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(54) **PROCESS FOR ELECTROLYTIC PRODUCTION OF ULTRA-PURE ZINC OR ZINC COMPOUNDS FROM ZINC PRIMARY AND SECONDARY RAW MATERIALS**

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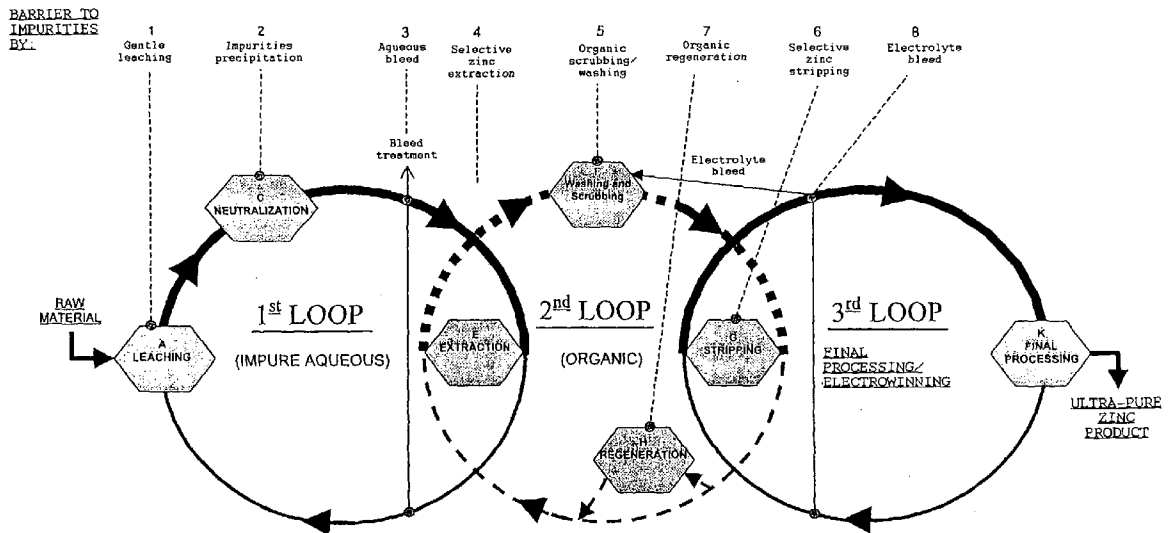
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(57) **ABSTRACT**

The process comprises the following stages: a) leaching; b) solid-liquid separation; c) neutralization of the aqueous solution; d) solid-liquid separation of the zinc-rich solution; e) zinc extraction; f) purification of the organic solvent from the extraction stage; g) stripping the ionic zinc loaded in the organic solvent; h) recovering the zinc contained in the aqueous acid solution from the stripping. The following barriers to impurities have been established: gentle leaching; alkaline pulp treatment; treatment of a small stream of aqueous solution, collected before and/or after the zinc extraction at step e); high selectivity of the dissolved zinc extraction; treatment of the zinc loaded in the organic solvent; cleaning treatment of the zinc-laden organic solvent, with an ultra-pure acid solution; partial bleeding and treatment of the stripped organic solvent; bleed of small stream of the final product producing loop, which will be recycled to the organic loop.



