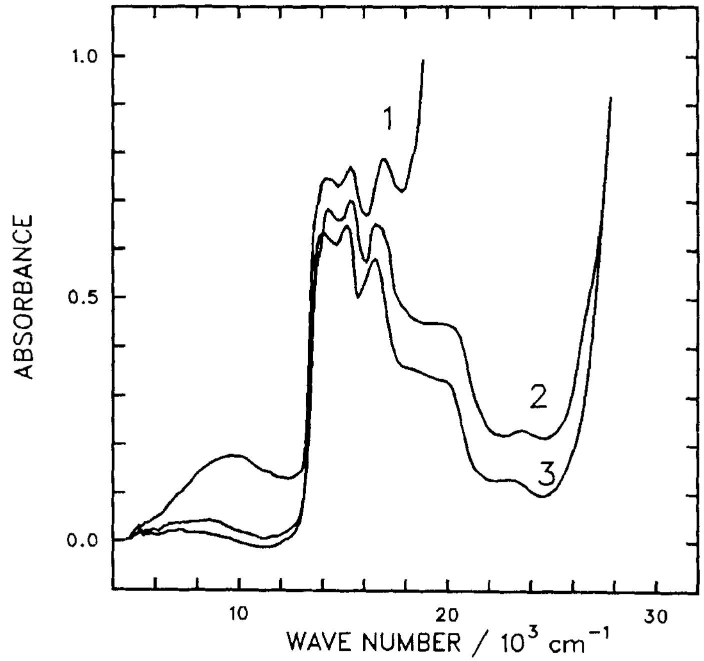

Fig. 1. Absorption spectra of the extract solution from a Pacific Nodule/$MgCl_2$-NaCl-KCl equilibration taken in a 10-mm-path-length cell. Curves 1 through 3 show the consequences of sequential evaporation of Fe^{3+} and Cu^{2+} chloride complexes.

Curve 1: Initial spectrum at 450°C.

Curve 2: Spectrum after ~6 hours at 450°C.

Curve 3: Spectrum after ~24 hours at 450°C.

further volatilization of the residual Cu^{2+} and Fe^{3+}. Chemical analyses confirmed that copper and iron chlorides were the major constituents of the condensate.

The results of the initial extraction tests with respect to solvolysis power of the two eutectics are given in Table 2. As is clearly illustrated in Table 2, the $MgCl_2$–NaCl–KCl eutectic proved to be a superior extraction medium for both cobalt and manganese, the two highest worth (*8*) transition metals in the nodules. Hence, all subsequent studies related to the solvolysis of these nodules (as reported herein) were done using the $MgCl_2$–containing eutectic.

A second series of 450°C extraction tests was conducted with $MgCl_2$–NaCl–KCl using nodule:salt weight ratios in the range 1:15 to 1:3 to determine the effect of this ratio on extraction efficiency. In these tests, the sealed tubes having nodule:salt

