United States Patent [19]

Kane et al.

[11] 3,869,360

[45] Mar. 4, 1975

[54] **REDUCTION METHOD FOR SEPARATING METAL VALUES FROM OCEAN FLOOR NODULE ORE**

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[21] Appl. No.: **310,604**

Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 251,089, May 8, 1972, abandoned, which is a continuation of Ser. No. 40,586, May 26, 1970, abandoned.

[52] **U.S. Cl.** ..... **204/105 R,** 204/105 R, 204/108, 204/112, 75/115, 75/117, 75/119, 75/121, 75/101 BE, 75/101 R, 423/140

[51] **Int. Cl.** **C22d 1/24,** C22d 1/14, C22d 1/16

[58] **Field of Search** ..... 75/115, 119, 117, 121, 75/101 R, 101 BE; 204/105 R, 105 M, 108, 112; 423/140

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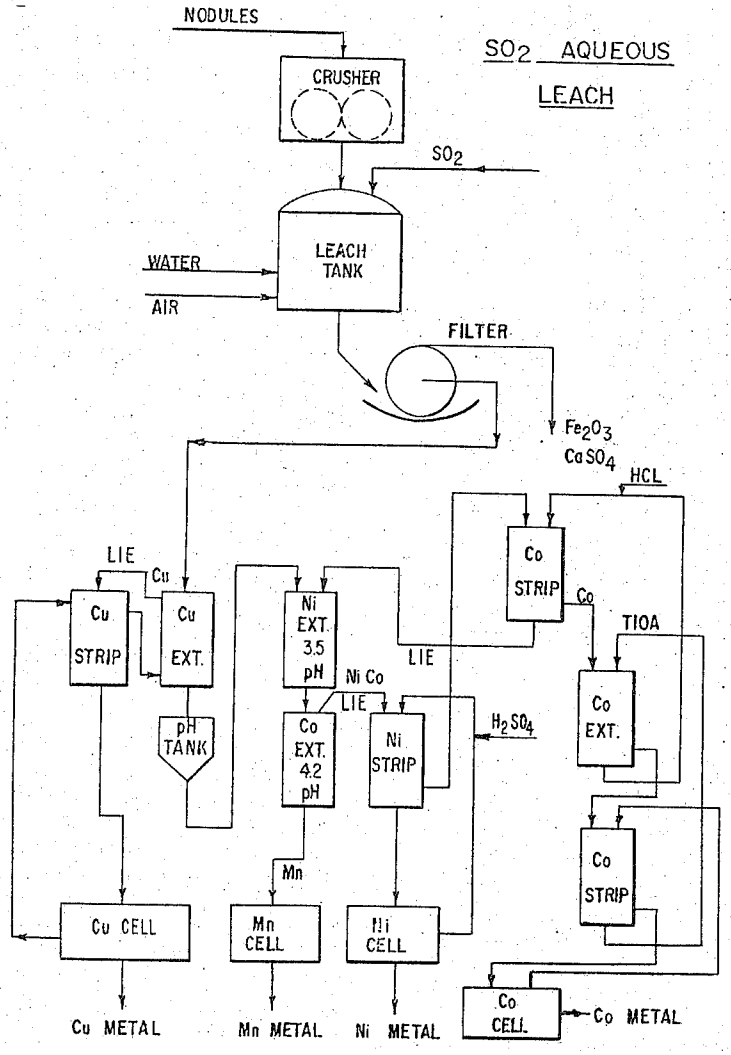
[57] **ABSTRACT**

This invention provides a process for obtaining the metal values from ocean floor nodule ore. The ore comprises primarily oxides of iron and manganese plus nickel, copper and cobalt compounds. The ore is treated with an acidic reagent, e.g., sulfur dioxide in the presence of oxygen, to form the water-soluble sulfates of manganese, nickel, copper and cobalt. The reacted ore is leached with water and the resultant leach solution is treated by liquid ion exchange processes to form separate solutions of each of nickel, copper, cobalt and manganese salts. These salts can then be cathodically reduced to form the respective metals.

