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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
20 December 2018 (20.12.2018)

WIPO | PCT

(10) International Publication Number
WO 2018/227237 A1

(51) International Patent Classification:
C22B 23/00 (2006.01) *C22B 3/20* (2006.01)
C22B 23/06 (2006.01) *C22B 3/44* (2006.01)

(21) International Application Number:
PCT/AU2018/050569

(22) International Filing Date:
08 June 2018 (08.06.2018)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
62/519,457 14 June 2017 (14.06.2017) US

(71) Applicants: **URBAN MINING PTY LTD** [AU/AU]; Level 1, 672 Murray Street, West Perth, Western Australia 6005 (AU). **NMR 360 INC** [CA/CA]; 5800 boulevard Thimens, Ville St. Laurent, Québec H4S 1S5 (CA).

(72) Inventors: **HARRIS, Bryn**; c/- 5800 boulevard Thimens, Ville St. Laurent, Québec H4S 1S5 (CA). **WHITE, Carl**; c/- 5800 boulevard Thimens, Ville St. Laurent, Québec H4S 1S5 (CA).

(74) Agent: **FPA PATENT ATTORNEYS PTY LTD**; Level 43, 101 Collins Street, Melbourne, Victoria 3000 (AU).

(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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2018/227237 A1

(54) Title: METHOD FOR THE PRODUCTION OF COBALT AND ASSOCIATED OXIDES FROM VARIOUS FEED MATERIALS

(57) Abstract: A method is disclosed for the recovery of cobalt, nickel and manganese from ores, concentrates, tailings, scrap alloys and spent batteries in an oxidic form, which is suitable for direct use in the manufacture of lithium-ion batteries, in particular. The process is unique in being able to recover cobalt, in particular, from concentrated solutions wherein the nickel to cobalt ratio is close to unity, rather than the more common 10:1 or 1:100. The process comprises selective oxidative precipitation of each metal under differing conditions of pH and ORP (oxidation-reduction potential). Sodium hypochlorite is the preferred precipitant, since it does not generate any acid, and is therefore self-buffering at the selected pH. A unique aspect of the process is to use Mn(VII) to effect the precipitation of Mn(II).

Method for the production of cobalt and associated oxides from various feed materials

Field of the invention

The present invention relates generally to methods for the production of cobalt and associated oxides from various primarily cobalt-bearing feed materials.

Background of the invention

The use of rechargeable Li-ion batteries has been growing steadily, and this growth will increase considerably as electric cars become more reliable and available, coupled with the increasing demand for off-peak mass electric power storage. It is variously estimated that there will be a significant shortfall of high-purity cobalt, in particular, by the year 2020.

There are no primary cobalt mines operating, with the metal generally being recovered as the by-product of copper (the African Copperbelt) or nickel (Canada and laterites) mining. With the former, the cobalt to nickel ratio is generally of the order of 100:1 in the cobalt sulphate solution derived from the leaching of concentrates, whereas in the latter, it is typically 1:10. Thus, in conventional processing, the requirement is either to remove a small amount of nickel from cobalt solutions, or a small amount of cobalt from nickel solutions.

Additionally, it can be expected that the recovery of cobalt and other metals from the recycling of spent Li-ion and similar batteries, and specialty alloys, will become significant, in order to recover specifically the cobalt, manganese and nickel. However, unlike the mining of by-product sources referred to above, the ratio of cobalt to nickel (and to manganese) can often be close to unity. Thus, rather than just a purification problem, each of the metals represents a major recovery opportunity, but also a separation problem. There are presently no operations that are separating all of these metals in a state of high-purity as valuable commodities from such feedstocks.

Douglas S. Flett, in an article entitled “Cobalt-Nickel Separation in Hydrometallurgy: a Review”, and published in Chemistry for Sustainable Development 12(2004), pages 81-91, reviewed all of the processes that have been used to effect

separation of small amounts of cobalt from nickel and vice versa. He concluded that solvent extraction processes were superseding precipitation processes for removing cobalt from nickel, and that ion exchange was the only method to effectively remove nickel from cobalt in a sulphate medium.

Oxidative precipitation processes for cobalt removal from nickel solutions, which have relevance to the current invention, were also reviewed. Much like is the case for the equivalent solvent extraction and ion exchange processes, it was noted that the issue with all of them was pH control, especially if significant amounts of cobalt were present, i.e. close to the 1:10 ratio referred to above. It was further noted that even strong oxidants such as Caro's Acid (H_2SO_5, peroxy monosulphuric acid), sometimes referred to as a superoxidant, were generally inadequate for effective and efficient cobalt removal. Additionally, all such reagents generate acid, requiring substantial amounts of base to be added at the same time.

