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(54) **Title**: RECOVERY OF ZINC AND MANGANESE FROM PYROMETALLURGY SLUDGE OR RESIDUES

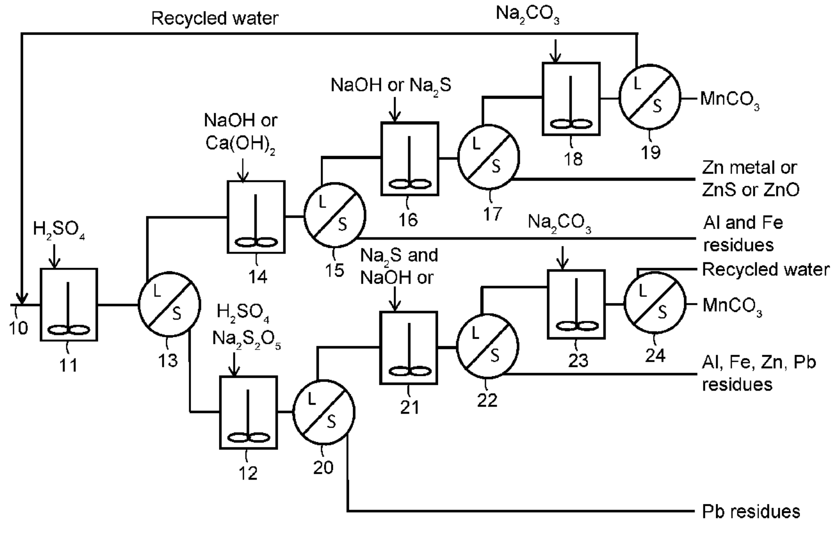

FIG. 4

(57) **Abstract**: Hydrometallurgical techniques for the selective recovery of Zn, Mn and Pb in that order from sludges or various metallurgical residues can include leaching steps to extract the zinc and manganese; the steps of removing iron, aluminum and silica from the leaching solutions; and recovering manganese and zinc by precipitation. Mn can be precipitated from an initial leaching solution as well as a secondary leaching solution obtained by leaching the slurry of the initial leaching step. Various other waste streams can also be treated.

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RECOVERY OF ZINC AND MANGANESE FROM PYROMETALLURGY SLUDGE OR RESIDUES

FIELD

The technical field relates to the treatment of pyrometallurgical sludge or residues, and more particularly to the recovery of components from such materials.

BACKGROUND

Among the numerous by-products generated by the steel industry, sewage sludge of smokes of blast furnaces can be very rich in manganese, zinc and lead (between 5 and 40%). These materials have generally been deposited in periphery of the sites of steel industry.

Zn is an important metal in metallurgical, chemical and textile industries. It mainly extracted from sulphide ores including Zn. Portions of Zn can be recovered from secondary sources such as electric furnace dust containing different levels of impurities depending on the source (Jha et al. 2001). Pyrometallurgical and hydrometallurgical processes are usually used to recover Zn in the ore or from secondary sources. Nevertheless, the pyrometallurgical processes consume significant energy and require process gas treatment during Zn recovery. The majority of studies have leached zinc with sodium hydroxide (Charpentier et al., 2007), ammonium chloride (Olper et al., 1993) and sulfuric acid (Dvorak et al., 2005).

Pyrolusite (MnO_2) is stable in acidic and alkaline conditions. Extraction of Mn (IV) must be carried out under reducing conditions (Naik et al. 2000). Various techniques for leaching ores or nodules have been studied for the last 20 years. Most studies function with sulfuric acid as a reducing agent, such as sulfuric acid leaching, coupled hydrogen peroxide (Allen et al, 1988; Jiang et al, 2004), to oxalic acid (Sahoo et al, 2001.), ferrous sulfate (Brantley et al, 1968), pyrite (Vracar et al, 2000) and aqueous sulfur dioxide (SO_2) Chow et al, 2012b, Ward (2005a), and Ward (2005b).

Leaching with hydrochloric acid (HCl) is also used with Ni (Chen et al, 1992), pyrite Kanungo (1999a) and hydrogen peroxide (El Hazek et al, 2006). Sayilgan et al. (2010)

conducted a series of studies of Mn ore leaching with hydrochloric acid or sulfuric acid in the presence of a reducing agent such as ascorbic acid, citric acid and oxalic acid.

Other studies have shown reducing properties using acidic carbohydrates waste from agriculture, renewable and non-hazardous such as glucose (Furnali et al 2006) molasses (Lasheen et al, 2009) lactose (Veglio et al, 2000), corn cobs (Tian et al, 2010) or sawdust (Hariprasad et al, 2007). Some authors use bacteria for bioleaching, as in Veglio et al. (1997).

Some studies have looked at hydrometallurgical process including the steps of leaching, extraction and purification of Mn in the form of oxides or salts. These methods mainly use reagents such as ferrous sulfate and SO_2 in sulfuric acid. Those chemicals are generally appreciated for their low cost and their effectiveness (see Chow et al., 2012 WO2012024294).

In a hydrometallurgical process, the principle of selective leaching is rarely used. Solution can contain impurities that can affect the production of pure Mn compounds. Purification is usually required to remove impurities present in aqueous solutions before proceeding to the recovery of the metal. The precipitation of the metals as hydroxides or sulfides are the main purification techniques used to recover the Mn and Zn in the solution. One challenge is to precipitate unwanted metals and to keep in solution Zn and Mn with a cost as low as possible.

Precipitation of metals as hydroxides is a common method for removing metals from a solution in hydrometallurgical processes (Zhang et al., 2007).

After precipitation of Fe^{3+} and Al^{3+} ions in the form of hydroxides, precipitation of the remaining impurities as sulphides is generally employed. This extraction is based on the difference in solubility between the metal sulfides as function of pH and temperature. Dihydrogen sulfide (H_2S), sodium sulfate (Na_2S), barium sulfate (BaS), or ammonium sulfate $(NH_4)_2SO_4$ are generally used for the precipitation of impurities in the form of metal sulfides. Pakarinen et al. (2011) use a precipitation with Na_2CO_3 under O_2 supply to allow the separation of Fe^{2+} and Mn^{2+} ions in solution. At pH 6 and under ORP > 200mV, it happens to precipitate the Fe^{2+} in $FeCO_3$ keeping the Mn^{2+} in solution. The $FeCO_3$ was then removed by filtration. The use of carbonate allows a good separation of Fe and Mn with an optimal price/quality ratio. Cementation is also a technique commonly used in hydrometallurgy. This technique includes the precipitation of a metal from an aqueous solution of a salt thereof with another metal. This redox reaction connects a more electropositive metal which is deposited on a less electropositive metal from solution. This technique is used in zinc hydrometallurgy to precipitate the metals present in the solution as Cu by adding Zn powder (Rizet et al, 2000).

There are various challenges in the treatment of pyrometallurgical sludge or residue, particularly for extracting components such as Zn and Mn.

SUMMARY

Techniques described herein relate selective extraction of zinc and manganese from metal sludge or dust by utilizing acidic leaching (e.g., using sulfuric acid) and generating a high-concentration lead slag. Various implementations are well suited to treating pyrometallurgic sludge or residue, and particularly to recover valuable constituents from sludge or residue, such manganese, zinc and lead in particular

In some implementations, the techniques enable steel residues to be treated by selectively and sequentially leaching the zinc and manganese, followed by effective purification to produce marketable product of each these metals.

Currently there is no method adapted to decontaminate and recover Zn, Mn and Pb contents in the dust generated by the ferromanganese industry. These residues have historically been deposited in basins bordering steel production plants, because legislation and metal prices over the last 100 years the industry did not promote the treatment of these waste streams. Given the market value of the metals and their general shortage, these brownfield sites can be considered as secondary resources. Techniques capable of profitably exploiting this type of residue (sludge), in order to produce compounds of Mn, Pb and Zn pure enough to be recoverable, can be advantageous for treating such wastes and also producing valuable products. In some implementations, the techniques include selectively leaching Zn, Mn and Pb in order to obtain a concentrate of Mn, a concentrate of Zn and residue rich in Pb.

Various tests have identified leaching agents and effective and affordable discount. Further steps include the purification of each leachate by removing unwanted metals such as iron (Fe), cobalt (Co), nickel (Ni), copper (Cu) and aluminum (Al), and then production of a marketable product of each valuable metal (e.g., Zn, Mn and Pb). In some scenarios, the techniques lead to the production of salts of Mn, Zn free from substantial impurities, as well as a final residue rich enough in Pb to be recycled.

In some implementations, there is provided a process for treating a matrix comprising zinc (Zn), manganese (Mn) and lead (Pb), comprising:

> leaching the matrix to generate a leaching solution enriched in Zn and a fraction enriched in Mn and Pb;
>
> subjecting the leaching solution to Zn-precipitation to produce Zn-based precipitates and a Zn-depleted fraction comprising Mn compounds;
>
> leaching the fraction enriched in Mn and Pb to produce a Mn-enriched leaching solution and a Pb-enriched fraction; and
>
> subjecting the Zn-depleted fraction and/or the Mn-enriched leaching solution to Mn-precipitation to produce Mn-based precipitates.

In some implementations, the leaching of the matrix is performed using an aqueous acidic solution.

In some implementations, the aqueous acidic solution comprises H_2SO_4.

In some implementations, the leaching of the matrix comprises multiple leaching runs with the aqueous acidic solution and multiple rinsing runs with an aqueous rinsing solution.

