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(54) Title : A METHOD FOR TREATING LIQUID EFFLUENTS AND RECOVERING METALS

(54) Título : PROCESSO PARA TRATAMENTO DE EFLUENTES LÍQUIDOS E RECUPERAÇÃO DE METAIS

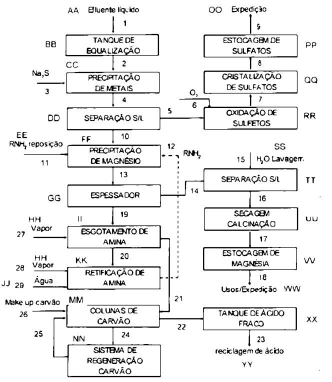

FIG. 2

AA	Liquid effluent
BB	EQUALIZATION TANK
CC	PRECIPITATION OF METALS
DD	S/L SEPARATION
EE	RNH_2 replenishment
FF	PRECIPITATION OF MAGNESIUM
GG	THICKENER
HH	Vapour
II	AMINE STRIPPING
JJ	Water
KK	AMINE RECTIFICATION
LL	Make up carbon
MM	CARBON COLUMNS
NN	CARBON REGENERATING SYSTEM
OO	Distribution
PP	SULPHATE STORAGE
QQ	SULPHATE CRYSTALLIZATION
RR	SULPHIDE OXIDATION
SS	H_2O Wash
TT	S/L SEPARATION
UU	DRYING CALCINATION
VV	MAGNESIA STORAGE
WW	Uses/Distribution
XX	WEAK ACID TANK
YY	acid recycling

(57) Abstract : A method for treating liquid effluents and recovering metals is described, which comprises the steps of: a) liquid effluent equalization; b) sulphide addition and precipitation of metals in the form of metal sulphides; c) solid/liquid separation of the metal sulphides produced in step (b) and formation of a metal-free liquid phase (10); the method for treating liquid effluents and recovering metals further comprising the following steps: d) addition of a 50 to 250 g/L amine solution to the liquid phase (10) precipitating magnesium in the form of magnesium hydroxide ($Mg(OH)_2$); and e) recovery of amine by stripping and rectification.

(57) Resumo : Descreve-se um processo para tratamento de efluentes líquidos e recuperação de metais compreendendo etapas de: a) equalização do efluente líquido; b) adição de sulfetos e precipitação de metais em forma de sulfetos metálicos; c) separação solido/líquido dos sulfetos metálicos obtidos na etapa (b) e formação de uma fase líquida (10) isenta de metais; o processo para tratamento de efluentes líquidos e recuperação de metais compreendendo, ainda, as seguintes etapas: d) adição de amina em solução na proporção de 50 a 250 g/L à fase líquida (10) com precipitação do magnésio na forma de hidróxido de magnésio - $Mg(OH)_2$; e e) recuperação da amina por esgotamento e retificação.

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Descriptive Report of Patent of Invention for **"A METHOD FOR TREATING LIQUID EFFLUENTS AND RECOVERING METALS"**

The present invention refers to a method for treating liquid effluents and recovering metals with the precipitation of magnesium hydroxide by means of amines, followed by the regeneration of the amines and exploitation of the sub-products magnesium and sulphur.

Description of the state of the art

The principal objectives of any method of treating liquid and solid effluents are (i) to neutralize and condition them properly for being released and returned to the environment and (ii) to obtain recyclable sub products that can be utilized in captive consumption and/or a commercial manner by third parties.

In taking advantage of lateritic nickel ore there are various factors that influence the process of producing nickel by the hydrometallurgical route of high pressure acid leaching (HPAL).

- the geological origin of the field;
- the mineralogical composition of the mineral;
- the grain size distribution of the mineral;
- the operating conditions of the processing;
- the configuration of the systems for preparing the mineral, leaching, precipitation, extraction by solvents and electrolysis.

The high pressure acid leaching process (HPAL) is recommended for predominantly limonite minerals, which present low quantities of magnesium – normally limited to 4%, maximum – since minerals with high magnesium content involve elevated consumption levels of sulphuric acid.

The process for the production of nickel by the HPAL route, known to the state of the art and illustrated in figure 1, consists, essentially, in the following steps: (i) preparation of lateritic nickel ore, (ii) high pressure leaching of nickel with Sulphuric acid, (iii) precipitation of nickel, (iv) re-leaching, (v) extraction of nickel by solvents and (vi) electrolysis for cathode nickel production (metallic nickel with 99.95% purity). Because of the significant presence of cobalt in the ore, cobalt will also be obtained as a co-product, also in the form of metal.

This technology is the most indicated for extraction of nickel and cobalt from limonite laterites due to the following characteristics:

- limonite laterites have low magnesium content and consequently, a low consumption of sulphuric acid;
- low operating cost in function of low cost of sulphuric acid and its low specific consumption;
- no drying or reduction steps are necessary because run of mine laterite is employed in the form of suspensions;
- high selectivity for the metals of interest;
- sulphur dioxide emissions below environmental standards;
- recovery of more than 90% of the nickel and cobalt contained in the ore.

