



## (51) International Patent Classification:

*C22B 3/10* (2006.01)      *C22B 19/28* (2006.01)  
*B01D 11/02* (2006.01)      *C22B 3/22* (2006.01)  
*C22B 19/20* (2006.01)      *C22B 3/44* (2006.01)

## (21) International Application Number:

PCT/CA2019/051710

## (22) International Filing Date:

29 November 2019 (29.11.2019)

## (25) Filing Language:

English

## (26) Publication Language:

English

## (30) Priority Data:

62/773,610      30 November 2018 (30.11.2018) US

(71) Applicant: 9203-5468 QUEBEC INC. DBA NMR360  
 [CA/CA]; 159-4148A Sainte-Catherine St. West, West-  
 mount, Québec H3Z 0A2 (CA).

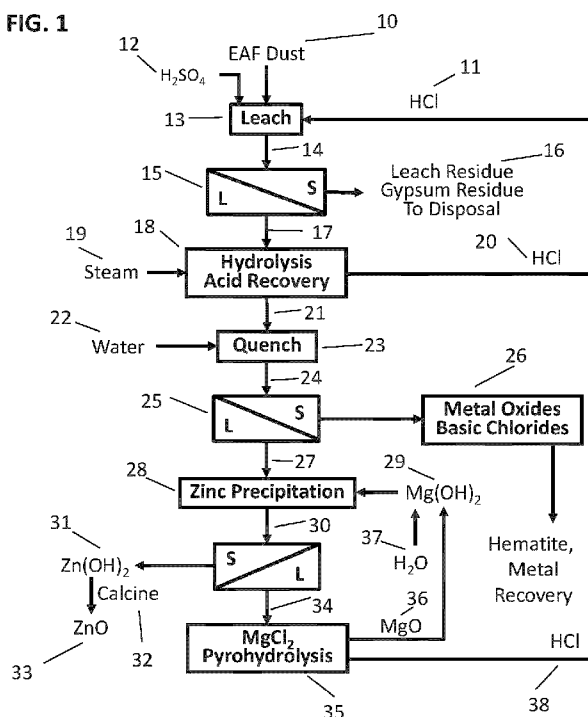
(72) Inventors: HARRIS, Bryn; 3312 Dornie Road, Alexan-  
 dria, Ontario K0C 1A0 (CA). WHITE, Carl; 5850 Thimens  
 Boulevard, Ville Saint-Laurent, Québec H4S 1S5 (CA).

(74) Agent: CALVET, Damien et al.; Gowling WLG (Canada)  
 LLP, 3700-1 Place Ville Marie, Montréal, Québec H3B 3P4  
 (CA).

(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,

(54) Title: PROCESS FOR THE RECOVERY OF VALUE METALS FROM ZINC-BEARING ORES, CONCENTRATES, INTER-  
 MEDIATES AND WASTES

FIG. 1



(57) Abstract: A process for recovering zinc and associated value metals from zinc-bearing ores, concentrates and intermediates, especially from electric arc furnace dust (EAFD) and spent steel mill zinc pickle liquor (ZPL), comprising leaching the feed material in recycled, concentrated hydrochloric acid, recovering iron as a pure form of hematite, precipitating pure zinc hydroxide and drying said product to form pure zinc oxide, and recovering magnesia via pyrohydrolysis. Value metals such as silver, copper, lead and cadmium are also recovered as pure products. A particular embodiment is to combine EAFD with spent steel plant pickling liquors, and in particular with spent steel plant ZPL. The present invention provides a single process which permits the recovery of iron, zinc and any other metals in a form of economic value, and to generate within the process its own reagents for internal recycle.



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))

## **PROCESS FOR THE RECOVERY OF VALUE METALS FROM ZINC-BEARING ORES, CONCENTRATES, INTERMEDIATES AND WASTES**

### **Cross-Reference to Related Applications**

- 5    **[0001]** The present patent application claims the benefits of priority of U.S. Provisional Patent Application No. 62/773,610 entitled “PROCESS FOR THE RECOVERY OF VALUE METALS FROM ZINC-BEARING ORES, CONCENTRATES, INTERMEDIATES AND WASTES”, and filed at the United States Patent and Trademark Office on November 30, 2018, the content of which is incorporated herein by reference.

### **Field of the Invention**

**[0002]** The present invention relates generally to processes for the recovery of zinc and associated value metals, such as lead, silver, copper, manganese, iron and cadmium in a marketable form from various zinc-bearing feedstocks.

### **Background of the Invention**

- 15   **[0003]** Primary zinc is generally recovered from ores and concentrates either pyrometallurgically by smelting, hydrometallurgically by pressure leaching combined with electrowinning, or a combination thereof by roasting and atmospheric leaching together with electrowinning (the so-called RLE process). All of these processes have significant issues with sulphur in one way or another, resulting in the requirement for either a sulphuric acid plant, or
- 20   a method of disposing of the excess sulphate. Disposal practices focus on the formation of jarosite, an iron-sulphate compound, or gypsum, both of which result in the need for dedicated large tailings ponds. Other valuable metals, such as silver, lead, copper and cadmium in zinc concentrates are generally not recovered, or are recovered as impure by-products, or disposed of.
- 25   **[0004]** A number of pyrometallurgical and hydrometallurgical techniques have been developed for recovering zinc and associated metals such as lead, silver, cadmium, copper and iron from various intermediate zinc-bearing sources, especially from steel plant EAFD (Electric Arc Furnace Dust).
- [0005]** The following Table summarises many of these processes, none of which, apart from
- 30   Ezinex and a number of Waelz Kiln operations, have achieved commercial operation.

| IRON PRODUCT                                                 | PROCESS                        | PROCESS TYPE                                   | ZINC PRODUCT       |
|--------------------------------------------------------------|--------------------------------|------------------------------------------------|--------------------|
| <b>Pig Iron</b><br>Total Fe: >90%<br>Metallization: 95%      | IBDR-ZIPP                      | Plasma furnace/hydrometallurgical              | Crude ZnO/Zn metal |
| Total Fe: >85%<br>Metallization: 95%                         | Kawasaki Steel                 | Vertical shaft furnace                         | Crude ZnO          |
| Total Fe: 97%<br>Metallization: >95%                         | ESI-MetWool                    | Cupola furnace                                 | Crude ZnO          |
| Total Fe: 94%<br>Metallization: n/a                          | Enviroplas                     | Plasma furnace                                 | Zn metal           |
| <b>DRI</b><br>Total Fe: ~ 80%<br>Metallization: >90%         | MRT (pyro/hydro)               | Rotary hearth furnace/NH <sub>4</sub> Cl leach | Crude ZnO          |
| Total Fe: 75-85%<br>Metallization: >90%                      | AllMet (pyro/pyro)             | Rotary hearth furnace/plasma furnace           | Crude ZnO/Zn metal |
| <b>Iron Rich Material</b><br>Total Fe: 53%<br>% metallized:  | ZTT                            | Inclined rotary reduction system               | Crude ZnO          |
| Total Fe: 55.3%<br>Metallic Fe: 35%                          | Horsehead Resource Development | Waelz kiln                                     | Crude ZnO          |
| Total Fe: n/a<br>Metallization: n/a                          | AICHI Steel/Toyota Motor Corp. | Vacuum heating reduction furnace               | Crude ZnO          |
| <b>Other Iron Product</b><br>Hematite                        | Terra Gaia Environmental       | Pressure leach                                 | ZnS                |
| Magnetite                                                    | Phoenix Environmental          | Oxygen lance furnace                           | Crude ZnO          |
| <b>Other</b><br>Iron Oxide: 50-60%<br>Zn: 8-12%<br>(ferrite) | Ezinex                         | Chloride leach                                 | Zn metal           |
| Iron Oxide Residue                                           | Zincex                         | Sulphuric acid leach                           | Zn metal           |
| Iron Oxide Residue                                           | Cashman                        |                                                | ZnO                |
| Inert Slag                                                   | Ausmelt                        | Plasma furnace                                 | Crude ZnO          |
| Inert Slag                                                   | Laclede Steel                  | Plasma furnace                                 | Zn metal           |

[0006] The most common technique currently practiced is pyrometallurgical, wherein the dust is smelted in a Waelz Kiln to fume off an impure zinc oxide. This zinc oxide invariably contains the other volatile materials in the EAFD, notably lead, cadmium and the halogens. All of these are detrimental to directly processing the zinc oxide in an electrolytic zinc refinery, such that secondary processing of the zinc oxide is usually required.