In some implementations, the leaching of the matrix comprises at least three leaching runs and/or at least three rinsing runs.

In some implementations, the process also includes, prior to the Zn-precipitation, removing additional metal components from the leaching solution enriched in Zn. In some implementations, the additional metal components include aluminum (Al). In some implementations, the additional metal components include iron (Fe).

In some implementations, the removing of the additional metal components comprises precipitating the additional metal components. In some implementations, precipitating of the additional metal components comprises adding a hydroxide of a divalent cation. In some implementations, the hydroxide of a divalent cation comprises $Ca(OH)_2$ or NaOH.

In some implementations, the Zn-precipitation comprises adding NaOH or Na_2S to produce ZnO or ZnS as the Zn-based precipitates.

In some implementations, the process also includes, prior to the Mn-precipitation, removing additional metallic impurities from the Zn-depleted fraction and/or the Mn-enriched leaching solution, including aluminum, iron, lead, zinc or a combination thereof. In some implementations, precipitating of the additional metal components prior to the Mn-precipitation comprises adding NaOH and Na_2S to the Zn-depleted fraction and/or the Mn-enriched leaching solution.

In some implementations, the Mn-precipitation comprises adding a carbonate compound to produce Mn-carbonates as the Mn-based precipitates. In some implementations, the carbonate compound comprises Na_2CO_3 to produce $MnCO_3$.

In some implementations, the process also includes, prior to the leaching of the matrix, a step of determining a composition of the matrix. In some implementations, determining the composition of the matrix comprises determining the concentrations of Zn and Mn. In some implementations, determining the composition of the matrix comprises determining the concentration of Pb. In some implementations, determining the composition of the matrix includes determining the concentrations of Al and/or Fe.

In some implementations, the process also includes treating the Pb-enriched fraction to recover Pb therefrom.

In some implementations, the process also includes subjecting the Zn-depleted fraction to Mn-precipitation in a first reactor to produce a first stream of Mn-based precipitates; and subjecting the the Mn-enriched leaching solution to Mn-precipitation in a second reactor to produce a second stream of Mn-based precipitates.

In some implementations, the process further includes producing a Mn-depleted stream in the second reactor; and subjecting at least a portion of the Mn-depleted stream to further Mn-precipitation. In some implementations, the further Mn-precipitation of the Mn-depleted stream is conducted in the first reactor.

In some implementations, the process further includes recycling a portion of the Mn-depleted stream from the second reactor for addition to the matrix before or during the leaching thereof.

In some implementations, the process further includes recovering a metals-depleted liquid from the Mn-precipitation in the first reactor and adding at least a portion of the metals-depleted liquid to the matrix before or during the leaching thereof.

In some implementations, the leaching of the matrix is performed in atmospheric pressure conditions.

In some implementations, one or more of the leaching steps are performed in a counter-current reactor.

In some implementations, one or more of the leaching steps are performed in an agitated tank reactor.

In some implementations, one or more of the leaching steps are performed in a batch reactor or a continuous.

It is noted that the leaching reactors can use recirculated streams derived from other units of the process. For instance, the recirculated streams can include leaching solutions from which one or more metals (e.g., valuable metal components) have been removed, such as streams that have been subjected to Mn-precipitation. It should be noted that the recirculation can be done at various points in the overall process, using different recycle streams depending on various factors, such as economic considerations, make-up water availability, build-up of certain components in the recycled streams, and so on.

In some implementations, the matrix comprises a powder or dust. In some implementations, the matrix comprises a by-product or waste stream derived from metals processing. In some implementations, the matrix comprises steel plant dust.

In some implementations, there is provided a process for treating a matrix comprising zinc (Zn), manganese (Mn) and lead (Pb), comprising selective and sequential leaching of Zn, Mn and Pb in order to obtain a Mn concentrate, a Zn concentrate, and a Pb-enriched residue.

In some implementations, there is provided a method for the hydrometallurgical treatment of a matrix comprising manganese (Mn), zinc (Zn), lead (Pb), iron (Fe), aluminum (Al), and at least one of calcium, chlorides, sodium and potassium as impurities, the method comprising:

> a first leaching step comprising:
>
> > leaching the matrix at atmospheric pressure in a reactor using a first leaching solution to product a first leach liquor and a first leach residue, the first leaching solution comprising a sulfuric acid solution; and
> >
> > separating the first leach liquor from the first leach residue after the first leaching;
>
> a second leaching step comprising:
>
> > leaching the first leach residue at atmospheric pressure using a second leaching solution to form a second leach liquor and a second leach residue, the second leaching solution comprising sulfuric acid and a reducing agent; and
> >
> > separating the second leach liquor from the second leach residue;
>
> a Mn-precipitation step wherein Mn compounds are precipitated from the first and second leach liquors, including contacting the liquors or streams derived therefrom, with a carbonate at a pH to precipitate Mn carbonate compounds.

In some implementations, the process also includes selecting a quantity of the carbonate to adjust the pH of the first and second leach liquor sufficiently to precipitate out Mn carbonate compounds.

In some implementations, the pH of the second leaching is between about 3 and about 5.

In some implementations, the reducing agent used in the second leaching step comprises $Na_2S_2O_5$.

In some implementations, the process further includes subjecting the first liquor to Zn-precipitation prior to Mn-precipitation.

In some implementations, the Zn-precipitation includes electroplating Zn as Zn metal.

In some implementations, the Zn-precipitation includes forming Zn sulfide and/or Zn oxide precipitates that are precipitated out of the solution.

In some implementations, the process includes separating the Zn sulfide and/or Zn oxide precipitates from the solution to form a Zn sulfide and/or Zn oxide containing residue, and a Zn-depleted first liquor that is subjected to the Mn-precipitation step.

In some implementations, the Zn-precipitation comprises adding alkali or sulfide to the first liquor to precipitate Zn compounds; and then preforming a solid-liquid separation to produce a Zn sulfide and/or oxide cake.

In some implementations, the process includes subjecting the first liquor to a Fe, silicate and Al precipitation step to form Fe, silicate and Al hydroxide compounds and a depleted liquor; separating the Fe, silicate and Al hydroxide compounds from the depleted liquor; and subjecting the depleted liquor to the Zn-precipitation.

In some implementations, the Fe, silicate and Al precipitation step comprises adding alkali to increase the pH between about 4 and about 5; and then preforming a solid-liquid separation to produce a mixed Fe, silicate and Al hydroxide cake.

In some implementations, the Mn-precipitation step comprises adding the carbonate to the first and second liquors to increase the pH to between about 7.5 and about 8.5; and then performing a solid-liquid separation to produce a Mn-carbonate cake.

In some implementations, the second leach residue contains between 10 wt% and 30 wt% of Pb.

In some implementations, a leaching period of mixing the sulfuric acid solution for the first and/or second leaching steps is between about 10 minutes and about 24 h.

In some implementations, the temperature of the sulfuric acid solution is between about 20°C and about 40°C.

In some implementations, the process includes one or more features of claims 1 to 34.

In some implementations, there is provided a system for treating a matrix comprising zinc (Zn) and manganese (Mn), comprising:

> a leaching unit for leaching the matrix to generate a Zn-enriched leaching solution, and a fraction enriched in Mn and Pb;
>
> a Zn-precipitation unit for subjecting the Zn-enriched leaching solution to Zn-precipitation to produce Zn-based precipitates and a Zn-depleted fraction comprising Mn compounds; and
>
> a leaching unit for leaching the fraction enriched in Mn and Pb to produce a Mn-enriched leaching solution and a Pb-enriched fraction; and
>
> a Mn-precipitation system for subjecting the Zn-depleted fraction and/or the Mn-enriched leaching solution, or streams derived therefrom, to Mn-precipitation to produce Mn-based precipitates.

In some implementations, the Mn-precipitation system comprises a first Mn-precipitation unit for subjecting the Zn-depleted fraction to Mn-precipitation; and a second Mn-precipitation unit for subjecting the Mn-enriched leaching solution to Mn-precipitation.

In some implementations, the systems includes an additional precipitation unit for receiving the Zn-enriched leaching solution and removing at least one of aluminum (Al), iron (Fe) and silicate therefrom, to produce a liquor for supplying to the Zn-precipitation unit.

In some implementations, there is provided a system for the hydrometallurgical treatment of a matrix comprising manganese (Mn), zinc (Zn), lead (Pb), iron (Fe), aluminum (Al), and at least one of calcium, chlorides, sodium and potassium as impurities, the system comprising:

> a first leaching unit for leaching the matrix at atmospheric pressure in a reactor using a first leaching solution to product a first leach liquor and a first leach residue, the first leaching solution comprising a sulfuric acid solution;

a first separation unit for separating the first leach liquor from the first leach residue after the first leaching;

a second leaching unit for leaching the first leach residue at atmospheric pressure using a second leaching solution to form a second leach liquor and a second leach residue, the second leaching solution comprising sulfuric acid and a reducing agent;

a second separation unit for separating the second leach liquor from the second leach residue; and

a Mn-precipitation system for precipitating Mn compounds from the first and second leach liquors, or streams derived therefrom, by contacting with a carbonate at a pH to precipitate Mn carbonate compounds.

In some implementations, the Mn-precipitation system comprises a first Mn-precipitation unit for subjecting the first leach liquor to Mn-precipitation; and a second Mn-precipitation unit for subjecting the second leach liquor to Mn-precipitation.