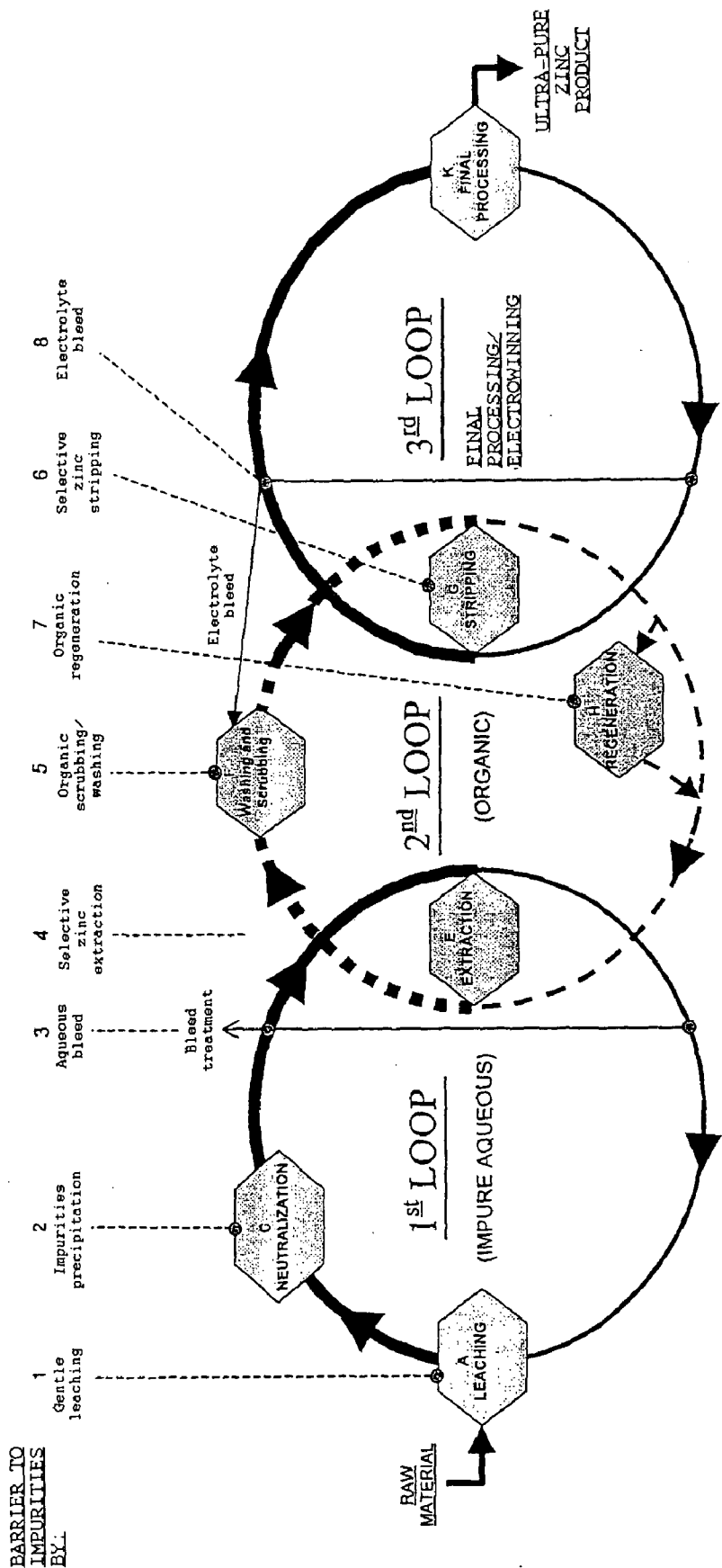


Figure 1

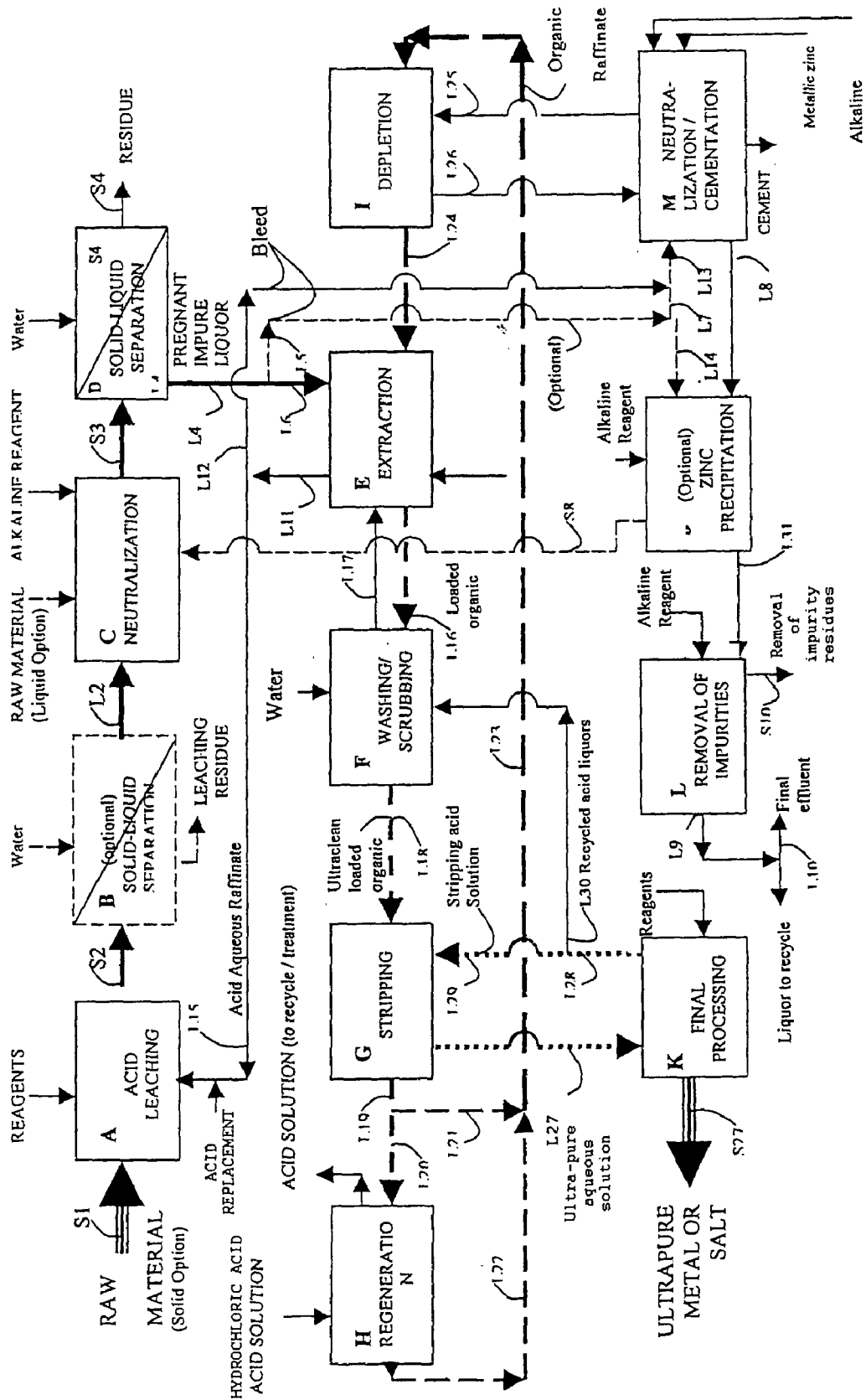


Figure 2

PROCESS FOR ELECTROLYTIC PRODUCTION OF ULTRA-PURE ZINC OR ZINC COMPOUNDS FROM ZINC PRIMARY AND SECONDARY RAW MATERIALS

OBJECT AND FIELD OF THE INVENTION

[0001] This invention relates to an improved process to produce zinc or its compounds, all of them ultra-pure, by a hydrometallurgical process starting from zinc primary and/or secondary raw materials through a new combination of purification loops incorporating barriers to impurities.

[0002] These barriers, according to the invention, consist of the combination of treatments that restrict the production or transport of impurities from the raw materials or from the outside to the product and/or permit their removal through successive depletions, and/or check the presence of impurities in the product, and/or prevent recontamination.

STATE OF THE ART

[0003] Several patented processes exist concerning the hydrometallurgical treatment of zinc primary and/or secondary raw materials. These processes, operating by employing appropriate means, are targeted towards the production of electrolytic zinc or zinc compounds. The ultimate objective of these processes is to produce zinc of the highest degree of purity.

[0004] The "Roast, leach and electrowin" process (RLE) treats primary raw materials, normally zinc sulphide concentrates. Roasting the concentrates leads to the production of an impure zinc oxide (calcine) and SO₂ gas which is converted into sulphuric acid. The calcine is then leached with a sulphuric acid solution recycled from the electrowinning stage.

[0005] The separation of the leaching pulp produces an impure solution. This impure solution is purified by cementation with zinc powder. The purified solution is sent to zinc electrowinning to produce the zinc plates, which are sent to the melting and casting stage. However, impurity concentration levels low enough to achieve extreme quality electrowinning are not achieved. This implies the production of zinc which is not ultra-pure, unless other difficult and/or expensive additional stages are applied.

[0006] Other generic processes use, in a first step, the acid leaching of the raw material to dissolve the zinc, then, in a second step, the selective extraction of the dissolved zinc present in the solution by means of an organic acid solvent which acts as an extractant (with pH control in some of them), in a third stage, the zinc-laden organic acid is treated to recover this zinc in the form of an aqueous solution and regenerate the organic solvent to be subsequently recycled.

[0007] A first process (U.S. Pat. No. 4,401,531) discloses the acid hydrometallurgical treatment of the zinc contained in secondary materials such as zinc alkaline solids, or impure solutions in sulphate or chloride media, e.g. smelting slag, galvanizing ashes, alkaline zinc slag, impure zinc oxides or hydroxides, impure zinc electrolytes, leaching effluents, etc. This process discloses a combination of resources which comprise the solvent extraction of the zinc present in the solution resulting from acid leaching with an organic acid solvent. In this process, the acidity produced during the zinc extraction, recovered as an acid solution, is recycled to the

leaching stage. This process has several drawbacks: the range of raw materials considered for the feed is exclusively restricted to secondary materials and, despite the presence of purification stages, both for the aqueous stream and the organic stream, the purity of the zinc produced is considered insufficient for some specific end-users and would be worth improving. Furthermore, there is a narrow range of process operative conditions (conditions such as temperature, residence time, acid concentration and zinc concentration).

[0008] Another patent (U.S. Pat. No. 4,552,629) discloses a process similar to that disclosed above, although, here, the zinc is produced as a direct electrogalvanizing product instead of as plates deposited from zinc electrowinning. The main object of this hydrometallurgical process to recover zinc from raw materials or secondary materials is to use a combination of stages similar to those of the patent U.S. Pat. No. 4,401,531. The leaching acid is formed by a blend of sulphuric acid and hydrochloric acid. The aqueous solution resulting from the leaching (rich in dissolved zinc) is treated with an organic acid solvent which acts as zinc extraction media. Then, the zinc loaded in the organic solution is treated with an acid solution (stripping), which permits recovering the zinc ions in a new aqueous phase and the regeneration of the organic acid. However, due to the possible use of the zinc produced, and in the absence of suitable organic washing before the zinc stripping, the zinc-rich aqueous solution originating in the stripping does not produce high-purity zinc.

[0009] Another hydrometallurgical process (U.S. Pat. No. 4,572,771) to specifically recover the zinc contained in the raw material, i.e. raw materials containing zinc, iron and lead, consists of a hydrochloric acid leaching stage. At the end of the leaching stage, the leached aqueous solution (zinc-laden solution clean from leaching residues) undergoes an oxidation stage with recycled chlorine and then undergoes iron and lead precipitation through calcium hydroxide. The zinc-laden aqueous solution (produced after the lead and iron removal) is subsequently treated by an extraction with an organic acid solvent. The organic containing the extracted zinc is treated with water or an acid solution such as, e.g. a HCl solution produced from zinc electrowinning and transforming the organic solvent in a discharged organic to be reused. Nevertheless, in this process, the solvent extraction does not contain a purification stage and, consequently, the organic solvent is not capable of producing high-purity zinc. Furthermore, the raw material feed is very specific. A hydrochloric acid leaching solution and an oxidation with chlorine from electrowinning is also used. Electrowinning is not the conventional process in sulphate media, as they operate with a membrane or separating diaphragm.

[0010] On the basis of said documents, it is demonstrated that the different processes referred to cannot produce extremely pure zinc, or zinc compounds, as they are essentially focussed on the raw material and are not sufficiently aimed towards the purification stages.

[0011] The first object of the invention is a hydrometallurgical process to produce extremely pure zinc from raw materials containing zinc of both primary and secondary origin, either solid or liquid, and also containing silicon, aluminium, iron, calcium, in variable quantities, in addition to other impurities, e.g. magnesium, manganese, sodium,

potassium, copper, nickel, cadmium, antimony, arsenic, cobalt, chlorine, fluoride and any other impurities.

[0012] Another object of this process is to permit the production of ultra-pure zinc in metal form by electrowinning or in the form of chemical compounds, e.g. zinc salts through a crystallization process, which permits recovering almost all the zinc contained in the raw material in gentle conditions.

[0013] Another object is that it is a process which combines three closed circuits to produce ultra-pure zinc, as is conceptually illustrated in **FIG. 1**. The first loop (impure aqueous) combines acid leaching of the raw material, when the considered raw material is a solid, neutralization, followed by extraction of the dissolved zinc using an organic acid solvent, and recycling the acid, which occurs in the aqueous phase during the zinc extraction, to the leaching stage. The second loop is an organic loop, transporting the zinc from extraction to stripping through a washing stage and transporting the acid in the opposite direction. The third loop is the combination of the stripping stages and final product production, which may be the electrowinning stage, using the acid produced in the electrowinning, to strip the organic phase zinc, a process wherein each loop is equipped with its own purification barriers.

[0014] Another object of the invention is the purification of the recycled leaching solution, through the complete control of the level of impurities present in said solution.

[0015] Another object of the invention is the ultra-purification of the zinc-laden organic produced in the extraction stage, which may be considered as an zinc-laden organic solution completely free from impurities

[0016] Another object of the invention is to avoid and/or remove the potential recontamination of the zinc-rich solution produced during the stripping stage and/or in the production of the final product.

