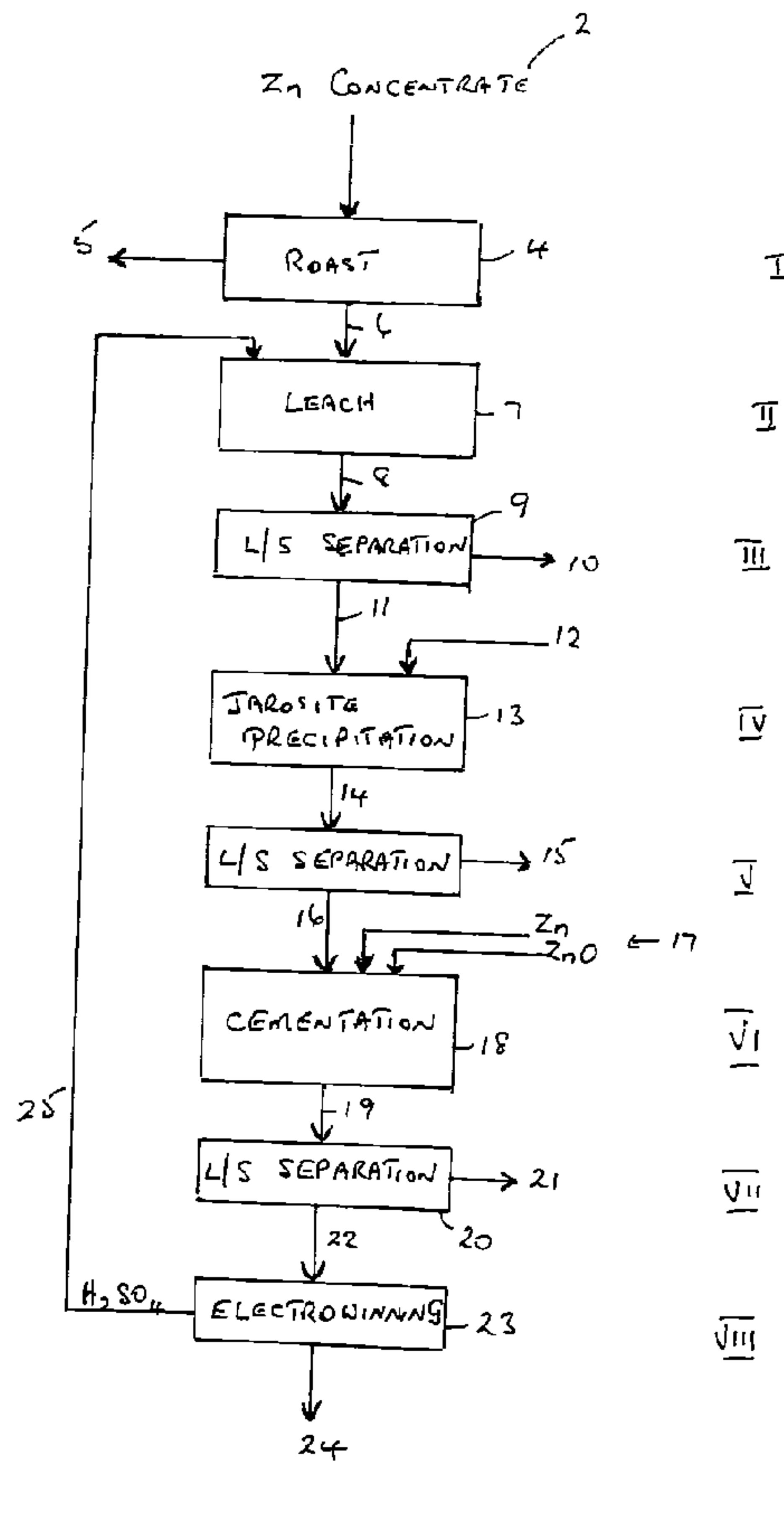




- (72) CONVEY, John Raymond, CA
 (72) LAUGHLIN, Robert Gardiner Willis, CA
 (72) LAKSHMANAN, Vaikuntam Iyer, CA
 (72) SRIDHAR, Ramamritham, CA
 (71) MORTIMER TECHNOLOGY HOLDINGS LIMITED, GB
 (51) Int.Cl.⁶ C22B 3/08
 (54) **PROCEDE HYDRO-METALLURGIQUE DE RECUPERATION
DU ZINC**
 (54) **HYDROMETALLURIGICAL PROCESS FOR RECOVERY OF
ZINC**



