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(54) Titre : PROCEDURE POUR LA PRODUCTION D'UN CONCENTRE D'ARGENT DE RESIDUS METALLURGIQUES
(54) Title: PROCEDURE FOR PRODUCING SILVER CONCENTRATE FROM METALLURGICAL RESIDUES

(57) Abrégé/Abstract:
A procedure for producing silver concentrate from metallurgical residues, in particular, from residues containing copper, iron, lead, silicon, silver and antimony, and which can optionally contain elements such as arsenic 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, and a first leached sludge having a content reduced in copper and iron, and optionally reduced in arsenic and rich in lead, germanium, silver 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) 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 a third leaching solution rich in silicon, and optionally arsenic, (iv) 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 silver, copper, lead and iron, and optionally arsenic, (v) silver precipitation from the fourth leaching solution rich in silver, copper 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, lead and silver, and optionally arsenic, (vi) leaching the first precipitate solid rich in iron, copper, lead 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 first silver and lead concentrate, and (viii) leaching the first silver concentrate with a second carboxylic acid salt solution, in order to produce a seventh leaching solution, and a second silver concentrate.

TITLE OF THE INVENTION

Procedure for producing silver concentrate from metallurgical residues.

ABSTRACT

A procedure for producing silver concentrate from metallurgical residues, in particular, from residues containing copper, iron, lead, silicon, silver and antimony, and which can optionally contain elements such as arsenic 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, and a first leached sludge having a content reduced in copper and iron, and optionally reduced in arsenic and rich in lead, germanium, silver 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) 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 a third leaching solution rich in silicon, and optionally arsenic, (iv) 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 silver, copper, lead and iron, and optionally arsenic, (v) silver precipitation from the fourth leaching solution rich in silver, copper 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, lead and silver, and optionally arsenic, (vi) leaching the first precipitate solid rich in iron, copper, lead 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 first silver and lead concentrate, and (viii) leaching the first silver concentrate with a second carboxylic acid salt solution, in order to produce a seventh leaching solution, and a second silver concentrate.

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TITLE OF THE INVENTION

Procedure for producing silver concentrate from metallurgical residues.

FIELD OF THE INVENTION

The invention relates to a procedure for producing silver concentrate from metallurgical residues, in particular, from residues containing copper, iron, lead, silicon and silver, 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.

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 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

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 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.

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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 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

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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.

The technology is based on lead recovery from lead waste using citric acid has been developed by Cambridge Enterprise Limited (WO2008056125A1) and 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) 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 WO2008056125A1 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.

Alkaline leaching

Mufakhir et al., *IOP Conf. Series: Materials Science and Engineering* 285 (2017) 012003 studied 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

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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 US 7329396 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 hydrochloric acid. 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.

A difference between the invention and patent application 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 CA 2820631A1 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

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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 silver leaching, unlike the application which requires temperatures above 125°C. Additionally, leaching of the material containing aluminum is performed with a hydrochloric acid concentration starting from 18%, while the present invention requires hydrochloric acid 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.

Description of the invention

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

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 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 alkaline leaching of the second leached sludge (6), wherein a base is added in order to form a first alkaline leaching solution (8), in order to obtain a third leached sludge having a content reduced in silicon (9), and a third leaching solution rich in silicon, and optionally arsenic (10),

a step (iv) of silver leaching of the third leached sludge (9), wherein an acid solution is used in chloride environment (11), in order to obtain a fourth leached sludge for final disposition (12) and a fourth leaching solution rich in silver, copper, iron, lead, and optionally arsenic (13),

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a step (v) of silver precipitation from the fourth leaching solution rich in silver, copper and iron, and optionally arsenic (13) with a neutralizing slurry (14), in order to produce a fifth solution rich in chloride (15) and a first precipitate solid rich in iron, copper, lead and silver, and optionally arsenic (16),

a step (vi) of leaching the first precipitate solid rich in iron, copper, lead and iron, and optionally arsenic (16) with a sulfuric acid solution (17), in order to produce a sixth leaching solution rich in copper, iron and optionally arsenic (18), and a first silver and lead concentrate (19),

a step (vii) of leaching the first silver concentrate (19) with a second carboxylic acid salt solution (20), in order to produce a seventh leaching solution (21), and a second silver 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 sulfuric acid.

