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(54) **Titre : TRAITEMENT DE MATERIAUX CONTENANT DU MANGANESE**
(54) **Title: TREATMENT OF MANGANESE-CONTAINING MATERIALS**

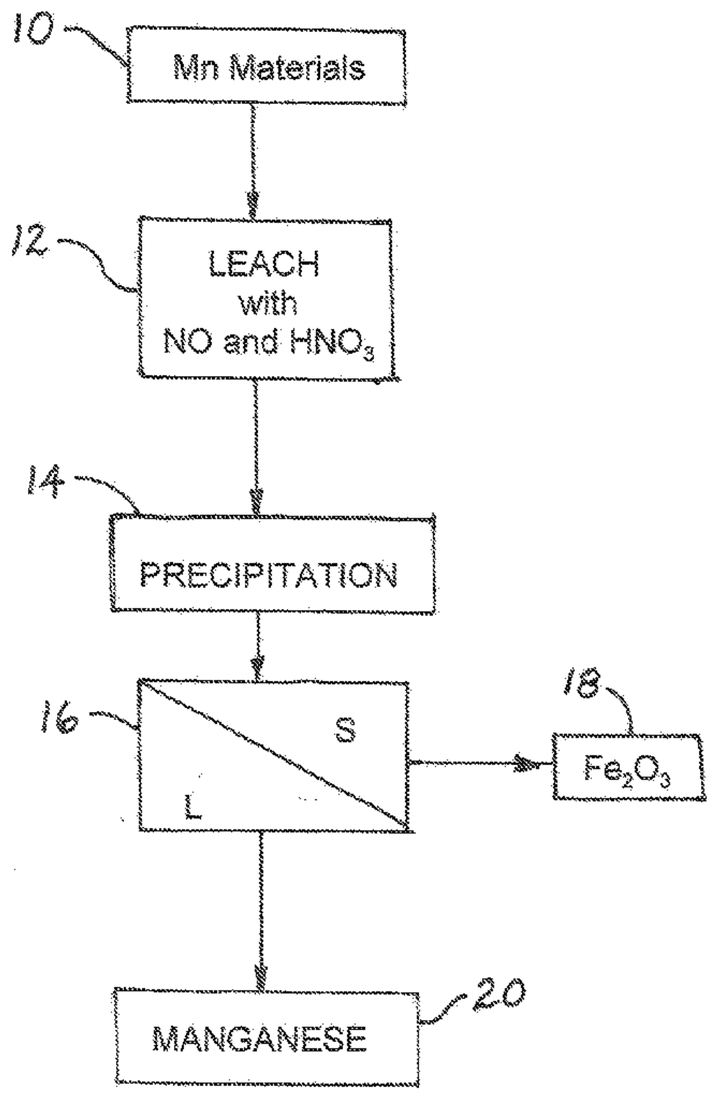


Fig. 1

(57) **Abrégé/Abstract:**
An improved method for treating manganese-containing materials, such as seafloor manganese nodules, by leaching with aqueous HNO3 and NO gas, and more particularly to methods for recovering valuable constituents from such nodules, especially manganese, cobalt, nickel, iron, and copper. It also provides a method to leach manganese material to release the titanium, vanadium, cerium, molybdenum and other metals from the manganese oxides and to make them available to be recovered.

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[Continued on next page]

(54) Title: TREATMENT OF MANGANESE-CONTAINING MATERIALS

(57) Abstract: An improved method for treating manganese-containing materials, such as seafloor manganese nodules, by leaching with aqueous HNO3 and NO gas, and more particularly to methods for recovering valuable constituents from such nodules, especially manganese, cobalt, nickel, iron, and copper. It also provides a method to leach manganese material to release the titanium, vanadium, cerium, molybdenum and other metals from the manganese oxides and to make them available to be recovered.

