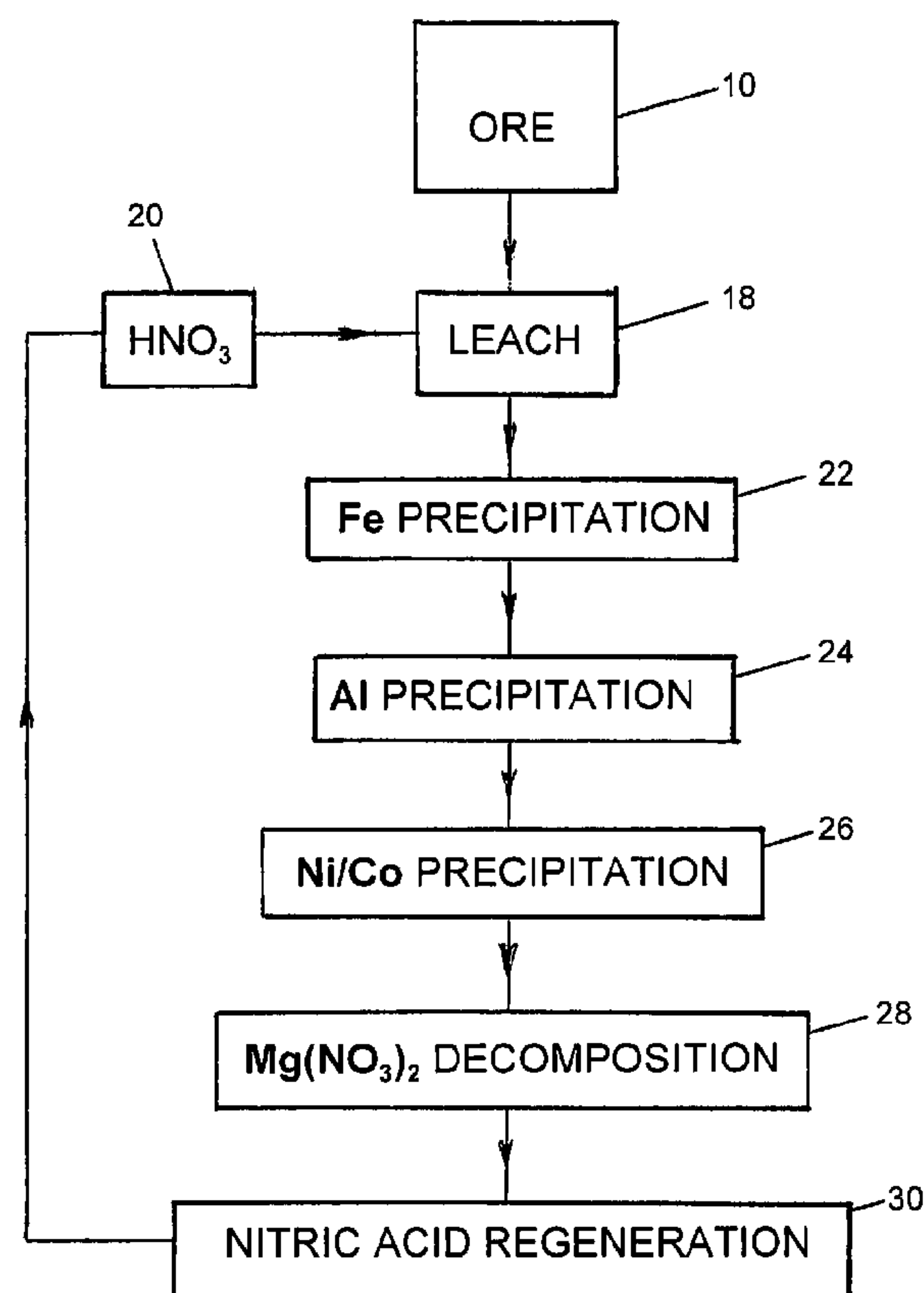




(86) Date de dépôt PCT/PCT Filing Date: 2008/05/01
(87) Date publication PCT/PCT Publication Date: 2008/11/13
(45) Date de délivrance/Issue Date: 2014/08/19
(85) Entrée phase nationale/National Entry: 2009/10/27
(86) N° demande PCT/PCT Application No.: US 2008/005600
(87) N° publication PCT/PCT Publication No.: 2008/137022
(30) Priorité/Priority: 2007/05/03 (US60/927,391)