14 Claims, 2 Drawing Figures



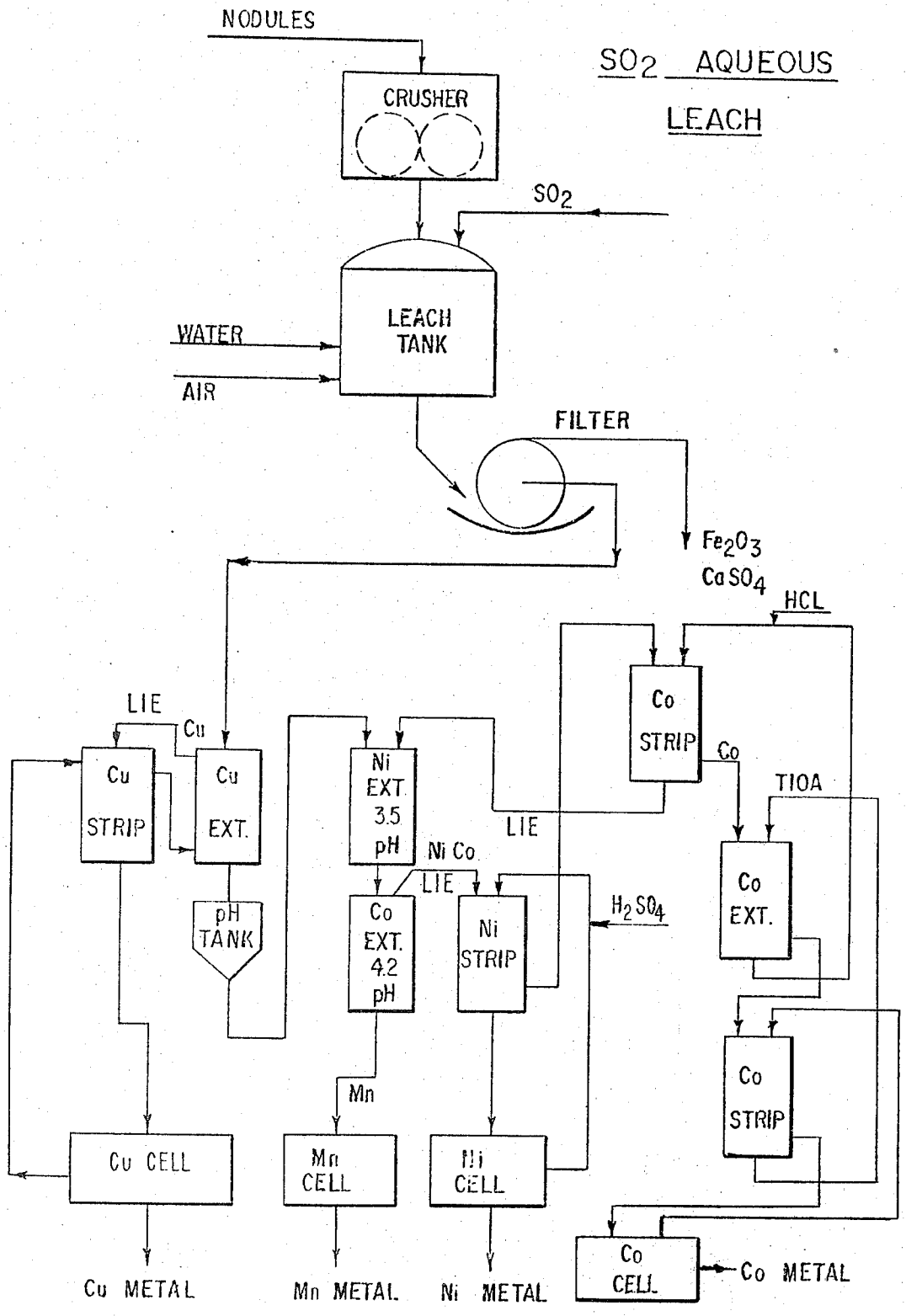
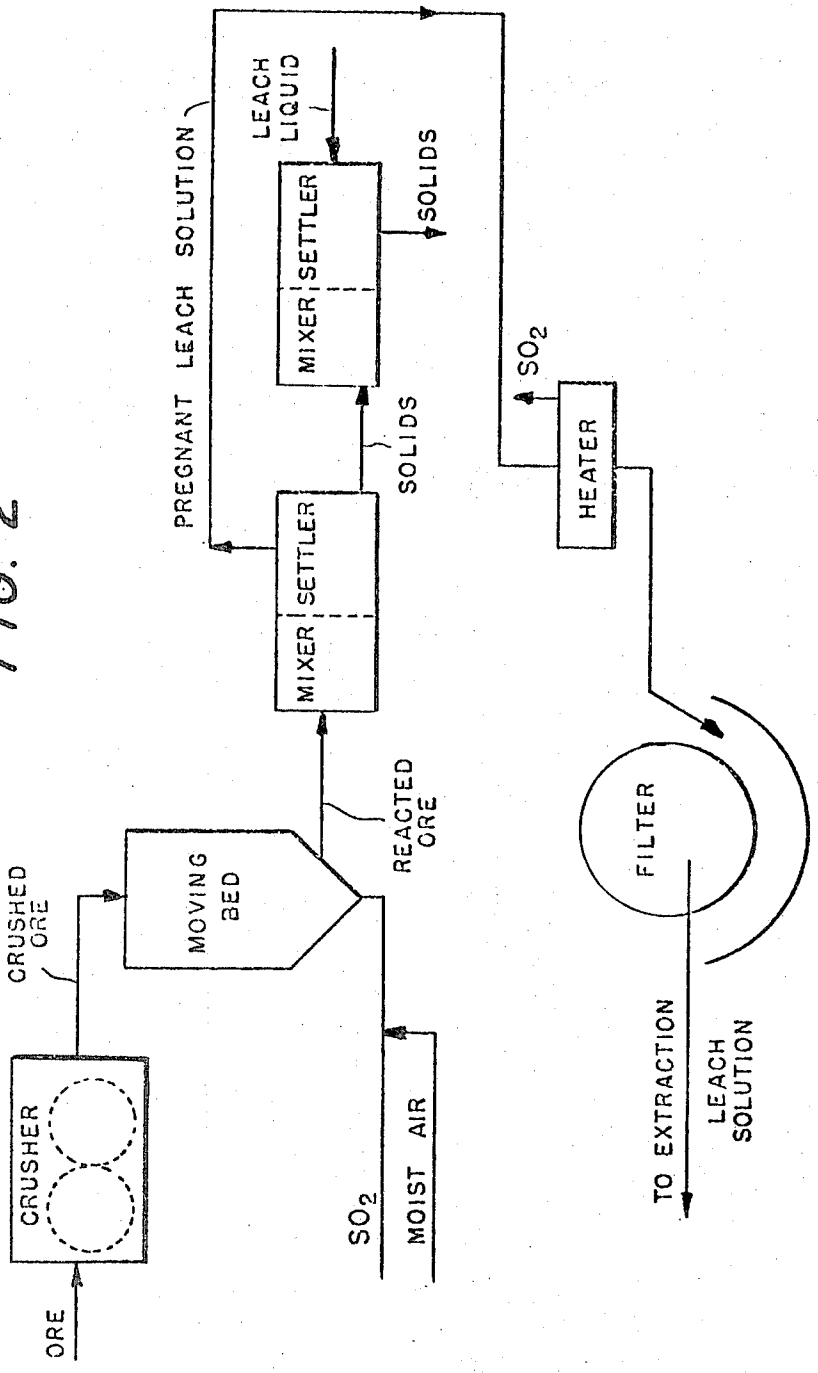

NODULES
CRUSHER
SO_2 AQUEOUS
LEACH
SO_2
WATER
AIR
LEACH TANK
FILTER
Fe_2O_3
$CaSO_4$
HCL
LIE
Cu
Cu STRIP
Cu EXT.
pH TANK
Ni EXT. 3.5 pH
Ni Co
LIE
Co EXT. 4.2 pH
Ni STRIP
LIE
Co STRIP
Co
TIOA
Co EXT.
H_2SO_4
Co STRIP
Mn
Cu CELL
Mn CELL
Ni CELL
Co CELL
Co METAL
Cu METAL
Mn METAL
Ni METAL

FIG. 1

FIG. 2


ORE
CRUSHER
CRUSHED ORE
MOVING BED
REACTED ORE
SO_2
MOIST AIR
MIXER
SETTLER
PREGNANT LEACH SOLUTION
SOLIDS
LEACH LIQUID
MIXER
SETTLER
SOLIDS
SO_2
HEATER
FILTER
TO EXTRACTION
LEACH SOLUTION

REDUCTION METHOD FOR SEPARATING METAL VALUES FROM OCEAN FLOOR NODULE ORE

This is a continuation-in-part of a copending U.S. Pat. application Ser. No. 251089 filed on May 8, 1972, which in turn is a continuation of U.S. application Ser. No. 40,586 filed May 26, 1970, both now abandoned.

It is not a common situation to obtain a relatively valuable nonferrous metal such as nickel, cobalt, copper, manganese, titanium, indium and zinc, from minerals which are primarily iron ores, i.e., containing a relatively high proportion of iron. A relatively untapped source of a high-quality manganiferous ore, however, is a material which is found on the ocean floor and has come to be known as ocean floor nodule ore.

With the increased awareness on the part of both the public and the metals industry of the ecological dangers that can arise from continued surface mining of minerals and the increased problems of pollution caused by the refining procedures required for most ores mined from the land, industry has been interested for several years now in the mining of minerals from the sea. This has been an extremely elusive target up to the present. The directions taken have included both attempts to wrest minerals directly from solution in sea water and the mining of ores which are available on the floor of the ocean. These ores do not require any digging into or stripping of the earth's crust; the ocean floor ores can merely be scooped up or in other ways removed from the ocean floor without actually rending the earth's surface.

Ocean floor nodules were first collected in the first half of the 1870s. They have been studied by many workers in an attempt to determine their composition, and after their composition had been determined to try to decipher ways to wrest from their peculiar structure the valuable metals contained therein. It is presently believed that these nodules are actually creations of the sea; they are somehow grown from the metal compounds which are dissolved in sea water, generally in the form of the metal oxides.

The metal values in the nodules are almost exclusively in the form of the oxides and moreover are present in a very peculiar physical configuration. The physical and chemical structure of the nodules are believed

to be a direct result of the conditions under which they were created and to which they have been exposed since their creation. First, the nodules have never been exposed to temperatures other than those at the bottom of the ocean at the location at which they were formed. They have an extremely large surface area, often better than 50 percent porosity and they are thus relatively chemically reactive ores.