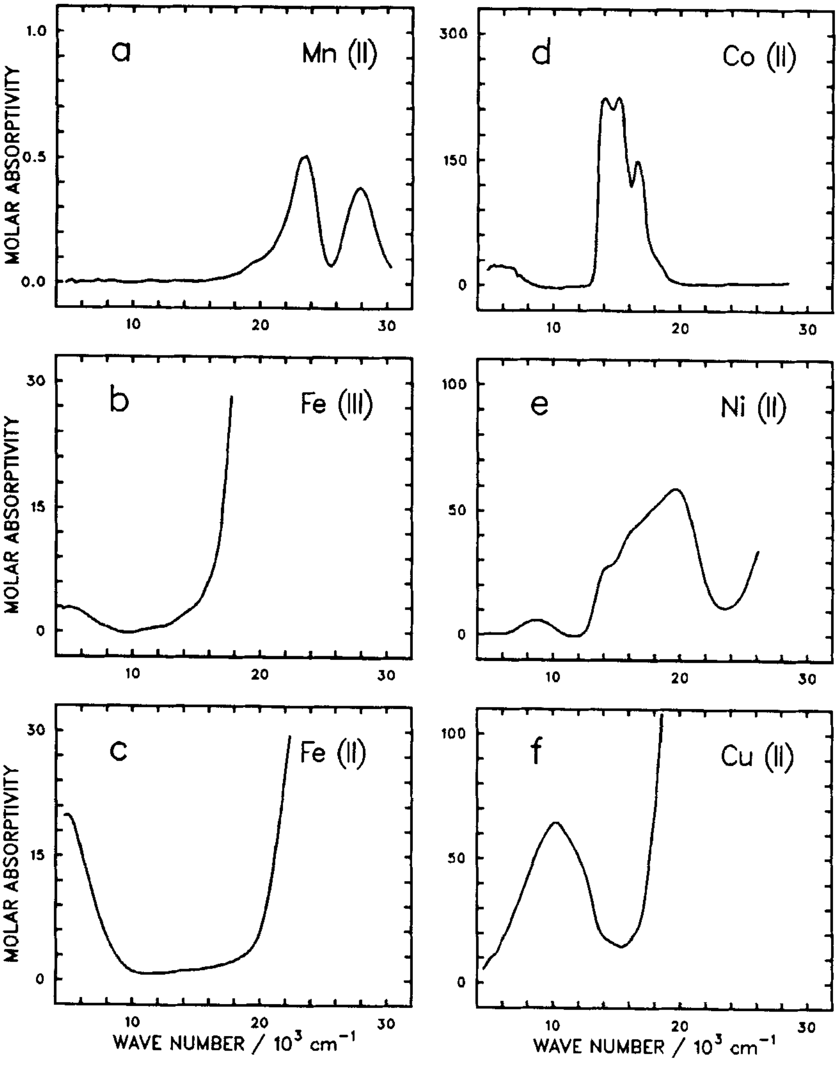

Fig. 2. Electronic absorption spectra of selected 3d transition metal cations in $MgCl_2$-NaCl-KCl eutectic at 450°C taken in a 1-mm-path-length cell.

TABLE 2.

Recovery (in Percent) of Transition Metals From Deep Sea Nodules by Molten Salt Extraction Using Chloride Eutectics

Transition Metal	LiCl-KCl[a] n:s=1/15	$MgCl_2$-NaCl-KCl[a] n:s=1/15	$MgCl_2$-NaCl-KCl[a] n:s=1/5
Co	46	100	100
Cu	93	100	94
Fe	<0.2	>44	(b)
Mn	14	100	85
Ni	<2	99	83

[a] n:s = nodule:salt weight ratio.

[b] Iron halides rapidly volatilize out of melt.

ratios of 1:5 or higher consistently burst during the extraction period. Subsequent studies of this problem ruled out evolution of water (in sufficient quantities to create a burst pressure) as the cause. Also, there was visual evidence of a yellow vapor in the tubes prior to bursting, and the odor of chlorine gas was quite noticeable after a burst. These observations prompted more detailed studies of the solvolysis reaction which are described further on in this section.

In order to complete the extraction tests at high nodule:salt ratios, it was necessary to use open ended tubes that vented into a hood through a pressure relief valve. The findings from the second series of tests are typified by the results shown in Fig. 3, where the absorbance of the filtrate at 700 nm is plotted as a function of nodule:salt weight ratio. Since care was taken to distill out most of the iron and copper chlorides in these samples prior to the spectroscopic measurements, it is safe to assume that the absorbance at 700 nm is due almost exclusively to Co^{2+}. The linearity of this plot with intercept at the origin gives evidence that quantitative extraction of cobalt is achieved at each nodule:salt weight ratio studied. ICP/AES analyses of several of the filtrates in this series confirmed that the cobalt is essentially 100% extracted from the nodules. It appears that the percent extraction of Cu, Mn, and Ni drops off only slightly with increasing nodule:salt ratio, as can be seen from a comparison of the results for the nodule:salt ratios of 1:15 and 1:5 in Table 1. It is difficult to keep track of the iron in these experiments by analysis of the filtrate alone because of the fact that iron chlorides tend to distill out of the extract salt. Overall mass balances, which include analyses of the undissolved residue from the solvolysis experiments, show that most of the iron is lixivated from the nodules at all nodule:salt ratios. Analyses of condensates obtained prior to filtration confirm that most of the iron is indeed in the volatile product that deposits in the unheated upper section of the filter tube.

