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(54) **Title:** RECOVERY OF NICKEL USING INTEGRATED CONTINUOUS ION EXCHANGE AND ELECTRO-WINNING PROCESS

(57) **Abstract:** A system and method for recovering nickel from a mixed metal product liquor solution containing nickel and at least copper or iron including the steps of: (a) passing the product liquor solution through an ion exchange bed to load nickel onto the ion exchange resin, (b) passing a sulfuric acid solution through the loaded ion exchange bed to strip nickel from the ion exchange resin and produce an eluate having a pH less than 3, (c) recovering the effluent and removing a portion of sulfuric acid sufficient to raise the pH of the effluent above 3, (d) electro-winning the eluate to produce electro-won nickel and a nickel-depleted raffinate, (e) combining at least a portion of the nickel-depleted raffinate with product liquor solution and repeating steps (a) through (d).



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RECOVERY OF NICKEL USING INTEGRATED CONTINUOUS ION EXCHANGE AND ELECTO-WINNING PROCESS

5 FIELD

The present invention is directed toward a continuous ion exchange process for recovering nickel from a mixed metal product liquor solution.

INTRODUCTION

10 Continuous ion exchange (CIX) processes are used to recover metals from product liquor solutions (PLS), see for example WO 1996/20291 and C. Bailey et al., Removal of Nickel From Cobalt Sulphate Electrolyte Using ISEP™ Continuous Ion Exchange. In general, CIX processes involve the use a metal recovery circuit including of a plurality of ion exchange beds, commonly arranged in carousal, which repetitively cycle through individual process zones including metal
15 loading and elution. US 7594951 describes a CIX process that includes an integrated electro-winning loop for recovering copper from the eluate. Unfortunately, interfering ions (e.g. iron, sulfate) quickly build up in the system and interfere with the intended electrochemistry of the electro-winning operation. This in turn requires eluate to be bled from the system or completely replaced. Given the low pH values of the eluate (e.g. less than 0.5), the described process is
20 applicable for recovery of other metals such as nickel.

SUMMARY

The present invention includes a system and method for recovering nickel from a mixed metal product liquor solution containing nickel and at least copper or iron comprising passing the
25 product liquor solution through a plurality of ion exchange beds containing nickel selective ion exchange resin that pass through process zones as part of a repeating nickel recovery circuit. In one embodiment, the method includes the steps of: (a) passing the product liquor solution through an ion exchange bed to load nickel onto the ion exchange resin, and (b) passing a sulfuric acid solution through the loaded ion exchange bed to strip nickel from the ion exchange resin and produce an
30 eluate having a pH less than 3. The method is characterized by the additional steps of: (c) recovering the effluent and removing a portion of sulfuric acid sufficient to raise the pH of the effluent above 3, (d) electro-winning the eluate to produce electro-won nickel and a nickel-depleted raffinate, (e) combining at least a portion of the nickel-depleted raffinate with product liquor solution and repeating steps (a) through (d). Many additional embodiments are described.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is schematic view of an embodiment the subject invention.

Figure 2 is a schematic view of an embodiment of a continuous exchange process applicable to the subject invention.

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DETAILED DESCRIPTION

The present invention includes a system and method for recovering nickel from a mixed metal product liquor solution, sometimes also referred to as “pregnant leach solution,” hereinafter collectively abbreviated as “PLS”. The source of the PLS is not particularly limited but is typically produced by heap leaching, vat leaching or pressure leaching lateritic ores. The PLS includes a sulfuric acid solution including at least copper or iron, nickel and other acid soluble impurities. The PLS preferably has a pH of less than 3, but more preferably less than 2.3 (e.g. from 1.3 to 2.2).

As part of the subject method, PLS is subject to continuous ion exchange (CIX) including the step of passing PLS through a plurality of ion exchange beds containing nickel selective ion exchange resin. The beds pass through individual process zones as part of a repeating nickel recovery circuit that is described below. In a preferred embodiment, the subject method further includes an integrated electro-winning cycle loop.