The nodules are formed as an extremely complex crystal matrix of iron and manganese oxides: tiny grains of each oxide of a size and type which are substantially impossible to separate with present available physical means. These iron and manganese oxides form the crystalline structure within which are held, by means not precisely known, other metal compounds, most likely oxides, including those of nickel, copper and cobalt, as the main ingredients, followed by chromium, zinc, tin, vanadium, and many more elements, including the rare metals silver and gold.

In addition to the crystals of compounds of the valuable metals present, there is also a large quantity of silt, or gangue material intimately admixed in the nodule ore. This silt, or gangue, is sand and clay, and includes the usual oxides of silicon and aluminum in varying proportions and some carbonates, especially calcium carbonate.

The precise chemical composition of the nodules varies depending upon their location in the ocean. The variation apparently is caused by differences in temperature in various places, differences in composition of sea water perhaps caused by the pressure and temperature variations at different depths and composition of adjacent land areas, variations in the amount of oxygen which is present in the water in different locations and perhaps other variables not readily apparent to observers. Generally, however, in almost all cases the metals which are present in primary proportions are manganese and iron. The following table (taken from an article entitled "The Geochemistry of Manganese Nodules and Associated Deposits from the Pacific and Indian Oceans" by Croonan and Tooms in Deep Sea Research (1969), Volume 16, pages 335–359, Pergamon Press (Great Britain) shows the relative compositions of the most valuable metals contained in nodules taken from different areas within the Pacific and Indian Oceans.

Table I

	1	2	3	4	5	6	7	8	9
Mn	13.95	16.87	15.71	15.85	22.33	19.81	16.61	13.56	15.83
Fe	13.10	13.30	9.06	12.22	9.44	10.20	13.92	16.75	11.31
Nl	0.393	0.564	0.956	0.348	1.080	0.961	0.433	0.322	0.512
Co	1.127	0.395	0.213	0.514	0.192	0.164	0.595	0.358	0.153
Cu	0.061	0.393	0.711	0.077	0.627	0.311	0.185	0.102	0.330
Pb	0.174	0.034	0.049	0.035	0.028	0.030	0.073	0.061	0.034
Ba	0.274	0.152	0.155	0.306	0.381	0.145	0.230	0.146	0.155
Mo	0.042	0.037	0.041	0.040	0.047	0.037	0.035	0.029	0.031
V	0.054	0.044	0.036	0.055	0.041	0.031	0.050	0.051	0.040
Cr	0.0011	0.0007	0.0012	0.0051	0.0007	0.0005	0.0007	0.0020	0.0009
Ti	0.773	0.810	0.561	0.489	0.425	0.467	1.007	0.820	0.582
L.O.I.	30.87	25.50	22.12	24.78	24.75	27.21	28.73	25.89	27.18
Depth (in)	1757	5001	5049	1146	4537	4324	3539	3793	5046

1. Mid-Pacific Mountains (6 samples)
2. West Pacific (23 samples)
3. Central Pacific (9 samples)
4. Southern Borderland Seamount Province (5 samples)
5. Northeast Pacific (10 samples)
6. Southeast Pacific (8 samples)
7. South Pacific (11 samples)
8. West Indian Ocean (10 samples)
9. East Indian Ocean (14 samples)

Nodules are also found in the Atlantic Ocean; however, it has been found that generally these nodules contain lower amounts of the more valuable metals and correspondingly high amounts of the less desirable metals which cannot be readily refined and which have little or no value; such as the alkaline earth metals.

Because of the peculiar and intricate crystal structure of the ocean floor nodules, the common refining techniques used for the refining of land ores are not generally suitable for the nodules.

Mero in U.S. Pat No. 3,169,856 discloses a scheme for "separating the nickel from the cobalt in ocean floor ore deposits." The Mero process is directed to a specific type of ocean floor nodule ore wherein the separate mineral phases of manganese and iron contain different metal constituents. Specifically, according to Mero nickel and copper are present only in the manganese phase of the material whereas cobalt is present solely in the iron phase. Mero further states that the oxides are in solid solution within the nodule. Mero reacts the nodule strong reducing agent for example, SO_2 or NO_2.

The Mero process is based upon the unique relationship of the metal constituents in being sub-divided between the manganese and iron phases. Mero states that as a result of the phase differences in the nodule ores, it is possible to carry out a process for differentially leaching these materials from the ore. In a first stage, the ore is contacted with an aqueous solution comprising SO_2 or NO_2 to selectively leach out manganese, nickel, copper and other mineral elements bound up in the manganese phase of the ore. The cobalt and iron are not leached out. The first solution containing the manganese, nickel and other elements is then treated by various chemical means to separate the different metal values.

Schaufelberger, in U.S. Pat. No. 2,778,729, discloses a process for the recovery of nickel and cobalt from land-based garnierite ores, i.e., ores containing metal values in a structure of magnesium silicate minerals. Such minerals contain as the valuable metal constituents manganese, copper, cobalt, nickel and iron. Aqueous slurries of the crushed minerals are treated with SO_2 gas. A major problem with refining of these ores is involved in the removal of the magnesium silicate which is a major constituent of these ores.

In accordance with the present invention an improved novel process is provided for extracting individual metal values from an ocean floor nodule ore. The process comprises: (1) reacting, in the presence of oxygen, the nodule ore with an acidic reducing agent, such as sulfur dioxide, which is capable of reacting with the metal values in the ore to form as reaction products the corresponding water-soluble Salts, e.g., the sulfates, of divalent manganese, nickel, cobalt and copper; (2) contacting the metal values with sufficient oxygen to convert substantially all of the iron to iron oxide; (3) leaching the reacted ore with water to form an aqueous pregnant leach solution comprising the water-soluble salts of divalent manganese, copper, nickel and cobalt; (4) separating the pregnant leach solution from any insoluble residue; (5) contacting the aqueous solution with a liquid ion exchange agent to separate out an individual metal value and to form a solution of the individual metal value in the form of a water-soluble salt; and (6) reducing the metal value to the elemental metal by cathodically electrodepositing from the solution of the water-soluble salt.

Steps (1), (2) and (3) above, are preferably carried out simultaneously by reacting the nodule ore with the acid-reducing agent in the presence of excess oxygen in an aqueous medium, e.g., a bath of an aqueous solution. For example, the ore can be comminuted and slurried in water and SO_2, with excess oxygen, can be bubbled therethrough, or a concentrated aqueous solution of SO_2, can be contacted with the comminuted ore with excess oxygen. Alternatively, the ore can first be contacted with SO_2gas plus oxygen, and then leached with water, preferably with additional oxygen being bubbled through the leach water.

The process of the present invention successfully and completely breaks up the matrix of the manganese oxide-iron oxided crystal structure in the nodule ore, freeing the valuable nonferrous metals from the ore in the form of soluble salts. The first steps of the process of the invention can be carried out over a wide range of temperatures. Preferably, however, the reactions are carried out in the presence of liquid water; therefore, unless elevated pressures are utilized, temperatures from about 0°C up to about 100°C, or the boiling point of the solution, are most generally utilized. Ambient pressures and temperatures are most preferred. The speed of the reaction, which is a first order reaction, is such that higher temperatures would not be of any advantage. The costs of heating the reaction mixture can be thus avoided. The preferred range of operating temperatures for the reaction in an aqueous medium is from about 10°to about 75°C. and optimum temperatures are from about 20° to about 50°C.