At this point in the research, the emphasis shifted to a study of the solvolysis mechanism and the significance of the apparent evolution of chlorine observed in

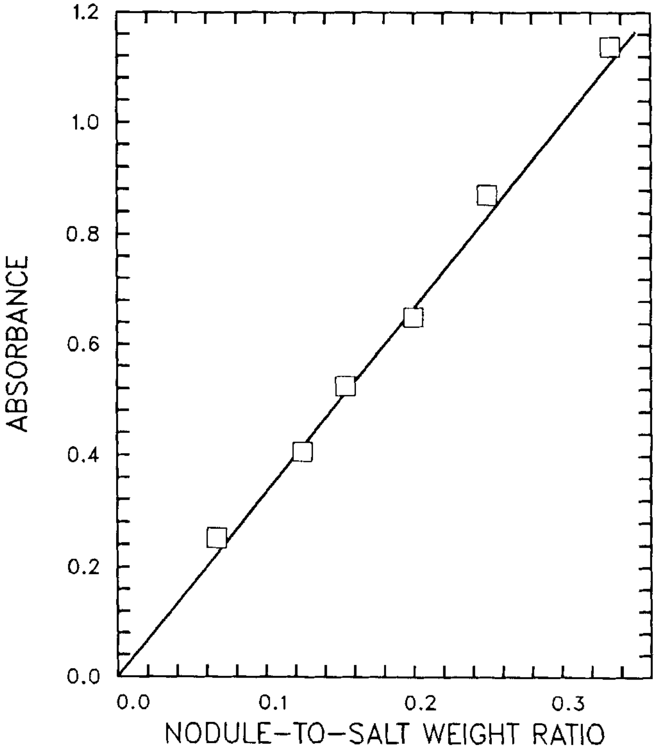

Fig. 3. Absorbance at 700 nm versus nodule-to-salt weight ratio. Salt = Mg, Na, K/Cl eutectic.

the second series tests. To follow up on this observation, several extractions were carried out in sparged reactor vessels designed to hold upwards of 250 grams of salt and 50 grams of nodule material. During the solvolysis period, a helium stream was passed over the reacting mixture, out of the tube, and through a series of pyrex gas bubblers filled with concentrated NaOH. With this technique any Cl_2, HCl, or other gases generated during the solvolysis could be collected and subsequently measured quantitatively. Normally, these sparged equilibrations were allowed to run for a day or two, as experience from the initial equilibrations had shown that the solvolysis would certainly be complete on such a time scale.

Analysis of (i) the trapped OCl^- from the reaction $Cl_2 + 2OH^- \rightarrow OCl^- + Cl^- + H_2O$ and (ii) total Cl^- in the bubblers after OCl^- titration showed that the ratio of total chlorine evolved (as Cl_2 and Cl^-) to OCl^- in the traps was in the 2.5:1 to 4:1 range. This implies that the sweep gas contained both Cl_2 and Cl^- in some form, presumably HCl. (If only Cl_2 was evolved, the total Cl^-/OCl^- ratio would be exactly 2.0, since OCl^-, which is analyzed first, is converted to Cl^- during its analysis.) Also, because of the way in which the large scale extraction tests were set up, it is certain that all of the chloride reaching the traps was in the form of species with high volatility at ambient temperature (*i.e.*, HCl or Cl_2). The volatile metal chlorides all condensed out in the tube leading from the extraction cell to the first NaOH trap. A glass frit at the entrance to the first trap prevented passage of any metal chloride particulate into the traps.