(57) A process for the recovery of zinc from a zinc ore. The process comprises leaching material obtained from a zinc ore with dilute sulphuric acid, in which essentially all of the zinc is in the form of zinc oxide. The leachate obtained is separated for recovery of zinc. Preferably, the material is substantially free of zinc ferrite. In preferred embodiments, the material is obtained from an iron-bearing zinc ore, especially zinc sulphide ore or concentrate, that has been subjected to a roasting step at a temperature of greater than 1050°C.



ABSTRACT OF THE DISCLOSURE

A process for the recovery of zinc from a zinc ore. The process comprises leaching material obtained
5 from a zinc ore with dilute sulphuric acid, in which essentially all of the zinc is in the form of zinc oxide. The leachate obtained is separated for recovery of zinc. Preferably, the material is substantially free of zinc ferrite. In preferred embodiments, the material is
10 obtained from an iron-bearing zinc ore, especially zinc sulphide ore or concentrate, that has been subjected to a roasting step at a temperature of greater than 1050°C.

HYDROMETALLURGICAL PROCESS FOR RECOVERY OF ZINC

The present invention relates to a hydrometallurgical process for the recovery of zinc, and especially to the recovery of zinc from an ore or concentrate in which the zinc values are in the form that may be leached in dilute sulphuric acid. In particular, the zinc values are in the form of zinc oxide, and the ore or concentrate is substantially free of zinc ferrite. In embodiments, the invention relates to the process for the recovery of zinc from the roasting of sulphide ores or concentrates containing zinc, especially iron-bearing zinc sulphide ores or concentrates, the zinc sulphide ore or concentrate having been roasted so as to convert zinc values to zinc oxide, in the absence of residual zinc sulphide and in which the amount of zinc ferrite that is typically formed in roasted iron-bearing zinc sulphide concentrate is reduced or eliminated. In particular, the present invention relates to a process for recovery of zinc in a hydrometallurgical process in which fewer steps and/or more economical steps may be used in the recovery of zinc values, and especially in which a single stage leaching step may be used to separate zinc values from roasted ore or concentrate (calcine). The calcine may be prepared for use in the process of the present invention by roasting at high temperature, especially above 1050°C. In embodiments, the calcine is treated to form magnetite, where the ore is an iron-bearing ore, which may be removed.

Processes for the recovery of zinc from zinc sulphide concentrates are well known. Such processes typically involve a fluid bed roasting. The fluid bed roasting results in the production of gaseous sulphur dioxide, and other volatile impurities, and a roasted zinc calcine that contains zinc oxide, zinc ferrite, and typically oxides of lead, cadmium, cobalt, indium and

other metals, depending on the particular composition of the zinc concentrate subjected to the roast and the roasting conditions that are used. The roasting is typically carried out at controlled temperatures, to
5 convert zinc sulphide to zinc oxide while attempting to limit the formation of zinc ferrite. Temperatures of greater than 850°C are used to obtain conversion of zinc sulphate formed in the roasting process to zinc oxide but temperatures are maintained below 950°C as zinc ferrite
10 tends to be formed from the reaction of the zinc oxide with iron oxide in the ore as the temperature increases. As noted below, other techniques are known for reduction of the amount of zinc ferrite that is formed.

The roasted calcine, after grinding if required, is
15 then subjected to a three-stage leaching step, typically involving leaching with a neutral aqueous solution, followed by leaching with a dilute sulphuric acid solution and followed further by leaching with a hot sulphuric acid solution. Liquid/solid separation steps
20 are used after each leach stage with the solids that are separated in the third liquid/solid separation step being sent to a tailings pond. The solids typically contain lead sulphate, some calcium sulphate and other materials.

The leachate from the final leaching stage is then
25 treated with manganese dioxide (MnO_2) and ammonium hydroxide to effect removal of iron as jarosite. A further liquid/solid separation step is used with the solids being sent to the tailings pond.