(51) Cl.Int./Int.Cl. *C22B 3/06* (2006.01),
C22B 21/00 (2006.01), *C22B 23/00* (2006.01),
C22B 3/20 (2006.01), *C22B 3/46* (2006.01)
(72) Inventeurs/Inventors:
DRINKARD, WILLIAM F., JR., US;
WOERNER, HANS J., US
(73) Propriétaire/Owner:
DRINKARD METALOX, INC., US
(74) Agent: GOWLING LAFLEUR HENDERSON LLP

(54) Titre : METHODE DE RECUPERATION DE VALEURS METALLIQUES DE MINERAIS
(54) Title: METHOD OF RECOVERING METAL VALUES FROM ORES



(57) Abrégé/Abstract:

An improved method for processing of nickel bearing saprolite and limonite ores to recover the valuable minerals contained therein, comprising leaching the ore with nitric acid to form a slurry; separating the iron values by precipitation, removing the iron values; forming a liquid/solid residue in which nickel, cobalt and magnesium are in solution, and manganese and aluminum are solid residues in oxide form; conducting a liquid-solid separation and removing the solids; and recovering the nickel, cobalt, and manganese from the liquid-metal concentrate. The leachate is recovered and nitric acid from the leachate is recycled.



(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau(43) International Publication Date
13 November 2008 (13.11.2008)

PCT

(10) International Publication Number
WO 2008/137022 A1(51) International Patent Classification:
C22B 23/00 (2006.01)

J. [DE/US]; 1017 Allman Extension, Mt. Pleasant, NC 28124 (US).

(21) International Application Number:
PCT/US2008/005600(74) Agent: **DOUGHERTY, Ralph, H.**; Ralph H. Dougherty, P.A., 4219 Kronos Place, Charlotte, NC 28210 (US).

(22) International Filing Date: 1 May 2008 (01.05.2008)

(81) Designated States (*unless otherwise indicated, for every kind of national protection available*): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(25) Filing Language: English

(26) Publication Language: English

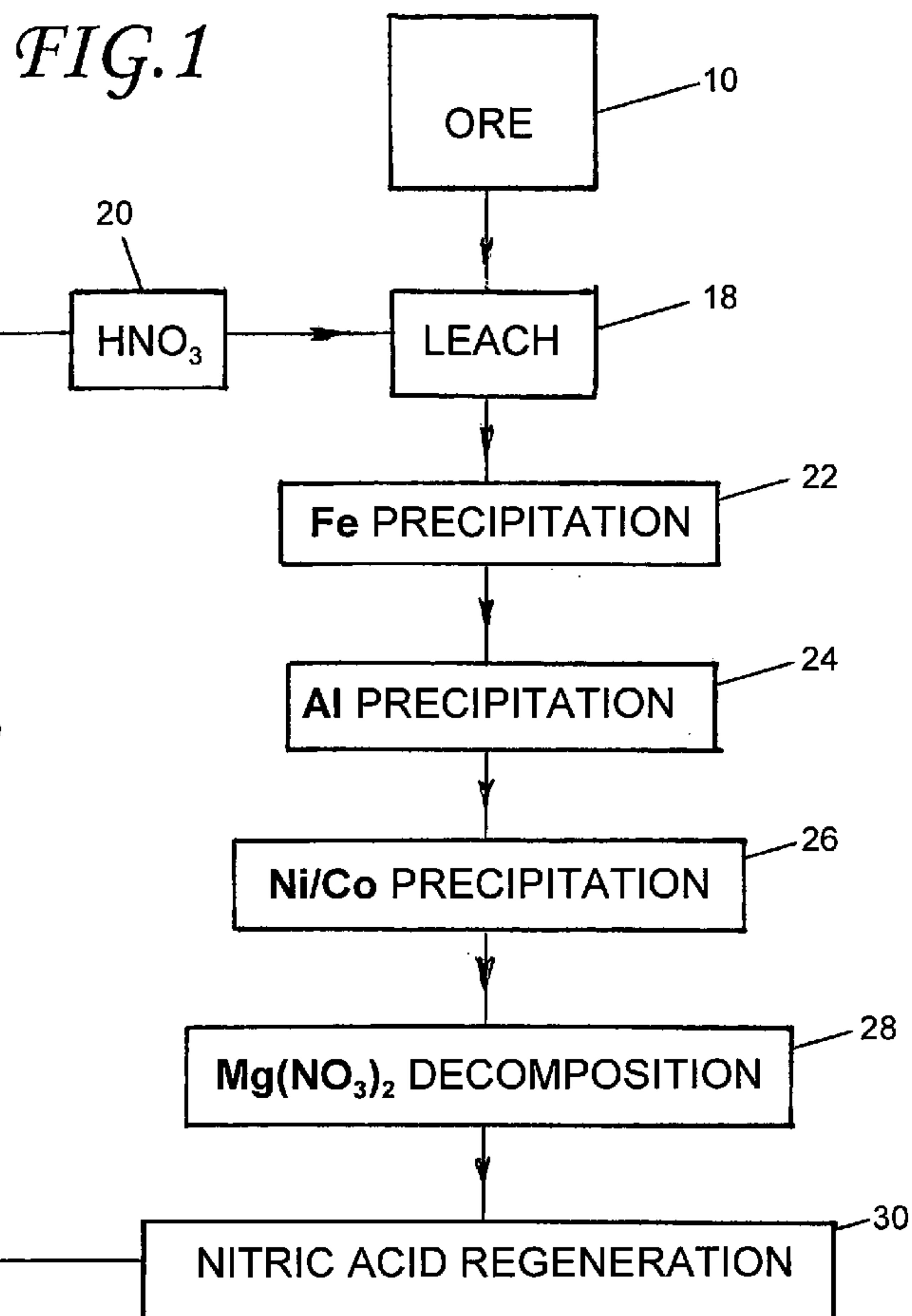
(30) Priority Data:
60/927,391 3 May 2007 (03.05.2007) US(71) Applicant (*for all designated States except US*):
DRINKARD METALOX, INC. [US/US]; P.O. Box 5471, Charlotte, NC 28299-5471 (US).