DESCRIPTION OF THE INVENTION

[0017] The invention relates to a continuous production process to produce ultra-pure electrolytic metallic zinc or zinc compounds from the zinc contained in raw materials from which it will be extracted using a hydrometallurgic treatment comprising the following stages:

[0018] a) If the raw material is solid, this raw material will be leached with an aqueous acid solution to dissolve the zinc.

[0019] b) optionally, depending on the nature of the raw material, if the leaching residue has any valuable elements, a solid-liquid separation can be included after leaching.

[0020] c) neutralization of the aqueous solution or leaching pulp, or the zinc-containing raw material when this is liquid.

[0021] d) solid-liquid separation of the zinc-rich solution (pregnant liquor) from the solids (inert residues and/or precipitates in the neutralizing stage).

[0022] e) extraction of the zinc contained in the pregnant liquor by an organic acid solvent,

[0023] f) purification of the zinc-laden organic solvent from the extraction step,

[0024] g) stripping of the ionic zinc loaded in the organic solvent by an aqueous acid solution.

[0025] h) recovery of the zinc contained in the aqueous acid solution produced from stripping by electrowinning and/or crystallization and/or precipitation,

[0026] and characterized in that:

[0027] the different steps of the process are organized in three interrelated loops, each containing successive barriers to impurities.

[0028] Within the first loop-leaching-neutralization-solvent extraction and further leaching, a first barrier to impurities, consisting of gentle leaching; a second barrier consists of alkaline treatment of the raw material pulp and aqueous solution, or of the zinc-rich aqueous solution originating in the leaching; a third barrier consists of the bleeding and treatment of a small aqueous solution stream, collected before and/or after the zinc extraction at step e) by an organic solvent; a fourth barrier consists of the high-selectivity extraction of the dissolved zinc.

[0029] Within the second loop, the organic loop, the fifth barrier consists of the zinc-laden organic solvent, through a physical and chemical purification system; a sixth barrier consists of the treatment to clean the zinc-laden organic solvent with an ultra-pure acid solution to strip the zinc from the ultra-pure organic solution; a seventh barrier consists of the partial bleeding and treatment of the stripped organic solvent.

[0030] Within the third loop, or final product producing loop, an eighth barrier consists of the bleed of a small stream of the final product producing loop, which will be recycled into the organic loop.

[0031] In the given description, the final product production loop is the final, ultimate step of the process through which ultra-pure zinc is produced in metallic form by electrowinning and/or in the form of chemical compounds such as, e.g. zinc salts by crystallization.

BRIEF DESCRIPTION OF THE DRAWINGS

[0032] To complement the preceding description and for the object of helping towards a better understanding of the characteristics of the invention, a set of drawings is attached to these specifications, forming an integral part thereof, and wherein the following has been represented with a merely illustrative, non-limiting character:

[0033] **FIG. 1** shows a conceptual diagram of the ultra-pure zinc metal or zinc compound purification loop process wherein A, C, E, F, G, H, K are the main stages.

[0034] **FIG. 2** shows a flow chart of the process object of the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0035] The raw material, considered for the process disclosed in this invention, contains zinc to be extracted, and can come from original raw materials or from secondary resources such as solids or liquids. Solids such as zinc oxide

minerals, mineral carbonates, mineral silicates, sulphates, calcines, smelting slag, galvanization residues, dust from arc furnaces, Waelz oxides, chemical precipitates, etc., all of which contain impurities in variable quantities such as silicon, aluminium, iron, calcium, magnesium, manganese, sodium, potassium, copper, antimony, arsenic, cobalt, nickel, cadmium, chlorides, fluorides and other elements and compounds. The zinc contained in these different solid feeds, expressed by weight, can range from 3% to 80%. For liquid raw materials, the zinc ion can be present as sulphate including unlimited, many and varied quantities of chlorides, nitrates, silicates, etc., not necessarily majorities.

[0036] The solid raw materials, before being used as feed according to the invention, can be finely ground until reaching the appropriate particle size, with a maximum size of 2 millimetres.

[0037] The invention is better understood through a description, schematically represented in a flow chart, which describes the three interrelated loops containing the barriers to the impurities. See **FIGS. 1 and 2**.

[0038] The first loop, (impure aqueous) consists of leaching (at A)—neutralizing (at C)—extracting with solvents (at E) and further leaching (L_{11} , L_{15} at A), with the bleeding of an aqueous moiety (L_5 , L_{12}) and corresponding treatments with these bleeds (at M and/or J).

[0039] Different barriers to impurities are used in the first loop.

[0040] The first barrier to impurities consists of the treatment (at A) of the solid raw material (if this is the case) by leaching in gentle temperature, acidity and pressure conditions with the aim of limiting the dissolution of the impurities accompanying the zinc, such as iron, aluminium or silicon, which are removed later with the solid after a solid-liquid separation (at D).

[0041] According to the process described in this invention, the gentle acid leaching of the solid raw material (S_1), according to step (A), should be carried out in the leaching area (at A) in, at least, one stirred reactor.

[0042] The acid solution used to leach the solid raw material can be a recycled solution (L_{11} , L_{15}) from the zinc extraction (at E) corresponding to stage e), which contains at least one strong acid and is complemented with a recovery acid, which can be a blend of acids. The acid or acids that may constitute the aqueous leaching solution are selected from a group formed by sulphuric acid, hydrochloric acid, nitric acid, hydrofluoric acid, or mixtures thereof, in different proportions. In the specific case where the leaching solution contains only one acid, this acid is preferably sulphuric acid.

[0043] The aqueous leaching solution (L_{15}) used to leach the zinc contained in the raw material is highly acidic, containing between 0.1 and 5 moles per litre acidity (H^+) regardless of its origin, including the addition of acid to compensate the alkalinity of the raw material.

[0044] The solid raw material leaching stage, with an acid solution, takes place in the leaching area in a pH range between 0 and 3, and, preferably, between 1.5 and approximately 2.5, with a residence time between 0.5 and 7 hours, preferably between 0.5 and 2 hours, and with a temperature below 95° C., preferably between 45° C. and 65° C.

[0045] Optionally, in stage b) a solid-liquid separation treatment can be carried out, separating the zinc-rich solution from the non-leached solid residue, which could be removed. The solid residue produced could thus be evaluated by undergoing further treatment, and can be separated from the stream at this stage without it undergoing neutralization.

[0046] The second barrier consists of an alkaline treatment (at C) of the aqueous raw material or zinc-rich solution originating in the leaching (at A).

[0047] For the time being, the zinc loaded in the leaching solution exits the leaching area as pulp, or as a solution if it undergoes the aforementioned solid-liquid separation phase. The leached solution (L_2) as pulp (S_2) or in separate phases, and containing solubilized impurities, undergoes a first purifying treatment consisting of controlled neutralization, step c), where the pH is set at a level compatible with the precipitation of each impurity, constituted by the group formed by silicon, iron, aluminium, antimony and arsenic.

[0048] The neutralization agent can be any typical alkaline agent, preferably cheap, such as hydroxides, carbonates, bicarbonates, in particular, calcium carbonates or hydroxides, and, more particularly, chalk or lime.

[0049] The neutralization stage is carried out (at C) at a temperature close to that reached in the final leaching step, i.e. at a temperature below 95° C., but generally between 40° C. and 60° C. The residence time is of the same order of magnitude as in the leaching section, i.e. between 0.5 and 7 hours but, preferably, between 1 and 4 hours. At the end of the neutralization stage, the pH of the neutralized leached solution is brought to a value between 3 and 5, preferably between 3.5 and 4.3.

[0050] Depending on the characteristics of the raw feed and plant capacity, the neutralization treatment can be carried out in several stages in cascade.

[0051] When the neutralization is carried out in several steps, the final pH post-neutralization can evolve in a controlled manner until reaching the value set for the different steps in order to selectively precipitate the impurities.

[0052] Having concluded the neutralization, a solid-liquid separation takes place (at D), permitting the separation of the neutralized zinc-rich solution (L_4), whilst separating the non-leached solid residue and/or the solid with precipitated impurities (S_4), which is removed.

[0053] The neutralized zinc-rich solution (L_4) can be partially or totally sent to the extraction stage (at E), wherein the zinc is extracted using an organic solvent.

[0054] The main stream leaving the extraction (zinc-discharged aqueous acid solution or raffinate (L_{13})) is recycled at the leaching stage.

[0055] The third barrier to impurities consists of the bleeding and treatment of a small stream (L_3) produced either from the neutralized zinc-rich aqueous solution (L_4) of this loop, prior to the extraction phase, and/or from the zinc-discharged aqueous acid solution called raffinate (L_{12}), produced after said extraction. Its object is to remove water and prevent the accumulation of different soluble impurities such as sodium, potassium, chlorides, fluorides, magnesium,

manganese, copper, nickel, cobalt, cadmium and other impurities, checking the transfer to subsequent steps and thus removing the dissolved impurities. If this stage did not exist, the impurities would accumulate in said solution as a result of the different loop processes used, as has been demonstrated by this invention.