The leachate solution obtained typically contains,
30 in particular, zinc, calcium and indium. Zinc oxide and zinc are then added sequentially to the leachate solution in a procedure known as cementation. A liquid/solid separation step is used to separate solid materials, these materials being for instance precipitates of lead,
35 tantalum, cobalt and indium. The liquid (leachate) contains zinc sulphate that is sufficiently pure that

zinc may be recovered, for example by being subjected to an electrowinning stage in sulphuric acid solution. Zinc metal is obtained, with sulphuric acid from the electrowinning solution being recycled to the leaching
5 stage on the roasted zinc calcine.

Many ores contain significant amounts of iron. In processes involving application of heat, especially under oxidizing conditions, complex multiple oxides of ferric oxide are formed, known as ferrites. In particular,
10 processes involving dead or sulphation roasting followed by treatment with sulphuric acid to recover zinc as soluble sulphates, generally result in failure to recover ferrites without subsequent severe leach conditions (high acid concentrations and elevated temperature). For
15 instance, dilute acid leaching to recover zinc values from zinc oxide formed during roasting does not recover zinc values from zinc ferrites. The latter zinc values must be recovered under more severe leaching conditions, with higher acid concentration and higher temperatures.
20 However, under the severe leaching conditions, iron values are not only recovered from zinc ferrite but also from other iron oxides in the roasted ore. Consequently, solutions containing zinc contain increased concentrations of iron, which affects subsequent steps to
25 recover zinc. In addition, the higher acid concentrations must be neutralized, thereby requiring use of greater quantities of lime or other bases, which also affects steps to recover metal values from tails and in other downstream processes.

30 Techniques for roasting of zinc ores or concentrates for reduction of formation of ferrites are known. For instance, U.S. 4 478 794 relates to the roasting of mixed zinc sulphide-lead sulphide concentrates to provide an oxidic feed for a smelting process, in which 2-20% by
35 weight of zinc oxide is mixed with the sulphide materials and roasting is conducted at at least two temperatures,

viz. 850-950°C for a first stage and 950-1050°C for the last stage.

U.S. 4 541 993 relates to sulphatization of non-ferrous metal sulphides in which an alkali metal carbonate or bi-carbonate is added to the roasting stage to promote the conversion of the metal sulphides to metal sulphates. Preferred roasting temperatures are from about 550°C to 650°C.

U.S. 4 619 814 describes a method for recovering zinc from sulphidic ores and concentrate. The material in a subdivided form is roasted in a fluidized bed reactor at a temperature of from 620-700°C with 20-60% excess air to obtain a calcine containing zinc primarily as sulphate and oxysulphate and iron primarily as hematite. The calcine is leached with water or dilute sulphuric acid at a temperature below 80°C, and then with hot strong sulphuric acid at a temperature above 80°C but below the boiling point of the solution. Most of the zinc ferrite and unreacted sulphide of zinc is converted to sulphates of iron and zinc, which dissolve in the leach solution.

U.S. 4 789 529 states that in conventional zinc recovery processes, zinc sulphide-bearing minerals are dead roasted at temperatures in the range of 850-1050°C such that essentially all the iron present is converted to zinc ferrite and only the remainder of the zinc present is in the form of zinc oxide. The patent describes a process for the recovery of zinc from sulphidic zinc-bearing ores and concentrates where oxidation roasting is controlled to retain a portion of the sulphides in the calcine, thereby retarding zinc ferrite formation. Roasting is carried out at 700-1050°C.

U.S. 4 889 694 describes roasting iron-bearing zinc sulphide concentrates with a oxidizing gas containing molecular oxygen at a temperature of at least about 900°C

but below the sintering temperature of the material to effect desulphurization and to convert zinc and iron values to the oxide form, while retaining residual sulphide-sulphur throughout. It is stated that it is
5 necessary to minimize the formation of ferrite because ferrites are insoluble in relatively dilute mineral acids. In the case of zinc processing, this lack of solubility of ferrites means that the solid residue remaining after the leaching step contains a significant
10 concentration of zinc which would be lost and significantly affect the overall efficiency of the leaching process if no steps were taken for recovery.

Notwithstanding the variations in processes for recovery of zinc values, especially from iron-bearing
15 zinc sulphide ores, hydrometallurgical processes that provide for recovery of the zinc values under mild leaching conditions and with less potential environmental impact, would be beneficial. Such a process has now been found.