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **DRINKARD, William, F., Jr.** [US/US]; 804 East Worthington Avenue, Charlotte, NC 28203 (US). **WOERNER, Hans,**(84) Designated States (*unless otherwise indicated, for every kind of regional protection available*): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI,

[Continued on next page]

(54) Title: METHOD OF RECOVERING METAL VALUES FROM ORES



(57) Abstract: An improved method for processing of nickel bearing saprolite and limonite ores to recover the valuable minerals contained therein, comprising leaching the ore with nitric acid to form a slurry; separating the iron values by precipitation, removing the iron values; forming a liquid/solid residue in which nickel, cobalt and magnesium are in solution, and manganese and aluminum are solid residues in oxide form; conducting a liquid-solid separation and removing the solids; and recovering the nickel, cobalt, and manganese from the liquid-metal concentrate. The leachate is recovered and nitric acid from the leachate is recycled.

WO 2008/137022 A1



FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL,
NO, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG,
CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— *with international search report*

METHOD OF RECOVERING METAL VALUES FROM ORES

FIELD OF THE INVENTION

The present invention relates to a method for processing of metal-containing ores, particularly for recovering of nickel and other metals, and more particularly to methods for recovery of iron, nickel, cobalt, magnesium, aluminum, chromium, and other valuable constituents of saprolite and limonite ores.

BACKGROUND OF THE INVENTION

The compositions of ores vary tremendously, even when taken from the same mining site. Limonite and saprolite ores usually contain iron, nickel, cobalt, magnesium, manganese, chromium, and/or aluminum. Known processes for treating high magnesium saprolite ores or high-iron limonite type ores are generally high cost processes, whereas the present invention is an improved, cost-effective process which can handle a full range of ores, including transitional ores. The term "ores" as used herein is intended to mean oxide and sulfide ores, metallurgical wastes, and metal-bearing materials, it being understood that metals can be combined with other elements.

SUMMARY OF THE INVENTION

The invention is a method for processing of nickel-bearing saprolite and limonite ores to recover the valuable minerals contained therein. The process acts on any oxide

or sulfide ores, metallurgical wastes, and metal-bearing materials, it being understood that in such materials, metals can be combined with other elements. The ores may be ground or comminuted, if desired, or may be blended with other metal-bearing materials. The ores are leached with nitric acid, then the iron is precipitated by
5 thermal hydrolysis or pH balancing. Optionally, aluminum is recovered by precipitation or crystalline recovery. Magnesium hydroxide is added to the solution, and a pH balance is effected to form nickel and cobalt hydroxides which are recovered as precipitates.