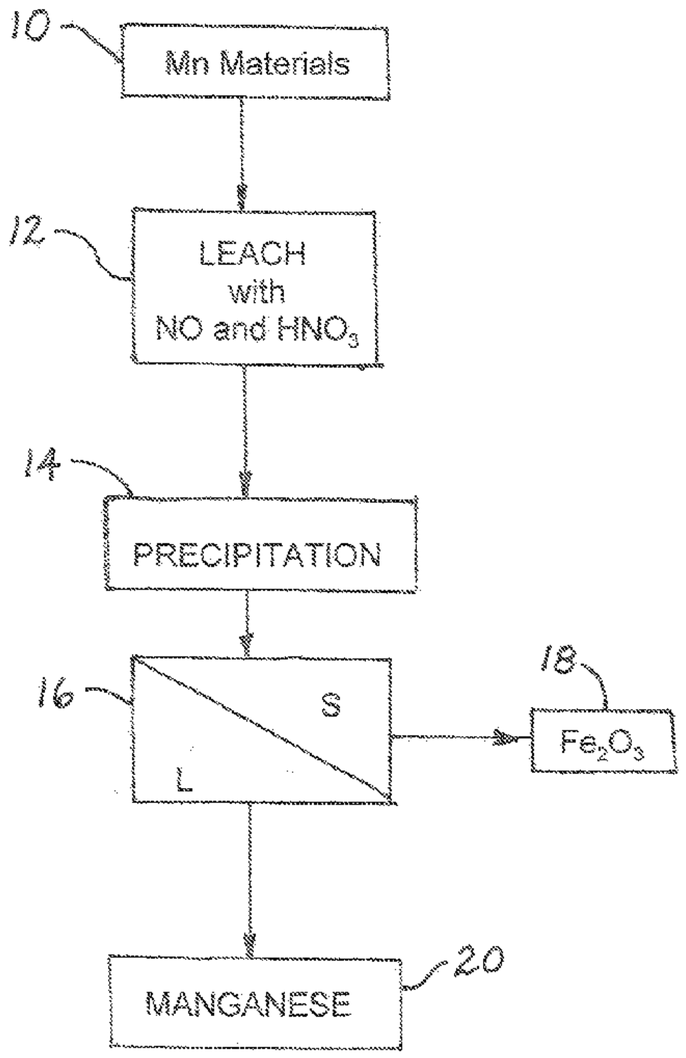


Fig. 1

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TREATMENT OF MANGANESE-CONTAINING MATERIALS

FIELD OF THE INVENTION

The present invention relates to a method for treating manganese-dioxide-containing materials, The invention is well suited to treating manganese-containing nodules recovered from the seafloor or lake floor, as well as manganese ores. The invention relates particularly to methods for leaching and recovering valuable constituents from such materials, especially manganese, and, if present, cobalt, nickel, copper, iron, and other valuable metals.

BACKGROUND OF THE INVENTION

Manganese-containing material treated by the invention can include manganese dioxide minerals in any form, including ores, or nodules, such as deep sea nodules.

Polymetallic or manganese nodules, are concretions formed of concentric layers of iron and manganese oxides around a core.

Deep sea nodules on the ocean floor include in their composition at least manganese (Mn) and usually nickel, cobalt, copper, zinc, and iron, with small amounts of titanium, vanadium, molybdenum, and cerium. Often present in addition are one or more of the following metals: magnesium, aluminum, calcium, cadmium, potassium, sodium, zirconium, titanium, lead, phosphorus, and barium.

All of the desired valuable metals in manganese nodules are tied up with insoluble oxidized manganese, such as MnO_2. Only about 5% of the manganese contained in the nodules is acid soluble. Thus it is necessary to reduce the MnO_2 by a suitable reducing agent

as a first step in order to recover the metal constituents. Historically, SO_2 has been used for this purpose. For deep sea nodules, carbon monoxide has also been used. However such prior art processes often do not recover a suitable manganese product, are capable of recovering only from about 80 to about 92% of the primary metal values, and often produce large quantities of waste. Moreover, a sulfate system requires large sized equipment with attendant high capital cost.

Unexpectedly, and contrary to earlier teachings, it has been found that reacting manganese-dioxide-containing materials with nitric oxide in the presence of nitric acid in aqueous solution results in recovery of at least 99% of the manganese values and associated metals (known as "pay metals" because they have higher commercial value than manganese).