[0056] This aqueous solution bleed (L_5) originating at (L_4) or (L_{12}) originating at (L_{11}) is treated in accordance with its characteristics, whilst the majority (L_6) of the neutralized zinc-rich solution (L_4) is sent to the extraction stage (at E).

[0057] If the bleed is that of a small stream (L_5) of the neutralized zinc-laden aqueous solution prior to extraction, the bleed (L_5 , L_{14}) can be directly sent to the zinc precipitation stage (at J). In another variant of the process, this bleed (L_5 , L_7 , L_{13}) can be previously treated at a cementation stage (at M) feeding metallic zinc and then the liquid L_8 , originating at M, is that which is later sent to that zinc precipitation stage (at J). In every case, this precipitation is followed by a solid-liquid separation where the solid moiety (S_8) containing zinc precipitate is recycled to the neutralization stage (at C) in the first loop. The liquid moiety (L_{31}) which exits J undergoes an impurity removal stage (at L) by controlled neutralization stage.

[0058] More precisely, in a first variant of the process, the small stream of neutralized zinc-laden aqueous solution undergoes controlled neutralization to precipitate (at J) the zinc from the solution, followed by a solid-liquid separation where the zinc-rich solid moiety (S_8) is recycled to the neutralization stage (at C) of the pulp and/or of the aqueous solution originating from the leaching of the raw material (stage A), whilst the liquid moiety (L_{31}) again undergoes an impurity removal stage (S_{10}) (at L) by controlled neutralization.

[0059] In a second variant of the process, the small stream (L_5) of the aqueous solution prior to extraction, can be sent (L_7 , L_{13}) to a cementation stage (at M) where it is treated with metallic zinc and where the liquid stream (L_8) produced at that stage (M) is sent to a solid-liquid separation stage (where the zinc-rich solid moiety (S_8) is recycled to the neutralization stage (at C) of the first loop, and the liquid moiety (L_{37}) undergoes an impurity removal step (at L) by controlled neutralization.

[0060] In a third variant of the process, the small stream (L_5 , L_7 , L_{13}) of the aqueous solution prior to extraction, can be sent to a cementation stage (at M) where metallic zinc can be introduced, and where the metallic zinc displaces solubilized metal impurities at the leaching stage (at A) whilst the resulting liquid moiety (L_{25}) is sent to the depletion stage (at I) to increase the zinc recovery efficiency of the complete process. Said depletion stage is found within the organic loop. In this depletion stage (I), the organic phase extracts the zinc present in the liquid moiety (L_{25}) contributing to the purification and increasing zinc recovery efficiency, whilst the zinc-depleted aqueous solution (L_{25}) is recycled to the neutralization and/or cementation step (at M). The liquid (L_8) originating at (M) is sent to the zinc precipitation stage (at J) and follows the same treatment as in the second variant of the process.

[0061] In a fourth variant of the process, variant one is combined with one of the two previous ones. In this case, a small moiety of the stream (L_{14}) is sent to the zinc precipi-

tation stage (J) followed by a solid-liquid separation, after which the solid with the zinc precipitate (S_8) is recycled to the neutralization stage (C) of the pulp and/or the aqueous solution originating in the leaching of the raw materials, whilst the other moiety (L_7 , L_{13}) of that small stream is sent to a cementation stage, at (I) wherein it is treated with metallic zinc and, optionally, to a depletion stage (at E). The aqueous liquid moieties (L_{25} , L_8 , L_{31}) resulting from the cementation stage (M) and, optionally, from the depletion stage (I) and of the zinc precipitation stage at (J), are sent to an impurity removal stage at (L) by controlled neutralization.

[0062] If the bleed is performed through the separation of a small stream (L_{12}) of the aqueous solution (L_{11}) (acid raffinate) of this loop, the treatment is performed by controlled neutralization of the solution (L_{12}) acidity, through (L_{13}) at (M) and/or through (L_7) and (L_{14}) at (J)), possibly followed by its corresponding solid-liquid separation.

[0063] The liquid moiety thus neutralized is treated with cementation (at M) and, optionally, undergoing a depletion (at I) and/or zinc precipitation (at J). Afterwards, the liquid (L_{31}) undergoes final impurity removal (at L), following the same stages (M, I, J, L) described for the case of the bleed (L_5).

[0064] All process variants disclosed for the bleed treatment (L_5) can be used for the treatment of (L_{12}) and are described hereunder.

[0065] As a first variant of the process, a small part of the aqueous solution stream from the extraction (L_{12} , L_7 , L_{14}) undergoes controlled neutralization with the object of precipitating (at J) the zinc in the solution, followed by a solid-liquid separation, from where the zinc-rich solid moiety (S_8) is recycled to the neutralization (at C) of the pulp and/or of the aqueous solution originating in the leaching of the raw material (A), whilst the liquid moiety (L_{31}) undergoes an impurity removal stage (S_{10}) at (L) by controlled neutralization—

[0066] As a second variant of the process, the small stream of the post-extraction aqueous solution (L_{12} , L_{13}) can be sent to the neutralization and/or cementation stage (at M) where it is treated with metallic zinc and from where the liquid stream (L_8) produced at that stage (M) is sent to the zinc precipitation stage (J) to subsequently be sent to a solid-liquid separation stage where the zinc-rich solid moiety (S_8) is recycled to the neutralization step (at C) of the first loop, and the liquid moiety (L_{31}) undergoes an impurity removal stage (at L) by controlled neutralization.

[0067] In the third variant of the process, the small stream (L_{12} , L_{13}) of the post-extraction aqueous solution, can be sent to the neutralization-cementation stage (M) where it will be treated with alkali and metallic zinc and the resulting liquid (L_{25}) is sent to the depletion stage (at I) to increase the zinc yield from the total process. Said depletion stage is located in the organic loop. The liquid (L_8) originating at (M) is sent to a zinc precipitation stage (at J), and follows the same treatment as described in the previous variant (second).

[0068] In a fourth variant of the process, it is possible to combine variant one with either of the two previous ones. In any case, a moiety of the small stream (L_7 , L_{14}) is sent to the zinc precipitation stage (J) followed by a solid-liquid separation after which, the solid containing the zinc precipitate

(S₈) is recycled to the neutralization stage (at C) of the pulp and/or of the aqueous solution originating in the leaching of the raw material. The other moiety L₁₃ of that small stream, is sent to the neutralization stage in (M) where it is treated with alkali and metallic zinc and, optionally, the liquid is sent to the depletion stage (at I). The aqueous liquid moieties (L₂₆, L₈, and L₃₁) resulting from the cementation stage at (M) and, optionally, from the depletion stage at (I) and from the zinc precipitation at (J), are sent to an impurity removal step at (L) by controlled neutralization.

[0069] As already mentioned, the depletion stage (at I) can be optionally used, taking place at the intervention of both loops. It consists of zinc extraction from the aqueous solution (L₂₅) fed to the organic loop, by treating it with a zinc-discharged, organic solvent (L₂₃) to deplete, as far as possible, the zinc contained in this aqueous solution, before its final treatment and removal, increasing the zinc recovery which is incorporated, in this manner, to the organic loop.

[0070] The two streams L₅ and L₁₂ can be treated individually or in combination.

[0071] The bleed treatment conditions (L₅ and/or L₁₂) are the following: whilst this bleed is treated (at M) by controlled neutralization with an alkaline agent, the pH is maintained between 2.0 and 4.0 and it is treated at that pH by cementation with metallic zinc powder to trigger the precipitation of the metal impurities such as copper, cadmium, cobalt, nickel and other impurities. The temperature is between 20° C. and 90° C. However, as previously mentioned, this bleed (L₅ and/or L₁₂) fulfils another object which is removing, with L₈ and/or L₃₁, L₉, soluble elements from the main, aqueous, solution circuit such as magnesium, sodium, potassium, as well as fluorides and chlorides, and also to attain water balance.

[0072] The soluble zinc present in this bleed (L₅ and/or L₁₂) and the added zinc (metallic) used in the cementation can be precipitated (at J) by an alkaline agent from pH 6.0 to pH 8.0 at a temperature between 70 and 90° C. and, after its solid-liquid separation, the resulting pulp is recycled to the neutralization stage (at C). Another possibility can be to recover this zinc at the depletion stage (at I) of the organic circuit as has been previously described.

[0073] In both cases, through the depletion stages (at I) and/or recycling the pulp (at J), the total zinc recovered is increased.

[0074] The cement (the solid material containing the precipitate of metal elements of M) is removed from the process or undergoes its own elimination treatment.

