Innovation, Sciences et Développement économique Canada
Office de la Propriété Intellectuelle du Canada

Innovation, Science and Economic Development Canada
Canadian Intellectual Property Office

CA 3143384 A1 2022/01/22

(21) 3 143 384

(12) DEMANDE DE BREVET CANADIEN
CANADIAN PATENT APPLICATION

(13) A1

(86) Date de dépôt PCT/PCT Filing Date: 2020/07/22
(87) Date publication PCT/PCT Publication Date: 2022/01/22
(85) Entrée phase nationale/National Entry: 2022/01/27
(86) N° demande PCT/PCT Application No.: IB 2020/056894
(87) N° publication PCT/PCT Publication No.: 2022/018489

(51) Cl.Int./Int.Cl. *C22B 7/00* (2006.01),
B01D 11/02 (2006.01), *C22B 13/00* (2006.01),
C22B 15/00 (2006.01), *C22B 3/04* (2006.01)

(71) Demandeur/Applicant:
ECOMETALES LIMITED, CL

(72) Inventeurs/Inventors:
ACUNA GOYCOLEA, MARCELO GUSTAVO, CL;
PEZOA CONTE, RICARDO MIGUEL, CL

(74) Agent: GOWLING WLG (CANADA) LLP

(54) Titre : PROCEDURE DE LIXIVIATION D'ELEMENTS PRECIEUX DE RESIDUS METALLURGIQUES
(54) Title: PROCEDURE FOR LEACHING VALUABLE ELEMENTS FROM METALLURGICAL RESIDUES

(57) Abrégé/Abstract:
A procedure for leaching copper and lead, metallurgical residues of smelting powders which have been subjected to a process of copper leaching and comprising copper, iron, lead, silicon, and optionally arsenic, antimony and bismuth, comprising: (i) copper leaching with a first acid solution of the metallurgical residue, in order to obtain a first leaching solution rich in copper and iron, and optionally arsenic, antimony and bismuth and a first leached sludge having a content reduced in copper and iron, and optionally reduced in arsenic and rich in lead and silicon, (ii) leaching the first leached sludge with a first solution of a carboxylic acid salt, in order to obtain a second leached sludge deficient of lead and a second leaching solution rich in lead, (iii) precipitation wherein a first base is added to the second leaching solution rich in lead in order to obtain a first lead concentrate, and a first precipitation solution deficient of lead, (iv) alkaline leaching of the second leached sludge, wherein a second base is added in order to form an alkaline leaching solution, in order to obtain a third leached sludge having a content reduced in silicon, and a third leaching solution rich in silicon, and optionally arsenic, (v) hydrochloric leaching of the third leached sludge, wherein an acid solution is used in chloride environment, in order to obtain a fourth leached sludge for final disposition and a fourth leaching solution rich in copper, lead and iron, and optionally arsenic, (vi), (vii) metal precipitation from the fourth leaching solution rich in copper, lead and iron, and optionally arsenic with a neutralizing slurry, in order to produce a fifth solution rich in chloride and a first precipitate solid rich in iron, copper and lead, and optionally arsenic, and (viii) leaching the first precipitate solid rich in iron, copper and iron, and optionally arsenic with a sulfuric acid solution, in order to produce a sixth leaching solution rich in copper, iron and optionally arsenic, and a second lead concentrate.

TITLE OF THE INVENTION

Procedure for leaching valuable elements from metallurgical residues.

Abstract

A procedure for leaching copper and lead, metallurgical residues of smelting powders which have been subjected to a process of copper leaching and comprising copper, iron, lead, silicon, and optionally arsenic, antimony and bismuth, comprising: (i) copper leaching with a first acid solution of the metallurgical residue, in order to obtain a first leaching solution rich in copper and iron, and optionally arsenic, antimony and bismuth and a first leached sludge having a content reduced in copper and iron, and optionally reduced in arsenic and rich in lead and silicon, (ii) leaching the first leached sludge with a first solution of a carboxylic acid salt, in order to obtain a second leached sludge deficient of lead and a second leaching solution rich in lead, (iii) precipitation wherein a first base is added to the second leaching solution rich in lead in order to obtain a first lead concentrate, and a first precipitation solution deficient of lead, (iv) alkaline leaching of the second leached sludge, wherein a second base is added in order to form an alkaline leaching solution, in order to obtain a third leached sludge having a content reduced in silicon, and a third leaching solution rich in silicon, and optionally arsenic, (v) hydrochloric leaching of the third leached sludge, wherein an acid solution is used in chloride environment, in order to obtain a fourth leached sludge for final disposition and a fourth leaching solution rich in copper, lead and iron, and optionally arsenic, (vi), (vii) metal precipitation from the fourth leaching solution rich in copper, lead and iron, and optionally arsenic with a neutralizing slurry, in order to produce a fifth solution rich in chloride and a first precipitate solid rich in iron, copper and lead, and optionally arsenic, and (viii) leaching the first precipitate solid rich in iron, copper and iron, and optionally arsenic with a sulfuric acid solution, in order to produce a sixth leaching solution rich in copper, iron and optionally arsenic, and a second lead concentrate.

Date reçue/ date received 2022-01-27

TITLE OF THE INVENTION

Procedure for leaching valuable elements from metallurgical residues.

FIELD OF THE INVENTION

The invention relates to a procedure for leaching valuable elements from metallurgical residues, in particular, focused on the recovery of elements such as copper and lead, and which can optionally contemplate leaching elements such as iron, arsenic, antimony, bismuth, silver and germanium.

In a more specific aspect, the invention relates to a procedure for leaching valuable elements from metallurgical residues for producing a final residue which is a stable residue, pursuant to TCLP (*Total characteristic leaching procedure*, and SPLP (*Synthetic precipitation leaching procedure*) hazard assays.

In another variant of the invention, a procedure is disclosed for obtaining a lead concentrate from metallurgical residues, which in an even more preferred aspect corresponds to lead carbonate.

In a more specific aspect, metallurgical residues are powders from a metal smelting process.

In an even more specific aspect, metallurgical residues are powders from a copper smelting process.

In an even more specific aspect, metallurgical residues, or in particular smelting powders, contemplate materials which have already been subjected to leaching process, such as sulfuric leaching.

In this description sludge are considered as any metallurgical residue which has been subjected to prior leaching processes.

State of the art

Copper leaching

The copper in the sludge is mainly composed of species such as ferrites and/or spinels in the form of $CuFe_2O_4$ as zinc, $ZnFe_2O_4$ and a relevant part of iron, $FeFe_2O_4$. Leaching of these species is based on temperature, acid concentration and residence time, as described in the study by B. S. Boyanov, et al. in World Academy of Science, Engineering and Technology, Vol 9, 2015, 1592-1598, who carried out a synthetic ferrite leaching study of

Date reçue/ date received 2022-01-27

zinc, copper and cadmium, evaluating the previously mentioned variables. The results of this study show that ferrites are better dissolved in HCl and H_2SO_4, at elevated temperatures and high acid concentrations.

At high acid concentrations it is observed that copper leaching has an asymptotic behavior regarding the leaching temperature, which once the 60 minutes reaction time had elapsed in sulfuric media, reaches copper leaching yields above 90% for the range of temperatures between 85 and 90ºC.

Leaching and precipitation of lead

World lead consumption for the year 2011 was above 10 million tons, of which about 80% of said lead was meant for the manufacturing of acid and lead batteries. These batteries contain lead amounts in the form of Pb, PbO_2 and $PbSO_4$. The most traditional way of recovering lead is the pyrometallurgical route, which is characterized by the addition of a reducing agent, such as carbon powder, iron scrap and sodium oxalate. The operation is carried out in ovens at temperatures above 1000°C, which results in a high demand of energy process He *et al.*, *Minerals* 7, no. 6 (2017): 93.

On the other hand, the hydrometallurgical route for recovering lead allows working at reduced temperatures, reducing energy consumption, and in turn sulfur dioxide, which is characterized for being a gas harmful for the environment, is not produced. The hydrometallurgical route uses desulphurizing agents such as sodium carbonate, ammonium carbonate, sodium bicarbonate, ammonium bicarbonate, sodium hydroxide, sodium citrate, acetic acid, sodium acetate, among others. The aim of these processes is to exchange the ion sulphate for other anions in order to form insoluble salts. Once recovered, lead salts such as lead citrate may be calcined in order to produce lead oxide (Zárate-Gutiérrez y Lapidus, *Hydrometallurgy* 144 (2014): 124-128.).

Desulphurization with citrate

In the particular case of the use of citrates, the citric acid and sodium citrate mixture is beneficial for leaching lead sulfate and the subsequent crystallization of lead citrate.