[0007] Further drawbacks of the Waelz Kiln Process are that zinc recoveries are generally in the range of 70%, and that a toxic slag is produced which requires a secure landfill. Occasionally, this slag can be suitable for use as road aggregate. There is no commercial process currently in operation for the re-processing of the slag, and nor could a secondary

treatment process be conceived of as being economic.

[0008] Numerous hydrometallurgical processes have been attempted, but the problem with such processes has been their inability to generate an iron-product suitable either for sale or for return to the steel plant. R.O. McElroy in U.S. Patent 5,336,297, issued to Terra Gaia on August 9, 1994, entitled "*Process for the Treatment of Electric Arc Furnace Dust*", and in a concurrent publication, R.O. McElroy and M. McClaren entitled "*Processing of Electric Arc Furnace Dust Via Chloride Hydrometallurgy*", published in Hydrometallurgy '94, Proceedings of an International Conference by IMM and SCI, Chapman and Hall publishers, July 1994, pp. 993-1010, describes a process wherein EAFD is leached in ferric chloride solution, and the iron precipitated as hematite in an autoclave. Zinc is recovered from the iron-free filtrate by solvent extraction and lead by cooling crystallisation. No methodology for the recovery of any silver, copper or cadmium is provided, nor is it mentioned how calcium, magnesium and manganese, all of which are normally present in most zinc feedstocks, are dealt with.

[0009] Ho In Lee, et al., in U.S. Patent 6,338,748 issued to Sangwon EnC Company on January 15, 2002, entitled "*Hydrometallurgical Method for Recovery of Zinc from Electric Arc Furnace Dust*", describe a hydrometallurgical process for the recovery of zinc metal from electric arc furnace dust. In this process, in order to selectively leach zinc and minimize iron dissolution by simultaneously precipitating it as FeOOH and Fe<sub>2</sub>O<sub>3</sub>, hot acid leaching is carried out with the aqueous solution containing 37-74 g/L HCl (i.e. 1-2M) and 104-270 g/L ZnCl<sub>2</sub>. The leach solution is purified by zinc oxide addition and then with activated carbon prior to electrowinning of zinc. The purpose of adding the zinc oxide is to raise the pH of the solution in order that residual iron and other impurities will be selectively precipitated.

[0010] This process wherein the dust itself is used to neutralise the iron must necessarily result in a low recovery of zinc, since if the residue were to be re-leached, there would be no outlet for the iron. Such a process also would not allow the effective recovery of minor metals such as silver and copper.

[0011] Further purification is proposed in the process by the addition of zinc powder to recover lead, copper and cadmium. This must be only as a polishing step, since most of these metals would have been removed either during iron precipitation or by activated carbon. This is certainly not a primary recovery step.

[0012] W.P.C. Duyvesteyn and M.C. Jha, in U.S. Patent 4,572,771 issued to Amax Inc. on February 25, 1986 entitled "*Zinc Recovery from Steel Plant Dusts and Zinciferous Materials*", describe a process wherein a zinc-bearing residue, and especially EAF dust, is leached with hydrochloric acid to provide a pregnant liquor containing zinc, iron, and lead. The iron and

other impurities such as lead are selectively removed from the pregnant liquor by precipitation with lime, and the zinc extracted from the purified liquor by solvent extraction. The zinc is subsequently stripped from the organic solvent using water or hydrochloric acid to provide a zinc chloride solution which is then fed to an electrowinning cell for the production of marketable electrolytic zinc. Chlorine gas from zinc electrowinning is burned with hydrogen to reconstitute the hydrochloric acid for recycle to the leaching stage.

[0013] C. Allen, et al. in U.S. Patent 6,395,242 B1, issued to Noranda Inc. on May 28, 2002, entitled "*Production of Zinc Oxide from Complex Sulfide Concentrates Using Chloride Processing*", describe a process for the recovery of zinc oxide from complex sulphide concentrates using chloride processing. In this process, the feed material is leached with hydrochloric acid and oxygen, the iron is precipitated oxidatively with magnesium oxide, and the lead, silver, copper, cadmium and cobalt are recovered as a single mixed product using zinc dust, and finally zinc hydroxide precipitated by magnesium oxide. The resultant magnesium chloride solution undergoes pyrohydrolysis to regenerate the magnesium oxide and recycle the hydrochloric acid. This necessarily generates a relatively dilute acid (<18%), thus limiting the concentration of zinc that can be taken into solution. Zinc chloride is very soluble (1800 g/L or 27M at 20°C), such that 18% acid (~6M) is very dilute in comparison, and does not take advantage of the high zinc solubility, therefore leading to appreciable water balance issues.

[0014] Using zinc dust to precipitate all of the copper, lead, silver, cadmium and cobalt is expensive, since zinc dust is a premium reagent. Normally, there are other impurities in these complex feeds such as aluminium, calcium and manganese. The process described by Allen et al. does not address these metals, all of which will report to the final magnesium chloride liquor. Calcium chloride, in particular, does not decompose during pyrohydrolysis, and will therefore both debase the magnesium oxide product, as will aluminium and manganese, as well as incurring significant chloride losses, and nor will it allow any bleed for calcium.

[0015] Spent zinc pickle liquor (ZPL) is the waste product containing zinc and ferrous chlorides from steel plant galvanizing pickling lines. At the present time, there is no method for treating this, and it is commonly disposed of by deep well injection.

[0016] Steel plant spent pickle liquor (SPL) is a waste material containing predominantly ferrous chloride. Current methodology for treating this is via spray or fluid bed roasting, which is costly and is only able recover acid at a strength of 18%, rather than concentrated acid at 33-35% strength.

[0017] In light of the foregoing, it would be advantageous to be able to not only separate, but also to selectively recover all the valuable components found in concentrates, EAFD and

similar feeds, such as, but not limited to, silver, copper, lead, cadmium, manganese, magnesium and calcium in a generally useful and pure form, together with concentrated (33-36% HCl) hydrochloric acid for recycle within the flowsheet.

[0018] Additionally, wherein there is significant sulphur in the feed, it would be advantageous to either recover, or at the very least dispose of this in its elemental form rather than either having to dispose of large volumes of toxic tailings, or the need to build a sulphuric acid plant.

[0019] Furthermore, it would be additionally advantageous to combine such a process with treating spent galvanizing zinc pickle liquor, for which there is no existing method of recovering the contained zinc, and also to combine this with treating this spent steel plant pickling liquor.

### Summary of the Invention

[0020] The shortcomings of the prior art are generally mitigated by the new process disclosed herein for treating zinc-bearing ores, concentrates, intermediates or residues.

[0021] According to a first aspect, the invention is directed to a process for recovering zinc and associated value metals from zinc-bearing feed material, the process comprising:

- a) providing a feed material comprising at least zinc and iron;
- b) leaching the feed material with a HCl leaching medium to generate a leachate and a solid residue, the leachate comprising at least zinc and iron;
- c) separating the solid residue from the leachate to generate a solution containing iron;
- d) heating the solution containing iron to cause precipitation of the metals, except zinc or calcium and any alkali metals if present, to generate a heated slurry and to recover hydrochloric acid in a concentrated form;
- e) quenching the heated slurry in water and filtering off resulting solids and a filtrate; and
- f) treating the filtrate from quenching to recover zinc hydroxide.

[0022] According to a preferred embodiment, the process may further comprise oxidising the solution containing iron to convert ferrous iron to ferric iron, the iron in the solution being predominantly in its ferric state or brought to ferric state. Preferably, the oxidation of ferrous iron is carried out electrolytically, including by adding HCl if necessary.

[0023] According to a preferred embodiment, the feed material may comprise other metals selected from the group consisting of copper, silver, lead, cadmium, manganese and magnesium, the process further comprising leaching the resulting solids in dilute hydrochloric

acid to effect re-dissolution of at least one of copper, silver, lead, cadmium, manganese and magnesium, if present. Preferably, the amount of hydrochloric acid as used is at least stoichiometric for the other metals present.