When reducing the ore with gaseous reducing agent (SO_2), the range of temperatures is broader. Generally, a temperature of from about −40° to about 500°C. is useful, preferably from about 20° to about 4,00°C. and optimally up to about 100°C. In both types of reaction, gaseous or aqueous medium, ambient conditions are most useful. when operating a large bed of ore on a commercial scale, cooling may be required. The reaction is first order and highly exothermic; it can be initiated at ambient or even lower temperatures. The maximum permissible temperature is a function of the reaction equipment and not limited substantially by the reaction.

The aqueous solution of the manganese, copper, cobalt and nickel salts which is produced during this process is preferably substantially free of iron. this is generally desirable when the metal values are to be separated by liquid ion exchange. The production of an iron-free solution is accomplished, generically, by maintaining the iron as the insoluble oxide or by converting any soluble iron sulfate formed to the insoluble oxide.

When treating bone dry nodule ore with SO_2in an anhydrous system, the iron is not converted to a soluble compound. The following reaction equations are believed to apply:

$$MnO_2 + SO_2 \rightarrow Mn\,SO_4$$
$$2\,NiO + 2\,SO_2 + O_2 \rightarrow 2\,NiSO_4$$
$$2\,CuO + 2\,SO_2 + O_2 \rightarrow 2\,CuSO_4$$
$$2\,Co_2O_3 + 4\,SO_2\,O_2 \rightarrow 4\,CoSO_4$$
$$2\,FeO(OH) \rightarrow 3\,Fe_2O_3 + H_2O$$

As shown the iron is converted to an insoluble oxide. When the reaction is carried out in the presence of water, and if, as is preferred, excess oxygen is present, i.e., it is in a net oxidizing atmosphere, the same reactions apply. If, however, excess SO_2 is used in the presence of water, i.e., net reducing conditions, the iron compound is believed to react as follows:

$$4\,FeO(OH) + 4SO_2 + O_2 \xrightarrow{H_2O} 4\,Fe\,SO_4 + 2H_2O$$

The iron sulfate product must then be oxidized to the iron oxide by the later addition of oxygen as follows:

$$4\,Fe\,SO_4 + O_2 + 4H_2O \rightarrow 2\,Fe_2O_3 + 4H_2SO_4$$

The acidic reducing agent can be added as a gas or as an aqueous solution. However, sulfur dioxide, is not sufficiently soluble in water to provide an economical reaction without the further addition of gas during the reaction.

The rate of reaction for SO_2 is sufficiently great that the amount of ore reacted per unit time is dependent substantially upon the rate at which the reducing agent is fed to the ore. Thus, if available, substantially pure reducing gas (e.g., SO_2) should be utilized, both for the vapor phase reaction and for the aqueous reaction. If only dilute gas is available: stack gases or by-products from another process, gas containing any proportion of SO_2can be used. Furthermore, highly dilute stack gases can be concentrated, if desired before contacting the nodules.

Oxygen-containing gas, usually air, is admixed together with the reducing agent. At least sufficient oxygen to react with the metal values and reducing gas to form the desired soluble salts should be provided to avoid wasting the relatively more costly reducing agent gas. Preferably, the oxygen is present in excess so as to form a net oxidizing atmosphere in order to avoid the formation of soluble iron sulfate when water is present. Preferably, the exit gas from the reactor is substantially free of SO_2.

Although the reaction between the ore and the reducing agent in an aqueous medium proceeds at substantially any concentration of the SO_2in the aqueous solution, it is preferred not to use solutions containing less than about 1 percent by weight of the reducing agent. Most preferably, a concentration of at least about 10percent by weight of the reducing agent is used. Optimally a saturated solution, wherein additional $SO_2$is continously bubbled through the water when is contact with the ore, is used.

It is preferred that the ore be comminuted and when reacting in an aquedous medium the ore is preferably mixed with the water to form a slurry or suspension into which the acidic reducing agent and oxygen are passed.

The nodule ore is preferably comminuted, as by grinding, crushing or pulverizing, into small particles so as to increase the surface area for reaction. Preferably, the ore is comminuted to a particle size of not greater than about 10 mesh on the U.S. seive scale and most preferably in the range of from about 35 to about 100 mesh.

If a soluble iron salt is formed and dissolved by leach water, the soluble salt, e.g., the sulfate, can be converted to the iron oxide and precipitated from the solution by bubbling oxygen into the solution at a temperature of at least about 30°C. Preferably, a temperature of from about 30°C. to about 80°C. is used and optimally of from about 40° to about 80°C.

The aqueous pregnant leach solution containing the dissolved soluble metal values are separated from the insoluble solids, i.e., the reacted residue or gangue, of the ore and the iron oxide, by any conventional liquid-solid separation procedure., e.. filtering, decanting, thickening or any other procedure for separating liquids from solids. This leaching and solid-liquid separation can be carried out batch-wise or continously but preferably by continuous countercurrent flow.

In the preferred procedure, steps **1**, **2** and **3** occur substantially simultaneously, The ore is contacted with an aqueous solution of, e.g., SO_2, in the presence of excess oxygen and the soluble metal salts formed are immediately leached into the solution which is separated from the remaining insoluble material, which includes iron oxide. In this preferred procedure, the ore is comminuted and contacted with the aqueous solution in conventional leaching apparatus. It is important to separate the iron value from the other metals early in the process. Dissolved iron in the solution tends to interfere with the preferred methods for separating and purifying the individual metal values remaining in the solution.

The pregnant leach solution, when sulfates are formed contains generally up to about 115 g/l of manganese value, but preferably contains manganese in a concentration of at least/about 25 g/l of metal, and optimally in a concentration of from about 25 to about 100 g/l. The concentrations of the other metals in the leach solution are proportional to their concentration in the nodule ore relative to manganese. Generally, the manganese salt has the limiting solubility so that substantially all of the remaining valuable metals can be leached out with the manganese. This especially true with regard to nickel, cobalt and copper.

Preferably, neutral water is not used as a leach liquid. The leach liquid is maintained acidic, having a pH of not greater than about 4 and preferably not greater than about 3. The optimum maximum pH of the leach liquid is about 2. A lower pH tneds to substantially increase the proportion of copper salt which tends dissolved. At higher pH, the copper salts tend to hydrolize, forming an insoluble precipitate.

It is desirable to insure that no unreacted acidic reducing agent, e.g., SO_2, remains in the pregnant leach solution. When the reaction is carried out in an aqueous medium, the resultant pregnant solution can be heated to evolve the SO_2 from the solution. Generally, a temperature of from about 60° to about 70° is sufficient. Bubbling sparge gas substantially inert to the present system, such as nitrogen, carbon dioxide, air or any of the noble gases, through the solution aids in the removal of the reducing agent. The SO_2 is preferably recovered and recycled for further use in the reduction step of the process.

Preferably the leach liquid is maintained at substantially ambient temperatures, There is substantially little or not advantage in utilizing higher temperatures. The term "leach liquid" in this specification is applied to the aqueous solution utilized for dissolving water-

soluble metal salts in order to separate them from insoluble gangue and iron oxides, following the vapor-phase reduction reaction, or to the liquid used as the aqueous reaction medium. The pregnant leach solution contains the dissolved metal values.

Because of the rather complex mixture of materials which are obtained from such ocean floor nodules, many of the standard hydrometallurgical methods for separating out metal values are not directly applicable because of the presence of various interfering ions. Preferably, the following procedures can be utilized for separating out at least the pure cobalt, copper and nickel values from the pregnant leach solution.