In some implementations, the system includes an additional precipitation unit for receiving the first leach liquor and removing at least one of aluminum (Al), iron (Fe) and silicate therefrom, to produce a metals depleted liquor comprising Zn and Mn; and a Zn-precipitation unit for receiving the metals depleted liquor and producing Zn precipitates and a Zn-depleted fraction, wherein the first precipitation unit is configured to receive the Zn-depleted fraction to be subjected to the Mn-precipitation.

In some implementations, the system also includes one or more operational or structural features of the processes described in the description or drawings.

Various implementations, aspects and features of the techniques will be described below and illustrated in the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a graph showing Zn concentration (mg/L) during electrolysis.

Figure 2 is a diagrammatic representation of a flow sheet depicting a method for the leaching of a metallic sludge.

Figure 3 is a diagrammatic representation of a process for treating a metallic sludge.

Figure 4 is a diagrammatic representation of another process for treating a metallic sludge.

DETAILED DESCRIPTION

Various implementations of techniques will be described for treating metallic sludges for recovering components, such as Zn and Mn.

Referring to Figures 3 and 4, in some implementations the process begins with metallic sludge 10, which may be obtained from “brownfield” or elsewhere. The metallic sludge 10 can contain between 1 and 40 percent of Zn, between 0.5 and 28 % of Mn and between 1 and 20 % of Pb, for example. It should be noted that the source material that is treated can be a mixture of metallic sludge streams from multiple sources and/or a pre-treated metallic sludge stream or another stream derived from metallic sludge.

In addition to manganese, zinc and lead, such metallic sludges may contain at least one of the following elements: iron, aluminum, calcium, silicates, sodium and magnesium.

In some implementations, the metallic sludge 10 is reacted at ambient temperature with sulfuric acid at step 11, referred to as Zn leaching step. The resource material pulp density can be between 5 and 15% by weight.

Optionally, there can be multiple (e.g., three) steps of leaching with a solution of sulfuric acid with a concentration of 0.25 M and multiple (e.g., three) steps of rinsing. Aqueous sulfuric acid reacts with zinc oxide according the following equation:

$$\text{Equation 1: } ZnO + H_2SO_4 \rightarrow Zn^{2+} + H_2O + SO_4^{2-}$$

H_2SO_4 reacts with divalent manganese (MnO) according the following equation:

$$\text{Equation 2: } MnO + H_2SO_4 \rightarrow Mn^{2+} + H_2O + SO_4^{2-}$$

In some implementations, the removal of impurities from leach liquor (“LL” which may also be referred to as pregnant leach solution “PLS”) can be accomplished in one stage. For example, in some implementations, the pH of the solution is changed from about 4.25 to about 4.75 to precipitate silicate, iron and aluminum at a mix tank, shown at step

14, referred to as Al and Fe precipitation step. This pH may be achieved in various way, including the addition to the solution of alkaline earth hydroxides or alkaline salt, such as NaOH, $Mg(OH)_2$ or $Ca(OH)_2$. The precipitated solid can be separated from the treated leach liquor in a thickener or a filter in a solid-liquid separation step 15.

In some implementations, the pH of the solution can then be raised; for example, sodium sulfide or Na_2S can be added to the solution to precipitate zinc as sulfides, the pH of the leach liquor can be about 4.25 to about 4.75. Zinc can also be precipitated and recovered as zinc oxide with a stoichiometric addition of sodium hydroxide, the pH of the leach liquor would be changed to about 7.0 to about 10.0, at step 16, referred to as Zn precipitation step. Zinc can also be recovered through electroplating with specific conditions. The sulphides or oxides precipitates can be separated from the treated leach liquor in a thickener or a filter in another solid-liquid separation step 17.

Optionally, the pH of the solution can then be raised to about 8.5 with Na_2CO_3 to precipitate and recover manganese carbonate, at step 18, referred to as Mn precipitation step The solid manganous carbonate is separated from the solution by a thickener or a filter, in another solid-liquid separation step 19.

In some implementations, after zinc leaching, the leached residue (from the first step 11 of Zn leaching) can be reacted in a stirred tank at ambient temperature with sulfuric acid and sodium metabisulfite to reduce manganese dioxide, at step 12, referred to as Mn leaching step. Optionally, there can be 2 steps of leaching and 2 steps of rinsing.

Sodium metabisulfite reacts with MnO_2 according the following equation:

$$\text{Equation 3: } 2MnO_2 + H_2SO_4 + Na_2S_2O_5 \rightarrow 2Mn^{2+} + H_2O + 3SO_4^{2-} + 2Na^{+}$$

In some implementations, the pH of the solution can be between about 3.0 and about 5.0 to leach manganese without leaching iron or aluminum.

In some implementations, additional removal of impurities from leach can be accomplished in one stage. For example, referring to Figure 4, the pH of the solution can be changed from about 4.80 to about 5.60 to precipitate aluminum, iron, lead and zinc in a mix tank, shown in step 21, referred to as Al, Fe, Pb and Zn precipitation step. Achievement of the desired pH may include the addition to the solution of sodium hydroxide and sulfide, such Na_2S, to precipitate impurities as sulfides. The precipitated solid can be separated from the treated leach liquor in a thickener or a filter in a solid-liquid separation step 22.

Referring to Figures 3 and 4, in some implementations, after filtration the pH of the solution is then raised to about 8.5 with Na_2CO_3 to precipitate and recover manganese carbonate, at step 23, referred to as another Mn precipitation step. The solid manganous carbonate can be separated from the solution by a thickener or a filter in another solid-liquid separation step 24.

Final residues can contain a high proportion of lead, between 10 and 30% for example, which can be revalorize by hydrometallurgical and/or pyrometallurgical methods.

EXAMPLE I: LEACHING

A leaching test was performed using steel dust. The composition of the dust is given in Table 1. In the test, 400 g of dust was lixiviated (i.e., leached) with 4 liters of water (10% pulp density by weight) in a stirred plastic reactor with baffle.

Table 1: Elements concentration in the metallic sludge (g/kg)

Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
198	72.9	45.3	6.88	56.3	52.3	11.5	13.1	18.7	3.23

After the leaching test for zinc, the slurry was filtered. A small portion was dried, crushed, digested and analyzed with ICP AES is given in Table 2. A sample of the filtrate was also analyzed.

Table 2: Elements concentration in the metallic sludge (g/kg)

Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
231	102	10.1	0.55	40.2	56.7	1.47	17.4	2.13	55.5

It is noted that by operating in a pH range of 1.5 to 3.5, the sulfuric acid concentration used for each leaching is 0.25 M, about 97% of the zinc and 13% of manganese is extracted. These results shows that as Mn is mainly found here as MnO_2 the first leaching step preferentially leaches Zn and not much Mn or Pb. Leaching times did not exceed 30 minutes and rinsing times did not exceed 10 minutes. The weight of dry residue after leaching was 252 g. After the zinc leaching, a second leaching step included leaching the first leach residue in a second leaching solution with sulfuric acid and reductant such as sodium metabisulfite. The elements concentration in the leach liquors are shown in the Table 3.

Table 3: Elements concentration in leach liquor (mg/L)

	Volume (mL)	$[H_2SO_4]$ (mol/L)	pH	Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
L1 Zn	3054	0.25	3.48	439	4.78	530	375	519	2.54	512	0.81	463	2882
L2 Zn	4168	0.25	2.49	967	7.16	1773	236	511	69.4	402	41.2	803	5915
L3 Zn	4176	0.25	1.46	740	6.30	988	95.6	593	1011	176	40.1	407	7466
R1 Zn	4000	0.0	1.74	272	4.68	353	33.7	562	211	59.6	12.4	134	2564
R2 Zn	4000	0.0	2.11	104	3.70	115	13.9	564	29.9	18.6	2.70	42.8	1171
R3 Zn	4000	0.0	2.40	51.1	3.83	40.7	7.87	593	6.58	6.31	0.68	16.4	824
Extraction %				12.8	0.41	83.7	100	58.0	26.3	93.7	7.72	96.7	-
L1Mn	2830	0.25	4.76	11998	9.90	0.00	13.5	573	0.00	49.3	12.0	44.3	17971
L2 Mn	2590	0.10	3.65	7954	9.04	155	8.25	548	5.44	45.2	6.45	93.4	14228
R1 Mn	2540	0.0	3.77	636	5.38	24.5	2.15	542	0.27	4.46	1.87	9.34	1561
R2 Mn	2540	0.0	3.79	2226	5.94	56.7	1.65	517	1.15	14.0	1.85	28.3	4263
Extraction %				90.9	0.70	87.1	100	83.5	26.4	100	8.87	100	-

After the second leaching, the slurry was filtered. A small portion was dried, crushed, digested and analyzed with ICP AES is given in Table 4. A sample of the filtrate was also analyzed.

Table 4: Elements concentration in the metallic sludge (g/kg)

Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
24.2	171	12.6	39.0	18.5	94.5	0.83	26.4	1.34	61.8

It is noted that by operating in a pH range 3.5 and 4.5, about 90.9 % of the manganese is extracted. Leaching times did not exceed 120 minutes and rising times did not exceed 10 minutes. The weight of dry residue after leaching is 138 g. This final residue contained 17.1% Pb and is recyclable by other processes.