G.M. Dunn, H.W. Schubert and H.E. Holliday, in an article entitled "Nickel Cobalt Separation with Superoxidants", published in Hydrometallurgy and Refining of Nickel and Cobalt, Volume 1 of Nickel Cobalt 97, Edited by W.C. Cooper and I. Mihaylov, CIM, Montreal, 1997, pages 197-210, describe the use of Caro's Acid and ozone as methods of oxidative precipitation. As with the article by Flett, it was noted that pH control is important, and also that the cobalt products contained significant amounts of nickel, requiring their re-processing. The large amounts of nickel co-precipitated were undoubtedly due to the long residence times employed.

With recycling, especially from the various types of lithium-ion batteries, more particularly from the so-called NMC (nickel-manganese-cobalt) batteries, and alloys such as alliages blancs, the ratios of cobalt to nickel are very much lower than those referred to above, often close to unity. The oxidative precipitative processes referred to above are inadequate, since they require large amounts of base, and generally co-precipitate large amounts of nickel along with the cobalt.

Different approaches to recovering cobalt are now being investigated, but none of them can generate a pure cobalt product directly suitable for use in battery manufacture. For instance, Retriev Technologies, in US Patent 8,882,007 B1, entitled "Process for Recovering and Regenerating Lithium Cathode Material From Lithium-Ion

Batteries", by W. Novis Smith and Scott Swoffer, published on November 11, 2014, describe a process wherein the original lithium cathode material is regenerated.

This process is also fundamentally pyrometallurgical, requiring a "low-temperature" (relative to smelting) roasting step combined with physical separation. Additional lithium hydroxide is then added to return the lithium content of the recovered cathode material to its original composition. It is not really a recovery process as such, but rather one of refurbishing the original component.

Akitoshi Higuchi et al., in an article entitled "Selective Recovery of Lithium from Cathode Materials of Spent Lithium Ion Battery", published in JOM, Volume 68, Number 10, October 2016, pages 2624-2631 noted that simpler metals recovery processes than presently exist are strongly required. Their somewhat surprising approach was to attempt to selectively recover the lithium, rather than the much more valuable cobalt. This was achieved by employing highly oxidising leaching conditions using sodium persulphate. High recoveries of lithium were obtained, whilst suppressing the dissolution of the other metallic components. The high oxidising potential of sodium persulphate effectively precludes any cobalt dissolution.

Eric Gratz, Qina Sa, Diran Apelian and Yan Wang, in an article entitled "A Closed Loop Process for Recycling Spent Lithium Ion Batteries", published in Journal of Power Sources 262 (2014), pages 255-262, describe a process for recycling spent batteries. Their mode of recovery is to precipitate a combined nickel-cobalt-manganese hydroxide, the composition of which is then adjusted to re-create the original battery material. This mode of recycling is also reported in a number of other articles.

Pratima Meshram, B.D. Pandey and T.R. Mankand, in an article entitled "Hydrometallurgical Processing of Spent Lithium Ion Batteries (LIBs) in the Presence of a Reducing Agent with Emphasis on Kinetics of Leaching", published in Chemical Engineering Journal 281 (2015), pages 418-427, describe a method of recovering cobalt from the leach solutions by precipitation of cobalt oxalate with oxalic acid. However, the considerable co-precipitation of nickel oxalate occurred, giving a cobalt purity of ~95%. A number of other researchers have reported similar processes using oxalic acid.

It is apparent from the foregoing that there is not yet any universal process, or combination of processes, for the high recovery of a pure form of cobalt from concentrated leach solutions. It would be beneficial if there were such a process, enabling high recoveries of cobalt, and the metals usually associated with cobalt, namely manganese and nickel, from a variety of different feedstocks. Such is important, since there is projected to be a significant shortfall in cobalt availability in the next half-decade.

In view of the above, it is desirable to provide a process for improving the recovery of cobalt while avoiding one or more of the problems of prior art processes.

Reference to any prior art in the specification is not an acknowledgment or suggestion that this prior art forms part of the common general knowledge in any jurisdiction or that this prior art could reasonably be expected to be understood, regarded as relevant, and/or combined with other pieces of prior art by a skilled person in the art.

Summary of the invention

In one aspect of the invention, there is provided a method for the recovery of cobalt from a Co- and Ni-containing aqueous solution, the method including:

providing a Co- and Ni-containing aqueous solution having a pH of from about 4.5 to about 6.5 and an oxidation-reduction potential of from about 750 to about 900 mV as measured against a Pt-Ag/AgCl electrode;

treating the Co- and Ni-containing aqueous solution with an amount of hypochlorite to oxidise and precipitate a portion of the cobalt to form a precipitate of CoOOH and to form a Co-lean Ni-aqueous solution; and

separating the CoOOH from the Co-lean Ni-containing aqueous solution.

This process advantageously recovers cobalt in a trivalent state oxidation state as opposed to prior art processes which typically recover cobalt salts in the divalent state. A cobalt product in the trivalent state is of particular economic value as it eliminates further processing steps, such as the oxidation of divalent cobalt, for

applications that require cobalt in the trivalent state – particularly in electrochemical processes such as those in battery operation.