Lead leaching in citrate solutions

The solubility product constant of anglesite at 20°C is $6.31 \cdot 10^{-7}$, indicating that $PbSO_4$ solubility is quite reduced. However, in the presence of citrate concentrated solutions, lead forms a series of soluble complexes. In solutions having 0.12 M Pb^{2+}, a great variety of citrate complex species are present in solution in the pH range of 4.6 to 11.5. At a pH lower

Date reçue/ date received 2022-01-27

than 4.6 the presence of lead sulphate is predominant, while at pH higher than 11.5 the lead hydroxide presence is dominant.

He *et al.*, *Minerals* 7, no. 6 (2017): 93, studied lead leaching of a paste with a lead sulphate to water weight ratio of 1:10, by the addition of 650 g/L sodium citrate at 35°C. These conditions allowed converting more than 99% lead sulphate into lead citrate once 60 min reaction time had elapsed. The increase in temperature up to 95°C, at a sodium citrate concentration of 300 g/L allowed obtaining an efficiency near 99% once 60 min reaction time had elapsed. However, when introducing citric acid to the mixture a decrease in the lead citrate production was observed. The optimum pH for producing lead citrate was within the range of 6 to 7. At a pH of 5.5 using citric acid and ammonium agents, elevated lead leaching efficiencies are also obtained from acid and lead batteries. Within the pH range of 5.2 to 5.5 the presence of trihydrate lead citrate ($[Pb_3(C_6H_5O_7)_2]\cdot[3H_2O]$) was reported as the main species. At higher pH within the range of 8 to 10 the lead recovery as citrate salt is lower due to the formation of lead hydroxide. When lead residues are rich in oxides such as PbO and PbO_2, leaching is performed with a citric acid to lead oxide (II) and (IV) molar ratio of 1:1 and 4:1 at 20°C between 15 and 60 min reaction, reaching leaching efficiencies higher than 99% by weight, obtaining $Pb(C_6H_6O_7)\cdot H_2O$ as the main species (Sonmez and Kumar, *Hydrometallurgy* 95, no. 1-2 (2009), 82-86.).

Pulp density is another import parameter for lead leaching with citrate solutions. Within the range of 10 to 50 g/L anglesite pulp, leachates with a sodium citrate solution 1 M, pH 7 at 600 rpm and 25°C, higher levels of lead extraction of 90 to 94% were reached with a pulp concentration of 10 g/L. At greater pulp concentration, lesser was the extracted lead amount.

Therefore, hydrometallurgical desulphurizing processes are affected by the citrate ion diffusion in the lead paste within the reactor due to the elevated density of lead paste. In this context it is key to design reactors maximizing the mass transfer in the system.

Technology based on lead recovery from lead waste using citric acid has been developed by Cambridge Enterprise Limited (WO2008056125A1). This technology basically comprises treating lead residues comprising lead oxide (II), lead oxide (IV) and lead sulphate with a citric acid solution, and which can be alternatively treated in combination with sodium citrate at a pH varying within the range of 1.4 to 6. Eventually, it is possible to add hydrogen peroxide in basic environment as reducing agent in order to accelerate the lead oxide (IV)

Date reçue/ date received 2022-01-27

leaching reaction so as to produce lead citrate (Sonmez and Kumar, *Hydrometallurgy* 95, no. 1-2 (2009), 82-86.).

The present invention differs from patent WO2008056125 A1 in which the pH required for leaching varies from 5.33 to 8.8, where preferably a pH equal to 7 is used. Additionally, the present invention presents recirculating the citrate solution obtained after a precipitation step with sodium carbonate, so as to again leach output metallurgical residue from the sulfuric leaching step.

Lead citrate crystallization

On the other hand, when crystallizing the lead citrate, both temperature variation and molar relation alteration between citric acid and sodium citrate, are effective alternatives. At temperatures above 75°C when the citric acid to sodium citrate molar ratio is equal to zero, a lesser amount of lead in the filtrate is observed, suggesting a greater precipitation of the lead citrate. In turn, at initial temperatures below 75°C a greater amount of lead in the filtrate was observed, suggesting a lesser fraction of lead was crystallized. Indeed, an elevated difference of temperature above 75°C favors lead citrate crystallization (US 8323373).

Another strategy so as to improve lead citrate crystallization is increasing the citric acid to sodium citrate molar ratio. For example, at an initial crystallization temperature of 35°C and a citric acid to sodium citrate molar ratio of 0.92, only 0.42% of lead was present in the filtrate, while the remaining fraction above 99% was crystallized. Using a citric acid to sodium citrate molar ratio of 1.7:1 at 20°C, with an acid and lead battery paste ratio of 1:5 and a reaction time of 8 h, allows converting 98% of the lead in lead citrate. With the aim of reducing costs and improving efficiency in the leaching step, the use of acetic acid has been suggested for dissolving lead paste. As a consequence, cooling the solution together with an increase in the citric acid to sodium citrate ratio (acidification) is observed to be effective in order to increase crystallization efficiency and obtain lead citrate recoveries above 99% (US 8323373).

Sodium carbonate precipitation

Most precipitation processes with sodium carbonate reported in the literature are based on lead battery processing.

Patent application AU2009350377A1 discloses a method for recovering lead contained in lead batteries electrolytic paste, by dissolving lead oxide in H_2SO_4 in the presence of acetate salts, in order to obtain lead sulphate soluble in such salts, such that after subsequently

Date reçue/ date received 2022-01-27

adding carbonate or hydroxide of the same cation for precipitating lead carbonate/oxycarbonate or lead oxide or hydroxide. The process claims recirculating the solution containing acetate salts obtained from the lead precipitation step such that the new fresh electrolytic paste is dissolved. Precipitation with sodium hydroxide is performed at 83°C, however, there are no specific details of how to carry out the precipitation with sodium carbonate. The application differs from the invention in that citrate salts are used for lead leaching, and in that there is no need of a sulphate removing step every time the invention contemplates a purge allowing to keep sulphate concentration below the saturation limit.

Patent US 8568670 discloses a method of producing lead carbonate from slags obtained from a bismuth refining process, wherein the slags are leached with sodium chloride in order to obtain lead chloride, which is filtered and neutralized so as to be added to a solution containing ammonium bicarbonate under an addition of 2 to 3 times the stoichiometric requirement of the reaction, in order to precipitate lead carbonate by adjusting the pH between 8 and 11 for a period of 1 to 2 h. The present invention differs from the application in that no chloride salts are used for lead leaching. Additionally, the precipitation is performed with sodium carbonate at a pH between 7 and 8 which is directly added to a lead leaching solution without need of prior lead chloride precipitation steps.

Patent US 5.545.805 claims a method for lead immobilization of materials containing elements which contribute hardness such as calcium and magnesium, wherein the material containing lead is contacted with a carbonate associated with alkaline metal in an amount sufficient for metals contributing hardness to react with the carbonate and adding polyprotic acid oxyanion. The carbonate salt is essentially sodium or potassium carbonate, while the polyprotic acid oxyanion is selected from phosphate, borate, selenate, arsenate, chromate or sulphate, for precipitating lead as an oxosalt of said oxyanions. In particular, the method also describes that the oxosalt may be a carbonate salt in which case lead carbonate would precipitate. In application examples the precipitation pH observed is elevated around 12.3. Patent application differs from the invention in that no polyprotic acid oxoanions are required for lead leaching.

Patent application WO2005007904A1 discloses a method for desulfurizing a resulting solid mixture of lead battery rupturing containing lead oxide, oxysulphate and sulphate residues, by contacting with ammonium, sodium or potassium carbonate in a molar ratio of between 0.1 and 10% in excess over the sulphate concentration, and the contact with solubilizing substance of lanarkite among which citric acid and citrates are mentioned, in a carbonate to

Date reçue/ date received 2022-01-27

solvent molar ratio is between 1 to 2.75. In the process, the lead residues are desulfurized by action of the solubilizing substances above mentioned, and subsequently the lead is precipitated by action of carbonates, wherein the process operation temperature is performed preferably between 60 and 100°C. This application differs from the present invention in that the amount of lead carbonate added does not require an addition over the stoichiometric amount necessary for precipitating lead based on the sulphate content of the solution, every time the purge considered keeps sulphate levels at certain level below saturation that does not impact on lead carbonate precipitation.

Alkaline leaching

Mufakhir et al., *IOP Conf. Series: Materials Science and Engineering* 285 (2017) 012003 studies silicon leaching in the presence of sodium hydroxide from slags from a ferronickel obtaining process. Alkaline leaching if slags was assessed at NaOH concentrations of between 6 and 14 mol/L, solid content between 5 and 25 % w/w and temperature between 25 and 110°C. Results are shown in a maximum yield of 31% of silicon leaching. In the invention object of the present application, a method is disclosed for maximizing copper and lead leaching including steps of sulfuric and citric leaching with the aim of removing Cu and Pb present in the sludge, for subsequently proceeding to alkaline leaching. Removing Cu, Fe and Pb in early steps allows chemically modifying the sludge, leaving silicon species more fragile to leaching as shown in the results obtained in the present application.