SUMMARY OF THE INVENTION

The present invention is a process for recovering manganese and, if present, other metal values from manganese-containing material, including deep sea manganese nodules, by treating manganese-containing material with nitric oxide (NO) in an aqueous nitric acid solution. The net reaction with the MnO_2 is as follows:

$$3MnO_2 + 2NO + 4\ HNO_3 \rightarrow 3Mn(NO_3)_2 + 2H_2O$$

liberating the trapped desired valuable metals. In the present process, the quantity of NO required per unit of manganese recovered is less than one-third of the quantity of SO_2 required per unit of manganese, or the quantity NO_2 required per unit of manganese. Thus, the invented process delivers substantial savings in reactant costs and byproduct disposal.

OBJECTS OF THE INVENTION

The principal object of the present invention is to provide an improved method of recovering manganese from manganese-bearing materials.

Another object of the invention is to provide an effective leach for recovering metal values from manganese-bearing materials, including, if present, nickel, cobalt, zinc, copper, magnesium, aluminum, iron, cadmium, zirconium, titanium, lead, cerium, molybdenum, phosphorus, barium, and vanadium.

Another object of the invention is to provide an effective method of recovering metal values from undersea manganese-containing materials including deepsea manganese nodules.

Another object of the invention is to produce fertilizer grade nitrate materials.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects will become more readily apparent by referring to the following detailed description and the appended drawings, in which.

Figure 1 is a schematic flow sheet of the invented process.

Figure 2 is a schematic flow sheet of a more detailed process to the process depicted in Figure 1.

DETAILED DESCRIPTION

Referring now to Figure 1, the invented method of recovering manganese from materials 10 containing manganese-dioxide and other metal values, comprises the steps of:

a. leaching 12 the manganese-dioxide containing materials with HNO_3 and NO gas in an aqueous solution to form MnO which dissolves in the nitric acid, releases the accompanying metals into solution, and leaves an acid-insoluble, essentially metal free residue;

b. precipitating 14 iron from the solution as a residue;

c. separating 16 the iron-containing residue 18 from the solution; and

d. precipitating and recovering manganese 20 from the solution.

The process begins with manganese-containing material, such as deepsea manganese nodules, which may be obtained from an ocean, sea, or other body of water. Sometimes such nodules are found in large lakes. The deep sea nodules often contain in excess of 20 percent manganese, usually about 30 percent.

In addition to manganese, such deep sea nodules usually contain at least one of the following metals: nickel, cobalt, zinc, copper, magnesium, aluminum, iron, calcium, cadmium, potassium, sodium, zirconium, titanium, lead, cerium, molybdenum, phosphorus, barium, and vanadium. The invented process includes the efficient leaching and recovery of many of these metal values.

Optionally, the nodules are crushed or ground to increase the surface area for leaching. Advantageously, any chlorides in the nodules, such as from salt water, are removed by any convenient method, such as washing. This step may be done before, during or after any crushing but preferably after. Crushing or grinding the nodules can occur during leaching in a wet mill or wet crusher.

Preferably, the nodules are leached in an aqueous nitric acid solution into which NO gas is introduced. Alternatively, the NO gas first may be introduced into an aqueous HNO_3 solution, followed by the introduction of nodules into the solution to complete the reaction.

The NO reacts with MnO_2 to form MnO and NO_2, and to release the other metals from the nodules. The MnO so produced dissolves in the nitric acid, leaving an acid-insoluble residue, which may be removed from the solution at that time, or the acid-insoluble residue

may be carried forward to the iron-precipitation step and removed with the iron, as desired. The temperature of the solution is preferably controlled to a temperature in the range of 30 to 120°C to achieve the reaction.

The pH of the solution is then changed to about 0.5 - 2.5 to precipitate hydrated iron oxide. The precipitated iron values are removed by solid-liquid separation techniques. This pH change may be achieved in various ways, including the addition to the solution of a precipitating agent, such as alkalis, alkaline earths, ammonia, or other acid- reducing agents. Alternatively, such precipitation can be effected by any other method of achieving iron hydrolysis and its precipitation, ensuring the separation of iron from the more valuable metals.