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.

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, at least 95% of the lead is found as lead sulphate(II).

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

In one preferred option, step (i) is performed at a sulfuric acid concentration of between 150 and 300 g/L, more preferably at a concentration of sulfuric acid 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 a temperature of 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 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, the base used in the leaching of step (iii) may be selected from potassium hydroxide, magnesium hydroxide or sodium hydroxide.

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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 regarding the total mass of the alkaline leaching solution.

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

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

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

In one preferred option, in step (v) the chloride environment is increased by the addition of chloride salt.

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

In one preferred option, in step (iv) the chloride is provided in a concentration of between 140 and 240 g/L.

In one preferred option, step (iv) is performed at a pH of between -1.5 and 0, preferably within the range of -0.73 and -0.65.

In one preferred option, step (iv) is performed at a temperature of between 40 to 95ºC.

In one preferred option, the neutralizing slurry of step (v) of silver 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 silver precipitation is a magnesium oxide slurry.

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

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

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

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

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

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

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

In another preferred option, the sulfuric acid solution of step (vi) 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, step (vi) of silver precipitate leaching is performed at a temperature of between 50 and 95ºC.

In one preferred option, the carboxylic acid salt form step (vii) of leaching the first silver concentrate is preferably sodium citrate.

In an even more preferred option, the sodium citrate concentration is between 0.5 and 1 M.

In one preferred option, step (vii) of leaching the first silver concentrate is performed at a temperature of between 25ºC and 90ºC.

In one preferred option, step (vii) of leaching the first silver concentrate is performed at a solid content between 5 and 10%.

In one preferred option, step (vii) of leaching the first silver precipitate is performed for 1 to 6 h.

In one preferred option, the seventh leaching solution is recirculated to step (ii) of leaching.

In one preferred option, the silver concentrate is composed of silver antimonate.

In an even more preferred option, the silver concentrate is composed of silver antimonate and lead antimonate.

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

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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 first leaching solution rich in copper is sent to an arsenic abatement process.

In another 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.

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

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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
$FeAsO_4*2H_2O$	%	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 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.

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

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Example 11

A refinery effluent dissolution was prepared to which the sulfuric acid 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. 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%.

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%.

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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 in 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
Temperature	°C	30	40	60	40	40	40	40
Stirring	RPM	500	500	500	500	500	500	500
Residence time	Hours	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

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 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 6.

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Table 6. Results examples 20 to 28

Variable/Example	Unit	20	21	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 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 7. Results examples 29 and 30

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

Hydrochloric leaching

Examples 31 to 38

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

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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 8.

Table 8. Results examples 31 and 38

Variable/Example	Unit	31	32	33	34	35	36	37	38
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									
Ag	%	64	57	71	68	80	70	86	31
Fe	%	72	70	84	73	96	62	96	99
Cu	%	27	21	31	26	84	67	97	82
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

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 4, 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.

Example 39

A silver precipitation solution with a 300 g/L concentration of magnesium chloride was subjected to an evaporation process until concentrating said broth at 500 g/L of magnesium

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chloride. A volume of 358 mL of said evaporation solution, 385 mL of concentrated hydrochloric acid and 94 mL of water were added to 274 g of sludge subjected to sequential leaching processes described in examples 1 to 28 in a 5 L reactor. The reactor was 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 showed a silver leaching yield of 86%, an iron leaching yield of 95% and copper of 94%. At least 98% of leached iron was ferric ion.