EXAMPLE II: LEACHING

Another leaching test was performed using steel dust more concentrated in zinc and less in manganese. The composition of the dust is given in Table 5. In the test, 20 g of dust was lixiviated with 200 mL of a solution with a sulfuric acid concentration of 0.25 mol/L (10% pulp density by weight) in an erlenmeyer with baffle. Table 6 presents the elements concentration in each leaching solution.

Table 5: Elements concentration in the metallic sludge (g/kg)

Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
0.74	108	19.8	0.0	10.2	62.3	2.03	0.54	392	15.9

After the leaching test of zinc, the slurry was filtered. A small portion was dried, crushed, digested and analyzed with ICP AES is given in Table 7. A sample of the filtrate was also analyzed. The sulfuric acid concentration used for each leaching is 0.25 mol/L, about 89.7% of the zinc is extracted. Times of leaching did not exceeded 30 minutes and times of rising did not exceeded 10 minutes. The weight of dry residue after leaching is 7.4 g. It is not necessary to do manganese leaching because the concentration of manganese in the metallic sludge is too low. This final residue contains 27.4% Pb and is recyclable by other processes.

Table 6: Elements concentration in leach liquor (mg/L)

	Volume (mL)	[H_2SO_4] (mol/L)	pH	Mn	Pb	Al	Ca	Fe	Mg	Sn	Zn
L1 Zn	190	0.25	5.66	8.33	13.0	18.0	248	23.5	33.1	0.0	10817
L2 Zn	210	0.25	5.36	7.42	8.75	30.2	138	43.3	27.9	0.0	12613
L3 Zn	226	0.25	2.89	13.2	11.5	1134	83.7	671	29.2	40.0	9445
R1 Zn	200	0.0	3.80	1.89	5.91	81.0	11.4	63.4	2.90	0.0	946
Extraction %				**44.1**	**0.4**	**71.4**	**47.7**	**14.3**	**47.2**	**83.5**	**89.7**

Table 7: Elements concentration in the metallic sludge (g/kg)

Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
1.0	274	24.0	1.0	16.1	136	4.0	-	39.7	24.0

EXAMPLE III: LEACHING

Another leaching test was performed using steel dust more concentrates in manganese and less in zinc and lead. The composition of the dust is given in Table 8. In the test, 20 g of dust was lixiviated with 200 mL of a solution with a sulfuric acid (10% pulp density by weight) in an erlenmeyer with baffle. Table 9 presents the element concentration in each leaching solution.

Table 8: Elements concentration in the metallic sludge (g/kg)

Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
278	3.93	58.0	7.88	56.7	12.7	16.6	0.51	7.74	5.60

Table 9: Elements concentration in leach liquor (mg/L)

	Volume (mL)	pH	Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
L1 Zn	150	3.31	173	0.0	617	250	662	1.50	652	0.0	99.4	2712
L2 Zn	204	1.83	744	0.9	1712	213	603	17.2	492	2.80	299	5641
L3 Zn	204	1.22	670	1.9	1152	107	632	79.0	258	2.00	178	6928
R1 Zn	202	1.56	200	0.0	541	45.0	591	8.00	111	0.60	67.2	2758
R2 Zn	202	1.94	61.2	0.0	230	24.8	612	0.80	47.3	0.0	22.8	1367
R3 Zn	202	2.34	23.1	0.0	109	14.2	639	0.0	26.1	0.0	8.20	889
L1 Mn	176	3.81	12846	4.65	22.2	26.8	562	0.14	86.6	7.92	40.7	19464
L2 Mn	162	3.62	8116	5.17	28.5	12.3	533	5.69	61.8	5.93	51.5	14078
R1 Mn	150	3.66	3063	1.57	9.17	3.79	507	0.77	21.7	2.00	18.1	5162
R2 Mn	152	4.11	1230	5.89	8.56	2.86	531	0.00	7.54	0.0	6.92	2147
Extraction %			82.6	4.3	74.7	80.9	93.9	8.9	95.7	36.8	97.8	-

After the leaching test of zinc and manganese, the slurry was filtered. A small portion was dried, crushed, digested and analyzed with ICP AES is given in Table 10. The weight of dry residue after leaching is 5.2 g. About 82.6% of manganese principally in the step of manganese leaching (L1 Mn to R2 Mn) and 97.8% of zinc is extracted principally in the steps of zinc leaching (L1 Zn to R3 Zn).

Table 10: Elements concentration in the metallic sludge (g/kg)

Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
66.3	13.1	80.8	2.4	116	52.4	9.0	23.9	6.9	125

EXAMPLE IV: LEACH LIQUOR PURIFICATION

In this example, the leach liquor purification is performed using a technique such as precipitation. The aim of precipitation is to remove iron and aluminum from the leach liquor after the zinc leaching test. The compositions of the leach liquor and the initial pH are in Table 11. For each precipitation step, 1 liter of leach liquor has been used.

Table 11: Elements concentration in the leach liquor (mg/L)

	pH	Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S	Na
L1 Zn	3.17	439	4.8	530	375	519	2.50	512	0.8	463	2882	28.5
L2 Zn	2.42	967	7.2	1773	236	511	69.4	403	41.2	803	5915	11.9
L3 Zn	1.46	740	6.3	988	95.6	593	1011	176	40.1	406	7466	4.70

The pH of the solution is changed to about 4.25 and 4.75 to precipitate silicate, iron and aluminum in a mix tank using lime or sodium hydroxide as precipitation agent. After pH stabilization and decantation the purified leach liquor and residues are analyzed. The compositions of the purified leach liquors, the final pH and the quantity of lime used in each precipitation are shown in Table 12. Table 12 shows that the majority of iron and aluminum have been precipitated without zinc and manganese.

The compositions of the precipitates are shown in Table 13.

Table 12: Elements concentration in the purified leach liquor (mg/L)

	pH	Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S	Na	$Ca(OH)_2$ (g)
L1 Zn	4.26	417	1.80	70.4	376	720	0.80	510	0.0	461	2109	27.1	1.6
L2 Zn	4.26	856	1.60	52.9	224	531	0.10	390	0.0	704	2082	10.5	6.3
L3 Zn	4.26	690	1.60	94.9	103	594	34.9	214	0.0	361	1691	4.30	14.1

Table 13: Elements concentration in the dry precipitates (g/kg)

	Moisture %	Mn	Pb	Al	K	Ca	Fe	Mg	Sn	Zn	S
L1 Zn	93.4	11.0	1.41	66.5	64.9	108	2.04	7.78	0.40	7.89	138
L2 Zn	90.5	11.1	0.43	57.0	28.5	120	3.98	4.26	1.34	8.50	146
L3 Zn	85.9	4.90	0.27	25.7	9.39	138	29.1	1.63	0.94	3.00	145

EXAMPLE V: ZINC OXIDE PRECIPITATION

Zinc oxide was precipitated from leach liquors after the zinc leaching (see EXAMPLE II) using stoichiometric quantity of NaOH as a precipitation agent (considering the concentration of Zn) at pH between 9.0 and 11.0. In the test, 1000 mL of leach liquor L1 Zn with 9339 mg Zn/L is precipitated with 114 mL of 100 g NaOH/L. The results are in Table 14.

Table 14: Initial concentration of elements in leach liquors (mg/L)

	Mn	Pb	Al	K	Ca	Fe	Mg	Zn	S	Na	pH ini	pH fin
L1 Zn	9.70	10.0	7.20	0.0	460	0.0	39.6	9339	5668	0.0	5.7	10.8
L2 Zn	11.5	6.90	24.7	1.4	357	8.3	37.1	11536	6845	0.0	5.4	10.0

After the precipitation, 20.0 g of ZnO for L1 Zn and 24.7 g of ZnO for L2 Zn are precipitated. The solid zinc oxide is separated from the solution by a filter. Concentrations of various elements of the finals cake are in Table 15. The concentration of zinc in the cake is 52.9 % for L1 Zn and 50.5 % for L2 Zn.

Table 15: Concentration of elements in g/kg in the final cake

	Mn	Pb	Al	K	Ca	Fe	Mg	Zn	S	Na

L1 Zn	0.52	0.53	0.48	0.15	8.87	0.02	6.63	529	60.2	48.6
L2 Zn	0.52	0.31	1.13	0.11	9.82	0.39	4.55	505	67.6	55.5

EXAMPLE VI: ZINC SULPHIDE PRECIPITATION

Zinc sulphide was precipitated from purified leach liquors using Na_2S as a precipitation agent at pH between about 4.5 and about 5.5. In this test 150 mL of leach liquor L Zn with 855.8 mg Mn/L and 704 mg Zn/L is precipitated with twice the stoichiometry (considering the concentration of Zn) of Na_2S. The Mn and Zn concentration after and before the precipitation are in Table 16.

Table 16: Concentration of elements in leach liquor (mg/L)

	Mn	Pb	Al	K	Ca	Fe	Mg	Zn	S
L Zn Before	856	1.6	52.9	224	531	0.1	390	704	2082
L Zn After	855	0.0	50.5	231	476	0.0	343	77.6	2334

Table 16 shows that most of zinc is precipitated in sulphides without manganese which will be precipitated as carbonate in another stage.