Once in solution, the metal values may be precipitated as oxides or sulfides. Any copper, lead, cadmium, and zinc present in the solution is removed therefrom. Preferably, the solution is adjusted to a low pH, preferably less than 3, and a heavy-metal precipitating agent, such as a sulfide or an organic reagent or a complexing agent, is introduced into the solution to precipitate any copper, lead, cadmium, and zinc which is present in the solution, and the precipitated metal values are removed by solid-liquid separation.

The pH of the solution is raised, and, if desired, a sulfide is added to the solution to precipitate cobalt and nickel as sulfides. Remaining aluminum and some remaining zinc may also be precipitated as sulfides in this step.

Preferably, the pH of the solution is then raised to a pH in the range of about 8 to 10 to precipitate manganese. After separating the manganese residue, the remaining solution is a fertilizer grade nitrate product. Alternatively, the manganese nitrate in the solution can be decomposed to recover manganese oxide and nitrogen dioxide, the latter of which can be readily converted to nitric acid.

Referring now to Figure 2, which depicts an embodiment of the present invention in greater detail than Figure 1, the method of recovering metal values from deep-sea manganese nodules, comprises the steps of:

a. obtaining manganese-containing nodules 22 which also contain at least one of the metals of the group consisting of: cobalt, nickel, lead, copper, magnesium, aluminum, iron, cadmium, zirconium, titanium, zinc, cerium, molybdenum, phosphorus, barium, and vanadium;

b. leaching the nodules at 12 with HNO_3 and NO gas in an aqueous solution to form manganese nitrate in solution and to release the other metals into solution;

c. adding pH adjusting agents 24 to the solution 26 to precipitate ferric hydroxide;

d. separating 28 the precipitated ferric hydroxide from the solution;

e. adjusting 30 the solution to a low pH and introducing a sulfide to the solution to precipitate copper, lead, cadmium, and zinc 32, if present in the solution;

f. raising 34 the pH of the solution and introducing additional sulfide to precipitate cobalt and nickel sulfides 36; and

g. raising the solution pH to about 8 to 10 to precipitate hydrated manganese oxide product.

SUMMARY OF THE ACHIEVEMENT OF THE OBJECTS OF THE INVENTION

From the foregoing, it is readily apparent that we have invented an improved method for treating manganese-containing material including the treatment of seafloor manganese nodules recovered by undersea mining to effectively leach the material to produce a manganese oxide product and release any valuable metals by reducing manganese dioxide with nitric oxide, and for recovering the metal values contained in the nodules more efficiently and more economically than heretofore has been possible. We have also invented an improved method of recovering manganese from manganese-bearing materials, including

an effective leach for recovering metal values from manganese-bearing materials, including, if present, nickel, cobalt, copper, magnesium, aluminum, iron, cadmium, zirconium, titanium, zinc, lead, cerium, molybdenum, phosphorus, barium, and vanadium; as well as an effective method of recovering metal values from undersea manganese-containing materials including deepsea manganese nodules, and for producing a fertilizer grade nitrate material.

It is to be understood that the foregoing description and specific embodiments are merely illustrative of the best mode of the invention and the principles thereof, and that various modifications and additions may be made to the apparatus by those skilled in the art, without departing from the spirit and scope of this invention.

What is claimed is:

1. A method of recovering manganese from materials containing manganese-dioxide and other metal values, comprising the steps of:

a. leaching the manganese-dioxide containing materials with HNO_3 and NO gas in an aqueous solution to form MnO which dissolves in the nitric acid and releases the accompanying metals into solution, and leaving an acid-insoluble residue;

b. precipitating iron from the solution as a residue;

c. separating the iron-containing residue from the solution; and

d. precipitating and recovering manganese from the solution.

2. A method according to claim 1 wherein the manganese-containing materials are leached in an aqueous nitric acid solution into which nitric oxide gas is then introduced.