In an embodiment, the Co- and Ni-containing aqueous solution is a chloride and/or sulphate solution.

In an embodiment, the Co is in the form of a Co^{2+} cation, and the Ni is in the form of a Ni^{2+} cation.

In an embodiment, the amount of hypochlorite is a sub-stoichiometric amount. Preferably, the sub-stoichiometric amount of hypochlorite is sufficient to precipitate up to 90% of the cobalt as CoOOH. Advantageously, the inventors have found that using a sub-stoichiometric amount of hypochlorite provides for a precipitate that is substantially pure CoOOH and substantially free of other metals. This high degree of purity is of particular importance as a number of applications, such as in electrochemical processes, demand high levels of purity if they are to be efficient. By substantially free of other metals, it is meant that on a comparative basis, other metals (for example Ni) are present in the precipitate in an amount of 0.5 wt% or less in comparison with Co (based on elemental Co). A preferred hypochlorite is NaOCl.

In embodiments where a sub-stoichiometric amount of hypochlorite is used, there is recoverable residual cobalt left in solution. Thus, in one form of this embodiment, the method further includes:

treating the Co-lean Ni-containing aqueous solution with an amount of hypochlorite to substantially oxidise and precipitate the remaining cobalt in the Co-lean Ni-containing aqueous solution as CoOOH and form a Co-barren Ni-containing aqueous solution; and

separating the CoOOH from the Co-barren Ni-containing aqueous solution.

In an embodiment, the pH of the Co- and Ni-containing aqueous solution is from about 5.0 to about 5.5.

In an embodiment, the oxidation-reduction potential of the Co- and Ni-containing aqueous solution is from about 800-850 mV.

In an embodiment, the step of treating the Co- and Ni-containing aqueous solution is conducted for a time of less than 2 hours.

In an embodiment, the step of treating the Co- and Ni-containing aqueous solution is conducted for a time of at least 30 minutes.

In an embodiment, the Co- and Ni-containing solution has a Co:Ni ratio of from about 100:1 to about 1:10. Preferably, the Co:Ni ratio is less than or equal to about 5.

In an embodiment, the method further includes a Ni-precipitating step including adding a precipitant to the Co-barren Ni-containing aqueous solution to precipitate nickel; and separating the nickel from the solution.

In one form of this embodiment, the precipitant is a carbonate.

In one form of this embodiment, prior to adding the precipitant, the pH of the Co-barren Ni-containing aqueous solution is adjusted to a value of from about 7.5 to 8.5.

In one form of this embodiment, the Ni-precipitating step is conducted at a temperature of from 45-80°C.

In an embodiment, the Co- and Ni-containing solution is substantially free of Cu, Fe, and Mn.

In an embodiment, the method includes:

treating a precursor solution containing at least Mn, Co, and Ni with a precipitant to selectively form a Mn-precipitate; and

separating the Mn-precipitate to form the Co- and Ni-containing aqueous solution.

In one form of this embodiment, prior to treating the precursor solution with the precipitant, the pH of the precursor solution is adjusted to a value of from about 3.5 to about 5.0.

In one form of this embodiment, the precipitant is a permanganate, and the permanganate oxidises the Mn to form a precipitate of MnO_2. Preferably, sufficient

permanganate is added to adjust the oxidation-reduction potential of the precursor solution to a value of from about 700 to about 800 mV as measured against a Pt-Ag/AgCl electrode.

In one form of this embodiment, prior to treating the precursor solution with the precipitant, the precursor solution is treated to remove iron and copper.

Further aspects of the present invention and further embodiments of the aspects described in the preceding paragraphs will become apparent from the following description, given by way of example and with reference to the accompanying drawings.

Brief description of the drawings

Figure 1: Process flow diagram of an embodiment of the invention.

Figure 2: XRD spectrum of solids produced according to an embodiment of the invention.

Detailed description of the embodiments

The description, and the embodiments described therein, is provided by way of illustration of examples of particular embodiments of principles and aspects of the present invention. These examples are provided for the purposes of explanation and not of limitation, of those principles of the invention. In the description that follows, like parts and/or steps are marked throughout the specification and the drawing with the same respective reference numerals.

The embodiments of the present invention shall be more clearly understood with reference to the following description and **Figure 1**.

Figure 1 provides a schematic representation of an embodiment of the invention for a method for the recovery of cobalt, manganese and nickel from a Co-, Ni- and Mn-containing aqueous feed solution. The Co, Ni and Mn are present in the solution in ionic form. The Co-, Ni-, and Mn-containing feed solution may be a sulphate and/or chloride based aqueous solution, in which case the Co, Ni, and Mn are present as sulphate and/or chloride salts and are in the form of Co(II) Ni(II), or Mn(II) respectively.