Figure 1 provides a schematic overview of an embodiment of the invention including an integrated CIX and electro-winning system generally shown at 10. The system includes a CIX unit (12) with multiple beds of nickel selective ion exchange resin for treating PLS (13), an acid removal unit (14) capable of removing a portion of sulfuric acid from the nickel eluate (16) exiting the CIX unit (12) in sufficient quantity to raise the pH above 3 (more preferably at least 3.2, 3.5 or even 4.0), an optional iron/copper removal unit (18) capable of removing a portion of iron or copper present in the pH adjusted eluate (20), and a nickel electro-winning unit (22) capable of electro-winning nickel from the eluate (24) resulting in a high grade nickel product (26) and a nickel depleted raffinate (28). The nickel depleted raffinate is recycled back to the CIX unit (12) and may be optionally supplemented with sulfuric acid (30). The system (10) may optionally include an acid recovery unit (32) for recovering sulfuric acid from the acid removal unit (14) and returning the acid to the CIX unit (12), recycling back to the PLS (13), for storage or disposal.

Figure 2 is a schematic overview of a CIX unit generally shown at 36 and adapted for use in the present method. The unit includes a plurality of ion exchange beds containing nickel selective ion exchange resin (e.g. DOWEX™ M4195) that sequentially pass through individual process zones (e.g. A, B, C) as part of a nickel recovery circuit. Each zone preferably includes at least one ion exchange bed or column, and in practice may include a plurality of individual beds. The method includes the following sequential steps:

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(a) passing the PLS (13) through an ion exchange bed (zone A) to load nickel onto the ion exchange resin and produce a raffinate solution (38), and

(b) passing a sulfuric acid solution (42) through the loaded ion exchange bed (zone C) to strip nickel from the ion exchange resin and produce an eluate (16) having a pH less than 3 (2.5, 2.3). The method may include additional process zones as is well known in the art, e.g. rinsing, washing, scrubbing. For example, optional Zone B is depicted as a rinsing step. PLS, rinse solution (e.g. water), elution solution (e.g. 20% sulfuric acid) may be maintained in tanks, 13, 40, and 42 respectively. The tanks are in selective fluid communication with the ion exchange beds. Fluid flow is controlled by a plurality of valves and a control panel (not shown) as the beds cycle through the individual process zones (A, B and C). CIX equipment for performing the subject method is available from PuriTech (e.g. IONEX™), Ionex Separations and Calgon Carbon (e.g. ISEP™) and is also described in US 7594951. Suitable nickel selective ion exchange resins include DOWEX™ M4195 and XUS-43578 chelating resins available from The Dow Chemical Company. These resins include a styrene-divinylbenzene copolymer matrix with bis-picolylamine functional groups.

The acid removal unit (14) is not particularly limited and may include an acid retardation unit including a fixed bed of suitable anion exchange resin (e.g. AMBERSEP™ 4200 Sulfate or DOWEX™ 21K XLT Sulfate resins). See for example: M. J. Hatch, J. A. Dillon, Acid Retardation. Simple Physical Method for Separation of Strong Acids from Their Salts, Ind. Eng. Chem. Process Des. Dev., 1963, 2 (4), pp 253–263. By way of further example, the acid removal unit (14) may include an engineered membrane system as described in Nystrom et al, MEMBRANE TECHNOLOGY, Volume 2000, Issue 117, January 2000, Pages 5–9.

The iron or copper removal unit (18) is not particularly limited and preferably includes an ion exchange resin, chelating resin or adsorbent that is selective for the metal or impurity of interest but is relatively non-selective for nickel. For example, the unit (18) may include a mixed bed of copper and iron selective resin such as AMBERLITE 747 or DIPHONIX™ resins.