10 Advantageously, the nitric acid for the leach is provided by the process described in US Patent Number 6,264,909, entitled Nitric Acid Production and Recycle, which issued on July 24, 2001.

The present invention is particularly useful for recovery of nickel, cobalt,
15 aluminum, iron, chromium, manganese, and magnesium.

OBJECTS OF THE INVENTION

The principal object of the present invention is to provide an improved method
20 of recovering nickel and cobalt from saprolite and limonite ores.

Another object of this invention is to provide a method of recovering metal values from ores, metallurgical wastes, and other metal-bearing materials.

Another object of the invention is to provide a method of producing nitrate salts, such as ammonium, sodium, potassium, calcium, or magnesium nitrates.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects will become more readily apparent by referring
5 to the following detailed description and the appended drawing in which:

Figure 1 is a schematic flowsheet of the invented process in its most basic form.

DETAILED DESCRIPTION

Referring now to the drawing, Figure 1 shows the invented process in its basic form. The process starts with run of the mine saprolite or limonite ores 10 or other metal
10 bearing materials.

The ore is leached with HNO_3 for a sufficient time to form a slurry. Although the ore may be crushed, it is not necessary to do so as the nitric acid will act efficiently regardless of the size of the ore particles. The ore is leached 18 with nitric acid 20 at a temperature of less than 160C, generally from about 70C to 130C, but preferably about
15 120 C for a period of time of about 30 minutes to about 3 hours. The acid can be a 10 to 90% (weight percent) nitric acid solution, but is preferably about 30 to 67% nitric acid, and optimally is about a 45 to 55 % acid solution.

The nitric acid 20 for the leaching process is preferably obtained from a nitric acid recycle process in accordance with US Patent 6,264,909, referred to above.

5 The temperature of the leach solution is raised by heating 22 to a temperature in the range of about 125 to 200C, preferably to about 165 C, to form a liquid/solid residue in which the nickel, cobalt and magnesium are in solution, and the iron, manganese, and aluminum are solid residues in oxide form. The heating is carried out in an enclosure from which the evolved gases (principally NO_x) are recovered for further treatment. The leaching and heating steps can be carried out in the same vessel, or in separate vessels.

10 Iron is precipitated at 22 as Fe_2O_3 , either by thermal hydrolysis or pH balancing of the solution to effect the precipitation.

The slurry undergoes a solid-liquid separation, the gangue materials being removed as solids. The remaining liquid solution is heated, the iron being precipitated as Fe_2O_3 , either by thermal hydrolysis or pH balancing of the solution to effect the precipitation.

15 The Fe_2O_3 is removed as a solid by liquid - solid separation (filtration), leaving a solution containing aluminum, nickel and cobalt values.

Aluminum is removed at 24 by precipitation. Alternatively, crystallization of the aluminum as a nitrate allows separation by filtration or by centrifuge. In either event, it leaves a nickel-cobalt solution.

Mg(OH)₂ is mixed with the nickel-cobalt solution, which then undergoes thermal hydrolysis or alternatively a pH balance (shift) to form Ni(OH)₂ and Co(OH)₂ in solid form which is removed as a precipitate (by filtration) at 26. The nickel and cobalt values can also be removed from solution by solvent extraction.

5 The filtrate is concentrated, usually in multiple effect evaporation until the remaining Mg(NO₃)₂ is almost anhydrous. The magnesium nitrate is then thermally decomposed at 28 to form MgO, HNO₃ and NO_x, and the nitric acid and nitric oxides are recycled. The resulting MgO can be used elsewhere in the invented process.

10 The NO_x containing gases are reformed at 30 into nitric acid utilizing the nitric recycle process described in US Patent Number 6,264,909.

Shifting of the pH of the solution is accomplished by adding or removing nitric acid, or by adding alkaline earths to the solution.

Precipitation of iron is usually accomplished at a pH of 2 to 3;

Precipitation of alumina is usually accomplished at a pH of 4-5;

15 Precipitation of nickel is usually accomplished at a pH of 6-7;

Precipitation of Manganese is usually accomplished at a pH of 8-9;

Precipitation of MgO is usually accomplished at a pH of 10-11;

Precipitation of Ca is usually accomplished at a pH of 12-13.

Precipitates are removed by filtration, or may be separated by other known methods such as centrifuging.

In any place throughout the process where nitric acid or oxide is removed, it may be recycled to the nitric acid recycle process for further use.