5 [0024] According to a preferred embodiment, the process may further comprise treating the filtrate from zinc precipitation using pyrohydrolysis to recover HCl. Preferably, a part of HCl recovered by pyrohydrolysis is recycled within the process.

[0025] According to a preferred embodiment, wherein the feed material is electric arc furnace dust (EAFD), or a complex lead-zinc-copper-silver ore or concentrate. Preferably, the spent zinc pickle liquor may be added to the electric arc furnace dust to provide additional iron and  
10 a portion of the HCl leaching medium.

[0026] According to a preferred embodiment, the leaching step is performed at a temperature of 25-110°C, preferably 80-100°C, more preferably 90-95°C.

[0027] According to a preferred embodiment, the leachate is cooled to crystallise out lead chloride.

15 [0028] According to a preferred embodiment, in step (d) the ferric solution is heated to a temperature of about 170-200°C, preferably about 180-190°C, in order to effect the hydrolysis of ferric iron and precipitation of hematite. Preferably, the reaction in step (d) may be allowed to proceed until no more HCl is evolved. More preferably, water or steam may be added at the end of the reaction in step (d) to ensure complete hydrolysis of all metals present except zinc,  
20 calcium and the alkali metals which do not hydrolyse.

[0029] According to a preferred embodiment, the amount of water used in the quenching step (e) is controlled to produce a magnesium chloride solution of 30 wt.% to 50 wt.%, when magnesium is present in the feed material.

25 [0030] In accordance with a broad aspect of the present invention, a process for treating zinc-bearing ores, concentrates, intermediates or residues, and in particular from steel plant toxic wastes such as electric arc furnace dust (EAFD) and spent pickle liquors, is disclosed. Such materials may contain lead, silver, cadmium, calcium, magnesium, manganese, aluminium and copper in addition to iron and zinc, all of which can be recovered in a marketable form, thereby maximising the value of the feed material. As discussed in the Background section above, no  
30 such process for achieving recovery of all of these metals currently exists.

[0031] As aforesaid, the process applies to electric arc furnace dust (EAFD) and complex zinc-

bearing ores and concentrates, and combined with SPL/ZPL (steel plant spent pickle and zinc pickle liquors). In a particular embodiment, the process combines EAFD and ZPL more efficiently than treating either on their own.

5 [0032] It is a further aspect of the invention that such feed materials may be advantageously combined with other steel plant wastes where appropriate, in particular spent zinc pickle liquor (ZPL) and/or spent pickle liquor (SPL). It is a further aspect of the invention that addition of ZPL or ZPL/SPL significantly improves the water balance of the process.

10 [0033] It is an aspect of the invention to provide a single process which permits the recovery of iron, zinc and any other metals in a form of economic value, and to generate within the process its own reagents for internal recycle.

[0034] Other and further aspects and advantages of the present invention will be better understood upon the reading of the illustrative embodiments about to be described or will be indicated in the appended claims, and various advantages not referred to herein will occur to one skilled in the art upon employment of the invention in practice.

15

#### **Brief Description of the Drawings**

[0035] The above and other aspects, features and advantages of the invention will become more readily apparent from the following description, reference being made to the accompanying drawings in which:

20 [0036] Figure 1 is a flowchart illustrating the process according to a preferred embodiment;

[0037] Figure 2 is a flowchart illustrating the process according to another preferred embodiment; and

[0038] Figure 3 is a flowchart illustrating the process according to yet another preferred embodiment.

#### **25 Detailed Description of the Preferred Embodiment**

[0039] A novel **process for treating zinc-bearing ores, concentrates, intermediates or residues** will be described hereinafter. Although the invention is described in terms of specific illustrative embodiments, it is to be understood that the embodiments described herein are by way of example only and that the scope of the invention is not intended to be limited thereby.

30 [0040] The terminology used herein is in accordance with definitions set out below.

[0041] As used herein % or wt.% means weight % unless otherwise indicated. When used herein % refers to weight % as compared to the total weight percent of the phase or composition that is being discussed.

5 [0042] By "about", it is meant that the value of weight % (wt.%), time, pH, volume or temperature can vary within a certain range depending on the margin of error of the method or device used to evaluate such weight %, time, pH, volume or temperature. A margin of error of 10% is generally accepted.

10 [0043] It is understood that the term "concentrate" used herein is a generic term used in mineral processing. Mined ore is crushed and ground, and then this undergoes some form of physical separation to separate the valuable minerals (concentrate) from the gangue (tailings). The method of separation may be for instance by flotation, gravity separation or dense medium, sieving, or magnetic separation, or any other known methods.

15 [0044] The description which follows, and the embodiments described therein are provided by way of illustration of an example 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.

20 [0045] In this particular example, the feed has been taken to be electric arc furnace dust (EAFD) containing recoverable amounts of iron, zinc, cadmium, copper, silver, lead, manganese, magnesium and, optionally, calcium. In the description that follows, like parts and/or steps are marked throughout the specification and the drawings with the same respective reference numerals.

25 [0046] According to a preferred embodiment, it is disclosed a process for treating a feed comprising zinc and/or iron, and optionally other metals selected from copper, silver, lead, cadmium, manganese and magnesium, the process comprising the following steps:

- i. leaching the feed material in hydrochloric acid to generate a solution containing at least zinc and iron and a solid residue;
- ii. separating the leach solution from the solid residue to generate a solution containing  
30 iron;
- iii. optionally, oxidising the ferric solution to convert any ferrous iron to ferric iron;
- iv. raising the temperature of the ferric solution to cause precipitation of the metals, except

zinc, or calcium and any alkali metals if present, to generate a heated slurry and to recover hydrochloric acid in a concentrated form;

- v. quenching the heated slurry in water and filtering off resulting solids and a filtrate;
- vi. leaching the solids in (dilute) hydrochloric acid to effect re-dissolution of copper, silver,
- 5       lead, cadmium, manganese and magnesium if present;
- vii. treating the filtrate from quenching to recover zinc hydroxide; and
- viii. treating the filtrate from zinc precipitation using pyrohydrolysis to recover HCl, part of which is optionally recycled.

10       [0047] According to a preferred embodiment, the oxidation, if needed, has to occur before the hydrolysis step, and the hydrolysis step preferably occur after solid/liquid separation of the leach.

[0048] According to a preferred embodiment, the feed material is electric arc furnace dust.

[0049] According to a preferred embodiment, the feed material is a complex lead-zinc-copper-silver ore or concentrate.

15       [0050] According to a preferred embodiment, the hydrochloric acid is recycled within the flowsheet. Preferably, for feeds containing sulphur, an oxidant optionally may also be used in the leaching step.

[0051] According to a preferred embodiment, electric arc dust and spent zinc pickle liquor are beneficially combined.

20       [0052] According to a preferred embodiment, spent steel plant pickle liquors are used to provide additional iron and to provide a portion of the chloride leaching medium. Preferably, the spent pickle liquors are used to replace fresh water and to improve the water balance.

[0053] According to a preferred embodiment, the temperature of the leaching reaction is 25-110°C, preferably 80-100°C, more preferably 90-95°C.

25       [0054] It has to be noted that the temperatures mentioned herein refer to temperatures measured under atmospheric pressure. It has to be understood that the process temperatures can be shifted by changing (increasing/decreasing) the pressure of reaction.

[0055] According to a preferred embodiment, the leach filtrate is optionally cooled to crystallise out lead chloride.

30       [0056] According to a preferred embodiment, the oxidation for ferrous iron is carried out electrolytically. Preferably, sufficient HCl is added to convert ferrous chloride to ferric.

Preferably, any temperature from ambient to 100°C may be used.

[0057] According to a preferred embodiment, the temperature is raised in step (iv) to 170-200°C, preferably 180-190°C, in order to effect the hydrolysis of ferric iron and precipitation of hematite.

5 [0058] According to a preferred embodiment, the reaction in step (iv) is allowed to proceed until no more HCl is evolved. Preferably, water, or more preferably steam, is added at the end of the reaction to ensure complete hydrolysis of all metals present except zinc, calcium and the alkali metals, which do not hydrolyse.