The system operates according to a method characterized by the integration of CIX and electro-winning unit operations into a single continuous process with cost effective recycling of nickel-depleted raffinate (28) and optionally, acid (32). More specifically, the subject method includes the sequential steps of:

(a) passing the PLS (13) through an ion exchange bed (12; zone A) to load nickel onto the ion exchange resin and produce a raffinate solution (38),

(b) passing a sulfuric acid solution (42) through the loaded ion exchange bed (zone C) to strip nickel from the ion exchange resin and produce an eluate (16) having a pH less than 3, more preferably less than 2.5 and still more preferably less than 2.3,

(c) recovering the effluent (16) and removing a portion of sulfuric acid (14) sufficient to raise the pH above 3, more preferably above 3.2 and still more preferably to at least 3.5,

(d) electro-winning (22) the eluate (24) to produce electro-won nickel (26) and a nickel-depleted raffinate (28), and

5 (e) combining at least a portion of the nickel-depleted raffinate (28) with PLS (13) and repeating steps (a) through (d). In a preferred embodiment, step (c) further includes the step of removing a portion of at least one of copper and iron (18) from the effluent (20), such as by way of ion exchange, chelation or adsorption.

10 Many embodiments of the invention have been described and in some instances certain embodiments, selections, ranges, constituents, or other features have been characterized as being “preferred.” Characterizations of “preferred” features should in no way be interpreted as deeming such features as being required, essential or critical to the invention. Stated ranges include end points. The entire subject matter of each of the aforementioned patent documents is incorporated herein by reference.

CLAIMS:

1. A method for recovering nickel from a mixed metal product liquor solution containing nickel and at least copper or iron comprising passing the product liquor solution through a plurality of ion exchange beds containing nickel selective ion exchange resin that pass through process zones as part of a repeating nickel recovery circuit, wherein the method comprises the steps of:
- 5 (a) passing the product liquor solution through an ion exchange bed to load nickel onto the ion exchange resin (and produce a raffinate solution), and
- (b) passing a sulfuric acid solution through the loaded ion exchange bed to strip nickel from the ion exchange resin and produce an eluate having a pH less than 3,
- 10 wherein the method is characterized by the steps of:
- (c) recovering the effluent and removing a portion of sulfuric acid sufficient to raise the pH of the effluent above 3,
- (d) electro-winning the eluate to produce electro-won nickel and a nickel-depleted raffinate,
- 15 (e) combining at least a portion of the nickel-depleted raffinate with product liquor solution and repeating steps (a) through (d).
2. The method of claim 1 wherein step (c) further comprises removing a portion of at least one of copper and iron from the effluent.
- 20