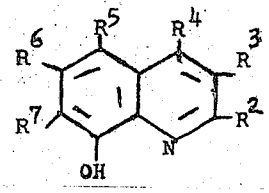
For separating each of the copper, cobalt, and nickel values from the leach solution a liquid extraction procedure is most preferred.

The liquid-liquid extraction procedure requires the use of an extracting medium which is readily separable from water, which is selective for extracting one or more of the metal values from the aqueous leach solution and from which the metal value can be readily stripped.

The extracting medium should be immiscible with water to improve the economic efficiency of the process. If the extracting medium were not immiscible with water, a substantial loss of the extracting reagent would occur during each extraction, by virtue of at least a partial solubility in the water phase and a loss of the extracting agent in the aqueous raffinate.

Extracting agents which are especially suitable because they are highly specific to the metal values in the leach solutions which are obtained, e.g., from ocean floor nodule ores, include, for example, certain substituted 8-hydroxyquinolines,α-hydroxy oximes and naphthenic acids.

The 8-hydroxyquinoline compounds, which are especially useful for the separation of the metal values in accordance with the present process, can generally be defined by the following formula:



wherein each of the R groups can be hydrogen or a hydrocarbyl group or inertly-substituted hydrocarbon groups, such as alkenyl, alkyl, alkynyl, cycloalkyl, cycloalkenyl, aryl or combinations thereof, such as alkaryl, aralkyl, aralkenyl, alkyl-cycloalkyl, etc.

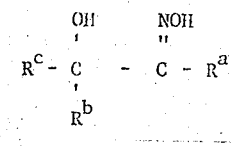
At least one of the R Groups, however, must be a hydrocarbon group. Any inert substituent can be present as long as it does not adversely affect the solubility of the substituted 8-hydroxyquinolines in organic solvents nor adversely affect the solubility in the organic solvent of the metal chelate formed therefrom.

The resulting metal chelate must remain soluble at least to the extent of approximately 2 percent by weight in the organic solvent.

The preferred position of the hydrocarbyl substituent of the 8-hydroxyquinoline nuclear structure is such as to preferentially complex with the desired metal ion in the aqueous solution. The sum of the carbon atoms in the R groups must be at least about 8 and can be high as 24 or more. The preferred R groups are alkylbenzyl groups or beta-alkenyl groups containing from 12 to 18 carbon atoms, preferably attached at the R^5, R^6, or R^7position. The optimum position for substitution is at the R^7position to obtain the highest degree of efficiency. For a more complete description of these hydrocarbyl-substituted 8-hydroxyquinolines, see Republic of South Africa specification No.69/4397 to Budde Jr. et al, assigned to Ashland Oil, Inc.

Representative compounds useful for ion exchange and within the scope of the above general formula I are: 7-octyl-benzyl-8-hydroxyquinoline, 7-dodecyl-benzyl-8-hydroxyquinoline, 7-nonylbenzyl-8-hydroxyquinoline, 7-ditertiarybutyl-benzyl-8-hydroxyquinoline, 7-hexadecenyl-8-hydroxyquinoline, 7-dibenzyl-8-hydrozyquinoline, 7-dimethyldicyclopentadienyl-8-hydroxyquinoline, 7-phenyl-dodecenyl-8-hydroxyquinoline, and the like where one or more of the hydrolcarbyl groups R are attached to ring carbon atoms in the 2nd, 3rd, 4th, 5th and 6th positions. Mixtures of these 8-hydroxyquinoline derivatives can be used if desired.

The second preferred type of metal extractants are the alphahydroxy oximes, which are disclosed inter alia in U.S. Pats. Nos. 3,224,873; 3,276,863 and 3,479,378. These materials have the general formula:



wherein the R^a, $R^b$and R^c groups can be any of a a of organic, hydrocarbon radicals such as aliphatic and alkyl aryl radicals. R^bcan also be hydrogen. Preferably $R^a$and R^c are unsaturated hydrocarbon or branched chain alkyl groups containing from about 6 to about 20 carbon atoms. R^a and R^o are also preferably the same, but when alkyl are preferably linked to the central carbon atoms by a secondary carbon atom. R^b is preferably hydrogen or unsaturated hydrocarbon or branched chain alkyl group containing from about 6 to about 20 carbon atoms. The oxime preferably contains a total of from about 14 to about 40 carbon atoms. Useful R^a, R^b and R^c groups include in addition to hydrogen, the mono-and polyunsaturated groups such as heptenyl, octenyl, decenyl, octadecenyl, octadecynyl, and 2-ethyl-octadecenyl.

Alkyl groups include 2-ethylhexyl, 2,3-diethylheptyl, 2-butyldecyl, 2-butylhexadecyl, 2,4-ethylbutyldodecyl, 4-butylcyclohexyl, and the like. Examples of the preferred alpha-hydroxy oximes include 19-hydroxyhexatriaconta-9,27-dien-18-oxime; 5,10-diethyl-8-hydroxytetradecan-7-oxime; 5,8-diethyl-7-hydroxydodecane-6-oxime.

The liquid ion exchange agents, which are used for the extraction of copper, cobalt and nickel values are generally chelates and thus remove only the metal values from the solution, leaving behind the anions.

The above hydroxyquinolines and oximes are compounds generally known to industry and commercially available. Any other compounds useful as selective extractants for the metal values in the aqueous systems obtained from the reduction of ocean floor nodules

ores can also be used in the process of this invention.

The extracting agent can be a liquid which is itself water-immiscible but generally can be dissolved in a solvent which is substantially immiscible with water. The oximes and hydroxyquinolines are at least partially insoluble with water. It has been found to be preferable to use them in solution in a water-immiscible solvent to form a water-immiscible extraction medium to prevent loss of the extraction agent in the aqueous raffinate.

It has been found when utilizing common commercially available water-immiscible solvents that solutions containing from about 2 to about 50 percent and preferably from about 5 to about 30 percent by wt. of the extracting agent is economically useful as being sufficiently active to remove the desired metal values selectively from the aqueous solution and being sufficiently dilute in the extracting agent so that substantially no extracting agent is leached out and lost in the aqueous raffinate. If it is desired, however, more concentrated solutions can be utilized. Mixtures of extracting agents can be used as long as they are not jointly reactive and do not interfere with the process of this invention.

Useful solvents include generally any inert hydrocarbons which are solvents for the extracting agent, per se, and for the metal chelate, or, extracting agent-metal complex, and which do not react with any of the other materials present, under the conditions of the extraction process. Generally, liquid aliphatic, cycloaliphatic, aromatic, cycloaliphatic-aromatic, aliphatic-aromatic or chlorinated such hydrocarbons are preferably utilized as the solvent-diluent for the extracting agent. Optimally, the diluent-solvent has a specific gravity in the range of from about 0.65 to about 0.95 and a mid-boiling point in the range of from about 120° to about 615°F. (ASTM distillation). However, substantially any liquid can be used as a solvent-diluent that meets the following criteria:

1. A solvent for the extracting agent;
2. A solvent for the extracting agent-metal complex, or chelate,
3. Immiscible with water; and
4. Readily separable from water.

Examples of suitable solvents include benzene, toluene, xylene, aliphatic and aromatic petroleum fractions such as naphtha and derivatives thereof and mixtures of the foregoing. In addition to the aliphatic, aromatic, cycloaliphatic-aromatic, aliphatic-aromatic hydrocarbons and cycloaliphatic hydrocarbons, chlorinated such hydrocarbon liquids can also be usefully utilized.