Hydrochloric leaching

Patent US7329396 describes a process for leaching valuable metal of oxidizing materials, such as a lateritic nickel mineral, comprising the step of leaching the mineral with a lixiviant comprising a cationic salt (for example, magnesium chloride) and HCl. An additional oxidizer or metal chloride may be added (as the one resulting from the leaching operation). In one embodiment, the process comprises recovery of a mineral valuable metal comprising the steps of: leaching the mineral with a lixiviant; separating a leachate value rich in mineral metals in a first solid-liquid separation; oxidizing and neutralizing the leachate value rich in metals thus obtained; and separating a magnesium chloride solution from the leachate thus obtained in a second solid-liquid separation. In another embodiment, the lixiviant solution is regenerated from a magnesium chloride solution. In an additional embodiment, regeneration of a leaching solution includes a step for producing magnesium oxide from the magnesium chloride solution.

Date reçue/ date received 2022-01-27

A difference between the invention and patent US7329396 is that it points out a preferred pH above 0.4 so as to precipitate hematite. In the case of the present invention, it is convenient to work at low pH, preferably below pH -0.25 with the aim of obtaining ferric ion in solution which favors the use of leaching solution in other leaching processes, such as those smelting powders leaching processes. Additionally, precipitation of iron hydroxides is entirely disadvantageous in the present invention, every time the silver to iron concentration rate amounts to 0.01 g Ag/g Fe, and as a consequence, the iron hydroxide precipitation may drag silver present in the solution.

Patent application CA2820631A1 relates to processes which may be efficient for treating several materials comprising many different metals. These materials may be leached with HCl so as to obtain a leachate and a solid. Then, they may be separated from each other and a first leachate metal may be isolated. Then, a second metal may be isolated from the leachate. The first and second metal may be isolated each one substantially from the leachates. This may be done by controlling the leachate temperature, adjusting the pH, reacting even more the leachate with HCl, etc. Metals that may be recovered in form of metal chlorides may be eventually converted into the corresponding metal oxides, thus allowing the recovery of HCl. Several metals may be selected from aluminum, iron, zinc, copper, gold, silver, molybdenum, cobalt, magnesium, lithium, manganese, nickel, palladium, platinum, thorium, phosphorus, uranium, titanium, rare earth and rare metal elements.

The present invention differs from patent application CA2820631A1 in that the former does not require temperatures above 90°C in order to efficiently perform metal leaching, unlike the application which requires temperatures above 125°C. Additionally, leaching of the material containing aluminum is performed with an HCl concentration starting from 18 % w/w, while the present invention requires HCl concentrations below 140 g/L (or below 11% w/w).

Description of the figures

Figure I shows the process diagram of the procedure disclosed by the present invention.

Figure II shows the X-ray diffraction spectrum of the lead concentrate obtained in the application examples.

Figure III shows the Raman spectrum of the lead concentrate obtained in the application examples.

Date reçue/ date received 2022-01-27

Description of the invention

In a broad aspect, the invention describes a procedure for leaching copper and lead, from metallurgical residues of smelting powders which have been subjected to a process of copper leaching and comprising copper, iron, lead, and silicon, and optionally arsenic, antimony and bismuth, maximizing the copper and lead recovery.

In another preferred option, the invention describes a procedure for leaching copper and lead, metallurgical residues of smelting powders which have been subjected to a process of copper leaching and comprising copper, iron, lead, and silicon, and optionally arsenic, antimony, silver, germanium and which leaves a final residue mainly composed of aluminosilicates and which undergoes hazard assays according to TCLP assay.

In another preferred option, the invention describes a procedure for obtaining a lead concentrate of metallurgical residues of smelting powders which have been subjected to a process of copper leaching and comprising copper, iron, lead, and silicon, and optionally arsenic, antimony, bismuth, silver and germanium.

The procedure of the present invention comprises the following steps:

a step (i) of copper leaching of the metallurgical residue (1), wherein a first acid leaching solution (2) is used, in order to obtain a first leaching solution rich in copper and iron, and optionally arsenic, antimony and bismuth (3) and a first leached sludge having a content reduced in copper and iron, and optionally reduced in arsenic and rich in lead and silicon (4),

a step (ii) of leaching the first leached sludge (4) wherein said first leached sludge (4) is processed with a first solution of a carboxylic acid salt (5), in order to obtain a second leached sludge deficient of lead (6) and a second leaching solution rich in lead (7),

a step (iii) of precipitation wherein a first base (8) is added to the second leaching solution rich in lead (7) in order to obtain a first lead concentrate (9), and a first precipitation solution deficient of lead (10),

a step (iv) of alkaline leaching of the second leached sludge (6), wherein a second base (11) is added in order to form an alkaline leaching solution, in order to obtain a third leached sludge having a content reduced in silicon (12), and a third leaching solution rich in silicon, and optionally arsenic (13),

Date reçue/ date received 2022-01-27

a step (v) of hydrochloric leaching of the third leached sludge (12), wherein an acid solution is used in chloride environment (14), in order to obtain a fourth leached sludge for final disposition (15) and a fourth leaching solution rich in copper, lead and iron, and optionally arsenic (16),

a step (vi) of metal precipitation from the fourth leaching solution rich in copper, lead and iron, and optionally arsenic (16) with a neutralizing slurry (17), in order to produce a fifth solution rich in chloride (18) and a first precipitate solid rich in iron, copper and lead, and optionally arsenic (19), and

a step (vii) of leaching the first precipitate solid rich in iron, copper and iron, and optionally arsenic (19) with a sulfuric acid solution (20), in order to produce a sixth leaching solution rich in copper, iron and optionally arsenic (21), and a second lead concentrate (22).

In one preferred optional, the metallurgical residue to be processed is powder obtained by a metal smelting process.

In a more preferred optional, said powder obtained by a copper smelting process is smelting powder.

In an even more preferred option, the metallurgical residue has been subjected to a copper leaching process.

In an even more preferred option, said metallurgical residue has been subjected to leaching with H_2SO_4.

In one preferred option, the metallurgical residue to be processed comprises the mineral species anglesite, covelline, cuprospinel in the form of $CuOFe_2O_3$, zinc spinels in the form of $ZnOFe_2O_3$, magnetite, iron oxide(III), pirite, scorodite, mucovite, kaolinite and lead sulphate(II).

In an even more preferred option, the copper contained in the metallurgical residue is present as copper sulphate, calcosine, covelline and cuprospinel in the form of $CuOFe_2O_3$.

In an even more preferred option, the copper contained in the metallurgical residue is present in at least 50% in the form of cuprospinel in the form of $CuOFe_2O_3$.

In one preferred option, the silicon contained in the metallurgical residue is present as muscovite and kaolinite.

Date reçue/ date received 2022-01-27

In another preferred option, the lead contained in the metallurgical residue is present as lead sulphate(II), galena or lead oxide(II).

In an even more preferred option, the lead is in at least 95% as lead sulphate(II).

In one preferred option, the first H2SO4 solution may comprise H_2SO_4 and/or a refinery effluent.

In one preferred option, step (i) is performed at a H_2SO_4 concentration of between 150 and 300 g/L, more preferably at a concentration of H_2SO_4 of 250 g/L.

In one preferred option, step (i) is performed at a temperature of between 50 and 130ºC, more preferably at a temperature of 85ºC.

In one preferred option, step (i) is performed for a period of between 3 and 12 hours, more preferably for a residence time of 6 hours.

In one preferred option, step (i) is performed at a solid concentration of between 5 and 20% w/w, more preferably at a solid concentration of 15% w/w.

In one preferred option, in step (ii) of leaching, the carboxylic acid salt is sodium citrate.

In one preferred option, in step (ii) the sodium citrate solution has a molar concentration of sodium citrate between 0.5 and 1 M.

In one preferred option, in step (ii) the first leached sludge is fed to the sodium citrate solution in a mass ratio of 1:9.

In one preferred option, step (ii) is performed at a temperature of between 20 and 60ºC, more preferably at 40ºC.

In one preferred option, step (ii) is performed for a residence time of between 1 and 23 h.

In one preferred option, step (ii) is performed at a pH of between 5.3 and 8.8, more preferably at a pH of 7.0.

In one preferred option, in step (ii), the acid corresponding to the carboxylic acid salt is added for adjusting the pH.

In an even more preferred option, in step (ii), a citric acid is added for adjusting the pH.

In one preferred option, the first base added to step (ii) is a carbonate salt, selected from sodium carbonate, sodium bicarbonate or magnesium carbonate.

Date reçue/ date received 2022-01-27

In an even more preferred option, the first base added to step (iii) is sodium carbonate.

In one preferred option, the sodium carbonate added to step (iii) is performed in stoichiometric ratio 1:1 regarding the lead concentration in the third leaching solution.

In one preferred option, in step (iii), the precipitation reaction is performed at a temperature of between 20 and 90ºC, more preferably at 70ºC.