Fig 1

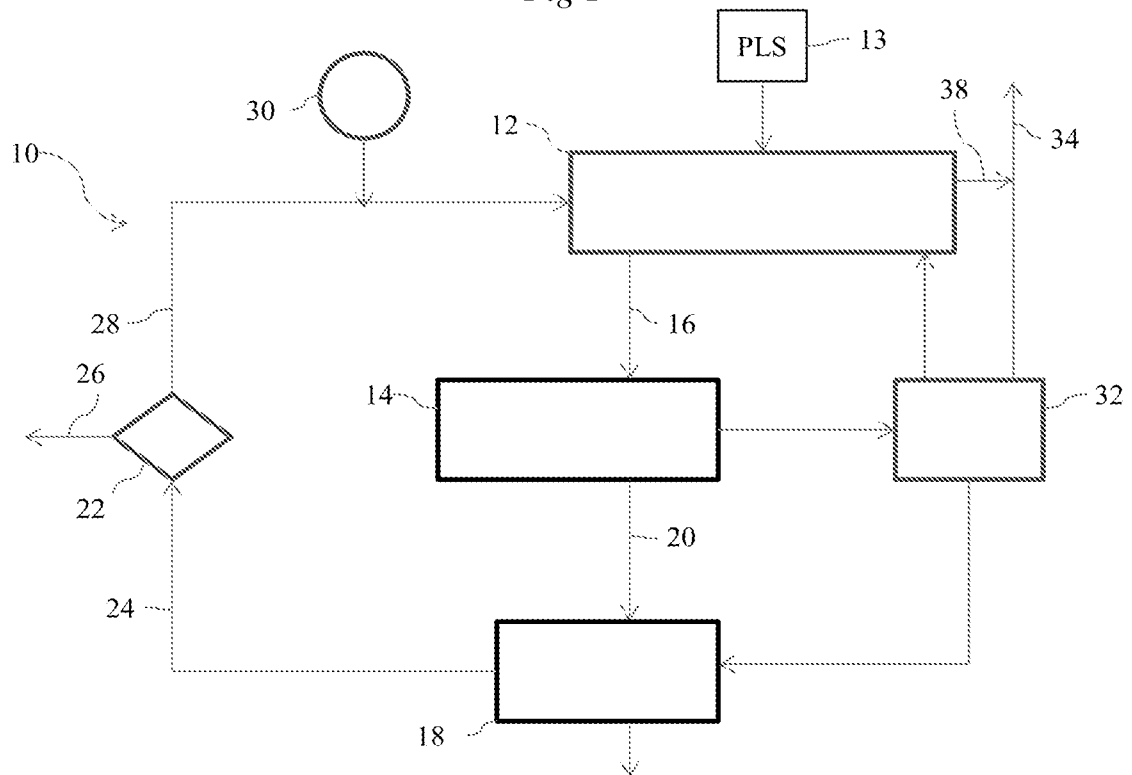
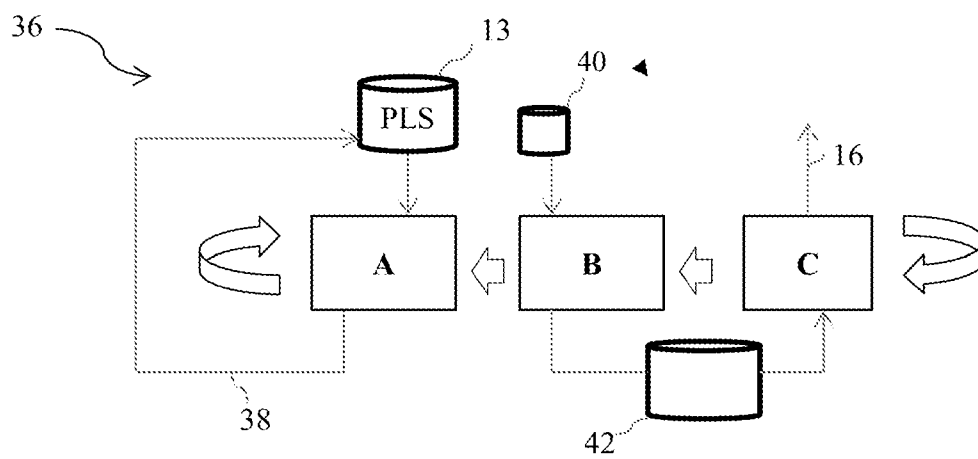


Fig 2



INTERNATIONAL SEARCH REPORT

International application No
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A. CLASSIFICATION OF SUBJECT MATTER
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ADD.

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

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96/20291 A1 (BHP MINERALS INT INC [US]; DUYVESTYEN WILLEM P C [US]; NEUDORF DAVID A) 4 July 1996 (1996-07-04) cited in the application the whole document	1,2
A	WO 2008/128278 A2 (METALLICA MINERALS LTD [AU]; GILLIES ANDREW LANGHAM [AU]; TREASURE PAT) 30 October 2008 (2008-10-30) the whole document	1,2
A	US 2001/001650 A1 (DUYVESTYEN WILLEM P C [US] ET AL) 24 May 2001 (2001-05-24) the whole document	1,2



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

"E" earlier application or patent but published on or after the international filing date

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

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"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

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9620291	A1	04-07-1996	AU 699127 B2 26-11-1998
		AU 4515396 A 19-07-1996	
		BR 9510115 A 30-12-1997	
		CO 4560388 A1 10-02-1998	
		OA 10492 A 10-04-2002	
		WO 9620291 A1 04-07-1996	
WO 2008128278	A2	30-10-2008	AU 2008241353 A1 30-10-2008
		WO 2008128278 A2 30-10-2008	
US 2001001650	A1	24-05-2001	AT 243773 T 15-07-2003
		AU 757360 B2 20-02-2003	
		AU 3515400 A 28-09-2000	
		DE 60003530 D1 31-07-2003	
		DE 60003530 T2 06-05-2004	
		EP 1159461 A1 05-12-2001	
		ES 2202079 T3 01-04-2004	
		GT 200000028 A 31-08-2001	
		US 2001001650 A1 24-05-2001	
		WO 0053820 A1 14-09-2000	