10 [0059] According to a preferred embodiment, the amount of acid added in step (vi) is at least stoichiometric for the base metals, silver and magnesium present.

[0060] According to preferred embodiments, the temperature in step (vi) is from ambient to 100°C, preferably ambient. Optionally, if the silver content is such as to produce a solubility of silver >100 mg/L, then sufficient recycled magnesium chloride is added to raise the chloride concentration to 2-5M, preferably 2-3M. More preferably, the silver is recovered by  
15 cementation with copper metal, and after silver is recovered, cadmium may be recovered by ion exchange with a strong sulphonic acid cationic resin or by ion exchange with a weak base quaternary amine resin. After silver and cadmium are recovered, copper is recovered by ion exchange with an iminodiacetate cationic resin or is recovered by ion exchange with a basic complex amine resin. The chloride content of the solution may be adjusted to 6-12M,  
20 preferably 8-10M, with recycled magnesium chloride, and manganese is recovered by ion exchange with a bis-picolyamine resin. Lead may be recovered by cementation with zinc dust, preferably with a temperature being from ambient to 100°C, preferably from 40-50°C. Preferably, air is excluded from the reactor. The residence time is limited from 2-10 minutes, preferably 5 minutes. The spent solution may be magnesium chloride with minor amounts of  
25 other metals including zinc, and may be recycled to the acid recovery stage of step (iv).

[0061] According to a preferred embodiment, the quenching step (v), the amount of water is controlled to produce a magnesium chloride solution of 30 wt.% to 50 wt.%, in step (vii). It is understood that some magnesium could be present where there is magnesium present in the feed.

30 [0062] Referring to Figure 1, there is shown a schematic representation of a process for the recovery of zinc in accordance with one embodiment of the invention. For simplicity, Figure 1 depicts the process as it applies to electric arc furnace dust (EAFD), but it is understood that

it equally applies to other zinc-rich feed materials. Broadly speaking, the process as shown in Figure 1 and Figure 2 combined involves the recovery of iron material, zinc material, a copper material, a silver material, a manganese material, a magnesium material, a cadmium material and a lead material, and where ZPL and SPL are included, of concentrated hydrochloric acid.

5 [0063] The feed material 10 is leached 13 with recycled hydrochloric acid 11 to dissolve all of the iron and zinc. Additionally, lead, copper, silver, cadmium, manganese and some flux/slag material within the dust containing magnesium and calcium also dissolve. Any aluminium present will also partially dissolve, the degree of dissolution being highly dependent on the source of the material.

10 [0064] Optionally, spent pickle liquor and/or spent zinc pickle liquor (not shown) may be added along with the recycled hydrochloric acid as an additional source of zinc, iron and/or hydrochloric acid, and in particular, in place of any fresh water that might be needed, to the solids concentration in the leach.

15 [0065] In this embodiment, sulphuric acid 12 is also added to the leach to precipitate any calcium as calcium sulphate, which may be in the form of gypsum, hemi-hydrate or anhydrite, with the former phase preferred. Adding sulphuric acid at this stage allows for maximum dissolution of the other metals, since the hydrochloric acid associated with the calcium is liberated. An added advantage of doing so is that the calcium phase markedly improves the subsequent solid/liquid separation step 15.

20 [0066] Alternative embodiments, especially if gypsum is a desired product in its own right, is to add the sulphuric acid in a separate step after the leach, or prior to magnesium chloride hydrolysis 35 at the end of the circuit.

25 [0067] The hydrochloric acid concentration may be of any value that causes leaching to take place, but ideally will be such to give metal ion concentration in the range of 70-100% of its solubility, and preferably 80-90% of its solubility. Since zinc, and to a lesser extent ferric iron, is highly soluble (>2000 g/L Zn in chloride media at leaching temperatures), realistically, the maximum acid concentration possible is used. This is a significant advantage over those processes employing pyrohydrolysis, where the acid concentration is limited to 6M. The addition of ZPL, in particular, allows for a very high zinc concentration, and a more efficient  
30 process.

[0068] The principal chemical reactions are as shown in reactions (1) and (2).





Similar reactions take place for other materials contained in the feed material.

[0069] The leaching stage 13 is carried out at atmospheric pressure.

[0070] The leaching temperature is maintained above 70°C, and preferably above 90°C.

5 [0071] Solid-liquid separation 15 of the leach slurry 14 may be effected by any convenient means, such as, but not limited to, flocculation and thickening, filter press or vacuum belt filter. The solids 16 will be predominantly silicate flux and calcium sulphate, and as such are environmentally benign. They are suitable for return to the steel plant or may be disposed of as landfill.

10 [0072] In a separate embodiment, where it is not added into the leaching circuit, the solution from the leach may be treated with sulphuric acid of concentration 50-98%, but preferably of 70-93%, and most preferably 93% in order to precipitate the majority of the calcium as a pure form of gypsum,  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  or hemihydrate,  $\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O}$ . The slurry so-generated may be filtered by any convenient means, such as, but not limited to, flocculation and thickening,  
15 filter press or vacuum belt filter. The calcium sulphate produced is pure and may be sold.

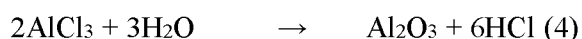
[0073] Normally, it would be expected that lead would precipitate as lead sulphate, which under most conditions is highly insoluble. However, in concentrated chloride media such as used here, this does not happen since the lead forms a soluble anionic chloro complex, and the lead therefore remains in solution. This is a novel aspect of the present invention, enabling the  
20 separate recovery of a lead product.

[0074] In a separate embodiment, if the feed is a complex zinc-bearing sulphide ore or concentrate, leaching will be carried out under oxidising conditions, with the addition of an appropriate oxidant such as, but not limited to, oxygen gas, chlorine, hydrogen peroxide or nitric acid. In such cases, the majority of the sulphur in the feed is converted to its elemental  
25 form rather than fully oxidised to sulphate, which is a distinct advantage of chloride leaching.

[0075] The solution 17 from the leaching circuit, irrespective of its original feed, will contain iron in its predominantly ferric state. Thus, an oxidation step for iron is not needed, which is a significant advantage of this process. This solution may be thermally decomposed 18 at a temperature of 160-200°C, and preferably in the range 170-190°C, resulting in the hydrolysis  
30 of ferric and any other trivalent ions present, such as aluminium, to form their respective oxides and evolve hydrogen chloride vapour 20. This HCl vapour may be used as-is in the leach

circuit, or condensed to concentrate (30-35% HCl) hydrochloric acid 11. If spent pickle liquor is added to the leaching circuit, then excess hydrochloric acid over and above that required for leaching is generated, which may be sold. In this respect, it is an advantage of this process that concentrated HCl is generated. Optionally, especially towards the end of the reaction, water  
 5 may be added, or more preferably, further heating may be effected by the addition of steam 19, which can also act a hydrolysis reagent if there is insufficient free water in the feed solution.

[0076] Heating is continued until no more hydrogen chloride vapour is evolved, signalling the completion of the reaction. The other metals present, such as copper, cadmium, lead, silver, magnesium and manganese, but with the exception of zinc which will not react, are  
 10 simultaneously hydrolysed to their corresponding basic metal chlorides. The reactions are shown as follows for iron, aluminium and copper, with similar reactions to that of copper for manganese, lead, cadmium and silver:

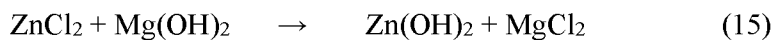


[0077] The slurry from the thermal decomposer, comprising the metal oxide and basic chlorides, with liquid, but highly concentrated (>2000 g/L Zn) zinc chloride is quenched  
 25 into water 22. The amount of water added is sufficient to give a zinc chloride solution of 200-250 g/L Zn, this concentration allowing for minimum water addition to the system.

[0078] The quench slurry 24 proceeds to solid-liquid separation 25, 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 26 will be predominantly hematite ( $\text{Fe}_2\text{O}_3$ ), together with some alumina and basic metal chlorides, which may be further treated (Figure 2) to separate and recover the various metals.

