

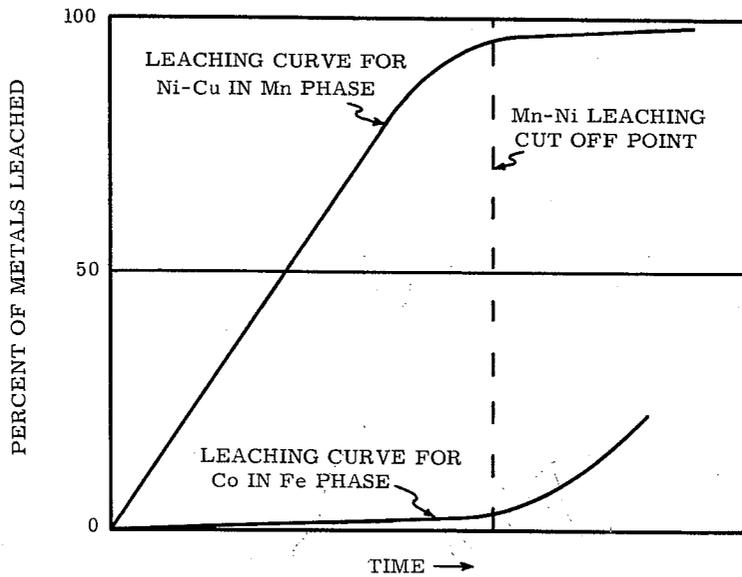
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PROCESS FOR SEPARATION OF NICKEL FROM COBALT IN
OCEAN FLOOR MANGANIFEROUS ORE DEPOSITS
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GRAPH SHOWING COMPARATIVE LEACHING RATES
OF MANGANESE AND OF IRON MINERALS



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PROCESS FOR SEPARATION OF NICKEL FROM COBALT IN OCEAN FLOOR MANGANIFEROUS ORE DEPOSITS

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My invention relates to a process for recovering nickel, cobalt and other metals from ocean floor manganiferous ore deposits, and more particularly relates to a process of separating the nickel from the cobalt found in ocean floor manganiferous deposits.

Although termed manganese deposits or manganiferous ore deposits by virtue of the fact that manganese, on a weight basis, is most frequently the major metallic constituent of these ore deposits, the ocean floor mineral deposits contain many other elements of economic interest as shown in the following table:

MAXIMUM, MINIMUM, AND AVERAGE WEIGHT PERCENTAGES OF 27 ELEMENTS IN MANGANESE DEPOSITS FROM THE PACIFIC AND ATLANTIC OCEANS

Weight percentages (dry weight basis)¹

Element	Pacific Ocean—Statistics on 54 Samples			Atlantic Ocean—Statistics on 4 Samples		
	Maximum	Minimum	Average	Maximum	Minimum	Average
B.....	0.06	0.007	0.029	0.05	0.009	0.03
Na.....	4.7	1.5	2.6	3.5	1.4	2.3
Mg.....	2.4	1.0	1.7	2.4	1.4	1.7
Al.....	6.9	0.8	2.9	5.8	1.4	3.1
Si.....	20.1	1.3	9.4	19.6	2.8	11.0
K.....	3.1	0.3	0.8	0.8	0.6	0.7
Ca.....	4.4	0.8	1.9	3.4	1.5	2.7
Sc.....	0.003	0.001	0.001	0.003	0.002	0.002
Ti.....	1.7	0.11	0.67	1.3	0.3	0.8
V.....	0.11	0.021	0.054	0.11	0.02	0.07
Cr.....	0.007	0.001	0.001	0.003	0.001	0.002
Mn.....	50.9	8.2	24.2	21.5	12.0	16.3
Fe.....	26.6	2.4	14.0	25.9	9.1	17.5
Co.....	2.3	0.014	0.35	0.68	0.06	0.31
Ni.....	2.0	0.16	0.99	0.54	0.31	0.42
Cu.....	1.6	0.028	0.53	0.41	0.05	0.20
Zn.....	0.08	0.04	0.047	-----	-----	-----
Ga.....	0.003	0.0002	0.001	-----	-----	-----
Sr.....	0.16	0.024	0.081	0.14	0.04	0.09
Y.....	0.045	0.033	0.016	0.024	0.008	0.018
Zr.....	0.12	0.009	0.063	0.064	0.044	0.054
Mo.....	0.15	0.01	0.052	0.056	0.013	0.035
Ag.....	0.0006	-----	² 0.0003	-----	-----	-----
Ba.....	0.64	0.08	0.18	0.36	0.10	0.17
La.....	0.024	0.009	0.016	-----	-----	-----
Yb.....	0.0066	0.0013	0.0031	0.007	0.002	0.004
Pb.....	0.36	0.02	0.09	0.14	0.08	0.10
L.O.I. ³	39.0	15.5	25.8	30.0	17.5	23.8