In this particular embodiment, the feed solution has been pre-treated to remove metal ions which may interfere with the recovery of cobalt from the Co-,Ni-, and Mn-containing aqueous feed solution to form a pre-purified feed solution 10. Such metal ions include at least Fe and Cu. Fe and Cu may be removed by methods known to those skilled in the art. Such methods may include precipitation with a base such as lime, electrowinning, solvent extraction or ion exchange. The Co-,Ni-, and Mn-containing aqueous feed solution may be subjected to additional treatment steps to remove other metal ion contaminants if necessary.

In this embodiment, the pre-purified feed solution 10 (being substantially free of Fe and Cu) additionally includes Mn ions (generally in the form of Mn(II)). The inventors have found that Mn(II) can be effectively removed in an oxidation/precipitation process that involves treating the pre-purified feed solution 10 with permanganate.

The pre-purified feed solution 10 is first adjusted 11 with caustic soda 12 to raise the pH to a value in the range of from about 3.5 to about 5.0, preferably from about 4.0 to about 4.5, and most preferably to a pH value of about 4.2. Sodium permanganate 14 is then added in order to preferentially and selectively oxidise the divalent manganese in solution 10 and form a precipitate slurry 15 that includes a manganese dioxide precipitate 17. In order to achieve this, sufficient permanganate is added to adjust the oxidation-reduction potential (ORP) of the pre-purified feed solution 10 to a value of from about 700 to about 800 mV (versus the Pt-Ag/AgCl electrode), and preferably to about 750 mV. Under these pH and ORP conditions, manganese can be selectively and quantitatively recovered while avoiding precipitation of cobalt or nickel according to Equation (1) below in a sulphate medium:

$$(1) \quad 3MnSO_4 + 2NaMnO_4 \rightarrow 5MnO_2 + H_2SO_4 + Na_2SO_4$$

It is important to adjust the concentration of the permanganate solution, such concentration being dependent upon the concentration of manganese in the feed solution (see equation (1)) and ensure that it is efficiently dispersed, since it may form localised areas of very high ORP promoting the formation of cobaltic oxide.

Sodium permanganate 14 is the preferred oxidant, because it is sufficiently powerful to affect the oxidation of divalent manganese in solution. Hydrogen peroxide,

for instance, a commonly-employed oxidant, does not work in this system. Potassium permanganate, a more common chemical than sodium permanganate, can also be used. However, this is more expensive to prepare than sodium permanganate.

The precipitation slurry 15 then undergoes solid-liquid separation 16. This may be effected by any convenient means, such as, but not limited to, flocculation and thickening, filter press or vacuum belt filter. The solids 17 are a pure form of manganese dioxide, part of which 19 are recycled to make sodium permanganate 14. To regenerate sodium permanganate, the solids portion 19 is first fused 20 with solid caustic soda 21, and the liquid melt 22 is quenched in water 23, where it dissolves 13 to form sodium permanganate solution 14. Sodium permanganate solution can be unstable if stored, but in this case it is used immediately, so no such issues arise. The remaining manganese dioxide solids 18 form a product for sale.

The treated feed solution 24 from solid-liquid separation 16 then proceeds to a first stage of cobalt precipitation 25 which is effected by the addition of sodium hypochlorite 27. The pH of the treated feed solution 24 is first adjusted by the addition of an alkali, such as caustic soda 26, to a value of from about 4.5 to about 6.5, preferably from about 5.0 to about 5.5. The ORP is then adjusted by the addition of sodium hypochlorite 27 to a value of from about 750 to about 900 mV, preferably from about 800 to about 850 mV (relative to the Pt-Ag/AgCl electrode). The inventors have found that these pH and ORP values allow for the preferential and selective oxidation of the cobalt (e.g. from Co(II) to Co(III)) and the precipitation of the cobalt in the form of a heterogenite, a hydrated cobaltic oxide, CoOOH. Equation (2) shows the reaction from a chloride medium:

$$(2) \quad 2CoCl_2 + 3NaOCl + H_2O_2 \rightarrow 2CoOOH + 3NaCl$$

Sodium hypochlorite is a common chemical, often referred to as household bleach, and is a powerful oxidising agent. It is rarely used in extractive metallurgy, however, because it introduces both sodium and chloride into predominantly sulphate-based processing schemes. However, it has been determined that its use is particularly suited to the recovery of cobalt when the concentration of both cobalt and nickel is high as described in this invention, since it does not generate any acid, unlike the processes

described in the prior art, and therefore requires no additional base, which is a major issue in conventional processing schemes.