Light fuel oil, high flash point kerosene and other petroleum hydrocarbons, such as hexane-heptane mixtures are preferred. Generally the aliphatic materials are most preferred because of their ready availability and ease of separation from the aqueous phase.

The concentration of the extracting agent in the solvent-diluent is determined not only by the solubility of the extracting agent per se, but also by the solubility of the extracting agent-metal complex, or chelate.

In addition to the solvent and the extracting agent, there can preferably also be present in the liquid extracting medium a phase modifier which prevents formation of an emulsion with, or entrainment of, the organic phase in the aqueous phase. This is accomplished, it is believed, by altering the surface tension and related physical properties of the organic-aqueous mixture during extraction. These phase modifiers are generally most useful when an aliphatic solvent-diluent is utilized and include, preferably, aliphatic alcohols containing from about 8 to about 16 carbon atoms such as n-octyl alcohol, n-decyl alcohol, n-dodecyl alcohol, n-tetradecyl alcohol, n-hexadecyl alcohol, isooctyl alcohol, 2-ethylhexyl alcohol, cyclohexanol and mixtures of these and other alcohols. Decanol is a preferred material.

Generally no more than the necessary amount of the phase modifier, e.g., alcohol, which is necessary to inhibit the formation of the emulsion or prevent entrainment, should be used. Usually no more than about 25 percent by volume of the phase modifier is necessary. Preferably, from about 2 to about 10 percent by volume is satisfactory and not more than about 5 percent is most preferred. The phase modifier can be completely eliminated if desired, and, therefore, is optional in the present procedure.

The present invention does not comprise solely the selection of the extracting medium. It is preferred that the extracting medium be a liquid, because liquid-liquid extraction of a normally solid material from solution is a relatively simple and common procedure. However, other extraction procedures can be followed and other types of extractants used.

When utilizing liquid-liquid extraction from an aqueous solution of mixed metal halides, a wide range of aqueous phase-to-aqueous-immiscible-phase volume ratios can be utilized in the present invention. Generally, using a 20 percent by wt. solution of the extracting agent, aqueous-to-aqueous immiscible phase volume ratios of from about 10:1 to about 1:10 are desirable. The useful range of volume ratios differ proportionately for other concentrations of the extracting agent.

The above two types of extraction agents are especially preferred for the separation of the metal values found in the leach liquid obtained from ocean floor nodules because it has been discovered, as an aspect of this invention, that a single one of these reagents can be utilized for the selective removal of all of the important metal values from the leach liquid. Thus, by utilizing either an α-hydroxy oxime or an 8-hydroxyquinoline, a single extracting medium can be utilized for removing, in seriatim, all of the desired metal values. It is unnecessary to utilize a multiple extractant system when utilizing these materials, but is merely necessary to vary the pH of the leach solution following each successive extraction.

Beginning withan aqueous leach solution containing dissolved copper salt, cobalt salt, nickel salt and manganese salt, as the primary solutes, plus a variety of other metal salts in monor concentrations, the extraction of the individual metals can preferably be carried out by the following general procedure with liquid ion exchange agents;

1. adjust the pH of the pregnant leach solution to a desirable pH, 2. mix the pregnant leach solution with an immiscible organic liquid containing an extractant specific to a metal at that pH; preferably, copper is extracted with an α-hydroxyoxime or an 8-hydroxyquinoline initially at a pH of not greater than about 2.5, preferably from about 1.5 to about 2.5 and optimally of from about 1.8 to 2.2; the best results are obtained at a pH of about 2; 3. separate the aqueous raffinate from step 2. from the extract phase, adjust the pH of the raffinate as necessary, mix the raffinate with an immiscible organic liquid containing an extractant specific to another metal at the pH of the aqueous

phase. Generally, nickel can be extracted using for example, an α-hydroxyoxime or 8-hydroxyquinoline at a pH of about 3 to about 6 and preferably about 3 to about 3.5 and cobalt can be extracted using these agents at a pH of from about 3.5 to about 7, preferably to about 6, optimally from about 3.5 to about 5 and the most economical results at from about 3.5 to about 4.5. At too high a pH, the manganese, nickel and cobalt tend to precipitate and this is preferably avoided. Further, increasing pH too much is expensive, in using up basic reagents. Nickel and cobalt can be extracted together.

The ratio of cobalt and nickel removed from the leach solution by the extractant is determined by the pH of the leach solution and by the volume phase ratio of organic to aqueous phases, i.e., the relative proportions of nickel and cobalt extract can be the same as that which is present in the pregnant leach solution or a greater proportion of nickel or a greater proportion of cobalt can be extracted. Generally, the higher the pH the greater the proportion of cobalt extracted. It is preferred, usually, to remove the nickel and cobalt. in the same proportions as the metals are present in the pregnant leach solution Therefore, the pH for this ratio should be maintained during the extraction.

It is usually necessary to continually add alkaline material during the extraction stages in order to maintain the desired pH. The chelating agents act by releasing hydrogen ions when extracting metals, and thus the pH would decrease during extraction. Caustic soda solution is preferably used. The sodium ion generally does not interfere with the further processing of any metal salt. However, other useful basic materials include generally the oxides, hydroxides and carbonates of alkali metals and alkaline earth metals. Such compounds include potassium hydroxide, lithium hydroxide, lithium carbonate and ammonium hydroxide and carbonate. Manganese hydroxide and manganese carbonate are especially useful as they do not introduce any additional metal value. Buffering agents can also be added; however, this can add an undesirable impurity to the leach liquid.

Each extraction step can be carried out with one or more extraction stages until the desired amount of metal is extracted.

4. The metal-containing organic extractant phases can be stripped of the metal values by contacting with an aqueous stripping liquid; generally an acidic solution is used. Generally, following stripping the extracting solution can be recycled to the process.

Copper can be readily stripped by an aqueous mineral acid. The amount of hydrogen ion provided by the stripping liquid must be at least slightly in excess (preferally at least about 5 percent in excess) of the stoichiometric amount needed to substitute for the metal in the extract. Preferably, the stripped copper is soluble in the stripping liquid. The preferred stripping acids include sulfuric acid, nitric acid, and hydrochloric acid. As the acid used determines the metal salt to be formed, this can be a basis for selecting the acid, if a particular salt is desired.

Where nickel and cobalt are extracted together, the nickel can first be stripped using a relatively weakly acidic aqueous solution, such as the mineral acids or the stronger organic acids, such as chloracetic acid, in a concentration of less than about 6N, preferably from about 0.01N to about 3N acid and most preferably from about 0.1N to about 1.ON. Cobalt can then be stripped from the chelate using a strong mineral acid aqueous solution in a concentration of at least 6N. hydrogen ion and 6N chloride ion. Strong hydrochloric acid, containing at least about 20 percent by weight HC1 is preferred.

Although the strong acid-chloride solution of cobalt can be directly used for the further reduction to cobalt metal, as in an aqueous electrolysis cell, it is preferred to extract the cobalt and then strip again to permit recycling and further use of the relatively expensive, strong, 6N acid-chloride solution. This can be done by contacting the cobalt solution with a tri-alkyl amine, or other material capable of extracting cobalt from an aqueous solution. The amine is preferably dissolved in a water-immiscible solvent to form a solution of the type described above for use with the hydroxyquinolines and oximes.