[0075] After this zinc recovery, the aqueous solutions (L₂₆, L₈ and/or L₃₁) exit the neutralization and/or cementation/depletion areas (at M and/or I) and/or zinc precipitation (at J) still containing dissolved impurities, where they should be sent to an impurity removal area (at L), where they are treated with an alkaline agent at a pH between 8.0 and 12.0 and, subsequently, the solid precipitate is separated from impurities (S₁₀) at a temperature between 30 and 90° C. Most of the liquid produced in this final stage of the bleed treatment should be recycled to the main circuit of the process as a base for the preparation of reagents or as process water. The remaining liquid is evacuated as final effluent (L₁₀)

[0076] The part of the solutions (neutralized zinc-rich solution (L₅) and/or zinc-discharged aqueous acid solution (L₁₂)) which are separated from the main stream (bleeds) to control the growth level of the dissolved impurities, increase zinc recovery and adjust the water and/or alkaline element balance, represents a maximum of 25% of the volume of the total stream and, preferably, between 8 and 15% in volume.

[0077] The fourth barrier consists of extraction with a high-selectivity organic acid solvent (at E) of the dissolved zinc, stage e). This selectivity is increased enormously as a result of the acid conditions during the zinc extraction and due to the operation conditions.

[0078] This barrier is produced at the interface between two loops: the leaching-neutralizing-extraction loop, and the organic loop.

[0079] The second loop, called "organic" loop is a solvent extraction system which has the advantages of the aqueous phase characteristics and its immiscibility with the aqueous phase. This second loop combines the zinc extraction stages (at E), the purification of the zinc-laden organic solvent, (L₁₆), (at F), the L₁₈ zinc stripping (at G), the total (L₁₉) or partial (L₁₉) regeneration of the organic acid solvent (at H) and, optionally, of the depletion (at I).

[0080] The majority or entire stream, (L₆) of the neutralized zinc-rich solution (pregnant liquor) at stage d) comes into contact at stage e) with an organic acid (L₂₄) whose mission is to permit zinc extraction. The solution undergoes the ionic chemical equilibrium reaction described below:



[0081] In this chemical reaction, HR represents said extraction organic acid reagent solution, and ZnR₂ represents the zinc-laden organic solution.

[0082] This pregnant liquor, fed at the extraction stage, has a pH over 2 and, preferably, between 3.5 and 4.3. During the zinc extraction, stage e), the aqueous solution increases its acidity to between 0.01 and 3.0 g/l of equivalent H⁺. This occurs because the protons are transferred from the organic phase to the aqueous phase throughout, preferably, 3 or 4 extraction steps at this stage, following the reaction (1). An alkaline agent can be added (as in other processes) to slightly increase the pH.

[0083] The zinc extraction temperature ranges from room temperature to 80° C. and, preferably, 40° C.

[0084] To attain the best selective extraction, acid conditions are used (without adding an alkaline agent) so that, in this way, only those cations with greater affinity for the organic solution, such as ferric and zinc, can be extracted. In these acid conditions, there is an increase in selectivity against other cation impurities. The aqueous solution that exits the extraction area (L₁₁-L₁₅) (acid raffinate), has acidity equivalent to that of the extracted zinc. This acidity (L₁₁-L₁₅) is used in the leaching stage (at A), thus reducing the necessary acid addition.

[0085] The organic acid, HR, is normally selected from the group formed by the acids: alkyl phosphoric acids, alkyl phosphonic acids, alkyl phosphinic acids, which have the capacity to extract zinc and, preferably within the group constituted by di-(2-ethylhexyl) phosphoric acid (D₂EPHA), di-(2-ethylhexyl) phosphonic acid and di-(2,4,4-trimethylpentyl)phosphinic acid.

[0086] For its use in zinc extraction, HR is dissolved in a mixture of organic compounds originating from an oil moiety, e.g. kerosene. The concentration of this organic agent in kerosene is between 5% and 75% and, preferably, between 30% and 50%.

[0087] During stage e), wherein the neutralized zinc-rich aqueous solution (L_{15}) comes into contact at (E) with the extraction solvent (L_{24}), in what is known as counter-current conditions, zinc extraction is achieved, releasing H^+ ions (two H^+ ions per each retained Zn^{2+} ion). The aqueous acid solution produced (L_{11}) at the extraction stage (at E), still containing residual zinc and a significant quantity of dissolved impurities can be, totally or partially, but always mostly, recycled at stage a) as a leaching solution to leach the solid raw material.

[0088] The ratio between quantities in the organic phase and aqueous phase at the extraction stage (at E) (O/A ratio) is selected according to the process conditions to successfully reach correct physical and chemical behaviour, generally positioned between 0.1 and 10 and, preferably, between 1.0 and 3.0.

[0089] The zinc-laden organic solution (L_{16}) (ZnR_2) exits the extraction stage e) at (E), containing co-extracted, entrained impurities in small quantities, is sent to stage f) for its ultra-purification (at F).

[0090] These remaining impurities together with zinc in the organic phase should be completely removed (at F), to avoid the contamination of the product resulting from the process according to the invention, which must be extremely pure. This is the reason for which the laden organic solution undergoes a treatment that can be described as an ultra-purification stage, step f) at (F) to remove all traces of remaining impurities still present. This is the object of the following barrier (the fifth) to impurities.

[0091] Within the second organic loop of the fifth barrier to impurities, consisting of the treatment of the zinc-laden organic solution (L_{16}), produced at the extraction stage e), at (E). This treatment, stage f) at (F), has a double purification system: scrubbing and washing using an aqueous acid solution (L_{30} and water) to remove both impurities entrained by the aqueous phase in the organic phase, and other impurities that, like calcium, are co-extracted with the zinc by the organic phase.

[0092] This barrier to impurities consists of a combination of successive physical and/or chemical treatments of the zinc-laden organic solvent, used at stage f). Herein, the impurities which, at concentration levels of ppm or ppb, can be co-extracted or entrained in the zinc-laden organic solvent that exits the extraction step, are removed.

[0093] This purification treatment (scrubbing/washing) (at F) can be formed by an array of counter-current stages. The number "q" of successive physical areas and/or "r" chemical areas, is in relation to the characteristics of the raw material, ("r"+"q" should be at least equal to one):

[0094] Number "q" of each physical purification treatment area (scrubbing) is at least 1 and, preferably between 1 and 4.

[0095] Number "r" of each chemical purification treatment area (washing) is at least 1 and, preferably, between 1 and 4.

[0096] The physical treatment of the organic phase, required to avoid aqueous entrainment in the organic phase, is achieved by adding acidulated water, with an acidity range between 0.01 and 4.0 g/l of equivalent H^+ , and in relation to organic/aqueous streams between 5 and 100 and, preferably, between 15 and 25.

[0097] The chemical treatment is carried out using an acidified recycled solution (mainly containing dissolved zinc) (L_{28} , L_{30} and water). This solution has between 10 g/l and 100 g/l of zinc and between 0.1 and 5 g/l of equivalent H^+ .

[0098] This treatment is based on the displacement of the co-extracted impurities (Me^{n+}) to the aqueous phase in the organic phase (MeR_2) by additional zinc extraction, achieving an organic solution of pure zinc according to the equilibrium reaction:



[0099] (Me has the valance of the metallic impurity. In this case, and as an example, a divalent ion has been considered).

[0100] Thanks to the use of a combination of different stages and to the selection of special process conditions, the zinc loaded in the organic solvent (L_{18}), ZnR_2 , reaches extremely high purity levels.

[0101] The sixth barrier to impurities, still within the second "organic" loop, consists of the treatment (at G) of the clean, zinc-laden organic solution (L_{18}) according to stage g) at (G), with a new aqueous acid solution (L_{28} , L_{29}), (this solution should itself be extremely pure), in special conditions according to the following chemical equilibrium reaction (3).



[0102] The stripping conditions (at G) should be so that impurities such as iron and aluminium, extracted together with the iron, are not stripped from the organic phase.

[0103] The acidity of the ultra-pure zinc acid solution used in the zinc stripping is between 0.5 and 5.0 g/l of equivalent H^+ , and contains between 0 g/l and 250 g/l of zinc.

[0104] The temperature of this stage is between 20° C. and 60° C. and, preferably, between 35° C. and 40° C.

[0105] The seventh barrier to impurities within the second organic loop is the regeneration step (at H).

[0106] Only very special cations, more specifically Fe^{3+} or Al^{3+} , are also extracted by the organic solution (at E/I) together with the zinc cations, but these cations are not as easily stripped as the zinc cations (at G), remaining in the organic solvent and, therefore, they do not contaminate the aqueous solution. To prevent their accumulation, a bleed of the organic stream, originating at stage g) is sent to the regeneration stage (at H). The bleed that is sent to regeneration represents, at most 20% of the total volume of the stream and, preferably, between 1% and 5% in volume.

[0107] In this regeneration stage (H), the small organic stream (L_{26}) is treated with hydrochloric acid solution with acidity between 2 and 10 mol/l, preferably between 4 and 8 mol/L, to strip those ions and regenerate the organic solution maintaining suitable quality and purity levels in the organic solution. This organic bleed, already regenerated, is recycled

to the main organic circuit and the depleted hydrochloric acid can be sent to leaching or to a hydrochloric acid recovery system.

