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(71) **Applicant** (for all designated States except US): **HYDRONICKEL ENGINEERING OOD** [BG/BG]; Ami Bue Str., 72, fl.5, 1612 Sofia (BG).

(72) **Inventors; and**

(75) **Inventors/Applicants** (for US only): **MITOV, Stoian Borissov** [BG/BG]; Yoan Ekzarh Str., 63, ap. 1, 1164 Sofia (BG). **MASHEV, Bozhidar Stoyanov** [BG/BG]; Georgi Benkovski Str., 24, entr. B1, ap. 3, Panagyurishte, Pazardzhik obi, 4500 (BG).

(74) **Agent:** GEORGIEVA, **Lilia Tsvetkova**; P.O. Box 21, 1797 Sofia (BG).

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(54) **Title:** METHOD FOR NICKEL AND COBALT EXTRACTION FROM OXIDE ORES

(57) **Abstract:** The method for extraction of nickel and cobalt comprises the steps of: pulp of ore and sulphuric acid solution is subjected to treatment in the cathode compartment of an electrolytic cell maintaining oxidation reduction potential at value of 200 to 300 mV which provides the reduction of Fe<sup>3+</sup> from the Fe<sub>2</sub>O<sub>3</sub>, contained in the ore, to Fe<sup>2+</sup> thus nickel, cobalt and iron are dissolved in the said sulphuric acid solution; the pulp is withdrawn from the electrolytic cell and the liquor containing nickel, cobalt, and iron is aerated with air at value of 100 to 130 m<sup>3</sup> per m<sup>3</sup> liquor in order to oxidize Fe<sup>2+</sup> to Fe<sup>3+</sup>; neutralizing agent comprising ammonia is added to the liquor to precipitate iron and to neutralize the free sulphuric acid; and nickel and cobalt are extracted from the liquor.



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## METHOD FOR NICKEL AND COBALT EXTRACTION FROM OXIDE ORES

## TECHNICAL FIELD

The present invention relates to a method for nickel and cobalt extraction from oxide ores and more specifically to a hydrometallurgical method for nickel and cobalt extraction from oxide ores which contain nontronitic serpentinites, chlorite, magnetite, hematite, goethite, and jarosite wherein the main nickel content in the ore substitutes the bivalent iron in the said minerals.

## BACKGROUND OF THE INVENTION

U.S. Patent 6,379,637 describes an atmospheric acid leaching method for extraction nickel and cobalt from highly serpentinized saprolitic fractions of nickel laterite deposits that are generally too low in nickel and cobalt, comprising the steps of: pulping a finely ground highly serpentinized saprolite ore with water to produce a pulped ore with a density of between 15 % and 33 % solids; heating said pulp ore; adding sulphuric acid to the heated pulped ore at atmospheric pressure in an amount of at least about 80 % by weight of the ore; agitating the mixture for an effective period of time, whereby metal oxides are leached from the heated pulped ore mixed with sulphuric acid to produce a hot leach pulp; separating said hot leach pulp into liquid and solids, wherein said liquid contains sulphates of said metals; neutralizing said liquid with limestone to precipitate dissolved iron contained therein; and recovering an intermediate product containing nickel and cobalt from said liquid.

U.S. Patent 4,410,498 describes a method for extraction of nickel and cobalt from serpentinitic laterite ores by leaching the ore with an aqueous solution of sulphuric acid while adding to the solution a reducing agent to maintain the redox potential of the solution at a value between 200 and 400 millivolts, measured against the saturated calomel electrode.

K.R. Patent Publication No. 890002035 discloses a method for extraction of nickel from the low quality laterite ore by leaching electrochemically in the electrolysis cell with a separator between cathode chamber and anode chamber. Nickel is recovered from 0.01-10.0 mol sulphuric acid solution with blowing the sulfurous

acid gas. Anode chamber consists of 0.01-10.0 mol. sulphuric acid solution including source ore powder under 10 mesh.

A disadvantage of the known methods is the low extraction degree of nickel and cobalt while treating low-grade oxide ores, containing the said metals, and more specifically while treating nontronitic serpentinites wherein the main nickel content in the ore substitutes the bivalent iron in the present minerals.