[0079] The solution 27 is predominantly pure zinc chloride, which is then treated with recycled slaked 37 magnesia 29 to effect precipitation 28 of zinc hydroxide 31. This may be carried out in any suitable reactor, preferably a stirred tank reactor. The temperature may be from ambient to 100°C, preferably from 60-65°C. The pH is from 6.0-8.5, preferably from 6.5-7.0. The precipitation may be carried out in one, two or three stages, with a single stage being shown  
 30 for convenience.

[0080] The chemical reaction involved is:



[0081] Solid-liquid separation of the precipitation slurry 30 may be effected by any convenient means, such as, but not limited to, flocculation and thickening, filter press or vacuum belt filter.

[0082] The solids 31 are pure zinc hydroxide, which are calcined 32 to generate pure zinc oxide 33. The temperature of calcination is low, from 150-300°C, preferably from 200-250°C.

[0083] The solution 34 is pure magnesium chloride, which may be treated by conventional pyrohydrolysis 35 to recover hydrochloric acid 38 for recycle to the leaching stage, or to the thermal decomposition stage to increase its concentration, and pure magnesia (MgO) 36. Part of the magnesia 42 is recycled to the impurity and zinc precipitation stages, and the balance 56, equivalent to fresh input from the feed, is suitable for sale.

[0084] The chemical reaction involved is:



[0085] Turning now to Figure 2, the metal oxides/basic chlorides solids 26 are treated with dilute HCl 39 in a re-dissolution reactor to selectively dissolve the basic chlorides. Such acid may be that from the magnesium chloride pyrohydrolysis stage 35. This is a novel and unique aspect of the current invention, separating valuable base and precious metals from more common metals such as iron and aluminium in this manner. The basic metal chlorides are readily soluble in very dilute acid, whereas the higher-valent metal oxides such as hematite and alumina are not. Any magnesium present will also dissolve.

[0086] The re-dissolution slurry 41 undergoes solid-liquid separation 42, 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 43 will be predominantly hematite, but may contain some alumina if there was any aluminium present in the feed which dissolved. If desired, this alumina may be conveniently separated by a simple caustic dissolution (not shown).

[0087] The solution 44 now comprises a mixture of magnesium, base metal and silver chlorides. Silver chloride, although nominally insoluble, does in fact have a small solubility, which is usually not exceeded, especially for feeds such as EAFD. However, if there is a large amount of silver present, its solubility can be enhanced by increasing the chloride content during re-dissolution so as to make it more soluble. This is conveniently achieved by adding recycled magnesium chloride 34.

[0088] Silver and the various base metal chlorides are separated by the following series of

steps. Silver is recovered via a cementation 46 reaction with scrap or recycled copper 45. The cementation slurry 47 undergoes solid-liquid separation 48, which may be effected by any convenient means, such as, but not limited to, flocculation and thickening, filter press or vacuum belt filter. In practice, a small vacuum pan filter is preferred. The solids 43 will be  
5 pure silver metal, which may be washed, melted and cast into bars.

[0089] The solution 50 then undergoes a series of ion exchange separations. Cadmium 51 is recovered first. If the silver content is low, then the chloride content of the solution will be low, close to stoichiometric for the metal ions present, and the pH of the solution will be around 2.0. In this case, cadmium will be present as a cation, and may be selectively recovered using  
10 a strong sulphonic acid cation ion exchange resin in its hydrogen form. Such resins are extremely effective for cadmium, and have a very high loading capacity (>100 g/L Cd per litre of wet settled resin). After washing, the resin may be stripped with either sulphuric or hydrochloric acid, the strength of the stripping solution being dependent on the amount of cadmium on the resin, but calculated to be stoichiometric for 100% stripping in two bed  
15 volumes, to give a cadmium salt solution 52.

[0090] Alternatively, if a high level of silver was present, necessitating the raising of the chloride content (not shown), then cadmium will form a very strong chloro complex. In this case, a weak base simple quaternary amine resin may be used, and stripping may be effected with water. Cadmium chloride 52 is the salt formed in this case.

[0091] Copper is recovered next, and a similar logic as for cadmium applies. If the chloride content is low (not shown), then copper will be present as a cation, and may be conveniently recovered with an iminodiacetic acid resin 55. In this case, loading up 30 g/L Cu per liter of wet settled resin can be achieved. After washing, the resin may be stripped with either sulphuric or hydrochloric acid, the strength of the stripping solution being dependent on the  
20 amount of copper on the resin, but calculated to be stoichiometric for 100% stripping in two bed volumes, to give a copper salt solution 56.

[0092] Alternatively, the chloride concentration may be adjusted with recycled magnesium chloride 54, wherein copper can be selectively loaded 55 onto a weak base complex amine resin, with similar loading to those achieved with the iminodiacetate resin. The copper chloro  
30 complex is not as strong as that of cadmium, and hence requires a strong base quaternary amine resin, and also is not efficiently stripped with water. In this case, copper is stripped with 5% HCl to generate a copper chloride salt solution 56.

[0093] Manganese is recovered next. It forms a very weak chloro complex, and is generally difficult to load onto resins. However, it has been found that in chloride media, a bis picolylamine resin 59 is effective for recovering manganese. Thus, the copper barren solution 57 is adjusted with recycled magnesium chloride 58 to raise the chloride content to 6-10M, the actual level depending on the amount of manganese present. Manganese can load up to similar levels as copper does for its resins, and may be stripped with 100 g/L H<sub>2</sub>SO<sub>4</sub> or HCl to yield a manganese salt 60.

[0094] Lead can be recovered from the manganese barren solution 61 by cementation 63 with zinc metal 62. Although this particular process is well-known in sulphate circuits, it is more difficult in chloride. There should be <5 g/L free HCl present and preferably <1 g/L, since the acid will not only consume the zinc powder added, but will also tend to re-dissolve the cemented lead. Recycled magnesia can be used to adjust the acidity if required (not shown). Additionally, it should also be carried out in the absence of air, and with a very short residence time of 5-10 minutes, preferably 5 minutes.

[0095] The cementation slurry 64 undergoes solid/liquid separation 65 in a manner analogous to that of the silver cement. The solids are pure lead 66, which may be washed, melted and cast to give lead bullion.

[0096] The solution 67 is predominantly magnesium chloride, with a small amount of zinc, which is recycled to acid recovery 18.

[0097] Referring to Figure 3, it is illustrated a process for recovering zinc and associated value metals from zinc-bearing feed material (1000), the process comprising:

providing a feed material comprising at least zinc and iron (1100);

leaching the feed material with a HCl leaching medium to generate a leachate and a solid residue, the leachate comprising at least zinc and iron (1200);

separating the solid residue from the leachate to generate a solution containing iron (1300);

heating the solution containing iron to cause precipitation of the metals, except zinc or calcium and any alkali metals if present, to generate a heated slurry and to recover hydrochloric acid in a concentrated form (1400);

quenching the heated slurry in water and filtering off resulting solids and a filtrate (1500); and

treating the filtrate from quenching to recover zinc hydroxide (1600).

[0098] The process will now be illustrated by way of several examples. These examples are provided for illustration of certain embodiments of the invention, and are not intended as limitations thereof.

### Example 1

- 5 [0099] Two samples of EAFD were leached with a mixture of concentrated hydrochloric acid and zinc pickle liquor (ZPL), which analysed 96.7 g/L Zn and 91.2 g/L Fe. The conditions were that 300 g of EAFD was added to a mixture of 600 mL 33% HCl and 100 mL ZPL, with the reaction taking place at 95°C for one hour. The following table shows the analysis of the dusts used and the metal extractions achieved.

| Sample | Chemical Analysis, % or (ppm) |      |      |        |      |       | Extraction, % |      |      |      |      |       |
|--------|-------------------------------|------|------|--------|------|-------|---------------|------|------|------|------|-------|
|        | Zn                            | Fe   | Pb   | Ag     | Cu   | Cd    | Zn            | Fe   | Pb   | Ag   | Cu   | Cd    |
| 1      | 16.1                          | 26.5 | 2.19 | (56.6) | 0.18 | (347) | 98.3          | 93.8 | 93.1 | 99.8 | 96.2 | 99.1  |
| 2      | 32.6                          | 21.5 | 1.53 | (94.7) | 0.18 | (776) | 100.0         | 99.9 | 99.9 | 99.9 | 99.8 | 100.0 |

- 10 [00100] This example shows that high metal extractions can be attained with different samples of EAFD even when spent ZPL is added.