Silver precipitate

Examples 40 to 46

450 g of PLS obtained from hydrochloric leaching tests were obtained with 508 mg/L Ag in a 600 mL precipitate flask and warmed at between 25 and 80°C. Neutralization of the silver 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 9. Results examples 40 to 46

Variable/Example	Unit	40	41	42	43	44	45	46
Neutralization pH	-	6	3	3	5	5	6	6
Temperature	°C	25	50	80	50	80	50	80
Precipitation yield								
Ag	%	>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

Silver concentrate

Examples 47 to 49

50 g of silver precipitate were placed with a 3,950 g/ton of Ag 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.

Table 10. Results examples 47 to 49

Variable/Example	Unit	47	48	49
Sulfuric acid concentration	-	60	80	120
Temperature	°C	60	60	60
Residence time	h	3	3	3

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Variable/Example	Unit	47	48	49
Law in the concentrate				
Ag	%	0.2	0.58	13
Fe	%			
Cu	%			

Examples 50 to 51

1,700 g of silver precipitate were placed with a 4,598 g/ton 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 11. Results examples 50 to 51

Variable/Example	Unit	50	51
Sulfuric acid concentration	-	275	275
Temperature	°C	25	80
Residence time	h	5	5
Law in the concentrate			
Ag	%	11.3	11.5
Fe	%	4.0	3.5
Cu	%	0.35	0.15
Pb	%	29.0	28.6

Silver concentrate cleaning

Examples 52 to 55

Due to the elevated presence of lead in the silver concentrate, silver concentrate leaching tests were performed with sodium citrate. In a 5 L glass reactor it was added 120 g of silver concentrate obtained from silver 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 Results showed there was no silver leaching in this step, while Sb leaching yield varied between 7 and 10%.

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Table 12. Results examples 52 to 55

Variable/Example	Unit	52	53	54	55
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					
Ag	%	0.1	<0.1	0.1	0.1
Pb	%	80	82	80	81
Sb	%	9.9	8.5	9.4	7.6
Law in the concentrate					
Ag	%	16.7	16.5	15.2	14.8
Pb	%	10.7	7.8	10.6	10.4
Sb	%	14.2	15.1	13.8	13.7

The Quemscan analysis performed to silver concentrates produces in the examples of the present invention revealed the presence of compounds such as silver antimonate and lead antimonate.

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CLAIMS

1. A procedure for producing silver concentrate from metallurgical residues, in particular, from residues containing copper, iron, lead, silicon, silver and antimony, and which can optionally contain elements such as arsenic 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, and a first leached sludge having a content reduced in copper and iron, and optionally reduced in arsenic and rich in lead, germanium, silver 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. 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 a third leaching solution rich in silicon, and optionally arsenic,

   iv. 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 silver, copper, lead and iron, and optionally arsenic,

   v. silver precipitation from the fourth leaching solution rich in silver, copper 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, lead and silver, and optionally arsenic,

   vi. leaching the first precipitate solid rich in iron, copper, lead 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 first silver and lead concentrate, and

   vii. leaching the first silver concentrate with a second carboxylic acid salt solution, in order to produce a seventh leaching solution, and a second silver 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.

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3. The procedure according to claim 2, characterized in that, said powder obtained by a 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 sulfuric acid.

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 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).

11. The procedure according to any one of claims 1 to 10, characterized in that, the first H2sulfuric acid solution may comprise sulfuric acid 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 sulfuric acid 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.

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.

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

25. The procedure according to any one of claims 1 to 24, 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.

26. The procedure according to any one of claims 1 to 25, characterized in that, the leaching reaction of step (iii) is performed at a temperature of between 90 and 140ºC.

27. The procedure according to any one of claims 1 to 26, characterized in that, the leaching reaction of step (iii) is performed for a residence time of between 1 and 6 hours.

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28. The procedure according to any one of claims 1 to 27, characterized in that, the acid used in the leaching of step (iv) is hydrochloric acid.

29. The procedure according to any one of claims 1 to 28, characterized in that, in step (iv) the hydrochloric acid is provided in a concentration varying from 50 to 140 g/L.