From the geology of the nodules used in this work, it is known (*2*) that the manganese is present mainly in the 3+ and 4+ oxidation states, *i.e.*, in MnOOH- and MnO_2-containing mineral forms. Yet, in the molten salt filtrates from the equilibrations, which contain >90% of the manganese in the original nodule material, the manganese has been shown by spectroscopy to be in the 2+ oxidation state. The following types of solvolysis reactions could account for these observations:

$$\text{"MnOOH"} + 2MgCl_2 \rightarrow MnCl_2 + 2MgO + HCl + \tfrac{1}{2}Cl_2 \qquad (1)$$

$$\text{"MnO}_2\text{"} + 2MgCl_2 \rightarrow MnCl_2 + MgO + Cl_2 \qquad (2)$$

$$\text{"FeOOH"} + 2MgCl_2 \rightarrow FeCl_3 + 2MgO + HCl \qquad (3)$$

where the compounds in quotation marks represent the general chemical form of the transition metals in what is known to be a complex mineral structure (*2*). Reaction 1 must also occur for "CoOOH" and "NiOOH" (the presumed major mineral forms of cobalt and nickel in the nodules), as the lixiviated cobalt and nickel have been shown to be present in the 2+ oxidation state.

A cursory experiment was carried out to study the products of reaction 2. Reagent grade MnO_2 was contacted with $MgCl_2$-NaCl-KCl eutectic at 500°C for several days in a vented tube. There was visual evidence of gas evolution during the initial stages of contacting. The spectrum of the molten extract salt (after filtration) confirmed the presence of appreciable amounts of dissolved Mn^{2+}. X-ray diffraction analysis of the filtered solid residue that had been in contact with the extract salt prior to filtration showed that $MgMnO_3$ and Mg_2MnO_4 were the major phases present. While these findings suggest that the reaction of MnO_2 with the $MgCl_2$ eutectic is more complex than indicated by reaction 2 (above), they do confirm that Mn^{2+} is a solvolysis product of Mn^{4+} oxide forms. The work of DeLarue (*7*) attests to the low solubility of MgO and Mn_2O_3 in alkali chloride eutectics. Related ternary oxide species, such as $MgMnO_3$ and Mg_2MnO_4, are also expected to have very little solubility in molten chloride eutectics. In fact, with a few exceptions, all the metal oxide solubility implications from the work presented herein are in agreement with the predictions in DeLarue's paper (*7*).

The pyroelectrolysis and cyclic voltammetry studies were carried out on salt samples from the large scale (250 gm) extraction tests that had been monitored for chlorine evolution. The salt/residue mixture from a single equilibration was loaded into a large filter tube, fused, and filtered to separate the salt from the residue. Both the residue and the salt were homogenized and samples (~500 mg in size) of each were submitted for ICP/AES analysis. The remaining filtered salt was loaded into the electrochemical cell constructed for the electrodeposition/cyclic voltammetry measurements (see Experimental section). After fusing the salt and establishing a stable e.m.f. at the counter and working electrodes (relative to the Ag/AgCl reference electrode), a starting cyclic voltammogram (CV) was recorded to establish a baseline for future measurements. A voltammogram that is typical of starting CV's recorded for electrodeposition experiments is shown as inset (a) in