5

SUMMARY OF THE ACHIEVEMENT
OF THE OBJECTS OF THE INVENTION

10

From the foregoing, it is readily apparent that we have invented an improved method of recovering nickel and cobalt from saprolite and limonite ores, and for recovering metal values from ores, metallurgical wastes, and other metal-bearing materials, more economically than heretofore has been possible.

15

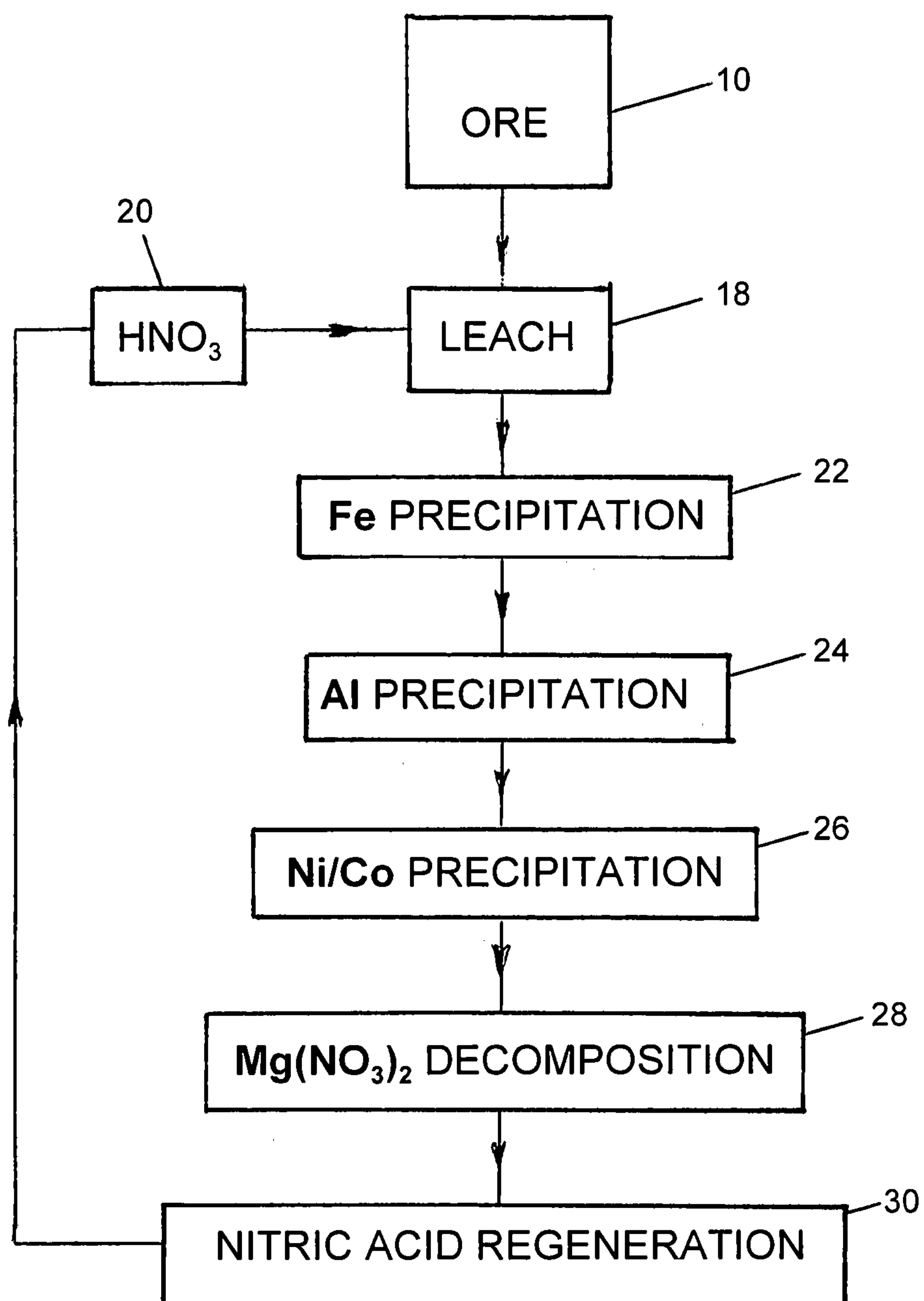
It is to be understood that the foregoing description and specific embodiments are merely illustrative of the best mode of the invention and the principles thereof, and that various modifications and additions may be made to the apparatus by those skilled in the art, without departing from the scope of this invention, which is therefore understood to be limited only by the scope of the appended claims as purposively construed.