¹ As determined by X-ray emission spectrography.
² Average of 5 samples in which Ag was detected.
³ L.O.I.=Loss on ignition at 1,100° F. for one hour. The L.O.I. figures are based on a total weight of air-dried sample basis.

Ocean floor mineral deposits containing substantial amounts of manganese, nickel, cobalt, and copper were discovered in 1873 by the British Oceanographic Challenger Expedition. Subsequent oceanographic expeditions have recovered samples of these deposits from many different locations in the ocean.

Ocean floor manganiferous deposits are found as nodules, loose-lying at the surface of the soft sea floor sediment, as grains in the sea floor sediments, as crusts on ocean floor hard rock outcrops, as replacement fillings in calcareous debris and animal remains, and in other less important forms. Samples of this potential ore material can readily be recovered on the ocean floor by drag dredging, a method used by oceanographers for many years, or by deep sea hydraulic dredging, a method that could be used in commercial operations to mine these deposits.

Of the many ingredients making up such ore deposits, nickel and cobalt are emphasized because, from an economic standpoint, they are the most significant metals in most of these sea floor ores. Other metals, normally present, will be recovered as by-products in the production of nickel and cobalt.

Known methods of separating nickel and cobalt as found in natural ores, generally depend on some method of indiscriminately leaching these elements and separating the same after they are in solution together. Such nickel-cobalt separations, however, are rather difficult and expensive to carry out.

The mining of the vast reserves of manganiferous deposits lying over the ocean floor, can best be economically justified, were a more economical process available to effect a separation and ultimate recovery of the nickel and cobalt elements.

Accordingly, among the objects of my invention are:

(1) To provide a novel and improved process of separating the nickel from the cobalt as found in ocean floor manganiferous deposits;

(2) To provide a novel and improved process of separating the nickel from the cobalt as found in ocean floor manganiferous deposits, which process shall be simple and straightforward;

(3) To provide a novel and improved process for separating the nickel from the cobalt as found in ocean floor deposits, which process, at the same time facilitates the recovery of the many other elements involved in such deposits.

(4) To provide a novel and improved process for separating the nickel from the cobalt as found in ocean floor deposits, which process provides simple but accurate controls for indicating substantially complete separation of such elements from each other.

Additional objects of my invention will be described in conjunction with the accompanying drawing wherein the figure is a graph depicting the principle underlying the present invention.

Following intensive investigation of these ocean floor mineral deposits, I have discovered them to consist of several separate mineral phases of manganese and of iron. These separate mineral crystallites of manganese and of iron are so fine-grained and so intimately mixed that no known physical process can be employed to separate them. The minor metallic constituents of the ocean floor manganiferous deposits, such as nickel, cobalt, and copper and other elements, are localized in different mineral phases of this material, some elements being contained in the manganese mineral phases and others in the iron mineral phases.