[0108] The organic acid solvent (L_{19}) from which the zinc has been removed, is totally or partially recycled (L_{21}) at the depletion stage at (I) and at the extraction stage e) at (E), except for a small stream (L_{20}). The organic stream (L_{23}) containing the mixture of the organic moiety thus treated at regeneration (L_{22}) and the stripped organic solution (L_{21}) is sent to the depletion and extraction stages (at I/E).

[0109] In another variant of the process, the entire stream L_{19} is made to pass through regeneration at (H) before being recycled to depletion/extraction (at I/E).

[0110] The final aqueous solutions of the solvent extraction system: acid raffinate from extraction, acid solution from stripping, and depleted hydrochloric acid from regeneration are passed through an active charcoal column to remove the organic content entrained by these streams, thus minimizing organic losses.

[0111] This treatment is another additional purification barrier, preventing the organic contamination of all aqueous solutions in general, and the ultra-pure stripped aqueous acid solution in particular.

[0112] Within the third loop, the final product producing loop, which is generally an electrowinning loop, is combined with stripping (at G) and the final product production stage (at K), the eighth barrier to impurities consisting of the bleeding of a small stream (L_{30}) of the aqueous of this loop. This bleed is sent to the scrubbing/washing stage (at F), to maintain the excellent quality of that aqueous stream acting as a purification system.

[0113] In this way, it permits the supply of an ultra-pure aqueous acid solution (completely free from impurities) L_{27} , to the scrubbing/washing stage which is used to produce a final product of ultra-pure zinc.

[0114] This bleed is an ultra-pure aqueous acid solution containing between 0.5 g/L and 5 g/L of equivalent protons and between 0 g/L and 250 g/l of zinc.

[0115] The ultra-pure aqueous acid solution bleed (L_{30}) is sent to the scrubbing/washing stage, which further contributes to assuring the extremely low impurity level required, itself acting as a medium for the extreme purification of the zinc-laden organic solvent. With this other barrier, the total purity in the aqueous stripping loop is maintained, and it is a tool to prevent external contamination at the stages of final product production.

[0116] The ultra-pure zinc-rich solution is now a practically pure aqueous solution. It is fed to the last stage of the process according to the invention. The ultra-pure zinc is recovered according to one of the following processes: electrowinning and/or crystallization and/or precipitation and/or any other known process to produce zinc compounds. In the case of electrowinning, the zinc purity will be higher than 99.995%, producing the best quality classification of the London Metal Exchange and following the maximum quality standards (ISO-752 Special High Grade (SHG), B6-98 5^a of ASTM, UNE 37-301-88, Zn 1 of BSL). Equivalent purity definitions will be applicable to other products or salts.

EXAMPLE

[0117] The invention will be better understood through a description of the process according to the invention, schematically represented in the flow chart wherein the stages of the process have been represented by capital letters from (A) to (M). See **FIG. 2**—

[0118] This example relates to the in-plant recovery of high-purity metallic zinc, by:

[0119] leaching the zinc contained in the raw material, achieved by the use of an aqueous solution of a blend of acids, a blend which contains sulphuric acid (representing 95% by weight equivalent of H^+ in the blend)

[0120] Extraction of the dissolved zinc using an organic acid solvent (D_2 EPHA),

[0121] Stripping the zinc using an acid treatment of the zinc loaded in the organic solvent.

[0122] The solid raw material used as feed (S_1) contains 10% by weight of zinc. The main impurities accompanying the zinc are: silicon (25% by weight), iron (2% by weight), calcium (2% by weight) and other impurities (magnesium, manganese, potassium, copper, cobalt, nickel, cadmium, chlorides, fluorides) which, with the sulphate and others, representing the balance of 100% by weight.

[0123] The raw material (100 t/h) is ground until 100% is under 1.29 millimetres, a K_{80} below than 500 microns, and, prepared in pulp form, is fed at leaching point (A) This stage contains 4 leaching areas in cascade. The raw material is introduced at the same time as the recycled leaching aqueous acid liquid/raffinate (L_{15}) which is suitably acidified by the addition of a concentrated acid which compensates for the raw material alkalinity.

[0124] The average leaching pH is maintained throughout the attack at a value below 1.4.

[0125] The average attack temperature is set at a constant value of approximately 55° C., and the time necessary for the raw material to reach the final leaching reactor is 2 hours.

[0126] The pulp (S_2) which exits the leaching stage (A) is, in this case, directly fed (without solid-liquid separation (B)) to the neutralization (C).

[0127] The zinc-laden aqueous solution (L_2) of the leached pulp (S_2) is neutralized in 4 neutralization reactors (C), simultaneously adding chalk, so that the average pH (at S_3), on concluding the neutralization, is set at a value of 4.2. The temperature is kept around 53° C. between the first and fourth neutralization reactor.

[0128] After the solid-liquid separation and the washing of the cake at (D), the residue (S_4) is removed whilst the zinc-rich solution (L_4) is sent, in this case the whole stream (L_6), to the extraction stage (E).

[0129] The solution (L_6), which constitutes the solution for the zinc extraction, is treated in several extraction stages (E) with an inorganic solvent (L_{24}) (a D_2 EPHA solution), by ion exchange according to the aforementioned equation (1). Each extraction stage comprises intimate contact between two immiscible phases, facilitating the zinc extraction

between each aqueous solution and each extraction organic solvent, and a separation area for the two liquids post-extraction.

[0130] During this zinc extraction by the organic acid solvent (organic raffinate) L₂₄, the aqueous phase is acidified in accordance with the reaction (1) and the aqueous solution produced, acid aqueous raffinate (L₁₁) is, in this case separated by two flows (L₁₅) and (L₁₂). The majority stream (L₁₅) is sent to leaching (A), and the minority or bleed (L₁₂) is passed (L₁₃) through a bleed treatment to remove impurities, consisting of neutralization and cementation (M).

[0131] The zinc-laden organic solvent (L₁₆) is sent to the extreme purification stage (F), which comprises two successive purification areas. One is a physical purification stage to remove aqueous solution impurities entrained by the organic stream, and the other, of chemical purification, wherein, in the appropriate conditions according to reaction (2), remove impurities co-extracted together with zinc. The purification (scrubbing/washing) is achieved, in suitable conditions, by a small flow, bleed from the recycled, ultra-pure aqueous acid solution (L₃₀) of the final product production loop—still containing zinc—and water. After this step, an ultra-pure zinc-laden organic solvent is produced, which is sent to stripping (G) in stream form (L₁₈), whilst (L₁₇) constituted by an aqueous acid solution, containing the impurities, is recycled to the extraction stage (E). The zinc-laden organic solution (L₁₈) which is produced by purification (F) is very pure and practically free from impurity residues. After stage (G), this is sent for zinc stripping and the release of the aforementioned extraction organic solvent according to the above reaction (3). This step produces a recycled aqueous acid solution (L₂₀) which contains 3.4 g/l of free equivalent H⁺ and 50 g (1 of zinc (zinc-depleted electrolyte).

[0132] The stripped organic stream (L₁₉) is divided in two flows, a small one (L₂₀) and a major one (L₂₁).

[0133] The small flow (L₂₀) of stripped organic solution, 2% of the total, is sent to the regeneration stage (H) where the iron and aluminium co-extracted in the organic stream (and not previously stripped) are now removed from said organic stream using a hydrochloric acid solution.

[0134] The entire organic acid solvent stream (organic raffinate) (L₂₃) exits the stripping and regeneration and is recycled to the extraction stage, passing through a depletion stage (I). This depletion stage is another extraction stage, wherein the zinc contained in the bleed (L₁₂) and the zinc dissolved in the cementation is recovered, all of which are present in the stream (L₂₅) coming from the neutralization and cementation stages (M). The last remaining impurities, present in the aqueous solution (L₂₆) are recycled to the neutralization and/or cementation at (M) and finally removed together with the hydroxide pulp produced in that neutralization (M). In this case, as with L₈/L₃₁, it is directly sent (without passing through the zinc precipitation stage (J)) to the final impurity removal stage (L). The pH is increased in this stage to precipitate the alkaline impurities which are removed at S₁₀. An aqueous liquor is also formed L₉ which is partially recycled to process L₁₀.

[0135] The aqueous solution (L₂₇) originating in the stripping stage (G) constitutes the ultra-pure zinc solution from which the ultra-pure metallic zinc can be produced (S₂₇), by zinc electrowinning.

[0136] In addition to the metallic zinc product of this final process (K), a depleted, ultra-pure zinc acid solution (L₂₉) is produced which is recycled to the stripping stage (G) thus reloading with more zinc. Stages (G) and (K) form the ultra-pure aqueous circuit. Only a small bleed from the ultra-pure aqueous acid solution (L₃₀) is sent to purification (scrubbing/washing) (F) to maintain the extreme purity of the solution throughout this loop.

[0137] All the impurities initially present in the raw material such as silicon, aluminium, iron, calcium, magnesium, potassium, copper, cobalt, nickel, and others, are removed at the different process stages in accordance with the invention. The recovered zinc has a minimum purity of 99.995% by weight.