EXAMPLE VII: MANGANESE CARBONATE PRECIPITATION

Manganese carbonate was precipitated from purified leach liquors using stoichiometry of Na_2CO_3 as a precipitation agent (considering the concentration of Mn) at pH between about 7.5 and 8.5. Before manganese carbonate precipitation, impurities like Al, Fe, Pb and Zn are removed as sulfide from the leach liquor. The pH of the solution is changed to about 4.80 and 5,80 to precipitate aluminum, iron, lead and zinc in a mix tank using sodium hydroxide and sodium sulfide as precipitation agent. After pH stabilization and decantation the purified leach liquor is filtrated, manganese carbonate is then precipitated with Na_2CO_3. Manganese precipitation is very fast at ambient temperature.

In the test, 1000 mL of leach liquor L1 Mn with 10125 mg Mn/L is precipitated with 23.4 g of Na_2CO_3. The results are shown in Table 17.

Table 17: Initial concentration in mg/L of elements in leach liquors after purification

	Mn	Pb	Al	K	Ca	Fe	Mg	Zn	S	pH ini	pH fin
L1 Mn	10125	2.1	0.1	23.4	545	1.1	34.1	0.5	13888	4.8	8.6
L2 Mn	7499	1.7	0.2	13.8	517	0.6	34.0	0.2	11279	5.6	8.6

After the precipitation, 26.9 g of $MnCO_3$ for L1 Mn and 16.4 g of $MnCO_3$ for L2 Mn are precipitated. The solid manganous carbonate is separated from the solution by a filter. Concentrations of various elements of the finals cake are in the Table 18. The elements concentration in leach liquors after precipitation of $MnCO_3$ are in Table 19, the majority of manganese have been precipitated but calcium, sodium and sulfides are also precipitated.

Table 18: Concentration of elements in g/kg in the final cake

	Mn	Pb	Al	K	Ca	Fe	Mg	Zn	S	Na
L1 Mn	439	0.5	0.1	1.7	13.2	0.1	0.0	1.6	17.8	19.3
L2 Mn	411	0.6	8.9	1.8	14.5	0.7	0.1	5.3	15.4	15.8

Table 19: Concentration of elements in leach purified liquor (mg/L)

	Mn	Pb	Al	K	Ca	Fe	Mg	Zn	S	Na
L1 Mn	5.6	1.1	0.0	21.6	58.2	0.0	29.0	0.0	11727	13518
L2	6.2	0.7	0.1	14.4	36.8	0.6	25.4	0.0	11722	10259

Mn

After the precipitation, it is preferred to wash the manganous carbonate precipitates to eliminate the sodium and sulfides. In the test, 20 g of manganous carbonate was rinsed with 200 mL of water (10% pulp density by weight), the results are shown in Table 20. The concentration of Mn in the cake is 44.6 % for L1 and 43.0 % for L2.

Table 20: Concentration of elements in g/kg in the final cake after rinsing

	Mn	Pb	Al	K	Ca	Fe	Mg	Zn	S	Na
L1 Mn	446	0,3	0,0	1.9	20.9	0,0	0,3	0.0	2.3	7,6
L2 Mn	430	0,2	0.0	0.7	28.9	0,0	0,7	0.0	1.8	6.4

EXEMPLE VIII: ZN ELECTROPLATING

Zn metal was electrodeposited from leach liquor using an electroplating cell. An electrical power source is connected to four cathodes and four anodes. The cathodes are made of stainless steel and the anodes are made of TiO_2. The area of each cathode is 220 cm^2. The solution is fed into electrolytic tank of 2 liters where zinc metal is deposited on the stainless steel cathodes during electrolysis. At the TiO_2 anodes an oxidation reaction occurs, generating oxygen gas, protons and giving electrons. The current is fixed of 15 A and every 60 minutes the cathodes full of Zn metal are replaced by news cathodes.

Reduction at cathode: $Zn^{2+} + 2e^- \rightarrow Zn$

Oxidation at anode: $H_2O \rightarrow 2H^+ + \frac{1}{2}O_2 + 2e^-$

Zinc metal was electrolysed from the mixture of leach liquors L1 and L2 after the zinc leaching (see EXAMPLE II). The results are shown in Table 21 and Figure 1 shows the Zn concentration during the electrolysis.

Table 21: Concentration of elements in leach liquors (mg/L)

	Mn	Pb	Al	K	Ca	Fe	Mg	Zn	S	Na
L1 and L2 Zn Before	8.2	7.7	17.3	0.0	240	14.6	33.5	10966	5713	0.0
L1 and L2 Zn After	2.9	0.0	20.8	0.0	186	12.3	26.7	1530	5714	0.0

With four change of cathode, about 86.0% of Zn is electrolyzed and the final concentration of Zn reaches 1530 mg/L.

While the techniques described herein apply to steel plant dust as well as various streams and materials derived therefrom, they can also be used for treating other matrices to extract valuable materials. For example, various waste or byproduct streams from the metals processing industry may be processed to extract compounds such as Zn, Mn and/or Pb, in particular when the concentration of such compounds is economically significant. Waste streams can include electric arc furnace (EAF) dust, various pyrometallurgical residues, and materials derived therefrom. Waste streams from the metals processing industry or other matrices can also be tested to determine the composition and extractability of desired components, prior to subjecting the waste streams to an implementation of the techniques described herein. Various other matrices, such as mining residues, can also be treated with techniques described herein.

CLAIMS

1. A process for treating a matrix comprising zinc (Zn), manganese (Mn) and lead (Pb), comprising:

   leaching the matrix to generate a leaching solution enriched in Zn and a fraction enriched in Mn and Pb;

   subjecting the leaching solution to Zn-precipitation to produce Zn-based precipitates and a Zn-depleted fraction comprising Mn compounds;

   leaching the fraction enriched in Mn and Pb to produce a Mn-enriched leaching solution and a Pb-enriched fraction; and

   subjecting the Zn-depleted fraction and/or the Mn-enriched leaching solution to Mn-precipitation to produce Mn-based precipitates.

2. The process of claim 1, wherein the leaching of the matrix is performed using an aqueous acidic solution.

3. The process of claim 2, wherein the aqueous acidic solution comprises H_2SO_4.

4. The process of claim 2 or 3, wherein the leaching of the matrix comprises multiple leaching runs with the aqueous acidic solution and multiple rinsing runs with an aqueous rinsing solution.

5. The process of claim 4, wherein the leaching of the matrix comprises at least three leaching runs and/or at least three rinsing runs.

6. The process of any one of claims 1 to 5, further comprising, prior to the Zn-precipitation, removing additional metal components from the leaching solution enriched in Zn.

7. The process of claim 6, wherein the additional metal components include aluminum (Al).

8. The process of claim 6 or 7, wherein the additional metal components include iron (Fe).

9. The process of any one of claims 6 to 8, wherein the removing of the additional metal components comprises precipitating the additional metal components.

10. The process of claim 9, wherein precipitating of the additional metal components comprises adding a hydroxide of a divalent cation.

11. The process of claim 10, wherein the hydroxide of a divalent cation comprises $Ca(OH)_2$ or NaOH.

12. The process of any one of claims 1 to 11, wherein the Zn-precipitation comprises adding NaOH or Na_2S to produce ZnO or ZnS as the Zn-based precipitates.

13. The process according to any one of claims 1 to 12, further comprising, prior to the Mn-precipitation, removing additional metallic impurities from the Zn-depleted fraction and/or the Mn-enriched leaching solution.

14. ,The process of claim 13, wherein the additional metallic impurities comprise aluminum, iron, lead, zinc or a combination thereof.

15. The process of claim 13 or 14, wherein removing the additional metallic impurities prior to the Mn-precipitation comprises adding NaOH and Na_2S to the Zn-depleted fraction and/or the Mn-enriched leaching solution.

16. The process of any one of claims 1 to 15, wherein the Mn-precipitation comprises adding a carbonate compound to produce Mn-carbonates as the Mn-based precipitates.

17. The process of claim 16, wherein the carbonate compound comprises Na_2CO_3 to produce $MnCO_3$.

18. The process of any one of claims 1 to 17, further comprising, prior to the leaching of the matrix, a step of determining a composition of the matrix.

19. The process of claim 18, wherein determining the composition of the matrix comprises determining the concentrations of Zn and Mn.

20. The process of claim 18 or 19, wherein determining the composition of the matrix comprises determining the concentration of Pb.

21. The process of any one of claims 18 to 20, wherein determining the composition of the matrix includes determining the concentrations of Al and/or Fe.

22. The process of any one of claims 1 to 21, further comprising treating the Pb-enriched fraction to recover Pb therefrom.

23. The process of any one of claims 1 to 22, further comprising:

    subjecting the Zn-depleted fraction to Mn-precipitation in a first reactor to produce a first stream of Mn-based precipitates; and

    subjecting the the Mn-enriched leaching solution to Mn-precipitation in a second reactor to produce a second stream of Mn-based precipitates.

24. The process of claim 23, further comprising:

    producing a Mn-depleted stream in the second reactor; and

    subjecting at least a portion of the Mn-depleted stream to further Mn-precipitation.

25. The process of claim 24, wherein the further Mn-precipitation of the Mn-depleted stream is conducted in the first reactor.

26. The process of any one of claims 23 to 25, further comprising recycling a portion of the Mn-depleted stream from the second reactor for addition to the matrix before or during the leaching thereof.

27. The process of any one of claims 23 to 26, further comprising recovering a metals-depleted liquid from the Mn-precipitation in the first reactor and adding at least a portion of the metals-depleted liquid to the matrix before or during the leaching thereof.