3. A method according to claim 1 wherein the manganese-containing material contains at least one of the metals of the group consisting of: nickel, cobalt, copper, magnesium, aluminum, iron, calcium, cadmium, potassium, sodium, zirconium, titanium, zinc, lead, cerium, molybdenum, phosphorus, barium, and vanadium.

4. A method according to claim 1 wherein the manganese-containing materials are manganese nodules obtained from any body of water, including a seafloor or lake floor.

5. A method according to claim 4, further comprising removing chlorides from the nodules prior to leaching.

6. A method according to claim 1 wherein the manganese-containing materials are dioxides or ores.

7. A method according to claim 4, further comprising crushing or grinding the nodules prior to leaching.

8. A method according to claim 4, further comprising crushing or grinding the nodules during leaching in a wet mill or wet crusher.

9. A method according to claim 5, wherein the chlorides are removed by washing the materials.

10. A method according to claim 9, wherein the chlorides are removed by washing the materials prior to leaching while crushing or grinding the nodules in a wet mill or wet crusher.

11. A method according to claim 1, further comprising removing the acid-insoluble residue prior to precipitating the iron.

12. A method according to claim 1 wherein following leaching, the pH of the leachant is changed to about 0.5 - 2.5 to precipitate hydrated iron oxide.

13. A method according to claim 12 wherein the pH of the leachant is changed by the addition to the solution of pH adjusting agents.

14. A method according to claim 13 wherein the pH adjusting agents are selected from the group consisting of alkalis, alkaline earths, or ammonia.

15. A method according to claim 12 wherein the precipitated ferric hydroxide is removed from the solution by solid-liquid separation.

16. A method according to claim 1 where any copper, lead, cadmium, and any zinc present in the solution are removed by precipitation at a low pH of less than 3.0, , followed by solid-liquid separation.

17. A method according to claim 16 where precipitation is effected by adjusting the solution to a pH of less than 3.0, then introducing a sulfide into the solution to precipitate as sulfides any copper, lead, cadmium, and zinc which is present in the solution, and the precipitated metal values are removed by solid-liquid separation.

18. A method according to claim 1, further comprising raising the pH of the solution, precipitating and removing any cobalt or nickel.

19. A method according to claim 18, wherein precipitation of cobalt and nickel is carried out by raising the pH of the solution and introducing additional sulfide thereto, and forming cobalt and nickel sulfides in solid form.

20. A method according to claim 1, wherein precipitation of manganese is carried out by raising the solution pH to about 8 to 10.

21. A method according to claim 1 further comprising, after the final step in which the solution contains manganese nitrate, thermally decomposing the manganese nitrate to form manganese dioxide and nitrogen dioxide.

22. A fertilizer grade nitrate product produced by the method of claim 1.

23. A method of recovering metal values from deep-sea manganese nodules, comprising the steps of:

a. obtaining manganese-containing nodules having a manganese content in excess of 20%, and containing at least one of the metals of the group consisting of: cobalt, nickel, lead, copper, magnesium, aluminum, iron, cadmium, zirconium, titanium, zinc, cerium, molybdenum, phosphorus, barium, and vanadium;

b. leaching the nodules with HNO_3 and NO gas in an aqueous solution to form manganese nitrate and to release the other metals;

c. adding pH adjusting agents to the solution to precipitate ferric hydroxide;

d. separating the precipitated ferric hydroxide from the solution;

e. adjusting the solution to a low pH and introducing a sulfide to the solution to precipitate copper, lead, cadmium, and zinc, if present in the solution;

f. raising the pH of the solution and introducing additional sulfide to precipitate cobalt and nickel sulfides; and

g. raising the solution pH to about 8 to 10 to precipitate hydrated manganese oxide.