[0138] The numerical data of the different process stages in accordance with the invention are summarized in the following table and are shown in accordance with the attached flow chart (See FIG. 2).

TABLE 1

Main streams characteristics													
LOOP	STEP or BARRIER	Stream	(S) t/H	(L) m³/H	Unit	Typical Zn/Acid and Impurities Evolution							
						Zn	Si	Al	Fe	Ca	Mg	Mn	K
1	LEACHING (A)	S1	100		%	10	25	5	2	2	0.5	0.3	0.9
		S2	89.3		%	0.45	27.8	4.6	2.37	2.0	0.59	0.3	0.98
1	1-Gentle Leaching	A.I. Removal (1)			%	4	99.4	83	94	90	95	90	97
	NEUTRAL. (C)-S/L (D)	S4	103.4		%	0.7	24.2	4.66	1.93	4.8	0.51	0.27	0.85
		A.I. Removal (1)			%	7.2	99.93	96.5	99.9	—	95	91	97.5
		L6		471	g/L	30	4E ⁻²	0.35	5E ⁻³	0.4	0.3	0.32	0.3
		L12		84.5	g/L	10	4E ⁻²	0.35	5E ⁻³	0.4	0.3	0.32	0.3
	3-Imp. Aqueo. Bleed	A.I. Removal (1)			%	15	99.95	97.1	99.9	—	100	100	100
1-2	EXTRACT. (E) (2)	L16		735	g/L	14	2E ⁻⁵	5E ⁻²	0.3	5E ⁻²	3E ⁻⁴	8E ⁻³	2E ⁻⁴
2	4-Select. org. extr.	A.I. Removal (1)			%	—	100	97.1	99.9	98.2	99.95	98.1	99.98
	WASHING (F)	L18		735	g/L	13	ND	5E ⁻²	0.3	1E ⁻³	ND	1E ⁻³	ND
2-3	5-Organic Washing	A.I. Removal (1)			%	—	100	97.1	99.9	99.96	99.99	99.8	99.99
	STRIPPING (G)	L19		735	g/L	0.5	ND	5E ⁻²	0.3	ND	ND	ND	ND
2	6-Select. org. strip	A.I. Removal (1)			%	—	100	97.1	99.9	99.96	99.99	99.8	99.99
	REGENERATION (H)	L22		16	g/L	0.0	ND	1E ⁻⁷	0.15	ND	ND	ND	ND
	7-Organ. Regenerat.	A.I. Removal (1)			%	0	100	99.99	100	99.96	99.99	99.8	99.99

TABLE 1-continued

Main streams characteristics													
3	Ultrapure Bleed	L30		9.4	g/L	50	—	0.1	5E ⁻³	7E ⁻²	2E ⁻²	8E ⁻²	6E ⁻³
	8-Ultrapure Bleed	A.I. Removal (1)			%	—	100	100	100	100	100	100	100
3	FINAL PRODUCT	S27	9.3		%	100	ND	<5E ⁻⁴	<2E ⁻⁴	ND	ND	ND	ND
Typical Zn/Acid and Impurities Evolution													
LOOP	STEP or BARRIER	Stream	(S) t/H	(L) m ³ /H	Unit	Cu	Co	Ni	Cd	Cl	F	H ⁺	Oth
1	LEACHING (A)	S1	100		%	0.1	2E ⁻³	1E ⁻²	2E ⁻²	5E ⁻²	5E ⁻²	—	54
		S2	89.3		%	4E ⁻²	5E ⁻¹	3E ⁻³	6E ⁻³	26E ⁻³	22E ⁻³	—	61
	1-Gentle Leaching	A.I. Removal (1)			%	40	30	30	30	50	40	—	—
1	NEUTRAL. (C)-S/L (D)	S4	103.4		%	4E ⁻¹	6E ⁻⁴	3E ⁻³	6E ⁻³	24E ⁻³	34E ⁻³	—	62
	2-Neutral precip.	A.I. Removal (1)			%	42	32	31	31	50	70	—	—
		L6		471	g/L	0.7	16E ⁻³	82E ⁻³	0.16	0.3	18E ⁻³	—	—
		L12		84.5	g/L	0.7	16E ⁻³	82E ⁻³	0.16	0.3	18E ⁻³	0.6	—
	3-Imp. Aqueo. Bleed	A.I. Removal (1)			%	100	100	100	100	100	100	—	—
1-2	EXTRACT. (E) (2)	L16		735	g/L	4E ⁻⁴	1E ⁻³	5E ⁻⁵	1E ⁻⁴	2E ⁻⁴	1E ⁻⁴	—	—
	4-Select. org. extr.	A.I. Removal (1)			%	99.7	98.5	99.6	99.6	99.7	98.5	—	—
2	WASHING (F)	L18		735	g/L	ND	ND	ND	ND	ND	ND	—	—
	5-Organic Washing	A.I. Removal (1)			%	100	100	100	100	100	100	—	—
2-3	STRIPPING (G)	L19		735	g/L	ND	ND	ND	ND	ND	ND	—	—
	6-Select. org. strip	A.I. Removal (1)			%	100	100	100	100	100	100	—	—
2	REGENERAITON (H)	L22		16	g/L	ND	ND	ND	ND	ND	ND	—	—
	7-Organ. Regenerat.	A.I. Removal (1)			%	100	100	100	100	100	100	—	—
3	Ultrapure Bleed	L30		9.4	g/L	—	—	—	—	<5E ⁻²	<5E ⁻²	3.4	—
	8-Ultrapure Bleed	A.I. Removal (1)			%	100	100	100	100	100	100	—	—
3	FINAL PRODUCT	S27	9.3		%	<5E ⁻⁴	ND	ND	<1E ⁻⁴	ND	ND	—	<3E ⁻³

Notes:

- (1) Accumulated Impurities Removal
- (2) Including Aqueous entrainment
- (ND) Not detectable

1. A process for the continuous production of ultra-high purity electrolytic zinc or ultra-high purity zinc compounds from raw materials containing zinc which can be extracted by a hydrometallurgic treatment characterized in that it comprises the following stages:

- a) if the raw material is solid, this raw material will be leached with an aqueous acid solution to dissolve the zinc;
- b) optionally, depending on the nature of the raw material, if the leaching residue has any valuable elements, a solid-liquid separation can be included after leaching;
- c) neutralization of the aqueous solution or leaching pulp, or of a zinc-laden solution when the zinc containing raw material is liquid;
- d) solid-liquid separation of the zinc-rich solution (pregnant solution) from the solids (inert residues and/or precipitates in the neutralizing stage);
- e) extraction of the zinc contained in the pregnant solution by an organic acid solvent;
- f) purification of the zinc-laden organic solvent from the extraction stage;
- g) stripping of the ionic zinc loaded in the organic solvent by an aqueous acid solution;
- h) recovery of the zinc contained in the aqueous acid solution produced from stripping by electrowinning and/or crystallization and/or precipitation, and

characterized in that:

the different stages of the process are organized in three interrelated loops, each containing successive combined barriers to impurities,

within the first loop-leaching-neutralization-solvent extraction and further leaching, the first barrier to impurities, consisting of leaching in gentle conditions; a second barrier consists of the alkaline treatment of the raw material pulp and aqueous solution or of the zinc-rich aqueous solution originating in the leaching; a third barrier consists of the bleeding and treatment of a small aqueous solution stream, collection before and/or after the zinc extraction in step e) by an organic solvent;

within the second loop, the organic loop, the fourth barrier consists of the highly-selective zinc extraction of the aqueous solution with said organic solvent; the fifth barrier consists of the treatment of the zinc-laden organic solvent, through a physical and chemical purification system; a sixth barrier consists of the treatment to clean the zinc-laden organic solvent with an ultra-pure acid solution to strip the zinc from the ultra-pure organic solution; a seventh barrier consists of the partial bleeding and treatment of the stripped organic solvent; and

within the third loop, the eight barrier consists of the bleed of a small stream of the final product producing loop, which will be recycled into the organic loop.

2. The process according to claim 1, characterized in that the raw material from which the zinc will be extracted is solid, either from primary or secondary materials, and contains between 3 and 80% by weight of zinc, which can be in the chemical form of oxides and/or salts and/or metal.

3. The process according to claim 1, characterized in that the raw materials are impure zinc aqueous solutions, with other cations and anions in variable quantities.

4. The process according to claim 1, characterized in that, within the first loop, the first barrier to impurities consists of leaching in gentle conditions of the raw material, conditions relating to temperature, acidity and residence time, to limit the solubilization of impurities, maintaining them in the solid raw materials.

5. The process according to claims 1, 2 or 4, characterized in that the leaching conditions, are maintained at a pH between 0 and 3.0 and, preferably, between 1.5 and 2.5.

6. The process according to claims 1, 2 or 4, characterized in that the leaching is carried out at a maximum temperature equal to 95° C., preferably, between 45° C. and 65° C.