20 Accordingly, one aspect of the present invention provides a process for the recovery of zinc from a zinc ore comprising the steps of:

- 25 (a) leaching material obtained from a zinc ore with dilute sulphuric acid, essentially all of the zinc in said material being in the form of zinc oxide; and
- (b) separating the leachate so obtained for recovery of zinc therefrom.

Another aspect of the present invention provides in
30 a process for the recovery of zinc from zinc sulphide concentrates, said process comprising roasting said concentrate, separating roasted concentrate containing zinc oxide, zinc ferrite and lead oxide therefrom, subjecting the separated roasted concentrate to multi-stage leaching, said multi-stage leaching including
35 leaching with dilute and with hot sulphuric acid, the improvement comprising roasting the zinc sulphide

concentrate at a temperature of greater than 1050°C, separating roasted concentrate and subjecting it to a single stage leach with dilute sulphuric acid.

The process of the present invention is illustrated by the embodiment shown in the drawing, in which:

FIG. 1 is a schematic representation of a process of the recovery of zinc.

In FIG. 1, a zinc recovery process is generally indicated by 1. Zinc recovery process 1 uses a zinc ore or zinc concentrate 2 as a feed material. The ore or concentrate will be a zinc sulphide ore, and typically a zinc sulphide ore or concentrate that also contains lead sulphide and iron-bearing materials. It is also to be understood that zinc sulphide ore will contain other metal values, possibly including indium, cadmium, cobalt and tantalum, depending on the particular ore. Methods for forming the zinc concentrate from ore, if desired, are known. The method will generally be described herein with reference to zinc concentrate.

Zinc concentrate 2 is transferred to a roasting step (Step I). In Step I, zinc concentrate 2 is subjected to a roast at a temperature of greater than 1050°C, for instance 1050-1200°C and preferably 1100-1150°C, to obtain a calcine product that has a reduced amount of zinc ferrite.

It has been understood, as noted herein, that roasting temperatures should be in the range of 850 - 950°C, as the formation of ferrite increases with increasing temperature. However, it has now been found that at high temperatures, greater than 1050°C and especially 1100 - 1150°C, zinc ferrite decomposes under the conditions of roasting.

In preferred embodiments, the calcine does not contain ferrite. In particular, the temperature of the roast is sufficiently high that ferrite is not formed, or

if formed is dissociated into zinc oxide and ferric oxide.

Step I results in the formation of volatile materials, particularly SO_2 , resulting from oxidation of the sulphides in the concentrate, as well as volatile metal values. In particular, depending on the composition of the concentrate, the volatile metal values may include indium, cadmium and particularly lead. Such volatile material may be treated for recovery of the SO_2 , in the form of sulphuric acid, and for the recovery of the metal values.

The roasted calcined ore or concentrate 6 from Step I is transferred to a leaching step, Step II. The leaching step is a single stage leaching step, in which the leaching material is dilute sulphuric acid. The dilute sulphuric acid may have a concentration typically in the range of 10-20 g/l. The leaching may be carried out over a range of temperature e.g. from ambient temperature to 95°C , and especially $50-90^\circ\text{C}$. It is believed to be not necessary to conduct leaching using neutral solution and/or hot concentrated sulphuric acid.

After a period of time in the leaching step, the mixture 8 obtained is transferred to a liquid/solid separation step (Step III). In this step, the solid material is transferred to tailings. The leachate 11 is then transferred to a step for removal of iron (Step IV). Leachate 11 would typically contain dissolved zinc compounds, iron(ferric) compounds, and optionally cobalt compounds and other soluble compounds from the leaching step, depending on the composition of the ore. In Step IV, MnO_2 and ammonium hydroxide are added to effect precipitation of iron as jarosite, 13. The mixture 14 from Step IV is transferred to a liquid/solid separation step (Step V) in which solids are separated, 15, and forwarded to a tailings pond.

The solution 16 passing from Step V, is then

subjected to a step for a removal of impurities. Such a step may be a so-called cementation step 18, (Step VI), in which zinc metal and zinc oxide are added. In such a step, zinc compounds selectively remain in solution
5 whereas other materials separate as precipitates. The resulting solution 19 is forwarded to a liquid/solid separation step 20 (Step VII) in which solid materials are separated (21). The liquid from Step VII, which is zinc sulphate in sulphuric acid solution is then
10 typically sent to an electrowinning step, 23 (Step VIII).