### Example 2

- [00101] A complex lead-silver ore, also containing copper, with a chemical analysis of 0.13% Ag, 0.11% Cu, 19.2% Fe, 5.5% Pb and 25.7% S was leached with the addition of 350 kg/tonne of hydrochloric acid and 200 kg/tonne of hydrogen peroxide at 90°C and 15% solids loading for a period of four hours. Metal extractions obtained were 85% for silver, 95% for lead and 90% for copper. This example demonstrates the viability of oxidative hydrochloric acid leaching for complex lead-silver ores, with the data being directly applicable to EAF dusts as above.

### Example 3

- [00102] A three-day miniplant leaching campaign was carried out using a large sample of dust from the same source as sample 1 in Example 1 as feed. Leaching was carried out at 20% solids loading with 750 kg/tonne acid addition (100% HCl basis), a temperature of 90-100°C, and a nominal residence time of 60 minutes in each of five cascading reactors.
- 25 [00103] The results showed consistently high zinc extraction (>95%) throughout the campaign, and close to 100% extraction for the other metals, although the data for iron were more variable, reflecting that, as for the laboratory tests, there is a fraction of the iron that

remained refractory to leaching. The results also confirmed, as in the laboratory test, that one reactor is actually sufficient to achieve the desired extraction levels.

[00104] This example demonstrates that the laboratory extraction results could be successfully translated into a continuous operation.

#### 5 Example 4

[00105] A solution containing 14 g/L copper, although high for a resin system, in a total of 2M chloride, was passed downflow at a constant 2BV/h (bed volumes/hour) through a strong base, complex amine, ion exchange resin. Breakthrough was seen after the passage of 3BV, which is good considering the high feed concentration. 85% of full loading was not seen after  
10 the passage of 10BV. After loading, the column was drained, and then stripped with a first pass of 5BV of DI water (de-ionised water), followed by 5BV of 5% HCl. The HCl was used, because it was clear that water had not fully stripped the resin. The water strip showed a concentration of 22 g/L Cu in the first BV, a concentration factor of 1.5 times. The 5% HCl strip showed 20 g/L Cu in the first bed volume. These data demonstrate that copper can be  
15 effectively recovered from chloride solutions, such as that obtained from the leaching of the hematite residue.

#### Example 5

20 [00106] Magnesium chloride brine, containing 61.9 g/L Mg, 34.0 mg/L Ni and 4.36 mg/L Mn, was passed through an ion exchange column containing a bis-picolylamine resin, at a flowrate of 10 BV/h for 1000BV (bed volumes). The objective of the test was to demonstrate the removal of nickel and manganese from chloride solutions, not specifically to recover manganese. Analysis of the solution exiting the column was <0.5 mg/L Ni and Mn for the first  
25 60 BV, and the resin was not fully loaded even after the passage of 1000 BV of feed solution. Stripping of the partially loaded resin (6.31% Ni, 0.036% Mg, 0.81% Mn) was effected by 5BV of 10% HCl, generating a solution analyzing 6.0 g/L Ni and 0.77 g/L Mn. This shows that manganese can be effectively recovered from chloride solutions, such as that obtained from the leaching of the hematite residue, or any remaining in the magnesium chloride solution after  
30 zinc precipitation.

#### Example 6

[00107] A sample of leach solution after removal of all impurities was precipitated using lime slurry. The zinc hydroxide produced was filtered off and well-washed, dried and analysed. The sample showed only calcium as an impurity at a concentration of 0.07%, showing that a purity for zinc oxide of >99.9% could be achieved.

5 [00108] This demonstrates that the process is capable of producing pure zinc oxide. In practice, however, magnesia would be used instead of lime, since calcium chloride does not hydrolyse and decompose, whereas magnesium does.

[00109] Iron is invariably present in all feedstocks, and is generally regarded as being a significant problem, one that has to be removed before the value metals can be recovered. It is  
10 also usually present in significant quantities, far more so than the value metals. Most processes regard iron in this light and the iron solids are first removed and then disposed of, usually by a neutralisation/precipitation process. This new process not only provides a novel and efficient method of separating iron from the value metals, but it also recovers the iron in a useful and valuable form of itself. It also allows for the recycle of hydrochloric acid in a concentrated  
15 form, which no other process is able to accomplish.

[00110] While illustrative and presently preferred embodiments of the invention have been described in detail hereinabove, it is to be understood that the inventive concepts may be  
20 otherwise variously embodied and employed and that the appended claims are intended to be construed to include such variations except insofar as limited by the prior art.

**Claims**

1. A process for recovering zinc and associated value metals from zinc-bearing feed material, the process comprising:
  - a) providing a feed material comprising at least zinc and iron;
  - 5 b) leaching the feed material with a HCl leaching medium to generate a leachate and a solid residue, the leachate comprising at least zinc and iron;
  - c) separating the solid residue from the leachate to generate a solution containing iron;
  - d) heating the solution containing iron to cause precipitation of the metals, except zinc or calcium and any alkali metals if present, to generate a heated slurry and to recover  
10 hydrochloric acid in a concentrated form;
  - e) quenching the heated slurry in water and filtering off resulting solids and a filtrate; and
  - f) treating the filtrate from quenching to recover zinc hydroxide.
- 15 2. The process of claim 1, further comprising oxidising the solution containing iron to convert ferrous iron to ferric iron, the iron in the solution being predominantly in its ferric state or brought to its ferric state.
3. The process of claim 2, wherein the oxidation of ferrous iron is carried out  
20 electrolytically or by adding HCl.
4. The process of any one of claims 1 to 3, wherein the feed material comprises other metals selected from the group consisting of copper, silver, lead, cadmium, manganese and magnesium, the method further comprising leaching the resulting solids in dilute hydrochloric  
25 acid to effect re-dissolution of at least one of copper, silver, lead, cadmium, manganese and magnesium if present.
5. The process of claim 4, wherein, the amount of hydrochloric acid as used is at least stoichiometric for the other metals present.  
30
6. The process of any one of claims 1 to 5, further comprising treating the filtrate from zinc precipitation using pyrohydrolysis to recover HCl.
7. The process of claim 6, wherein a part of HCl recovered by pyrohydrolysis is recycled

within the process.

8. The process of any one of claims 1 to 7, wherein the feed material is electric arc furnace dust (EAFD), or a complex lead-zinc-copper-silver ore or concentrate.

5

9. The process of claim 8, wherein spent zinc pickle liquor is added to the electric arc furnace dust to provide additional iron and a portion of the HCl leaching medium.

10. The process of any one of claims 1 to 9, wherein the leaching step is performed at a temperature of 25-110°C, preferably 80-100°C, more preferably 90-95°C.

10

11. The process of any one of claims 1 to 10, wherein the leachate is cooled to crystallise out lead chloride.

12. The process of any one of claims 1 to 11, wherein in step (d) the ferric solution is heated to a temperature of about 170-200°C, preferably about 180-190°C, in order to effect the hydrolysis of ferric iron and precipitation of hematite.

15

13. The process of claim 12, wherein the reaction in step (d) is allowed to proceed until no more HCl is evolved.

20

14. The process of claim 12, wherein water or steam is added at the end of the reaction in step (d) to ensure complete hydrolysis of all metals present except zinc, calcium and the alkali metals which do not hydrolyse.

25

15. The process of any one of claims 1 to 14, wherein the amount of water used in the quenching step (e) is controlled to produce a magnesium chloride solution of 30 wt.% to 50 wt.%, when magnesium is present in the feed material.