7. The process according to claims 1, 2 or 4, characterized in that the leaching is carried out with a residence time of 0.5 to 7 hours and, preferably, with a residence time between 0.5 and 2 hours.

8. The process according to claim 1, characterized in that, within the first loop, the second barrier to impurities consists of the precipitation of several impurities, co-leached with the zinc and/or present in aqueous solution, by neutralizing an aqueous solution at a controlled pH between 3 and 5, and, preferably, between 3.5 and 4.3 to selectively precipitate each impurity, in particular, silicon, iron, aluminium and antimony, removing them from the solution.

9. The process according to claim 8, characterized in that the operating temperature of the neutralization stage in 95° C. maximum and, preferably between 40° C. and 60° C.

10. The process according to claim 8, characterized in that the neutralization is carried out with a residence time of between 0.5 and 7 hours, preferably between 1 and 4 hours.

11. The process according to claims 1, characterized in that, within the first loop, the third barrier to impurities consists of the bleed of a small stream of neutralized zinc-laden aqueous solution and/or the zinc-discharged, aqueous solution originating in the zinc extraction to remove water and other soluble impurities, in particular magnesium, sodium, potassium, manganese, copper, nickel, cobalt, chlorides and fluorides, thus avoiding their accumulation in the circuit.

12. The process according to claim 11, characterized in that a small stream of the zinc-laden aqueous solution originating at the zinc extraction stage c) and/or zinc-discharged aqueous acid solution originating at the zinc extraction stage e) undergoes controlled neutralization followed by zinc precipitation and a subsequent solid-liquid separation, from where the solid zinc precipitate moiety is recycled to the neutralization stage c) of the pulp and/or solution originating in the raw material leaching, and the liquid moiety undergoes an impurity removal stage by controlled neutralization.

13. The process, according to claim 11, characterized in that the small stream of the neutralized zinc-laden aqueous

solution originating at stage c), undergoes a cementation stage by introducing metallic zinc and removing the solid with the metallic impurities, followed by zinc precipitation of the resulting aqueous solution and a subsequent solid-liquid separation, from where the solid zinc precipitate moiety is recycled to the neutralization stage at c) of the pulp and/or solution originating from the raw material leaching, and the liquid moiety undergoes an impurity removal stage by controlled neutralization.

14. The process according to claim 11, characterized in that the small stream of zinc-laden aqueous acid solution originating in the extraction stage e) undergoes neutralization and/or cementation stages by controlled neutralization of the acidity and subsequent zinc precipitation from the resulting aqueous solution and followed by a solid-liquid separation, from where the solid moiety of zinc precipitate is recycled to the neutralization stage at c) of the pulp and/or of the solution originating in the raw material leaching, and the liquid moiety undergoes an impurity removal stage by controlled neutralization.

15. The process according to claims 13, characterized in that the liquid moiety is sent to a depletion stage within the organic loop, where the zinc present in the aqueous stream is extracted in a depletion stage by the organic phase, whilst the zinc depleted aqueous solution originating in the depletion stage is recycled to neutralization and/or cementation.

16. The process according to claim 12, characterized in that:

a moiety of the small stream of the neutralized zinc-laden aqueous solution and/or the zinc discharged aqueous acid solution originating in the extraction, is/are sent to the zinc precipitation stage, followed by a solid-liquid separation after which, the zinc precipitate is recycled to the neutralization stage c) of the pulp and/or of the leached solution originating in the raw material leaching stage;

the other moiety of the small stream is sent to the neutralization and/or cementation stage and, in the case that the small stream comes from the zinc-discharged, aqueous acid solution, after neutralization, it is optionally sent to the depletion stage;

and the liquid fractions, resulting from the zinc precipitation and/or neutralization and/or cementation and/or depletion are sent to the impurity removal stage by controlled neutralization.

17. The process according to claims 13, 14 or 15, characterized in that the pH of the controlled neutralization treatment of the acidity with an alkaline/cementation agent with metallic zinc, is between 2.0 and 4.0.

18. The process according to claim 12, characterized in that the zinc in solution in the small stream in the neutralized zinc-laden aqueous solution and/or the zinc-discharged, aqueous acid solution originating in the zinc extraction, is precipitated with an alkaline agent at a pH between 6.0 and 8.0.

19. The process according to claim 17, characterized in that the temperature of the neutralization, cementation and zinc precipitation treatments is between 70° C. and 90° C.

20. The process according to claim 1, characterized in that the aqueous solution containing impurities, originating, by the bleed treatment, in neutralization, cementation, depletion and/or zinc precipitation, is treated with an alkaline agent, at a pH between 8.0 and 12.0 to precipitate the impurities

which are removed, whilst the liquid obtained after the separation of impurities is recycled to the process.

21. The process according claim 11, characterized in that the moieties of neutralized zinc-rich liquid and or zinc-discharged aqueous acid solution, originating at the extraction stage e), represents, at most, 25% of the volume of the total stream and, preferably, between 8% and 15% in volume.

22. The process according to claim 1, characterized in that, within the first loop and second loop, the fourth barrier to impurities consists of the highly-selective extraction of dissolved zinc, by an organic acid solvent, stage e) feeding the aqueous zinc solution neutralized to a pH between 2.0 and 5.0 and, preferably, between 3.5 and 4.3.

23. The process according to claim 1, characterized in that the extraction of the zinc contained in the neutralized zinc-rich aqueous solution, takes place in an acidity range between 0.01 and 3.0 g/l of equivalent H^+ and at a temperature between room temperature and 80° C., preferably 40° C.

24. The process according to claim 1, characterized in that the extraction of the zinc contained in the neutralized zinc-rich aqueous solution, is performed using an organic acid solvent, dissolved in kerosene, chosen from the group constituted by alkyl phosphoric acids, alkyl phosphonic acids, alkyl phosphinic acids and, preferably within the group constituted by di-(2-ethylhexyl) phosphoric acid (D_2EPHA), di- (2-ethylhexyl) phosphonic acid and di-(2,4,4-trimethylpentyl) phosphinic acid.

25. The process according to claim 22, characterized in that the ratio of phases between the organic solvent and the aqueous solution (ratio written as O/A) is between 0.1 and 10 and, preferably, between 1.0 and 3.0.

26. The process according to claim 1, characterized in that the fifth barrier to impurities consists of the treatment of the zinc-laden organic solvent from the extraction, with a double purification system, physical and chemical treatment (scrubbing/washing), used in the aqueous acid solution to remove impurities from the aqueous phase entrained in the organic phases, and other impurities co-extracted with the zinc.

27. The process according to claim 26, characterized in that the physical treatment consists of washing the organic solvent with zinc from the extraction, with acidulated water containing between 0.01 and 4.0 g/L of equivalent H^+ , with an organic/aqueous ration between 5 and 100 and, preferably, between 15 and 25.

28. The process according to claim 26, characterized in that the chemical treatment is carried out with a recycled acidulated solution containing between 0.1 and 5 g/L of equivalent H^+ .

29. The process according to claim 26, characterized in that the physical and chemical purification is carried out counter-current, in successive area(s) which are "q" physical and/or "r" chemical, so that "r"+"q" should be at least equal to one, number "q" for areas of physical purification treatment (scrubbing) should be preferably between 1 and 4 and number "r" for chemical purification treatment areas (washing) should, preferably between 1 and 4.

30. The process according to claim 1, characterized in that the sixth barrier to impurities, still within the second loop, consists of the treatment of the loaded organic solvent, in the stripping stage, with an aqueous acid solution wherein the acidity is between 0.5 and 5 g/L or equivalent H^+ .

31. The process according to claim 30, characterized in that the aqueous acid solution used in stripping contains a maximum of 250 g/l of dissolved zinc.

32. The process according claim 29, characterized in that the treatment temperature is between 20° C. and 60° C. and, preferably, between 35° C. and 40° C.

33. The process according to claim 1, characterized in that, within this second loop, the seventh barrier to impurities is that sent from a small bleed stream of the stripped organic phase to the regeneration phase, treating this organic solution with a hydrochloric acid solution, and subsequently recycling this treated organic bleed to the circuit.

34. The process according to claim 33, characterized in that the hydrochloric acid solution has an acidity between 2 and 10 mol/L and, preferably, between 4 and 8 mol/L.

35. The process according to claim 31, characterized in that the organic bleed sent to regeneration represents, at most, 20% of the volume of the total stream and, preferably, between 1% and 5% in volume.

36. The process according to claim 1, characterized in that, within the third loop to produce the final product, the eighth barrier to impurities is the bleed from a small stream of ultra-pure aqueous acid solution, which is sent to the scrubbing/washing stage, to purify the zinc-laden organic solution.

37. The process according to claim 36, characterized in that the small stream of ultra-pure aqueous acid solution contains between 0.5 and 5 g/L of equivalent H^+ and between 0 and 250 g/L of zinc

38. Ultra-pure zinc or ultra-pure zinc compounds, characterized in that they are produced according to the process of claim 1.

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