28. The process of any one of claims 1 to 27, wherein the leaching of the matrix is performed in atmospheric pressure conditions.

29. The process of any one of claims 1 to 27, wherein one or more of the leaching steps are performed in a counter-current reactor.

30. The process of any one of claims 1 to 28, wherein one or more of the leaching steps are performed in an agitated tank reactor.

31. The process of any one of claims 1 to 28, wherein one or more of the leaching steps are performed in a batch reactor or a continuous.

32. The process of any one of claims 1 to 31, wherein the matrix comprises a powder or dust.

33. The process of any one of claims 1 to 32, wherein the matrix comprises a by-product or waste stream derived from metals processing.

34. The process of any one of claims 1 to 33, wherein the matrix comprises steel plant dust.

35. The process of any one of claims 1 to 34, including one or more features of claims 33 to 53.

36. A process for treating a matrix comprising zinc (Zn), manganese (Mn) and lead (Pb), comprising selective and sequential leaching of Zn, Mn and Pb in order to obtain a Mn concentrate, a Zn concentrate, and a Pb-enriched residue.

37. The process of claim 36, including one or more features of claims 1 to 35 and 38 to 56.

38. A method for the hydrometallurgical treatment of a matrix comprising manganese (Mn), zinc (Zn), lead (Pb), iron (Fe), aluminum (Al), and at least one of calcium, chlorides, sodium and potassium as impurities, the method comprising:

a first leaching step comprising:

leaching the matrix at atmospheric pressure in a reactor using a first leaching solution to product a first leach liquor and a first leach residue, the first leaching solution comprising a sulfuric acid solution; and

separating the first leach liquor from the first leach residue after the first leaching;

a second leaching step comprising:

leaching the first leach residue at atmospheric pressure using a second leaching solution to form a second leach liquor and a second leach residue, the second leaching solution comprising sulfuric acid and a reducing agent; and

separating the second leach liquor from the second leach residue;

a Mn-precipitation step wherein Mn compounds are precipitated from the first and second leach liquors, including contacting the liquors or streams derived therefrom, with a carbonate at a pH to precipitate Mn carbonate compounds.

39. The method of claim 38, further comprising selecting a quantity of the carbonate to adjust the pH of the first and second leach liquor sufficiently to precipitate out Mn carbonate compounds.

40. The method of claim 38 or 39, wherein the pH of the second leaching is between about 3 and about 5.

41. The method of any one of claims 38 to 40, wherein the reducing agent used in the second leaching step comprises $Na_2S_2O_5$.

42. The method of any one of claims 38 to 41, further comprising subjecting the first liquor to Zn-precipitation prior to Mn-precipitation.

43. The method of claim 42, wherein the Zn-precipitation includes electroplating Zn as Zn metal.

44. The method of claim 42, wherein the Zn-precipitation includes forming Zn sulfide and/or Zn oxide precipitates that are precipitated out of the solution.

45. The method of claim 44, further comprising separating the Zn sulfide and/or Zn oxide precipitates from the solution to form a Zn sulfide and/or Zn oxide containing residue, and a Zn-depleted first liquor that is subjected to the Mn-precipitation step.

46. The method of claim 44 or 45, wherein the Zn-precipitation comprises:

adding alkali or sulfide to the first liquor to precipitate Zn compounds; and then

preforming a solid-liquid separation to produce a Zn sulfide and/or oxide cake.

47. The method of any one of claims 44 to 46, further comprising:

subjecting the first liquor to a Fe, silicate and Al precipitation step to form Fe, silicate and Al hydroxide compounds and a depleted liquor;

separating the Fe, silicate and Al hydroxide compounds from the depleted liquor; and

subjecting the depleted liquor to the Zn-precipitation.

48. The method of the claim 47, wherein the Fe, silicate and Al precipitation step comprises:

adding alkali to increase the pH between about 4 and about 5; and then

preforming a solid-liquid separation to produce a mixed Fe, silicate and Al hydroxide cake.

49. The method of any one of claims 38 to 48, wherein the Mn-precipitation step comprises:

adding the carbonate to the first and second liquors to increase the pH to between about 7.5 and about 8.5; and then

performing a solid-liquid separation to produce a Mn-carbonate cake.

50. The method of any one of claims 38 to 49, wherein the second leach residue contains between 10 wt% and 30 wt% of Pb.

51. The method of any one of claims 38 to 50, wherein a leaching period of mixing the sulfuric acid solution for the first and/or second leaching steps is between about 10 minutes and about 24 h.

52. The method of any one of claims 38 to 51, wherein the temperature of the sulfuric acid solution is between about 20°C and about 40°C.

53. The method of any one of claims 38 to 52, further comprising one or more features of claims 1 to 34.

54. A system for treating a matrix comprising zinc (Zn) and manganese (Mn), comprising:

    a leaching unit for leaching the matrix to generate a Zn-enriched leaching solution, and a fraction enriched in Mn and Pb;

    a Zn-precipitation unit for subjecting the Zn-enriched leaching solution to Zn-precipitation to produce Zn-based precipitates and a Zn-depleted fraction comprising Mn compounds; and

    a leaching unit for leaching the fraction enriched in Mn and Pb to produce a Mn-enriched leaching solution and a Pb-enriched fraction; and

    a Mn-precipitation system for subjecting the Zn-depleted fraction and/or the Mn-enriched leaching solution, or streams derived therefrom, to Mn-precipitation to produce Mn-based precipitates.

55. The system of claim 54, wherein the Mn-precipitation system comprises:

    a first Mn-precipitation unit for subjecting the Zn-depleted fraction to Mn-precipitation; and

    a second Mn-precipitation unit for subjecting the Mn-enriched leaching solution to Mn-precipitation.

56. The system of claim 54 or 55, further comprising an additional precipitation unit for receiving the Zn-enriched leaching solution and removing at least one of aluminum (Al), iron (Fe) and silicate therefrom, to produce a liquor for supplying to the Zn-precipitation unit.

57. A system for the hydrometallurgical treatment of a matrix comprising manganese (Mn), zinc (Zn), lead (Pb), iron (Fe), aluminum (Al), and at least one of calcium, chlorides, sodium and potassium as impurities, the system comprising:

a first leaching unit for leaching the matrix at atmospheric pressure in a reactor using a first leaching solution to product a first leach liquor and a first leach residue, the first leaching solution comprising a sulfuric acid solution;

a first separation unit for separating the first leach liquor from the first leach residue after the first leaching;

a second leaching unit for leaching the first leach residue at atmospheric pressure using a second leaching solution to form a second leach liquor and a second leach residue, the second leaching solution comprising sulfuric acid and a reducing agent;

a second separation unit for separating the second leach liquor from the second leach residue; and

a Mn-precipitation system for precipitating Mn compounds from the first and second leach liquors, or streams derived therefrom, by contacting with a carbonate at a pH to precipitate Mn carbonate compounds.

58. The system of claim 57, wherein the Mn-precipitation system comprises:

a first Mn-precipitation unit for subjecting the first leach liquor to Mn-precipitation; and

a second Mn-precipitation unit for subjecting the second leach liquor to Mn-precipitation.

59. The system of claim 58, further comprising:

an additional precipitation unit for receiving the first leach liquor and removing at least one of aluminum (Al), iron (Fe) and silicate therefrom, to produce a metals depleted liquor comprising Zn and Mn;

a Zn-precipitation unit for receiving the metals depleted liquor and producing Zn precipitates and a Zn-depleted fraction, wherein the first precipitation unit is configured to receive the Zn-depleted fraction to be subjected to the Mn-precipitation.

60. The system of any one of claims 54 to 59, further comprising one or more operational or structural features of claims 1 to 53 and/or described in the description or drawings.