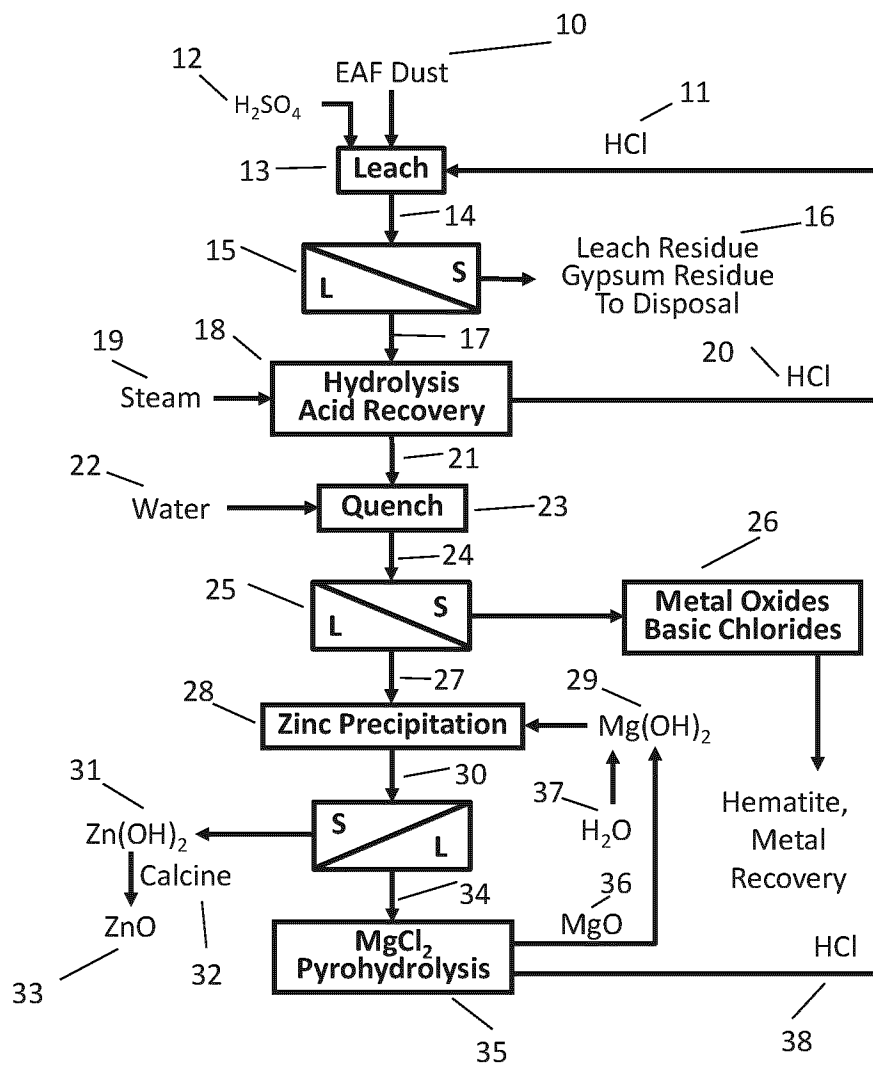


FIG. 1

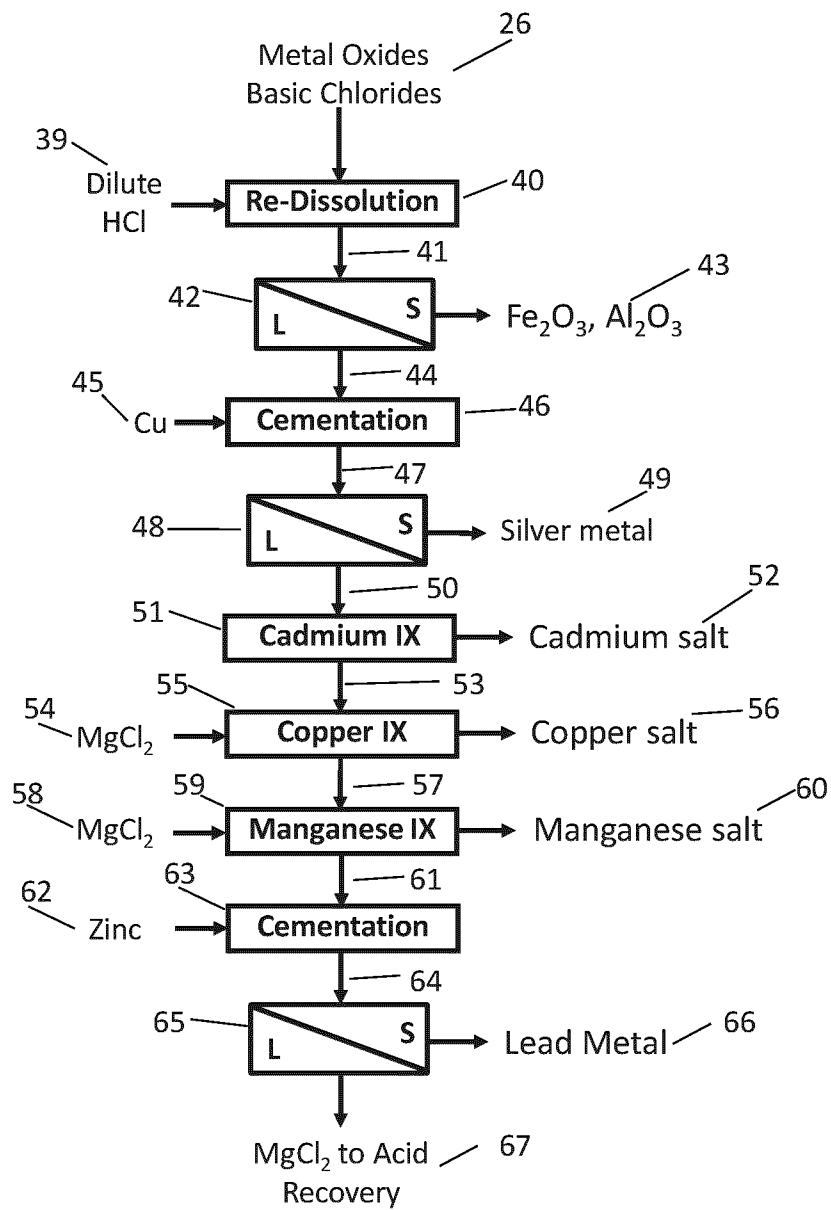
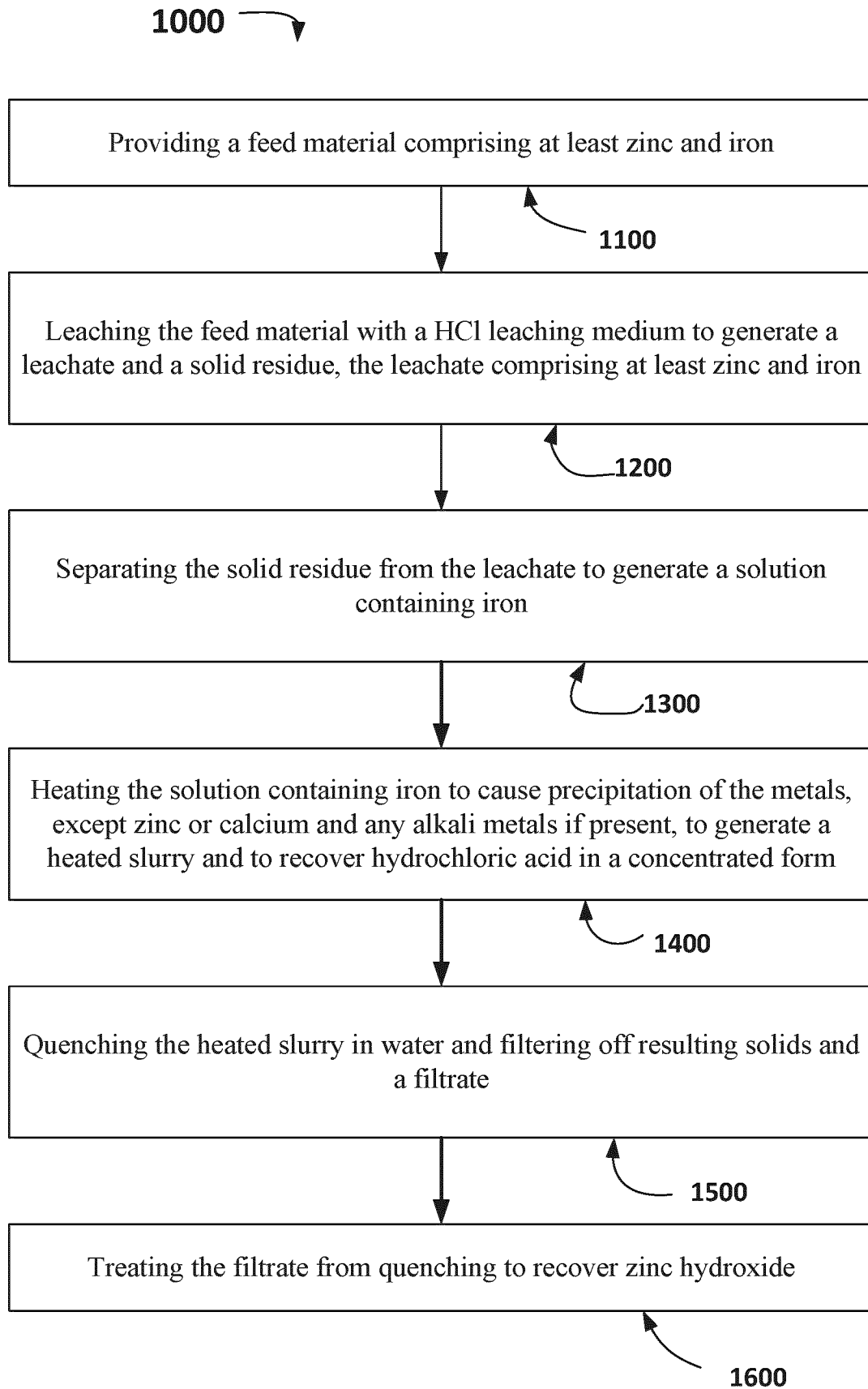