I have found, through my extensive investigations, that the nickel and copper are contained in the manganese mineral phases of this material, apparently in solid solution in the manganese minerals. Cobalt, on the other hand, I have discovered to exist in the iron mineral phases of this material to the exclusion of the manganese phase. This is unlike the situation existing in connection with conventional ore involving nickel and cobalt, in which ores, when the nickel and cobalt are intimately mixed, must be indiscriminately leached from the ore, as the first step in effecting a separation thereof, but which step, unfortunately places them both in solution together, which in turn raises the problem of separation of the nickel from the cobalt.

The present invention is predicated upon the aforementioned discovery of mine relating to the phase characteristics of the ocean floor mineral deposits under consideration herein, and basically involves a process for differentially leaching these metals from the manganiferous ore before they are both in solution together, which process is made possible by such discovery.

To accomplish such separation of the nickel from the cobalt in the manganiferous deposits found on the ocean floor, the ore is first crushed preferably to about minus forty mesh. The crushed ore material is then mixed with water to form an aqueous slurry which consists of not more than about 40 percent of crushed ore by weight. The amount of crushed ore in this slurry is not critical but should be sufficient to allow the mixture to act fluid. Leaching gases, which may be sulphur dioxide, nitrogen dioxide or other gases that reduce manganese and iron oxides of a high oxidation state, are then mixed with the aqueous slurry. This may be accomplished by percolating the gas up through the slurry while maintaining the slurry in a constant state of agitation. When the slurry is thus exposed to the gas, the manganese along with the nickel, copper and other mineral elements bound up in the manganese phase of the ore, will go into solution in accordance with the leaching curve of the drawing, designated as "Leaching Curve for Ni—Cu in Mn Phase," while the iron along with the cobalt bound up in the iron phase, will leach out in accordance with the leaching curve identified on the drawing as "Leaching Curve for Co in Fe Phase."

A comparison of the two curves establishes that the nickel, copper and such other elements in the manganese phase, will go into solution before any appreciable amounts of the cobalt and such other elements as may be bound up in the iron phase. After all the available manganese, nickel, copper, etc., are in solution, additional amounts of gas added to the aqueous slurry, will cause a change in the pH of the slurry toward the acidic and only then will much of the cobalt or iron start to dissolve. It is at this point, that the process is stopped and the separation effected, because at this point, the nickel and associated elements are all in solution, while the cobalt and its associated elements are still in solid state. This critical point can thus be controlled by continuous monitoring of the pH of the aqueous slurry.

Another indication of the complete dissolution of the nickel and other metals associated in the manganese phase, will be the evolution of leaching gas from the top of the leaching cell. Evolution of such leaching gas or the sudden change in the pH of the slurry, therefore, can be used as controls to prevent the dissolving of the cobalt and other elements associated with the iron phase in the ore material.

This leaching process may be batch-wise or continuous. At the completion of the leaching operation in a batch process, the leaching gases are stopped and the solution is separated from the tailings. In a continuous process, solution would be continuously drawn off, ore, leaching gases, and water continuously added and the tailings continuously removed. The pH of the solution and the evolution of leaching gases would be closely monitored to determine the rate at which new slurry is added to the system and the rate at which solution is withdrawn.

The amount of leaching gas required to complete the dissolution of the elements in the manganese phase can be determined by calculation, but, in practice, a small excess of gas is always required to assure complete dissolution of the manganese, nickel, copper, etc., and the controls previously described, are of practical value in determining when these elements have been completely dissolved.

The rate at which the manganese, nickel, and associated elements are dissolved will depend somewhat on the temperature, pressure, and agitation of the slurry, but such variables are not critical nor essential features of the process constituting the present invention.

There need be no external control of the pH of the aqueous slurry or resulting solutions. The pH of the slurry will be controlled by the reaction between the gases, the water, and the dissolving elements, and will be on the acidic side of 7, while the manganese, nickel and associated elements are dissolving. The value of the pH will depend somewhat on the rate of the reaction and

the excess of the leaching gas used, but the exact value of the pH is not critical nor an essential feature of this process.