### SUMMARY OF THE INVENTION

An object of the present invention is a hydrometallurgical method for nickel and cobalt extraction from oxide ores which provides high-degree extraction of nickel and cobalt from low-grade ores with low content of the said metals.

According to the invention, the method for nickel and cobalt extraction from oxide ores comprises the steps of:

a) pulp of ore and sulphuric acid solution with concentration of 50 to 250 g/l is subjected to treatment in the cathode compartment of an electrolytic cell at a temperature of 55°C to 85°C maintaining oxidation-reduction potential at 200 to 300 mV which provides the reduction of  $\text{Fe}^{3+}$  from the  $\text{Fe}_2\text{O}_3$ , contained in the ore, to  $\text{Fe}^{2+}$  thus the contained nickel, cobalt and iron are dissolved in the said sulphuric acid solution;

b) the pulp, treated in the cathode compartment, is withdrawn out of the electrolytic cell and liquor, containing nickel, cobalt, and iron, is separated from the solid residual;

c) the liquor, containing nickel, cobalt, and iron is aerated with air at values of 100 to 130 m<sup>3</sup> per m<sup>3</sup> liquor in order to oxidize  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$ ;

d) the liquor is heated to a temperature of 75-85°C, and neutralizing agent comprising ammonia is added to precipitate iron and to neutralize the free sulphuric acid;

e) the neutralized liquor is separated from the solid residue;

f) nickel and cobalt are extracted from the neutralized liquor via ion exchange extraction or liquid extraction or precipitation or crystallization.

In an embodiment of the present invention, the anode and the cathode compartments of the electrolytic cell are separated by a diaphragm.

In an alternative embodiment of the present invention, the anode and the cathode compartments of the electrolytic cell are separated by an impenetrable separator, and the electric circuit is closed via a salt bridge.

The advantages of the method for nickel and cobalt leaching from oxide ores, and more specifically from nontronitic serpentinites, reveal in the following: during the treatment of pulp of ore and sulphuric acid solution in the cathode compartment of an electrolytic cell under conditions providing reduction of  $\text{Fe}^{3+}$  from the contained in the ore  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}^{2+}$ , the structure of the crystal lattice of the magnetite and the other iron and magnesium minerals is destroyed which accelerates the dissolution process of nickel and cobalt in the sulphuric acid solution. As a result, nickel and cobalt extraction grade in the solution is increased. In the subsequent solution aeration with air, oxidation of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  occurs which ensures more complete process of iron recovery from the sulphuric acid solution, and the sulphuric acid solution, resultant from the neutralization phase, containing nickel and cobalt, is of low iron content (up to 2-3 g/l).

#### DETAILED DESCRIPTION OF THE INVENTION

The method in accordance with the present invention is used for treatment of ochre nontronitic serpentinite with a general formula of  $(\text{Na,K,Ca})\text{Fe}_2[(\text{Si,Al})_4\text{O}_{10}](\text{OH})_2n\text{H}_2\text{O}$ , and contains 36.68%  $\text{Fe}_3\text{O}_4$  and 35.84%  $\text{SiO}_2$ , low concentration of MgO - 6.26%, and low concentration of precious components: Ni - 0.712 %, and Co - 0.034% which substitute the iron in the mineral structure. The average Fe content is 29.6%.

The ore is subjected to grinding and water in a solid to liquid ratio = 4:1 is fed to fraction of -0.080 mm. The mixture is pulped, and sulphuric acid is added to the resultant pulp up to concentration in the range of 50 to 250 g/l.

The treatment of pulp takes place in an electrolytic cell with a cathode of lead or of stainless steel. The anode may be of lead or graphite.

In an embodiment of the present invention, the anode and the cathode compartments in the electrolytic cell are separated by a filter fabric diaphragm.

In an alternative preferred embodiment of the present invention, an electrolytic cell is used wherein the anode and the cathode compartments are separated by an impenetrable separator, and the electric circuit is closed via a salt bridge.