Nickel can also react under these conditions which is undesirable. The reaction with nickel is very slow, given this, one option for preventing the reaction of nickel is by limiting the residence time. The inventors have found that by limiting the residence time, such as to a time of limited to less than two hours (and preferably of from about 30 to about 60 minutes) the co-precipitation of nickel can be avoided allowing an essentially pure cobalt product to be obtained (i.e. a cobalt precipitate that does not include additional metal co-precipitate). Further, using a sub-stoichimetric amount of sodium hypochlorite relative to cobalt can also avoid co-precipitation of nickel. In this regard, a multi-stage cobalt oxidation and precipitation process can be used. By way of example, and as shown in **Figure 1** in the first cobalt precipitation stage 25, sufficient sodium hypochlorite is used to precipitate 80 to 90% of the cobalt to ensure that no other metals, notably nickel, co-precipitate. The precipitation slurry 28 undergoes solid-liquid separation 29, which may be effected by any convenient means, such as, but not limited to, flocculation and thickening, filter press or vacuum belt filter. The solids 30 may, if desired, be dried to form cobaltic oxide, Co_2O_3.

The solution 31 then undergoes a second stage of cobalt precipitation 32 by the addition of excess sodium hypochlorite 33. This ensures that all of the cobalt is recovered. This may also result in the co-precipitation of a small amount of nickel. The second cobalt precipitation slurry 34 undergoes solid-liquid separation 35, which may be effected by any convenient means, such as, but not limited to, flocculation and thickening, filter press or vacuum belt filter. The solids 36 are returned to the leaching stage (not shown) of the flowsheet.

The solution 37 now substantially free of cobalt, then undergoes nickel precipitation 38. This is achieved by the addition of sodium carbonate 39 at a temperature from about 45 to about 80°C, preferably from about 60 to about 65°C. The pH of the solution is adjusted to and/or controlled at about 7.5 to about 8.5, and preferably about 8.0 to about 8.2. The precipitation slurry 40 undergoes solid-liquid separation 41, which may be effected by any convenient means, such as, but not limited

to, flocculation and thickening, filter press or vacuum belt filter. The solids 42 are pure nickel carbonate.

The solution 43, containing a mixture of sodium sulphate and sodium chloride if the original solution was sulphate, or just sodium chloride if the original solution was chloride, may be treated for their recovery if warranted, or simply disposed of.

The principles of the present invention are illustrated by the following example, which is provided by way of illustration, and should not be taken as limiting the scope of the invention.

Example 1

A solution containing 80 g/L Co and 20 g/L Ni was adjusted to pH 5.5 with caustic soda, and then sodium hypochlorite was added to raise the ORP to 850 mV (versus Pt-Ag/AgCl). Black solids were formed immediately, which after filtering, washing and air drying were found to contain 59% Co and just 0.2% nickel, with the balance being primarily oxygen. **Figure 2** shows an XRD scan of the solids which indicates that the solids are primarily heterogenite (CoOOH), together with a small amount of a mixed cobaltic-nickelic oxide.

This example demonstrates the ability of the process to recover a high-purity form of trivalent cobalt oxide from a solution containing high levels of nickel.

It will be understood that the invention disclosed and defined in this specification extends to all alternative combinations of two or more of the individual features mentioned or evident from the text or drawings. All of these different combinations constitute various alternative aspects of the invention.

CLAIMS

1. A method for the recovery of cobalt from a Co- and Ni-containing aqueous solution, the method including:

providing a Co- and Ni-containing aqueous solution having a pH of from about 4.5 to about 6.5 and an oxidation-reduction potential of from about 750 to about 900 mV as measured against a Pt-Ag/AgCl electrode;

treating the Co- and Ni-containing aqueous solution with an amount of a hypochlorite to oxidise and precipitate a portion of the cobalt as CoOOH and form a Co-lean Ni-aqueous solution; and

separating the CoOOH from the Co-lean Ni-containing aqueous solution.

2. The method of claim 1, wherein the amount of hypochlorite is a sub-stoichiometric amount.

3. The method of claim 2, wherein the sub-stoichiometric amount of hypochlorite is sufficient to precipitate up to 90% of the cobalt as CoOOH.

4. The method of claim 2, wherein the method further includes:

treating the Co-lean Ni-containing aqueous solution with an amount of hypochlorite to substantially oxidise and precipitate the remaining cobalt in the Co-lean Ni-containing aqueous solution as CoOOH and form a Co-barren Ni-containing aqueous solution; and

separating the CoOOH from the Co-barren Ni-containing aqueous solution.

5. The method of claim 1, wherein the pH of the Co- and Ni-containing aqueous solution is from about 5.0 to about 5.5.

6. The method of claim 1, wherein the oxidation-reduction potential of the Co- and Ni-containing aqueous solution is from about 800-850 mV.

7. The method of claim 1, wherein the step of treating the Co- and Ni-containing aqueous solution is conducted for a time of less than 2 hours.

8. The method of claim 1, wherein the step of treating the Co- and Ni-containing aqueous solution is conducted for a time of at least 30 minutes.

9. The method of claim 1, wherein the Co- and Ni-containing solution has a Co:Ni ratio of from about 100:1 to about 1:10.