In Step VIII, zinc is recovered as metallic zinc, as a cathode, and the sulphuric acid may be recycled 25, to the initial leaching step, Step II.

In Step I, volatile impurities are removed as a
15 result of the high roasting temperature that is used. The gas stream from the roasting step must be treated to separate solid calcine particles from the gas containing the volatiles before any volatiles condense and coat the particles. This effects removal of such metal values,
20 and simplifies subsequent separation steps in the process. It is understood that the gas stream containing the volatile compounds would typically be treated for recovery of SO_2 , as sulphuric acid, and for recovery of metal values, in an environmentally acceptable manner.

In addition, zinc ferrite, if formed in the roasting
25 step, will tend to dissociate at the temperature used into zinc oxide and ferric oxide (Fe_2O_3), both of which may be leached in a single dilute sulphuric acid leaching step (Step II). Ferric oxide may be converted to
30 magnetite (Fe_3O_4), which may be removed magnetically. Fe_3O_4 is less readily leached than Fe_2O_3 .

Step II has the advantage that it is a single stage
step using dilute sulphuric acid, rather than three
stages using a variety of concentrations, and in
35 particular hot concentrated sulphuric acid. It is not necessary to use hot concentrated sulphuric acid in the

process of the present invention. A single-stage leaching step has the advantage of lower acid consumption, and the use of more dilute acid. In addition, only one liquid/solid separation stage should
5 be required, as opposed to three such stages that are typically required. The single stage leaching step may be conducted at or about ambient temperature up to 95°C. It is not necessary to heat the leaching solution.

The roasted ore or concentrate obtained from Step I
10 may need to be ground, crushed or otherwise broken into smaller particulate matter to make the leaching step, Step II, more effective and efficient.

Notwithstanding the description of the embodiment of FIG. 1, it is to be understood that any method of
15 conversion of zinc sulphide ore, including zinc sulphide concentrate, to calcine in which the zinc is in the form of zinc oxide and with the substantial absence of zinc ferrite may be used. Roasting at a temperature greater than 1050°C is one such method.

The calcine obtained from the ore, or concentrate,
20 has zinc in the form of zinc oxide. The calcine should be substantially free of zinc ferrite. In preferred embodiments, the calcine has less than 2% of the zinc in the form of zinc ferrite, especially less than 1% and
25 particularly less than 0.5% in the form of zinc ferrite.

In order to minimize iron leaching without compromising zinc leaching efficiency, it has been found that the calcine obtained from roasting at about 1050-1200°C can be transferred to a subsequent reduction
30 pretreatment step which utilizes the enthalpy of the calcine. This can be done by maintaining mildly reducing conditions e.g. partial combustion of fuel to retain some CO and H₂ in the gas. The reducing condition should be such that Fe₂O₃ is reduced to FeO. Under these conditions
35 the zinc remains as oxide but any ferrite formed dissociates. On cooling the calcine, any iron in the

form of FeO, which is not stable at room temperature, reverts to Fe₃O₄ and there is essentially no effect on the subsequent leaching steps, except no zinc is tied up as ferrite and the zinc extraction in the leaching is
5 maximized. The reduction is carried out at 700 to 900°C and advantageously at about 800°C. An additive e.g. lime or sodium-containing compounds e.g. Na₂O, can be injected into the reactor to facilitate formation of more stable calcium or sodium ferrites. In addition, such additives
10 will tend to effect decomposition of any residual zinc sulphide.

A further advantage of the reduced amount of acid used in Step II of the process of the present invention is that in Step IV i.e. jarosite precipitation, less
15 neutralizing agent is required to neutralize acid and obtain the precipitate. Typical neutralizing agents are NH₃ and Na₂CO₃. In addition, there is a lower volume of precipitate and a lower volume of liquid for storage. Similarly, it is to be expected that the solid separated
20 in Step VI should have a reduced volume, which would reduce the size of the tailings pond.

It is further expected that Step VII would be a single stage, compared with two or three stages used in other processes as zinc values are predominantly present
25 as zinc oxide, and less iron is present in the solution.