In one preferred option, in step (iii), the precipitation reaction is performed for between 0.5 and 6 h.

In one preferred option, in step (ii) the precipitation reaction is performed at a pH of between 6 and 9, more preferably at a pH of 7.5.

In one preferred option, in step (iii) the pH adjustment is performed with a neutralizer such as sodium hydroxide without considering neutralizers providing hardness to the calcium and/or magnesium based solution.

In one preferred option, the first precipitation solution of step (iii) is recirculated to step (ii) in order to leach the first leached sludge of step (i).

In one preferred option, a part of the first lead concentrate is recirculated to step (iii) in order to act as seed.

In an even more preferred option, the part of the first lead concentrate recirculated corresponds to a 30% of the total of said first precipitated solid.

In one preferred option, the recycling ratio of the first precipitation solution deficient of lead to step (iii) is of 90%.

In one preferred option, the first precipitation solution deficient of lead recirculated to step (ii) requires a sodium citrate restitution.

In one preferred option, the sodium citrate restitution is a solution containing sodium citrate in a mass ratio of 0.35:1 regarding water used for preparing said solution and is added such as to obtain a pulp having 10% w/w of solids regarding the second leached sludge.

In one preferred option, the first precipitation solution deficient of lead recirculated to step (ii) requires a pH adjustment to 7.0.

In an even more preferred option, the pH adjustment in step (ii) is performed with a citric acid solution of between 600 and 900 g/L.

Date reçue/ date received 2022-01-27

In one preferred option, the first precipitation solution deficient of lead obtained from step (ii) does not require a step for removing the sodium sulphate.

In one preferred option, the first lead concentrate consists of lead carbonate.

In one preferred option, the second base used in the leaching of step (iv) is selected between $Mg(OH)_2$, KOH or NaOH.

In one preferred option, the second base added in step (iv) is added at a ratio of between 5 and 10% w/w regarding the total mass of alkaline leaching solution, more preferably at a ratio of 6.0% w/w.

In one preferred option, the leaching reaction of step (iv) is performed at a temperature of between 70 and 150ºC, more preferably at a temperature of 130ºC.

In one preferred option, the leaching reaction of step (iv) is performed for a residence time of between 1 and 12 hours, more preferably for a residence time of 3 hours.

In one preferred option, the acid used in the leaching of step (iv) is HCl.

In one preferred option, in step (v) the HCl is provided in a concentration varying from 50 and 140 g/L.

In one preferred option, in step (v) a chloride salt is added.

In an even more preferred option, in step (v) the chloride environment is increased by the addition of magnesium chloride.

In one preferred option, in step (v) the chloride salt is provided such that the chloride concentration is within 140 and 240 g/L.

In one preferred option, step (v) is performed at a pH of between -1.5 and -0.25, preferably within the range of -0.73 and -0.65.

In one preferred option, step (v) is performed at a temperature in a range of 40 to 95ºC.

In one preferred option, the neutralizing slurry of step (vi) of metal precipitation is selected from among calcium hydroxide, calcium oxide, calcium carbonate, lime, dolomitic lime, magnesium carbonate, magnesium hydroxide or magnesium oxide.

In an even more preferred option, the neutralizing slurry of step (vi) of metal precipitation is a magnesium oxide slurry.

Date reçue/ date received 2022-01-27

In another preferred option, step (vi) is performed at a temperature of between 50 to 95ºC.

In one preferred option, the neutralizing slurry added in step (vi) is provided until reaching a pH between 3 and 7.

In another preferred option, step (vi) has a residence time of between 0.5 and 3 h.

In one preferred option, the fifth solution rich in chloride of step (vi) is sent to a crystallization process of magnesium chloride.

In another preferred option, the fifth solution rich in chloride of step (vi) is recirculated to the fourth step of silver precipitation.

In another preferred option, the sulfuric acid solution of step (vii) has a sulfuric acid concentration of between 60 and 275 g/L.

In another preferred option, the sulfuric acid solution of step (vii) is a sulfuric leaching solution of smelting powders.

In another preferred option, the sulfuric acid solution of step (vii) is the first leaching solution rich in copper and iron, and optionally arsenic and bismuth of step (i) to which acidity has been adjusted to between 60 and 275 g/L.

In one preferred option, the step (vii) of leaching the first precipitate solid rich in iron, copper and lead, and optionally arsenic, is performed at a temperature of between 50 and 95ºC.

In one preferred option, the second lead concentrate is recirculated to step (ii).

In one preferred option, the first leaching solution rich in copper, iron and optionally arsenic is sent to a copper leaching process of smelting powders.

In one preferred option, the first leaching solution rich in copper, iron and optionally arsenic is sent to an arsenic abatement process.

In one preferred option, the sixth leaching solution rich in copper, iron and optionally arsenic is sent to a copper leaching process of smelting powders.

In one preferred option, the sixth leaching solution rich in copper, iron and optionally arsenic is sent to an arsenic abatement process.

In one preferred option, the arsenic abatement process is selected from those contemplating the ferric arsenate production.

Date reçue/ date received 2022-01-27

In an even more preferred option, the arsenic abatement process is a scorodite production process.

Application examples

The examples below should be considered as embodiments of the present invention and in any case should they be considered as limiting thereof, since different adaptations which may be performed therein shall be covered within the claimed subject matter by this invention.

Sulfuric leaching

Examples 1 to 7

Between 2.550 and 2.850 g of a sulfuric acid solution with a con concentration of between 150 and 250 g/L of H_2SO_4 were prepared, which were arranged in 5 L glass reactor, wherein the sludge previously subjected to a copper leaching process was added to a solid content of between 5 and 10% w/w. Mineralogy of said sludge is shown in Table 1. The reactor was stirred at 300 rpm for 3 to 6 hours at 85°C. Once the reaction time is ended, the pulp was filtered in a Büchner system. Results are shown in Table 2.

Table 1. Sludge mineralogy

Species	Unit	Value
$PbSO_4$	%	12.84
PbS	%	0.1
PbO	%	0.1
$CuSO_4$	%	2.54
Cu_2S	%	0.63
CuS	%	4.02
CuO	%	0.71
$CuOFe_2O_3$	%	15.09
$ZnOFe_2O_3$	%	4.46
ZnS	%	2.94
Fe_3O_4	%	4.74
Fe_2O_3	%	4.91
FeS_2	%	6.32
Ag_2S	%	0.1

Date reçue/ date received 2022-01-27

Species	Unit	Value
$FeAsO_4*2H_2O$	%	5.18
Bi_2O_3	%	0.59
Sb_2O_3	%	0.5
$KAl_3Si_3O_{10}(OH)_2$	%	7.01
$Al_2Si_2O_3(OH)_4$	%	2.92
Ge	g/ton	548

Table 2. Sulfuric leaching results examples 1 to 7

Variable/Example	Unit	1	2	3	4	5	6	7
H_2SO_4 concentration	g/L	150	250	150	250	250	150	250
Solid content	% w/w	5	5	15	15	15	20	20
Leaching time	h	6	6	6	3	6	6	6
Cu leaching yield	%	75.9	76.1	68.0	60	69.7	64.8	67.7

Examples 8 to 10

2,550 g of a 250 g/L of H_2SO_4 solution were prepared, which were arranged in 4 L autoclave, wherein the sludge previously subjected to a copper leaching process was added to a solid content of 15% w/w. The reactor was stirred at 300 rpm for 1 to 6 hours at 130°C. Once the reaction time is ended, the pulp was filtered in a Büchner system. Results are shown in Table 3.

Table 3. Sulfuric leaching results examples 8 to 10

Variable/Example	Unit	8	9	10
Leaching time	h	1	3	6
Cu leaching yield	%	75.9	76.1	82.0
Mass loss	%	35.0	41.0	42.0

Example 11

A refinery effluent dissolution was prepared (table 4) to which the H_2SO_4 concentration was adjusted at 250 g/L, which was arranged in a 5 L glass reactor, wherein 450 g of sludge previously subjected to a copper leaching process were added, in order to create a pulp with 15% w/w solids. The reactor was stirred at 300 rpm for 6 hours at 85°C. Once the reaction

Date reçue/ date received 2022-01-27

time is ended, the pulp was filtered in a Büchner system. Results showed a leaching yield of Cu of 72.0%, a leaching yield of Fe of 62.0%, a leaching yield of As of 71.5%, a leaching yield of Zn of 57.0% and a mass loss of 38.5%.

Table 4. Refinery effluent composition

Elements	Unit	Value
H_2SO_4	g/L	35.73
Cu	g/L	11.37
Fe	g/L	0.10
As	g/L	1.80
Bi	g/L	0.00
Zn	g/L	0.00
SO_4	g/L	53.66
Sb	g/L	0.04
Pb	g/L	0.00
Al	g/L	0.00
Ca	g/L	0.51
Ag	ppm	0.00
Ge	ppm	0.00

Citric leaching

Example 12

A solution was prepared with 40 L of water to which it was added 14 kg of sodium citrate and the pH adjusted to 7.0 with a citric acid solution of 800 g/L. Once the reagents are dissolved 6 kg of leached sludge were added pursuant to example 3. The head sludge has a Pb content of 15.4%. Leaching was carried out at 20°C and stirred at 1,000 rpm for a 9 h period. A Pb leaching efficiency of 94% was obtained, thus obtaining a leached sludge reducing its mass in 24% with a Pb content of 1.19%.

Examples 13 to 19

A solution was prepared with 2 L of water with a concentration of between 323 and 368 g/L of sodium citrate at a pH between 5.3 and 8.8. The pH was adjusted with a citric acid solution of 800 g/L. Once reagents are dissolved the sludge processed under example 3 at a ratio of between 1.2 and 2.3 g of sodium citrate/g of sludge, is added. The head sludge has a Pb

Date reçue/ date received 2022-01-27

content of between 15.0 and 15.1%. Leaching was carried out between 30 and 60°C and stirred between 500 and 700 rpm for a period between 2 and 4 h. Results are shown in Table 5.

Table 5. Citric leaching results examples 13 to 19

Variable/Example	Unit	13	14	15	16	17	18	19
Sodium citrate:sludge ratio	g:g	2.3	2.3	2.3	2.3	1.2	2.3	2.3
Sodium citrate concentration	g/L	350	350	350	350	323	368	368
pH		8.8	8.8	8.8	5.3	5.6	5.3	5.3
Temperature	°C	30	40	60	40	40	40	40
Stirring	RPM	500	500	500	500	500	500	500
Residence time	H	4	2	2	4	4	4	4
Head Pb law	%	15.1	15.1	15.1	15.1	15.1	15.0	15.0
Sludge Pb law	%	2.1	2.2	1.6	0.6	0.9	0.7	0.9
Pb leaching yield	%	90	89	92	97	96	97	96
Mass loss	%	24	25	24	26	28	32	29

Lead precipitation

Examples 20 to 25

447 mL of a lead leaching solution were taken with a Pb concentration of 15.8 g/L. The pH was adjusted at a range between 7.0 and 8.0 adding a NaOH solution of 400 g/L. An amount of sodium carbonate equimolar to the amount of Pb present in the leaching solution. The precipitation was carried out during 1 h at a temperature of between 40 and 70°C.

Table 6. Lead precipitation results examples 20 to 25

Variable/Example	Unit	20	21	22	23	24	25
pH		7	7.5	8	7	7.5	8
Temperature	°C	40	40	40	70	70	70
Pb precipitation yield	%	72	89	91	95	96	97

Date reçue/ date received 2022-01-27

Example 26

A solution was prepared with 4.7 L of water to which it was added 1,633 g of sodium citrate adjusting the pH at 7.0 with a citric acid solution of 800 g/L. Once the reagents are dissolved 700 g of leached sludge were added pursuant to example 3. The head sludge has a Pb content of 17.4%. Leaching was performed at 40°C and stirred at 700 rpm for 3 h. Subsequently, the pulp was filtered and the filtered solution used for performing a lead carbonate precipitation. The pH of the solution was adjusted at 7.5 with a NaOH solution of 400 g/L, and then an equimolar amount of sodium carbonate was added. The precipitation was carried out for 1 h, and then the pulp was filtered while 90% of the filtered solution of the precipitation step was used for leaching fresh sludge. For said second leaching cycle, a sodium citrate solution was added in a sodium citrate:water ratio equal to 0.35:1 fresh for adjusting the solid contents of the pulp at 10% w/w regarding the sludge content. Additionally, the pH of the solution was adjusted to 7.0 with a citric acid solution of 800 g/L. Once the leaching pH was adjusted, the second Pb leaching cycle was performed and then a second Pb precipitation cycle following the same precipitation conditions as described at the beginning of example 18. Recirculation of filtering solution of the precipitation step was repeated until completing a total of 15 cycles. For the last 5 cycles, precipitated solid of lead carbonate was used as seed in the precipitation step. The average leaching efficiency was of 94%, with a leached solid with a Pb content of 1.33% average. In the precipitation step a Pb precipitate was obtained with a Pb content of 76%. The sulphate content reached a maximum value of 96 g/L, which was kept constant for the last five test cycles. Other analytes concentrated in the execution of different leaching cycles were Fe, reaching 4 g/L, Bi reaching 1.5 g/L and K reaching 1.5 g/L. The element more significantly leached in tests was Bi, with an average leaching of 66%. Cu, Fe, Ag, Ge, Sb, As, Si, Al and K has negligible leaching efficiencies. In this context, the semi continuous test did not require a step for removing sodium sulphate, every time the concentration obtained did not affect leaching.

DRX analysis was performed on precipitated solids, showing the presence of lead carbonate associated to sodium hydroxide ($NaPb_2(CO_3)_2OH$). In turn, Raman analysis was performed which showed two peaks at 635.6 cm^{-1} and 1,011.9 cm^{-1} which correspond to lead carbonate.

Date reçue/ date received 2022-01-27

Alkaline leaching

Examples 27 to 35

A pulp was prepared with a sodium hydroxide solution with a concentration between 5.4 and 8.7% w/w and leached sludge subjected to sulfuric and citric leaching consecutive processes with a solid content between 5.0 and 7.0 % w/w. The pulp was arranged in a 4 L autoclave and warmed at a temperature of between 100 and 140°C for between 1 and 6 hours at 600 rpm. Once the leaching time is fulfilled, the pulp was cooled and filtered in Büchner system. Results are shown in Table 7.

Table 7. Results examples 27 to 35

Variable/Example	Unit	27	28	29	30	31	32	33	34	35
NaOH Concentration	% w/w	5.6	5.6	5.6	5.6	5.6	7.2	5.4	8.7	5.7
Solid content in pulp	% w/w	5.0	5.0	5.0	5.0	5.0	5.0	7.0	5.0	5.0
Temperature	°C	100	140	120	120	130	130	140	140	130
Residence time	h	3	3	1	6	3	3	3	6	3
Stirring	rpm	600	600	600	600	600	600	600	600	900
Leaching yield										
Si	%	79.5	75.4	75.7	67.1	66.9	68.1	62.0	71.5	77.0
As	%	90.9	94.1	92.2	93.1	94.3	93.3	95.0	95.5	90.0
K	%	73.6	79.4	76.6	78.9	80.2	81.8	75.3	84.3	91.0

Examples 36 to 37

A pulp was prepared with 6.230 mL of water to which 420 g of sodium hydroxide and 350 g of leached sludge subjected to copper and lead leaching consecutive processes, were added, in order to obtain a concentration of 6.0% w/w of NaOH and 5.0% w/w of solids. The pulp was arranged in a 10 L glass reactor and warmed at 90°C for between 1 and 6 hours and stirred at 900 rpm. Once the leaching time is fulfilled, the pulp was cooled and filtered in Büchner system.

Table 8. Results examples 36 and 37

Variable/Example	Unit	36	37
Residence time	h	1	6

Date reçue/ date received 2022-01-27

Variable/Example	Unit	36	37
Leaching yield			
Si	%	63.2	63.0

Hydrochloric leaching

Examples 38 to 45

A solution was prepared with an HCl concentration between 54 and 160 g/L and with a chloride concentration of 140 to 237 g/L. The chloride concentration was increased by adding hexahydrated magnesium chloride. Such solution was added 180 g of sludge subjected to sulfuric and citric leaching processes, and on the other hand subjected to sulfuric, citric and alkaline leaching processes as described in experiments 1 to 37. The pulp was fed to a 5L glass reactor, heated at 90°C and kept constant stirring for 6 hours. Once the pulp test is concluded, the pulp was filtered in Büchner system. Results of these tests are shown in table 9.

Table 9. Results examples 38 and 45

Variable/Example	Unit	38	39	40	41	42	43	44	45
Sludge		Step i and ii	Step i and ii	Step (i) and ii	Step (i) and ii	Step i. ii and iii	Step (i). ii and iii	Step (i). ii and iii	Step (i). ii and iii
HCl concentration	g/L	80	130	130	100	54	130	130	160
Chloride concentration	g/L	230	230	230	140	230	230	230	170
Temperature	°C	90	50	90	90	90	50	90	90
Leaching yield									
Fe	%	72	70	84	73	96	62	96	99
Cu	%	27	21	31	26	84	67	97	82
Pb	%	80%	70%	80%	65%	83	73%	97%	81%
Mass loss	%	28	20	32	26	38	31	45	44
Fe^{3+}/FeT ratio	mol:mol	0.98	0.98	0.98	0.98	0.98	0.98	0.98	0.98

Date reçue/ date received 2022-01-27

Results show a clear contribution to copper leaching including the alkaline leaching step, which allows increasing the copper leaching yield of the global process. This observation is explained by the existence of chrysocolla in the matrix of sludge from step ii, which are effectively modified in step ii by the addition of the silicon removal base, leaving the copper more fragile for the alkaline attack of step (v), such as appreciated in the results herein expressed.

The final residue of hydrochloric leaching tests was subjected to stability test pursuant to TCLP and SPLP protocol, thus obtaining cadmium, arsenic and lead values released below the values allowed by the standard.

Metal precipitation

Examples 46 to 52

450 g of PLS obtained from hydrochloric leaching tests were obtained in a 600 mL precipitate flask and warmed at between 25 and 80°C. Neutralization of the hydrochloric leaching solution was performed using magnesium oxide slurry at 15% in volume until a pH within the range of 3 and 6. Subsequently, the pulp was filtered with 45 µm filter paper.

Table 10. Results examples 46 to 52

Variable/Example	Unit	46	47	48	49	50	51	52
Neutralization pH	-	6	3	3	5	5	6	6
Temperature	°C	25	50	80	50	80	50	80
Precipitation yield								
Pb	%	>99.5	>99.5	>99.5	>99.5	>99.5	>99.5	>99.5
Fe	%	97	85	80	98	97	100	99
Cu	%	18	5	2	16	15	20	23

Lead concentrate

Examples 53 to 55

50 g of metal precipitate were placed with a 17.1% Fe, 1.3% Cu and 0.44% Pb content in a 600 mL precipitate flask and sulfuric acid was added in order to obtain a concentration between 60 and 257 g/L of H_2SO_4. The pulp was stirred with a magnetic bar and taken to a temperature of 60°C for 5 h, and once the pulp leaching time is fulfilled the pulp was filtered with 45 µm paper.

Date reçue/ date received 2022-01-27

Table 11. Results examples 53 to 55

Variable/Example	Unit	53	54	55
Sulfuric acid concentration	-	60	80	120
Temperature	°C	60	60	60
Residence time	h	3	3	3
Law in the concentrate				
Pb	%	2.0	5.4	14.0
Fe	%	37.6	29.3	6.2
Cu	%	0.12	0.09	0.04

Examples 56 to 57

1.700 g of metal precipitate were placed with a 17.1% Fe, 1.3% Cu and 0.44% Pb content in a 20 mL glass reactor, to which it was added 15,300 g of a 275 g/L of H_2SO_4 solution. The pulp was kept between 25 and 80°C and with mechanical stirring at 450 rpm for 5 h, and once the leaching time is fulfilled the pulp was filtered in filter paper N°42.

Table 12. Results examples 56 to 57

Variable/Example	Unit	56	57
Sulfuric acid concentration	-	275	275
Temperature	°C	25	80
Residence time	h	5	5
Law in the concentrate			
Fe	%	4.0	3.5
Cu	%	0.35	0.15
Pb	%	29.0	28.6

Citric leaching of lead concentrate

Examples 58 to 61

The lead concentrate was recirculated to the citric leaching step. In a 5 L glass reactor it was added 120 g of lead concentrate obtained from metal precipitate leaching tests and a sodium citrate solution between 0.5 and 1 M at pH 7 adjusted with citric acid. The pulp was kept between 20 and 70°C and stirred at 700 rpm for 3 h. The lead leaching yield varied between 80 and 82%

Date reçue/ date received 2022-01-27

Table 13. Results examples 58 to 61

Variable/Example	Unit	58	59	60	61
Sodium citrate concentration	M	1	1	0.5	1
Temperature	°C	70	20	70	70
Residence time	h	3	3	3	3
Solid content	% w/w	5	5	5	10
Leaching yield					
Pb	%	80	82	80	81

Date reçue/ date received 2022-01-27

CLAIMS

1. A procedure for leaching copper and lead, from metallurgical residues of smelting powders which have been subjected to a process of copper leaching and comprising copper, iron, lead, silicon, and optionally arsenic, antimony and bismuth, characterized in that it comprises:

i. copper leaching with a first acid solution of the metallurgical residue, in order to obtain a first leaching solution rich in copper and iron, and optionally arsenic, antimony and bismuth and a first leached sludge having a content reduced in copper and iron, and optionally reduced in arsenic and rich in lead and silicon,

ii. leaching the first leached sludge wherein said first leached sludge is processed with a first solution of a carboxylic acid salt, in order to obtain a second leached sludge deficient of lead and a second leaching solution rich in lead,

iii. precipitation wherein a first base is added to the second leaching solution rich in lead in order to obtain a first lead concentrate, and a first precipitation solution deficient of lead,

iv. alkaline leaching of the second leached sludge, wherein a second base is added in order to form an alkaline leaching solution, in order to obtain a third leached sludge having a content reduced in silicon, and a third leaching solution rich in silicon, and optionally arsenic,

v. hydrochloric leaching of the third leached sludge, wherein an acid solution is used in chloride environment, in order to obtain a fourth leached sludge for final disposition and a fourth leaching solution rich in copper, lead and iron, and optionally arsenic,

vi. metal precipitation from the fourth leaching solution rich in copper, lead and iron, and optionally arsenic with a neutralizing slurry, in order to produce a fifth solution rich in chloride and a first precipitate solid rich in iron, copper and lead, and optionally arsenic, and

vii. leaching the first precipitate solid rich in iron, copper and iron, and optionally arsenic with a sulfuric acid solution, in order to produce a sixth leaching solution rich in copper, iron and optionally arsenic, and a second lead concentrate.

Date reçue/ date received 2022-01-27

2. The procedure according to claim 1, characterized in that, the metallurgical residue to be processed is powder obtained by a metal smelting process.

3. The procedure according to claim 1, characterized in that, said powder obtained by a copper smelting process is smelting powder.

4. The procedure according to claim 1, characterized in that, the metallurgical residue has been subjected to a copper leaching process.

5. The procedure according to claim 4, characterized in that, said metallurgical residue has been subjected to leaching with H_2SO_4.

6. The procedure according to any one of claims 1 to 3, characterized in that, the metallurgical residue to be processed comprises the mineral species anglesite, covelline, cuprospinel in the form of $CuOFe_2O_3$, zinc spinels in the form of $ZnOFe_2O_3$, magnetite, iron oxide(III), pirite, scorodite, mucovite, kaolinite and lead sulphate(II).

7. The procedure according to claim 6, characterized in that, the copper contained in the metallurgical residue is present as copper sulphate, calcosine, covelline and cuprospinel in the form of $CuOFe_2O_3$.

8. The procedure according to any one of claims 1 to 7, characterized in that, the silicon contained in the metallurgical residue is present as muscovite and kaolinite.

9. The procedure according to any one of claims 1 to 7, characterized in that, the lead contained in the metallurgical residue is present as lead sulphate(II), galena or lead oxide(II).

10. The procedure according to claim 9, characterized in that at least 95% of the lead is found as lead sulphate(II).

11. The procedure according to any one of claims 1 to 10, characterized in that, the first H_2SO_4 solution may comprise H_2SO_4 and/or a refinery effluent.

12. The procedure according to any one of claims 1 to 11, characterized in that, step (i) is performed at a H_2SO_4 concentration of between 150 and 300 g/L.

13. The procedure according to any one of claims 1 to 12, characterized in that, step (i) is performed at a temperature of between 50 and 130ºC.

Date reçue/ date received 2022-01-27

14. The procedure according to any one of claims 1 to 13, characterized in that, step (i) is performed for a period of between 3 and 12 hours.

15. The procedure according to any one of claims 1 to 14, characterized in that, step (i) is performed at a solid concentration of between 5 and 20% w/w.

16. The procedure according to any one of claims 1 to 15, characterized in that, in step (ii) of leaching, the carboxylic acid salt is sodium citrate.

17. The procedure according to any one of claims 1 to 16, characterized in that, in step (ii) the sodium citrate solution has a molar concentration of sodium citrate between 0.5 and 1 M.

18. The procedure according to any one of claims 1 to 17, characterized in that, in step (ii) the first leached sludge is fed to the sodium citrate solution in a mass ratio of 1:9.

19. The procedure according to any one of claims 1 to 18, characterized in that, step (ii) is performed at a temperature of between 20 and 60ºC.

20. The procedure according to any one of claims 1 to 19, characterized in that, step (ii) is performed for a residence time of between 1 and 23 h.

21. The procedure according to any one of claims 1 to 20, characterized in that, step (ii) is performed at a pH of between 5.3 and 8.8.

22. The procedure according to any one of claims 1 to 21, characterized in that, in step (ii) a citric acid is added in order to adjust the pH.

23. The procedure according to any one of claims 1 to 22, characterized in that, the pH adjustment in step (ii) is performed with a citric acid solution of 600 and 900 g/L.

24. The procedure according to any one of claims 1 to 23, characterized in that, the first base added to step (ii) is a carbonate salt, selected from sodium carbonate, sodium bicarbonate or magnesium carbonate.

25. The procedure according to claim 24, characterized in that, the first base added to step (ii) is sodium carbonate.

Date reçue/ date received 2022-01-27

26. The procedure according to claim 25, characterized in that, the sodium carbonate added to step (ii) is performed in stoichiometric ratio 1:1 regarding the lead concentration in the third leaching solution.

27. The procedure according to any one of claims 1 to 26, characterized in that, in step (iii) the precipitation reaction is performed at a temperature of between 20 and 90ºC.

28. The procedure according to any one of claims 1 to 27, characterized in that, in step (iii) the precipitation reaction is performed for 0.5 to 1 hour.

29. The procedure according to any one of claims 1 to 28, characterized in that, in step (iii) the precipitation reaction is performed at a pH of between 6 and 9.

30. The procedure according to claim 29, characterized in that, in step (iii) the pH adjustment is performed with a neutralizer such as sodium hydroxide.

31. The procedure according to any one of claims 1 to 30, characterized in that, the first precipitation solution of step (iii) is recirculated to step (ii) in order to leach the first leached sludge of step (i).

32. The procedure according to any one of claims 1 to 30, characterized in that, a part of the first lead concentrate is recirculated to step (iii) in order to act as seed.

33. The procedure according to claim 31, characterized in that, the part of the first lead concentrate recirculated corresponds to a 30% of the total of said first precipitated solid.

34. The procedure according to any one of claims 1 to 33, characterized in that, the recycling ratio of the first precipitation solution deficient of lead to step (iii) is of 90%.

35. The procedure according to claim 34, characterized in that, the first precipitation solution deficient of lead recirculated to step (ii) requires the addition of an additional contribution of sodium citrate.

36. The procedure according to claim 35, characterized in that, the additional contribution of sodium citrate in a mass ratio of 0.35:1 regarding water used for preparing said solution and is adjusted for the solid content of the pulp to be 10% w/w regarding the amount of second leached sludge.

Date reçue/ date received 2022-01-27

37. The procedure according to any one of claims 35 to 36, characterized in that, the first precipitation solution deficient of lead recirculated to step (ii) requires a pH adjustment to 7.0.

38. The procedure according to claim 37, characterized in that, the pH adjustment in step (ii) is performed with a citric acid solution of 600 to 900 g/L.

39. The procedure according to any one of claims 35 to 37, characterized in that, the first precipitation solution deficient of lead obtained from step (ii) does not require a step for removing the sodium sulphate.

40. The procedure according to any one of claims 1 to 39, characterized in that, the first lead concentrate is lead carbonate.

41. The procedure according to any one of claims 1 to 40, characterized in that, the second base used in the leaching of step (iv) is selected between $Mg(OH)_2$, KOH or NaOH.

42. The procedure according to any one of claims 1 to 41, characterized in that, the second base added in step (iv) is added at a ratio of between 5 and 10% w/w regarding the total mass of alkaline leaching solution.

43. The procedure according to claim 42, characterized in that, the second base added in step (iv) is added at a ratio of 6.0% w/w regarding the total mass of alkaline leaching solution.

44. The procedure according to any one of claims 1 to 43, characterized in that, the leaching reaction of step (iv) is performed at a temperature of between 90 and 140ºC.

45. The procedure according to any one of claims 1 to 44, characterized in that, the leaching reaction of step (iv) is performed for a residence time of between 1 and 6 hours.

46. The procedure according to any one of claims 1 to 45, characterized in that, the acid used in the leaching of step (v) is HCl.

47. The procedure according to claim 46, characterized in that, in step (v) the HCl is provided in a concentration varying from 50 to 140 g/L.

Date reçue/ date received 2022-01-27

48. The procedure according to any one of claims 1 to 47, characterized in that, in step (v) the chloride environment is increased by the addition of chloride salt.

49. The procedure according to claim 48, characterized in that, in step (v) the chloride environment is increased by the addition of magnesium chloride.

50. The procedure according to any one of claims 48 to 49, characterized in that, in step (v) the chloride is provided in a concentration between 140 and 240 g/L.

51. The procedure according to any one of claims 1 to 50, characterized in that, step (v) is performed at a pH of between -1.5 and -0.25, preferably within the range of -0.75 and -0.65.

52. The procedure according to any one of claims 1 to 51, characterized in that, step (v) is performed at a temperature of between 40 and 95°C.

53. The procedure according to any one of claims 1 to 52, characterized in that, the neutralizing slurry of step (vi) of metal precipitation is selected from among calcium hydroxide, calcium oxide, calcium carbonate, lime, dolomitic lime, magnesium carbonate, magnesium hydroxide or magnesium oxide.

54. The procedure according to any one of claims 1 to 53, characterized in that, step (vi) is performed at a temperature of between 50 and 95°C.

55. The procedure according to any one of claims 1 to 53, characterized in that, the neutralizing slurry added in step (vi) is provided until reaching a pH between 3 and 7.

56. The procedure according to any one of claims 1 to 55, characterized in that, step (vi) has a residence time of between 0.5 and 3 hours.

57. The procedure according to any one of claims 1 to 56, characterized in that, the fifth solution rich in chloride of step (vi) is sent to a crystallization process of magnesium chloride.

58. The procedure according to any one of claims 1 to 57, characterized in that, the fifth solution rich in chloride of step (vi) is recirculated to the fourth step of silver precipitation.

Date reçue/ date received 2022-01-27

59. The procedure according to any one of claims 1 to 58, characterized in that, the sulfuric acid solution of step (vii) has a sulfuric acid concentration of between 60 and 275 g/L.

60. The procedure according to any one of claims 1 to 59, characterized in that, the sulfuric acid solution of step (vii) is the first leaching solution rich in copper and iron, and optionally arsenic and bismuth of step (i) to which acidity has been adjusted to between 60 and 275 g/L.

61. The procedure according to any one of claims 1 to 60, characterized in that, the sulfuric acid solution of step (vii) is a sulfuric leaching solution of smelting powders.

62. The procedure according to any one of claims 1 to 61, characterized in that, the sulfuric acid solution of step (vii) is the first leaching solution rich in copper and iron, and optionally arsenic and bismuth of step (i).

63. The procedure according to any one of claims 1 to 62, characterized in that, the step (vii) of leaching the first precipitate solid rich in iron, copper and lead, and optionally arsenic, is performed at a temperature of between 50 and 95°C.

64. The procedure according to any one of claims 1 to 63, characterized in that, the second lead concentrate is recirculated to step (ii).

65. The procedure according to any one of claims 1 to 64, characterized in that, the first leaching solution rich in copper is sent to a copper leaching process of smelting powders.

66. The procedure according to any one of claims 1 to 65, characterized in that, the first leaching solution rich in copper is sent to an arsenic abatement process.

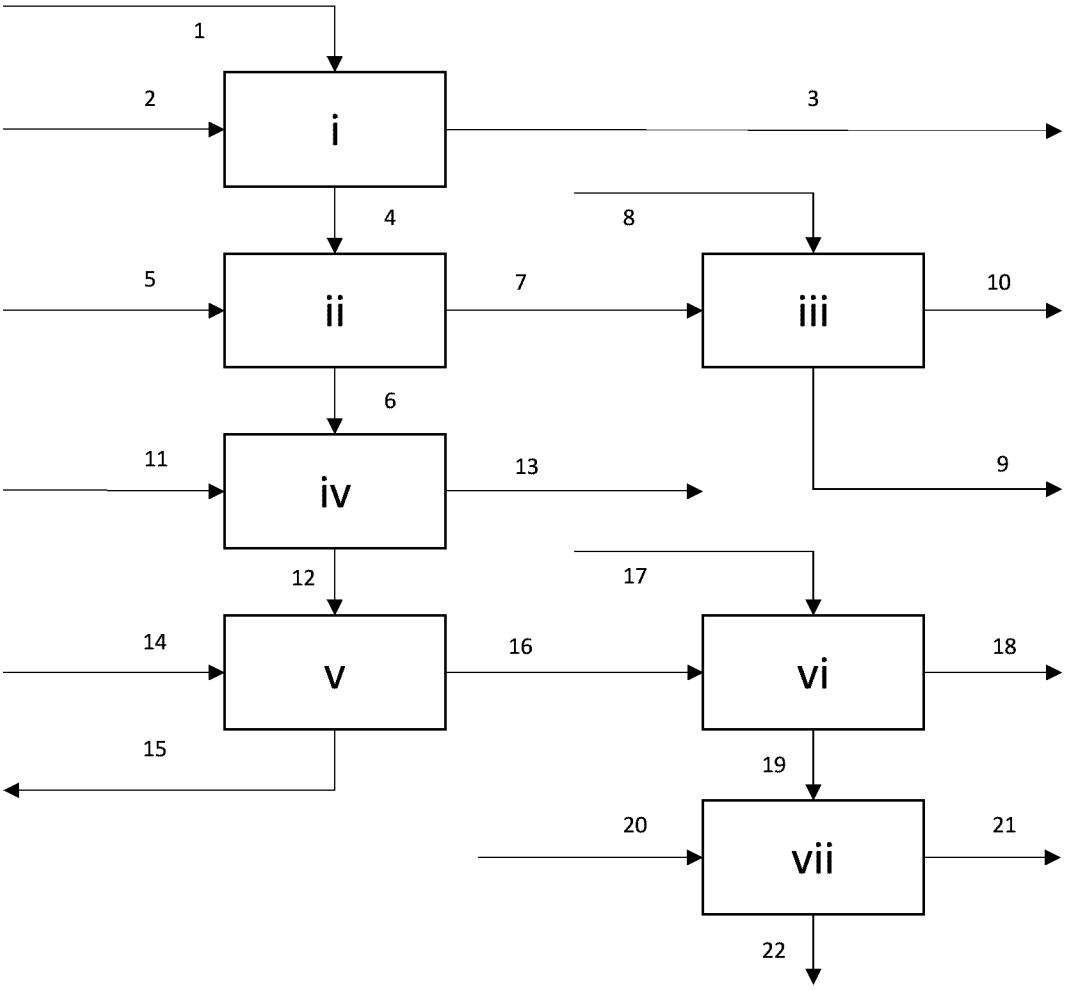
67. The procedure according to any one of claims 1 to 66, characterized in that, the arsenic abatement process is selected from those contemplating the ferric arsenate production.

68. The procedure according to claim 67, characterized in that, the arsenic abatement process is a scorodite production process.

Date reçue/ date received 2022-01-27

Sheet 1/3

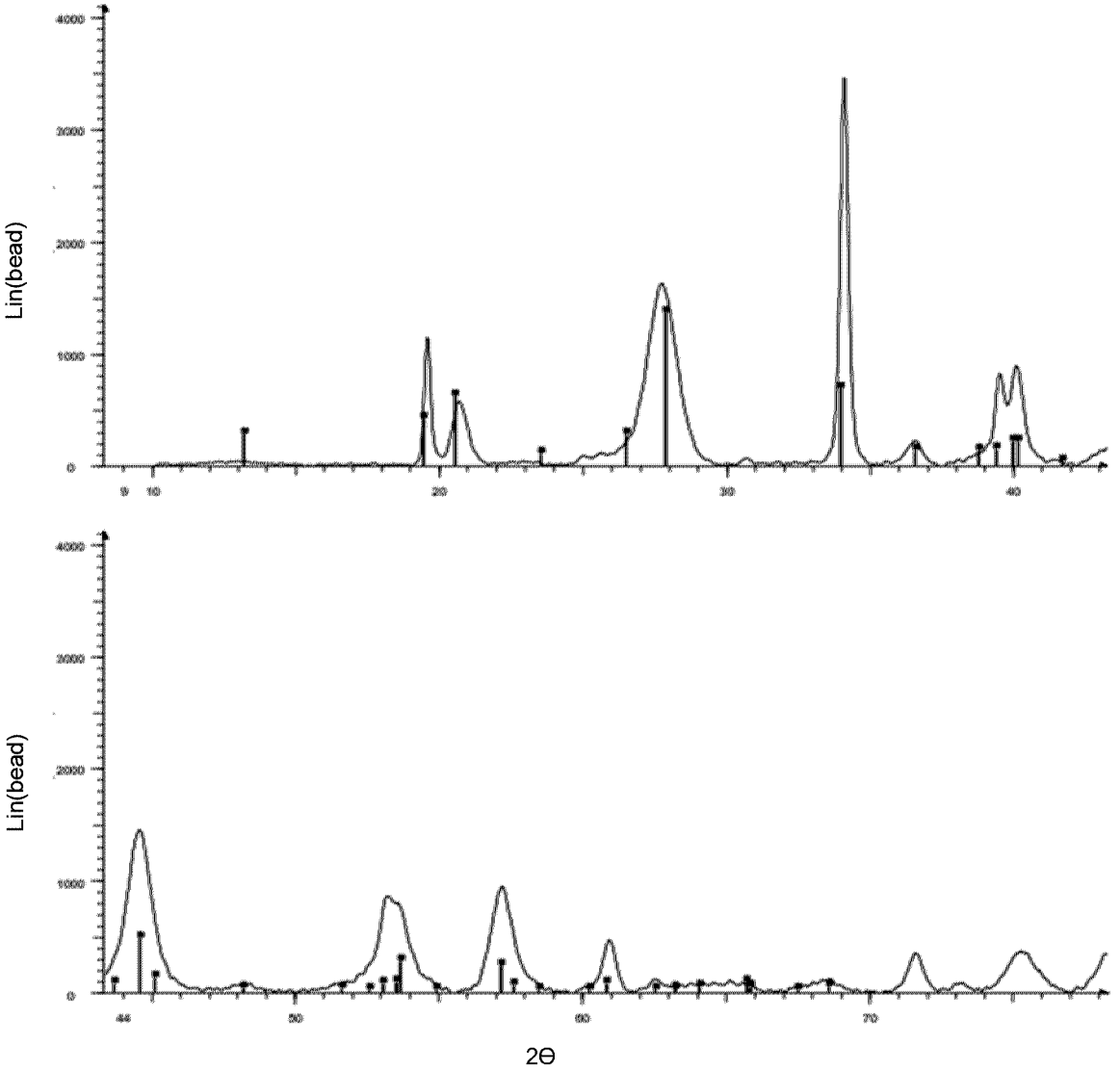
Figure I



Date reçue/ date received 2022-01-27

Sheet 2/3

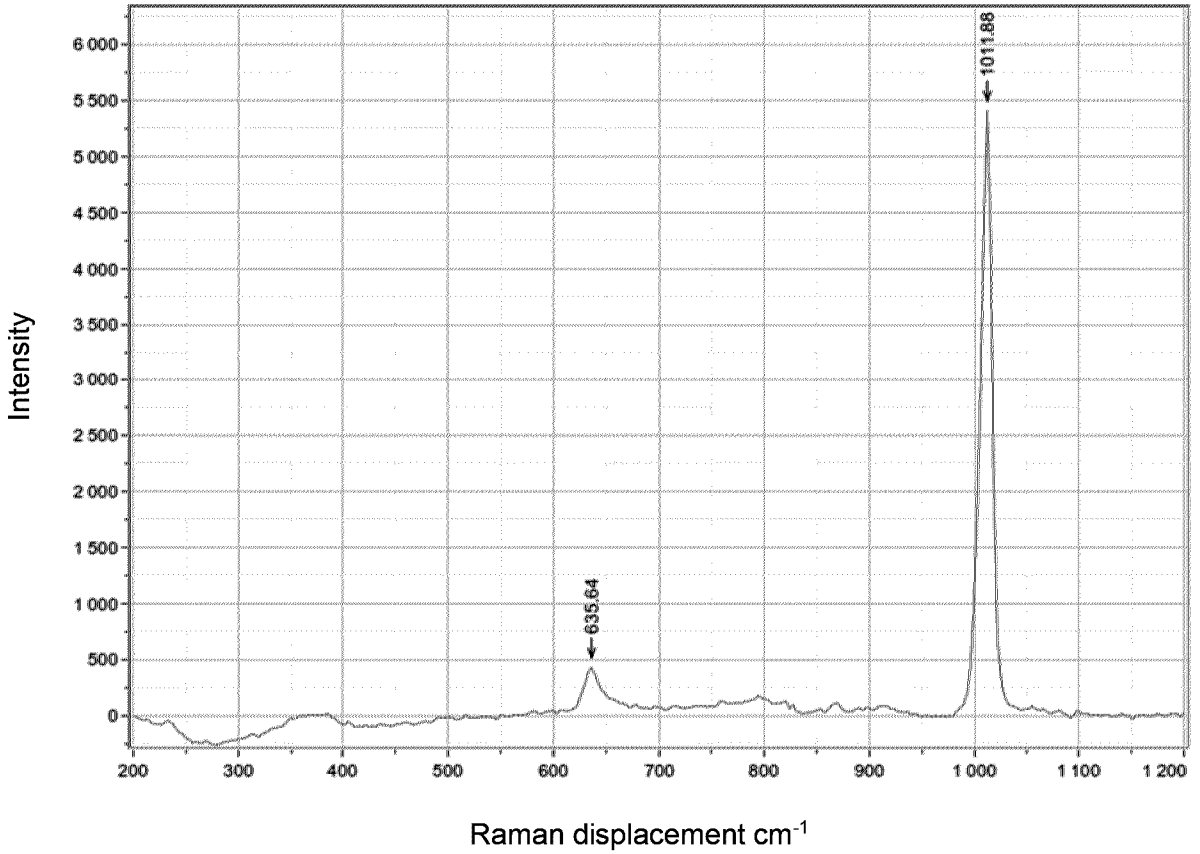
Figure II



Date reçue/ date received 2022-01-27

Sheet 3/3

Figure III



Date reçue/ date received 2022-01-27