10. The method of claim 9, wherein Co:Ni ratio is less than or equal to about 5.

11. The method of claim 1, wherein the method further includes a Ni-precipitating step including adding a precipitant to the Co-barren Ni-containing aqueous solution to precipitate nickel; and separating the nickel from the solution.

12. The method of claim 11, wherein the precipitant is a carbonate.

13. The method of claim 11, wherein prior to adding the precipitant, the pH of the Co-barren Ni-containing aqueous solution is adjusted to a value of from about 7.5 to 8.5.

14. The method of claim 11, wherein the Ni-precipitating step is conducted at a temperature of from 45-80°C.

15. The method of claim 1, wherein the Co- and Ni-containing solution is substantially free of Cu, Fe, and Mn.

16. The method of claim 1, wherein the method includes:

treating a precursor solution containing at least Mn, Co, and Ni with a precipitant to selectively form a Mn-precipitate; and

separating the Mn-precipitate to form the Co- and Ni-containing aqueous solution.

17. The method of claim 16, wherein prior to treating the precursor solution with the precipitant, the pH of the precursor solution is adjusted to a value of from about 3.5 to about 5.0.

18. The method of claim 16, wherein the precipitant is a permanganate, and the permanganate oxidises the Mn to form a precipitate of MnO_2.

19. The method of claim 18, wherein sufficient permanganate is added to adjust the oxidation-reduction potential of the precursor solution to a value of from about 700 to about 800 mV as measured against a Pt-Ag/AgCl electrode.

20. The method of claim 16, wherein prior to treating the precursor solution with the precipitant, the precursor solution is treated to remove iron and copper.

1/2

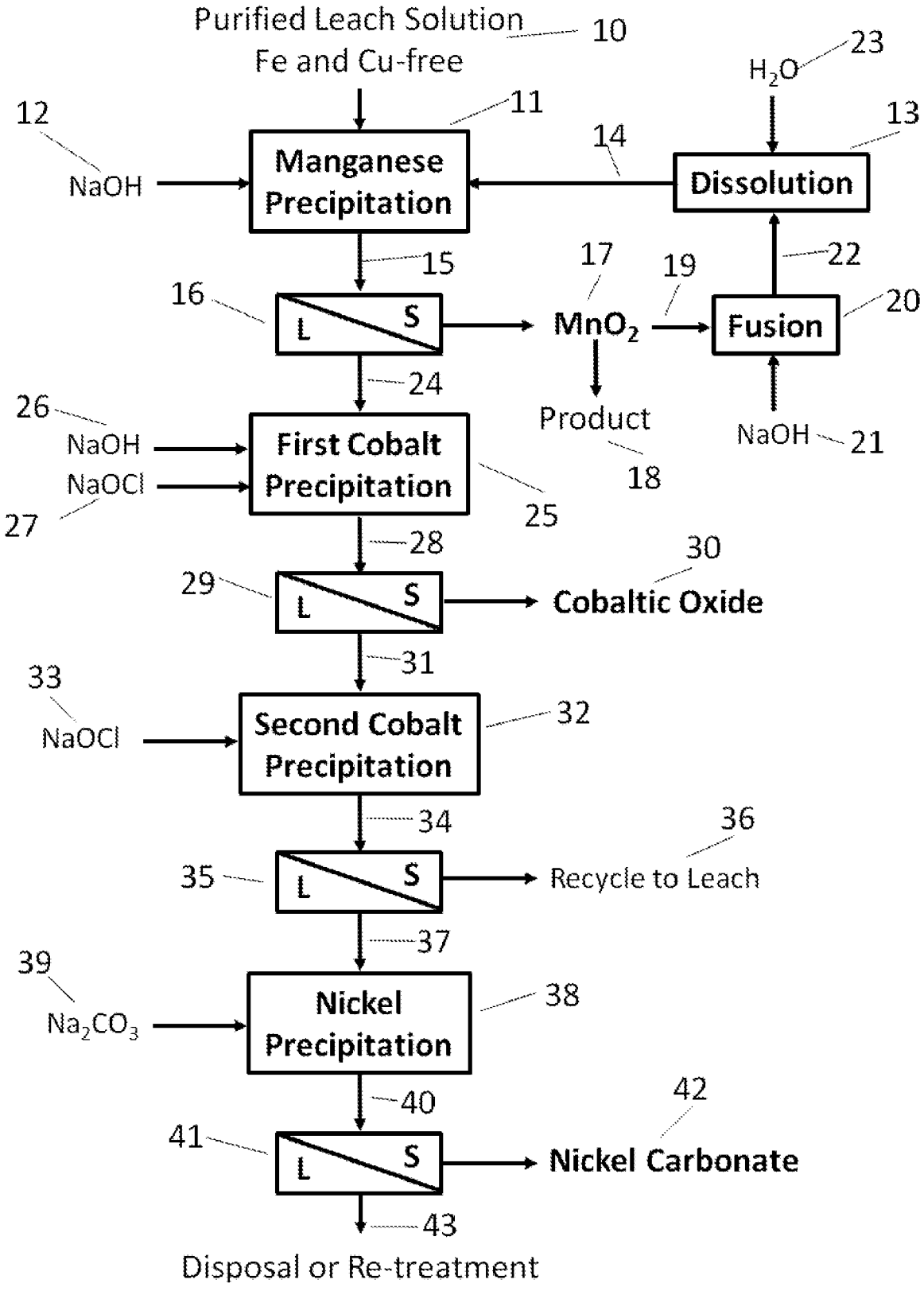
Purified Leach Solution
Fe and Cu-free
10
H_2O
23
12
NaOH
11
Manganese Precipitation
14
Dissolution
13
15
17
19
22
16
L
S
MnO_2
Fusion
20
24
Product
18
NaOH
21
26
NaOH
NaOCl
27
First Cobalt Precipitation
25
28
30
29
L
S
Cobaltic Oxide
31
33
NaOCl
Second Cobalt Precipitation
32
34
36
35
L
S
Recycle to Leach
37
39
Na_2CO_3
Nickel Precipitation
38
40
42
41
L
S
Nickel Carbonate
43
Disposal or Re-treatment