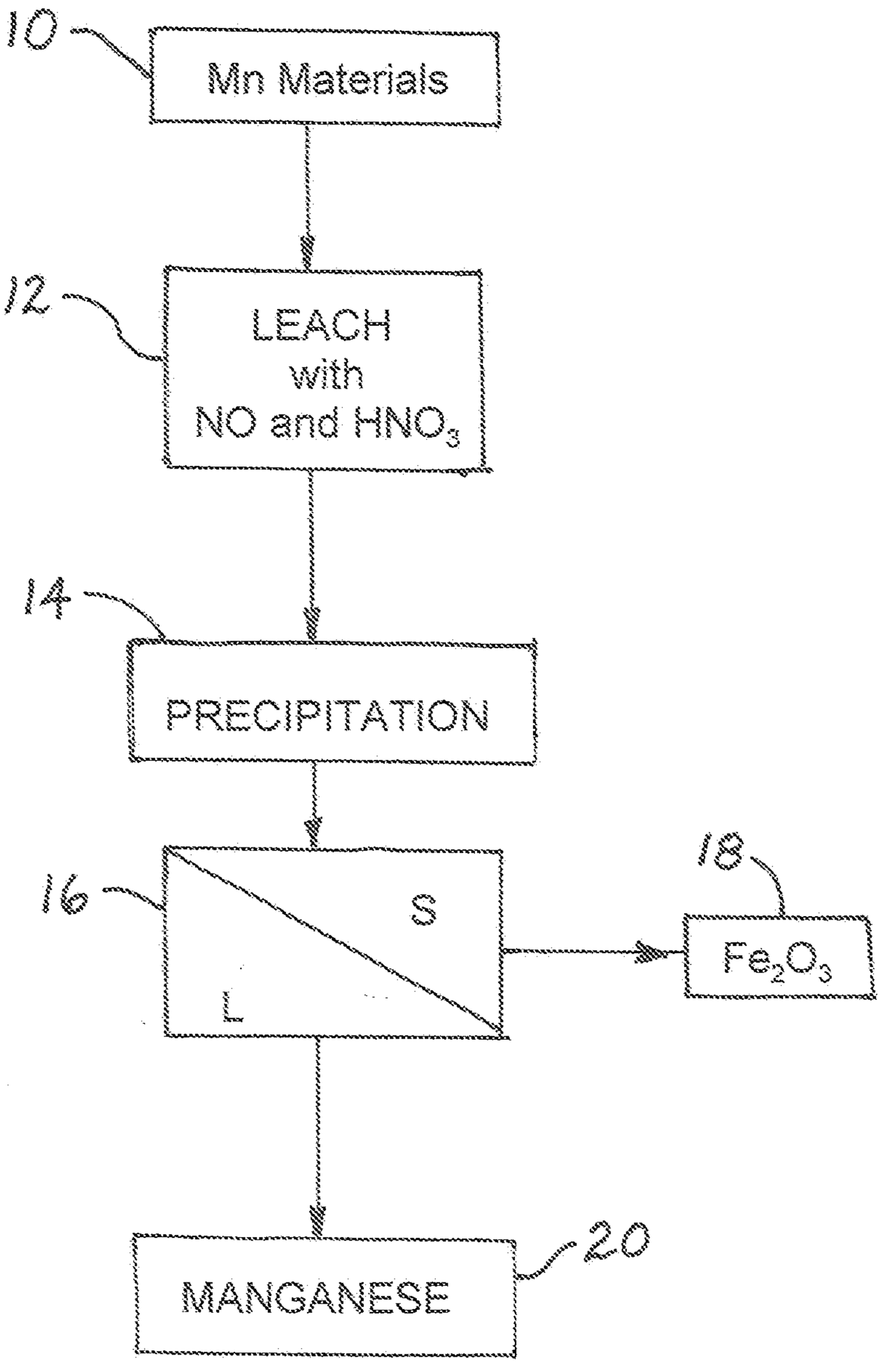

10
Mn Materials
12
LEACH
with
NO and HNO_3
14
PRECIPITATION
16
S
L
18
Fe_2O_3
MANGANESE
20

Fig. 1

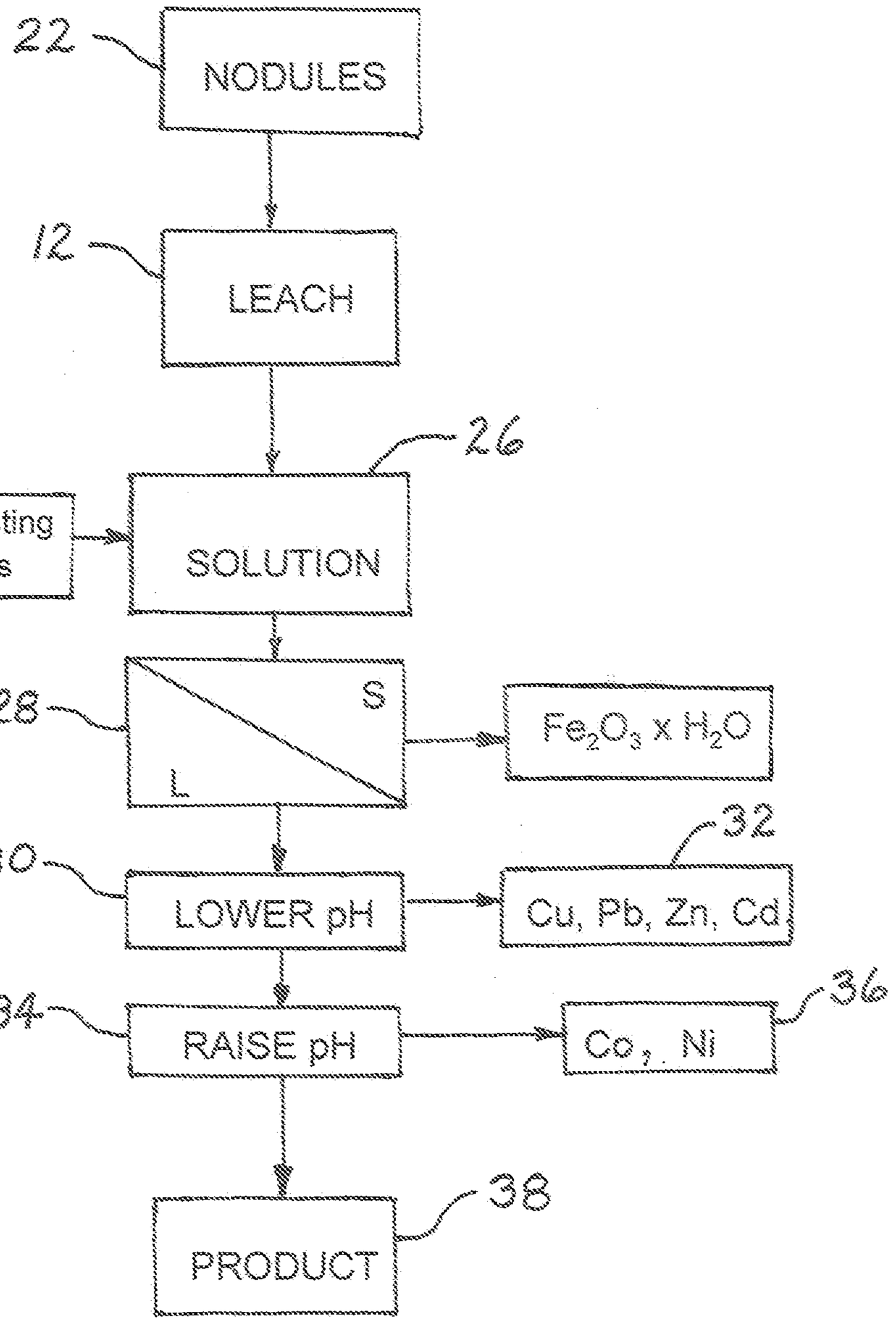

22
NODULES
12
LEACH
24
pH Adjusting Agents
26
SOLUTION
28
S
L
$Fe_2O_3 \times H_2O$
30
LOWER pH
32
Cu, Pb, Zn, Cd
34
RAISE pH
36
Co, Ni
38
PRODUCT