In preferred embodiments, iron oxide is present in the calcine in the form of magnetite (Fe₃O₄), which may be removed magnetically prior to the initial leaching of the dilute sulphuric acid or, if present, tends to be less
30 readily leached than FeO under the leaching conditions that are used. Consequently, a reduced amount of iron is present in the leachate, which reduces the amount of jarosite that is precipitated. Precipitated jarosite tends to be voluminous. In addition, if impurities are
35 removed in a roasting stage, there is a reduced requirement for removal subsequently in the process e.g.

in step VII.

While a preferred embodiment has been described with respect to FIG. 1, it is to be understood that Steps IV-VIII could be varied, depending on the impurities in the solution and other techniques known to persons skilled in the art.

As discussed herein, the use of higher operating temperatures for the roast, $>1050^{\circ}\text{C}$, can assist in the dissociating of the ferrite and reducing the ferrite content in the calcine.

The use of calcine having zinc in the form of zinc oxide, with the substantial absence of zinc ferrite, in the leaching step simplifies subsequent treatment steps in the process, and tends to utilize less chemicals, particularly sulphuric acid, for separation of metallic zinc. Thus, the process of the invention offers the advantages of a single stage dilute acid leaching step, one liquid/solid separation step, followed by steps for removal of impurities and recovery of zinc by electrowinning. Such a process would offer the advantages of lower acid consumption, lower amounts of neutralization reagents, lower precipitation/storage volumes, a lesser number of liquid/solid separation stages, milder leach conditions and consequently less demand on the materials of construction, and a single stage impurity removal stage subsequent to separation of iron.

CLAIMS:

1. A process for the recovery of zinc from a zinc ore comprising the steps of:

5 (a) leaching calcine obtained from a zinc ore with dilute sulphuric acid, essentially all of the zinc in said calcine being in the form of zinc oxide; and

(b) separating the leachate so obtained for recovery of zinc therefrom.

10

2. The process of Claim 1 in which calcine subjected to the leach of step (a) is substantially free of zinc ferrite.

15 3. The process of Claim 2 in which the calcine is obtained from an iron-bearing zinc ore.

4. The process of any one of Claims 1-3 in which the calcine is a roasted zinc sulphide ore or
20 concentrate.

5. The process of Claim 4 in which the ore or concentrate has been subjected to a roasting step at a temperature of greater than 1050°C.

25

6. The process of Claim 5 in which the temperature is 1050-1200°C.

7. The process of Claim 5 in which the temperature
30 is 1100-1150°C.

8. The process of any one of Claims 1-7 in which said roasting is carried out in the presence of lime or sodium-containing additives.

35

9. The process of any one of Claims 1-8 in which

sulfur dioxide and metal compounds volatile at 1050°C have been separated from said calcine in said roasting step.

10. The process of Claim 9 in which the volatile
5 compounds include lead compounds.

11. The process of Claim 9 in which said volatile
metal compounds include indium, cadmium and lead
compounds.
10

12. The process of Claim 3 in which the calcine has
been treated for removal of magnetite therein prior to
leaching with sulphuric acid.

13. The process of any one of Claims 1-12 in which
15 step (a) is a single stage leaching step.

14. In a process for the recovery of zinc from zinc
sulphide concentrates, said process comprising roasting
20 said concentrate, separating roasted concentrate
containing zinc oxide, zinc ferrite and lead oxide
therefrom, subjecting the separated roasted concentrate
to multi-stage leaching, said multi-stage leaching
including leaching with dilute and with hot sulphuric
25 acid, the improvement comprising roasting the zinc
sulphide concentrate at a temperature of greater than
1050°C, separating roasted concentrate and subjecting it
to a single stage leach with dilute sulphuric acid.

15. The process of Claim 14 in which the roasted
30 concentrate subjected to the single stage leach with
dilute sulphuric acid is substantially free of zinc
ferrite.

16. A process for the forming of a calcine from a
35 zinc ore containing iron-bearing compounds, comprising

roasting said zinc ore at a temperature of greater than 1050°C, and treating the roasted ore to convert iron oxides therein into magnetite.

5 17. The process of Claim 16 in which the roasted ore is subjected to a temperature of 700-900°C under reducing conditions.

10 18. The process of Claim 17 in which the reducing conditions are an atmosphere of CO and H₂.

 19. The process of Claim 18 in which magnetite is separated from the calcine so obtained.

15 20. A process for the recovery of zinc from a zinc ore comprising the steps of:

 (a) leaching calcine obtained from a zinc ore with dilute sulphuric acid, said calcine containing iron in the form of magnetite; and

20 (b) separating the leachate so obtained for recovery of zinc therefrom.