High pressure leaching is generally carried out in titanium-clad autoclaves at temperatures that vary within the range of 245 to 270°C. In this process the suspension fed into the autoclave contains approximately 40 to 45% solids, having been heated by steam. Due to the nature of the clayish minerals present in some ores the concentration of solids may be limited to 25 to 30%. The level of density of the suspension significantly influences the capacity of the autoclave, a piece of equipment that involves elevated capital costs. The leaching mechanism involves the acid dissolution at high temperatures of the nickel and cobalt contained in the matrix of the host ore. Under these conditions, the dissolution of the iron in ores occurs first, followed by the formation of sulphates, which, under high temperature conditions, react with the water to form hematite and, in consequence, regenerate the sulphuric acid:

$$2FeOOH + 3H_2SO_4 = Fe_2 (SO_4)_3 + 4H_2O$$

$$Fe_2Si_4O_{10}(OH)_2 + 3H_2SO_4 = Fe_2(SO_4)_3 + 4SiO_2 + 4H_2O$$

$$Fe_2(SO_4)_3 + 2 H_2O = 2Fe(OH)SO_4 + H_2SO_4$$

$$2Fe(OH)SO_4 + H_2O = Fe_2O_3 + 2 H_2SO_4$$

Extraction levels of this process attain values of 92 to 96% for nickel and 90 to 92% for cobalt. Normally, to obtain that degree of extraction the reaction suspension should present a residual free acid concentration of 30 to 50 g/L after the chemical reaction.

After the leaching, the suspension exiting from the autoclave is depressurized and cooled in expansion chambers ("flash vessels"), to approximately 100°C. The remaining solids are then separated from the liquid phase. Solid-liquid separation is carried out in counter current decanters (CCD), generating a liquor charged with sulphates of nickel, magnesium, manganese, zinc, copper and iron, among other metals. The nickel and cobalt present in the liquor are then precipitated in the form of sulphides (utilizing H_2S), carbonates (utilizing ammonium carbonate) or as hydroxides, utilizing magnesium (MgO). These intermediate products normally present purities of 55% (Ni+Co) for the case of sulphides (MSP – Mixed Sulphide Precipitate) and 40 to 45% (Ni+Co) for the case of hydroxides (MHP – Mixed Hydroxide Precipitate). It is also possible to recover these metals by means of extraction by solvents applied directly to the liquor coming from the decanting system. It should be observed that the MSP process makes it possible to obtain a product with a higher valuable metal content and a lower level of contamination with manganese, magnesium and sulphates. However, production utilizing the MSP process involves a high capital cost for auxiliary installations because of the necessity for hydrogen and hydrogen sulphide units, which require sophisticated safety systems for handling those products.

In the following stage, refining, the intermediate products (sulphides or hydroxides of nickel and cobalt) are re-leached and, thus dissolved, are submitted to purification treatments, such as (i) extraction by solvents for the separation of nickel and cobalt and (ii) electrolysis (electro-refining) in order to attain greater levels of purity.

In the process of producing nickel by the HPAL route, based on ore containing magnesium silicates and magnesium carbonate, the generation of liquid effluent occurs in proportions of 250 to 400 m^3/t Ni produced, essentially containing magnesium and sulphate and, in small quantities, cobalt, zinc, manganese, nickel, iron, chromium, among other elements. Table 1 presents the chemical composition of the effluent to be treated and shows the significant contents of sulphate and magnesium.

Table 1. Composition of the effluent to be treated

Components	Units	Proportion
Ni	ppm	2.00
Co	ppm	6.00
Zn	ppm	0.90
Mn	ppm	40.00
Fe	ppm	10.00
Cr	g/L	4.45
Mg	g/L	18.00
SO_4	g/L	75.00
NH_3	g/L	0.50
pH		7.5

Various types of effluent treatments, with steps that target recovering reagents utilized in the process of leaching and/or recovering metals dispersed in effluents generated through liquid ore treatment processes, are known in the state of the art.

Along those lines, the document GB 1,520,175 describes a process for recovering metals such as, for example, the magnesium, coming from aqueous sulphate solutions, by means of the utilization of lime or chalk to precipitate the magnesium and sulphate. In this system the magnesium forms a compound, magnesium hydroxide, which precipitates in conjunction with calcium sulphate. The separation and recovery of these two elements is complicated by the fact that they are presented in fine granules with similar physical properties, which limits the employment of existing industrial processes for physical separation. In addition, recovery of the sulphur contained in the calcium sulphate requires complex calcination installations that demand intensive energy usage. In that aspect, there is a great disadvantage, from the point of view of costs, operational ease and simplicity of installation when compared with the method the object of the present invention, in which the precipitation of magnesium is realized employing amines.

Another method known in the state of the art is described in the document US 2009/0148366, which deals with a process for the recovery of metals and magnesium oxide on the basis of magnesium sulphate solutions. This process makes use of the crystallization of magnesium by evaporation, requiring, in function of the degree of hydration of the sulphate, the evaporation of practically all the water contained in the effluent. That evaporation, in the case of using a vacuum, can occur at temperatures in the range of 70°C to 90°C. In a following stage, in order to exploit the magnesium, the magnesium sulphate precipitated must be subjected to calcination so as to transform it into magnesium oxide. That operation must be accomplished at elevated temperatures, 700°C to 800°C, which demands an intensive consumption of energy. For the recovery of sulphur from the gas resulting from that calcination, sulphur dioxide, it must first be compounded into sulphur trioxide with the employment of a catalyst bed for later transformation into sulphuric acid. These operations must be carried out in complex, expensive sulphuric acid plants.

Another process known in the state of the art is described in the document US 2009/0180945, which deals with a system for the recovery of the magnesium and sulphate contained in effluents arising from the acid leaching of lateritic ores in the form of magnesium hydroxide and magnesium oxide. In that process ammonia is utilized as agent of precipitation; the sulphur is recovered as ammonia sulphate. The employment of ammonia constitutes a great disadvantage in relation to the method the object of the present invention, which utilizes amines, since ammonia is a highly toxic gas and difficult to manage. And, once combined with sulphate, it cannot be regenerated, while amines can be handled in liquid form at environmental temperatures and, most importantly, can be regenerated for reutilization in the process.

Objectives of the Invention

The objective of the present invention is to provide a process for the treatment of liquid effluents and the recovery of metals with the precipitation of magnesium hydroxide by means of amines, followed by the regeneration of amine and exploitation of the sub products magnesium and sulphur.

Brief Description of the Invention

Disclosed herein is a method for treatment of liquid effluents and recovery of metals including steps of:

a) equalization of the liquid effluent;
b) addition of sulphides and precipitation of metals in the form of metallic sulphides;

c) solid/liquid separation of the metallic sulphides obtained in stage (b) and formation of a liquid phase free of metals;

The process the object of the present invention also includes the following steps:

d) addition of amine - in solution and in the proportion of 50 to 250 g/L – to the liquid phase, with precipitation of magnesium in the form of hydroxide – $Mg(OH)_2$; and
e) recovery of the amine by stripping and rectification.

According to a first aspect of the present invention there is provided aprocess for treating liquid effluents and recovering metals comprising the steps of:

a) homogenizing the liquid effluent;
b) adding a sulfide so as to precipitate one or more metals in the form of metal sulfide(s);
c) separating the metal sulfide(s) obtained in step (b) from the liquid effluent in a solid/liquid separation operation so as to form a liquid phase free of all metals except magnesium;
d) adding an amine solution to the liquid phase so as to precipitate magnesium hydroxide $Mg(OH)_2$, wherein:
    i) the precipitated magnesium hydroxide is separated from the liquid phase and washed; and
    ii) the washed magnesium hydroxide is dried and calcined to form magnesia;
e) recovering the amine by a two-step process comprising:
    iii) a stripping step, comprising heating the liquid phase whilst continually feeding in low pressure vapour so as to form: a tower bottom mass stream comprising weak acids and traces of amine; and, an amine rich vapour which is sent to a rectification step; and
    iv) a rectification step, comprising continually feeding in low pressure vapour to the amine rich vapour, so as to form a top vapour current that is condensed through heat exchangers,

wherein said amine is selected from a group consisting of low boiling point amines.

Summary Description of the Figures

The present invention will be explained below in more detail on the basis of an example of execution represented in the designs. The figures show:

Figure 1 is a flow chart of the process of nickel production by the HPAL route known to the state of the art, and

Figure 2 is a flow chart of the method for treating liquid effluents and recovering metals the object of the present invention.

Detailed Description of the Figures

In accordance with a preferred formulation and, as may be seen in Figure 2, the method for treating liquid effluents and recovering metals the object of the present invention was developed for the recovery of (i) magnesium and (ii) sulphur. The first, to be recycled for agricultural purposes (correctives and fertilizers) in the hydrometallurgical nickel extraction process and as a raw material for industry, in general. The second, in the form of diluted sulphuric acid, that can be recycled in the leaching process.

The process the object of this invention also makes it possible to remove the remaining metals in the liquid effluent such as manganese (Mn), zinc (Zn), cobalt (Co) and copper (Cu), among others, thus creating conditions for its complete recycling in the industrial process, in addition to providing an additional production of micronutrients for agricultural use, among other applications.

As shown in the flowchart of Figure 2, in the method of treating liquid effluents and recovering metals that is the object of this invention, the liquid effluent 1 is routed to agitator tanks for equalization. Then the homogenized (equalized) effluent 2 receives the addition of sulphides 3, in the form of Na_2S and/or H_2S for the precipitation of remaining metals such as Ni, Co, Mn, Zn and Cu, among others, in the form of metal sulphides 4. In the following stage, such sulphides are submitted to a solid/liquid separation operation, which results in a rich flow of metal sulphides 5. Appropriately washed, the sulphides are oxidated in agitating reactors with the injection of oxygen 6 and the resulting solution 7 is submitted to crystallization to obtain the respective salts 8, separated or mixed, which are stocked and sent for shipment 9.

The liquid phase or liquid effluent so treated is practically free of metals 10 and is transferred to the reactor system, which is made up of agitator tanks, where it is brought into contact with low boiling point recovered amine 12 and replacement amine 11, which results in a magnesium hydroxide suspension 13. At this stage the amine is added in a ratio of 50 to 250 g/L at a temperature of 25 to 70°C, with a solid content of 1 to 10% p/p, dwelling time of 0.5 to 2 hours and a suspension recycle ratio of 5 to 40:1.

This suspension is conducted to a condenser; the magnesium hydroxide is removed by underflow 14, transferred to a solid/liquid separator and washed with water 15, which results in a magnesium hydroxide cake 16. In contrast to the processes known to the state of the art, in the process the object of the present invention the magnesium hydroxide is precipitated in isolation and is easily recovered using conventional solid/liquid separators.

In the sequence of operations, this cake is submitted to drying and calcination, which results in obtaining magnesium 17, which is stocked, part being recycled to the process of extraction of nickel and the rest commercialized 18. In the reaction system, the ratio of amine to effluent must be kept in the range of 100 to 200 g/L, being optimized in function of the amount of magnesium in the solution. Part of the precipitated magnesium hydroxide suspension is recirculated from the compressor underflow to the contact reactors for the purpose of promoting the growth of $Mg(OH)_2$ crystals by seeding. Gas emitted from the magnesium hydroxide precipitation and drying reactors is transferred to an amine absorption system and returned from there for reprocessing in the precipitation reactors.

The floating liquid phase of the condenser 19 continues for the amine recovery step via distillation in two steps, stripping followed by immediate rectification.

Stripping of the amine is carried out by heating the weak acid solution containing amine 19 to temperatures in the range of 90 to 120°C with vapour 27 at low pressure - 1.5 to 3.0 kgf/cm^2 (man.) - continually fed. That results in a mass current from the base of tower 21, constituted of weak acid and amine traces, which are transferred to the columns of activated carbon, for the purpose of removing the residual quantities of amine contained. The resulting weak acid 22 is transferred to the stocking area, going from there 23 for reuse in the hydrometallurgical process. The saturated activated carbon 24 continues to the regeneration stage, after which 25 it is recomposed with the addition of new carbon 26.

After the stripping stage in the distillation a current of vapours rich in amine 20 continues to the rectification stage, in which low pressure vapour 28 is again injected in the distillation column 27, with pressures in the range of 1.5 to 3.0 kgf/cm^2 (man.) continually fed. Also, the upper vapour currents are condensed in this equipment by the intermediation of heat exchangers operating with cooling water 29, creating reflux of 3 to 5.1 in relation to the production of high purity amine 12 in the distillation apparatus.

The amine replacement current 11, along with the recovered amine current 12, is then fed into the precipitation reactors, closing the processing circuit.

Example

Simulation tests of the process the object of the present invention, realized on a laboratory scale, demonstrate the possibility of obtaining sub products (recyclable solids) with commercial value and recovered acid water adequate for reutilization in the industrial process, which allows the condition of zero effluent to be attained in regard to liquid effluents. Such trials were conducted in a 500 mL beaker, adding a known volume of diethylamine in a known mass of the solution ($MgSO_4$ aqueous, in concentration of 30g/L Mg). With the hydrolysis of the water and the liberation of OH^* for the solution there was a precipitation of $Mg(OH)_2$. Table 2 presents the experimental results of precipitation of magnesium hydroxide utilizing diethylamine (Et_2NH).

Table 2. Results of Magnesium Hydroxide Precipitation Tests

Quantity of diethylamine in relation to the stoichiometric (%)	Concentration of remaining Mg (g/L)	Recovery of Mg (%)
0	18.00	0.0
50	9.90	42.7
75	6.50	60.2
100	1.90	87.8
125	0.17	98.9
150	0.09	99.4

As the results of Table 2 indicate, increasing the quantity of diethylamine favoured the elevation of the removal of magnesium from the solution, as observed in the recovery of Mg. However, there was no great variation in the recovery of magnesium for additions of amine equal to 125 and 150% in relation to the stoichiometric mass of the cation Mg^{2+}.

Tests for the recovery of amine were performed in a laboratory distiller, coupled to a reactor-crystallizer, with the objective of recycling the amine, by separate distillation and recovery of the $Mg(OH)_{2.}$ The reactor was warmed with a bath with thermostat at a temperature of 70°C. A condenser coil was connected to the reactor. The condenser jacket was supplied with water at 60°C, its circulation effected by means of a peristaltic pump to maintain a constant temperature. The gaseous amine continued to bubble in a solution of H_2SO_4 (10% p/p). The acid solution, receptor of all the recovered amine, was later analysed in order to calculate the recovery of the organic reagent. A current of air was kept blowing through the interior of the reactor during the time of the experiment. The pH of the solution was monitored throughout the experiment utilizing a digital meter. An amine/Mg relationship in a quantity 50% above the stoichiometric value was utilized. Therefore the mixture taken for distillation tests contained: 90 mg/L Mg; 71.1g/L SO_4^{2-}, 162.2 g/L Et_2H and pH=12. Each trial lasted 3 hours. The average amine recovery was equal to 99.6% and the final pH of the solution was equal to 5.5.

Table 3 shows the evolution of the quality of the liquid effluent during the course of the treatment process the object of this invention.

Table 3. Evolution of the quality of the liquid effluent during the course of the treatment process

Parameters	Unit	Effluent	Additions Precipitants	Effluent after Removal of Magnesium	Effluent after Removal of Amine	Effluent after Removal of Organic Matter
Mg	g/L	18.00		0.10	0.11	0.11
SO_4	g/L	75.00		66.17	74.78	74.78
Amine	g/L			115.87	0.88	0.00
pH	-	6.5	13.0	12	5.5	5.5
Temperature	°C	27	27	35	70	35
Discharges						
. effluent	m^3/h	1,000		1133	1003	1002
. Mg	kg/h	18,000		110	110	110
. SO_4	kg/h	75,000		75,000	75,000	75,000
. Amine	kg/h		131,328	131,328	878	0
. $Mg(OH)_2$ pcpt	kg/h		44,726			
. water - lavage	kg/h		36,594			

Sub products obtained were (i) magnesium oxide (MgO) after the calcination of $Mg(OH)_2$, with adequate quality for re-utilization in the nickel extraction process, (ii) metal sulphides as raw material for obtaining agricultural micronutrients and (iii) acid water adequate for purposes of re-use in the industrial process of nickel extraction.

The amine, the principal reagent of the present process, is recovered by means of evaporation; it is recycled, which favours the reduction of operating costs.

In addition to that, another advantage of the process the object of this invention in comparison to methods already known in the state of the art is the fact that the resulting sulphate solution, after passing through the carbon columns, constitutes an acid solution that is again exploited in the lateritic ore leaching process itself. With that, the magnesium and sulphur are recovered in a simple form from the effluents containing these elements.

Another advantage of the present process lies in the fact that Mg is recovered in the form of a magnesium hydroxide precipitate that can be easily recycled into earlier steps of the process, constituting an alternative low in operational costs when compared with state of art techniques. It happens, as pointed out earlier, that the sulphur is recovered in the acid water that results from the polishing operation in the carbon columns. Thus, with a simpler flow chart and lower operating costs, amine evaporation is accomplished at lower temperatures, allowing the magnesium and sulphur recovered at this step of the process to be recirculated for the leaching operation.

In that sense, along general lines, the method for treating liquid effluents the object of the present invention presents new and inventive characteristics in comparison with the state of the art:

a) utilization of amines with a low boiling point, substances generating alkaline conditions and easily separable for the purposes of recovery and recycling, which are applied directly to effluent solutions containing magnesium and sulphates;
b) removal of soluble magnesium, derived from the acid solubilization of nickel laterite, in the form of $Mg(OH)_2$ precipitate and its transformation into magnesium, MgO, and as a raw material for agricultural uses and industrial applications;

c) transformation of the liquid effluent into acid water with a low concentration, possessing characteristics that allow its reuse in the processing circuit, providing for operations in “zero effluent” condition, with a significant reduction of the consumption of replacement water in the industrial complex;

d) removal of metals remaining in the liquid effluent (Co, Mn, Ni, Zn, Cu, etc.) and their exploitation as raw material in the production of micronutrients for agricultural purposes;

e) amplification of the exploitation of the other mineral resources associated with nickel; and

f) additionally, this process for the treatment of liquid effluents presents great operational flexibility and can be implemented in the form of modules.

Having described an example of a preferred implementation, it must be understood that the scope of the present invention embraces other possible variations and is limited only by the content of the claims appended, the possible equivalents included therein.

CLAIMS:

1. A process for treating liquid effluents and recovering metals comprising the steps of:
   a) homogenizing the liquid effluent;
   b) adding a sulfide so as to precipitate one or more metals in the form of metal sulfide(s);
   c) separating the metal sulfide(s) obtained in step (b) from the liquid effluent in a solid/liquid separation operation so as to form a liquid phase free of all metals except magnesium;
   d) adding an amine solution to the liquid phase so as to precipitate magnesium hydroxide $Mg(OH)_2$, wherein:
      i) the precipitated magnesium hydroxide is separated from the liquid phase and washed; and
      ii) the washed magnesium hydroxide is dried and calcined to form magnesia;
   e) recovering the amine by a two-step process comprising:
      iii) a stripping step, comprising heating the liquid phase whilst continually feeding in low pressure vapour so as to form: a tower bottom mass stream comprising weak acids and traces of amine; and, an amine rich vapour which is sent to a rectification step; and
      iv) a rectification step, comprising continually feeding in low pressure vapour to the amine rich vapour, so as to form a top vapour current that is condensed through heat exchangers,

   wherein said amine is selected from a group consisting of low boiling point amines.

2. The process for treating liquid effluents and recovering metals according to claim 1, wherein the amine in said step (d) is added in the ratio 50 – 250 g amine/L liquid phase.

3. The process for treating liquid effluents and recovering metals according to claim 1 or claim 2, wherein adding the amine in solution to the liquid phase in step (d) occurs at a temperature of 25 to 70°C, solid content of 1 to 10% p/p, residence time of 0.5 to 2 hours and recycle ratio of slurry of 5 to 40:1.

4. The process for treating liquid effluents and recovering metals according to any one of claims 1 to 3, wherein in the amine solution added at step (d) comprises amine condensed in step e) iv).

5. The process for treating liquid effluents and recovering metals according to any one of claims 1 to 4, wherein the floating liquid phase in stripping step (e) iii) is heated to a temperature ranging from 90 to 120 °C and low pressure vapour has a pressure in the range of 1 to 10 kgf/cm^2.

6. The process for treating liquid effluents and recovering metals according to any one of claims 1 to 5, wherein the tower bottom mass stream formed by weak acids and traces of amine is transferred to an activated charcoal column in which residual amine is removed and resulting weak acids are transferred for storage.

7. Treated liquid effluent and recovered metals produced by the method of any one of claims 1 to 6.

8. A process according to any one of claims 1 to 6 substantially as hereinbefore described with reference to the Example or to Figure 2.

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Patent Attorneys for the Applicant/Nominated Person
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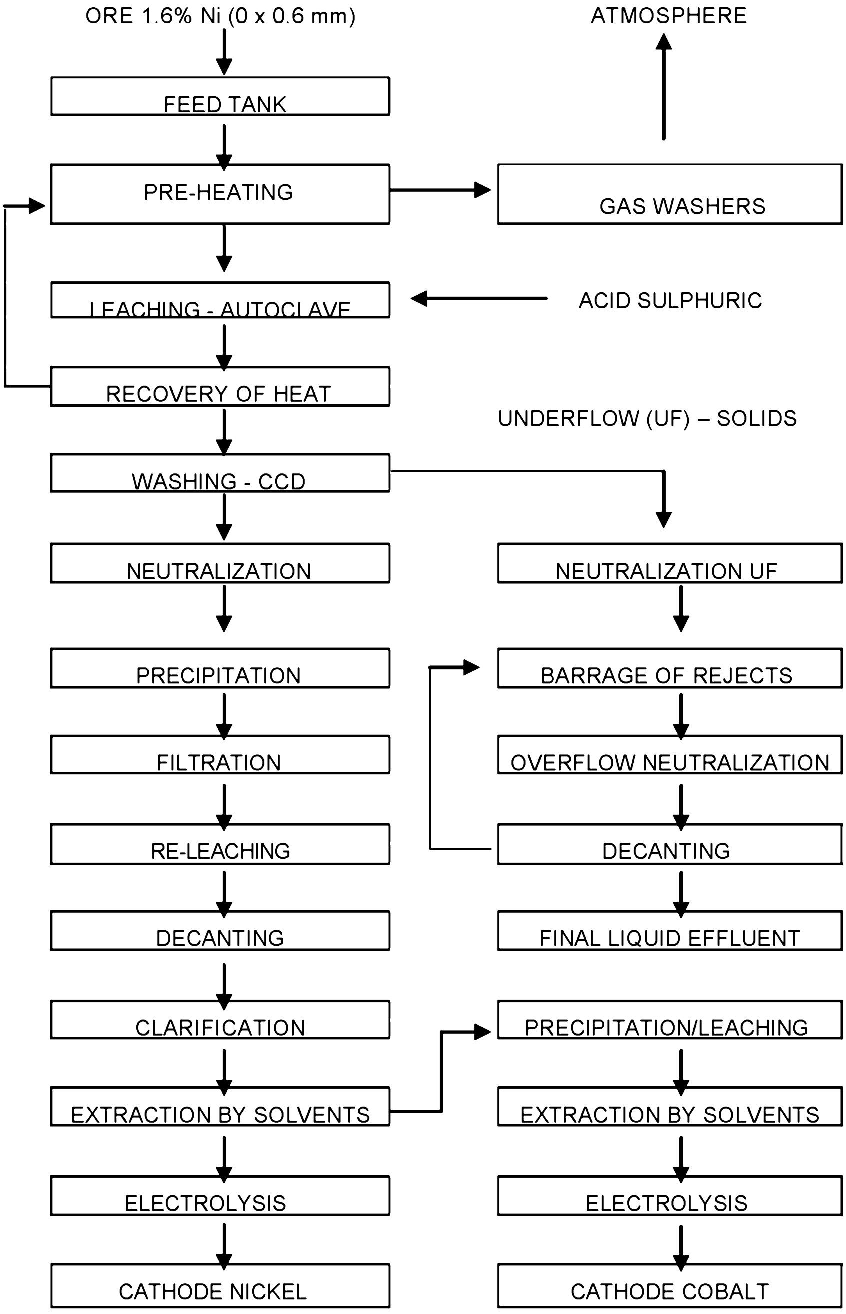
ORE 1.6% Ni (0 x 0.6 mm)
ATMOSPHERE
FEED TANK
PRE-HEATING
GAS WASHERS
LEACHING - AUTOCLAVE
ACID SULPHURIC
RECOVERY OF HEAT
UNDERFLOW (UF) – SOLIDS
WASHING - CCD
NEUTRALIZATION
NEUTRALIZATION UF
PRECIPITATION
BARRAGE OF REJECTS
FILTRATION
OVERFLOW NEUTRALIZATION
RE-LEACHING
DECANTING
DECANTING
FINAL LIQUID EFFLUENT
CLARIFICATION
PRECIPITATION/LEACHING
EXTRACTION BY SOLVENTS
EXTRACTION BY SOLVENTS
ELECTROLYSIS
ELECTROLYSIS
CATHODE NICKEL
CATHODE COBALT

FIG.1

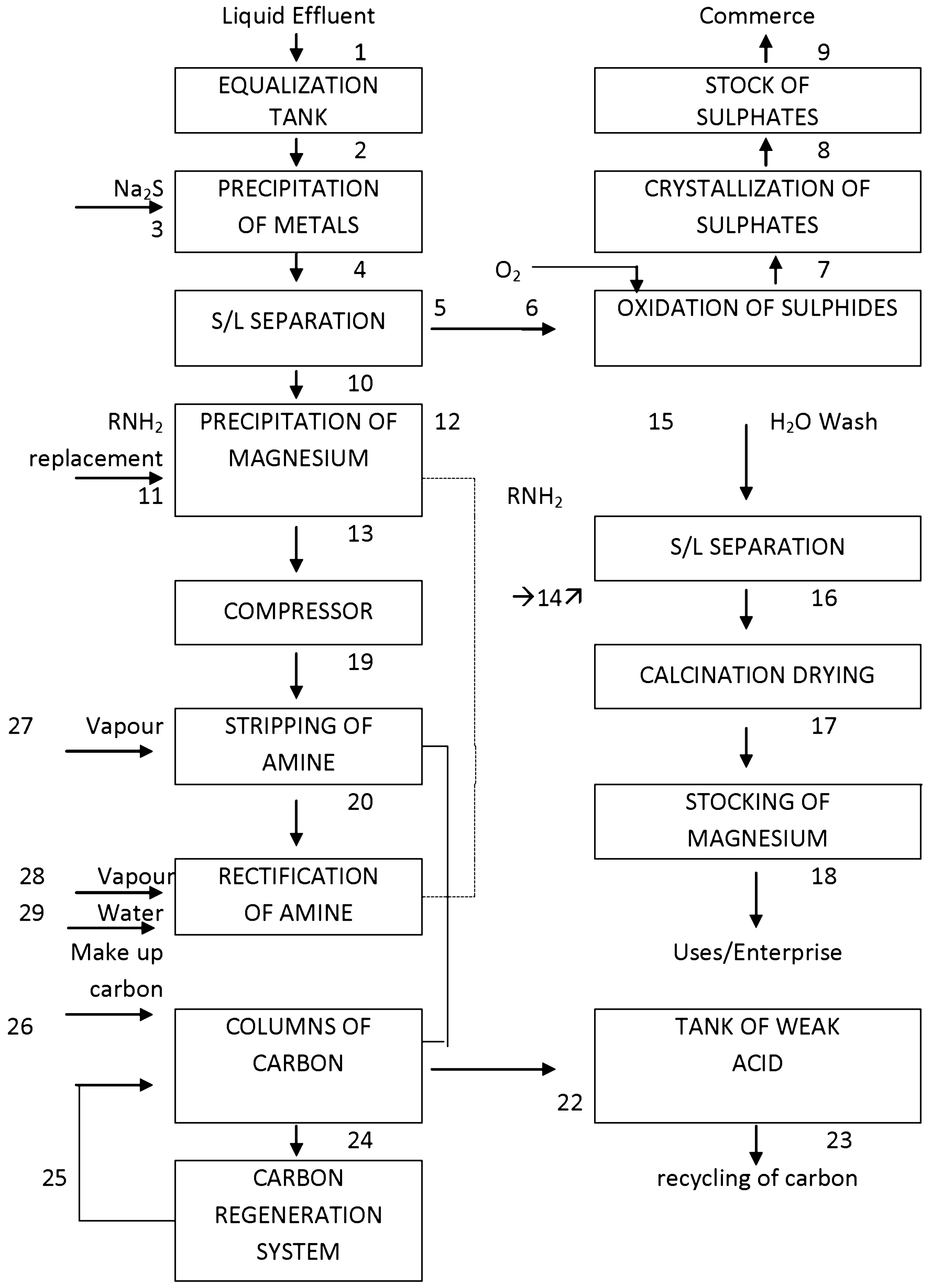
Liquid Effluent
1
EQUALIZATION TANK
2
Na_2S
3
PRECIPITATION OF METALS
4
S/L SEPARATION
5
6
10
RNH_2 replacement
11
PRECIPITATION OF MAGNESIUM
12
13
COMPRESSOR
19
27
Vapour
STRIPPING OF AMINE
20
28
Vapour
29
Water
RECTIFICATION OF AMINE
Make up carbon
26
COLUMNS OF CARBON
24
25
CARBON REGENERATION SYSTEM
Commerce
9
STOCK OF SULPHATES
8
CRYSTALLIZATION OF SULPHATES
O_2
7
OXIDATION OF SULPHIDES
15
H_2O Wash
RNH_2
S/L SEPARATION
→14↗
16
CALCINATION DRYING
17
STOCKING OF MAGNESIUM
18
Uses/Enterprise
22
TANK OF WEAK ACID
23
recycling of carbon

FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/BR2011/000274

A. CLASSIFICATION OF SUBJECT MATTER

IPC: C22B 3/20 (2006.01), C22B 26/22 (2006.01), C02F 1/62 (2006.01), C02F 103/10 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C22B 3/20 (2006.01), C22B 26/22 (2006.01), C02F 1/62 (2006.01), C02F 103/10 (2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

INPI BR, Scielo, PAJ, Epo-Internal, USPTO, DIALINDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2009089613 A1 (SILVA ROBERTO MATTIOLI [BR]) 23 July 2009 (2009-07-23), see abstract and page 7, paragraph [0023] to page 8; paragraph [0025].	1 a 9
A	US 2006228279 A1 12 October 2006 (2006-10-12), see abstract	1
A	GB 1520175 A (INCO LTD) 02 August 1978 (1978-08-02), see pag 9; Lines 6 to 61 Claims 1, 5, 7, 8 e 10, and Figure 1.	1, 3 a 6
A	US 20070212765 A1 31 December 1969 (1969-12-31), see abstract	1

☐ Further documents are listed in the continuation of Box C.　☒ See patent family annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search **17/11/2011**	Date of mailing of the international search report 30 11 11
Name and mailing address of the ISA/BR INPI INSTITUTO NACIONAL DA PROPRIEDADE INDUSTRIAL Rua Mayrink Veiga nº 9, 18º andar cep: 20090-050, Centro - Rio de Janeiro/RJ Facsimile No. +55 21 3037-3663	Authorized officer **Alciciéa da Conceição Pereira Monteiro** Telephone No. +55 21 3037-3493/3742

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/BR2011/000274

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		US 8043585 B2	2011-10-25
		WO 2009089613 A8	2009-10-22
US 2006228279 A1	2006-10-12	CA 2534035 A1	2006-10-07
		US 7387767 B2	2008-06-17
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		AU 1213176 A	1977-09-22
		BR 7601977 A	1976-10-05
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		CA 1041304 A1	1978-10-31
		FR 2306272 A1	1976-10-29
		JP 51122603 A	1976-10-26
		JP 59019973 B	1984-05-10
		JP 1244312 C	1984-12-14
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		NO 144154 B	1981-03-23
		US 4006215 A	1977-02-01
		ZA 7601353 A	1977-02-23
US 20070212765 A1	2007-09-13	NONE	

INTERNATIONAL SEARCH REPORT

International application No.
PCT/BR2011/000274

A. CLASSIFICATION OF THE OBJECT

IPC: C22B 3/20 (2006.01), C22B 26/22 (2006.01), C02F 1/62 (2006.01), C02F 103/10 (2006.01)

In accordance with the International Patent Classification (IPC) or in conformity with national classification and (IPC)

B. FIELDS SEARCHED BY THE RESEARCH

Minimum documentation searched (classification system followed by the classification symbol)

IPC: C22B 3/20 (2006.01), C22B 26/22 (2006.01), C02F 1/62 (2006.01), C02F 103/10 (2006.01)

Additional documentation searched, other than the minimum, to the extent that such documents are include in the fields searched

Electronic data base consulted during the international search (name of the data base and, if necessary, search terms used)

INPI BR, Scielo, PAJ, Epo-Internal, USPTO, DIALINDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Documents cited, with indication of relevant parts, if appropriate	Relevant to Claims No.
A	WO 2009089623 A1 (SILVA ROBERTO MATTIOLI [BR]) 23 July 2009 (23/07/2009), see abstract and page 7, paragraph [0023] to page 8, paragraph [0025].	1 to 9
A	US 2006228279 A 1 12 October 2006 (12/10/2006), see abstract.	1
A	GB 1520175 A (INCO LTD) 2 August 1978 (02/08/1978), see page 9, lines 6 to 61 Claims 1, 5, 7, 8 and 10, and Figure 1.	1, 3 to 6
A	US 20070212765 A 1 31 December 1969 (31/12/1969) see abstract.	

☐ Additional documents are listed in the continuation of Box C.

☒ See the patent family annex.

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"L" document which may cast doubt on priority claim(s) or in which it is cited in order to determine the date of another citation or for other special reason.
"O" document referring to an oral disclosure, use, exhibition or other means
"F" document published prior to the international filing, but later than the priority date claimed
"I" document published after the international filing date, or of priority and which do not conflict with the application, but cited to understand the principal or theory on which the invention is based.
"X" document of particular relevance; the invention claimed cannot be considered new and cannot be considered to involve an inventive activity when the document is considered in isolation.
"Y" document of particular relevance; the invention claimed cannot be considered to involve an inventive step when the document is combined with one or more other documents, such combination being obvious to a technician in the matter
"&" document member of the same patent family

Date of the actual completion of the international search
17 November 2011

Date of mailing of the international search report
30 NOVEMBER 2011

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/BR2011/000274

Documents of patents cited in the search report	Date of publication	Member(s) of the family of patent	Date of publication
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		US 8043585 B2	2011-10-25
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		JP 1244312 C	1984-12-14
		NO 761118 A	1976-10-05
		NO 144154 B	1981-03-23
		US 4006215 A	1977-02-01
		ZA 7601353 A	1977-02-23
US 20070212765 A1	2007-09-13	**None**	