Figure 1

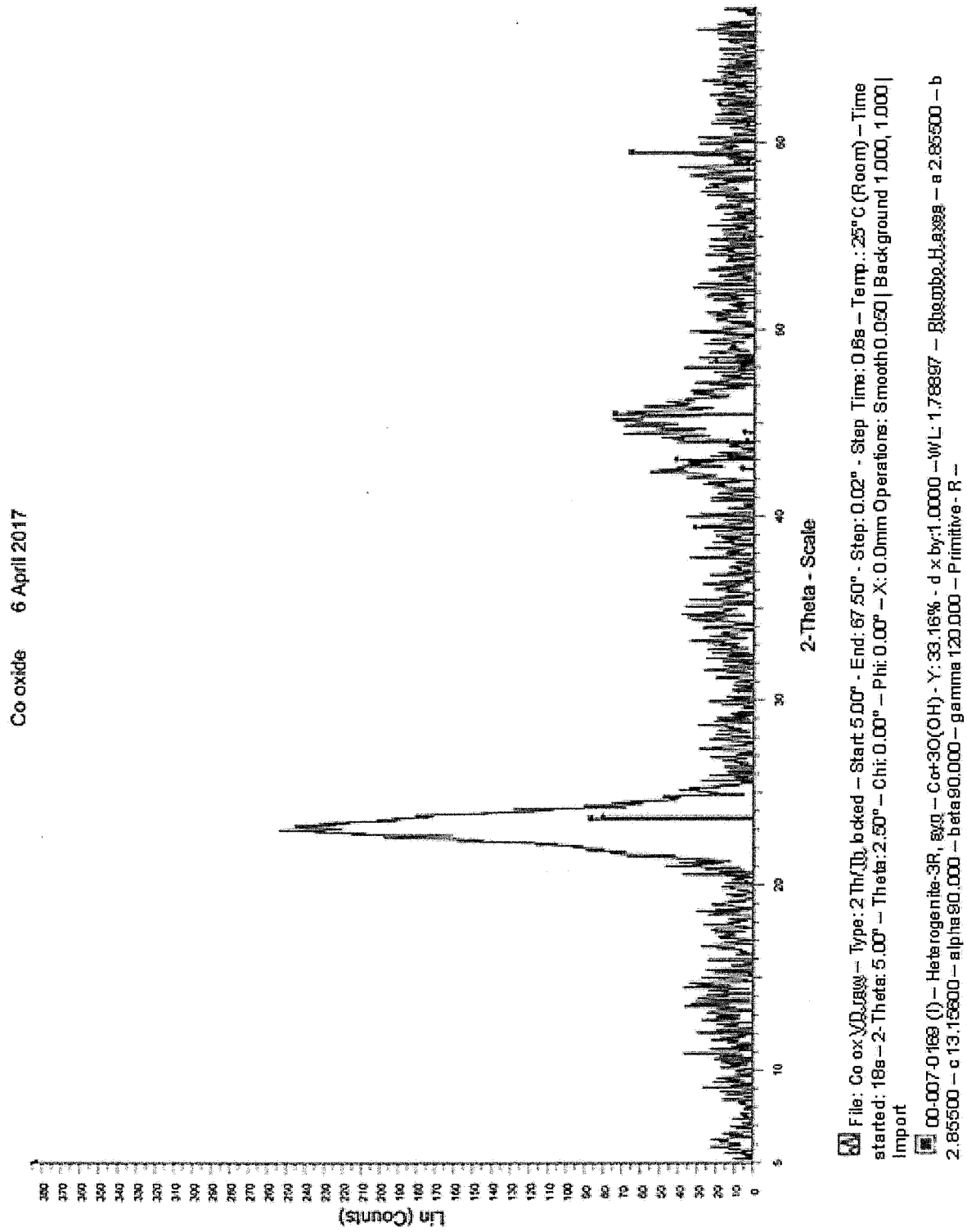
Co oxide 6 April 2017
Lin (Counts)
2-Theta - Scale
File: Co ox.XRAW – Type: 2Th/Th locked – Start: 5.00° - End: 67.50° - Step: 0.02° - Step Time: 0.8s – Temp.: 25°C (Room) – Time started: 18s – 2-Theta: 5.00° – Theta: 2.50° – Chi: 0.00° – Phi: 0.00° – X: 0.0mm Operations: Smooth 0.050 | Background 1.000, 1.000 | Import
00-007-0169 (I) – Heterogenite-3R, syn – Co+3O(OH) - Y: 33.16% - d x by: 1.0000 – WL: 1.78897 – Rhombo.H.axes – a 2.85500 – b 2.85500 – c 13.15600 – alpha 90.000 – beta 90.000 – gamma 120.000 – Primitive - R –