 21. The process of Claim 20 in which essentially all of the zinc in said calcine is in the form of zinc oxide.

25 22. The process of Claim 21 in which calcine subjected to the leach of step (a) is substantially free of zinc ferrite.

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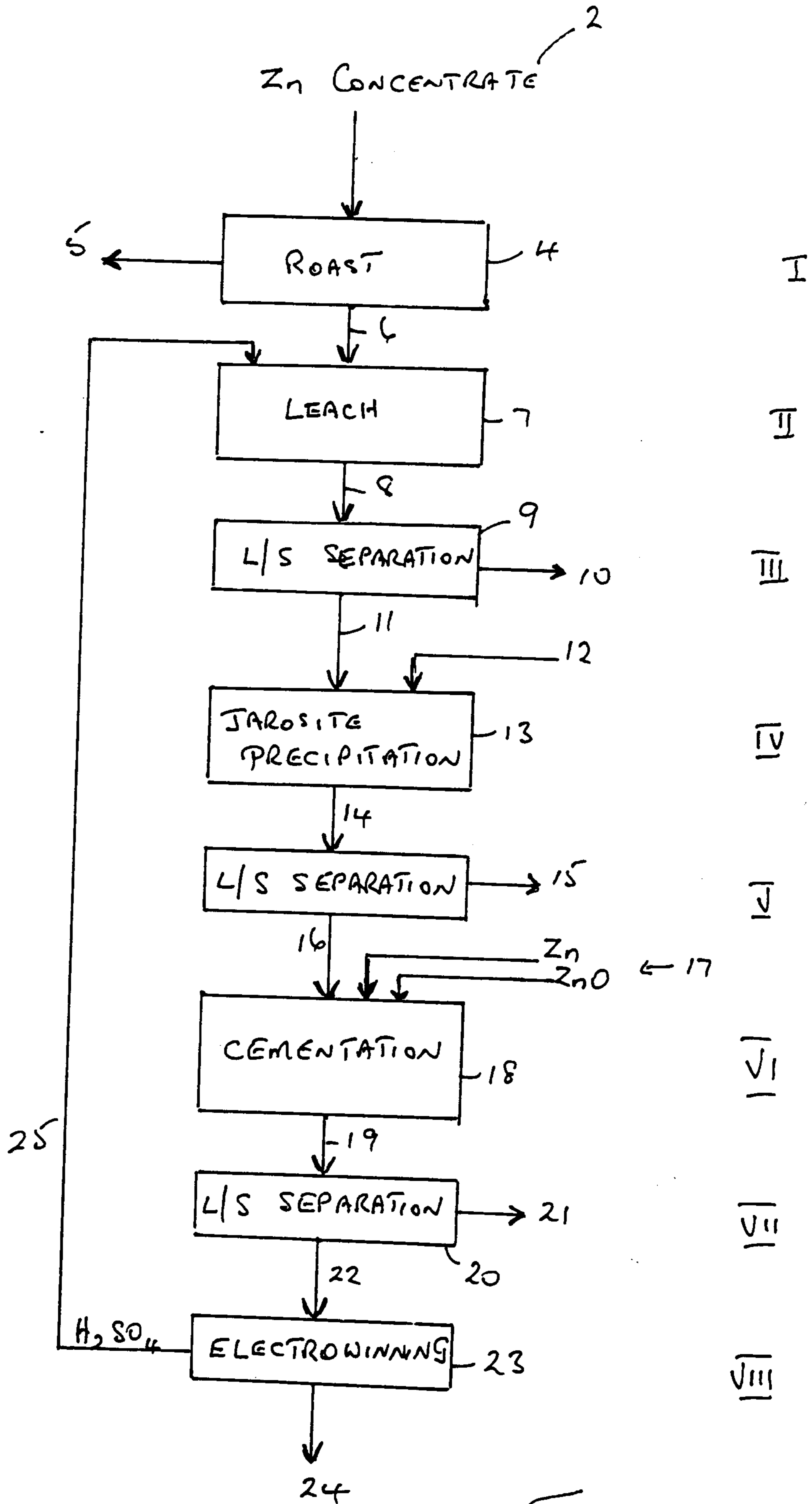


Fig. 1