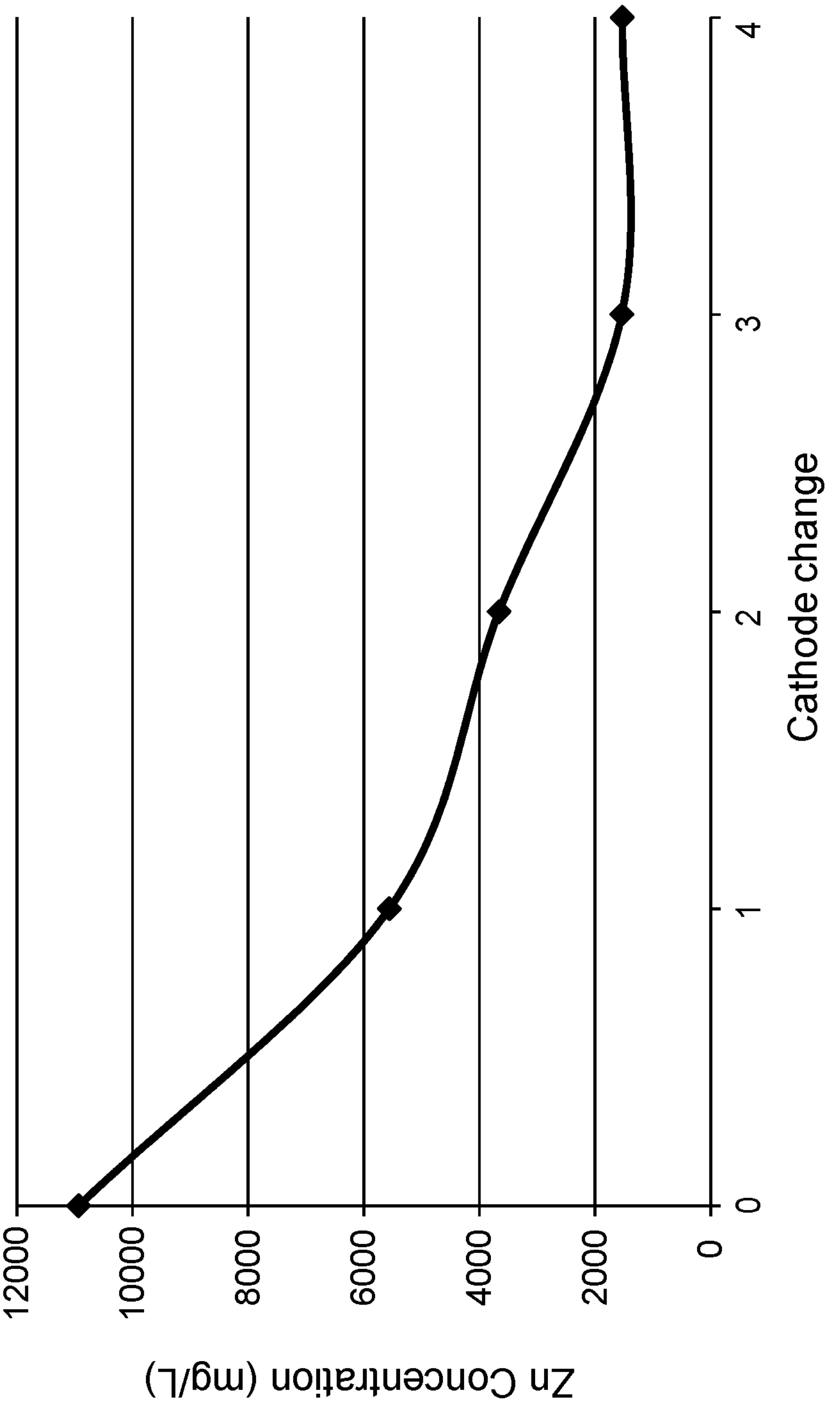
Zn Concentration (mg/L)
12000
10000
8000
6000
4000
2000
0
0
1
2
3
4
Cathode change

FIG. 1

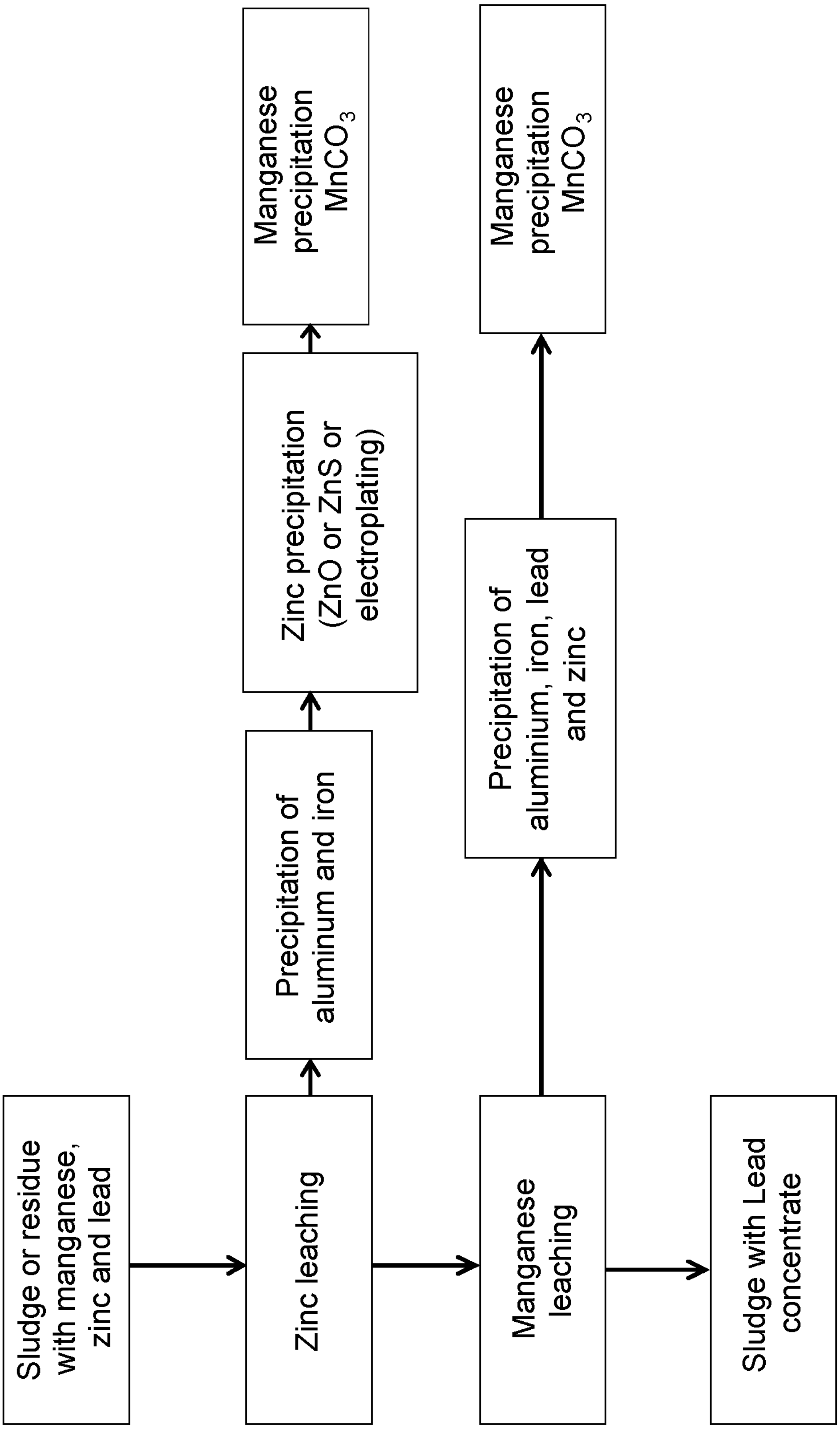
Sludge or residue with manganese, zinc and lead
Zinc leaching
Precipitation of aluminum and iron
Zinc precipitation (ZnO or ZnS or electroplating)
Manganese precipitation MnCO3
Manganese leaching
Precipitation of aluminium, iron, lead and zinc
Manganese precipitation MnCO3
Sludge with Lead concentrate

FIG. 2

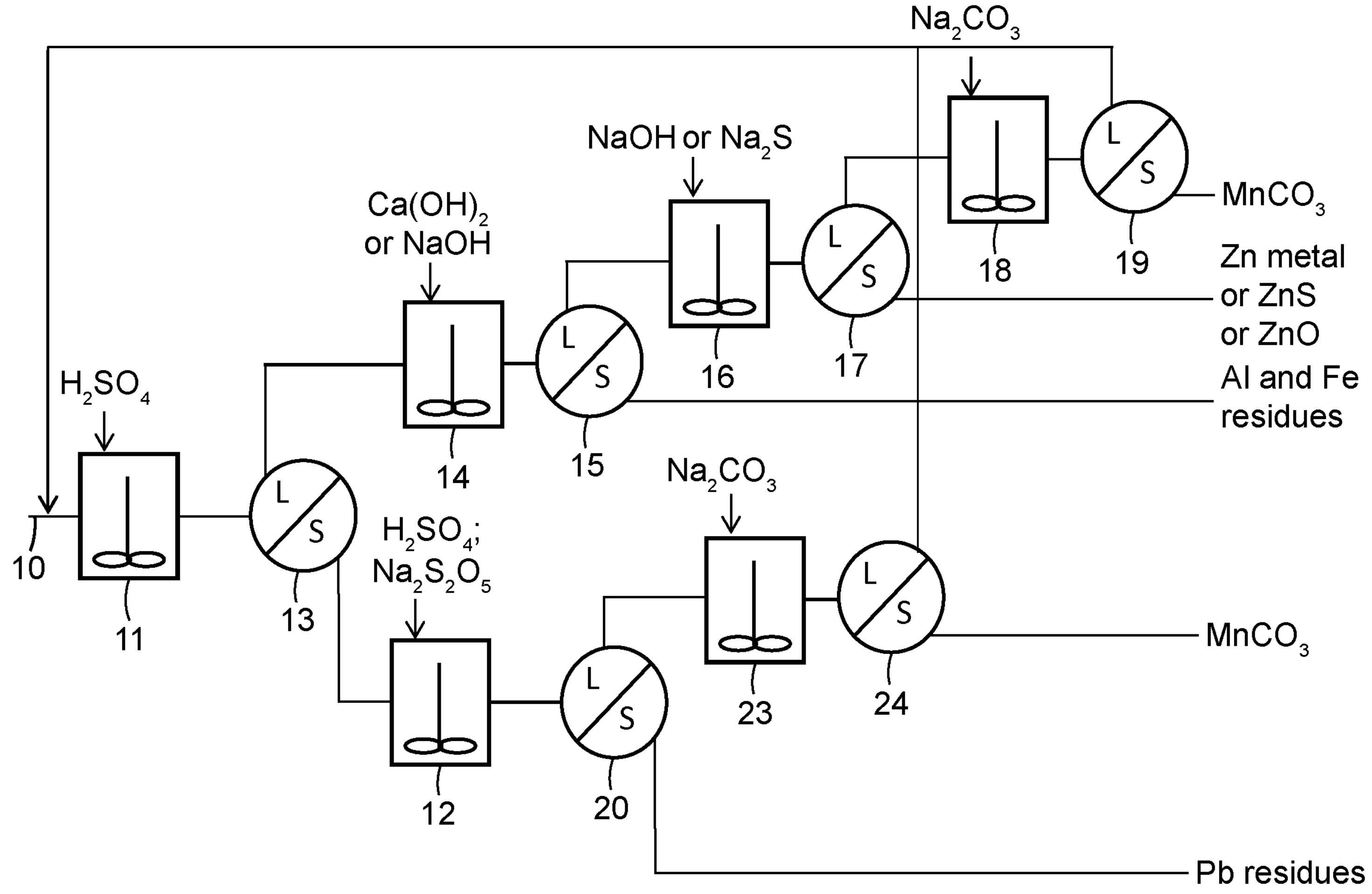
Na$_2$CO$_3$
NaOH or Na$_2$S
Ca(OH)$_2$ or NaOH
H$_2$SO$_4$
MnCO$_3$
Zn metal or ZnS or ZnO
Al and Fe residues
H$_2$SO$_4$; Na$_2$S$_2$O$_5$
Na$_2$CO$_3$
MnCO$_3$
Pb residues
L
S
10
11
12
13
14
15
16
17
18
19
20
23
24