Figure 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU2018/050569

A. CLASSIFICATION OF SUBJECT MATTER

C22B 23/00 (2006.01) C22B 23/06 (2006.01) C22B 3/20 (2006.01) C22B 3/44 (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)

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)

EPOQUE tools: PATENW, XFULL and abstract cluster (EPODOC, WPIAP) with IPC/CPC Class marks: C22B3/04, C22B23, C22B3/04, C22B23/06, C22B3/20 C22B23/0423, C22B23/0453, C22B7, C22B7/006, C01G51/04, Y02P10/234; and keywords (cobalt, nickel, extraction, heterogenite, CoOOH, cobaltic oxide, cobaltous hydroxide, cobaltic oxyhydroxide, trivalent cobalt, oxidant, hypochlorite, hypohalite, ORP, oxidation reduction , potential eh, vollts, millivolts, ph, precipitate, filtration, separation and like terms); Google, Google Advanced Patent Search, Google Scholar, Espacenet search using keywords (cobalt, Nickel, heterogenite, hypochlorite, precipitate, pH, ORP and like terms); Applicant(s)/Inventor(s) name searched in Esapcenet, Auspat and in internal databases provided by IP Australia.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	

[X] Further documents are listed in the continuation of Box C [X] 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

"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)

"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	Date of mailing of the international search report
7 August 2018	07 August 2018

Name and mailing address of the ISA/AU	**Authorised officer**
AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustralia.gov.au	Kosala Gunatillaka AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. +61262223652

INTERNATIONAL SEARCH REPORT C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		International application No. **PCT/AU2018/050569**
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2011157604 A (SUMITOMO METAL MINING CO.) 18 August 2011, Abstract and specification - English translation retrieved from Esapcenet Abstract; paragraphs [0003] and [0026] - [0030]	1 - 20
A	US 2014/0023572 A1 (VAUGHAN et al.) 23 January 2014 Abstract, paragraphs [0058] – [0070]	1 - 20
A	US 2004/0228783 A1 (HARRIS et al.) 18 November 2004 Abstract; paragraphs [0110] - [0111] and claim 1, 19 & 39	1 - 20
A	US 2011/0232421 A1 (HERNANDEZ et al.) 29 September 2011 Abstract; claim 16 and paragraphs [0051] – [0058]	1 - 20

INTERNATIONAL SEARCH REPORT Information on patent family members	International application No. **PCT/AU2018/050569**

This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document/s Cited in Search Report		**Patent Family Member/s**	
Publication Number	**Publication Date**	**Publication Number**	**Publication Date**
JP 2011157604 A	18 August 2011	JP 2011157604 A	18 Aug 2011
US 2014/0023572 A1	23 January 2014	US 2014023572 A1	23 Jan 2014
		US 9447480 B2	20 Sep 2016
		AU 2012211033 B2	20 Oct 2016
		CA 2825583 A1	02 Aug 2012
		CN 103459621 A	18 Dec 2013
		CN 103459621 B	03 Feb 2016
		EP 2668303 A1	04 Dec 2013
		JP 2014504677 A	24 Feb 2014
		JP 6081926 B2	15 Feb 2017
		KR 20140006875 A	16 Jan 2014
		KR 101861885 B1	28 May 2018
		US 2016355906 A1	08 Dec 2016
		WO 2012100293 A1	02 Aug 2012
US 2004/0228783 A1	18 November 2004	None	
US 2011/0232421 A1	29 September 2011	US 2011232421 A1	29 Sep 2011
		US 8758479 B2	24 Jun 2014
		AU 2008251010 A1	20 Nov 2008
		AU 2008251010 B2	12 Jul 2012
		CN 101680053 A	24 Mar 2010
		CO 6321141 A2	20 Sep 2011
		WO 2008138039 A1	20 Nov 2008

End of Annex

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.