30. The procedure according to any one of claims 1 to 29, characterized in that, in step (iv) the chloride environment is increased by the addition of chloride salt.

31. The procedure according to any one of claims 1 to 30, characterized in that, in step (iv) the chloride environment is increased by the addition of magnesium chloride.

32. The procedure according to any one of claims 1 to 31, characterized in that, in step (iv) the chloride is provided in a concentration between 140 and 240 g/L.

33. The procedure according to any one of claims 1 to 32, characterized in that, step (iv) is performed at a pH of between -1.5 and -0.25, preferably within the range of -0.75 and -0.65.

34. The procedure according to any one of claims 1 to 33, characterized in that, step (iv) is performed at a temperature of between 40 and 95ºC.

35. The procedure according to any one of claims 1 to 34, characterized in that, the neutralizing slurry of step (v) of silver precipitation is selected from among calcium hydroxide, calcium oxide, calcium carbonate, lime, dolomitic lime, magnesium carbonate, magnesium hydroxide or magnesium oxide.

36. The procedure according to claim 35, characterized in that, the neutralizing slurry of step (vi) of silver precipitation is a magnesium oxide slurry.

37. The procedure according to any one of claims 1 to 36, characterized in that, step (v) is performed at a temperature of between 50 and 95ºC.

38. The procedure according to any one of claims 1 to 37, characterized in that, the neutralizing slurry added in step (v) is provided until reaching a pH between 3 and 7.

39. The procedure according to any one of claims 1 to 38, characterized in that, step (v) has a residence time of between 0.5 and 3 hours.

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40. The procedure according to any one of claims 1 to 39, characterized in that, the fifth solution rich in chloride of step (v) is sent to a crystallization process of magnesium chloride.

41. The procedure according to any one of claims 1 to 40, characterized in that, the fifth solution rich in chloride of step (v) is recirculated to the step (iv) of silver precipitation.

42. The procedure according to any one of claims 1 to 41, characterized in that, the sulfuric acid solution of step (vi) has a sulfuric acid concentration of between 60 and 275 g/L.

43. The procedure according to any one of claims 1 to 42, characterized in that, the sulfuric acid solution of step (vi) 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.

44. The procedure according to any one of claims 1 to 43, characterized in that, step (vi) of leaching the silver precipitate is performed at a temperature of between 50 and 95ºC.

45. The procedure according to any one of claims 1 to 44, characterized in that, the carboxylic acid salt of step (vii) of leaching the first silver concentrate is preferably sodium citrate.

46. The procedure according to any one of claims 1 to 45, characterized in that, the sodium citrate concentration in step (vii) is between 0.5 and 1 M.

47. The procedure according to any one of claims 1 to 46, characterized in that, step (vii) of leaching the first silver concentrate is performed at a temperature of between 25 and 70ºC.

48. The procedure according to any one of claims 1 to 47, characterized in that, step (vii) of leaching the first silver concentrate is performed at a solid content of between 5 and 10%.

49. The procedure according to any one of claims 1 to 48, characterized in that, step (vii) of leaching the first silver concentrate is performed for 1 to 6 h.

50. The procedure according to any one of claims 1 to 49, characterized in that, the seventh leaching solution of step (vii) is recirculated to step (ii) of leaching.

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51. The procedure according to any one of claims 1 to 50, characterized in that, the second silver concentrate is composed of silver antimonate.

52. The procedure according to any one of claims 1 to 51, characterized in that, the second silver concentrate is composed of silver antimonate and lead antimonate.

53. The procedure according to any one of claims 1 to 52, characterized in that, the first leaching solution rich in copper is sent to a copper leaching process of smelting powders.

54. The procedure according to any one of claims 1 to 53, characterized in that, the first leaching solution rich in copper is sent to an arsenic abatement process.

55. The procedure according to claim 54, characterized in that, the arsenic abatement process is selected from those contemplating the ferric arsenate production.

56. The procedure according to claim 54 and/or 55, characterized in that, the arsenic abatement process is a scorodite production process.

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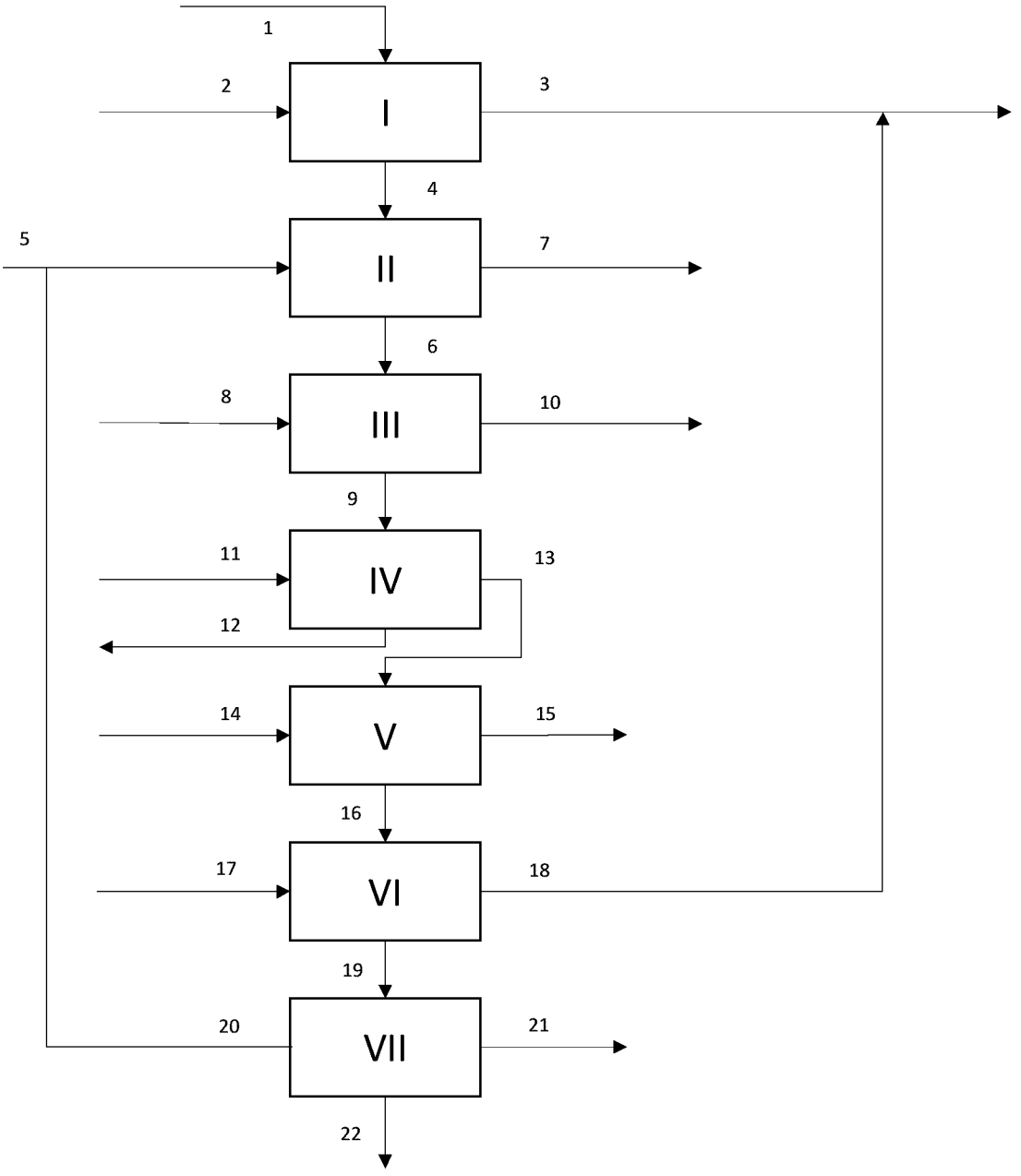
Figure I



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