FIG. 2

**FIG. 3**

## INTERNATIONAL SEARCH REPORT

International application No.

**PCT/CA2019/051710**

## A. CLASSIFICATION OF SUBJECT MATTER

IPC: **C22B 3/10** (2006.01), **B01D 11/02** (2006.01), **C22B 19/20** (2006.01), **C22B 19/28** (2006.01),  
**C22B 3/22** (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)

IPC: **C22B 3/10** (2006.01), **C22B 19/+** (2006.01), **C22B 7/02** (2006.01), **C22B 3/44** (2006.01)

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

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

Google Scholar, FAMPAT (Questel), Scopus

Zinc, leach+/dissol+/extract+/lixiv+, iron/ferr+, hydroly+/precipit+, heat+/decompos+/thermal+, hydrochloric/hcl/hci/hcl/chlorhydric, recover+/regenerat+

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|-----------|------------------------------------------------------------------------------------|-----------------------|
| A         | WO2011100820A1 (HARRIS et al.) 25 August 2011 (25-08-2011)                         |                       |
| A         | CN105776140A (ZHU FULONG et al.) 20 July 2016 (20-07-2016)                         |                       |
| P/A       | WO2019006545A1 (HARRIS et al.) 10 January 2019 (10-01-2019)                        |                       |

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

☒ See patent family annex.

|                                             |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                      |                          |                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          |
|---------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| *<br>"A"<br>"D"<br>"E"<br>"L"<br>"O"<br>"P" | Special categories of cited documents:<br>document defining the general state of the art which is not considered to be of particular relevance<br>document cited by the applicant in the international application<br>earlier application or patent but published on or after the international filing date<br>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)<br>document referring to an oral disclosure, use, exhibition or other means<br>document published prior to the international filing date but later than the priority date claimed | "T"<br>"X"<br>"Y"<br>"&" | 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<br>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<br>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<br>document member of the same patent family |
|---------------------------------------------|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|

Date of the actual completion of the international search

12 February 2020 (12-02-2020)

Date of mailing of the international search report

04 March 2020 (04-03-2020)

Name and mailing address of the ISA/CA  
Canadian Intellectual Property Office  
Place du Portage I, C114 - 1st Floor, Box PCT  
50 Victoria Street  
Gatineau, Quebec K1A 0C9  
Facsimile No.: 819-953-2476

Authorized officer

Jay Fothergill (819) 639-8455

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

International application No.  
**PCT/CA2019/051710**

| Patent Document<br>Cited in Search Report | Publication<br>Date          | Patent Family<br>Member(s) | Publication<br>Date            |
|-------------------------------------------|------------------------------|----------------------------|--------------------------------|
| WO2011100820A1                            | 25 August 2011 (25-08-2011)  | AR081403A1                 | 29 August 2012 (29-08-2012)    |
|                                           |                              | AU2011213512A1             | 16 August 2012 (16-08-2012)    |
|                                           |                              | AU2011217756A1             | 16 August 2012 (16-08-2012)    |
|                                           |                              | AU2011217756B2             | 14 July 2016 (14-07-2016)      |
|                                           |                              | AU2011217757A1             | 23 August 2012 (23-08-2012)    |
|                                           |                              | AU2016204038A1             | 14 July 2016 (14-07-2016)      |
|                                           |                              | AU2016204038B2             | 24 May 2018 (24-05-2018)       |
|                                           |                              | AU2016204101A1             | 04 August 2016 (04-08-2016)    |
|                                           |                              | AU2016204101B2             | 05 July 2018 (05-07-2018)      |
|                                           |                              | BR112012020460A2           | 17 September 2019 (17-09-2019) |
|                                           |                              | CA2788384A1                | 11 August 2011 (11-08-2011)    |
|                                           |                              | CA2788384C                 | 19 February 2019 (19-02-2019)  |
|                                           |                              | CA2788965A1                | 25 August 2011 (25-08-2011)    |
|                                           |                              | CA2788965C                 | 21 May 2019 (21-05-2019)       |
|                                           |                              | CA2789095A1                | 25 August 2011 (25-08-2011)    |
|                                           |                              | CA2789095C                 | 06 March 2018 (06-03-2018)     |
|                                           |                              | CA3012343A1                | 25 August 2011 (25-08-2011)    |
|                                           |                              | CA3012343C                 | 31 December 2019 (31-12-2019)  |
|                                           |                              | CL2012002290A1             | 13 December 2013 (13-12-2013)  |
|                                           |                              | CN102892907A               | 23 January 2013 (23-01-2013)   |
|                                           |                              | CU20120119A7               | 17 December 2012 (17-12-2012)  |
|                                           |                              | DOP2012000223A             | 30 November 2012 (30-11-2012)  |
|                                           |                              | EA201290730A1              | 30 April 2013 (30-04-2013)     |
|                                           |                              | EA032086B1                 | 30 April 2019 (30-04-2019)     |
|                                           |                              | EP2531628A1                | 12 December 2012 (12-12-2012)  |
|                                           |                              | EP2536858A1                | 26 December 2012 (26-12-2012)  |
|                                           |                              | EP2536860A1                | 26 December 2012 (26-12-2012)  |
|                                           |                              | JP2013527307A              | 27 June 2013 (27-06-2013)      |
|                                           |                              | KR20130135724A             | 11 December 2013 (11-12-2013)  |
|                                           |                              | MX2012009550A              | 15 May 2015 (15-05-2015)       |
|                                           |                              | MX356807B                  | 13 June 2018 (13-06-2018)      |
|                                           |                              | US2013220079A1             | 29 August 2013 (29-08-2013)    |
|                                           |                              | US8894740B2                | 25 November 2014 (25-11-2014)  |
|                                           |                              | US2013052104A1             | 28 February 2013 (28-02-2013)  |
|                                           |                              | US9889421B2                | 13 February 2018 (13-02-2018)  |
|                                           |                              | US2013195738A1             | 01 August 2013 (01-08-2013)    |
|                                           |                              | WO2011094858A1             | 11 August 2011 (11-08-2011)    |
|                                           |                              | WO2011100821A1             | 25 August 2011 (25-08-2011)    |
|                                           |                              | ZA201206582B               | 26 March 2014 (26-03-2014)     |
|                                           |                              | ZA201206954B               | 26 March 2014 (26-03-2014)     |
|                                           |                              | ZA201206955B               | 26 March 2014 (26-03-2014)     |
| CN105776140A                              | 20 July 2016 (20-07-2016)    | None                       |                                |
| WO2019006545A1                            | 10 January 2019 (10-01-2019) | CA3068794A1                | 10 January 2019 (10-01-2019)   |