CLAIMS

1. A method of recovering metal values from ores containing iron, nickel, cobalt, magnesium, and aluminum, comprising:
 - a) leaching the ore with HNO_3 for a sufficient time to form a slurry;
 - 5 b) precipitating the iron from the slurry as Fe_2O_3 ;
 - c) precipitating aluminum as Al_2O_3 , and leaving a solution containing nickel and cobalt values;
 - d) mixing $\text{Mg}(\text{OH})_2$ with the nickel-cobalt solution, then performing thermal hydrolysis, or pH shift or solvent extraction to form $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ in solid form,
 - 10 and removing the nickel-cobalt values as a precipitate;
 - e) recovering HNO_3 and NO_x from the process; and
 - f) reforming the removed NO_x containing gases into nitric acid for further use.
2. A method according to claim 1 wherein the leach is carried out at a temperature of
 - 15 70°C to 160°C for a period of time of from about 30 minutes to about 3 hours.
3. A method according to claim 1 wherein the nitric acid in the leach is a solution of 10 to 90 percent nitric acid.
- 20 4. A method according to claim 3 wherein the nitric acid in the leach is a solution of 30 to 67 percent nitric acid.
5. A method according to claim 1 wherein the leach step is followed by heating to a temperature of from about 125°C to about 200°C to form a liquid/solid residue in which
 - 25 the nickel, cobalt and magnesium values are in solution.
6. A method according to claim 5 wherein the leach step is followed by heating to a temperature of from about 125°C to about 200°C to form a liquid/solid residue in which the nickel, cobalt and magnesium values are in solution, and the iron, manganese, and
 - 30 aluminum value are solid residues in oxide form.

7. A method according to claim 1, wherein precipitation of iron is accomplished by thermal hydrolysis.
8. A method according to claim 1, wherein precipitation of iron is accomplished by
5 pH balancing of the solution.
9. A method according to claim 1 wherein the ore is crushed prior to leaching.
10. A method according to claim 1 further comprising: during or after the step of
10 mixing $\text{Mg}(\text{OH})_2$ with the nickel-cobalt solution, performing thermal hydrolysis, pH balance (shift) or solvent extraction to form $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ or Ni/Co salts in solid form, and removing the nickel-cobalt values as a precipitate.
11. A method of recovering metal values from sulfide ores containing iron, nickel,
15 cobalt, magnesium, and aluminum, comprising:
- a) leaching the ore with HNO_3 for a sufficient time to form a slurry;
 - b) precipitating the iron from the slurry as Fe_2O_3 ;
 - c) precipitating aluminum as Al_2O_3 , and leaving a solution containing nickel and cobalt values;
 - 20 d) mixing $\text{Mg}(\text{OH})_2$ with the nickel-cobalt solution, then performing thermal hydrolysis, or pH shift or solvent extraction to form $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ in solid form, and removing the nickel-cobalt values as a precipitate;
 - e) recovering HNO_3 and NO_x from the process; and
 - f) reforming the removed NO_x containing gases into nitric acid for further use.
- 25
12. A method according to claim 11 wherein the leach is carried out at a temperature of 70°C to 160°C for a period of time of from about 30 minutes to about 3 hours.
13. A method according to claim 11 wherein the nitric acid in the leach is a solution
30 of 30 to 67 percent nitric acid.

14. A method according to claim 11 wherein the leach step is followed by heating to a temperature of from about 125°C to about 200°C to form a liquid/solid residue in which the nickel, cobalt and magnesium values are in solution, and other metal values are solid residues in oxide form.
- 5
15. A method according to claim 11, wherein precipitation of iron is accomplished by thermal hydrolysis.
16. A method according to claim 11, wherein precipitation of iron is accomplished by
- 10 pH balancing of the solution.
17. A method according to claim 11 wherein the ore is crushed prior to leaching.
18. A method according to claim 11 further comprising:
- 15 during or after the step of mixing $\text{Mg}(\text{OH})_2$ with the nickel-cobalt solution, performing thermal hydrolysis, pH balance (shift) or solvent extraction to form $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$ or Ni/Co compounds in solid form, and removing the nickel-cobalt values as a precipitate.

*FIG.1*