Fig. 2

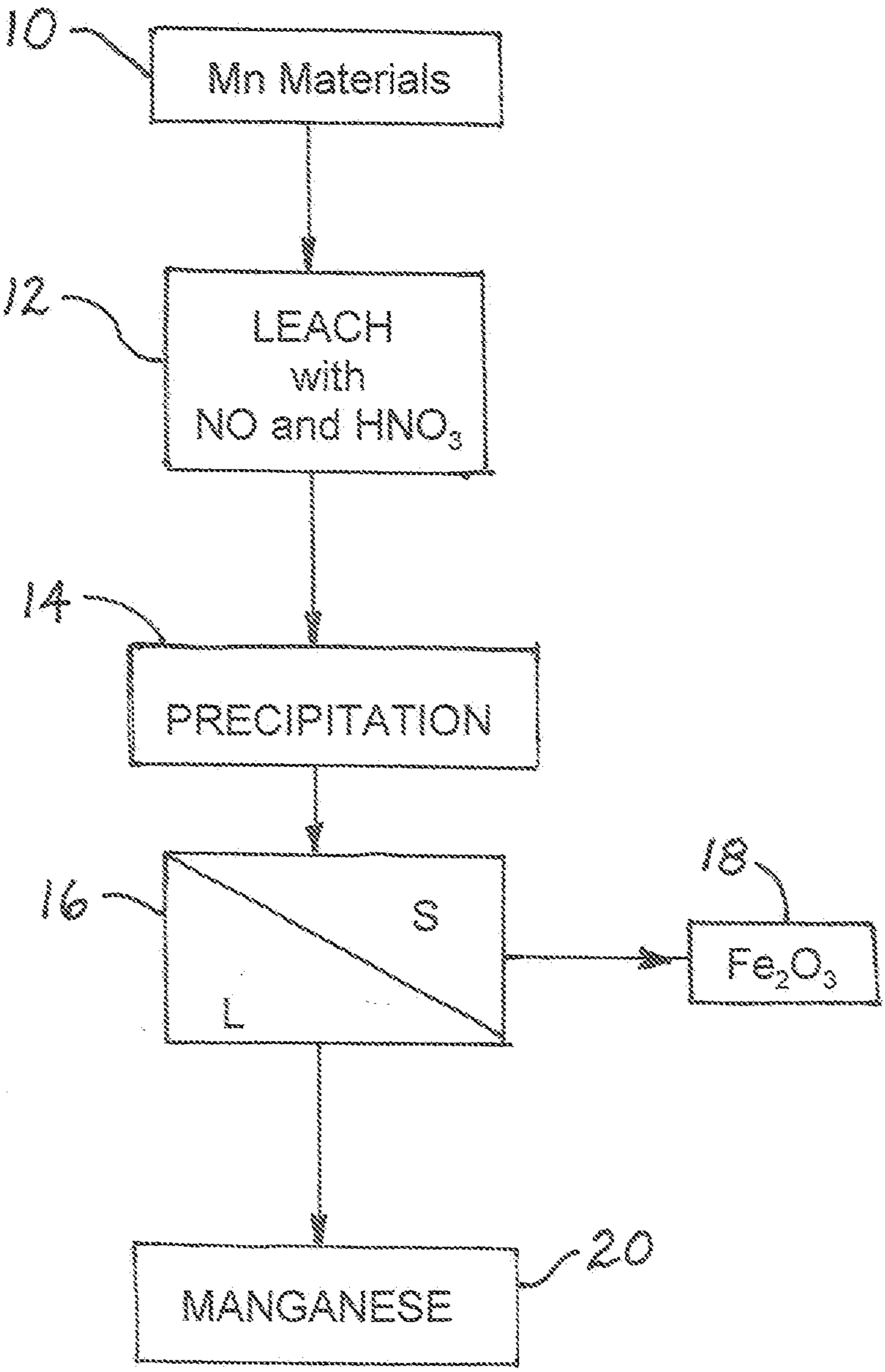

10
Mn Materials
12
LEACH
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PRECIPITATION
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MANGANESE

Fig. 1