As previously indicated, the resulting solution of manganese, nickel, copper etc., is separated from the resulting cobalt-iron solid tails, before the iron and cobalt can dissolve appreciably. In a batch process, the cut off point of the leaching process would be at the point at which the cobalt or iron content of the resulting solution begins to rise rapidly, as illustrated in the drawing.

The iron-cobalt tails are then removed from the vessel, dewatered, filtered, and washed, and then treated in a standard manner with acid to leach the cobalt from the iron. The leaching of the cobalt from the iron with acid is a standard process in the metallurgical industry.

The solution of manganese, nickel, copper, etc., can be treated with hydrogen sulphide to precipitate the copper, which is then separated from the remaining manganese-nickel solution by standard dewatering and filtering techniques. Nickel can then be separated from the manganese by precipitation with hydrogen gas, or the manganese can be first separated from the nickel by differential thermal reduction. The separation of the nickel from the manganese or the manganese from the nickel would be conducted according to standard procedures.

The make up of the manganiferous ores found strewn over the ocean floor, lends itself to other methods of differentially leaching to effect separation of the nickel from the cobalt. One such additional method which comes to mind, involves subjecting the ore material to preleaching reduction roasts. The common factor in carrying out the present process, however, is to effect a differential leaching of the ore material, regardless of the particular steps carried out in effecting such differential leaching.

While I have described my invention in its preferred form and in considerable detail, it will be apparent that the same is subject to alteration and modification without departing from the underlying principles involved, and I, accordingly, do not desire to be limited in my protection to the specific details described, except as may be necessitated by the appended claims.

I claim:

1. The method of separating the nickel from cobalt in ocean floor manganiferous deposits, in which the nickel is present in a manganese oxide phase and the cobalt in an iron oxide phase, comprising,

breaking up such ore,

leaching under reducing conditions in a solution, the manganese phase and included nickel from the iron phase including the cobalt, then removing such manganese phase in solution before any appreciable amount of the elements in the iron phase are dissolved, and processing the same to remove the nickel, and separately processing the iron phase remaining, to remove the cobalt.

2. The method of separating the nickel from cobalt in ocean floor manganiferous deposits, in which the nickel is present in a manganese oxide phase and the cobalt in an iron oxide phase, comprising,

breaking up such ore,

mixing said ore in its broken up state with water to form a slurry,

mixing with said slurry a leaching agent capable of reducing manganese and iron oxides,

continuing the addition of such leaching agent and halting the same before any appreciable amount of the elements in the iron phase are dissolved, and then removing the solution of manganese and nickel from the resulting cobalt-iron tails.

3. The method of separating the nickel from cobalt in ocean floor manganiferous deposits, in which the nickel is present in a manganese oxide phase and the cobalt in an iron oxide phase, comprising,

crushing such ore to about minus forty mesh,

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mixing said ore in its crushed state with water to form an aqueous slurry,

mixing with said slurry a reducing and leaching agent capable in the presence of water of reducing manganese and iron oxides,

continuing the addition of such leaching agent and halting the same before any appreciable amount of the elements in the iron phase are dissolved, and then removing the solution of manganese and nickel from the resulting cobalt-iron tails.

4. The method of separating the nickel from cobalt in ocean floor manganiferous deposits, in which the nickel is present in a manganese oxide phase and the cobalt in an iron oxide phase, comprising,

crushing such ore to about minus forty mesh,

mixing said ore in its crushed state with water to form an aqueous slurry,

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mixing with said slurry a reducing and leaching gas capable in the presence of water of reducing manganese and iron oxides,

continuing the addition of such leaching gas and halting the same before any appreciable amount of the elements in the iron phase are dissolved, and then removing the solution of manganese and nickel from the resulting cobalt-iron tails.

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