The tri-alkyl amine solution forms a complex with the cobalt halide and can then be readily separated from the strong acid solution. The cobalt halide can be stripped from the extractant by a weakly acidic aqueous solution, i.e., a pH of not greater than about 3, which can then be used, for example, as an aqueous electrolyte for refining to the elemental metal by cathodic electroplating.

The aqueous raffinate leach solution remaining after the cobalt and nickel are removed contains substantially all of the manganese value which was leached from the nodule plus minor amounts of the salts of other metals. The raffinate can be utilized per se to obtain relatively impure manganese, the degree of impurities being very slight. However, if a high quality manganese is needed, it is advisable to separate the manganese from the other metals. This can be done in various ways: "cementation," passing the solution through a bed of manganese metal particles, which results in the removal of the more noble metals by substitution therefore by manganese, or precipitation, as by sulfide precipitation of the other metals present. The remaining manganese salt in solution can then be utilized for the preparation of manganese metal by any conventional means. The presence of alkali or alkaline earth metals results in no interference at this point.

The solutions of the individual metal salts can then be treated in a conventional manner to reduce them to the elemental metals, e.g., by cathodic electroplating techniques. For example, manganese sulfate can be reduced to manganese in an aqueous electrolytic cell.

Copper, nickel and cobalt salts can be reduced to the respective metals from aqueous solutions in electrolytic cells.

The electrolytic procedures include the conventional methods for electrolytically reducing the salts to the elemental metals and the exact procedure forms no part of this invention. However, preferably, aqueous electrolysis procedures are followed wherein the electrolysis solution can be utilized in stripping the metal value from the liquid ion exchange medium and thencan be reused directly, with or without preliminary treatment, in the electrolysis, so as to continuously replenish the supply of electrolyte salt.

It should be noted that under this procedure the electrolyte salt, which is obtained from the liquid ion exchange medium, need not be the original salt, e.g., sulfate produced in the reaction.

Generally, it has been found that the halides are especially effective as electrolyte solutes for cobalt, producing an elemental halogen, e.g., chlorine, in addition to the elemental metal.

Although the initial product formed during the reaction between the nodules and the reducing gas are, e.g., sulfate salts, when the metal values are stripped from the liquid ion exchange medium the salt formed depends upon the acid which is used for the stripping.

For a more complete explanation and description of various electrolysis, or cathodic electroplating, refining procedures, see, Graham Electroplating and Engineering Handbook (1971), for example.

Referring to the drawings accompanying this application:

FIG. I is a schematic flow diagram of a procedure wherein sulfur dioxide is reacted with crushed nodules in an aqueous medium.

FIG. 2 is a portion of a procedure wherein SO_2vapor is reacted with the ore.

Referring to FIG. 1, nodules crushed to a particle size of from about 35 to about 100 mesh are passed into a leach tank where they are slurried with water while SO_2 and excess air are bubbled up through the water.

The liquid slurry is next passed to a filter to separate the solid residue, comprising the ore gangue $CaSO_4$ and iron oxide, from the aqueous solution comprising the manganese, cobalt, nickel, copper and other metal values dissolved as the sulfate salts. The sulfate solution is then passed to a liquid ion exchange system to separate out the individual metal values.

The leach/solution filtrate is extracted with a liquid ion exchange agent specific to copper at the pH of the filtrate, approximately 2.0. The liquid ion exchange agent, e.g., an oxime or an 8-hydroxyquinoline is dissolved in organic solvent medium which is immiscible with the aqueous leach liquid. The extractant solution and leach solution are contacted in any conventional liquid-liquid extraction equipment. Preferably a multistage counter-current flow extraction is carried out, either multiple mixer-settler stages or in an extraction column. The aqueous raffinate from the final stage is substantially depleted of copper.

The organic extract phase is stripped of its copper by contact with a sulfuric acid solution having a hydrogen ion concentration of about 2N to about 6N, in this case recycled from the copper electrolytic cell. The copper is stripped out as copper sulfate, which can be directly fed to the electrolytic cell. The organic extracting solution is then recycled.

To the aqueous raffinate is then added an alkaline material to increase the pH to the desired value, about 3.5. The raffinate is then extracted again with a liquid ion exchange agent, preferably the same α– hydroxy oxime or 8-hydroxyquinoline used for copper extraction.

The pH of the aqueous phase is monitored and maintained at the necessary pH (3–3.5 for oximes or hydroxyquinolines) until most of the nickel is extracted, and the pH is then increased to/and maintained within the range of 3.5 to 4.5 until the remaining cobalt is extracted. The organic extract phase from the extraction system contains the cobalt and nickel, and the final raffinate aqueous phase is substantially depleted of these metals, and contains primarily manganese sulfate plus small quantities of salts of other metals.

Alternatively, all of the nickel and cobalt can be removed in a single unit by maintaining the pH of the aqueous phase constant during this extraction such that the ratio of nickel-to-cobalt which is extracted is substantially that in the pregnant leach solution. This can be predetermined and the pH of the aqueous phase maintained to correspond to this proportion by continously adding basic material during the extraction. Generally, the higher the pH the greater the proportion of cobalt which is extracted relative to the nickel, and vice versa.

The organic extract, which contains cobalt and nickel, is then stripped first of its nickel content using the aqueous solution from a nickel electrolysis cell. To this solution is added sufficient make-up sulfuric acid to increase hydrogen ion concentration to a degree sufficient to at least stoichiometrically replace the nickel from the extract; generally from about 2N to about extract; N hydrogen ion concentration is preferred. This is sufficient to strip out nickel without removing cobalt. The aqueous phase containing nickel is then fed to the nickel electrolytic cell.

The remaining organic phase layer is then further treated with very strong aqueous solution of HC1 containing at least 6N hydrogen ion concentration and 6N chloride ion concentration. It is necessary that there be a sufficiently high chloride ion concentration to form the tetrachlorocobalt complex, which it is believed is needed in order to strip out cobalt. Although hydrochloric acid is preferred, as this provides both the necessary hydrogen concentration and chloride concentration, other strong mineral acids can be utilized in combination with soluble halide salts. The strongly acidic aqueous solution containing cobalt as the only metal can then be contacted with a 5 –30 percent solution of an organic tertiary amine, e.g., tri-2-ethylhexyl amine, to extract cobalt. The cobalt can be readily stripped from the amine solution using the electrolyte solution from a cobalt cell, and the aqueous stripping phase fed directly to the electrolysis cell. The 6N HC1 solution can then be recycled.

The manganese sulfate nickel sulfate and cobalt chloride solutions are electrolyzed in aqueous electroplating cells of conventional type. The electrolysis solutions from the nickel and cobalt cells are continously recycled as stripping liquids to pick up fresh metal salt feed for the cells.

Referring to FIG. 2 the crushed nodule ore is passed into a moving bed reactor and countercurrently contacted with SO_2 and air. The reacted nodules are than passed through a series of mixer-settler tanks countercurrently to water, preferably with additional air bubbled through the water. The liquid from the final settler tank is passed to a filter to insure the removal of all solid material. The liquid filtrate containing the manganese, nickel, cobalt and copper values from the ore can then be passed to a liquid ion exchange separation system as in FIG. 1.

The water which is utilized in the leach system is originally preferably at a pH of not greater than about 2.

The following examples set forth preferred embodiments of the present invention, but are exemplary and not exclusive of the full range of this invention.