Fig. 4. The estimated voltage ranges of the anodic peaks for Ni/Ni^{2+}, Co/Co^{2+}, and Cu/Cu^{+} are indicated in the inset. These estimates are based on extrapolations of redox couple potentials for the same metals in molten LiCl-KCl (*9*). Controlled potential electrodeposition was then performed at a voltage near the Ni^{2+} reduction potential (LV in Fig. 4). Inset (b) in Fig. 4 shows a CV taken near the end of the low-voltage deposition of Ni^{2+} from the melt. When it became clear from the CV's that most of the Ni^{2+} had been deposited, the deposition electrode was removed, a fresh deposition electrode was inserted, and electrodeposition was continued at a higher voltage near the Co^{2+}/Co reduction potential. A CV taken near the end of this high-voltage electrodeposition (HV in Fig. 4) is shown as inset (c) in Fig 4. Unfortunately, the metallic deposits did not adhere well to the carbon deposition electrodes, and as a result, most of the deposits fell to the bottom of the cell. However, in post-experiment examination of the cell contents, two well-separated types of deposits were found. One type of deposit, which constituted the major fraction of the total recovered deposit, was a dendritic, highly magnetic material. ICP/AES analysis revealed that this material was 96+% nickel. Its X-ray powder diffraction pattern was that of nickel with a slightly expanded lattice indicating the presence of some solid solution, possibly due to codeposition of small quantities of other metals. Because (i) the amount of this deposit was consistent with the relative number of coulombs passed during low-voltage electrolysis and (ii) it was almost pure nickel, it was assumed to be the low-voltage product.

The second type of deposit was reddish, mossy, and also highly magnetic. The analysis of this material (by ICP/AES) showed that its major constituents (90% of total weight) were copper, nickel, and cobalt in a ratio of $3:1:0.6_5$; the remaining 10% was mainly carbon particles presumably dislodged from the electrode surface. Based on chemical composition and quantity relative to the number of coulombs passed during high-voltage electrolysis, this deposit was taken to be the high-voltage product. To complete the assay data base for a full extraction cycle, the depleted electrolyte from the electrolysis cell was filtered to remove remaining deposits and electrode debris and then submitted for ICP/AES analysis.

DISCUSSION

The sequence of experiments described in this paper was not optimized for quantitative recovery of the individual transition metals in the nodules, hence, only a qualitative assessment of the recovery potential of the pyroelectrochemical process in this application is possible. The separations that can be achieved are best illustrated by the results in Table 3. In this table, the relative concentrations of Mn, Co, Ni, Cu, Fe, and Al (normalized to Ni = 1) are listed for the as-received nodule material, for the filtered extract salt from nodule/salt equilibration, for the "low-voltage" and "high-voltage" electrodeposition deposits, and for the filtered, depleted salt from an essentially complete electrolysis as evidenced by cyclic voltammetry and ICP/AES. Data for aluminum are included because the fate of Al in these experiments was found (from analytical results) to parallel that of the fourth and fifth row transition metals and most of the other nontransition metals found in the nodules.

The comparisons that can be made from the results in Table 3 show the uniform extraction of the five 3d transition metals; their separation from the other metallic constituents in the nodules during solvolysis; the isolation of nickel during the "low-voltage" electrolysis; the cobalt enriched product of the "high-voltage" electrolysis

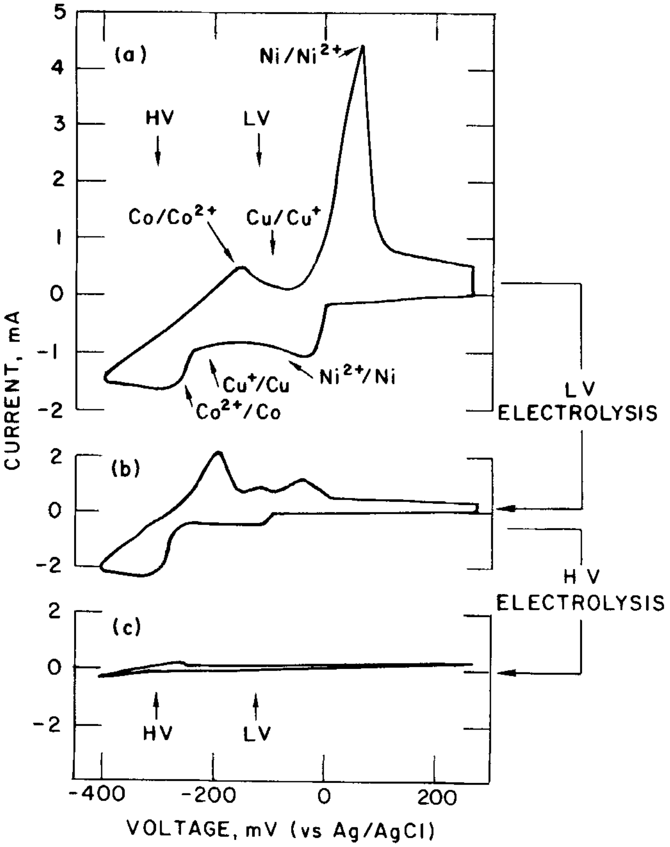

Fig. 4. Cyclic voltammograms obtained during the electrolysis of deep sea nodule extracts in $MgCl_2$-NaCl-KCl eutectic at 450°C: LV = low voltage; HV = high voltage. Scan rate = 10 mV/s.

(from 0.25 wt% in the nodule to ~13 wt% in the "high-voltage" product); and the isolation of Mn in the post electrolysis salt. The actual fate of Fe and Cu is not accurately reflected in Table 3. Iron chlorides and complexes thereof with other metal halides (*10*), continually volatilize out of the extract salt during all phases of the processing (equilibration, filtration, deposition, etc.). By the time electrolysis is actually started, very little of the original iron extracted from the nodules is still present in the extract salt. The copper mass balance and oxidation state in the electrolysis stages must be considered somewhat spurious, as it was found in post electrolysis examinations that copper from the electrical lead to the micro (CV) working electrode and the counter electrode was making its way into the salt. By proper selection of lead wire material, it should be possible to avoid this problem in future electrodeposition studies.

TABLE 3.
Relative Concentrations of Transition Metals During Consecutive Stages of the Pyroelectrochemical Processing of Deep Sea Nodules (Results Normalized to Nickel = 1 at all Process Stages)

Stage	Mn	Co	Ni	Cu	Fe	Al[a]
As-received Nodules	24	0.2	1	0.9	5.4	1.9
Extract Salt[b]	24	0.2	1	0.9	<5	0.04
Low Volatge Deposit	$<10^{-3}$	$<10^{-2}$	1	$<10^{-1}$	$<10^{-3}$	$<10^{-3}$
High Voltage Deposit	$<10^{-2}$	0.6_5	1	3.0	$<10^{-3}$	$<10^{-3}$
Depleted Salt[c]	2300	1.5	1	40	2.2	5.5

[a] The fate of aluminum in these experiments typifies that of the fourth and fifth row transition metals and most of the other nontransition metals contained in the nodules.

[b] After equilibration with nodules and filtration.

[c] After both low voltage and high voltage electrolysis.

There is considerable room for optimization of the process steps represented in Table 3. For example, more extensive volatilization to remove copper prior to "high-voltage" electrodeposition could lead to a cobalt-rich product with little or no copper in it. In the same vein, optimization of both the "low-voltage" and "high-voltage" deposition potentials should yield purer grades of the respective products. On the other hand, an electrode deposit that is a mixture of cobalt and nickel would be a commercially useful product by itself, *i.e.*, without need for further separation. Clearly, more work must be done to develop electrodes which retain the deposited metals in a readily recoverable form.

Up to this point, no attempts have been made to recover the manganese remaining in the depleted electrolysis salt. Electrodeposition of manganese metal will probably not occur below the voltage at which alkali and alkaline earth metals begin to react with the carbon deposition electrode. However, the observation has been made that introduction of dry oxygen to the melt leads to precipitation of Mn_2O_3, giving evidence of a relatively simple and practical means for recovering the Mn in a useable form. The elucidation of these and other details of an integrated pyroelectrochemical process will be the subject of future research planned in connection with this project.

One of the most attractive features of the process depicted in Table 3 is the separation of the higher 3d transition metals (*i.e.*, Mn, Fe, Co, Ni, and Cu) from the other mineral matter present in the nodules, as represented by the aluminum results in Table 3. The chemistry behind this separation has not been fully elucidated, but it is clear that the aluminum, titanium, molybdenum, lead, and other heavier metals remain in the residue after molten salt extraction. Presumably, the oxygen potential that is reached in the extract salt after contacting the nodules is high enough to keep the aluminum and titanium from forming chlorides. The residue chemistry, as determined by X-ray diffraction and ICP/AES analysis, is very complex, with many ternary and higher order phases, which makes a detailed assessment of the process thermodynamics virtually impossible. Nonetheless, it is clear that there are no significant amounts of aluminum, titanium, or molybdenum in the extract salt or the distillates. All evidence suggests that these metals are mainly in the post-extraction residue.

An authoritative assessment of the economic incentives for developing pyroelectrochemical processes of the type described above and in reference (*1*) is beyond the scope of this paper. The need for such capability in the case of cobalt and manganese has been documented in many publications and reports that have appeared over the past several years alone, *e.g.*, reference (*11*). In particular, the economic potential of deep sea nodules and crusts has been explored and discussed, *e.g.*, by Manheim *et al.*, (*12,13*). While deep sea mining must be viewed more as an undertaking for the future rather than the present, there are already available in the U.S. a number of accessible ore concentrates (*1*) and scrap materials that could be used today as sources of both cobalt and manganese. There is indeed potential for application of pyroelectrochemical processes to all of these sources.

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REFERENCES

1. V. A. Maroni and R. M. Yonco, in "Pyrochemical Solvolysis of Ore-bound Transition Metals," Proceedings of the International Symposium on Electrochemistry in Mineral and Metal Processing, Volume 84-10, The Electrochemical Society, Inc., Pennington, NJ (1984) p. 417.

2. B. W. Haynes, S. L. Law, and D. C. Barron, *Mineralogical and Elemental Description of Manganese Nodules*, U.S. Department of Interior/Bureau of Mines Information Circular 8906 (1982).

3. B. W. Haynes, Bureau of Mines, Avondale, MD (letter communication, June 22, 1984).

4. V. A. Maroni, C. E. Philbin, and R. M. Yonco, *Separation Science and Technology 18*, 1699 (1983).

5. C. E. Philbin and V. A. Maroni, *Inorg. Chem.* *24*, 443 (1985).

6. D. M. Gruen and R. L. McBeth, *J. Pure and Applied Chemistry 6*, 23 (1963).

7. G. DeLarue, *Chimie Analytique 44*, 91 (1962).

8. Highest in worth in terms of gross value based on concentration and price per unit weight as discussed for example in reference (*12*) below.

9. *Encyclopedia of Electrochemistry of the Elements*, Volume X, A. J. Bard and J. A. Plambeck, Eds., Marcel Dekker, Inc., New York, NY (1976) pp. 68–71.

10. G. N. Papatheodorou, "Vibrational Spectroscopy of High Temperature Metal–Halide Vapor Complexes," in *Metal Bonding and Interactions in High Temperature Systems*, J. L. Gole and W. C. Stwalley, ACS Symposium Series, No. 179, ACS (1982) p. 309.

11. *Strategic and Critical Nonfuel Minerals: Problems and Policy Alternatives*, Congressional Budget Office Report, August 1983; available through Superintendent of Documents, U.S. Government Printing Office, Washington, D.C.

12. P. Halbach and F. T. Manheim, *Marine Mining*, *4*, 319 (1984).

13. R. F. Commeau, A. Clark, C. Johnson, F. T. Manheim, P. J. Aruscavage, and C. M. Lane, "Ferromanganese Crust Resources in the Pacific and Atlantic Oceans," in Proceedings of Oceans '84, IEEE Publication 84CH2066-9 (1984) p. 421.