The pulp of oxide ore and sulphuric acid solution with concentration of 50 to 250 g/l is fed to the cathode compartment of an electrolytic cell, and the anode compartment is fed with sulphuric acid solution with the same concentration as the above said solution in the cathode compartment. Said pulp is treated for 2 to 4 hours at temperature of 55 to 85<sup>0</sup>C at continuous agitating, the cathode current density and resistance being maintained within ranges providing maintenance of redox media in the cathode compartment and redox potential at 200 to 300 mV. Under these conditions Fe<sup>3+</sup> from the contained in the ore Fe<sub>2</sub>O<sub>3</sub> reduces to Fe<sup>2+</sup>.

The crystal lattice structure of the magnetite and the other iron and magnesium minerals is destroyed during the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>, and as a result, the process of dissolution of nickel and cobalt in the sulphuric acid solution is enhanced, and the extraction degree of those metals is increased. Iron is also dissolved in the sulphuric acid solution.

The treated pulp is withdrawn from the cathode compartment of the electrolytic cell, and the liquor obtained is separated from the solid residue. The liquor is aerated with air or with air enriched with oxygen in an amount of .100 to 130 m<sup>3</sup> per m<sup>3</sup> liquor in order to achieve oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> aiming to more complete precipitation of the iron.

Upon completion of the oxidation process the liquor is heated to a temperature of 75-85<sup>0</sup>C, and ammonia is added to it in an amount, stoichiometric to the iron content. As a result, the main amount of iron is precipitated, and the free sulphuric acid is neutralized.

Upon separation of the liquid from the solid phase, the iron content in the resultant neutralized liquor is up to 2-3 g/l. Nickel and cobalt are recovered from the neutralized liquor using conventional methods such as ion exchange extraction, liquid extraction, precipitation, and crystallization.

The degree of nickel extraction is 90 - 92 %, and of cobalt is 80-85 %.

The method in accordance with the present invention is explained by the following non-limiting examples.

## Example 1.

The method in accordance with the present invention is used for processing of oxide nickel-bearing ore which contains nontronitic serpentinites, chlorite, and magnetite. The ore contents: 0.74% nickel, 35-38% iron, 0.051 % cobalt, 1.95 % magnesium, and 1.29 % aluminium. The nickel is not presented by natural minerals, and it substitutes the bivalent iron in the specified minerals.

The ore is subjected to grinding and water in a solid to liquid ratio = 4:1 is fed to fraction of -0.080 mm. Upon pulping sulphuric acid is added to concentration of 200 g/l.

The treatment of pulp takes place in an electrolytic cell with a stainless steel cathode and lead anode which are of the same surface. The cathode compartment is separated from the anode compartment by a filter fabric diaphragm.

A portion of pulp is fed to the cathode compartment of the electrolytic cell, and the anode compartment is fed with a sulphuric acid solution with concentration of 200 g/l. The treatment of said pulp is carried out for 4 hours at 60°C temperature, and at continuous agitation.

The cathode and the anode current densities are 300 A/m<sup>2</sup>, and the cell voltage is 5.4 V. Under these conditions a reduction medium is created in the cathode compartment, and a redox potential is maintained at 250-270 mV. As a result of this treatment, Fe<sup>3+</sup> reduces to Fe<sup>2+</sup> under the action of the electric current, and iron, nickel, and cobalt are solubilized. The portion of pulp already treated in the cathode compartment is withdrawn from the electrolytic cell, and said cathode compartment is fed with a new portion of pulp comprising ore and sulphuric acid solution.

The results of a chemical analysis exhibit the following: upon filtration the catholyte contains nickel, 1.2 g/l; iron, 24 g/l; the solid residue contains nickel 0.15 % and iron 13.5 %.

Energy consumption is 7600 kW h per ton of nickel (7600 kW h/t Ni).

Upon withdrawal from the cathode compartment of the electrolytic cell, the pulp is filtrated to separate liquor from the solid residue. The resultant liquor is blown with air at consumption of 120 m<sup>3</sup> per m<sup>3</sup> of liquor, as a result of which Fe<sup>2+</sup> from the solution oxidizes to Fe<sup>3+</sup>. Thereafter, precipitating of the dissolved in the sulphuric acid solution iron is carried out. The pulp is heated to a temperature of 80°C, and 25 %

ammonia solution is fed for precipitating of the dissolved iron and neutralization of the free sulphuric acid.

Upon separation of the liquid from the solid phase by filtration, the neutralized liquor contains nickel 1.05 g/l, cobalt 0.1 g/l, iron 2.7 g/l, magnesium 0.480 g/l, and aluminium 0.081 g/l. The degree of nickel extraction is 91 %, and of cobalt is 85%.

The neutralized liquor is subjected to three-stage extraction using LIX84-I, the pH values being priorly adjusted to 2.8-3.2. The concentrated extractant is regenerated in two stages with a solution of sulphuric acid.

Example 2.

The method in accordance with the present invention is used for processing of oxide nickel-bearing ore which contains nontronitic serpentinites, chlorite, and magnetite. The content is: 0.74% nickel, 35-38% iron, 0.051 % cobalt, 1.95 % magnesium, and 1.29 % aluminium. The nickel substitutes the bivalent iron in the specified minerals.

The ore is subjected to grinding and water in a solid to liquid ratio = 4:1 is fed to fraction of -0.080 mm. Upon pulping sulphuric acid is added to concentration of 200 g/l.

The treatment of pulp takes place in an electrolytic cell with lead cathode and lead anode which are of the same surface. The cathode compartment is separated from the anode compartment by an impermeable diaphragm, and electric connection is effected via high resistance liquid salt bridge.

A portion of pulp is fed to the cathode compartment of the electrolytic cell, and the anode compartment is fed with a sulphuric acid solution with concentration of 200 g/l. The treatment of said pulp in the cathode compartment is carried out for 4 hours at 60°C temperature, and at continuous agitation. The cathode and the anode current densities are 10 A/m<sup>2</sup>, and the cell voltage is 14 V. Under these conditions a reduction medium is created in the cathode compartment of the electrolytic cell, and a redox potential is maintained at 250-270 mV. As a result of this treatment, Fe<sup>3+</sup> reduces to Fe<sup>2+</sup>, and iron, nickel, and cobalt are solubilized. The portion of pulp already treated in the cathode compartment is withdrawn from the electrolytic cell, and said cathode compartment is fed with a new portion of pulp comprising ore and sulphuric acid solution.

The results of a chemical analysis exhibit the following: upon filtration the catholyte contains nickel, 1.1 g/l; iron, 24 g/l; the solid residue contains nickel 0.19 % and iron 17.1 %.

Energy consumption is 5300 IcW MNi.

5        Upon withdrawal from the cathode compartment of the electrolytic cell, the pulp is filtrated to separate liquor from the solid residue. The resultant liquor is blown with air at consumption of 120 m<sup>3</sup> per m<sup>3</sup> of liquor, as a result of which Fe<sup>2+</sup> from the solution oxidizes to Fe<sup>3+</sup>. Thereafter, precipitation of the dissolved in the sulphuric acid solution iron is carried out. The pulp is heated to a temperature of 80<sup>0</sup>C, and 25 %  
10        ammonia solution is fed for precipitation of the dissolved iron and neutralization of the free sulphuric acid.

Upon filtration the neutralized liquor contains nickel 1.05 g/l, iron 2.7 g/l, magnesium 0.480 g/l, and aluminium 0.081 g/l.

The degree of nickel extraction is 92 %, and of cobalt is 84%.

15        The neutralized liquor is subjected to three-stage extraction using LIX84-I for the nickel and cobalt recovery, the pH values being priorly adjusted to 2.8-3.2. The concentrated extractant is regenerated in two stages with a solution of sulphuric acid.

## CLAIMS

1. A method for nickel and cobalt extraction from oxide ores, characterized in that said method comprises the steps of:

- 5 a) pulp of ore and sulphuric acid solution with concentration of 50 to 250 g/l is subjected to treatment in the cathode compartment of an electrolytic cell at a temperature of 55<sup>0</sup>C to 85<sup>0</sup>C maintaining oxidation-reduction potential at 200 to 300 mV which provides the reduction of Fe<sup>3+</sup> from the Fe<sub>2</sub>O<sub>3</sub>, contained in the ore, to Fe<sup>2+</sup> thus the contained nickel, cobalt and iron being dissolved in the said sulphuric acid solution;
- 10 b) the pulp, treated in the cathode compartment, is withdrawn out of the electrolytic cell and the liquor, containing nickel, cobalt, and iron, is separated from the solid residual;
- c) the liquor, containing nickel, cobalt, and iron is aerated with air at values of 100 to 130 m<sup>3</sup> per m<sup>3</sup> liquor in order to oxidize Fe<sup>2+</sup> to Fe<sup>3+</sup>;
- 15 d) the liquor is heated to a temperature of 75-85<sup>0</sup>C, and neutralizing agent comprising ammonia is added to precipitate iron and to neutralize the free sulphuric acid;
- e) the neutralized liquor is separated from the solid residue;
- f) nickel and cobalt are extracted from the neutralized liquor via ion exchange  
20 extraction or liquid extraction or precipitation or crystallization.

2. A method according to claim 1, characterized in that the anode compartment and the cathode compartment of the electrolytic cell are separated by a diaphragm.

3. A method according to claim 1, characterized in that the anode compartment and the cathode compartment of the electrolytic cell are separated by an impenetrable  
25 separator, and the electric circuit is closed via a salt bridge.

# INTERNATIONAL SEARCH REPORT

International application No PCT/BG2008/000012
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**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C22B3/08 C22B3/44 C22B23/00 C25C1/08

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)  
 C22B C25C

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 practical, search terms used)

EPO-Internal , WPI Data, COMPENDEX, INSPEC

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
A	LEE H Y ET AL: "Electrochemical leaching of nickel from low-grade laterites" HYDROMETALLURGY, ELSEVIER SCIENTIFIC PUBLISHING CY. AMSTERDAM, NL, vol. 77, no. 3-4, 1 June 2005 (2005-06-01), pages 263-268, XP004856299 ISSN: 0304-386X the whole document <div style="text-align: center; margin-top: 10px;">----- -/--</div>	1-3

Further documents are listed in the continuation of Box C

See patent family annex

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|---|---|
| <p>* Special categories of cited documents</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P<sup>1</sup>" document published prior to the international filing date but later than the priority date claimed</p> | <p>"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</p> <p>"X<sup>1</sup>" 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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p> |
|---|---|

Date of the actual completion of the international search  <b>9 June 2009</b>	Date of mailing of the international search report  24/06/2009
Name and mailing address of the ISA/ European Patent Office, P B 5818 Patentlaan 2 NL - 2280 HV RIJSWIJK Tel (+31-70) 340-2040, Fax (+31-70) 340-3016	Authorized officer  <b>Juhart, Matjaz</b>

## INTERNATIONAL SEARCH REPORT

International application No  
PCT/BG2008/000012

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>MCDONALD ET AL: "Atmospheric acid leaching of nickel laterites review" HYDROMETALLURGY, ELSEVIER SCIENTIFIC PUBLISHING CY. AMSTERDAM, NL, vol. 91, no. 1-4, 28 November 2007 (2007-11-28), pages 35-55, XP022524528 ISSN: 0304-386X Chapter 4.2 Redox-controlled leaching page 41 - page 42</p> <p>-----</p>	1-3
A	<p>KR 890 002 035 B1 (KOREA INST SCIENCE TECHNOLOGY [KR]) 8 June 1989 (1989-06-08) cited in the application the whole document</p> <p>-----</p>	1-3
A	<p>US 4 159 232 A (BACON WILLIAM G [CA] ET AL) 26 June 1979 (1979-06-26) claim 1; figures 1,2</p> <p>-----</p>	1-3
A	<p>US 6 379 637 B1 (CURLOOK WALTER [CA]) 30 April 2002 (2002-04-30) cited in the application the whole document</p> <p>-----</p>	1-3

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/BG2008/000012

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
KR 890002035	B1	08-06-1989	NONE
US 4159232	A	26-06-1979	NONE
US 6379637	B1	30-04-2002	AU 776553 B2 16-09-2004
		AU 1371202 A	15-05-2002
		WO 0236838 A2	10-05-2002
		EP 1337677 A2	27-08-2003