EXAMPLE 1

Ocean floor nodule ore was obtained having the following composition:

Component	Percent by Wt.
Manganese	17.65
Iron	10.6
Nickel	0.65
Cobalt	0.32
Copper	0.12
Other Metals	Traces

The nodule ore was ground to an average particle size of less than 100 mesh and 100 gram samples of the nodules were slurried in 500 grams water. $SO_2$was bubbled through the aqueous slurry at a rate of approximately 0.1 liter/min.STP, and air at a rate of 0.5 liter/min. STP, for about 10 minutes. The flow of SO_2 and air was discontinued. The solids are then separated from the liquid by passing the slurry through a filter.

A second sample was treated identically except that the air flow was omitted. The aqueous leach solution filtrate from each sample was analyzed and the following percentages of the original metal values present in the nodule were found to have been dissolved in the leach solution as shown in Table I.

TABLE I

Air Flow liter/min.	Metal Dissolved in Solution (% by wt.)				
	Manganese	Iron	Copper	Cobalt	Nickel
0.5	88.6	0.0	78.2	96.4	92.1
0	69.8	79.4	76.7	94.3	80.7

As shown by the above table the addition of excess air served to substantially eleminate the iron which was carried over into the solution and increased the proportions of the other valuable metals dissolved.

EXAMPLE 2

A bed comprising 100 gms. of the crushed nodule ore of Example 1 was maintained in a fluidized condition by passing 1 liter/minute STP of a mixture of SO_2 and air containing 10 percent SO_2 and 5 percent O_2 through a fluidized bed reactor. After 3 minutes, the ore particles were removed and passed through a two stage mixer-settler leaching system countercurrently to water having an initial pH of 2. The final liquid was filtered to remove solids and the liquid leach solution was analyzed. Substantially the same results were obtained as in Example 1; the amount of dissolved iron was reduced to substantially zero, i.e., it was not detectable.

The patentable embodiments of this invention which are claimed are as follows:

1. A process for separating metal values from ocean floor nodule ores, the ore comprising as primary components the oxides of manganese and iron and as secondary components compounds of copper, cobalt and nickel, the process comprising the steps of:

1. reacting the nodule ore, in the presence of oxygen, with a sulfur dioxide acidic reducing agent to form as reaction products the water-soluble sulfates of divalent manganese, nickel, cobalt and copper (2) contacting the metal values with sufficient oxygen to convert substantially all of the iron present to insoluble iron oxide. (3) leaching the reacted ore with an aqueous leach liquid to form an aqueous pregnant leach solution comprising the water-soluble salts of divalent manganese, copper, nickel and cobalt;
(4) separating the solution from any insoluble residue of the ore;
(5) separating out an individual metal value by treating the aqueous solution in a liquid ion exchange process to form a solution of the individual metal in the form of a water-soluble salt;
(6) reducing the metal value to the elemental metal by cathodically electroplating from the solution of the water-soluble salt.

2. The process of claim **1** wherein the liquid ion exchange process comprises contacting the aqueous pregnant leach solution with a liquid ion exchange medium selective for the metal, separating the medium from the aqueous solution and stripping the metal value from the medium with an aqueous stripping solution.

3. The process of claim **2** wherein the medium comprises a metal extractant selected from the group consisting of alpha-hydroxyoximes and 8-hydroxyquinolines.

4. The process of claim **3** wherein the metal extractant is dissolved in a water-immiscible organic liquid solvent.

5. The process of claim **1** wherein the nodule ore is reacted with the sulfur dioxide and in excess of oxygen in an aqueous medium to form directly an aqueous pregnant leach solution of the water-soluble salts of divalent manganese, copper, nickel and cobalt.

6. The process of claim **5** wherein the nodule ore is comminuted and the ore particles are slurried in an aqueous medium prior to reaction with the sulfur dioxide in the presence of oxygen.

7. The process of claim **1** wherein oxygen is present in excess when the ore is reacted with sulfur dioxide.

8. The process of claim **1** wherein the nodule ore is reacted with sulfur dioxide in an anhydrous environment.

9. The process of claim **1** wherein the ore and the sulfur dioxide are both at substantially ambient temperatures when they are reacted.

10. The process of claim **1** wherein the aqueous leach liquid is at substantially ambient temperature when it contacts the reacted ore.

11. The process of claim **1** wherein the leach liquid has a pH of not greater than about 3.

12. A process for separating metal values from ocean floor nodule ore, the ore comprising as primary components the oxides of manganese and of iron and as secondary components compounds of copper, cobalt and nickel, the process comprising the steps of: (1) comminuting the nodule ore; (2) reacting the nodule ore with sulfur dioxide in the presence of excess oxygen; (3) forming a pregnant leach solution comprising a solution in water of manganese sulfate, nickel sulfate, cobalt sulfate and copper sulfate and separating the pregnant leach solution from the insoluble solids; (4) separating individual metal values from the pregnant leach solution by subjecting said leach liquid to a liquid ion exchange medium and stripping individual metal values therefrom to form separate aqueous solutions of soluble copper salt, nickel salt, cobalt salt, and manganese salt; (6) reducing the copper to copper metal by cathodically electroplating the aqueous solution of copper (7) reducing the nickel salt and cobalt salt to elemental cobalt and nickel by cathodically electroplating respectively, and (8) reducing the manganese sulfate to

manganese metal by cathodically electroplating the aqueous solution of manganese sulfate.

13. The process of claim 12 wherein the liquid ion exchange agent is selected from the group consisting of 8-hydroxyquinolines and alphahydroxyoximes.

14. A process for separating metal values from ocean floor nodule ores, the ore comprising as primary components the oxides of manganese and iron and as secondary components compounds of copper, cobalt and nickel, the process comprising the steps of:

1. reacting the nodule ore, in the presence of oxygen and water with an acidic reducing agent capable of reducing the tetravalent manganese and trivalent iron present in the ores and to form a product comprising the water-soluble salts of divalent manganese, divalent iron, divalent nickel, divalent copper and divalent cobalt and insoluble residue;
2. Contacting the product with sufficient oxygen to convert all of the iron compounds to insoluble iron oxide;
3. leaching the reacted ore with water to form an aqueous leach solution comprising the water-soluble salts of divalent manganese, copper, nickel and cobalt;
4. separating the solution from any insoluble residue of the ore;
5. Separating out an individual metal value by treating the aqueous solution in a liquid ion exchange process to form a solution of the individual metal in the form of a water-soluble salt;
6. reducing the metal value to the elemental metal by cathodically electroplating from the solution of the water-soluble salt.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,869,360

DATED : March 4, 1975

INVENTOR(S) : William S. Kane, et al

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Add at the end of "(63)" the following:

--a continuation-in-part of Ser. No. 309,714, November 27, 1972 and Ser. No. 309,713, November 27, 1972, now U. S. Patent numbers 3,809,624 and 3,810,827, respectively.

Column 1, line 6, after "abandoned.", add the following:

--This application is further a continuation-in-part of co-pending U. S. Application Serial No. 309,714 filed on November 27, 1972 and U. S. Application Serial No. 309,713 filed on November 27, 1972, now U. S. Patent Nos. 3,809,624 and 3,810,827 respectively.--

Column 16, line 26 (Claim 5 line 2) change "in" to --an-- (see application Claim 2, line 2).

Column 17, line 5 (Claim 13 line 3) correct "alphahydroxyoximes" to --alpha-hydroxyoximes-- (application Claim 13, lines 2 and 3)

Signed and Sealed this

first Day of June 1976

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks