



(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: 2022/01/27

(85) Entrée phase nationale/National Entry: 2021/12/20

(86) N° demande PCT/PCT Application No.: IB 2020/056895

(87) N° publication PCT/PCT Publication No.: 2022/018490

(51) Cl.Int./Int.Cl. *C22B 7/00* (2006.01),
C22B 3/04 (2006.01), *C22B 3/42* (2006.01),
C22B 41/00 (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 POUR LA PRODUCTION D'UN CONCENTRE DE GERMANIUM DE RESIDUS
METALLURGIQUES

(54) Title: PROCEDURE FOR PRODUCING GERMANIUM CONCENTRATE FROM METALLURGICAL RESIDUES

(57) Abrégé/Abstract:

Procedure for producing germanium concentrate from metallurgical residues, 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, silicon, and germanium, (ii) leaching the first leached sludge wherein said first leached sludge is processed with a first solution of sodium citrate, in order to obtain a second leached sludge deficient of lead and a second leaching solution rich in lead, (iii) alkaline leaching of the second leached sludge, wherein a 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 germanium and a third leaching solution rich in germanium and silicon, and optionally arsenic, (iv) charging in an ion exchange column, wherein the germanium is captured by the resin, in order to obtain a fourth alkaline solution deficient of germanium and rich in silicon, (v) washing the ion exchange column, wherein a fifth solution of column charge wash is obtained, (vi) eluting the ion exchange column with an HCl solution, in order to obtain a sixth elution solution rich in germanium, (vii) distillation, wherein the sixth elution solution rich in germanium is distilled in order to obtain a seventh solution of germanium and an eighth solution deficient in germanium and (viii) hydrolysis, wherein the seventh solution of germanium is contacted with a solution of water to produce a first germanium dioxide concentrate.



TITLE OF THE INVENTION

Procedure for producing germanium concentrate from metallurgical residues.

ABSTRACT

Procedure for producing germanium concentrate from metallurgical residues, 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, silicon, and germanium, (ii) leaching the first leached sludge wherein said first leached sludge is processed with a first solution of sodium citrate, in order to obtain a second leached sludge deficient of lead and a second leaching solution rich in lead, (iii) alkaline leaching of the second leached sludge, wherein a 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 germanium and a third leaching solution rich in germanium and silicon, and optionally arsenic, (iv) charging in an ion exchange column, wherein the germanium is captured by the resin, in order to obtain a fourth alkaline solution deficient of germanium and rich in silicon, (v) washing the ion exchange column, wherein a fifth solution of column charge wash is obtained, (vi) eluting the ion exchange column with an HCl solution, in order to obtain a sixth elution solution rich in germanium, (vii) distillation, wherein the sixth elution solution rich in germanium is distilled in order to obtain a seventh solution of germanium and an eighth solution deficient in germanium and (viii) hydrolysis, wherein the seventh solution of germanium is contacted with a solution of water to produce a first germanium dioxide concentrate.

TITLE OF THE INVENTION

Procedure for producing germanium concentrate from metallurgical residues

FIELD OF THE INVENTION

5 The invention relates to a procedure for producing germanium concentrate from metallurgical residues, in particular, from residues containing copper, iron, lead, and germanium, and which can optionally contain elements such as arsenic, antimony, and bismuth.

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.

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

In a broad aspect, the germanium concentrate may be understood as a germanium-rich liquid fraction, consisting mainly in germanium tetrachloride, or in a solid germanium concentrate
15 which, in a more specific aspect may relate to germanium dioxide.

In the present disclosure, any metallurgical residue which has been subjected to prior leaching processes shall be considered as sludge.

State of the art

Copper leaching

20 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 zinc, copper and
25 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 has elapsed in

sulfuric media, reaches copper leaching yields above 90% for the range of temperatures between 85 and 90°C.

Lead leaching

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, PbO₂ and PbSO₄. 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 and 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 PbSO₄ 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 Pb²⁺, 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 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
5 obtained from acid and lead batteries. Within the pH range of 5.2 to 5.5 the presence of trihydrate lead citrate ($[\text{Pb}_3(\text{C}_6\text{H}_5\text{O}_7)_2] \cdot [3\text{H}_2\text{O}]$) 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 PbO₂, 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
10 60 min reaction, reaching leaching efficiencies higher than 99% by weight, obtaining $\text{Pb}(\text{C}_6\text{H}_5\text{O}_7) \cdot \text{H}_2\text{O}$ 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
15 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 desulphurization 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.

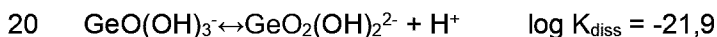
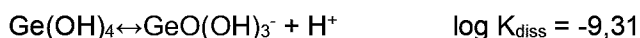
20 Technology based on lead recovery from lead waste using citric acid has been developed by Cambridge Enterprise Limited (WO2008056125A1). This technology basically comprises treating lead residues comprising lead oxide (II), lead oxide (IV) and lead sulphate with a citric acid solution, and which can 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
25 environment as reducing agent in order to accelerate the lead oxide (IV) leaching reaction so as to produce lead citrate (Sonmez and Kumar, *Hydrometallurgy* 95, no. 1-2 (2009), 82-86.).

The present invention differs from application (WO2008056125A1) in that 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
30 with sodium carbonate, so as to again leach output metallurgical residue from the sulfuric leaching step.

Germanium leaching

Germanium is a metal which is widely used in the field of optical fiber, infrared fiber, photovoltaic cells, and aeronautic, aerospace and military industry, among others. In general, germanium is not abundant in the Earth's crust, since it constitutes between 1 – 7 ppm of Earth's crust, with a total estimated amount of 8600 tons. Germanium is usually associated with copper, lead, zinc, and carbon deposits, whereas deposits with an elevated content of germanium are limited. Most of the germanium is recovered from vapors of lignite subjected to pyrometallurgical processes, and from lead-zinc mineral smelting. However, pyrometallurgical processes have lost importance every time they generate environmental issues associated with germanium (II) oxide and germanium sulphide volatility.

There are various methods for the recovery of germanium from electrolytic solutions of zinc, from which tannin precipitation, germanium tetrachloride distillation, flotation, activated carbon adsorption, precipitation, solvent extraction and chelating resin adsorption stand out (US 455332). Germanium is usually present in the form of germanic acid $\text{Ge}(\text{OH})_4$, the most predominant species being within the pH range of pH 1 to 8, whereas between pH 9 to 13 the most predominant species is $\text{GeO}(\text{OH})_3^{1-}$ and at pH greater than 13, the dominant species is $\text{GeO}_2(\text{OH})_2^{2-}$. The first dissociation constant of germanic acid is 4,9-10 mol.L⁻¹ ($\log K_{\text{diss}} = -9,31$) (Wood and Iain, *Ore Geology Reviews* 28, no. 1 (2006): 57-102.).



Acid leaching

Germanium may be leached using H_2SO_4 , at temperatures of between 40 and 60°C, at a H_2SO_4 concentration of 100 g/L for a period of 30 min and with a solid:liquid ratio of 1:4, recovering 78% germanium. At higher temperatures, in the order of 85°C, and at a H_2SO_4 concentration of 150 g/L and a residence time of 1 h, collective leaching of different metals is produced, wherein the extraction of germanium was of 92.7% (Rutledge et al., *Metals* 5, no. 3 (2015): 1520-1542.).

Patent application CN108486390A describes a process for separating germanium and gallium from a germanium- and gallium-containing material. In a first step, the germanium and gallium material is added to a solution of 50 to 150 g/L H_2SO_4 at a ratio of 5 to 10% w/w, and subsequently adjusted to a pH between 1 and 3. The leaching solution is neutralized at pH 1 to 3, for the subsequent addition of zinc powder to the neutralized liquid at a temperature of 40-80°C, in order to obtain germanium concentrates and a liquid solution. To this liquid solution

is again added zinc powder at a temperature of 40-80°C, in order to obtain gallium residues and a liquid solution

Alkaline leaching

Patent application CN108300876A describes a method for leaching gallium and germanium from slags of processes for obtaining zinc. In a first step, the slag is milled to a size of 50-100 microns, then 0.1-1 mol/L H_2SO_4 solution is added in a liquid-solid ratio of 4-10: 1 mL/g, at a leaching temperature of 25-80°C, stirring at 100-600 rpm for 0.25-4 h. Then the liquid-solid separation is carried out to obtain leaching residues with H_2SO_4 to which a solution of 0.2-2 mol/L hydrogen peroxide is added at a liquid-solid ratio of 4-10: 1 mL/g, adding 0.1-1 mol / L NaOH to adjust the pH of the leaching solution to 5.0 - 8.0. This alkaline leaching is carried out at 25-80°C, stirring at 100-600 rpm for 0.25-4 h, in order to obtain a germanium-rich leaching solution. In the case of the present invention, in order to be able to leach germanium values, the sulfuric leaching and citric leaching steps are necessary in order to remove the elevated levels of lead in the metallurgical residue and thus increase the content of germanium in the residue due to the loss of metallurgical residue mass in the citric leaching step. Further, the presence of lead in the metallurgical residue by generating a process such as the one of the application would result in a greater consumption of soda, due to the conversion of lead sulfate into lead hydroxide, which would affect germanium leaching yield.

Ion exchange

Subsequent to the leaching step, the obtained germanium must be concentrated by different alternatives such as solvent extraction, precipitation with chelating agents or ion exchange. For the present invention, the ion exchange step has been considered every time since it is the one with better recovery levels and it also allows increasing the germanium concentration ratio vs. other metals present in the leaching solution such as lead, aluminum, silicon and arsenic.

Patent US4525332 describes the adsorption of germanium-containing solutions in ion exchange resins consisting of a polymer having functional groups selected from secondary, tertiary and quaternary ammonium groups, which have a relative selectivity of germanium to antimony of 50:1, followed by an elution of germanium collected by the resin in an aqueous medium. The present invention makes use of a resin containing N-methylglucamines as functional group. Patent US4525332 does not specify that the charge solution may contain silicon. In the application examples of patent US4525332, the charge is carried out with acid or slightly acid solutions, and not with alkaline solutions, as shown by the present invention. By being an element belonging to the same group as germanium, silicon may interfere when recirculating

charge solutions used within the process. In the same way, the elution of the resin used in the examples of patent US4525332 is carried out with H₂SO₄ or sodium hydroxide, depending of the resin used, in contrast with the elution with HCl which is carried out herein, and which is necessary for the subsequent step of germanium tetrachloride distillation. Further, the present invention differs from patent US4525332 in that the latter does not teach how to remove silicon from alkaline solutions in order to recirculate the solution as a leaching medium of metallurgical residues to obtain germanium.

Patent application GB933563A teaches the processing of aqueous, neutral or slightly acid solutions of germanium in ion exchange resins containing hydroxy phenyl groups in which germanium is collected, for it to be later eluted with hydrochloric solutions on 7 N for it to be later distilled and the germanium tetrachloride hydrolyzed to produce germanium dioxide. Patent application GB933563A does not teach how to carry out the charge of strongly alkaline solutions with the presence of silicon. Since there is silicon present in solution, the neutralization of the solution in order to carry out the charge of germanium in the resin is not obvious, since when lowering the pH the silicon would precipitate and drag the germanium. In this scenario, it is necessary to carry out the charge without the prior precipitation and remove the silicon once the solution has passed through the column and is deficient of germanium. In addition, unlike patent application GB933563, in this invention the elution may be carried out with solutions with Ge concentrations of less than 6 N with no evidences of considerable loss of germanium.

Germanium distillation

Powell et al. J. Appl. Chem. 1951, 541-551, teaches the leaching of smelting powders with HCl, in order to generate germanium tetrachloride in situ which could be distilled at a temperature of 84°C. One of the problems of this method is the presence of arsenic trichloride because, even though it boils at 130°C, its vapor pressure at 84°C is high enough so as to co-distill with germanium tetrachloride. In this sense the present invention differs from the teachings of Powell in the sense that there is a series of prior leaching steps and ion exchange separation which prevent elements such as arsenic to be present in elevated concentrations which interfere with germanium distillation.

Patent US3102786 teaches a continuous process for purifying germanium tetrachloride using an HCl solution with a minimum concentration of 6 N, and keeping the column at a temperature of between 83 and 110°C. The present invention differs from US3102786 in that the distillation may be carried out at acid concentrations of less than 6 N, allowing to distill germanium in an effective way with distillation rates over 95%.

Patent US2811418 teaches a process for purifying germanium tetrachloride, using an HCL solution, of 12 N concentration, and saturated with chlorine gas, allowing the mixture to separate in two phases, wherein the heavier phase contains purified germanium tetrachloride. The present invention differs from US2811418 in that the distillation may be carried out at acid concentrations lower than 12 N, in particular lower than 5 N, allowing to distill germanium in an effective way with distillation rates over 95%, minimizing arsenic drags.

Germanium hydrolysis

Patent US3455645 discloses a process for the production of amorphous germanium dioxide, characterized in that it precipitates germanium present in the aqueous solution wherein the pH is at least 5 and at most 9. In particular, the experiments disclosed by US3455645 teach about the addition of germanium tetrachloride to a solution containing 10 parts NaOH by 90 parts water up to a pH lower than 8, or preferably lower than 6. Patent US3455645 differs from the present invention in that the distillation solutions obtained are sent directly to a cooling reactor wherein germanium dioxide precipitation is verified, with no need of controlling the pH at the values stated by US3455645.

James E. Hoffmann in Extracting and Refining Germanium, *Journal of Metals*, June 1987, 42-45, states that at HCl concentrations of less than 5.5, germanium is mainly found as germanic acid, and that 3 grams of water are enough to hydrolyze 1 g germanium with a yield of 95%. In addition, it states that it is preferable for the precipitation to be carried out at a temperature close to 0°C, and that it is possible to use germanium dioxide to act as center of nucleation of germanium precipitation. The present invention shows that it is possible to obtain elevated germanium precipitation yields with no need to use germanium dioxide as a seed to verify germanium precipitation. The present invention proves that by using sufficiently concentrated solutions of germanium it is possible to precipitate germanium dioxide, and that low HCl concentrations negatively affect germanium dioxide precipitation process compared to HCl concentrations close to 3.7 N (135 g/L HCl).

Description of the figures

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

Figure II shows the distillation curve of germanium from ionic exchange solutions.

Figure III shows the second distillation curve of germanium from primary distillation solutions. Second distillation refers to a distillate solution which has been collected following a first distillation cycle.

Figure IV shows the third distillation curve of germanium from secondary distillation solutions. Third distillation refers to a distillate solution which has been collected following a second distillation cycle.

Description of the invention

5 In a broad sense, the invention describes a procedure for the production of germanium from metallurgical residues.

In one preferred option, the invention describes a procedure for the production of germanium tetrachloride.

10 In a still more preferred option, the invention describes a procedure for the production of a solid-state germanium concentrate.

In a still more preferred option, the invention describes a procedure for producing technical-grade germanium dioxide, with a concentration ranging from 60 and 70%.

15 In one broad aspect, the invention describes a procedure for producing germanium concentrate from metallurgical residues, in particular, from residues containing copper, iron, lead, silicon, and germanium, and which can optionally contain elements such as arsenic, antimony and bismuth, characterized in that it comprises:

20 a step (i) of copper leaching with a first acid solution (2) of the metallurgical residue (1), 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, silicon and germanium (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),

25 a step (iii) of alkaline leaching of the second leached sludge, wherein a base (8) 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 germanium (9), and a third leaching solution rich in germanium and silicon, and optionally arsenic (10),

30 a step (iv) of charging the third leaching solution rich in germanium and silicon (10), and optionally arsenic in an ion exchange column, wherein the germanium is captured by the resin, in order to obtain a fourth alkaline solution deficient of germanium and rich in silicon (11),

a step (v) of washing the ion exchange column, which is carried out with water (12), wherein a fifth solution of column charge wash (13) is obtained,

a step (vi) of eluting the ion exchange column, which is carried out with an HCl solution (14), in order to obtain a sixth elution solution rich in germanium (15),

- 5 a step (vii) of distillation, wherein the sixth elution solution rich in germanium (15) is distilled in order to obtain a seventh solution of germanium (16) and an eighth solution deficient in germanium (17), and

- a step (viii) of hydrolysis, wherein the seventh solution of germanium (16) is contacted with a solution of water (18) to produce a first germanium dioxide concentrate (19) and a ninth solution deficient of germanium (20).
10

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

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

- 15 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, covellite, cuprospinel in the form of $CuOFe_2O_3$, zinc spinels in the form of $ZnOFe_2O_3$, magnetite, iron oxide (III), pyrite, scorodite, muscovite, kaolinite and lead sulphate (II).
20

In an even more preferred option, the copper contained in the metallurgical residue is present as copper sulphate, calcosine, covellite 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 $CuOFe_2O_3$.

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

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 H_2SO_4 solution of step (i) 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.

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

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.

- 10 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.

- 15 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 60°C, more preferably at 40°C.

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

- 20 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 corresponding acid of 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.

- 25 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.

In one preferred option, step (iii) is a germanium leaching step.

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

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

- 5 In one preferred option, the leaching reaction of step (iii) is performed at a temperature of between 70 and 150°C, more preferably at a temperature of 130°C.

In one preferred option, the leaching reaction of step (iii) 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, step (iv) is performed with a resin with a nitrogen atom group (*N-donor group*).

- 10 In one preferred option, step (iv) is performed charging the third leaching solution rich in germanium and silicon at a ratio of between 2 and 3 bed volumes.

In an even more preferred option, step (iv) is performed charging the third leaching solution rich in germanium and silicon at a ratio of 10 bed volumes.

- 15 In one preferred option, step (v) is performed charging the fourth solution of charge wash at a ratio of between 5 and 15 bed volumes.

In one preferred option, step (vi) of elution is performed with a HCl solution.

In an even more preferred option, step (vi) of elution is performed with an HCl solution at a concentration of between 2 and 8 N, more preferably 6 N.

- 20 In one preferred option, step (vi) is performed by charging the HCl solution at a ratio of between 1 and 5 bed volumes, more preferably at a ratio of 3 bed volumes.

In another preferred option, the fourth alkaline solution deficient of germanium is subjected to a silicon removal process.

In another preferred option, in said silicon removal process, slaked lime or aluminum sulphate is added.

- 25 In an even more preferred option, in said silicon removal process, slaked lime is added.

In an even more preferred option, slaked lime is added at a molar ratio of 1:1 with respect to the silicon contained in the fourth alkaline solution deficient of germanium, in order to generate a regenerated alkaline solution and a solid consisting of calcium silicate.

In another preferred option, the silicon removal step is performed at a temperature of between 20 and 90°C.

In an even more preferred option, the regenerated alkaline solution is recirculated to step (iii) of alkaline leaching.

- 5 In another preferred option, step (vii) of distillation is performed at a temperature of between 86.5°C and 107°C, and at a bulb temperature of between 86.5 and 108°C.

In another preferred option, the seventh germanium solution is redistilled between 1 to 5 times in order to produce a concentrated germanium solution and a distilled HCl solution.

- 10 In an even more preferred option, the seventh germanium solution is redistilled 3 times in order to produce a concentrated germanium solution and a distilled HCl solution.

In one preferred option, the distilled HCl solution is recirculated at a previous distillation step with the purpose of increasing HCl concentration at the entry to the distiller.

- 15 In another preferred option, the concentrated germanium solution is contacted with deionized water at a volumetric ratio of between 1:1 and 1:6 to precipitate germanium as a germanium concentrate.

In an even more preferred option, said germanium concentrate is germanium dioxide.

In an even more preferred option, the concentrated germanium solution that is contacted with deionized water in step (viii) is performed at a temperature of between 2 and 15°C.

- 20 In another preferred option, the concentrated germanium solution sent to the hydrolysis step has a germanium concentration between 8.1 and 24.8 g/L.

In another preferred option, the concentrated germanium solution sent to the hydrolysis step has a HCl concentration between 55 and 135 g/L.

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

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

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

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 no case should they be considered as limiting thereof, since different adaptations which may be performed thereto shall be covered within the subject matter claimed by this invention.

Sulfuric leaching

Examples 1 to 7

Between 2.550 and 2.850 g of a sulfuric acid solution with a concentration of between 150 and 250 g/L of H_2SO_4 were prepared, which were arranged in a 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 ₂ S	%	0.63
CuS	%	4.02
CuO	%	0.71
CuOFe ₂ O ₃	%	15.09
ZnOFe ₂ O ₃	%	4.46
ZnS	%	2.94
Fe ₃ O ₄	%	4.74
Fe ₂ O ₃	%	4.91
FeS ₂	%	6.32
Ag ₂ S	%	0.1
FeAsO ₄ *2H ₂ O	%	5.18
Bi ₂ O ₃	%	0.59
Sb ₂ O ₃	%	0.5
KAl ₃ Si ₃ O ₁₀ (OH) ₂	%	7.01
Al ₂ Si ₂ O ₃ (OH) ₄	%	2.92
Ge	g/ton	548

Table 2. Cu leaching results examples 1 to 7

Variable/Example	Unit	1	2	3	4	5	6	7
H ₂ SO 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

- 5 2,550 g of a 250 g/L H₂SO₄ solution were prepared, which were arranged in a 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.

10

Table 3. Cu 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 H₂SO₄ concentration was adjusted to 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 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%.

20

Table 4. Refinery effluent composition

Elements	Unit	Value
H ₂ SO ₄	g/L	35.73
Cu	g/L	11.37
Fe	g/L	0.10

Elements	Unit	Value
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

- 5 A solution was prepared with 40 L of distilled 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%.

10 Examples 13 to 19

- 15 A solution was prepared with 2 L of distilled 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 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

Variable/Example	Unit	13	14	15	16	17	18	19
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
Flock 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

Alkaline leaching

Examples 20 to 28

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 copper and lead 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 to 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 a Büchner system. Results are shown in Table 6.

10

Table 6. Results examples 20 to 28

Variable/Example	Unit	20	18	22	23	24	25	26	27	28
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										
Ge	%	78.2	86.4	81.1	84.2	86.0	85.5	77.8	83.7	83.0
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 29 and 30

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

15

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 a Büchner system.

Table 7. Results examples 29 and 30

Variable/Example	Unit	29	30
Residence time	h	1	6
Leaching yield			
Ge	%	78.1	82.0
Si	%	63.2	63.0

5

Ion exchange

Examples 31 to 38

12,500 mL of a solution derived from alkaline leaching of sludge were taken, with concentrations of 28 to 34 mg/L of Ge and 7.2 to 8.6 g/L of Si, and were passed in an ion exchange column with 400 mL resin with a nitrogen atom group. The charge flow was 67 mL/min to 133 mL/min at a rate of 3.4 to 6.7 cm/min. The column was washed with 2000 mL water, with no germanium elution observed in any of the experiments. Germanium elution was performed with HCl at a rate of 99 g/L passing between 1 and 2 bed volumes. The elution flow was between 20 and 67 mL/min at a rate of between 1 and 3.4 cm/min. Lastly, the column was washed with 2000 mL water, with no Ge drag observed in any of the experiments. Results are shown in Table 8.

15

Table 8. Results experiments 31 to 38

Example/Variable	Unit	31	32	33	34	35	36	37	38
Resin		IRA743	IRA67	WP-2	IRA743	IRA743	IRA743	IRA743	IRA743
Charge flow	mL/min	67	67	67	100	133	67	67	67
Charge rate	cm/min	3.4	3.4	3.4	5.1	6.7	3.4	3.4	3.4
Number of elution bed volumes	-	1.5	1.5	1.5	1	1.25	1	2	2
Elution flow	mL/min	20	20	20	20	20	20	40	67
Elution rate	cm/min	1	1	1	1	1	1	2	3.4
Number of bed volumes for charge breaking point	-	10	8	7	10	10	10	10	10

Maximum concentration of Ge	mg/L	254	174	135	600	483	331	277	290
Si charge with respect to the feed	%	4	6	5	2	2	0.5	0.7	0.2

Silicon removal

Examples 39 to 41

- 2,000 mL of the charge solution derived from the ion exchange column were taken with a concentration of 18.5 g/L Si and pH 3.7, to which it was added tetradecahydrate aluminum sulphate at a molar ratio Al/Si of 0.43 and 1.0. The mixture was stirred at 400 rpm and a temperature of 80°C for 60 minutes. Once the reaction was finished, the pulp was filtered and a Si removal efficiency of 74% was obtained, lowering the Si concentration to 2.8 g/L and that of Al to 130 mg/L with a pH of 13.4.

10

Table 9. Results examples 39 to 41

Variable/Example	Unit	39	40	41
Al/Si ratio	h	0.43	0.70	1.00
Si precipitation yield	%	74	98	99
Si concentration following precipitation	g/L	2.8	0.41	0.12
Al concentration following precipitation	g/L	0.13	1.00	3.5
pH following precipitation		13.4	13.4	12.5

Examples 42 to 45

- 4,200 g of a IX (ion exchange) discharge solution were taken, with 17.4 g/L Si in a 5 L reactor at a temperature within the range of 20 to 70°C, to which calcium hydroxide was added at a molar ratio within the range of 0.9 to 1.1 mol Ca/mol Si, with continuous stirring at 300 rpm for 60 minutes. Once the reaction is concluded, the pulp was filtered in filter paper No.42.

Table 10. Results examples 42 to 45

Variable/Example	Unit	42	43	44	45
Ca/Si ratio	h	0.9	1.1	1.1	1.1
Temperature	°C	70	20	50	70

Variable/Example	Unit	42	43	44	45
Si precipitation yield	%	82	70	83	95

Germanium distillation

Example 46

18,000 mL of a solution with 454 mg/L Ge, 1,039 mg/L Pb, 294 mg/L Al, 7 mg/L As and 150 g/L HCl were taken as an output solution of the ion exchange column elution. The solution was disposed in a distillation balloon of 20 L and heated to 108°C. Once the bulb temperature reached 108°C, the distillate solution output was observed, which was kept in fractions between 300 and 1,200 mL. The evaporated solution was condensed in a coil through which cold water was circulated at 5°C, and received in a jacketed collecting cup through which water circulated at 5°C. A total of 100% Ge was collected in the distillate, obtaining fractions with up to 1,960 mg/L Ge. 0.02% of the Pb present in the solution passed to the distillate, whereas 0.19 and 50% of Al and As, respectively, were dragged by the distillate.

Example 47

14,000 mL of a solution with 1,060 mg/L Ge and 100 g/L HCl were taken as germanium distillation solution. The solution was disposed in a distillation balloon of 20 L and heated to 108°C. Once the bulb temperature reached 108°C, the distillate solution output was observed, which was kept in fractions of 500 mL. The evaporated solution was condensed in a coil through which cold water was circulated at 5°C, and received in a jacketed collecting cup through which water circulated at 5°C. A total of 100% Ge was collected in the distillate, obtaining fractions with up to 4,330 mg/L Ge.

Example 48

16,000 mL of a solution with 2,630 mg/L Ge and 117 g/L HCl were taken as germanium distillation solution. The solution was disposed in a distillation balloon of 20 L and heated to 108°C. Once the bulb temperature reached 108°C, the distillate solution output was observed, which was kept in fractions of 1.000 mL. The evaporated solution was condensed in a coil through which cold water was circulated at 5°C, and received in a jacketed collecting cup through which water circulated at 5°C. A total of 100% Ge was collected in the distillate, obtaining fractions with up to 15,000 mg/L Ge.

Example 49

16,000 mL of a solution with 10,400 mg/L Ge and 150 g/L HCl were taken as germanium distillation solution. The solution was disposed in a distillation balloon of 20 L and heated to 108°C. Once the bulb temperature reached 108°C, the distillate solution output was observed,

which was kept in fractions of 1.000 mL. The evaporated solution was condensed in a coil through which cold water was circulated at 5°C, and received in a jacketed collecting cup through which water circulated at 5°C. A total of 100% Ge was collected in the distillate, obtaining fractions with up to 25,000 mg/L Ge.

5 Germanium hydrolysis

Examples 50 to 57

250 mL of a germanium solution with a concentration within the range of 4.1 to 24.8 g/L Ge and an HCl concentration between 54 and 134 g/L were taken, which were disposed in a jacketed 500 mL reactor, through which 5,000 mL of water were circulated in a 1% volume mixture of ethylene glycol and cooled by a cooling equipment at 1°C. The solution was mechanically stirred at 250 rpm for 5 h at a temperature between 2 and 3°C. At the end of the process the solution was filtered in filter paper of 0.45 µm.

Table 11. Results examples 50 to 57

Variable/Example	Unit	50	51	52	53	54	55	56	57
Start									
Ge	g/L	4.1	4.1	8.3	8.3	16.5	16.5	24.8	24.8
HCl	g/L	54	134	54	134	54	134	54	134
Precipitate	g	s/p	s/p	s/p	1.1	2.7	4.6	4.5	7.8
Ge	%	-	-	-	69	66	66	63	68

CLAIMS

1. Procedure for producing germanium concentrate from metallurgical residues, in particular, from residues containing copper, iron, lead, and germanium, and which can optionally contain arsenic, antimony and bismuth, characterized in that it comprises:
 - 5 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, silicon, and germanium,
 - 10 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,
 - 15 iii. alkaline leaching of the second leached sludge, wherein a 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 germanium, and a third leaching solution rich in germanium and silicon, and optionally arsenic,
 - iv. charging in an ion exchange column, wherein the germanium is captured by a resin, in order to obtain a fourth alkaline solution deficient of germanium and rich in silicon,
 - v. washing the ion exchange column, which is carried out with water, wherein a fifth solution of column charge wash is obtained,
 - 20 vi. eluting the ion exchange column, which is carried out with an HCl solution, in order to obtain a sixth elution solution rich in germanium,
 - vii. distillation, wherein the sixth elution solution rich in germanium is distilled in order to obtain a seventh solution of germanium and an eighth solution deficient in germanium, and
 - 25 viii. hydrolysis, wherein the seventh solution of germanium is contacted with a solution of water to produce a first germanium dioxide concentrate.
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 2, characterized in that said powder obtained by a
30 copper smelting process is smelting powder.

4. The procedure according to any one of claims 1, 2 or 3, 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 .
- 5 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, covellite, cuprospinel in the form of CuOFe_2O_3 , zinc spinels in the form of ZnOFe_2O_3 , magnetite, iron oxide(III), pyrite, scorodite, mucovite, kaolinite and lead sulphate(II).
- 10 7. The procedure according to claim 6, characterized in that the copper contained in the metallurgical residue is present as copper sulphate, calcosine, covellite 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.
- 15 9. The procedure according to any one of claims 1 to 7 or 1 to 8, 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).
- 20 11. The procedure according to any one of claims 1 to 10, characterized in that the first H_2SO_4 solution from step i 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 130°C.
- 25 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 relation 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 60°C.
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 step (iii) is a germanium leaching step.
25. The procedure according to any one of claims 1 to 24, characterized in that the base used in the leaching of step (iii) is sodium hydroxide.
26. The procedure according to any one of claims 1 to 25, characterized in that the base added in step (iii) is added in a ratio of between 5 and 10% w/w regarding the total mass of alkaline leaching solution.
27. The procedure according to any one of claims 1 to 26, characterized in that the leaching reaction of step (iii) is performed at a temperature of between 90 and 140°C.
28. The procedure according to any one of claims 1 to 27, characterized in that, the leaching reaction of step (iii) is performed for a residence time of between 1 and 6 hours.

29. The procedure according to any one of claims 1 to 28, characterized in that step (iv) is performed with an ion exchange resin with a nitrogen atom group.
30. The procedure according to any one of claims 1 to 29, characterized in that step (iv) is performed charging the third leaching solution rich in germanium and silicon at a ratio of between 2 and 3 bed volumes.
31. The procedure according to any one of claims 1 to 30, characterized in that step (v) is performed charging the fourth charge wash solution at a ratio of between 5 and 15 bed volumes.
32. The procedure according to any one of claims 1 to 31, characterized in that step (vi) of elution is performed with an HCl solution.
33. The procedure according to any one of claims 1 to 32, characterized in that step (vi) of elution is performed with an HCl solution at a concentration of between 2 and 8 N.
34. The procedure according to any one of claims 1 to 33, characterized in that step (vi) is performed charging the HCl solution at a ratio of between 1 and 5 bed volumes.
35. The procedure according to any one of claims 1 to 34, characterized in that the fourth alkaline solution deficient of germanium is subjected to a silicon removal process.
36. The procedure according to any one of claims 1 to 35, characterized in that in said silicon removal process, slaked lime is added.
37. The procedure according to any one of claims 1 to 36, characterized in that slaked lime is added at a molar ratio of 1:1 with respect to the silicon contained in the fourth alkaline solution deficient of germanium, in order to generate a regenerated alkaline solution and a solid consisting of calcium silicate.
38. The procedure according to any one of claims 1 to 37, characterized in that the silicon removal state is performed at a temperature of between 30 and 90°C.
39. The procedure according to any one of claims 1 to 38, characterized in that the regenerated alkaline solution is recirculated to step (iii) of alkaline leaching.
40. The procedure according to any one of claims 1 to 39, characterized in that step (vii) of distillation is performed with a temperature of between 86.5 and 107°C and a bulb temperature of between 86.5 and 108°C.

41. The procedure according to any one of claims 1 to 40, characterized in that the seventh germanium solution is redistilled between 1 to 5 times in order to produce a concentrated germanium solution and a distilled HCl solution.
- 5 42. The procedure according to claim 41, characterized in that, the seventh germanium solution is redistilled 3 times in order to produce a concentrated germanium solution and a distilled HCl solution.
43. The procedure according to any one of claims 1 to 42, characterized in that the distilled HCl solution is recirculated in a previous distillation step with the purpose of increasing HCl concentration at the entry to the distiller.
- 10 44. The procedure according to any one of claims 1 to 43, characterized in that the concentrated germanium solution that is fed in step (viii) is contacted with deionized water at a volumetric ratio of between 1:1 and 1:6 to precipitate germanium as a germanium concentrate.
- 15 45. The procedure according to claim 44, characterized in that said germanium concentrate obtained in step (viii) is germanium dioxide.
46. The procedure according to any one of claims 1 to 45, characterized in that the concentrated germanium solution that is contacted with deionized water in step (viii) is performed at a temperature of between 2 and 15°C.
- 20 47. The procedure according to any one of claims 1 to 46, characterized in that the concentrated germanium solution sent to the hydrolysis step has a germanium concentration of between 8.1 and 24.8 g/L.
48. The procedure according to any one of claims 1 to 47, characterized in that the concentrated germanium solution sent to step (viii) has an HCl concentration of between 55 and 135 g/L.
- 25 49. The procedure according to any one of claims 1 to 48, characterized in that the first leaching solution rich in copper is sent to a copper leaching process of smelting powders.
50. The procedure according to any one of claims 1 to 49, characterized in that the first leaching solution rich in copper is sent to an arsenic abatement process.

51. The procedure according claim 50, characterized in that the arsenic abatement process is selected from those contemplating the ferric arsenate production.
52. The procedure according to claim 51, characterized in that the arsenic abatement process is a scorodite production process.

Figure I

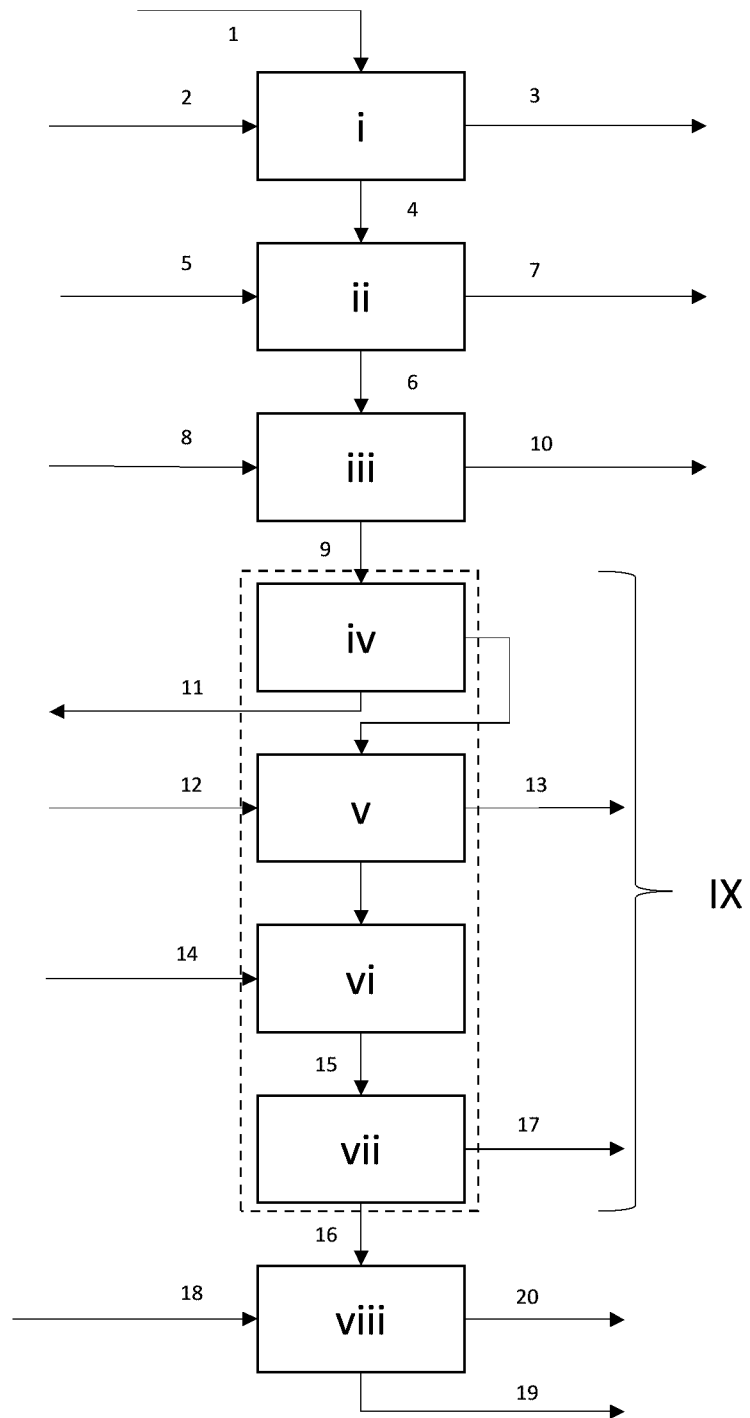


Figure II

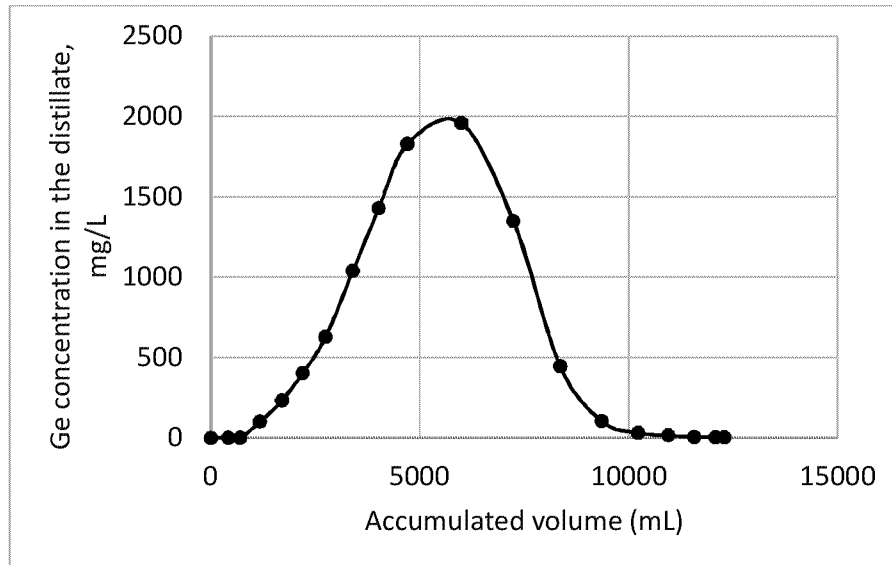


Figure III

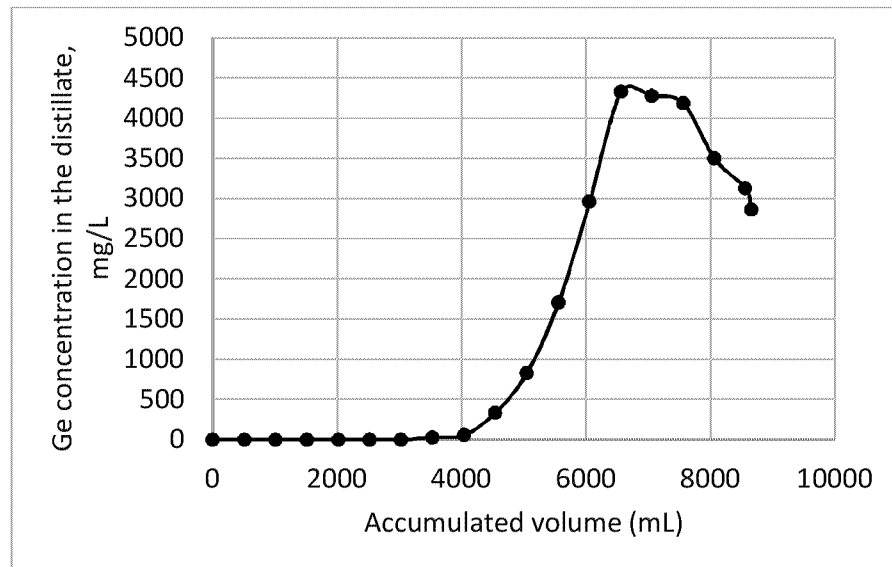


Figure IV