FIG. 3

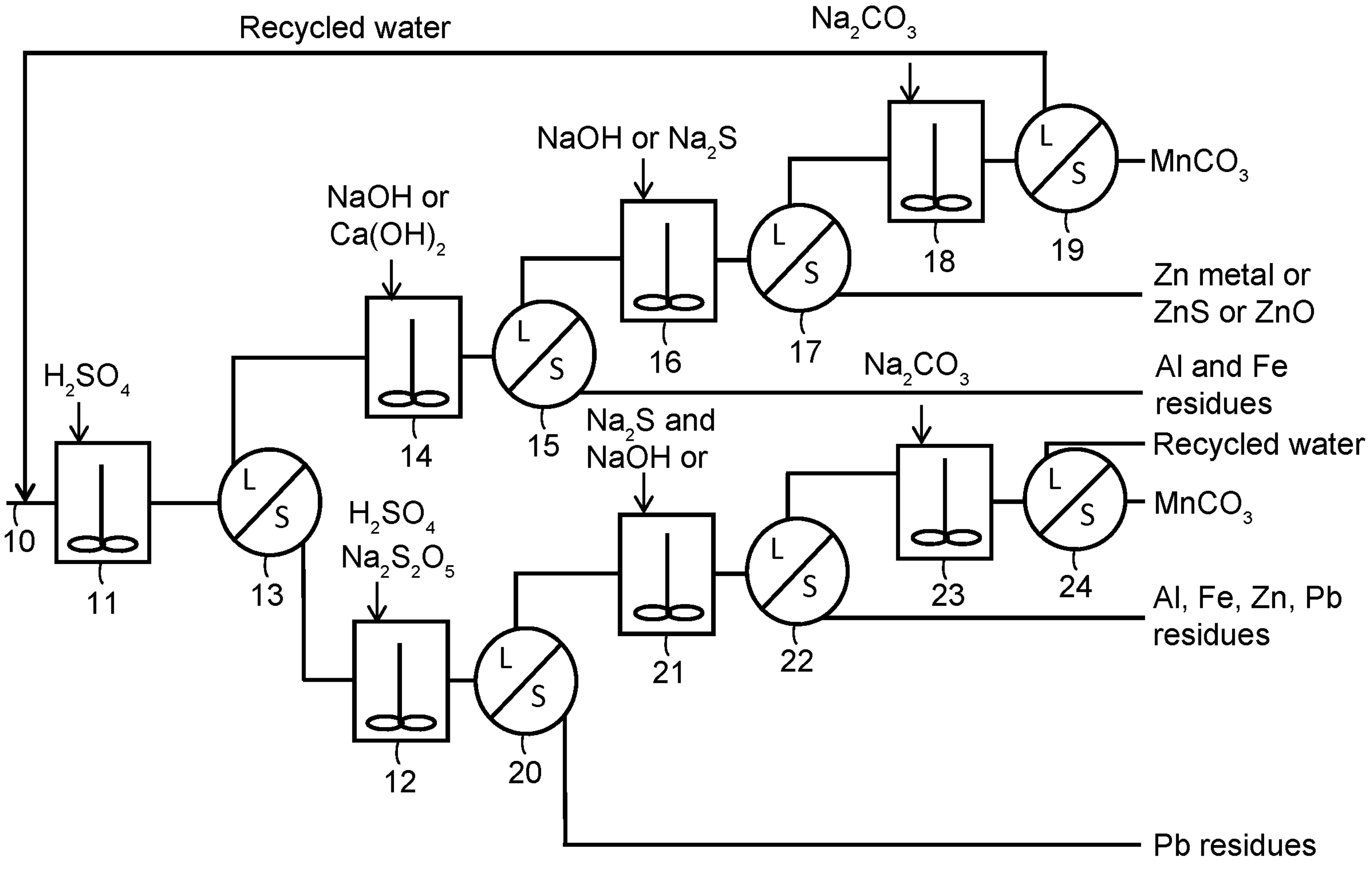
Recycled water
Na_2CO_3
NaOH or Na_2S
NaOH or $Ca(OH)_2$
H_2SO_4
$MnCO_3$
Zn metal or ZnS or ZnO
Al and Fe residues
Na_2CO_3
Na_2S and NaOH or
Recycled water
$MnCO_3$
H_2SO_4 $Na_2S_2O_5$
Al, Fe, Zn, Pb residues
Pb residues
L
S
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24

FIG. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2015/050547

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C22B 3/08*** (2006.01) , ***C22B 3/46*** (2006.01) , ***C22B 7/00*** (2006.01) , ***C22B 7/02*** (2006.01) ,
C22B 13/08 (2006.01) , *C22B 19/00* (2006.01) (more IPCs on the last page)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC: C22B 3/08 (2006.01), C22B 19/00 (2006.01), C22B 19/20 (2006.01), C22B 47/00 (2006.01), C22B 7/02 (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)
FAMPAT (Questel), Scopus, Google

Leach*/dissol*/solubili*/digest*, zinc*/zn*, mangan*/mn*, lead/pb*, residu*/cake/solid*/under_flow/fraction, precipit*/cement*, reduc*

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X -- Y	CN102586599A (LIU et al.) 18 July 2012 (18-07-2012)	36-37 -- 1-22, 28-35
Y	GB1290672A (SNELGROVE) 27 September 1972 (27-09-1972)	1-22, 28-35
X	US3976743A (LANDUCCI et al.) 24 August 1976 (24-08-1976)	54-60
A	WO2006119611A1 (PUVVADA et al.) 16 November 2006 (16-11-2006)	

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

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search 04 September 2015 (04-09-2015)	Date of mailing of the international search report 18 September 2015 (18-09-2015)
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.: 001-819-953-2476	Authorized officer Jay Fothergill (819) 997-4842

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CA2015/050547

Patent Document Cited in Search Report	Publication Date	Patent Family Member(s)	Publication Date
CN102586599A	18 July 2012 (18-07-2012)	CN102586599A	18 July 2012 (18-07-2012)
		CN102586599B	31 July 2013 (31-07-2013)
GB1290672A	27 September 1972 (27-09-1972)	None	
US3976743A	24 August 1976 (24-08-1976)	US3976743A	24 August 1976 (24-08-1976)
		AU8448475A	10 March 1977 (10-03-1977)
		BE832924A1	16 December 1975 (16-12-1975)
		CA1035580A1	01 August 1978 (01-08-1978)
		DE2540641A1	01 April 1976 (01-04-1976)
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		FR2284682B1	24 December 1981 (24-12-1981)
		GB1509537A	04 May 1978 (04-05-1978)
		JPS5154825A	14 May 1976 (14-05-1976)
		JPS5621813B2	21 May 1981 (21-05-1981)
		NL7510779A	16 March 1976 (16-03-1976)
		NL180022B	16 July 1986 (16-07-1986)
		NL180022C	16 December 1986 (16-12-1986)
		NO753098A	16 March 1976 (16-03-1976)
		NO142995B	18 August 1980 (18-08-1980)
		NO142995C	26 November 1980 (26-11-1980)
WO2006119611A1	16 November 2006 (16-11-2006)	WO2006119611A1	16 November 2006 (16-11-2006)
		CA2590927A1	16 November 2006 (16-11-2006)
		CN101184856A	21 May 2008 (21-05-2008)
		CN100567524C	09 December 2009 (09-12-2009)
		EP1880030A1	23 January 2008 (23-01-2008)
		EP1880030A4	03 March 2010 (03-03-2010)
		JP2008540835A	20 November 2008 (20-11-2008)
		JP5149163B2	20 February 2013 (20-02-2013)
		KR20080016607A	21 February 2008 (21-02-2008)
		KR101011382B1	28 January 2011 (28-01-2011)
		MX2007013950A	12 December 2008 (12-12-2008)
		TR200707718T1	21 April 2008 (21-04-2008)
		US2008145289A1	19 June 2008 (19-06-2008)
		US7666372B2	23 February 2010 (23-02-2010)

C22B 47/00 (2006.01)